

# Quantum diffusion in liquid water from ring polymer molecular dynamics

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We have used the ring polymer molecular-dynamics method to study the translational and orientational motions in an extended simple point charge model of liquid water under ambient conditions. We find, in agreement with previous studies, that quantum-mechanical effects increase the self-diffusion coefficient  $D$  and decrease the relaxation times around the principal axes of the water molecule by a factor of around 1.5. These results are consistent with a simple Stokes-Einstein picture of the molecular motion and suggest that the main effect of the quantum fluctuations is to decrease the viscosity of the liquid by about a third. We then go on to consider the system-size scaling of the calculated self-diffusion coefficient and show that an appropriate extrapolation to the limit of infinite system size increases  $D$  by a further factor of around 1.3 over the value obtained from a simulation of a system containing 216 water molecules. These findings are discussed in light of the widespread use of classical molecular-dynamics simulations of this sort of size to model the dynamics of aqueous systems. © 2005 American Institute of Physics. [DOI: 10.1063/1.2074967]

## I. INTRODUCTION

The anomalous properties of liquid water and its role in chemistry and biology have made it a subject of intense research for many decades. On the computational side, the earliest atomistic simulations of the ambient liquid using a simple empirical potential were performed almost 40 years ago.<sup>1</sup> Since then, many improved potentials have been developed and shown to provide better agreement with experiment when used in classical molecular-dynamics and Monte Carlo simulations,<sup>2–8</sup> and these simulations have been extended to study the properties of liquid water in a much wider variety of regimes.<sup>8–12</sup> The first quantum-mechanical simulations of the static equilibrium properties of the liquid were performed in the mid-1980s, when the path-integral Monte Carlo (PIMC) method was used to assess the effect of quantum-mechanical fluctuations on the liquid structure.<sup>13,14</sup> However, it is only comparatively recently that the role of quantum-mechanical effects in the dynamics of the liquid have been investigated.<sup>15–20</sup>

The first people to consider these effects were Lobaugh and Voth,<sup>15</sup> who used the centroid molecular-dynamics (CMD) method to study the dynamics of a flexible simple point-charge (SPC/F) model of ambient water. This was followed shortly afterwards by a study in which the less sophisticated Feynman-Hibbs effective potential approach was used to calculate the self-diffusion coefficients of light and heavy water over a rather wide temperature range.<sup>16</sup> Several CMD studies of the orientational and translational motions in a rigid-body (TIP4P<sup>2</sup>) water model have since appeared,<sup>17,18</sup> and two very recent studies have considered the dynamics of a flexible water model using the Feynman-Kleinert linearized path-integral (FK-LPI) approach.<sup>19,20</sup>

The general conclusion of these papers is that quantum-

mechanical fluctuations tend to increase the diffusion in the ambient liquid, the calculated increase in the self-diffusion coefficient over that obtained in a purely classical simulation varying from a factor of 1.4–2.0 depending on the interaction potential and the approximate quantum dynamical method employed.<sup>15–20</sup> This increase in the diffusion coefficient is consistent with the decrease in the structure of the liquid owing to quantum-mechanical effects that was observed in the earlier PIMC calculations.<sup>13,14</sup> Quantum-mechanical fluctuations evidently disrupt the hydrogen-bonding network in ambient water leading to a less structured liquid through which the water molecules diffuse more rapidly.

In the present paper, we report a further study of quantum-mechanical effects in the dynamics of liquid water using the recently developed ring-polymer molecular-dynamics (RPMD) method.<sup>21–25</sup> This is a simple approximate quantum dynamical technique that generalizes the exact path-integral molecular-dynamics (PIMD) method for calculating the static equilibrium properties of quantum-mechanical systems.<sup>26</sup> So far, it has been applied to the calculation of chemical reaction rates,<sup>22,25</sup> and to the diffusion in<sup>23</sup> and the inelastic neutron scattering from<sup>24</sup> a strongly quantum-mechanical liquid (parahydrogen). In particular, it has been found to give a self-diffusion coefficient for liquid parahydrogen that agrees very well with experimental measurements when extrapolated to the limit of infinite system size.<sup>23</sup> Since liquid water at 298 K is considerably less quantum mechanical than liquid parahydrogen at 14 K, and since the RPMD approximation becomes exact in the classical limit,<sup>21</sup> one would expect this approximation to give quite a satisfactory description of the dynamics of ambient water.

The outline of the paper is as follows. Section II reviews the theory of the RPMD method<sup>21–25</sup> and describes how this method can be used to study both the translational and orientational motions in liquid water. Particular emphasis is given to certain moment (or sum rule) constraints that are

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satisfied by the exact Kubo-transformed<sup>27</sup> orientational correlation functions of a molecular liquid and which can be used to assess the accuracy of the RPMD approximation. The section ends by presenting the details of our calculations on an extended simple point-charge (SPC/E) model<sup>3</sup> of liquid water, including a discussion of why we chose to use this particular effective potential model. Our computed RPMD velocity autocorrelation functions and orientational correlation functions of the liquid at 298 K and a density of 0.998 g cm<sup>-3</sup> are then presented and discussed in light of earlier work in Sec. III. Section IV summarizes what we have accomplished in the present study and suggests some interesting directions for future research.

## II. THEORY

### A. Ring-polymer molecular dynamics

The exact quantum-mechanical self-diffusion coefficient of liquid water is given by a Green-Kubo relation in terms of the time integral of a Kubo-transformed velocity autocorrelation function,<sup>28</sup>

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

where

$$\tilde{c}_{\mathbf{v},\mathbf{v}}(t) = \frac{1}{\beta N} \int_0^\beta d\lambda \sum_{i=1}^N \langle \mathbf{v}_i(-i\lambda\hbar) \cdot \mathbf{v}_i(t) \rangle, \quad (2)$$

with  $\beta = 1/(k_B T)$ . The sum in Eq. (2) is over the  $N$  molecules in the liquid,  $\mathbf{v}_i(t)$  is the Heisenberg-evolved center-of-mass velocity operator of molecule  $i$  at time  $t$ , and the angular brackets denote an average over the equilibrium distribution of the liquid at temperature  $T$ .

The RPMD approximation to  $\tilde{c}_{\mathbf{v},\mathbf{v}}(t)$  is simply<sup>23,24</sup>

$$\begin{aligned} \tilde{c}_{\mathbf{v},\mathbf{v}}(t) &\approx \frac{1}{(2\pi\hbar)^{9Nn} Z_n} \int \int \prod_{j=1}^{3N} \prod_{k=1}^n d\mathbf{p}_j^{(k)} d\mathbf{r}_j^{(k)} \\ &\times e^{-\beta_n H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\})} \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i(0) \cdot \mathbf{v}_i(t), \end{aligned} \quad (3)$$

where

$$Z_n = \frac{1}{(2\pi\hbar)^{9Nn}} \int \int \prod_{j=1}^{3N} \prod_{k=1}^n d\mathbf{p}_j^{(k)} d\mathbf{r}_j^{(k)} e^{-\beta_n H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\})} \quad (4)$$

is an  $n$ -bead path-integral approximation to the canonical partition function of the liquid.<sup>29,30</sup> Here  $\beta_n = \beta/n$ , and  $H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\})$  is the classical Hamiltonian of a three-dimensional system of  $3N$  atomic ring  $n$  polymers that interact through the physical interaction potential  $V(\mathbf{r}_1, \dots, \mathbf{r}_{3N})$ ,

$$\begin{aligned} H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\}) &= \sum_{j=1}^{3N} \sum_{k=1}^n \left[ \frac{(\mathbf{p}_j^{(k)})^2}{2m_j} + \frac{1}{2} m_j \omega_n^2 (\mathbf{r}_j^{(k)} - \mathbf{r}_j^{(k-1)})^2 \right] \\ &+ \sum_{k=1}^n V(\mathbf{r}_1^{(k)}, \dots, \mathbf{r}_{3N}^{(k)}), \end{aligned} \quad (5)$$

where  $m_j$  is the mass of atom  $j$ ,  $\omega_n = 1/(\beta_n \hbar)$ , and  $\mathbf{r}_j^{(0)} \equiv \mathbf{r}_j^{(n)}$ .

The classical equations of motion generated by this ring-polymer Hamiltonian are used to evolve the integration variables in Eq. (3) forward in time,

$$\dot{\mathbf{p}}_j^{(k)} = -m_j \omega_n^2 (2\mathbf{r}_j^{(k)} - \mathbf{r}_j^{(k-1)} - \mathbf{r}_j^{(k+1)}) - \frac{\partial V(\mathbf{r}_1^{(k)}, \dots, \mathbf{r}_{3N}^{(k)})}{\partial \mathbf{r}_j^{(k)}}, \quad (6)$$

$$\dot{\mathbf{r}}_j^{(k)} = \frac{\mathbf{p}_j^{(k)}}{m_j}, \quad (7)$$

and the molecular center-of-mass velocity  $\mathbf{v}_i(t)$  is obtained from an average over the beads of the ring polymers in molecule  $i$  at time  $t$ :

$$\mathbf{v}_i(t) = \frac{1}{nm_{\text{H}_2\text{O}}} \sum_{j \in i} \sum_{k=1}^n \mathbf{p}_j^{(k)}(t). \quad (8)$$

As we have stressed throughout our recent papers,<sup>21-25</sup> this RPMD model simply provides a convenient way to combine quantum statistical effects with classical molecular dynamics, without retaining any real-time quantum phase information. The expression for  $\tilde{c}_{\mathbf{v},\mathbf{v}}(t)$  in Eq. (3) is therefore not exact. However, there are good reasons to believe that it will provide a satisfactory approximation to the Kubo-transformed velocity autocorrelation function of liquid water. In particular, Eq. (3) reduces correctly to a purely classical velocity autocorrelation function in the classical ( $n=1$  bead) limit,<sup>21</sup> and it coincides with the exact quantum-mechanical (Kubo-transformed) velocity autocorrelation function in the limit as  $t \rightarrow 0$  (with a leading error<sup>31</sup> of order  $\hbar^2 t^4$ ).

### B. Orientational correlation functions

A more challenging test for the RPMD approximation is provided by the calculation of orientational correlation functions of the form<sup>32,33</sup>

$$\tilde{c}_l(t) = \frac{1}{\beta N} \int_0^\beta d\lambda \sum_{i=1}^N \langle P_l[\hat{\mathbf{e}}_i(-i\lambda\hbar) \cdot \hat{\mathbf{e}}_i(t)] \rangle, \quad (9)$$

where  $\hat{\mathbf{e}}_i(t)$  is the Heisenberg-evolved operator for the orientation of one of the three principal inertial axes of molecule  $i$  in the liquid at time  $t$ . This calculation is more difficult for two reasons. First, the accuracy of the RPMD approximation is known to degrade for correlation functions involving nonlinear operators,<sup>21,24,34</sup> and  $\hat{\mathbf{e}}_i(t)$  is a highly nonlinear function of the coordinate operators  $\mathbf{r}_j(t)$ . Second, the orientational motion of water molecules is predominantly a hydrogen-atom motion and therefore inherently more quantum mechanical than the molecular center-of-mass motion that determines  $\tilde{c}_{\mathbf{v},\mathbf{v}}(t)$ .

When  $l=1$ , Eq. (9) reduces to

$$\tilde{c}_1(t) = \frac{1}{\beta N} \int_0^\beta d\lambda \sum_{i=1}^N \langle \hat{\mathbf{e}}_i(-i\lambda\hbar) \cdot \hat{\mathbf{e}}_i(t) \rangle, \quad (10)$$

the RPMD approximation to which is simply

$$\begin{aligned} \tilde{c}_1(t) \approx & \frac{1}{(2\pi\hbar)^{9Nn}Z_n} \int \int \prod_{j=1}^{3N} \prod_{k=1}^n d\mathbf{p}_j^{(k)} d\mathbf{r}_j^{(k)} \\ & \times e^{-\beta_n H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\})} \frac{1}{N} \sum_{i=1}^N \mathbf{e}_i(0) \cdot \mathbf{e}_i(t), \end{aligned} \quad (11)$$

where  $\mathbf{e}_i(t)$  involves a ring-polymer average over unit vectors along the chosen inertial axis of molecule  $i$  at time  $t$ :

$$\mathbf{e}_i(t) = \frac{1}{n} \sum_{k=1}^n \hat{\mathbf{e}}_i^{(k)}(t). \quad (12)$$

These unit vectors  $\hat{\mathbf{e}}_i^{(k)}$  are normalized eigenvectors of the inertia tensors<sup>35</sup>

$$\begin{aligned} \mathbf{I}_i^{(k)} = & \sum_{j \in i} m_j [(\mathbf{r}_j^{(k)} - \bar{\mathbf{r}}_i^{(k)})^T (\mathbf{r}_j^{(k)} - \bar{\mathbf{r}}_i^{(k)}) \mathbf{1} \\ & - (\mathbf{r}_j^{(k)} - \bar{\mathbf{r}}_i^{(k)}) (\mathbf{r}_j^{(k)} - \bar{\mathbf{r}}_i^{(k)})^T], \end{aligned} \quad (13)$$

where

$$\bar{\mathbf{r}}_i^{(k)} = \frac{1}{m_{\text{H}_2\text{O}}} \sum_{j \in i} m_j \mathbf{r}_j^{(k)}, \quad (14)$$

and they are therefore highly nonlinear functions of the ring-polymer coordinates.<sup>36</sup>

When  $l=2$ , Eq. (9) becomes

$$\tilde{c}_2(t) = -\frac{1}{2} + \frac{3}{2\beta N} \int_0^\beta d\lambda \sum_{i=1}^N \langle [\hat{\mathbf{e}}_i(-i\lambda\hbar) \cdot \hat{\mathbf{e}}_i(t)]^2 \rangle, \quad (15)$$

the RPMD approximation to which is

$$\begin{aligned} \tilde{c}_2(t) \approx & -\frac{1}{2} + \frac{3}{2(2\pi\hbar)^{9Nn}Z_n} \int \int \prod_{j=1}^{3N} \prod_{k=1}^n d\mathbf{p}_j^{(k)} d\mathbf{r}_j^{(k)} \\ & \times e^{-\beta_n H_n(\{\mathbf{p}_j^{(k)}\}, \{\mathbf{r}_j^{(k)}\})} \frac{1}{N} \sum_{i=1}^N \text{tr}[\mathbf{M}_i(0)\mathbf{M}_i(t)], \end{aligned} \quad (16)$$

where  $\mathbf{M}_i(t)$  is the  $3 \times 3$  matrix

$$\mathbf{M}_i(t) = \frac{1}{n} \sum_{k=1}^n \hat{\mathbf{e}}_i^{(k)}(t) \hat{\mathbf{e}}_i^{(k)}(0)^T, \quad (17)$$

and the “tr” denotes a matrix trace.

The generalization to higher values of  $l$  proceeds along the same lines by expanding the Legendre polynomial  $P_l(x)$  and writing each term as a Kubo-averaged autocorrelation function between a tensor operator at imaginary time  $-i\lambda\hbar$  and the same operator at real time  $t$ . However, both the equations and the objects that are correlated within the RPMD approximation become increasingly complicated as  $l$  increases, the most complicated object that arises for a given  $l$  being a three-dimensional Cartesian tensor of rank  $l$ . Because of this, and because it suffices to make the points we want to make, we shall stop in the present study at  $l=2$ .

### C. Moment (sum rule) constraints

It follows from the general properties of the RPMD approximation that Eqs. (11) and (16) will give the exact Kubo-

transformed orientational correlation functions in the limit as  $t \rightarrow 0$ , in this case with a leading error<sup>31</sup> of order  $\hbar^2 t^2$ . However, because of the nonlinearity of the correlated operators in Eqs. (10) and (15), it is not at all clear *a priori* that the approximation will be reliable at longer times.<sup>21,24,34</sup> A theoretical test of the accuracy of the RPMD approximations to  $\tilde{c}_1(t)$  and  $\tilde{c}_2(t)$  would therefore be very desirable.

Such a test can be constructed by noting that, since  $P_l(1)=1$  for all  $l$ , the standard orientational correlation functions

$$c_l(t) = \frac{1}{N} \sum_{i=1}^N \langle P_l[\hat{\mathbf{e}}_i(0) \cdot \hat{\mathbf{e}}_i(t)] \rangle \quad (18)$$

all tend to one in the short-time limit. This implies a constraint on  $\tilde{c}_l(t)$  by virtue of its relationship to  $c_l(t)$ . If  $\tilde{C}_l(\omega)$  is the Fourier transform of  $\tilde{c}_l(t)$ ,

$$\tilde{C}_l(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} \tilde{c}_l(t) dt, \quad (19)$$

and  $C_l(\omega)$  is that of  $c_l(t)$ , one has<sup>27,28</sup>

$$C_l(\omega) = \frac{\beta\hbar\omega}{(1 - e^{-\beta\hbar\omega})} \tilde{C}_l(\omega), \quad (20)$$

and so by inverting the Fourier transform one obtains

$$c_l(0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\beta\hbar\omega}{(1 - e^{-\beta\hbar\omega})} \int_{-\infty}^{\infty} dt e^{-i\omega t} \tilde{c}_l(t). \quad (21)$$

If  $\tilde{c}_l(t)$  were calculated exactly, the double integral on the right-hand side of this equation would give  $c_l(0)=1$ , but this is not guaranteed to be the case when  $\tilde{c}_l(t)$  is calculated using an approximate quantum dynamical method such as RPMD. Equation (21) therefore provides a useful moment (or sum rule) test of the accuracy of the calculation. An interesting aspect of this test is that, while  $c_l(0)$  is purely real, the right-hand side of Eq. (21) will in general be complex when it is combined with an approximation to  $\tilde{c}_l(t)$ . In principle, the equation therefore provides two separate tests of an approximate Kubo-transformed quantum correlation function. However, it is clear that the imaginary part of the right-hand side will be identically zero if  $\tilde{c}_l(t)$  is a real and even function of  $t$ . Since this is the case in RPMD, one of the two constraints in Eq. (21) is satisfied exactly, and the other provides a numerical test of the accuracy of the calculation.

Note also from Eq. (20) that, since  $C_l(0)=\tilde{C}_l(0)$ , the molecular orientational relaxation times

$$\tau_l = \frac{1}{2} \int_{-\infty}^{\infty} c_l(t) dt \equiv \text{Re} \int_0^{\infty} c_l(t) dt \quad (22)$$

can be calculated equivalently as

$$\tau_l = \frac{1}{2} \int_{-\infty}^{\infty} \tilde{c}_l(t) dt \equiv \int_0^{\infty} \tilde{c}_l(t) dt, \quad (23)$$

where we have again used the fact that  $\tilde{c}_l(t)$  is a real and even function of  $t$ .<sup>21</sup>

TABLE I. Parameters in the SPC/E water potential.

$r(\text{OH})$ (Å)	1.0
$\angle$ (HOH) (deg)	109.47
$10^{-6}A$ (kJ Å <sup>12</sup> mol <sup>-1</sup> )	2.633
$10^{-3}B$ (kJ Å <sup>6</sup> mol <sup>-1</sup> )	2.617
$Q_{\text{O}}( e )$	-0.8476
$Q_{\text{H}}( e )$	0.4238

#### D. Computational details

The above ring-polymer molecular-dynamics equations and the classical molecular-dynamics limit were used to simulate liquid water at a temperature of 298 K and a density of 0.998 g cm<sup>-3</sup>. All calculations were repeated with system sizes of 216, 343, and 512 water molecules. For the purposes of this study, the RPMD method was implemented in the DL\_POLY molecular-dynamics simulation package.<sup>37</sup>

Interactions between molecular pairs were described using the extended simple point-charge (SPC/E) model<sup>3</sup>

$$V_{ij} = \sum_{k \in i} \sum_{k' \in j} \frac{Q_k Q_{k'}}{R_{kk'}} + \frac{A}{R_{\text{OO}}^{12}} - \frac{B}{R_{\text{OO}}^6}, \quad (24)$$

which includes a Coulomb contribution from the fixed partial charges on the atom centers and a Lennard-Jones interaction between the oxygen atoms. The potential-energy parameters are reported in Table I. Although this effective pair potential provides a very simple model for the interaction between water molecules, we expect it to be realistic enough for our present purposes, which are simply to assess the magnitude of quantum-mechanical effects in the dynamics of the room-temperature liquid.

The reason why we chose to use this potential rather than one of the (many other) empirical water potentials that are now available is that it has been widely used in the past in classical molecular-dynamics simulations. In particular, it has been shown to give a self-diffusion coefficient in good agreement with the experimental value of 0.23 Å<sup>2</sup>/ps in classical molecular-dynamics simulations of a system of 216 water molecules at 298 K.<sup>3,4</sup> One of the key questions we shall investigate is by how much this value changes when quantum statistical effects are included using RPMD and the resulting diffusion coefficient is extrapolated to the limit of infinite system size.

The remaining details of our simulations were as follows. Cubic periodic boundary conditions were applied using the minimum image convention.<sup>38</sup> Short-range interactions were truncated at an atom-atom distance of 9 Å, and electrostatic interactions beyond this distance were included using Ewald summation.<sup>38</sup> Individual simulations were performed by equilibrating the system for 200 ps and then calculating the velocity autocorrelation function [Eq. (3)] and the orientational correlations functions [Eqs. (11) and (16)] for 10 ps by averaging over 80 consecutive 20 ps trajectories with a time step of 2 fs. The temperature was controlled by resampling the atomic momenta from the Maxwell distribution at inverse temperature  $\beta_n$  between each trajectory. Five such simulations were performed for each system size, yielding an average value for (and a standard error in) the center-of-mass

diffusion coefficient and the orientational relaxation times. The starting configurations for the simulations were obtained from uncorrelated steps in an equilibrated, classical SPC/E water calculation.

The equations of motion in Eqs. (6) and (7) were integrated with the velocity Verlet method,<sup>39</sup> using the SHAKE (Ref. 40) and RATTLE (Ref. 41) algorithms to preserve the internal geometry of each ring-polymer bead of each water molecule. In the RPMD simulations (with  $n$  beads), the contributions to the momentum evolution were split between the forces arising from the physical potential and the interbead harmonic potential [see Eqs. (5) and (6)]. The evolution of the interbead term was performed using  $n$  multiple time-step cycles.<sup>42</sup> As expected from the earlier PIMC and CMD calculations,<sup>13,17,18</sup> we found that  $n=6$  ring-polymer beads sufficed to converge the results at 298 K. The classical results were obtained using the same computer code but with just  $n=1$  ring-polymer bead. Since most of the computational effort was spent in evaluating the forces arising from the SPC/E potential, the RPMD calculations were found to be just over six times more expensive than the classical calculations.

### III. RESULTS AND DISCUSSION

#### A. Orientational motion

We shall begin the discussion of our results with the orientational dynamics of liquid water embodied in the single-molecule correlation functions  $\tilde{c}_1^\eta(t)$  [Eq. (10)] and  $\tilde{c}_2^\eta(t)$  [Eq. (15)], where  $\eta=x, y$ , or  $z$  indicates one of the principal inertial axes of the water molecule. These correlation functions were calculated for all three principal axes using both classical molecular dynamics and RPMD. The results for the  $z$  axis, which coincides with the dipole moment axis of the molecule, are plotted in Fig. 1. The computed correlation functions for the  $x$  (the remaining in-plane) and  $y$  (out-of-plane) axes were found to be very similar to those shown in this figure.

The orientational correlation functions in Fig. 1 share the same basic features and both can be interpreted in terms of the motion of a single water molecule surrounded by its liquid environment.<sup>33</sup> At very short times ( $t < 30$  fs), rapid decorrelation occurs as the molecule rotates freely between collisions with its neighbors. This trend is broken by the glitch in the correlation functions at  $t \approx 50$  fs, the signature of librational rebound in a molecular liquid with a cagelike structure. Finally, at longer times, the orientational motion enters a diffusive regime in which the solvent cage breaks up and the correlation functions decay exponentially to zero.<sup>32,33</sup>

Comparison of the classical and RPMD results in the figure reveals at least two interesting quantum effects. First, in Fig. 1(a), we note that the RPMD correlation function  $\tilde{c}_1^\eta(t)$  differs from the classical result of unity at time zero. This can be interpreted as arising from quantum dispersion in the orientational coordinates. From Eq. (12), it is clear that when one ring-polymer bead is employed ( $n=1$ ), the vectors  $\mathbf{e}_i$  that appear in Eq. (11) have unit length and give rise to the classical result. However, when  $n > 1$ , Eq. (12) corresponds to an average of unit vectors which are not perfectly aligned,



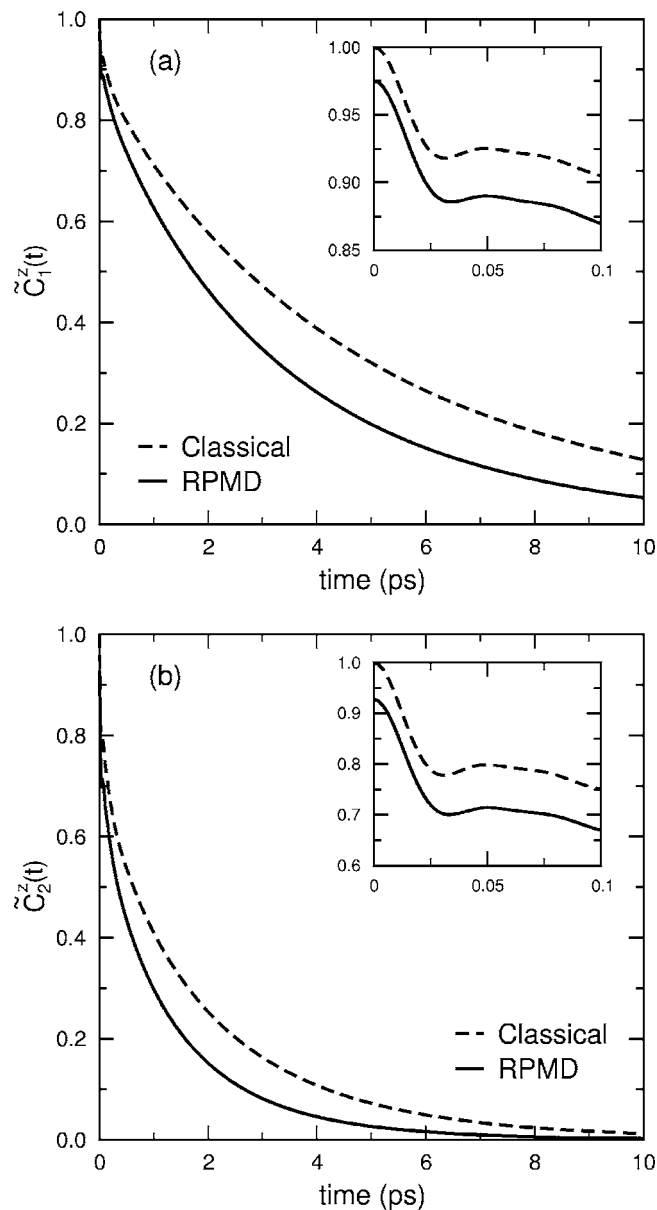


FIG. 1. Kubo-transformed orientational correlation functions for SPC/E water at the  $T=298$  K,  $\rho=0.998$  g cm $^{-3}$  state point, obtained from the classical and RPMD simulations of a system of 512 water molecules.

resulting in vectors  $\mathbf{e}_i$  with less than unit length. In Fig. 1(b), we see that the deviation of the quantum result from unity at time zero becomes more pronounced for the higher-order orientational correlation function  $\tilde{c}_2^z(t)$ . Note that this is a genuine quantum-mechanical effect and not simply an artifact of the RPMD approximation; unlike CMD,<sup>15,17,18</sup> RPMD is exact for all coordinate-dependent Kubo-transformed correlation functions in the limit as  $t \rightarrow 0$ .<sup>21</sup>

The second difference between the classical and RPMD results in Fig. 1 is that the RPMD method predicts a more rapid exponential decay of the correlation functions in the diffusive regime. Quantum zero-point energy and tunneling disrupt the hydrogen-bonding network in classical liquid water and enable the molecules to more rapidly lose memory of their original orientation. We shall see below that this simple

TABLE II. Calculated relaxation times (in ps) for the principal axes of the water molecule. The  $z$  axis is coincident with the dipole moment axis of the water molecule; the  $x$  axis is also in the plane of the molecule. The index  $l$  indicates the order of the orientational correlation function from which the relaxation time is calculated. The numbers in parentheses are the standard errors in the last digit from five statistically independent calculations. The results in this table were obtained from a simulation of 512 water molecules, but the orientational correlation functions and relaxation times were not found to exhibit any significant system-size dependence.

$l$	$\eta$	Classical $\tau_l^\eta$	RPMD $\tau_l^\eta$	RPMD/Classical
1	$x$	4.30(3)	2.79(3)	0.65
1	$y$	2.76(2)	1.80(2)	0.65
1	$z$	4.40(3)	2.94(3)	0.67
2	$x$	1.90(1)	1.19(1)	0.63
2	$y$	1.11(1)	0.68(1)	0.61
2	$z$	1.48(1)	0.93(1)	0.63

molecular picture qualitatively explains virtually all of the quantum-mechanical effects we have found in our calculations.

The rate of orientational diffusion can be numerically characterized by the relaxation times  $\tau_l$  in Eq. (23). We report the first- and second-order orientational relaxation times for all three principal axes of the water molecule in Table II. Each  $\tau_l^\eta$  was calculated by integrating the corresponding  $\tilde{c}_l^\eta(t)$  after analytically fitting its exponential tail. The numbers shown in the table were obtained from our largest simulation (of 512 water molecules), but the relaxation times obtained from the smaller simulations were found to be very similar.

Table II shows that the quantum effects included in RPMD consistently reduce the orientational relaxation times to approximately 2/3 of their classical values. This reduction is insensitive to the moment of inertia around the chosen principal molecular axis, because the dominant contribution to the relaxation time is from the exponential tail of the orientational correlation function; inertial free rotation occurs only at very short times ( $t < 30$  fs).

For the thermodynamic state point we have considered, the experimental value of  $\tau_2^x$  inferred from the NMR measurements is 2.5 ps.<sup>43</sup> The SPC/E potential is known to underestimate this result,<sup>4</sup> even in the classical treatment of the dynamics for which it was parametrized,<sup>3</sup> and we see from Table II that the addition of quantum effects only makes the comparison with experiment worse. However, previous theoretical work that utilized a different model potential has also found a quantum/classical ratio of approximately 2/3 for the orientational relaxation times,<sup>17</sup> suggesting that this result is relatively independent of the choice of potential.

It is also of interest to consider the spectra of our orientational correlation functions,

$$I_l^\eta(\omega) = \omega^2 \tilde{C}_l^\eta(\omega), \quad (25)$$

where  $\tilde{C}_l^\eta(\omega)$  is the Fourier transform of  $\tilde{c}_l^\eta(t)$  [see Eq. (19)]. Figure 2 shows these spectra calculated using both the classical molecular-dynamics and the RPMD methods for the case where the principal axis is in the direction of the dipole moment of the water molecule ( $\eta=z$ ). We note that this form

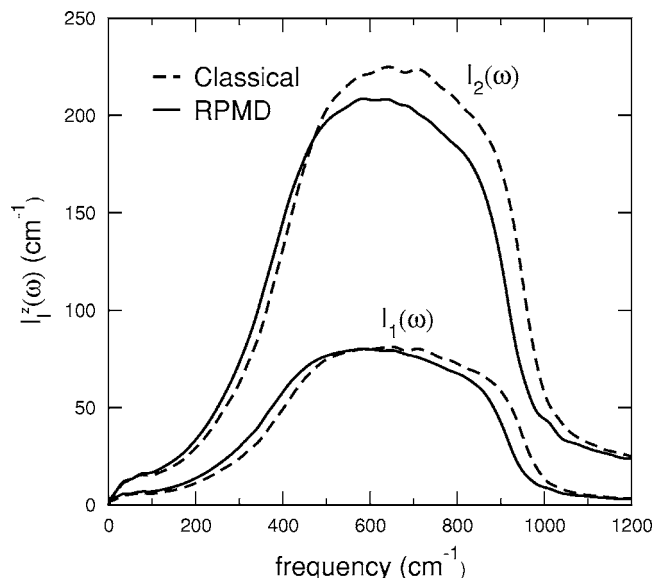


FIG. 2. Spectral functions  $I_l^z(\omega)$  obtained from the orientational correlation functions in Fig. 1.

of the classical spectrum includes the so-called harmonic detailed balance correction factor.<sup>44–47</sup> We also note that  $I_1^z(\omega)$  can be related to the infrared dipole absorption spectrum of the liquid, upon neglecting interaction-induced moments and collective contributions to the spectrum.<sup>33</sup>

The dominant feature of the spectra in Fig. 2 is a broad absorption band centered around  $600\text{ cm}^{-1}$ . This band, which arises from the glitch in the correlation functions at  $t \approx 50\text{ fs}$  in Fig. 1, is associated with the librational motions of the molecules in the liquid. Quantum effects cause a slight redshift of both the  $I_1^z(\omega)$  and  $I_2^z(\omega)$  absorption bands, reflecting the anharmonicity of the intermolecular potential. Like the shortening of the quantum orientational relaxation times, this redshift suggests that the hydrogen-bonding network of the quantum liquid is less rigid than that of the classical liquid. The spectra in Fig. 2 are similar to those obtained using the CMD method in Ref. 17, with the exception that the RPMD method predicts quantum effects to decrease (rather than increase) the intensity of the  $I_2^z(\omega)$  absorption band.

## B. Sum-rule tests

It is clear from the above results that the RPMD method predicts substantial quantum effects in the orientational dynamics of liquid water. But how does one know that this description is correct? Comparison of the calculated RPMD results with experiment is not a useful indicator, because the SPC/E water potential was parametrized on the basis of classical simulations.<sup>3</sup> However, the sum rules in Eq. (21) provide a purely theoretical test of the RPMD orientational correlation functions that should be satisfied regardless of the inadequacies of the interaction potential.

Table III reports the results of these sum-rule tests for the first- and second-order RPMD orientational correlation functions for all three principal axes of the water molecule. In addition, the third column of the table shows the moments of inertia around the principal axes and the fourth gives the

TABLE III. Results of the orientational correlation function sum rule test in Eq. (21).  $I_\eta$  is the moment of inertia around axis  $\eta$ .  $\tilde{c}_l^\eta(0)$  is the value of the Kubo-transformed orientational correlation function at time zero, which is given exactly by the RPMD method. The value of  $c_l^\eta(0)$  obtained by Fourier inversion of the RPMD approximation to  $\tilde{c}_l^\eta(t)$  is given in the final column; the exact sum rule is  $c_l^\eta(0)=1$ . The statistical errors in  $\tilde{c}_l^\eta(0)$  and  $c_l^\eta(0)$  were found to be significantly smaller than the  $\approx 1\%$  errors in the relaxation times reported in Table II; the standard errors in  $\tilde{c}_l^\eta(0)$  and  $c_l^\eta(0)$  from our five statistically independent calculations were never larger than  $5 \times 10^{-4}$ .

$l$	$\eta$	$I_\eta(\text{amu } \text{Å}^2)$	$\tilde{c}_l^\eta(0)$	$c_l^\eta(0)$
1	x	0.59	0.985	1.000
1	y	1.93	0.972	1.001
1	z	1.33	0.975	1.001
2	x	0.59	0.956	1.001
2	y	1.93	0.920	1.000
2	z	1.33	0.928	1.001

values of the Kubo-transformed orientational correlation functions at time zero. As we have already noted in connection with the  $\eta=z$  results in Fig. 1, the RPMD values for  $\tilde{c}_l^\eta(t)$  are exact when  $t=0$  and so it is correct that these values in Table III deviate from unity. We further note that the amount of deviation is correlated with the moments of inertia around the principal axes, because the orientation of a particular axis exhibits greater quantum dispersion when the remaining two axes have lower moments of inertia.

The final column in Table III reports the values of the standard orientational correlation functions at time zero,  $c_l^\eta(0)$ , obtained from the RPMD method using Eq. (21). An exact Kubo-transformed quantum correlation function would yield the result  $c_l^\eta(0)=1$ . In all six cases considered in the table, one sees that the RPMD approximation passes this test with an error of at most 0.1%. It is particularly encouraging that the results for the second-order orientational correlation functions (which involve cross terms as well as autocorrelated contributions) remain excellent. We stress that because the real part of  $c_l^\eta(0)$  includes contributions from  $\tilde{c}_l^\eta(t)$  at all times [via Eq. (21)], this is a genuine test of the real-time orientational dynamics obtained from the RPMD approximation.

The success of these sum-rule tests is particularly interesting because the RPMD method is known to fare poorly in strongly quantum-mechanical situations for correlation functions that involve nonlinear functions of coordinate operators. A recent example is provided by the inelastic neutron scattering from liquid parahydrogen at 14 K.<sup>24</sup> Although it does well for low-momentum transfers where the correlated density operators are approximately linear functions of the coordinates, moment tests analogous to those in Table III have shown that the direct RPMD approximation to the self-part of the Kubo-transformed intermediate scattering function becomes quite inaccurate in the impulsive (high-momentum transfer) regime.<sup>24</sup>

The interesting question, therefore, is why the present moments of the Kubo-transformed orientational correlation functions of liquid water are obtained as accurately as they are (to within 0.1%). This is certainly not because the orientational correlation functions  $\tilde{c}_1^\eta(t)$  and  $\tilde{c}_2^\eta(t)$  are well suited to calculation by RPMD, since it is clear from the discussion

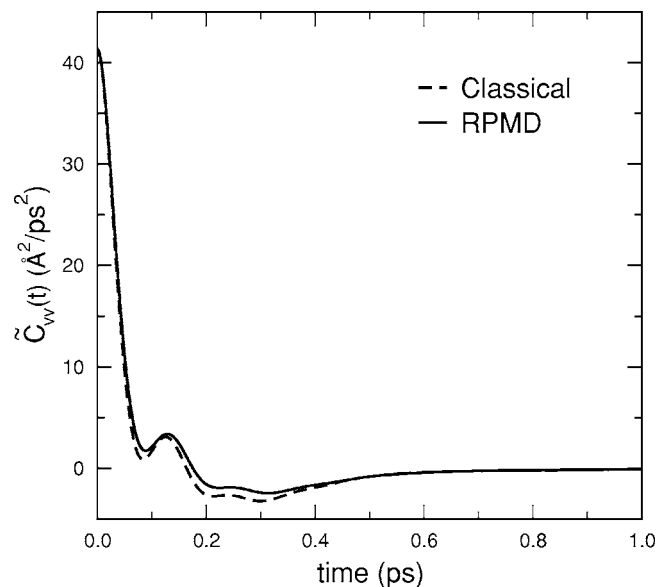


FIG. 3. Kubo-transformed velocity autocorrelation functions for SPC/E water at the  $T=298$  K,  $\rho=0.998$  g cm $^{-3}$  state point, obtained from the classical and RPMD simulations of a system of 512 water molecules.

in Sec. II B (and Ref. 36) that they are not. It must therefore be associated with the fact that liquid water at 298 K is far less quantum mechanical than liquid parahydrogen at 14 K. The RPMD approximation becomes exact in the classical (high-temperature) limit even for correlation functions involving nonlinear operators,<sup>21</sup> and ambient water is evidently close enough to this limit for the approximation to work very well indeed.

### C. Translational motion

Having thus verified that the RPMD method is capable of providing a reasonable description of quantum-mechanical effects in the dynamics of liquid water, let us now move on to consider the translational motion in the liquid embodied in the center-of-mass velocity autocorrelation function in Eq. (2).

The RPMD approximation to this Kubo-transformed autocorrelation function is compared with the purely classical ( $n=1$  bead) approximation in Fig. 3, again for a system of 512 water molecules. One sees from this figure that, for this less quantum-mechanical property, the differences between the RPMD and classical results are considerably smaller than they were for the orientational correlation functions in Fig. 1. However, one also sees that there is a systematic difference that arises from the quantum statistical effects included in RPMD: the classical velocity autocorrelation function is smaller than the RPMD velocity autocorrelation function at all times. This is consistent with the results of an earlier study that used the CMD method and a different intermolecular potential.<sup>17</sup>

The clear implication of this systematic difference is that the self-diffusion coefficient  $D$  obtained from the RPMD simulation will be larger than that obtained from the classical simulation [see Eq. (1)]. That this is the case is demonstrated in Table IV, which lists the diffusion coefficients obtained in the two simulations as a function of the system size (from

TABLE IV. Calculated self-diffusion coefficients for SPC/E water (in  $\text{\AA}^2/\text{ps}$ ).  $N$  is the number of water molecules in the simulation.  $L$  is the side length of the cubic simulation box. The numbers in parentheses after the tabulated diffusion coefficients are the standard errors in the last digit from our five statistically independent calculations. The values in the last row were obtained from the linear regressions in Fig. 4.

$N$	$L$ ( $\text{\AA}$ )	Classical $D$	RPMD $D$	RPMD/Classical
216	18.64	0.242(3)	0.343(2)	1.42
343	21.74	0.250(2)	0.358(2)	1.43
512	24.85	0.254(1)	0.365(2)	1.44
$\infty$	$\infty$	0.29(1)	0.43(1)	1.48

216 to 512 water molecules). It can be seen from this table that the RPMD diffusion coefficient is larger than the classical diffusion coefficient by a factor of between 1.4 and 1.5. It is also clear that, unlike the orientational relaxation times reported in Table II, the self-diffusion coefficients calculated using the two methods increase quite significantly with an increase in the system size.

The reason for this system-size dependence of  $D$  is well established. As was first shown by Dünweg and Kremer,<sup>48</sup> and has recently been reiterated by Yeh and Hummer,<sup>49</sup> the leading system-size dependence of the calculated diffusion coefficient will be given by the hydrodynamic relation

$$D(L) = D(\infty) - \xi \frac{k_B T}{6\pi\eta L}, \quad (26)$$

where  $\eta$  is the shear viscosity,  $L$  the length of the simulation cell, and  $\xi$  a numerical coefficient that depends on the geometry of the simulation<sup>50</sup> (with  $\xi \approx 2.837297$  for a cubic cell<sup>50,51</sup>).

As Yeh and Hummer have emphasized,<sup>49</sup> the vast majority (>80%) of the correction for finite-size effects in Eq. (26) comes from the fact that the average momentum of the atoms in the simulation must be set equal to zero to satisfy Newton's third law. This clearly restricts the motion of the atoms in a small simulation cell more so than in a large one, leading to an increase in the calculated diffusion coefficient with increasing system size. A point we made in our recent study of liquid parahydrogen<sup>23</sup> is that there is no reason why the same argument, nor indeed the entire hydrodynamic argument that leads to the more precise result in Eq. (26),<sup>48,49</sup> should not also apply to an exact quantum-mechanical (or an approximate RPMD) simulation. The calculated RPMD self-diffusion coefficient of liquid parahydrogen does, in fact, satisfy Eq. (26) extremely well.<sup>23</sup>

Figure 4 shows that the equation is also satisfied to within the statistical accuracy of the present classical and RPMD simulations of SPC/E water. This figure plots the diffusion coefficients in Table IV as a function of  $L^{-1}$ . One sees that both (classical and RPMD) simulations obey Eq. (26) with a shear viscosity  $\eta$  that is approximately independent of the system size. That this is also true of purely classical molecular-dynamics simulations of TIP3P water<sup>2</sup> was demonstrated in the recent paper by Yeh and Hummer.<sup>49</sup> The shear viscosities obtained from the slopes in Fig. 4 are 0.38 g m $^{-1}$  s $^{-1}$  in the RPMD calculations and 0.64 g m $^{-1}$  s $^{-1}$  in the classical limit. For comparison with these values, the

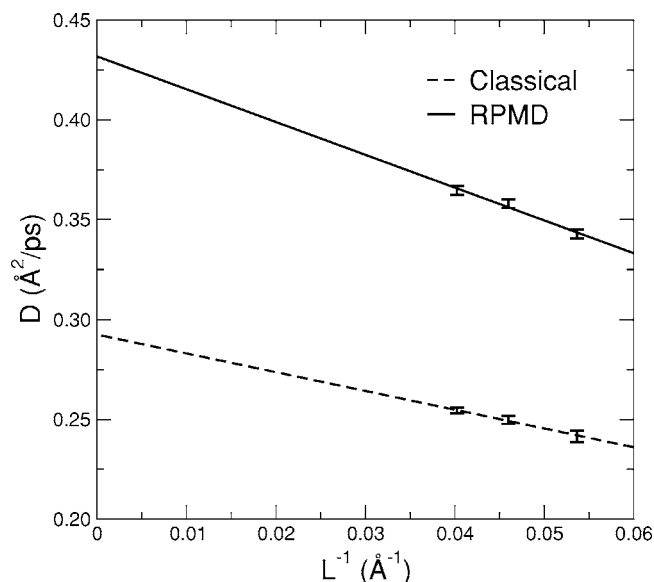


FIG. 4. System-size scaling of the classical and RPMD self-diffusion coefficients for SPC/E water at the  $T=298$  K,  $\rho=0.998$  g cm $^{-3}$  state point, showing the extrapolation to infinite system size.

experimental shear viscosity of ambient water is<sup>52</sup> 0.89 g m $^{-1}$  s $^{-1}$ , and a classical molecular-dynamics simulation of TIP3P water gives<sup>49</sup>  $\eta=0.31$  g m $^{-1}$  s $^{-1}$ . The values of  $D(\infty)$  obtained from the present classical and RPMD simulations of SPC/E water are listed in the final row of Table IV.

#### D. Discussion

The results for the orientational and translational motions in liquid water we have just presented have a natural physical interpretation. Within a simple Stokes-Einstein model, one would expect the self-diffusion coefficient of a molecular liquid to be inversely proportional to, and the orientational relaxation times directly proportional to, the liquid viscosity.<sup>53</sup> According to the slopes of the lines in Fig. 4, and the hydrodynamic explanation for these slopes in Eq. (26), the quantum-mechanical effects included in RPMD decrease the viscosity of ambient SPC/E water from the value obtained in the classical limit by a factor of around 2/3. This is consistent with the decrease in the orientational relaxation times in Table II by approximately the same factor and the increase in the diffusion coefficients in Table IV by a factor of around 3/2.

The upshot is therefore simply that quantum fluctuations disrupt the hydrogen bonding in SPC/E water and make it approximately one-third less viscous than it is in the classical limit. This reduction in the viscosity speeds up both the orientational and the translational motions of the molecules in the liquid. The results of several earlier studies in which quantum effects have been included using other empirical potential models can also be explained in the same way. The precise amount by which the self-diffusion coefficient increases on including quantum effects depends on the interaction potential and the approximate dynamical method employed, but it has never been found to be smaller than a factor of 1.4 (Ref. 15) or larger than a factor of 2.0.<sup>20</sup>

As has recently been shown in classical molecular-dynamics simulations of TIP3P water,<sup>49</sup> and as we have confirmed here in the present simulations of the SPC/E model, there is also a significant additional increase in the self-diffusion coefficient over that obtained in a small simulation when one extrapolates to the limit of an infinite system size (see Fig. 4). When combined with the reduction in the viscosity owing to quantum fluctuations, this results in a quantum diffusion coefficient for the infinite liquid that is substantially larger than that obtained in a typical classical molecular-dynamics simulation. For example, one sees from Table IV that the RPMD estimate of the self-diffusion coefficient of ambient SPC/E water is 0.43  $\text{\AA}^2/\text{ps}$ , whereas a classical simulation of a system of 216 molecules gives a value of 0.24  $\text{\AA}^2/\text{ps}$ . In this case, roughly half of the increase in the self-diffusion coefficient comes from quantum effects and the remainder from the extrapolation to infinite system size.

Since the vast majority of the (very many) computational studies of liquid water that have appeared over the last four decades have been based on the classical molecular dynamics of a (typically rather small) periodic system, the implications of this result are quite profound. The experimental self-diffusion coefficient of ambient water<sup>54</sup> (0.23  $\text{\AA}^2/\text{ps}$ ) is one of the key quantities that has been (and is still being<sup>8</sup>) used to assess the quality of water interaction potentials. According to classical molecular-dynamics simulations of a system of 216 water molecules at 298 K, the SPC/E potential reproduces this quantity rather well.<sup>3,4</sup> However, it can be seen from the results in Fig. 4 and Table IV that when quantum-mechanical and finite-size effects are taken into account this potential overestimates the experimental diffusion coefficient by a factor of nearly 2.

The present results are also relevant to those of a very recent *ab initio* molecular-dynamics study of liquid water at 315 K.<sup>55</sup> This study employed the Becke-Lee-Yang-Parr<sup>56,57</sup> (BLYP) density functional in a number of independent simulations of systems of 64 and 128 water molecules. The resulting self-diffusion coefficient was found to be  $0.04 \pm 0.02$   $\text{\AA}^2/\text{ps}$ —nearly an order of magnitude smaller than the experimental value of 0.35  $\text{\AA}^2/\text{ps}$  at 315 K.<sup>58</sup> Insofar as we can tell from the present results, quantum-mechanical effects in the nuclear motion and finite-size effects are unlikely to be the only causes of such a large discrepancy. However, it is clear that if these effects were included in the *ab initio* molecular-dynamics simulations they would each make quite a significant contribution to the calculated self-diffusion coefficient and bring it closer to the experimental result.

#### IV. CONCLUSIONS AND FUTURE WORK

In this paper, we have presented a detailed study of the translational and orientational motions in ambient SPC/E water using the recently developed ring-polymer molecular-dynamics (RPMD) method.<sup>21–25</sup> We have calculated orientational relaxation times and self-diffusion coefficients that are consistent with those found in a number of earlier approximate quantum-mechanical studies.<sup>15–20</sup> In addition, we have



presented some sum-rule tests which suggest that the RPMD approximation provides a reliable description of the quantum effects in the ambient liquid, and we have investigated the system-size dependence of our computed results.

Our main conclusion is that quantum effects in the nuclear motion and finite-size effects in the translational diffusion are too large to be neglected in simulations of liquid water. In particular, we have shown that these effects combine to increase the self-diffusion coefficient of ambient SPC/E water by a factor of nearly 2 over the value obtained from a classical molecular-dynamics simulation of 216 water molecules. It is clear that classical molecular-dynamics simulations of systems of this sort of size do not therefore provide a very reliable way to assess the accuracy of water interaction potentials.

Since the SPC/E potential gives a rather poor description of the dynamics of liquid water when quantum fluctuations and finite-size effects are taken into account, one wonders whether any of the (many) other water interaction potentials that have been proposed over the years will fare any better. We suspect on the basis of the present results that at least one of the proposed (effective) interaction potentials will. Watanabe and Klein (WK) have developed a potential that accounts correctly for mean-field self-polarization and so gives a good description of the static dielectric properties of the ambient liquid.<sup>4</sup> However, according to classical molecular-dynamics simulations of a system of 216 water molecules, this potential gives a self-diffusion coefficient that is approximately half of the experimental value and a NMR relaxation time that is too large by a factor of  $\sim 3/2$ .<sup>4</sup> We anticipate on the basis of our present results for SPC/E water that combining quantum-mechanical and finite-size effects with the WK potential will rectify both of these deficiencies and lead to much better agreement with experiment.

It will be interesting in future work to see whether or not this is the case, and also to apply the RPMD method to a flexible water model so as to assess the importance of quantum-mechanical effects in the higher-frequency intramolecular vibrations (for example, by comparing the classical and RPMD simulations of the liquid water infrared absorption spectrum). A key point here is that the coupling between the intramolecular and intermolecular motions has recently been shown to lead to quite a significant quantum effect on the structure of liquid water in Car-Parrinello PIMD simulations of H<sub>2</sub>O and D<sub>2</sub>O.<sup>59</sup> This coupling may well lead to a quantum effect in the liquid dynamics that goes beyond what we have seen in the present rigid-body simulations. It will also be interesting to see what effect the quantum fluctuations included in RPMD have on the hydration dynamics of simple ions and polar molecules.

## ACKNOWLEDGMENTS

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- <sup>36</sup>This is certainly true for flexible water molecules. However, the situation is somewhat different when rigid-body constraints are applied, as in the present simulations of SPC/E water. With these constraints, the unit vectors along the in-plane inertial axes ( $x$  and  $z$ ) of a given water molecule become linear functions of its Cartesian atomic coordinates, and the unit vector along the out-of-plane ( $y$ ) axis becomes a quadratic function of these coordinates. We have glossed over this subtlety in the text because it does not make any difference to our argument. The reason why the RPMD method works best for linear operators is that it gives the exact quantum-mechanical Kubo-transformed correlation function for a harmonic potential when one or other of the correlated operators is a linear function of the coordinates (see Ref. 21). The RPMD result is only approximate for nonlinear operators, and it is also only approximate for correlation functions involving linear operators when holonomic constraints are applied to the dynamics of an otherwise harmonic system. The orientational correlation functions  $\bar{c}_i(t)$  are thus expected to provide a challenging test of the RPMD approximation in both flexible and rigid-body simulations.
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