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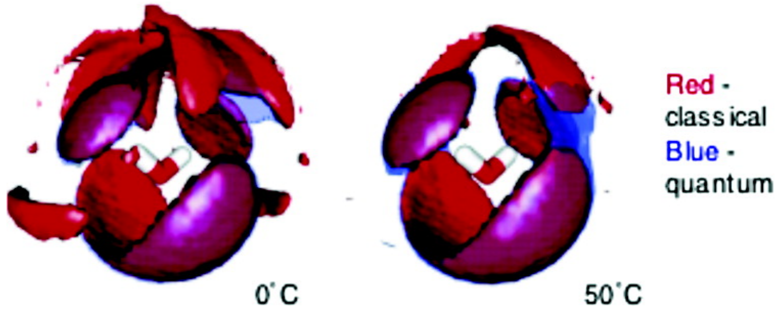

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Temperature Dependence of Quantum Effects in Liquid Water

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Abstract: Quantum and classical simulations are carried out on model water systems over a wide range of temperatures, from 100 to −35 °C. A detailed examination of the equilibrium and dynamical properties of liquid water is presented, together with a discussion of the interplay between quantum mechanical tunneling and dynamics. The study shows that quantum effects are essential for a description of the dynamical behavior of liquid water, particularly in the low-temperature (supercooled) region. The similarities and differences between quantum effects and the effects associated with increasing the temperature are explicitly characterized.

I. Introduction

Despite the enormous literature accumulated on the study of liquid water, its equilibrium and dynamical properties remain the focus of much research. Since the differences in the equilibrium properties of H_2O and D_2O have a quantum origin, quantum effects must have some impact in liquid water. To assess the relevance of the proton uncertainty in the properties of liquid water, a number of path integral simulations have been carried out to date[1−7] using a variety of methods and models. Equilibrium path integral Monte Carlo (PIMC) and path integral molecular dynamics (PIMD) simulations on rigid[1,3] and flexible water[2,4] models offered the first insights into the impact of quantum effects on structural properties and energy. Quantum liquid water was found to be less structured and with somewhat higher (7−9%) intermolecular energy than classical liquid water.[1−4] Kuharsky and Rossky[1] suggested that the structural properties of quantum liquid water at room temperature were similar to the structural properties of classical water 50 °C hotter. This analogy, which has been verified by other authors,[1−7] is a useful way to illustrate, at least, the qualitative importance of quantization in liquid water. In addition, information on the changes occurring in the dynamical properties of liquid water systems when quantum mechanics is taken into account has become available within the past decade.[5−9] Several studies[5−7] have indicated that quantum effects are very important in the dynamical properties of liquid water at room temperature, where quantities such as the self-diffusion coefficient and relaxation times were shown to be significantly affected by quantization. Moreover, it has been demonstrated that whereas classical simulations[10] with simple model potentials for water are unable to reproduce isotopic effects in the dynamical properties, quantum simulations[7] can successfully reproduce the experimentally observed shifts.

Changes in temperature can be expected to modify the influence of quantization. In the path integral representation of statistical mechanics,[11,12] this is clearly seen by noting that in the limit $\beta \to 0$, where $\beta = 1/kT$, the imaginary time (τ) "trip" collapses to 0 (since the path integral representation of statistical mechanics is recovered by using the identity, $\tau = -i\beta\hbar$), and the quantum mechanical partition function approaches the classical one. In the discretized path integral picture,[12] the harmonic interaction between "beads" becomes dominant, and the particle's uncertainty shrinks to 0 in the $\beta \to 0$ limit. Furthermore, the liquid water results of Guillot and Guissani,[6] obtained with a Feynman−Hibbs effective potential, suggest that the impact of quantum effects on the self-diffusion coefficient at lower temperatures is even more pronounced than at room temperature, in agreement with expectations. The study of Guillot and Guissani[6] is the only work to date to consider temperature dependence.

In this paper, we present a detailed examination of the structure and dynamics of quantum liquid water over a wide range of temperatures and explore the interplay between structure and dynamics in the context of "effective tunneling". The discussion focuses on two issues: the increasing importance of quantum effects in equilibrium and dynamical properties with decreasing temperature, and the analogy (and distinction) between quantum effects and temperature changes. We demonstrate that quantum effects are an essential component of the

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Table 1. Details of the Present Classical and Quantum Liquid Simulations of TIP4P Water

T (°C)	system	run length (ns)	density (g/cm^3)
−35	classical	2	0.973250[a]
	quantum	1	
−20	classical	1.6	0.993490[b]
	quantum	1	
0	classical	1	0.999868[b]
	quantum	1	
25	classical	0.4	0.997075[b]
	quantum	0.5	
50	classical	0.4	0.988066[b]
	quantum	0.25	
100	classical	0.4	0.958384[b]
	quantum	0.25	

[a] From refs 14 and 15. [b] From ref 16.

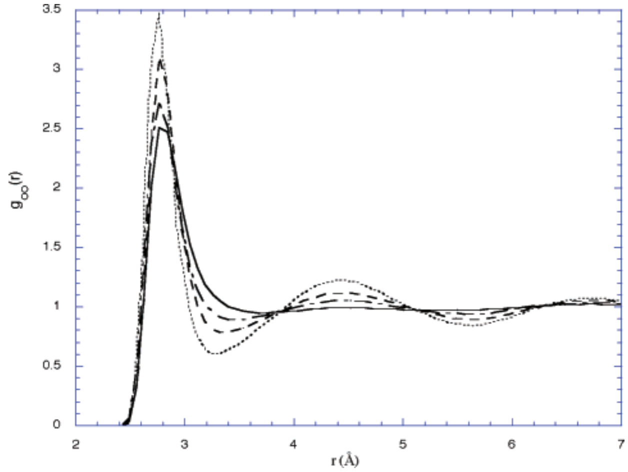

Figure 1. Oxygen−oxygen radial distribution function of liquid TIP4P water at −20 and 50 °C. The dotted, dashed, dashed-solid, and solid lines correspond to the −20 °C classical, −20 °C quantum, the 50 °C classical, and 50 °C quantum simulation results, respectively.

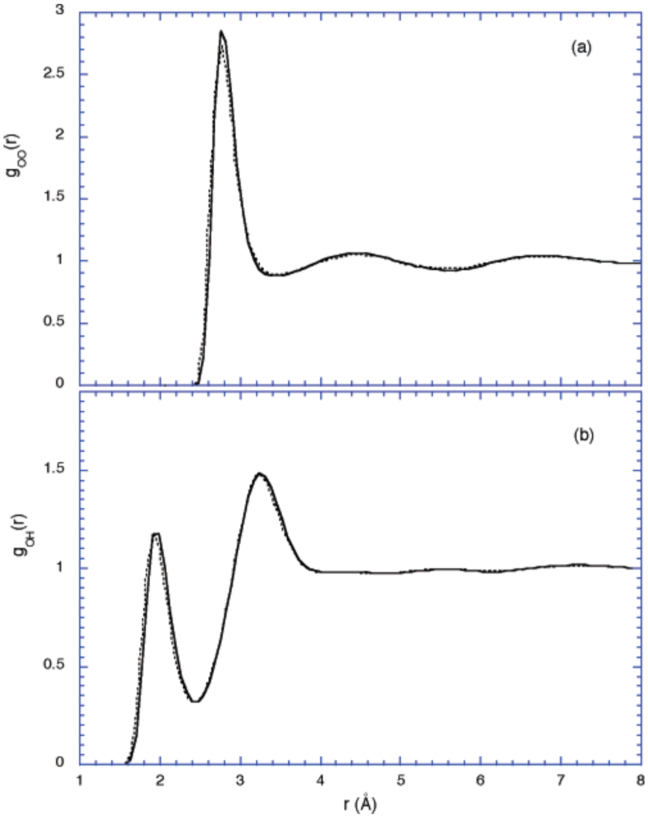

Figure 2. Oxygen−oxygen (a) and oxygen−hydrogen (b) radial distribution functions of liquid TIP4P water at 0 and 50 °C. The solid lines correspond to the quantum simulation results at 0 °C, while the dotted lines correspond to classical results at 50 °C.

description of molecular behavior in liquid water, particularly at lower temperatures, and that they can be only qualitatively captured by rescaling potentials. We remark that although the "model" experiment carried out in this study, where quantum and classical systems characterized by the same interaction potential are compared, has no real analogue, it is nonetheless extremely useful and insightful since it directly probes the effect of interest. The validity of the present approach has been previously verified[7] by its ability to reproduce known isotope effects in liquid water.

This article is organized as follows. In Simulation Details, we present the methods used for the simulations; in Results and Discussion, we show and discuss our results, and finally, Conclusions are given in section IV.

II. Simulation Details

Quantum and classical simulations were carried out on the rigid TIP4P water model[13] over a range of temperatures, from 100 to −35 °C. The classical simulations were realized with a standard molecular dynamics code, and the quantum simulations were performed via rigid body centroid molecular dynamics (CMD),[7,9] where only the rotational degrees of freedom of the water molecules have been quantized. The computational details were identical to those given in ref 7. The run lengths and the (experimental) densities used in the simulations are given in Table 1. The values at 25 °C (results from ref 7) have been included for completeness. It is important to note that the length in real time of the quantum simulations at 0, −20, and −35 °C was 1 ns. These relatively long simulation times are reflective of the computational efficiency of the present (rigid-body) approach. To help achieve these long runs, the evaluation of the forces and torques for each bead was performed in parallel in the simulation code by using the Open-MP protocol.

III. Results and Discussion

A. Equilibrium Properties. The oxygen−oxygen radial distribution functions (RDFs) at −20 and 50 °C for classical and quantum liquid water are presented in Figure 1. The classical results reveal that there is a very strong temperature dependence of the maximum of this function at 2.8−2.9 Å (see also Figure 5 in ref 7). Although both maxima in the classical results decrease with quantization, the effect of the softening of the structure is more pronounced at the lower temperature. At 50 °C, while the classical $g_{OO}(r)$ retains some structure, the quantum radial distribution function exhibits only a "nearest neighbor" first peak, which indicates that structural quantum effects are still significant at this temperature. The oxygen−hydrogen RDFs (not shown), which more directly probe the hydrogen bonding in these systems, confirmed the observations made in Figure 1.

A direct examination of the analogy between quantum and temperature effects is made in Figure 2, where the RDFs from quantum simulations at 0 °C are compared with the RDFs of classical liquid water at 50 °C. The functions exhibit very similar behavior, in agreement with Kuharsky and Rossky's observations[1]. This constitutes further clear evidence that quantum effects in liquid water are significant. The quantum oxygen−oxygen RDF at 0 °C has a slightly higher maximum at ∼2.8 Å

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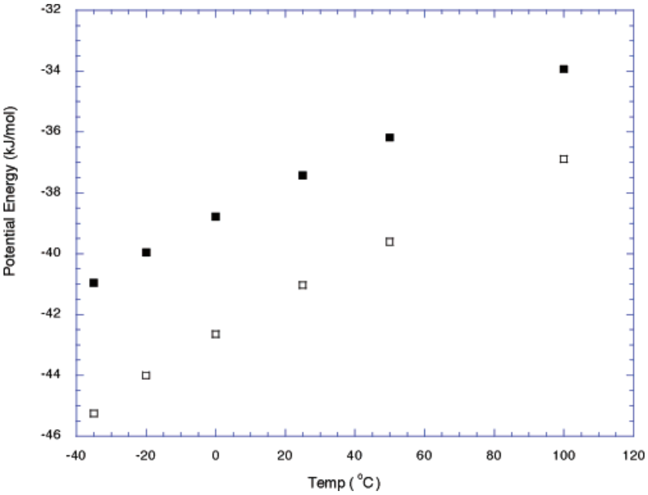

Figure 3. Average intermolecular potential energies (in kJ/mol) as a function of temperature. The solid squares are values from the quantum simulations, and the open squares are the classical results.

in comparison with the classical oxygen−oxygen RDF at 50 °C. The first peak in the quantum oxygen−hydrogen RDF at 0 °C, however, appears shifted slightly toward larger radii in relation to the classical RDF at 50 °C. These differences suggest that although the analogy is qualitatively valuable, its quantitative implications may change with the property under examination. We will explore this issue in further detail below.

The values obtained for the average potential energy in the classical and quantum simulations are plotted in Figure 3 as a function of temperature. At all temperatures, the quantum energy is higher than the classical one, and the difference between them increases as temperature decreases. Interestingly, the energy difference, quantum − classical, grows almost linearly in this temperature range, indicating a consistently smaller heat capacity for the quantum system, in agreement with Kuharsky and Rossky results.[1] It is easily observed from Figure 3 that the average energy from the quantum simulation at −35 °C is very similar to the classical result at 25 °C, suggesting a temperature "shift" due to quantization of 60 °C for this property. This observation again agrees with the analogy between the impact of quantum effects on the equilibrium or structural properties and an apparent temperature increase,[1] although the shift is somewhat larger than the one found in the RDF comparisons (Figure 2).

It is clear that the differences between the classical and quantum systems are a consequence of the quantum mechanical molecular (orientational) uncertainty of the quantum water molecule. However, it is interesting to note that the quantum mechanical uncertainty does not have a monotonic behavior over this range of temperature, as has been discussed in ref 17. The observed reduction in the quantum mechanical uncertainty at lower temperatures has been demonstrated[17] to be due to the increasing influence of the local molecular structure that more than offsets the direct influence of decreased temperature. This result further emphasizes that care is required when considering quantum effects in liquid water.

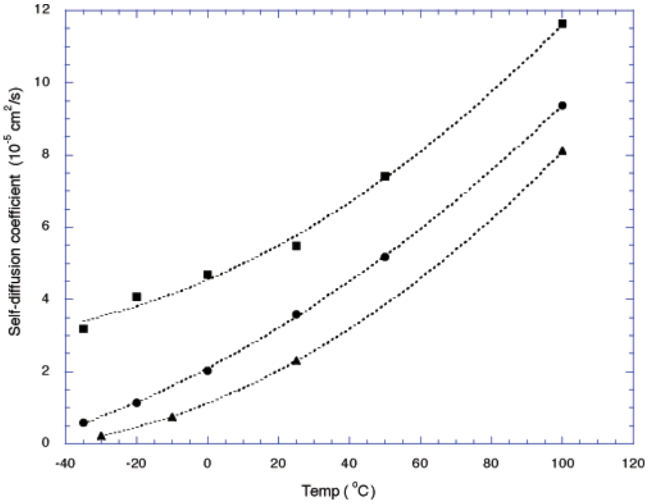

Figure 4. Self-diffusion coefficient as a function of temperature. The circles, squares, and triangles represent the classical, quantum, and experimental values, respectively. Experimental values were taken from ref 18. (The dotted lines are a convenient polynomial fit to aid the eye.)

B. Dynamical Properties. According to previously reported quantum simulations,[5−7] quantization has a significant impact on the dynamical properties of liquid water at 25 °C. It is important then to analyze the temperature dependence of quantum effects in the dynamical properties of model water systems.

Figure 4 shows the values of the self-diffusion coefficients as a function of temperature obtained from the classical and quantum simulations and compares them with experimental results.[18] It is clear that classical simulations with the TIP4P potential overestimate the experimental values at all temperatures. The results from the quantum simulations appear still further above the classical values, as expected. It is apparent from Figure 4 that the classical values decay slightly faster than the experimental ones, whereas the temperature dependence of the quantum results exhibits a greater curvature, more reminiscent of the experimental data.

An interpretation of a systematically higher diffusion coefficient in the quantum simulation in relation to the classical liquid deserves careful examination. In a classical MD simulation, the forces and torques acting on a molecule are just the appropriate derivative of the classical potential evaluated at the position and orientation of the molecule (i.e., $\mathbf{F}_i = (\partial V(\mathbf{r})/\partial \mathbf{r})_{\mathbf{r}_i}$ and $\mathbf{T}_i = (\partial V(\Omega)/\partial \Omega)_{\Omega_i}$). Within the rigid-body−CMD method,[7,9] the forces and torques acting on the centroid are an average of the local (or classical) forces, and torques over the appropriate uncertainty and can be written as[7,9]

$$\mathbf{F}_{c,i} = \langle (\partial V(\mathbf{r})/\partial \mathbf{r})_{\mathbf{r}_i} \rangle_{\Delta\Omega_i} = \langle \mathbf{F}_i \rangle_{\Delta\Omega_i} \qquad (1)$$

and

$$\mathbf{T}_{c,i} = \langle (\partial V(\Omega)/\partial \Omega)_{\Omega i} \rangle_{\Delta\Omega_i} = \langle \mathbf{T}_c \rangle_{\Delta\Omega_i} \qquad (2)$$

where $\Delta\Omega_i$ denotes the orientational uncertainty associated with the centroid i. This averaging process leads to the relationships $|\mathbf{F}_{c,i}| \leq |\mathbf{F}_i|$ and $|\mathbf{T}_{c,i}| \leq |\mathbf{T}_i|$. In other words, the centroid must

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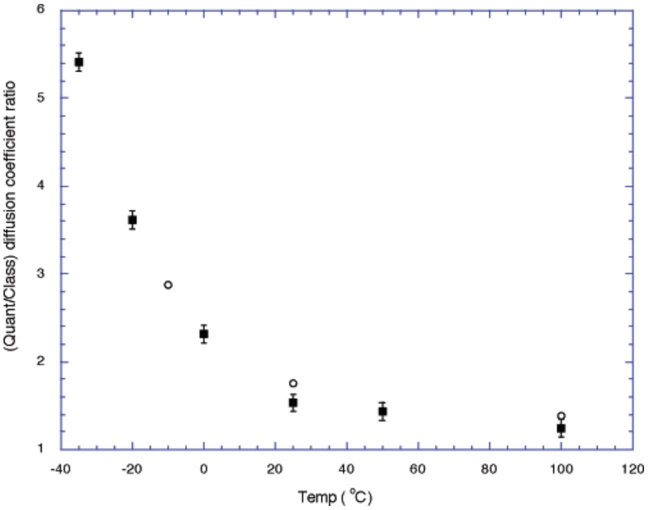

Figure 5. Diffusion coefficient ratio of Quantum/Classical as a function of temperature. The solid squares are the calculated results, whereas the circles are from ref 6.

always experience smaller forces and torques (in magnitude) than a classical particle would, assuming the same configuration and potential for each. This result implies that as the interaction becomes nonlocal, it undergoes an effective "smoothing" (the effective centroid interaction potential could, in fact, be calculated by the appropriate integration of eqs 1 and 2). Therefore, the centroid dynamics evolve on a potential energy surface with higher minima and lower maxima in comparison with the classical potential surface. Since this smoothing only occurs at the scale of the molecular uncertainty, the higher minima can be interpreted as a zero-point vibrational effect and the lower maxima as an "effective tunneling". The latter must certainly be connected to the enhanced dynamical behavior of quantum water in comparison with the model classical liquid.

The impact of quantization in the present context can be perhaps better judged by using the Quantum/Classical diffusion coefficient ratios. Figure 5 shows the behavior of the calculated ratios as a function of temperature, as well as the ratios obtained by Guillot and Guissani.[6] The results obtained here via rigid-body−CMD agree remarkably well with the ones published by Guillot and Guissani,[6] especially considering that this previous work used a different model potential and simulation method. It is clear from Figure 5 that the effect of quantization, which is already more that 50% at 25 °C, grows quite significantly as the temperature of the system decreases. These results suggest that while the diffusive motion in classical dynamics is very significantly impeded by decreasing the temperature, the dynamics in the quantum system is less affected. In other words, while a quantum molecule with a certain kinetic energy is able to escape from the local environment of its neighbors, the classical molecule with that same kinetic energy would remain effectively trapped.

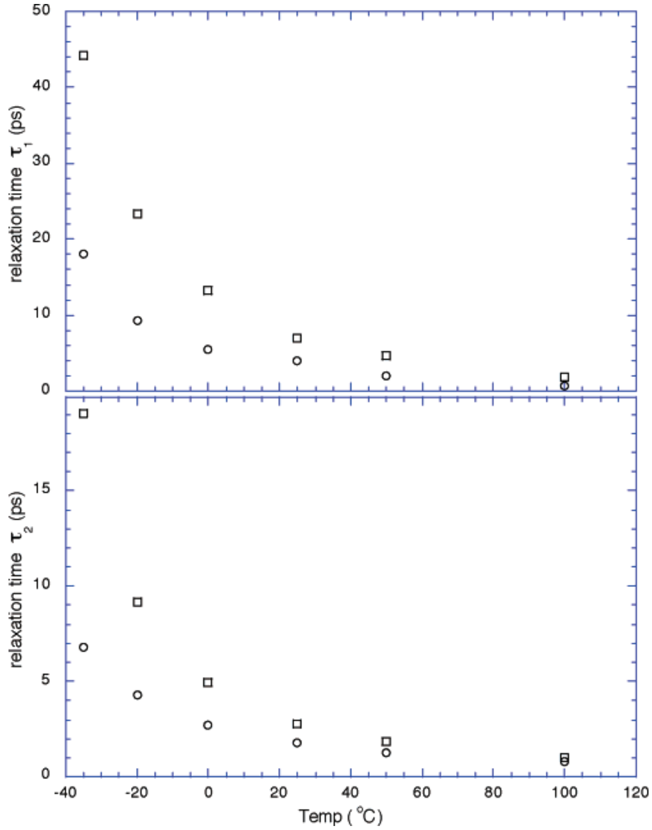

Figure 6. Classical and quantum relaxation times (τ_1 and τ_2) as a function of temperature. The squares and circles correspond to the classical and quantum results, respectively.

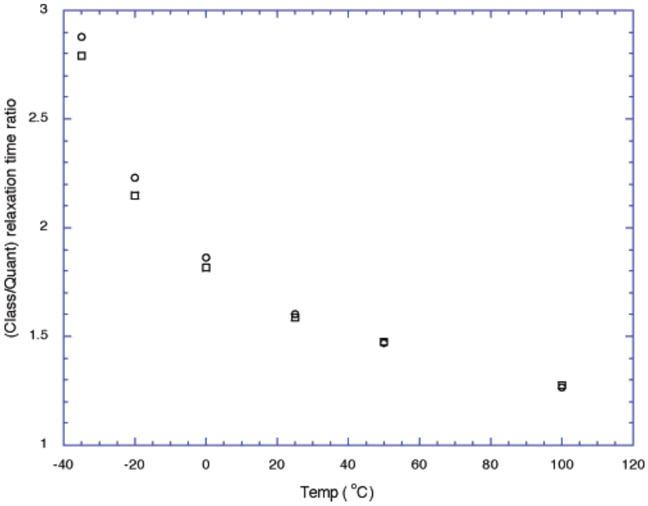

Figure 7. Classical/Quantum relaxation time ratio as a function of temperature. The square and the circles correspond to τ_1 and τ_2 ratios, respectively.

Further confirmation of the increasing importance of quantum effects at lower temperatures can be found by calculating the appropriate orientational relaxation times. Figure 6 shows the classical and quantum relaxation times as a function of temperature. The values of τ_1 and τ_2 were calculated from the corresponding dipole time correlation functions (for the first- and second-order Legendre polynomials, respectively) as described in ref 7. Clearly, the relaxation times are significantly diminished in the quantum liquid, in agreement with the observed faster dynamics. In addition, the quantum effect becomes more important at lower temperatures, as revealed in Figure 7, with the Classical/Quantum relaxation time ratios for τ_1 and τ_2. Despite the difference in the absolute values of τ_1 and τ_2 (as observed in Figure 6), the ratios for τ_1 and τ_2 exhibit very similar behavior. Figure 7 indicates that although the relaxation times grow for both the classical and quantum systems, their growth is much more pronounced in the classical than in the quantum liquid. This result is in agreement with the observations made above with respect to effective tunneling behavior.

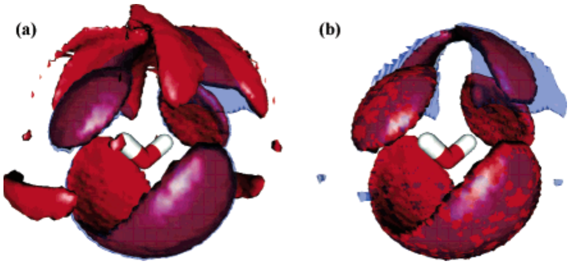

Figure 8. (a) Oxygen−oxygen spatial distribution functions of classical (red) and quantum (semitransparent blue) liquid water at 0 °C. (b) Oxygen−oxygen spatial distribution functions of classical (red) liquid water at 50 °C and quantum (semitransparent blue) liquid water at 0 °C. All isosurfaces represent $g_{OO}(\mathbf{r}_{ij}) = 1.43$.

C. Interplay between Equilibrium and Dynamical Properties. One of the major differences between classical and quantum simulations of water is that the latter allows for tunneling behavior. As has been discussed above, its impact on the dynamical properties of water is significant. An unambiguous identification of the nature of this effective tunneling in water can be carried out with the aid of oxygen−oxygen spatial distribution functions (SDFs), $g_{OO}(\mathbf{r}_{ij})$ (see refs 17, 19, and 20). The effects of quantization have already[1] been compared to the effects associated with increasing the temperature (see Figure 2).

Figure 8 shows the oxygen−oxygen SDFs of quantum liquid water at 0 °C in comparison with the oxygen−oxygen SDFs of classical liquid at 0 (a) and 50 °C (b). All isosurfaces displayed in this figure are at the same threshold value (corresponding to 1.43 times the bulk oxygen density). Figure 8a depicts the effect of quantization on the local structure of water at 0 °C; analogous to the effects described in ref 17 at higher temperature (25 °C), we observed that quantization shifts the first neighbor features slightly outward and has a major impact in the interstitial water region (somewhat above and perpendicular to the plane of the molecule). In Figure 8b, the spatial analogous to Figure 2a, we compare the effect of quantization and the effect of temperature in the structure of liquid water. We see that the increase in temperature (red isosurfaces) shifts the first neighbor features to somewhat larger separations, very similar to the shift produced by quantization (blue isosurfaces in Figure 8b). The gap between the interstitial and the H-bond donor first-neighbor features decreases when the temperature is increased in the classical system, although not to the same extent as demonstrated by the effective tunneling exhibited in the quantum system. The second-neighbor features in classical water are seen in Figure 8 to disappear on increasing the temperature, in qualitative agreement with the diminished structure in the corresponding RDFs. However, the quantum SDF (see Figure 8b) exhibits some second-neighbor features not apparent in the 50 °C classical system. We remark that further detailed comparisons with data at other temperatures (not shown) reveal that the analogy to a temperature shift cannot be improved overall by considering a slightly different value. We can conclude that the effects of quantization are equivalent to a temperature shift (or equivalently a simple rescaling of the water−water interaction potential) only to a first approximation. Such a result is not surprising in light of the potential modifications implied by eqs 1 and 2.

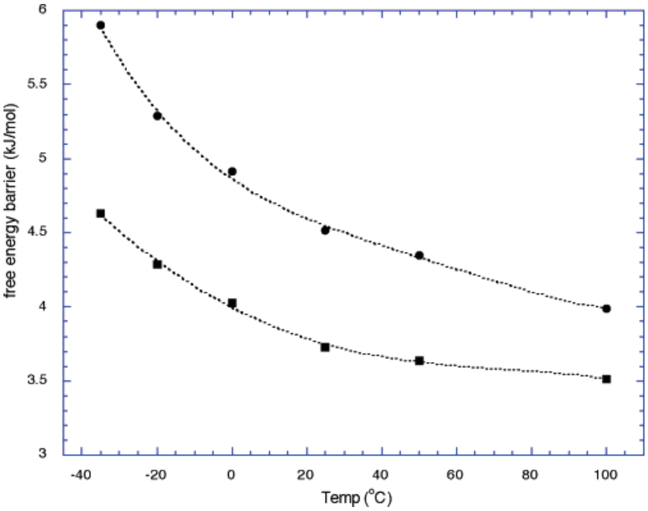

Figure 9. Free-energy barrier associated with molecular displacements across the tunneling region in classical (circles) and quantum (squares) liquid water as a function of temperature (see text).

The spatial distribution function can be related to a free-energy difference by the straightforward generalization of the relationship,[21] $\Delta F = -kT\ln g(r)$, where ΔF becomes the change in free energy associated with the displacement of a molecule initially at infinity (relative to the central molecule) to the position $\mathbf{r}_{ij}$. Therefore, by recording SDF values across the tunneling region, the magnitude of the associated free-energy barrier can be easily estimated. We note that this barrier has been previously shown to represent a principal mechanism for the breaking and making of H-bonds in liquid water.[22−24] Values for this free-energy barrier in the classical and quantum systems are plotted as a function of temperature in Figure 9. It can be clearly seen that the quantum system has, at all temperatures, an effective barrier lower than the classical one, in complete agreement to the concept of tunneling. Additionally, it is observed that the values of the classical system grow more rapidly with decreasing temperature than the quantum results, again confirming that tunneling is becoming more significant at lower temperatures.

IV. Concluding Remarks

In this work, we have explored the relevance of quantum effects in liquid water over a wide range of temperatures, from −35 to 100 °C, through a comparison of classical and quantum molecular dynamics simulation results carried out on the TIP4P water model. In general, the classical simulations are able to capture the qualitative behavior of liquid water over this range of temperatures. However, the consistent increase of the relative effects of quantization, especially in the dynamical properties of liquid water upon supercooling, indicates that while quantum effects are important at 25 °C, their relevance grows dramatically as temperature is decreased. In addition, the similarities and differences between quantum effects and the effects associated with increasing the system's temperature have also been explicitly examined. We have demonstrated that while the effects

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of quantization can be approximately related to a temperature shift, a simple scaling of the water−water interaction potential does not capture the full detail of the phenomenon.

The quantum simulations presented here (carried out in a context of a rigid water model) account for the quantum mechanical uncertainty, which is an inherent property of real water molecules, by including an orientational uncertainty. This orientational uncertainty allows for effective tunneling, thereby, enhancing a water molecule's ability to make and break hydrogen bonds as well as to respond much more rapidly to an evolving local molecular environment. It is also important to point out that since rotational and translational motions are very strongly coupled in liquid water, the orientational uncertainty associated with the molecule has a strong influence on its translational behavior. Therefore, the impact of quantum mechanics manifest in the rotation of a water molecule causes the molecule to diffuse in a way that is (qualitatively similar but) quantitatively different from its otherwise classical behavior.

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