Hydrogen bonding in supercritical water

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We study the hydrogen bonding structure of water models at supercritical conditions by molecular dynamics to directly compare with recent microstructural data obtained by neutron diffraction with isotopic substitution (NDIS) experiments. We also study the angular dependence of the hydrogen–oxygen pair distribution function to gain insight into the hydrogen bonding mechanism in the molecular models for water. The simulation results suggest that the angle-averaged radial distribution function $g_{OH}(r)$ measured by NDIS experiments may not provide a complete picture of the degree of hydrogen bonding.

INTRODUCTION

Supercritical water (water at temperatures above the critical temperature and typically at high pressure) is increasingly attracting scientific and engineering scrutiny because of its importance in many natural situations (such as geothermal formations and deep sea vents) and technological applications (such as process water for power generating facilities and oxidation of organic wastes using supercritical water as the reaction solvent). As a consequence of this interest, in recent years there have been several molecular simulation studies whose goal has been to elucidate the structure and physical properties of supercritical water and supercritical aqueous solutions.\(^1\)\textsuperscript{-7} For the first time, the accuracy of the microstructural information provided by these simulation studies can now be assessed with the recent publication of experimentally measured correlation functions obtained in neutron diffraction with isotopic substitution (NDIS) experiments.\(^\textsuperscript{8}\) A preliminary comparison by Postorino et al.\(^\textsuperscript{8}\) between the NDIS measurements and molecular dynamics (MD) simulation by Cummings et al.\(^\textsuperscript{5}\) suggested that the simple point charge (SPC) model for water\(^\textsuperscript{9}\) predicted more pronounced hydrogen bonding structure than was observed in the NDIS experiments. This conclusion was based on comparing NDIS experiments and MD simulations at quite different state points. In this letter, we compare NDIS experiments and MD simulations at the same state points with a simple point charge (SPC) model for water, SPC\(^\textsuperscript{9}\) in which the molecules are represented as a set of three or four point charges distributed in either a linear, triangular, or tetrahedral arrangement. We find much better agreement with NDIS experiments at the same state points with this model. Based on the simulations, we also present MD simulations for SPCG, a version of the SPC model suggested by Strauch and Cummings\(^\textsuperscript{11}\) which has a dipole moment equal to the bare molecule dipole moment of water. We find much better agreement with NDIS experiments at the same state points with this model. Based on the simulations, we also present evidence that the angle-averaged radial distribution function $g_{OH}(r)$ measured by NDIS experiments does not provide a complete picture of the degree of hydrogen bonding.

INTERMOLECULAR POTENTIALS AND MOLECULAR DYNAMICS SIMULATIONS

The theoretical description of the properties of water have typically been based on intermolecular potential models, such as SPC,\(^\textsuperscript{9}\) in which the molecules are represented as a set of three or four points charges distributed in either a rigid or a flexible geometry plus a non-Coulombic soft contribution (usually Lennard-Jones). While these models are able to capture many of the structural and dynamical properties of water, none of them has built in the specifically directional properties that characterize the hydrogen bond. The molecular simulation of these models therefore portrays the hydrogen bond as a cooperative Coulombic effect that occurs when the oxygen and the hydrogen sites of two different water molecules in the condensed phase approach each other. Even though this picture might be at odds with the traditional one which describes the hydrogen bond as a form of weak covalent bond, there is no evidence of any major flaw or inconsistency in it. Postorino et al.\(^\textsuperscript{8}\) have suggested a way to test the validity of such a model by studying the breakdown of the hydrogen bonding as the water moves from ambient to supercritical conditions and investigating whether the molecular simulation of the model reproduces the structural changes observed in the NDIS experiments.

An important and somewhat surprising feature is that two closely related rigid molecule models for water, the SPC model and the modified SPC model known as SPCE, predict quite different critical points—$T_c\sim587$ K and $\rho_c\sim0.27$ g/cc for the SPC\(^\textsuperscript{12}\) and $T_c\sim625$ K and $\rho_c\sim0.326$ g/cc for the SPCE,\(^\textsuperscript{11}\) the latter being much closer to the real one—even though their density dependence in the correlation functions. The advantage of SPCE over SPC for the purpose of comparison with experiment, including the NDIS experiment, is that since the critical point is so much closer to the real critical point of water, it is meaningful to compare SPCE to experiments at the same absolute state conditions. That is, there is no need to compare theory and experiment at the same reduced state conditions (temperature and density reduced by their critical values) as is the case for SPC.

The simulated supercritical state conditions were those
FIG. 1. Comparison between the experimental and the simulated SPCE and SPCG H–H, $g_{HH}(r)$, radial distribution functions of water at $T=573$ K and $p=0.72$ g/cc. Note that the NDIS results include an intramolecular peak at short range which is not included in the simulation results.

of the NDIS experiments: $T=573$ K and $p=0.72$ g/cc, and $T=673$ K and $p=0.66$ g/cc. The simulation methodology is fully described in Refs. 5 and 7. According to the results at the supercritical condition $T=573$ K and $p=0.72$ g/cc, shown in Figs. 1–3, the SPCE model captures qualitatively the main features of the oxygen–oxygen, oxygen–hydrogen, and hydrogen–hydrogen radial distributions functions, $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$, respectively, for real water, with the main differences observed in $g_{OH}(r)$, where the SPCE model shows a first peak shifted $\sim 0.5$ Å to the left, and $\sim 50\%$ higher than that observed by NDIS. Note, however, that the model describes quite well the position and size of the first valley of $g_{OH}(r)$. We should note that we have also performed simulations of SPC at the same conditions and find essentially no difference from the SPCE results.

DISCUSSION

One feature that makes the SPC and SPCE models accurate at ambient conditions is their effective dipole moments—2.774 D for the SPC and 2.351 D for the SPCE—which are considerably higher than that for the bare dipole moment of a water molecule, 1.85 D. This high value of the dipole moment in SPC and SPCE, which comes about as a result of regarding the point charges as adjustable parameters in fitting to the ambient experimental data, is attributed to polarizability effects present at liquidlike densities. However, at supercritical conditions where the water behaves as a gaslike fluid, the polarization effects are likely to be much less important. Therefore, the bare dipole moment of water appears to be a more appropriate choice for the effective dipole moments for the SPC and SPCE models at supercritical conditions. The model we obtain simply by rescaling the SPC point charges to give the gas phase dipole moment is denoted by the SPCG model. It is encouraging to find that the SPCG model captures the disappearance of the first peak of $g_{OH}(r)$ (Fig. 2), the resulting shoulder has the right size but shifted $\sim 0.5$ Å to the left. The agreement between the simulated and the experimental correlation functions becomes even better for the $g_{HH}(r)$ (Fig. 1), indicating that the rationale behind the charge scaling is correct. The only negative aspect of the SPCG model is that $g_{OO}(r)$ is predicted less accurately than by SPC or SPCE (Fig. 3).

At the second supercritical condition, $T=673$ K and $p=0.66$ g/cc, the SPC and SPCE models accurately predict the position, and qualitatively well the shape of the first two peaks of $g_{HH}(r)$. The difference between the two models is negligibly small, and neither one captures the disappearing (formation of a shoulder) of the first peak of the $g_{OH}(r)$ (Fig. 4). With regard to $g_{OO}(r)$ none of SPC, SPCE, and SPCG predicts the more pronounced shoulder in the NDIS experiments, which appears as a degeneration of the original "bump" at the base of the first peak at ambient conditions. The agreement between the $g_{OH}(r)$ (Fig. 4) and $g_{HH}(r)$ predicted by the SPCG model and the NDIS becomes even better at these conditions.

Because the SPC and SPCE models predict very similar structures, and the SPCG model gives the best agreement with the NDIS results for supercritical water, we now exam-
The temperature/density effect on the hydrogen bonding structure predicted by the SPCE and SPCG models when we move from ambient to supercritical conditions. We define a new correlation function, \( g_{OH}(r) \), so that it is the relative (to the bulk value) probability of finding two water molecules separated by distance \( r \) in the geometric configuration of a hydrogen bond according to the definition of Mezei and Beveridge\(^{14} \) used by Cummings and co-workers in their study of supercritical water.\(^{36} \) It is thus a specific angular slice of \( g_{OH}(r) \) which contributes \( \frac{1}{2} \) of the total value of \( g_{OH}(r) \)\(^{13} \) [i.e., \( g_{OH}(r) = \frac{1}{2} g_{HB}(r) + \frac{1}{2} g_{NHB}(r) \) where \( g_{NHB}(r) \) is the relative (to the bulk value) probability of finding two water molecules separated by distance \( r \) not in the geometric configuration of a hydrogen bond]. In Fig. 5 we show the behavior of the correlation functions \( g_{HB}(r) \) and \( g_{OH}(r) \) for the SPCE and SPCG models at \( T = 673 \) K and \( \rho = 0.66 \text{ g/cc} \). The very interesting feature we note here is that even though the first peak of \( g_{OH}(r) \) for the SPCE model is reduced by a factor of \( \sim 1.8 \), becomes wider, and is more skewed than that at ambient conditions, its relative size with respect to that for \( g_{OH}(r) \) remains approximately the same as for ambient conditions, i.e., \( \sim 4.3 \). In addition, the second peak in \( g_{OH}(r) \) at ambient conditions disappears as a “flat bump.” Similar behavior is exhibited by the SPCG model which in \( g_{OH}(r) \) has a lower first peak than the corresponding one for SPCE which is very skewed with a clear shoulder, the result of the disappearance of the first peak of the \( g_{OH}(r) \). Yet, the relative strength of the first peak of \( g_{OH}(r) \) for SPCG is \( \sim 4.3 \), i.e., similar to that for the SPCE (and other models).\(^{13} \) This behavior strongly suggests that the temperature/density dependence of \( g_{OH}(r) \) and \( g_{OH}(r) \) are similar, and the relative values of the two correlation functions are insensitive to the magnitude of the Coulombic charges. To see just how insensitive this ratio is, we reduced the dipole moment from 2.274 to 0.0074 D, i.e., \( \sim 250 \) times smaller than the bare dipole moment of water (the SPC0 model). A revealing feature, shown in Fig. 5 is that even for the hypothetical water molecule with practically zero dipole moment, \( g_{OH}(r) \) exhibits a relatively strong \( g_{HB}(r) \) component, even though the first peak of \( g_{OH}(r) \) has disappeared completely. These results suggest two things: first, a definition for hydrogen bonding based solely on geometrical considerations is probably insufficient, since in the case of SPC0 there can be no hydrogen bonding yet the geometrical definition would suggest a measurable degree because of the value of \( g_{OH}(r) \); second, in view of this, one cannot infer the degree of hydrogen bonding with any degree of certainty solely from \( g_{OH}(r) \) alone. As we show elsewhere in greater detail,\(^{13} \) various theoretical models predict similar \( g_{OH}(r) \) but with quite different \( g_{HB}(r) \), thus implying that the degree of hydrogen bonding—even using a purely geometric definition—cannot be inferred from \( g_{OH}(r) \) alone.

We point out one other surprising finding from our simulations, and that is that the SPC and other models predict a counterintuitive density dependence for the \( g_{OH}(r) \) along the isotherm \( T_r = T/773 \)\(^{1.04} \) in the density range \( 1.0 = \rho = p/p_c \approx 2.0 \). At these conditions the height of the first peak of the \( g_{OH}(r) \) decreases from \( \sim 0.95 \) at \( \rho_c = 1.0 \), to \( \sim 0.75 \) at \( \rho_c = 2.0 \). We point this out since Postorino \textit{et al.} \(^8 \) evidently expected that \( g_{OH}(r) \) would increase with density so that O–H correlations between water nearest neighbors should be absent at near-critical densities because, according to the NDIS results, they are already absent at liquidlike densities. However, the corresponding coordination number \( n_{OH}(r) = 4\pi r^2 g_{OH}(r) \) where \( r = 2.5 \text{ Å} \) indicates the location of the first valley of the \( g_{OH}(r) \) predicted by the SPCE model—changes from \( \sim 9 \) at \( \rho_c = 1.0 \) to \( \sim 13 \) at \( \rho_c = 2.0 \), even though the height of the peak of the \( g_{OH}(r) \) decreases as the density increases along the isotherm \( T_r = 1.04 \). This result also suggests that the size of the peak of \( g_{OH}(r) \) may not, in itself, be representative of the strength of the hydrogen bonding.

**CONCLUSIONS**

We have presented molecular simulation results of SPCE water and modifications thereof and compared the resulting structure to NDIS experimental results. Our simulation results indicate that the SPC and SPCE models for water pre-
dict a significant degree of orientational correlation between nearest neighboring water molecules which is consistent with hydrogen-bonded states and which contributes approximately 4 of the total radial distribution function $g_{OH}(r)$, according to the normalization constants of the corresponding correlation functions. This orientational correlation function, $g_{OH}^{BB}(r)$, exhibits a rather strong temperature/density dependence, even though the relative values of $g_{OH}^{BB}(r)$ to $g_{OH}(r)$ in the vicinity of the first peak remain practically unchanged. Because we have found that several different models predict similar $g_{OH}(r)$'s but differing $g_{OH}^{BB}(r)$'s, these results suggest that the interpretation of either the first peak of $g_{OH}(r)$ or its volume integral as representative of the degree of hydrogen bonding may be inappropriate.

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