MOLECULAR DYNAMICS SIMULATION OF SUB-CRITICAL AND SUPERCRITICAL WATER AT DIFFERENT DENSITIES

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Abstract

Interest in both the fundamental and applied chemistry of supercritical water (SCW) has recently increased, especially in environmental science but also because of the possibility in developing a new generation of water-cooled nuclear reactors operating with the coolant at supercritical temperatures. Such a state corresponds to water above its critical temperature: T_c = 373.95 °C, P_c = 22.06 MPa, ρ_c = 0.322 g/cm^3. Controlling the water chemistry of an SCW reactor requires the ability to understand and mitigate the effects of water radiolysis. As experiments at very high temperatures and pressures, and especially beyond the critical point of water, are difficult to perform, computer simulation becomes a very valuable alternative tool of investigation. Preliminary results suggest that a key requirement for predicting water radiolysis in an SCW reactor is to have access to a detailed picture of the heterogeneous molecular structure of SCW, and to see how this influences radiation energy deposition and the subsequent radiolysis reactions. Local density and molecular configurational fluctuations (associated with criticality) are also believed to play a pivotal role in the understanding of the detailed atomistic picture underlying the mechanism of localization of excess electrons in sub-critical water and SCW. Relevant information concerning the microscopic aspects of this particularly interesting molecular system can be gained from all-atomistic computer simulations. In this work, molecular dynamics (MD) simulations with a full description of the atomic interactions through the use of a force field have been carried out on water systems at different densities (0.17, 0.31, and 0.55 g/cm^3) and different temperatures (360 and 400 °C). Having access to a complete molecular description of those systems, radial distribution functions (RDF) can then be computed. Detailed analysis of these RDF reveals the formation of water clusters whose behavior as a function of temperature and density is in agreement with experimental data.

Keywords: Sub-critical and supercritical water, Radiolysis of water, Electron localization, Molecular dynamics, Radial distribution functions, Clusters.

1. Introduction

Sub-critical and supercritical water (SCW), i.e. water at temperatures and pressures near the critical point, has become a very attractive subject of scientific research and industrial application [1]. From an industrial standpoint, its importance lies in the fact that SCW can be used as an alternative single-phase, environmentally friendly "green" reaction medium for the chemical industry [2]. The planned next generation (Generation IV) of water-cooled nuclear reactors can also operate with the coolant at supercritical temperature [3]. From a fundamental point of view, understanding the continuous change with the density for various properties in the sub-critical and SCW regimes is a particularly challenging topic [4-6]. For instance, due to the high compressibility, a small variation in the pressure and temperature leads to significant changes in density, engendering a heterogeneous medium with high and low-density regions [7]. Local density fluctuations in sub-critical water and SCW play a fundamental role in the localization mechanism of excess electrons [8].

Recently, using electron pulse radiolysis techniques, the optical absorption spectra of the hydrated electron (e^{-}_{aq}) in sub-critical and SCW were measured by Jay-Gerin et al. [8] at different temperatures and densities. They found, for all studied densities (0.2–0.65 g/cm^3), that the e^{-}_{aq} absorption maximum shifts to the red with decreasing density. More precisely, the position of e^{-}_{aq} absorption maximum ($E_{A\mathrm{max}}$) varies linearly with density in a double logarithmic plot for the investigated temperatures: 375, 380, 390, and 400 °C. It was also observed that $E_{A\mathrm{max}}$ decreases monotonically with increasing temperature at fixed pressure. However, at fixed density, the variation of $E_{A\mathrm{max}}$ with temperature exhibits a minimum near the critical point. It was argued that the presence of clusters in sub-critical and SCW can act as trapping sites for excess electrons [8]. Moreover, the formation of clusters in SCW was also considered by Tassaing et al. [9] in order to explain the change in the infrared absorption spectra of supercritical water at 380 °C as a function of pressure and density. Experimentally, the development of clusters in supercritical conditions was attributed to the large density fluctuations and the highly disrupted hydrogen-bond network associated with criticality [10]. Using molecular dynamics (MD) simulations in supercritical fluids, it was found that the hydrogen bonding and dipolar interactions strongly increase the local density fluctuations [11]. MD simulation performed with 200 water molecules in the canonical (N,V,E) ensemble revealed that SCW, even at vapor-like densities ($\rho < 0.2$ g/cm^3), can contain quite large molecular clusters [12]. Skarmoutsos et al. [13] employed the time correlation function to study the time evolution of the local density distribution around each molecule in the vicinity of the critical point. This study showed that the bulk density of water influences significantly the effective average local densities in pure SCW.

The MD approach is a powerful tool to better understand the behavior of sub-critical water and SCW, and to create realistic configurations to learn more about the molecular-level mechanisms underlying the localization and hydration of an excess electron at subpicosecond times. This detailed atomistic picture information is not available or difficult to obtain from experimental measurements. The aim of this work was thus to use MD simulations to examine the microstructure of SCW for different densities (0.17, 0.31, and 0.55 g/cm^3) at 400 °C, and sub-critical water at 360 °C and a density of 0.55 g/cm^3, for which experimental data exist [8,14].

2. Simulation details

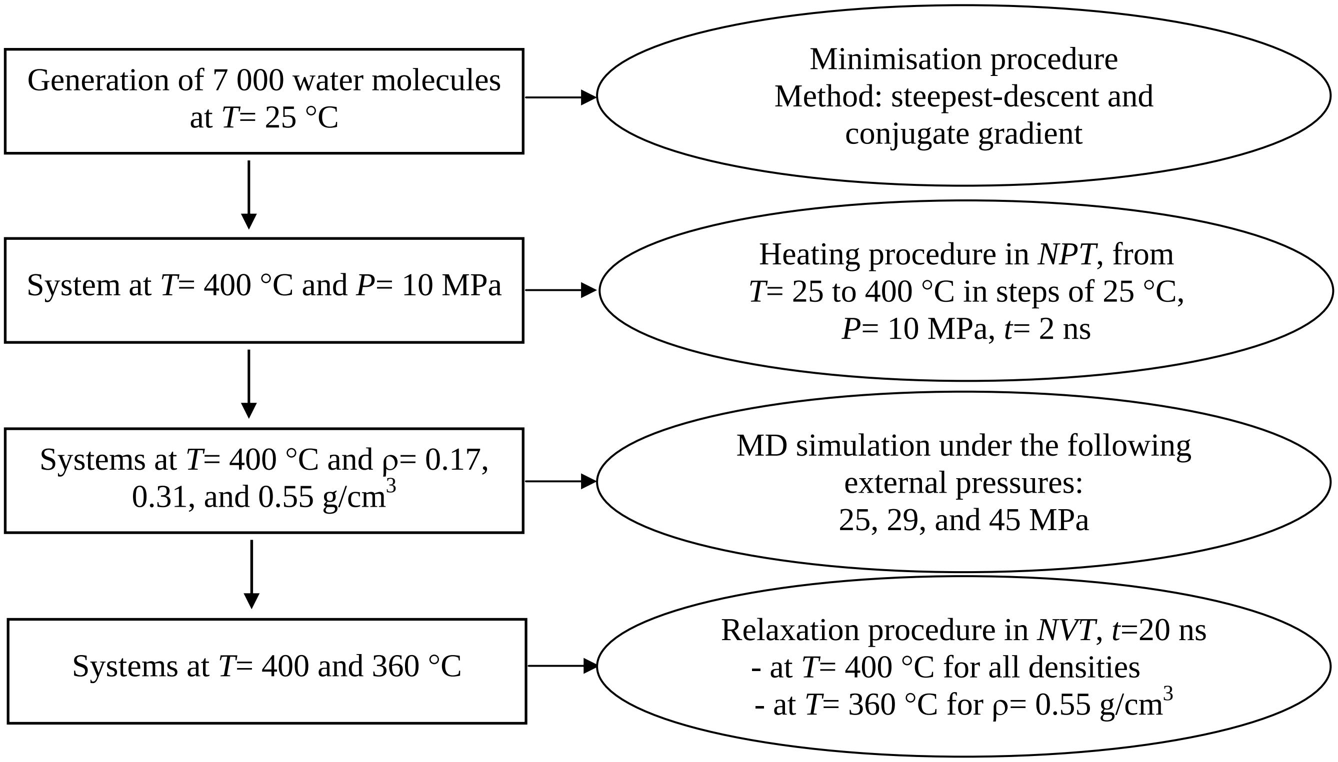
To represent interactions between water molecules, we used the extended simple point charge (SPC/E) potential model [15]. The SPC/E model differs from the original simple point charge (SPC) model of water [16] by inclusion of a self-energy correction. The model pictures a water molecule by three point masses with the O-H distance constrained at 1 Å and the HOH angle equal to the tetrahedral angle, with charges located at the hydrogen and oxygen sites equal to +0.4238 and –0.8476 *e* (*e*: electronic unit charge), respectively. It also includes a repulsion-dispersion term modeled by a Lennard-Jones (LJ) potential. The intermolecular interactions that result from three point charges located at the hydrogen and oxygen atoms are depicted by the following equation:

$$U = \sum_{i>j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} , \qquad (1)$$

where r_{ij} is the non-bonding distance between two atoms i and j, q_i is the partial charge on atom i, and ε_{ij} and σ_{ij} stand for the LJ interaction parameters. The SPC/E force field is considered to accurately describe the structure and the properties of SCW [17]. Moreover, the SPC/E model reproduces with a good agreement the liquid-vapor coexistence curve of water and predicts critical parameters which are very close to experimental data [18].

Simulations have been performed in a cubic box containing N = 7 000 water molecules, with a cutoff radius of 9.5 Å for LJ interactions. It is argued that this number is sufficient to adequately represent the thermodynamic limit ($N \rightarrow \infty$), i.e., to enable the configuration space to be accurately depicted. Periodic boundary conditions (PBC) have been employed. The Ewald summation method was used to calculate long-range electrostatic interactions. To preserve intramolecular constraints, the SHAKE iterative procedure [19] with a relative tolerance of 10^{-4} was used, enabling us to use an integration time step of 2 fs. All MD calculations were performed using the LAMMPS ("Large-scale Atomic/Molecular Massively Parallel Simulator") simulation package [20].

Two configurations have been initially generated using the MSI Materials Studio *Amorphous Cell* interface under normal conditions. A classical minimisation procedure consisting of a series of steepest-descent and conjugate gradient algorithms was then applied to these configurations. The system was thereafter gently heated to T = 400 °C in 25 °C steps under an external pressure of 10 MPa. The MD simulation was carried out for 2 ns in the (N,P,T) ensemble (i.e., constant number of molecules, pressure, and temperature). To keep the system at prescribed temperature and pressure the Nose-Hoover algorithm was employed [21]. We then carried out several simulations using different imposed external pressures. For each external pressure, simulation was carried out until an equilibrated density was reached. Densities of the final systems under external pressures of 25, 29, and 45 MPa have been found to be 0.17, 0.31, and 0.55 g/cm^3, respectively. These densities are in excellent agreement with experiment. An additional relaxation step was imposed to these structures at 400 °C during 20 ns in the N,V,T ensemble (i.e., constant number of particles, volume, and temperature). Finally, another simulation was performed at T = 360 °C using configurations with a density of 0.55 g/cm^3 (Schema 1). The last 10 ns of these runs were used to collect data.



Schema 1: Simulation procedure.

3. Results and discussion

Figure 1 shows water systems over a range of densities: ρ = 0.55, 0.31, and 0.17 g/cm^3 at T = 400 °C. Similar pictures have been obtained for ρ = 0.55 g/cm^3 at T = 360 °C. Figure 1 reveals the three-dimensional (3D) distribution of oxygen atoms in red and hydrogen atoms in white, after 20 ns of equilibration. It also clearly reveals, as the bulk water density decreases, the heterogeneous character of the medium with distinct high- and low-density regions. This water “clustering” behavior is consistent with that observed in previous studies [13] and supports the previously proposed interpretation [8,22] of the role played by those pre-existing molecular clusters or local density fluctuations in the trapping of excess electrons in sub-critical water and SCW. In order to confirm that sub-critical water and SCW are characterized by strong local density fluctuations and that the microstructure is heterogeneous, the projection of the density in the XY plan is shown in Fig. 2. Images observed in Fig. 2 are consequences of the heterogeneity of the systems. From the snapshots shown in this figure, we infer that water molecules form high-density regions separated by low-density regions. Structures observed in Figs. 1 and 2 can be qualitatively understood through intermolecular interactions resulting from the breaking of the hydrogen bonding network [10]. Nevertheless, qualitative and quantitative analysis was performed as it is difficult to draw any firm conclusions by visualization of structures alone. The water center of mass (COM) radial distribution function was used to get more information.

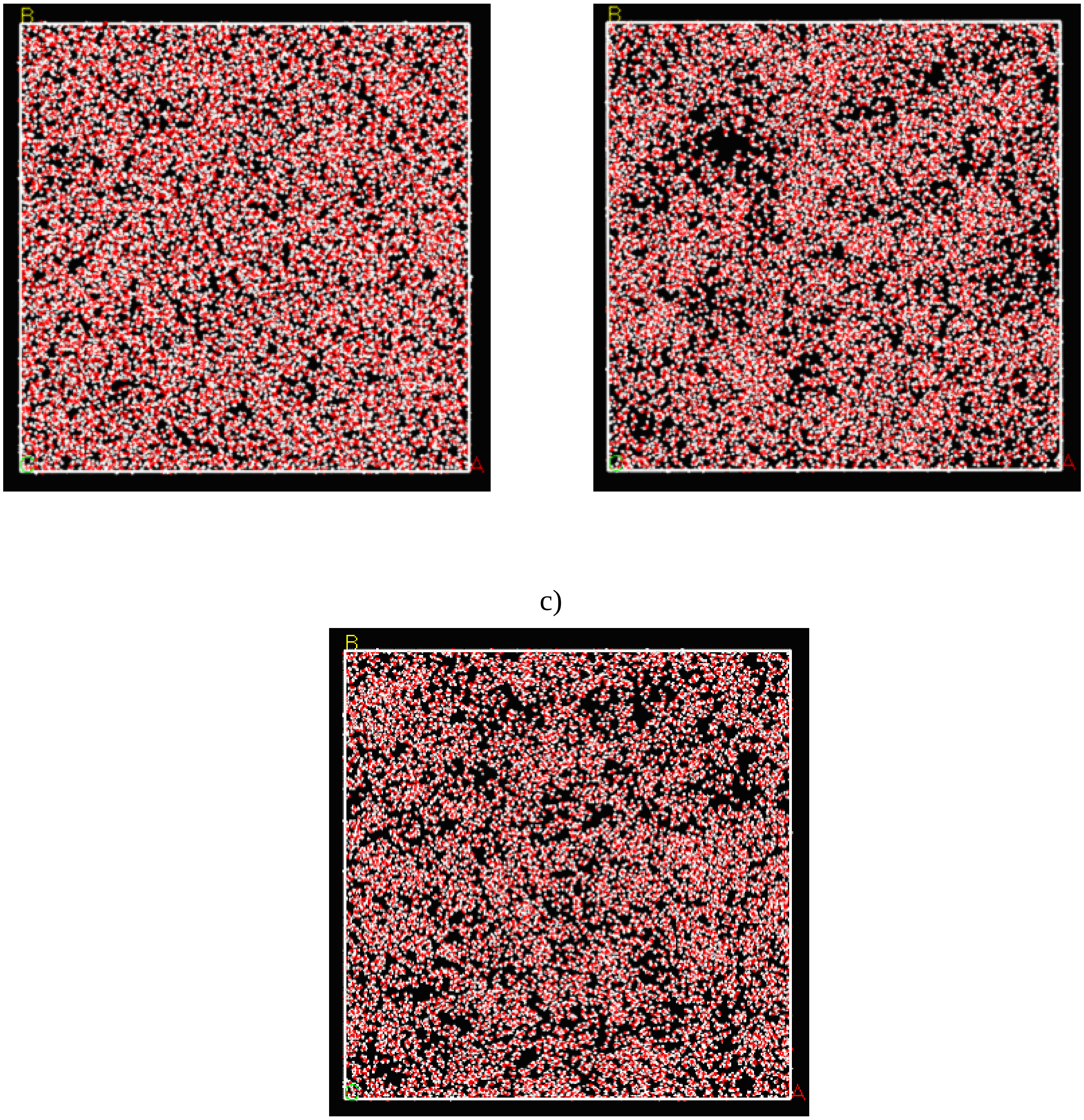

a)
b)
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Figure 1: The simulation cell showing the SCW systems at *T* = 400 °C:
a) ρ = 0.55, b) ρ = 0.31, and c) ρ = 0.17 g/cm^3.

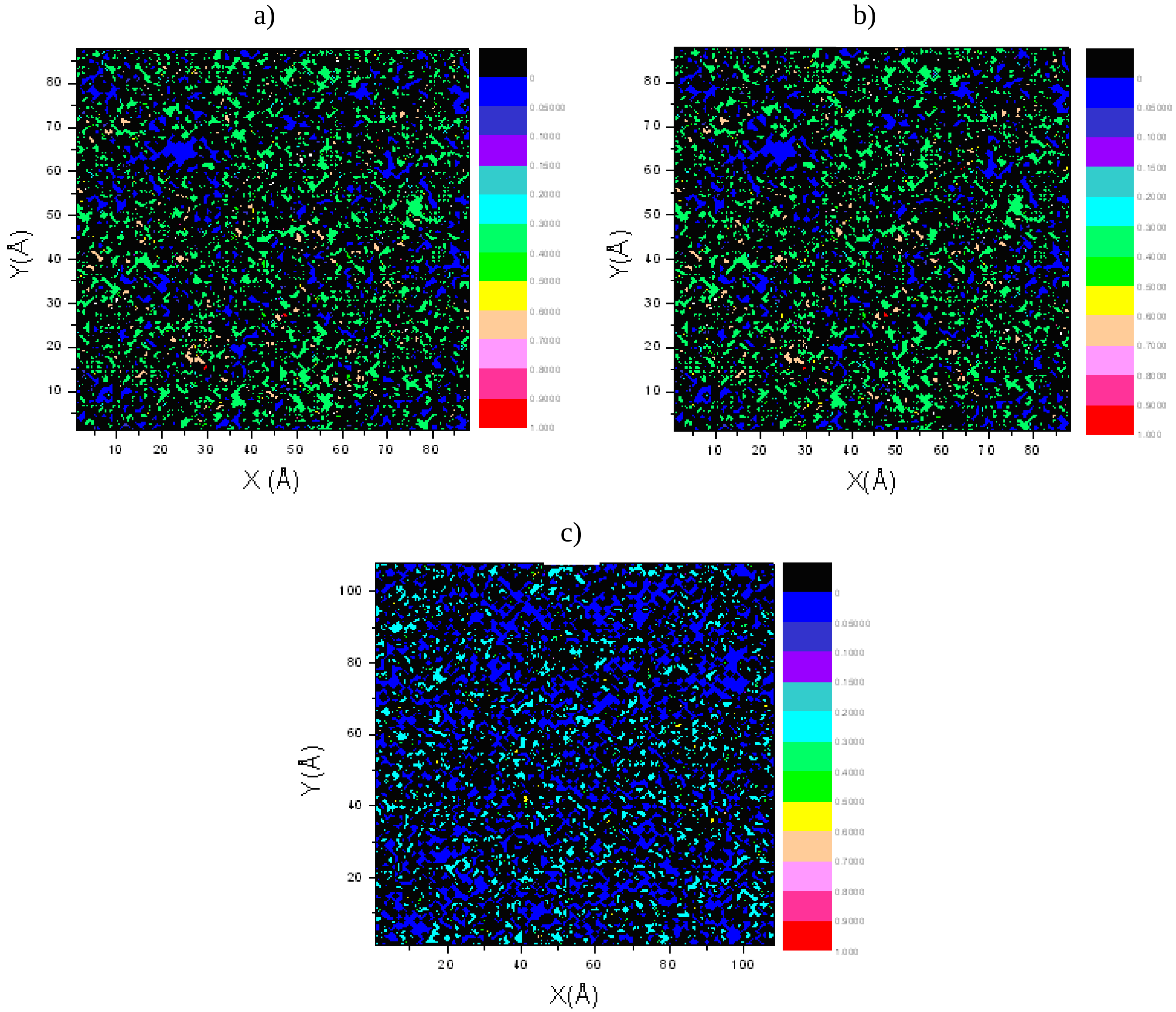
a)

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Figure 2: The simulated 2D contour plots of the SCW density at T = 400 °C:
a) $\rho = 0.55$, b) $\rho = 0.31$, and c) $\rho = 0.17$ g/cm^3.

To investigate the local density fluctuations, the radial distribution function $g(r)$ was computed. It describes the probability of finding a molecule at distance r and $r+\delta r$. This function allows the description of the liquid structure. It is defined by:

$$g(r) = \frac{n(r)}{4\pi r^2 \delta r\, \rho}\ , \tag{2}$$

where *n(r)* is the number of molecules that are present in a spherical shell between *r* and $r+\delta r$, and ρ is the density. The calculated radial distribution functions between water molecule centers of mass for structures at *T* = 400 °C for different densities (0.55, 0.31, and 0.17 g/cm^3) are shown in Fig. 3. A sharp peak is localized at a distance of 2.8 Å, which originates from the first sphere of solvation and is due to strong hydrogen bonding in water. The location of this peak is independent of density, although its intensity is larger when the density is decreased. As the distance increases, *g(r)* reaches a minimum, which is considered as the end of a water cluster. It is observed that the distance corresponding to this minimum increases as the density decreases (Table 1). The presence of a second peak indicates the occurrence of a cluster that is always located at *r*= 5.5 Å independent of the density. A third peak of low intensity can be revealed around *r*= 8.3 Å only for ρ = 0.55 g/cm^3.

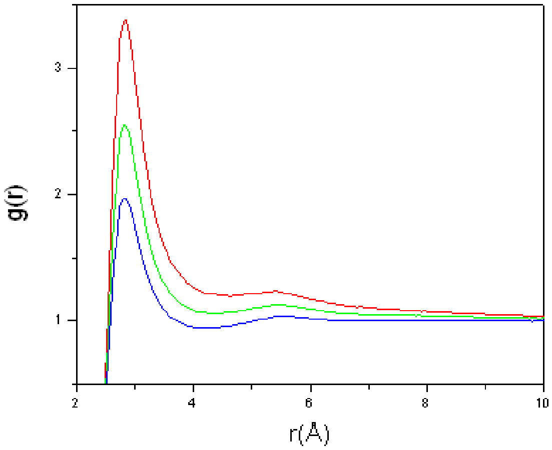

Figure 3: Simulated COM radial distribution function at *T* = 400 °C:
— ρ = 0.55 (lower curve), — ρ = 0.31 (middle curve), and — ρ = 0.17 (upper curve) g/cm^3.

Density (g/cm^3)	First minimum (Å)
0.17	4.55
0.31	4.35
0.55	4.2

Table 1: First minimum for all studied densities at *T*= 400 °C.

The behavior of the calculated radial distribution function with respect to the temperature for ρ= 0.55 g/cm^3 is shown in Fig. 4. The first peak intensity is temperature dependent: as the temperature decreases its intensity increases. Moreover, the second peak intensity is slightly temperature dependent. This dependency is interpreted as changes in the hydrogen bonding as the temperature is varied [23]. These results are in agreement with estimated values obtained by Jay-Gerin et al. [8] in comparison with the $(H_2O)_n^-$ cluster data of Ayotte and Johnson [24] and data of Coe [25]. However, more systematic investigations of sub-critical and SCW local densities are needed in order to quantify the number of water molecules present inside the clusters. This remains one of our further goals in this field of investigation.

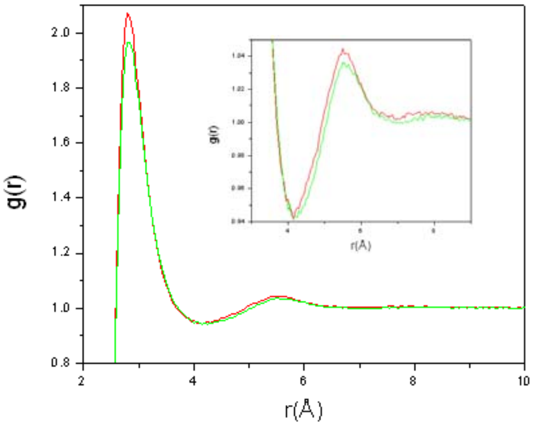

Figure 4: Simulated COM radial distribution function of the ρ = 0.55 g/cm^3 system versus temperature: — T= 400 °C (lower curve) and — T= 360 °C (upper curve).

4. Conclusion

In this preliminary study, the local molecular structures of supercritical water for different densities (0.55, 0.31, and 0.17 g/cm^3) at 400 °C and sub-critical water with density of 0.55 g/cm^3 at 360 °C were examined using molecular dynamics simulations. These simulations have shown that structures of sub-critical water and SCW are heterogeneous and characterized by low- and high-density regions. These results are in agreement with experimental observations. Configurations inferred from these simulations can therefore be used in the study of the localization and hydration of excess electrons in subcritical water and SCW. Such a study would be most useful to explore the mechanism(s) by which excess electrons are stabilized by local density fluctuations as well as to estimate the time scales that are involved in the formation of the molecular structures of e^-_{aq}. These molecular configurations will be further employed to model the radiation energy deposition and the subsequent radiolysis reactions in SCW.

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