



# Local structural fluctuations, hydrogen bonding and structural transitions in supercritical water



Ioannis Skarmoutsos<sup>a,\*</sup>, Elvira Guardia<sup>b</sup>, Jannis Samios<sup>c</sup>

<sup>a</sup> Institut Charles Gerhardt Montpellier, UMR 5253 CNRS, Université de Montpellier, Place E. Bataillon, 34095 Montpellier Cedex 05, France

<sup>b</sup> Departament de Física, Universitat Politècnica de Catalunya, Campus Nord-Edifici B4-B5, Jordi Girona 1-3, Barcelona E-08034, Spain

<sup>c</sup> National & Kapodistrian University of Athens, Department of Chemistry, Laboratory of Physical Chemistry, Panepistimiopolis, 157-71, Athens, Greece

## ARTICLE INFO

### Keywords:

Supercritical water  
Hydrogen bonding  
Density inhomogeneities  
Molecular dynamics simulation  
Structural transitions

## ABSTRACT

The contribution of hydrogen bonding interactions to the formation of local density inhomogeneities in supercritical water at near-critical conditions has been extensively studied by means of molecular dynamics simulations. The results obtained have revealed the strong effect of water molecules forming one and two hydrogen bonds on the determination of the local density augmentation in the fluid. The local structural order has also been studied in terms of the trigonal and tetrahedral order parameters, revealing the correlation between local orientational order and hydrogen bonding. The dynamics of the structural order parameters exhibit similarities with local density ones. The local structural analysis performed in terms of nearest neighbors around the individual molecules provides additional significant evidence about the existence of a liquid-like to gas-like structural transition in supercritical water at the density range close to  $0.2 \rho_c$ , further supporting previous suggestions based on the interpretation of experimental thermodynamic data.

## 1. Introduction

Supercritical water (SCW) is an environmental friendly solvent and a cheap alternative to organic ones, having thus a wide applicability in several green chemical processes [1–5]. The main reason for this wide applicability is that by slightly adjusting the thermodynamic conditions, the dielectric properties of SCW can be drastically altered, allowing thus the eclectic dissolution of several types of polar or non-polar solutes in SCW. Such a behavior, in combination with the low viscosity of SCW, has promoted its use in new emerging applications such as hazardous waste treatment, biomass processing and materials synthesis. Apart from the technological applications, the study of the properties of SCW is also very important in Geochemistry. SCW acts as a medium in several hydrothermal reactions in the Earth's crust and mantle [6] and can also be dissolved in silicate minerals, strongly affecting in this way many important geochemical processes.

The properties of SCW exhibit in general significant differences with its liquid state ones [7–20]. According to several existing experimental and simulation data [21–41] the hydrogen bonding (HB) network in SCW is much weaker and the fraction of water molecules forming hydrogen bonds is much lower at supercritical conditions. However, water molecules can still form hydrogen bonds even at these high temperature

conditions and quite recent experimental studies have confirmed the existence of hydrogen bonds up to at least 873 K and 132 MPa [20]. Previous studies have also confirmed the existence of local density inhomogeneities [29,42] in SCW and have revealed that the local density augmentation is much more pronounced in comparison with non-HB fluids [29,42–44]. Taking into account the importance of density inhomogeneities in determining a wide range of properties of supercritical fluids [45], a deeper insight on the interplay between hydrogen bonding and the local structural fluctuations in SCW would lead towards a better understanding of its behavior.

Molecular simulation has become a very important tool to investigate the properties of supercritical fluids and their solutions, as pointed out in recent reviews [46]. The present study has been therefore devoted to a more thorough investigation of this interplay by performing a series of molecular dynamics simulations of SCW along a near critical isotherm, aiming to shed light on open questions regarding the interrelation between hydrogen bonding, local density inhomogeneities and structural order in SCW. Moreover, attention has been paid to provide information related to recent observations [41], according to which at near-critical temperatures there might be a supercritical fluid – gas transition at densities lower than  $0.2 \rho_c$ , due to the collapse of the short-range order. This work aims therefore to provide

Abbreviations: SCW, supercritical water; HB, hydrogen bonding; MD, molecular dynamics; rdf, radial distribution function; LDA, local density augmentation

\* Corresponding author.

E-mail address: [iskarmoutsos@hotmail.com](mailto:iskarmoutsos@hotmail.com) (I. Skarmoutsos).

<http://dx.doi.org/10.1016/j.supflu.2017.08.004>

Received 17 June 2017; Received in revised form 3 August 2017; Accepted 7 August 2017

Available online 10 August 2017

0896-8446/© 2017 Elsevier B.V. All rights reserved.

**Table 1**  
Simulated thermodynamic state points of supercritical water, along the supercritical isotherm of  $T = 666$  K.

Simulated State Points	Density ( $\text{g}/\text{cm}^3$ )
1	0.0322
2	0.0644
3	0.1288
4	0.1932
5	0.2576
6	0.322
7	0.3864
8	0.4508
9	0.5152
10	0.5796
11	0.644

additional insight towards a deeper understanding of a wide-range of properties of SCW, often related to its peculiar behavior near the critical point.

The computational details of the performed simulations are presented in Section 2 of the manuscript. The results obtained and the following discussion is presented in Section 3. Finally, Section 4 contains the general conclusions and remarks drawn from the present study.

## 2. Computational details

Eleven thermodynamic state points of SCW were simulated in the framework of the present study. Ten molecular dynamics (MD) atomistic simulations of SCW were performed at a constant near-critical temperature of  $T = 666$  K ( $T_c = 647.1$  K) and for densities in the range  $0.0644$ – $0.644$   $\text{g}/\text{cm}^3$  ( $\rho_c = 0.322$   $\text{g}/\text{cm}^3$ ) in order to reveal the effect of hydrogen bonding interactions on the local structural order and density inhomogeneities in SCW. An additional MD simulation was later performed at the lower density of  $0.0322$   $\text{g}/\text{cm}^3$  and at the same temperature, in order to investigate the possible existence of structural transitions in SCW. The simulated state points of SCW are presented in Table 1. The simulations were carried out with 500 molecules, using the DL\_POLY software [47]. Each simulation was extended to 1 ns to achieve equilibrium, starting from an initial configuration created with the packmol software [48], and the properties of SCW were evaluated in subsequent simulations with duration of 2 ns. In all simulations the equations of motion were integrated using a leapfrog-type Verlet algorithm and the integration time step was set to 1 fs. The Nose-Hoover thermostat [49] with a temperature relaxation time of 0.5 ps was also used to constrain the temperature during the simulations. The intramolecular geometry of the molecules was also constrained by employing the shake algorithm [50].

The rigid SPC/E potential model [51] was employed to describe the site-site interactions between the water molecules. This three-site potential model has been successfully used in previous studies of liquid water and SCW, as well as in the case of several aqueous mixtures. Therefore, our choice has been based upon previously reported simulation results concerning the accuracy of this model in approximating sufficiently the critical point of water [35,36], as well as various properties of the fluid [35,51–53]. Taking into account that the performance of SPC/E in predicting the properties of SCW is very reasonable, as well as that our previous studies on SCW have also been performed with the same model [29,30,42,52,54], we decided to employ it in the present treatment as well. In such a way our findings could be also correlated to the findings of our previous works, providing in this way a more complete picture of the behavior of SCW at near-critical, supercritical conditions. It has to be noted that in the presentation of the results in this study, the simulated fixed densities have been presented as reduced densities  $\rho/\rho_c$ , taking the experimental critical density as a reference. The reason to do so is that the reported values for

the calculated critical density using the SPC/E model are close to the experimental one (for instance  $0.29$   $\text{g}/\text{cm}^3$  in Reference [35] and  $0.308$   $\text{g}/\text{cm}^3$  in Reference [36]). Moreover, since depending on the method used to extract the value of the critical density in the simulations the calculated values can be slightly different (as in References [35,36]), it was considered as a more standard approach to use the experimental critical density as a reference point. The temperature of the simulated isotherm in our case is also higher than the predicted critical temperatures of SPC/E water [35,36], ensuring that the simulated fluid is at supercritical conditions [45]. In our simulations a cut-off radius of  $12.0$  Å has been applied for LJ interactions and long-range corrections have been also taken into account. To account for the long-range electrostatic interactions the Ewald summation technique was used.

## 3. Results and discussion

### 3.1. HB effect on local structure and density augmentation

In order to obtain a clearer picture of the effect of HB interactions on the local structural properties of SCW the individual water molecules in the fluid were classified in different types according to the number of hydrogen bonds they form with other water molecules. Note that there are several definitions of the hydrogen bond in the literature [28], but a well-established geometric criterion, also used in several previous studies [25–27,29,30], was used in order to analyze the HB network in SCW. According to this criterion a hydrogen bond between two water molecules exists if the interatomic distances are such that  $RO...O \leq 3.6$  Å,  $RH...O \leq 2.4$  Å and the donor-acceptor angle  $H-O...O \leq 30^\circ$  (the symbol ... corresponds to intermolecular distances). Since our previous studies [29] have revealed that the main trends of the density dependence of the number of hydrogen bonds in several supercritical fluids and corresponding statistics can be realistically represented by simple geometric criteria and since the systematic study of HB definitions is way out of the scope of the present treatment, this simple definition was employed in the present study. Based on this criterion the fractions of water molecules forming 0–4 hydrogen bonds were estimated for all the investigated state points and are presented as a function of the bulk density of the fluid in Fig. 1. From this figure it can be clearly seen that in the range of the simulated bulk densities the majority of water molecules form mainly 0–2 hydrogen bonds and there is also a small fraction of water molecules forming 3 hydrogen bonds, which increases with the density. The fraction of water molecules forming 4 hydrogen bonds is almost negligible. It is interesting to notice

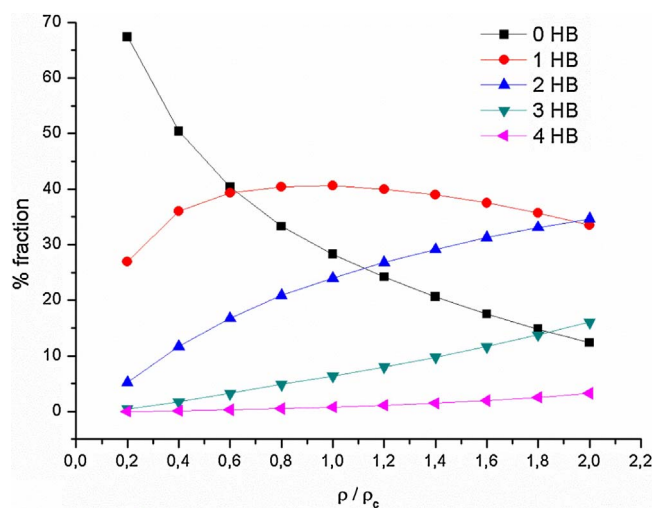


Fig. 1. Calculated fractions of water molecules forming 0–4 hydrogen bonds as a function of the bulk density of SCW.

Download English Version:

<https://daneshyari.com/en/article/6477648>

Download Persian Version:

<https://daneshyari.com/article/6477648>

[Daneshyari.com](https://daneshyari.com)