THEORETICAL DETECTION OF A HDA-LDA LIQUID-LIQUID TRANSITION PHASE FOR WATER USING MOLECULAR SIMULATION

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ABSTRACT – Recent work concerning liquid-phase water simulation and theory suggests that some anomalies observed may be related to a transition between two liquid states, the so called HDA-LDA transition. For example, the density maximum at 4 °C and the minimum in the isothermal compressibility at 46 °C are believed to be due to the existence of this phase transition. In this paper we will present the results of molecular simulations using the TIP4P model for water at very low temperatures and high pressures. In those simulations we were able to obtain a liquid phase transition that can be identified through a change in density. An increase in the coordination number, a discontinuity in water density and a change in the radial distribution function as a function of temperature were observed.

1. INTRODUCTION

In 1992, Peter Poole and coworkers theoretically predicted the formation of a second liquid phase for water in supercooling conditions (Poole et al., 1992). This transition would be characterized by a change in density; for that reason, it was called the HDA-LDA transition (high density to low density). Poole’s team was able to verify this behavior with molecular dynamics using the ST2 model for water interaction (Stilinger, 1974). In their work, experimental data for a transition in the solid phase (HDA-LDA transition in ice) was presented, and the radial distribution function was studied through neutron scattering. Their work suggested that some anomalies presented by water can be ascribed to this liquid-liquid transition.

In 1996, Hideki Tanaka (Tanaka, 1996) built a phase diagram for water using the TIP4P (Jorgensen et al., 1983) model. This phase diagram also presented a liquid-liquid transition at low temperatures and regular pressure (0.1 MPa).

Until recently, this behavior was not experimentally observed. Woutersen et al. (2018) were able to experimentally determine a phenomenon that is believed to occur due to this liquid-liquid phase transition. Those authors lower the crystallization point to avoid the formation of ice, by adding a salt, and were able to observe a phase transition believed to be related to the HDA-LDA water liquid-liquid transition.
In this work we present several molecular simulations using the TIP4P model for water to map this liquid-liquid transition. These computer simulations were carried out considering high pressure and low temperature, without any salt added. The analysis of radial distribution function and of the density profile showed the HDA-LDA liquid-liquid phase transition. The formation of a new hydration shell, the increase in the coordination number and a discontinuity in the density profile are observed as the temperature decreased.

2. METHODOLOGY

Molecular simulations were performed with the software GROMACS 5.1.4. (Berendsen et al., 1995). HPC clusters available at the Universidade de São Paulo, particularly the cluster Lince, were used to carry out the simulations. Post-processing codes were implemented to analyze the results.

The molecular dynamics simulations were performed as follows. The time step used was 1 fs, the total number of steps were 132 billion for production and 20 billion for equilibration, totalizing 152 microseconds. An energy minimization step was performed before the equilibration. For equilibration, the Berendsen rescale for the thermostat and standard Berendsen for the barostat (Berendsen et al., 1984) were used. For production, we used an annealing algorithm in the NTP ensemble so we could vary temperature stepwise. The system was left to equilibrate at each new temperature for 4 nanoseconds before production. Pressure values were considered to vary from 6000 bar to 14000 bar. The thermostat was changed to Nose-Hoover (Nose, 1984) and the barostat to Parrinello-Rahman (Parrinello & Rahman, 1980) for production. The simulation box was cubic with 3 nanometers in each side and we had 884 water molecules inside (2652 particles).

3. RESULTS AND DISCUSSION

Not all the results will be shown here, but as an example, Figure 1 shows the radial distribution function of oxygen-oxygen for 6000 bar from 263 K to 113K:

Figure 1 – Oxygen-oxygen radial distribution function for water at 6000 bar with varying temperature.
As pointed out before, one can clearly observe the formation of a hydration shell as a second peak appears. Beyond that, the increasing size of the first peak indicates the increase in the coordination number as the temperature decreases. This is confirmed by calculating the coordination number from the radial distribution function, using the following equation:

\[ n(r) = 4\pi \rho \int_{0}^{r'} g(r)r^2 dr \]  

(1)

where \( n \) is the coordination number, \( r \) is the space coordinate, \( r' \) is the distance \( r \) for the first minimum, \( \rho \) is the bulk density and \( g(r) \) is the radial distribution function.

For the identification of the liquid-liquid phase transition the evolution in density for the simulations performed for 8000 bar from 263 K to 113K is shown in Figure 2. A discontinuity at approximately 170 K is observed, showing that a second-order phase transition occurs:

![Figure 2 – Density profile for the simulation of water with TIP4P model with 6000 bar going from 263K to 113K.](image)

4. CONCLUSION

Results obtained from molecular simulations using the TIP4P model for water were presented. At supercooling and high pressure conditions, we were able to verify a second-order transition and a structure modification in water through the analysis of the density profile and the radial distribution function showing the predicted HDA-LDA liquid-liquid transition.
5. REFERENCES

BERENDSEN, H. J. C.; POSTMA, H. P. M. VAN GUNSTEREN, W. F.; DINOLA, A.; HAAK, J. R.; Molecular-dynamics with coupling to na external bath. J Chem. Phys., v. 81, p. 3684-3690, 1984.

BERENDSEN, H. J. C.; VAN DER SPOEL, D.; VAN DRUNEN, R.; GROMACS: A message-passing parallel molecular dynamics implementation. Comp. Phys. Com., v. 91, p. 43-56, 1995.

JORGENSEN, W. L.; CHANDRASEKHAR, J.; MADURA, J. D.; IMPEY, R. W.; KLEIN, M.; Comparison of simple potential functions for simulating water. J Chem. Phys., v. 79, p. 926-935, 1983.

NOSE, S.; A unified formulation of the constant temperature molecular dynamics methods. J Chem. Phys., v. 81, p. 511-519, 1984.

PARRINELLO, M.; RAHMAN, A.; Crystal structure and pair potentials: a molecular-dynamics study. Phys. Rev. Let., v. 45, p. 1196-1199, 1980.

POOLE, P. H.; SCIORTINO, F.; ESSMANN, U.; STANLEY, H. E.; Phase behaviour of metastable water. Nature, v. 360, p. 324-328, 1992.

STILINGER, F. H.; Improved simulation of liquid water by molecular dynamics. J Chem. Phys., v. 60, p. 1545-1567, 1974.

TANAKA, H.; A self-consistent phase diagram for supercooled water. Nature, v. 380, p. 328-330, 1996.

WOUTERSEN, S.; ENSING, B.; HILBERS, M.; ZHAO, Z.; ANGELL, C. A.; A liquid-liquid transition in supercooled aqueous solution related to the HDA-LDA transition. Science, v. 359, p. 1127-1131, 2018.