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Transition of liquid water to the supercritical state

Yuri Gorbaty, Galina V. Bondarenko *

Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow Region, Russia

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ABSTRACT

As was a long time believed, liquid and its gas can be distinguished one from another, if only they exist simultaneously below the critical point. This is because there is seemingly no qualitative difference between these two states. So there should not be a difference between a liquid and dense supercritical fluid. However, many experimental facts about water, cast doubt on this viewpoint. Especially interesting appears the enigmatical behavior of experimental pair correlation functions at the transition of liquid water to the supercritical state. Here we present a qualitative model for the transition based on the experimental data only. It is shown that the probability of hydrogen bonding approaches the percolation threshold near the critical isotherm. This means that the infinite cluster of hydrogen bonded molecules, which is characteristic for the liquid water, cannot exist in the supercritical fluid. The explanation of observed phenomena in terms of the percolation theory gives rise to a new conception of the transition of liquid water into the supercritical state. It also sheds light on the structure of the dense supercritical fluid and interrelation between all fluid states.

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1. Introduction

The role of supercritical water in the Earth environment cannot be overestimated. The very Earth crust, transport of elements, ore deposits, volcanism, etc. are the consequences of the activity of hot compressed aqueous solution of many compounds [1]. During the last two decades, industrial applications of supercritical water had been developed pursued the environment-friendly and energy-saving chemical technologies [2]. However, it is problematic to present a correct description of the dense supercritical water fluid. Meanwhile, this is a very specific state of a substance requiring better understanding. It is also touches upon one of the basic question of statistical physics – is there a *qualitative* difference between a liquid, gas, and supercritical fluid?

In the P-T diagram of any substance the critical isotherm is considered to be the border between the liquid state and the supercritical fluid (SCF). However, no explicit changes in the state of a substance have been observed at crossing the critical isotherm along an isobar, isochore or a random line. It may mean that the critical isotherm is simply a conventional boundary between these two states. But may we be sure that a qualitative distinction between the intrinsic liquid and supercritical fluid does not exist? Some time ago, such a question could not be even put into discussion. Indeed, it has been strictly defined that there is only a *quantitative* difference between a liquid and its vapour [3]. In other words, there is no such a property as, for example, the symmetry that would be intrinsic for one of the phases and could

not be found in another. So one can only distinguish between a liquid and gas, if both these phases coexist below the critical temperature.

Such an approach has led to confusion in understanding the properties of supercritical state. The necessity to describe supercritical fluid, existing in the large range of temperature and pressure, compelled researchers to introduce the terms “liquid-like SCF” and “gas-like SCF”. There were numerous attempts in the past to outline approximate borders of liquid-like and gas-like supercritical states in the phase diagram, in particular, of water. Unfortunately, almost all of them were based on the erroneous idea that the two-phase curve has a “hidden” continuation in the supercritical region. As a possible boundary between liquid-like and gas-like states of a supercritical fluid some authors referred to the critical isochore, the line of maximums of thermal expansion, the line of maximums of C_p and C_v , etc. Regrettably, they neglected the fact that each of the curves bears a definite physical meaning. For example, the critical isochore corresponds to maximums of the density fluctuations, the line of C_p and C_v maximums corresponds to maximal fluctuations of entropy, and so forth. Certainly, the fluctuations of entropy are not in any aspect better than the fluctuations of density or any other thermodynamic quantities. The very fact that lines of maximal fluctuations of thermodynamic quantities diverge above the critical point proves that there is not and cannot be a prolongation of the two-phase equilibrium curve into the supercritical region.

Another definition of SCF shared by many scientists is that the SCF is simply or at least technically [4] gas. This description is not far from truth, especially if we leave out the word “simply”.

It is beyond any doubt that hydrogen bonds exist in supercritical water (the only exception is the work [5]) but it is hardly possible to find the infinite hydrogen bonded networks in this state. In this paper

* Corresponding author.

E-mail address: bond@iem.ac.ru (G.V. Bondarenko).

we are trying to clear up two important questions – at which conditions the infinite network vanishes and what is the form of hydrogen bonded finite clusters. We present here a few experimental facts, which evidence significant changes in the state of a substance in the vicinity of critical isotherm. The peculiarities are discovered in the behavior of water or water solutions. Due to the strong intermolecular interaction induced by hydrogen bonding, the critical temperature of water is fairly high (374 °C). As distinct from simple liquids, the bonds between molecules clearly manifest themselves, e.g., in the vibrational spectra, NMR, and the pair correlation functions. The hydrogen bonds between water molecules provide a powerful probe that allows one to peep into the incessantly changed and reconfigured structure.

2. Experimental

As is well-known, the specific feature of the water structure is the tetrahedral nearest ordering arising due to the hydrogen bonding between water molecules. Each molecule can join four nearest molecules by means of hydrogen bonds. The main indication of the tetrahedral structure of such aggregates is the peak at ~ 4.5 Å in the pair correlation function [6]. The peak corresponds to the separation between the vertices of more or less perfect tetrahedron. Fig. 1 shows the experimental molecular pair correlation functions $g_m(r)$ [7,8]. To focus on the behavior of the peak at 4.5 Å, only a part of $g_m(r)$ is presented. With the temperature rise the quantity of relatively strong hydrogen bonds decreases, the bonds become longer and distorted. It seems natural that the peak practically disappears at approaching the critical isotherm. Quite mystically, the peak reappears above the critical isotherm and even tends to grow with the further temperature increase. The same is observed for aqueous solutions [9]. Such a behavior seems unbelievable. One can hardly seem unbelievable. One can hardly suggest any other assignment of the peak, except that it corresponds to the rib of a full or even incomplete tetrahedron built up from H-bonded molecules. Neither, it is possible that the number of hydrogen bonds in water becomes larger above the critical temperature. The temperature dependence of the mole fraction of bonded OH groups in water P_b (probability of hydrogen bonding) obtained with different methods in the wide range of pressures is shown in Fig. 2 [10]. One can see that P_b decreases in the whole explored temperature range. At critical temperature P_b amounts to 0.34 ± 0.03 . This quantity is fairly close to the percolation threshold $P_c = 0.39$ calculated by Stanley and Teixeira for the diamond-like crystal lattice (bond problem) [11]. In the real system P_c depends, of course, on many factors, for example, on the cutoff of energy

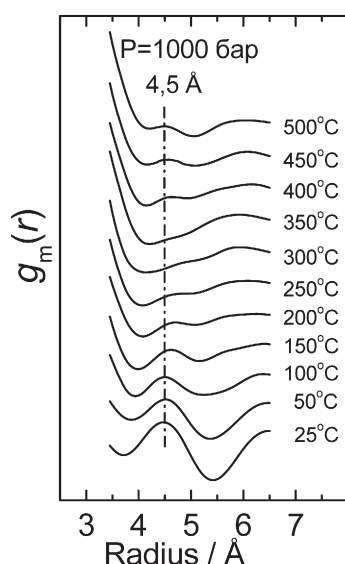


Fig. 1. The pair correlation functions of water at a constant pressure of 1000 bar.

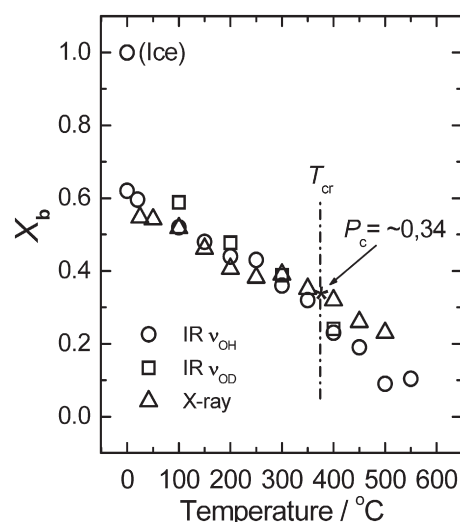


Fig. 2. The temperature dependence of the mole fraction of bonded OH groups in water obtained with different techniques¹⁰.

and geometry of hydrogen bonds, perfection of the tetrahedral ordering, etc.

This observation gives rise to an assumption that the line of percolation threshold for the water network is close to the critical isotherm. Above the percolation threshold a substance is in the liquid state due to the spanning infinite cluster of H-bonded molecules, which holds the molecules together. Such an infinite network cannot exist in the supercritical state. Only clusters of finite dimensions may be found in the supercritical fluid. The ruining of the infinite cluster leads to the appearance of freely (inertially) rotating monomers and aggregates of water molecules linked by the remaining hydrogen bonds.

The important role in forming such aggregates plays the effect of cooperativity of hydrogen bonds [12,13]. It consists in the increasing of average energy of hydrogen bonding in the H-bonded aggregate with every new molecule joined to it. Therefore, seeking the minimum of free energy, the molecules tend to assemble tetrahedrally ordered clusters of finite dimensions. This is the reason for the reappearing of the main indication of tetrahedral ordering above the critical isotherm.

Now the question arises – why MD and MC calculations never revealed this surprising effect? Apparently, one of the reasons is that these methods cannot as yet take into account the phenomenon of cooperativity. Therefore, the result of such calculations is close to the statistical distribution of molecules with different number of hydrogen bonds. It leads to the conviction that at high supercritical temperatures the molecules with four and three hydrogen bonds are practically absent. The computer simulations, even highly sophisticated, are not able to reveal the fact that, despite of low probability of hydrogen bonding above the critical temperature, the most of bonded molecules are four-bonded. The typical example is work [14]. The authors state that the second peak of the pair correlation function at 4.5 Å disappears, “indicating a uniform distribution beyond the first shell” above ~ 220 °C. The experimental $g_m(r)$ functions (Fig. 1) show that this conclusion is far from the real situation. We wish to stress that we criticize neither this particular work, nor other numerous computer calculations. In many aspects they are very helpful and often give a unique possibility to solve a problem. We believe that with the further development of the computational techniques a better conformity with experimental results may be achieved. But at the present state of the method all the attempts to reproduce the experimental correlation functions in a wide temperature range are not much successful. Even the data on the behavior of the first peak of $g_{OO}(r)$ at ~ 2.8 Å are controversial. This peak corresponds to the separation between the hydrogen bonded oxygen atoms. In some calculations, the height of the first peak h increases [14,15] at certain thermodynamical conditions while in others [16] it

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