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# Transition of liquid water to the supercritical state

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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

\* Corresponding author. E-mail address: bond@iem.ac.ru (G.V. Bondarenko). 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 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  $\sim$  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 seems 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  $P_{\rm b}$ (probability of hydrogen bonding) obtained with different methods in the wide range of pressures is shown in Fig. 2 [10]. One can see that  $P_{\rm b}$ decreases in the whole explored temperature range. At critical temperature  $P_{\rm b}$  amounts to 0.34  $\pm$  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  $P_{\rm c}$ 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 techniques<sup>10</sup>.

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 decreases. Krishtal et al. [14] explained the controversy. They have found a deep minimum in the temperature trend of the height of the first peak close to the critical temperature. As is shown below, the minimum of h may be explained in the same way, as the behavior of the peak at 4.5 Å. Another important inference drawn from this study is the assumption that the infinite hydrogen bonded network ceases to exist near the critical point. The preceding discussion makes it clear that there is no way to explain the surprising behavior of the experimental pair correlation functions with the use of theoretical or calculation methods. We can only illustrate the idea with an imaginary, speculative model presented in Fig. 3. Let us assume that hydrogen



**Fig. 3.** The speculative model for transition of liquid water into the supercritical state. (a) Ambient temperature. (b) Close approach to the critical isotherm. (c) Supercritical state. The frames around pictures in Fig 3a and 3b symbolize infinity.

bonds form a square two-dimensional network with the separation between nodes L (see insertion in Fig. 3a). Then the next nearest distance should be 1.41 L (diagonal of the square), then 2 L, and so on. These separations correspond to the peaks in the correlation function of the twodimensional rather incomplete and distorted network at ambient temperature (Fig. 3a). The peak at 1.41 L should be necessarily present in the pair correlation function of such a network. This peak is the full analogue of the peak at 4.5 Å in the real three-dimensional network of water.

As temperature approaches the critical isotherm and the quantity of hydrogen bonds decreases, the square nearest order becomes much more distorted and large holes arise in the network. That is again a consequence of the cooperativity effect. The loss of hydrogen bonds in some places of the network leads to the lesser average energy of bonding, making easier the destruction of bonds in the local neighborhood. The remaining bonds become longer and bent, and the peak at 1.41 L disappears (Fig. 3b). However, the infinite cluster exists still, preventing the scatter of molecules. Above the critical isotherm, that is, below the percolation threshold (Fig. 3c) the infinite cluster disintegrates so that only non-bonded molecules and H-bonded groups of molecules remain. These tiny pieces of the initial network have free borders; they do not undergo stretching stress from the other parts of the former infinite network. So, nothing prevents the square geometry (tetrahedral in the real case) from being restored. The peak at 1.41 L reappears. The smaller the finite clusters are, the more perfect is the tetrahedral order. Incidentally, MD simulations [17] have shown that large clusters uniting more than one hundred molecules exist even at 500 °C. Although the authors suggest a different interpretation, we believe that these clusters have to be tetrahedrally ordered.

The behavior of the height of the first peak h described in the study [14] may be explained in the same way. Close to the critical point hydrogen bonds in the highly strained (but still infinite) network should be greatly distorted and the height of the peak reaches minimum. In the small finite clusters at higher temperatures hydrogen bonds came back to the normal geometry.

Looking at the pictures in Fig. 3, one must bear in mind that the lifetime of hydrogen bonds is very short (typically  $1 \times 10^{-12}$  s. at ambient temperature). The lifetime of the finite clusters in Fig. 3c is not much longer. They incessantly come asunder and arise again, most likely in the different parts of space due to the fluctuations of thermodynamic parameters. Such a state can hardly be called "liquid-like" as is commonly accepted.

That is the only explanation of the behavior of the experimental pair correlation functions we are able to suggest. On the other hand, one can imagine many other molecular configurations, which could lead to the appearance of "tetrahedral" peak. Suppose, for example, that below the percolation threshold a significant part of bonded molecules forms trimers **A** or chains **AAA...A**. Much as this looks fantastic, the correlation functions would necessarily contain the peak at 4.5 Å.

Theoretically, it would be sufficient if only one last bond providing unlimited percolation gets broken to induce the collapse of the infinite network. In the real situation, some changes in the state of a substance may be found only if noticeable number of bonds vanishes. Due to the thermodynamic fluctuations the infinite cluster disappears not exactly at a definite temperature point but alternatively disappears and arises in some temperature zone around the critical isotherm. Therefore, the percolation transition in the case of water manifests itself mainly in the first and the second derivatives of thermodynamic parameters. We think but intuitively that the zone may widen at high pressures and its center may shift to slightly higher temperature.

#### 3. Some other results and discussion

There are many evidences that properties of a substance show specific behavior at the critical isotherm. A few examples are presented in Fig. 4.





**Fig. 4.** The behavior of some properties of water at isobaric heating. (a) The derivative of speed of sound. (b) The coefficient of isotope distribution. (c) Concentration of the main components in the water-sulfur solution.

The temperature derivative of the sound velocity in water reveals minimums on the critical isotherm in the wide range of pressure [18] as Fig. 4a shows. The coefficient of the isotope distribution undergoes something like a jump (Fig. 4b) near critical temperature [19]. Fig. 4c shows the specific behavior of the concentrations of main components of the solution resulting from the interaction between water and crystalline sulfur taken as a precursor. The data have been obtained with the use of Raman spectroscopy directly at high temperatures and a constant pressure of 1000 bar [20]. The reactions in the system are rather slow, especially at low temperatures; therefore the non-stop experiment lasted for some 50 days. As is seen, maximums of concentrations for all the components take place in the region of the critical isotherm. Moreover, the reactions are reversible and the same maximums appear at decreasing temperature. This result is important for practical applications inasmuch as it may serve as a model for the industrial supercritical chemical technologies.

Another important fact is that the intensity of rotational movement strongly increases just above the critical temperature, when the prevailing quantity of water molecules gains the ability to rotate inertially. At supercritical pressures up to 500 bar well-defined rotational branches of rotational-vibrational IR spectra of  $(v_2 + v_3)$  combination mode of D<sub>2</sub>O become apparent above the critical isotherm [21]. At high pressures rotational branches become poorly resolved but one can see the sharp growth of the halfwidths immediately above  $T_{\rm cr}$  as a result of increasing rotational movement [9].

In this paper, we have only handled a problem of transition of liquid water into the supercritical state. There have been many theoretical works aimed at the finding positions of percolation lines in the phase diagram of simple liquids (see, for example, the excellent review of Sator [22]). The results, however, were rather ambiguous and very different, which is not at all surprising, taking into account a large variety of cluster models, that have been so far suggested. Unfortunately, when studying simple liquids, such effective experimental tools as, for example, the pair correlation functions are not much enlightening. That is for, we cannot state with confidence that the conception suggested here can be applied to simple liquids.

Paradoxically, the complicated systems with hydrogen bonds give more information. Studying a series of alcohols [12], we have arrived at the same conclusion as in the case of water. However, the percolation threshold for the alcohols occurs at  $P_b$  equal to ~0.65–0.7. OH group in alcohols can form 2H-bonds, whereas the water molecule can form 4H-bonds. It is easy to see that the value ~0.7 for alcohol and the value ~0.34 for water correspond to the same average number ~1.4 hydrogen bonds per molecule.

#### 4. Conclusion

In conclusion we would like to present a brief summary of the results of this work.

As is shown in the paper, the probability of hydrogen bonding in water approaches the percolation threshold close to the critical temperature. This means that the infinite cluster of hydrogen bonded molecules cannot exist in supercritical water, however the probability of hydrogen bonding is still high. We suppose that the percolation state of a substance can serve as a qualitative criterion. Analyzing our own and literature data, we arrived at the conclusion that an inherent property of liquid water is the infinite cluster of H-bonded molecules that cannot exist in the supercritical state. So, the critical isotherm is not merely a formal border but separates qualitatively different states of a substance. The same is true for the liquid and gas. We found the term "liquid-like supercritical water" to be inadequate for description of the fluid. It does not give proper weigh to the qualitative difference between liquid and gas. The dense supercritical water is a non-uniform medium containing microscopic clusters typical for liquid and free monomers typical for gas. However, the term "gas-like SCF" may be used to characterize the fluid at high temperature and low density [21]. Above the specific volume of ~10 cm<sup>3</sup>  $g^{-1}$ , practically all the water molecules take part in the free rotational movement.

Finally, we have to admit that the conception described in this paper is just a hypothesis requiring further experimental and theoretical validation. We would be happy, if our work can serve as a base for a helpful discussion.

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