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HYDROGEN-BOND PUZZLE

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A scientist creating the models of material structures works in a way similar to the artist painting from the nature. Various models, similarly as different images may describe the *same* reality in a better or worse way. We think that it is the time to admit that the models of the percolating lattice and dynamic clusters are two images of the same structure of water, viewed from different perspectives. We believe that the most important will be such improvement of the basic model of the structure of water molecule that both ways of its modeling would give practically the same consistency with experimental results.

key words: hydrogen bond, percolating lattice, connectivity of bonds, water clusters

The molecule of water is one of the smallest in the Nature. Prof. Kamieński has even used to say that it is an atom of a double negative oxygen, that has hidden in its orbitals two protons of not fully compensated charges. This results in huge electric moments of the molecules that are the source of hydrogen bonds. To describe the interactions of charges located at atomic distances in each water molecule a modification of the coulomb potential rather than the „diameter" of these molecules is needed.

Such necessity clearly results from Prof. Adamczyk's statement, that „everything" is determined by charges. In the newest works much attention is paid to the Yukawa potential, (Blum et al. (1999) and to the experiments that combine the power of the hydrogen bond with the local charge densities in the anti-bonding orbitals σ_{OH}* (Kumar et al. (2007)).

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Maybe this year is the last one, when we can call the hydrogen bond a mysterious one. Although in one of the recent papers, Gilli et al. (2009), concerning the structure of liquid water the statement '*H-bond puzzle'* appears, several other papers indicate that in reviews published in Chemical Review 2010 this puzzle should practically disappear.

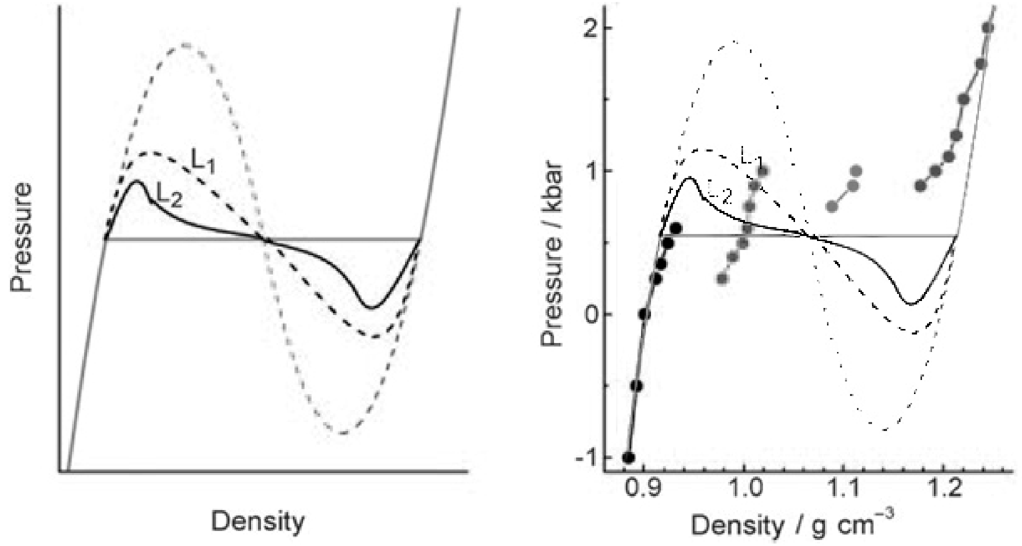
It is therefore reasonable to summarize the long period of the development of various competing descriptions of the hydrogen bond with the expectation that the *present generation of our PhD graduates* will develop a homogeneous and generally accepted theory of this bond. Why do we think so? After a long period of the competition of various basic assumptions concerning different models of the water molecule, the ideas of their combination have appeared. Two theories of the structure of liquid water that apply *the same* models of water molecule lead to the results equally close to experimental results.

Somewhat older theory, known as the theory of the *percolating lattice* of the liquid water was developed in the late 70-ties, by Stanley and Teixeira (1980) and 10 years later come up the theory of *water clusters* (Chaplin, 2008). The first one describes water as the dynamic lattice of locally variable structures, while the second one treats it as the equilibrium mixture of dynamic aggregates of water molecules, differing in size and structure.

In some more recent works there has appeared the proposal of creating the model of water molecules, based on the known parameters of all studied structures of ice, including those anisotropic ones, starting from the experimentally confirmed fact that the *average* strength of hydrogen bonding is the function of both, temperature and pressure (Dougherty, 1998; Dougherty and Howard, 1998). In such a virtual molecule, whose construction uses both the model lengths of bonds and their angles between the hydrogen bonds, might take the values remaining within the regions *known from the experiments* carried out in the wide range of pressure and temperature values. The modeling is usually performed in the NTV system that takes into account also the structures present in the equilibrium interface regions. The laws of the statistical thermodynamics make possible the transfer of the results of the calculations onto the *pVT* system.

The experimental works prove that water is not a „van der Waals" liquid because it does not meet the assumptions of this model. No single molecules but their aggregates, „clusters", are the objects of translational movements. The condition required that the vdW equation describes the behavior of water to a good approximation is that the dynamic *clusters* of water should be sufficiently large and „stable" so as to interact with the *neighboring clusters* only by the London dispersive forces, due to the saturation of their *internal* hydrogen bonds (depending on the value of the parameters of state, the strength of a hydrogen bond may be of the order of kT). It is assumed that large, symetric clusters contain the tetrahedrally combined molecules of water but the *strength of a local* hydrogen bond within the cluster, within the range of the whole order of values, depends on its location

Particularly important seems to be the fact that water, in addition to the „classical" triple point has two additional breaks on the density – temperature curve. („Light" water – at about 4^{o}C and about 45^{o}C, and the „heavy" one – at about 11^{o}C and about 60^{o}C). The first *kink* corresponds to the temperature of maximum density, while the second one – to the minimum solubility of hydrophobic compounds.



a b

Fig. 1. a) Isotherm of a fluid at subcritical temperature. Meta-stable and unstable parts of the Van der Waals loop are shown by different lines. Respectively. L1 and L2 show isotherms of finite systems of different sizes, with L1<L2. b) Isotherm of a macroscopic fluid. Model isotherm of supercooled ST2 water at T=235 K, simulated in the restricted NPT ensemble. Four branches of this isotherm, (given by points, on separate lines) correspond to the four phases of supercooled liquid water.

Such behavior is typical for mixed solvents, and in the case of water – for the *mixture* of its structures. (This reminds rather the „resonance of structures" than the *homogeneous* mixture with its local fluctuations. It causes the necessity of considering at equilibrium the simultaneous run of several processes of different relaxation times.

The condition necessary for the system to create the lattice of percolating hydrogen bonds during reduction of volume (*V*), containing (*N*) particles, at fixed temperature (*T)* is that the system must reach the so called "*percolation threshold"* , Blumberg et al. (1984). In the work of Bernabei et al. (2008), it has been shown that the probability of the increase of the number of these bonds may be higher in the lattice points neighboring with oxygen atoms of four bonds. Hydrogen bonds are formed even in the gaseous phase, in water vapor. But the condition required for their

„*connectivity*" is the threshold value of the average number of bonds n_{HB}, per one oxygen atom in the lattice point. For the three-dimensional lattice the critical percolation threshold takes the value of: $n_c = 1.55$ per one water molecule in the system considered. It is rather commonly accepted that after the melting of ice there remain on average 3.6 hydrogen bonds from each 4 bonds, and at the boiling point there remain still 3.2 bonds, per each oxygen atom. At present, the possibility of the existence of the percolation lattices even in the supercritical states of water (Bernabei et al., 2008) has become the subject of interest.

The tetrahedral system with four water molecules at the corners, characteristic for the crystals of hexagonal ice (Ih) is generally accepted for hydrogen bonds. Oxygen atoms of five molecules are bound with hydrogen bridges: —O••••H——O , and each of them is both a donor and an acceptor of electric charges[ii]. In this idealized system the length of a hydrogen bond is equal to about 2.82Å, and the angle between the bonds of the hydrogen bridge and the covalently bound hydrogen atom (O—H) takes about 109.5°. In various places of the percolation lattice the local and temporary locations of water molecules cause a significant deformation of both the above given distances and angles, as well as the local electron density of the $\sigma_{\mathrm{OH}}{}^*$ orbitals.

The graphs shown above are taken from a most recent work of Brovchenko and Oleinikova (2008). They illustrate the trend in such application of the experimental data on the influence of temperature and pressure on the radial distributions of oxygen and hydrogen atoms, and on the electric densities of liquid water and ice, that it would make possible the use of this information for improving the models of water molecule. The final goal is an equation of state for liquid water, showing clearly inadequacy of the van der Waals equation.

Under the imposed *NTV* conditions the model calculations should give the dependence of the average energy of hydrogen bond upon temperature and pressure for liquid water consistent with experiments. This labor-consuming way has been confirmed by the early work by Berendsen et al. (1987), in which the theory of percolating bonds has been applied. It has been shown that the results of calculations carried out using the SPC model of water are clearly approaching the experimental ones, when in addition to the stable dipole moment (in the SPC/E model) also the existence of induced moments is taken into account.

The more complex attempt to describe the structure of liquid water, using the information on the defined lattice elements has been presented in the already cited work of Brovchenko and Oleinikova (2008). The authors have assumed that liquid water formed after melting ice has the structure of a percolating lattice, where in addition to the structures of the parameters characteristic for the hexagonal lattice of ice appear also increasing numbers of groups of molecules in the pentagonal system. In the latter case, the angle between hydrogen bonds and hydroxide bonds is reduced to 108°. The number of pentagonal structures increases up to about 4°C. At this temperature the tetrahedral structures (Ih ice) are transformed into the plane hexagonal groups of the bond angle equal to 120°. This last structure is the most numerous at about 45° C when large hydrophobic molecules are the least soluble in water. Starting from this temperature, in the percolating lattice, the systems of pentagonal symmetry are replaced by the groups of molecules characteristic for the simple cubic lattice of the overheated water and critical regions. The authors have simulated radial distributions of water molecules for each of the assumed models of its particles and have obtained the results similar to the results of experiments carried out for water at varying temperature.

Summing up, we may state that the scientist creating the models of material structures works in a way similar to the artist painting from the nature. Various models, just as different images, may describe the *same* reality in a better or worse way. We think that it is the time to admit that the models of the percolating lattice and dynamic clusters are two images of the same structure of water, viewed from different perspectives. We believe that the most important will be such improvement of the basic model of the structure of water molecule that both ways of its modeling would give practically the same consistency with experimental results.

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Uczony – tworząc modele struktur materialnych – postępuje jak artysta malujący obrazy *z natury*. Podobnie jak różne obrazy, tak też różne modele mogą lepiej lub gorzej opisywać *tę samą* rzeczywistość. Sądzimy, że nadszedł czas aby uznać, że modele, zarówno perkolującej sieci, jak też dynamicznych klasterów to dwa obrazy tej samej struktury wody, lecz oglądanej z innych perspektyw. Odnosimy wrażenie, że *środek ciężkości* zagadnienia przenosi się wyraźnie na *takie* udoskonalenie *podstawowego* modelu *molekuły wody*, aby obie *drogi* modelowania jej struktury, dawały praktycznie taką samą zgodność z wynikami prac doświadczalnych.

słowa kluczowe: wiązania wodorowe, klastery wody, łączność wiązań