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## Cluster structure of water and its argon-like equation of state

Nikolay P. Malomuzh

Odessa I.I. Mechnikov National University, <http://onu.edu.ua/>

Odessa 65026, Ukraine

E-mail: [mnp@onu.edu.ua](mailto:mnp@onu.edu.ua)

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*Abstract.* The paper is devoted to the discussion of the physical nature for water properties having similarity with ones for argon-like liquids and ones for their amorphous states. The strong clusterization of molecules in liquid water is a natural basis for so wide diapason of its physical properties. It is taken into account that the cluster composition and their properties strongly depend on temperature and pressure. The averaged life time  $\tau_0$  of clusters is one of the chief characteristics of clusters. If behavior of some water characteristics is determined by molecular configurations with their life times  $\tau_c >> \tau_0$ , one can speak that they are determined by the averaged interparticle potentials between water molecules. The position of vapor-liquid binodal can serve as a typical example of such properties. At the same time, the entropy and heat capacity of water are mainly determined by thermal excitations of clusters for which:  $\tau_{ex} << \tau_0$ . From here it follows that at beginning we should clear understand what slow or quick molecular processes are dominating in the formation of considered characteristics of water.

*Keywords:* water, clusters, cluster excitations, equation of state, coexistence curve, heat capacity, dielectric permittivity

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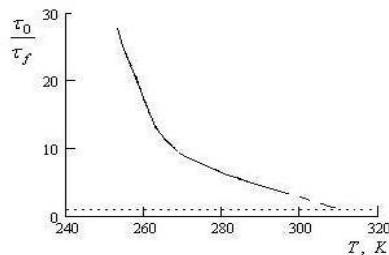
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- ### 1. INTRODUCTION
- Water plays very important role in alive and lifeless nature. This circumstance is connected with its many properties caused by H-bonds. The lasts, in particular, determine and its local

structure remembering that in the hexagonal ice [1]. In more details H-bonds, whose interaction energy exceeds the dispersion one more than one order of magnitude, stimulate the formation of different clusters. Among them there are hexamers determining the hexagonal ice structure [1]. However clusters in liquid water are short-living objects. During its life time water molecules, belonging to some cluster, can only oscillate similarly to that in the hexagonal ice. The spatial displacement of molecules becomes possible only after destruction of corresponding cluster. At that a molecule rotates on some angle. Sometime the similar picture of displacements and rotations of molecules describes with the help of two characteristic times:  $\tau_0$  and  $\tau_f$  [2, 3], where the first is interpreted as the residence time and the other - as the transition one. In accordance with our reasons the residence time can be considered as the life time of hexamers and tetramers determining mainly the local water structure. We can speak about the crystal-like thermal motion in water if the condition:  $\tau_f \ll \tau_0$  is carried out. Since  $\tau_0$  and  $\tau_f$  depend on temperature, this condition can only be carried out in some temperature interval. At that with suitable accuracy  $\tau_f$  can be approximated by the expression:  $\tau_f \sim a/v_T$ , where  $a$  is the average interparticle spacing between the nearest neighbors and  $v_T$  is the average value for the thermal velocity of a molecule.

The temperature dependence of the ratio:  $\tau_0/\tau_f$  is studied in [4-6] with the help of incoherent neutron scattering data. The results are presented in **Fig. 1** (see also [6, 7]). As we



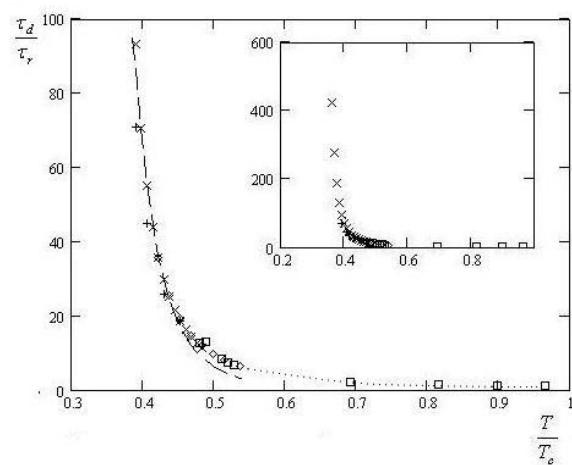
**Fig. 1.** Temperature dependence of the ratio  $\tau_0/\tau_f$ , where  $\tau_f \approx 5 \cdot 10^{-13}$  s, obtained in [4, 5].

can see, the crystal-like representations for the description of thermal motion in water are only applicable in the narrow temperature interval:  $273 \text{ K} < T < T_H$ ,  $T_H = 315 \text{ K}$ , of its normal states as well as for its supercooled ones:  $T < 273 \text{ K}$ .

The temperature dependence of the dipole relaxation time  $\tau_d$  presented in **Fig. 2**, is the important addition to Fig. 1. This quantity characterizes the rotational motion of water molecules.

Here  $\tau_r$  has meaning of the period for free rotation of water molecules,  $\tau_r \sim 2\pi/\omega_T$ , where  $\omega_T \sim \sqrt{k_B T/I}$  is the characteristic value of angular velocity,  $I = m_H r_{OH}^2$  is the inertia moment for a molecule ( $m_H$  is the hydrogen mass and  $r_{OH}$  is the distance between the oxygen and hydrogen in water molecule). By order of magnitude:  $\tau_r \sim 0.5 \cdot 10^{-12}$  s. As we can see, temperature dependences of the dipole relaxation time are different in the temperature intervals (see [7, 8]): 1)  $T < T_{IP}$ , where  $\tau_d \gg \tau_r$  and 2)  $T > T_{IP}$ , where  $\tau_d \leq \tau_r$ . The first temperature interval corresponds to the rotation of a molecule beginning after cluster destruction, the second one – to the quasi-free rotation of molecules.

It is very essential that the information about translational and rotational motions of water



**Fig. 2.** Temperature dependence of the ratio:  $\tilde{\tau}_d(t) = \tau_d(t)/\tau_r$ , where  $\tau_d$  is taken from works: + – from [1],  $\square$  – [9],  $\times$  – [10],  $\diamond$  – [11]. Points present the interpolation data for  $\tau_d$

molecules, obtained by different methods, is consistent with each other.

Considerable deviations of  $\tilde{\tau}_d(t)$  from unity are observed for:  $T < T_{H_p}$ , where the temperature dependence of  $\tilde{\tau}_d(t)$  is approximated by the exponential function (dashed line in Fig. 2):

$$\tilde{\tau}_d = \tilde{\tau}_d^{(0)} \exp(\varepsilon_H / t), \quad \tilde{\tau}_d^{(0)} = 5.1 \cdot 10^{-4}, \quad \varepsilon_H = 4.71.$$

At that, the value of the activation energy for the dipole relaxation time,  $\varepsilon_H = E_H / k_B T_s$ , coincides practically exactly with the H-bonding energy [1] between water molecules.

From our consideration it follows that physical characteristics of water are divided into two main totalities: 1) those, which properties are determined by molecular configurations having the life times more than the typical ones for clusters and 2) those, peculiarities of which are determined by properties of clusters, in particular, by their thermal excitations.

It is clear that the equation of state (EoS), the structure of the coexistence curve as well as the coefficients of self-diffusion and shear viscosity belong to characteristics of the first type. Changes of these quantities take place only on times exceeding  $\tau_o$ . Since these quantities can be also described in two-particle approximation, the corresponding interparticle potentials should consider as the averaged ones. The averaging is carried out on angular variables (pairs of molecules have different angular orientations).

The entropy, heat capacity as well as dielectric permittivity of water relate to characteristics of the second type. The essential contributions to their formation are caused by thermal excitations of clusters. It is evident that we can speak about thermal excitations only on times lesser than  $\tau_o$ .

In our paper we present 1) the averaged interparticle potential between water molecules, having the argon-like structure and the EoS for water constructed in argon-like approximation; 2) the influence of H-bonds on the EoS of water; 3) the character of thermal excitations and 4) peculiarities of their contributions to

the heat capacity and dielectric permittivity of water.

## 2. EQUATION OF STATE OF WATER IN ARGON-LIKE APPROXIMATION

In this Section the main attention is focused on the equation of state of water constructed in argon-like approximation. For this aim the structure and properties of the averaged interparticle potentials are considered. It is taken into account that the rotation of molecules creates the natural conditions for self-averaging of interparticle potentials. The Section is ended by the description of the H-bonds role.

### a) THE AVERAGED POTENTIAL OF INTERPARTICLE INTERACTION IN WATER

By definition, the averaged potential  $U(r)$  of interparticle interaction between water molecules is determined by the equation:

$$\exp(-\beta U(r)) = \langle \exp(-\beta \Phi(r, \Omega_1, \Omega_2)) \rangle,$$

where the angular brackets designates the averaging of the bare potential  $\Phi(r, \Omega_1, \Omega_2)$  on its angular variables  $\Omega_1$  and  $\Omega_2$ ,  $\beta = 1/k_B T$  (see details in [12, 13]). Due to such a definition the free energy of a system in two-particle approximation is invariant relatively transformation from bare to averaged potential. The bare potential is modelled by the sum:

$$\Phi(r, \Omega_1, \Omega_2) = \Phi_{dis}(r, \Omega_1, \Omega_2) + \\ + \Phi_{el}(r, \Omega_1, \Omega_2) + \Phi_H(r, \Omega_1, \Omega_2),$$

where the first term describes the dispersion interaction between water molecules, the second – the electrostatic one, modelled by potentials of type SPC, and the third – the irreducible one, caused by weak overlapping of electronic shells for interacting molecules [14]. In fact namely the last generates the irreducible part of H-bonding. In [12] it had been shown that the dominating contribution to the averaged potential  $U(r)$  is given by electrostatic interactions, which after the averaging take the Lennard-Jones structure:

$$U_{el}(r) \approx 4\varepsilon_a \left[ \left( \frac{\sigma_a}{r} \right)^{12} - \left( \frac{\sigma_a}{r} \right)^6 \right].$$

**Table 1**  
 Parameters of the averaged interparticle potentials for water corresponding to the standard bare ones (dimensionless  $\varepsilon_a$  equals to  $\varepsilon_a = \varepsilon_w^{(el)} / k_B T_{tr}^{(w)}$ , where  $T_{tr}^{(w)}$  – is the triple point temperature).

	SPC	SPC/E	TIPS	TIP3P	MP
$\varepsilon_a$	1.43	1.42	1.42	1.42	0.86
$\sigma_a$ , Å	2.78	2.78	2.77	2.77	2.89

In particular, for several often used interaction potentials the values  $\varepsilon_a$  and  $\sigma_a$  are presented in **Table 1**.

The designations SPC, SPC/E, TIPS, TIP3P correspond to potentials taken from [15-18]. The abbreviation MP denotes the multipole-multipole interaction potential considered in [14,19].

### b) ESTIMATES FOR THE CRITICAL TEMPERATURE OF WATER IN ARGON-LIKE APPROXIMATION

The simplest estimate for the critical temperature of water can be obtained with the help of Van der Waals formula [20]:

$$T_c = \frac{8a}{27b}. \quad (1)$$

coefficients  $a$  and  $b$  of which are determined by the averaged potential according to:

$$a = -2\pi \int_0^\infty U(r)r^2 dr, \quad b = \frac{2}{3}\pi\sigma^3.$$

Since the parameter  $\varepsilon_a$  and  $\sigma_a$  of the averaged potential  $U(r)$  depend on temperature, the formula (1) transforms in fact to the equation for the critical temperature:

$$T_c = \frac{8a(T_c)}{27b(T_c)}.$$

The intermediate calculation shows that for the bare potentials SPC and SPCM the critical temperature takes the values:

$$T_c^{(SPC)} = 626K, \quad T_c^{(SPCM)} = 561K.$$

Here the index “M” for potential notes that the electrostatic interaction in it is described by a segment of the multipole series including in itself the quadrupole-octupole interactions [19].

If the coefficient  $a(T)$  is calculated in accordance with more exact formula:

$$a(T) = -2\pi T \int_0^\infty (1 - \exp[-U(r)/T]) r^2 dr,$$

correct for  $\varepsilon_a/(k_B T_{tr}) > 1$ , we get the following estimates for the critical temperature:

$$T_c^{(SPC)} = 650K, \quad T_c^{(SPCM)} = 604K.$$

The critical temperature can be also estimated with the help of relation:

$$T_c^{(w)} \approx \frac{\varepsilon_w^{(el)} + \varepsilon_w^{(dis)}}{\varepsilon_{Ar}} T_c^{(Ar)} = 638K.$$

following from the similarity principle [20, 21].

The relative width of the temperature interval for liquid states of argon equals to  $\frac{T_c^{(Ar)} - T_{tr}^{(Ar)}}{T_c^{(Ar)}} \approx 0.56$ . In the argon-like approximation the relative width of the corresponding interval  $\frac{T_c^{(w)} - T_{tr}^{(w)}}{T_c^{(w)}}$  for water should be the same:  $\frac{T_c^{(Ar)} - T_{tr}^{(Ar)}}{T_c^{(Ar)}} \approx 0.56$ . From here we get the following estimate for the triple point temperature of water:

$$T_{tr}^{(w)} \approx 0.44 T_c^{(w)} = 280K.$$

Thus, the using of the averaged interparticle potentials for water and the argon-like approximation for its EoS allows us to get the quite satisfactory values of temperatures for its critical and triple points.

### c) TEMPERATURE DEPENDENCE OF THE SPECIFIC VOLUME PER MOLECULE ON THE WATER BINODAL

The similarity of the averaged interparticle potential in water and that in argon allows us to write the following relation between the specific volumes on their coexistence curves:

$$\nu_w(t) \approx \left( \frac{\sigma_w}{\sigma_{Ar}} \right)^3 \nu_{Ar}(t), \quad (2)$$

where  $t = T / T_{tr}^{(i)}$ ,  $i = w, Ar$ . From (2) it follows that 1) the temperature dependences for the specific volumes of water and argon on their coexistence curves are practically identical and 2) in their triple points the specific volumes are connected between each other by the relation:

$$\frac{\nu_w(t=1)}{\nu_{Ar}(t=1)} \approx \left( \frac{\sigma_w}{\sigma_{Ar}} \right)^3 = \begin{cases} 0.56, & \text{SPC,} \\ 0.62, & \text{MP.} \end{cases}$$

Its corresponding experimental value equals to:

$$\frac{v_w(t=1)}{v_{Ar}(t=1)} \approx \frac{m_w}{m_{Ar}} \frac{\rho_{Ar}(t=1)}{\rho_w(t=1)} = 0.63.$$

The closeness of theoretical estimates for  $\frac{v_w(t=1)}{v_{Ar}(t=1)}$  to its experimental value as well as corresponding correlations between predictions and real positions of the critical and triple points point show explicitly on satisfactoriness of argon-like approximation for the EoS of water. Here it is especially important that a theoretical estimate for the ratio  $\frac{v_w(t=1)}{v_{Ar}(t=1)}$  is a few lesser than its experimental value. It means that the argon-like approximation should be naturally completed by a contribution caused by short-living H-bonds. In accordance with [22-24] their averaged life time at the room temperature does not exceed (1 ÷ 3) ps. Due to them some increase of the specific volume becomes possible. The similar effect takes also place for hexagonal ice, where it is caused by the regular network of H-bonds. Since the lasts are stable they lead to essentially more increase of the specific volume, more than that in liquid water on 3 order of magnitude.

**d) MANIFESTATION OF H-BONDS IN WATER EoS**  
For the description of temperature dependence of the specific volume we will use henceforth the reduced variables following from the van der Waals analysis of critical phenomena [20,21]:  $\tilde{v}_w(t) = v/v_c$  and  $t = T/T_c$ . In accordance with said above they should describe by the equation:

$$\tilde{v}_w(t) = k\tilde{v}_{Ar}(t) + \tilde{v}_H(t), \quad k = \left( \frac{\sigma_w}{\sigma_{Ar}} \right)^3 \frac{v_c^{(Ar)}}{v_c^{(w)}}, \quad (3)$$

generalizing the formula (2) where  $\tilde{v}_H(t)$  is the contribution caused by H-bonds. By order of magnitude:  $k \geq 0.85$  and  $\tilde{v}_H(t) \sim 0.05\tilde{v}_w(t)$  or  $\tilde{v}_H(t) \sim 0.05\tilde{v}_{Ar}(t)$ , i.e. its relative value does not exceed 5%. In [25-27] it had been shown that this contribution is formed by short-living H-bonds in water and it is proportional to the averaged number  $n_H(t)$  of H-bonds per molecule:

$$\tilde{v}_H(t) = \tilde{v}_H^{(0)} n_H(t) + \dots \quad (4)$$

It is necessary to note that the influence of H-bonds weakens with increase of temperature and reduced specific volume  $\tilde{v}_w(t)$  per water

molecule asymptotically approaches to that  $\tilde{v}_{Ar}(t)$  for argon. On the contrary, the contribution  $\tilde{v}_H(t)$  increases with approaching the water triple point. Only in the narrow vicinity of the critical point these our conclusions should be préciséd [20, 27].

The careful analysis of the temperature dependence for  $\tilde{v}_w(t)$  allows us to conclude that  $n_H(t)$  changes linearly with temperature [25-27]:

$$n_H(t) = 4(1 - \lambda t + \dots), \quad \lambda = 0.85. \quad (5)$$

Near the triple and critical points values of  $n_H(t)$  are correspondingly equal to:  $n_H(t=0.42) \approx 0.26$  and  $n_H(t=1) \approx 0.6$ , that satisfactory correlates with results of computer modeling in [28, 29] and estimates of the dimerization degree of water molecules near the critical point [30].

Similar estimates for  $n_H(t)$  are obtained in [26, 27] from the analysis of the evaporation heat.

In conclusion of this subsection it is necessary to note that the representation of the specific volume of water in the view (3) – (5) allows us to explain naturally the physical nature of the mass density maximum at  $T_m = 277$  K. It is a result of superposition of two contributions having opposite character of temperature dependences: the argon-like contribution weakens if temperature falls and H-bond one increases at the same condition.

### 3. EXCITATIONS OF CLUSTERS AND THEIR MANIFESTATION IN DIELECTRIC PERMITTIVITY OF WATER

This not great Section is devoted to the discussion of the physical nature for dielectric permittivity in vapor and liquid states of water

**a) DIELECTRIC PERMITTIVITY OF WATER VAPOR**  
Water vapor is the simplest system for illustration of clusters role. At that, if vapor is not too dense, water dimers dominate among clusters. Considering such a system as a mixture of monomers and dimers its dielectric permittivity  $\epsilon$  can represent in the view [31]:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \frac{\rho}{m_w} \alpha_{eff},$$

where  $\rho$  is the mass density,  $m_w$  is the mass of a water molecule,  $\alpha_{eff}$  is the effective polarizability per molecule. With good accuracy the electronic polarizability of a dimer can be approximated by the doubled one for a monomer: ( $\alpha_d \approx 2\alpha_m$ ), and the dipole moment of a dimer in its ground state satisfies the equation:  $\vec{d}_d^2 = 2\vec{d}_m^2$  [31], where  $d_m$  is the dipole moment for a water monomer. Taking into account these relations we obtain the following expression for the effective polarizability per molecule for water vapor:

$$\alpha_{eff} = \alpha_m + \frac{\vec{d}_m^2}{3T_c t} + \dots$$

Due to collisions between monomers and dimers the lasts are excited and the effective polarizability per molecule becomes to be equal:

$$\alpha_{eff} = \alpha_m + \frac{c_d}{1+c_d} \alpha_v^{(d)}(t) + \frac{\vec{d}_m^2}{3T_c t} + \dots$$

where  $c_d = n_d / (n_m + n_d)$  is the dimer concentration ( $n_m$  and  $n_d$  are the numerical densities of monomers and dimers), and the contribution  $\alpha_v^{(d)}(t)$  to the effective polarizability:

$$\alpha_v^{(d)}(t) = \frac{\langle \delta \vec{d}_d^2 \rangle}{3T_c t}$$

is caused by the thermal excitations of dimers, i.e. their vibrations.

In [31] it had been shown that the numerical value of  $\alpha_v^{(d)}(t)$  exceeds the electronic polarizability  $\alpha_m \approx 1.05 \cdot 10^{-24} \text{ cm}^3$  of water monomer in several times:  $\alpha_v^{(d)}(t) / \alpha_m \sim (1 \div 10)$ . It is very important that  $\alpha_v^{(d)}(t)$  is independent on temperature (since  $\langle \delta \vec{d}_d^2 \rangle \sim T$ ).

The careful comparison of theoretical predictions with experimental data allows us to get the temperature dependence of dimer concentration (see [31]).

### b) DIELECTRIC PERMITTIVITY OF LIQUID WATER

The structure of the hexagonal ice is determined by hexamers [1]. At the fusion of ice the global molecular ordering is violated and hexamers become unstable. In this situation it seems to be natural to assume that the structure of liquid

water is mainly formed by clusters of lower order – cyclic tetramers and dimers having simpler structure and more stable relatively effect of irregular molecular surrounding. At that, the dipole moment of a cyclic tetramer in its ground state is equal to zero. In accordance with this the effective polarizability of a water molecule equals to:

$$\begin{aligned} \alpha_{eff}(t) = \alpha_m &+ \frac{c_d}{2(2-c_d)} \left( \alpha_2^{(d)} + \frac{2\vec{d}_m^2}{3k_B T} \right) + \\ &+ \frac{(1-c_d)}{2(2-c_d)} \alpha_4^{(t)} + \dots \end{aligned} \quad (6)$$

where

$$c_d = \frac{n_d}{n_d + n_t}, \quad c_t = \frac{n_t}{n_d + n_t},$$

are the concentrations of dimers and tetramers, and  $n_i$ ,  $i = d, t$ , are their densities,

$$\alpha_2^{(d)} = \frac{\langle \delta \vec{d}_d^2 \rangle}{3k_B T}, \quad \alpha_4^{(t)} = \frac{\langle \delta \vec{d}_t^2 \rangle}{3k_B T}, \quad (7)$$

are the contributions to the effective polarizability of water molecule caused by vibrations of dimers and tetramers. Here it is also taken into account that the electronic polarizability of tetramer satisfies the relation:  $\alpha_t \approx 4\alpha_m$  with quite good accuracy. We also assume that the energy of electrostatic field in media tends to its minimal value, in consequence of the dimer concentrations in water should be close to zero. This requirement is only violated in the vicinity of the critical point, where a system becomes spatially inhomogeneous due to large-scale fluctuations.

The comparison of  $\alpha_{eff}(t)$ , determined according to  $\alpha_{eff}(t) = \frac{3}{4\pi} \frac{m_w}{\rho} \frac{\epsilon - 1}{\epsilon + 2}$ , with experimental values of  $\epsilon$  and  $\rho$ , and calculated with the help of (6) and (7), testifies about their full compatibility. Details of this comparison are presented in [31] and they show the leading role of tetramers in liquid water. At that the large values of the dielectric permittivity for liquid water are mainly formed by thermal excitations

of tetramers. The role of dimers is only essential near the critical point.

#### **4. MANIFESTATION OF THERMAL EXCITATIONS OF CLUSTERS IN HEAT CAPACITY OF WATER**

Here we will show that peculiarities of the heat capacity are determined by fine properties of H-bonds.

##### **a) H-BOND STRUCTURE**

In works [14, 32-36] it had been shown that the H-bonding energy is determined by sum of electrostatic interaction, responsible for the formation of clusters, and relatively weak exchange one, arising due to the overlapping of electronic shells for molecules [14]:

$$\varepsilon_H = \varepsilon_{el} + \varepsilon_h, \quad \varepsilon_h \leq 0.2\varepsilon_{el}.$$

As noted above,  $\varepsilon_h$  should be interpreted as an irreducible part of H-bonding energy. With this value additional vibrations of electronic density are connected and they generate independent contributions to the heat capacity of water. Since the overlapping region for electronic shells reminds a string connecting the oxygen of one water molecule with hydrogen of other molecule, we can speak about two transversal and one longitudinal vibration degrees of freedom. The excitation energy for transversal vibrations is as rule lesser than that for longitudinal one, therefore we can take into account only transversal vibrations of electronic density.

##### **b) CONTRIBUTION OF CLUSTER THERMAL EXCITATIONS TO THE HEAT CAPACITY OF WATER VAPOR**

Similarly to dielectric permittivity the role of cluster thermal excitations is the simplest in non-dense water vapor. It is evident that the heat capacity  $\zeta_v$  of such a vapor at constant volume per molecule is determined by the expression:

$$\zeta_v = \frac{\zeta_m + c_d(\zeta_d - \zeta_m)}{1+c_d}, \quad (8)$$

where  $\zeta_m$  and  $\zeta_d$  are the heat capacities per monomer and dimer correspondingly. If dimers are not excited than  $\zeta_m$  and  $\zeta_d$  are only caused by translational and rotational degrees of freedom:

$\zeta_m = 6, \zeta_d = 6$  in units  $1/2k_B$ . In this case (8) is essentially simplified:

$$\zeta_v = \frac{6}{1+c_d}.$$

If dimers are excited the formula (8) is generalized:

$$\zeta_v = \frac{\zeta_m + c_d \xi_v}{1+c_d},$$

where  $\xi_v$  is the contribution caused by vibration degrees of freedom. In classic approximation 6 vibration degrees of freedom lead to  $\zeta_v = 12$ . From here it follows:

$$\zeta_v = 6 \left( 1 + \frac{c_d}{1+c_d} \right). \quad (9)$$

If we will take into account the vibrations of electronic density connected with the irreducible part of H-bonding, the formula (9) transforms to:

$$\zeta_v = 6 \left( 1 + \frac{c_d(1+(1.6)\xi_v^{(e)}(t))}{1+c_d} \right), \quad (10)$$

where  $\xi_v^{(e)}(t) = \sum_{i=1}^3 \xi_v^{(i)}(t)$  and the summation is carried out on three additional degrees of freedom [20]. Fitting the experimental values of the heat capacity with the help of (10) we can estimate the concentration  $c_d$  of dimers in a water vapour. In [31] it had been shown that values of  $c_d$  obtained from the analysis of dielectric permittivity and heat capacity, agree with each other quite satisfactory.

It is necessary to note that talking into account of internal vibration degrees of freedom is standard for the description of the heat capacity of alcohols belonging to the methanol series [27].

##### **c) CONTRIBUTION OF CLUSTER THERMAL EXCITATIONS TO THE HEAT CAPACITY OF WATER**

The heat capacity  $\zeta_w$  of liquid water at constant volume can be represent by the sum:

$$\zeta_w = \zeta_w^{(0)} + \xi_v^{(e)}. \quad (11)$$

Here the first term describes the constituent caused by translational and orientation vibrations of rigid water molecules having the same

physical nature as the molecular motion for a water homologue  $H_2S$ . In liquid states of the last H-bonds absent and the heat capacity is mainly determined by vibration degrees of freedom. This contribution is estimated as:

$$\zeta_w^{(0)} \approx 12. \quad (12)$$

that practically coincides with the experimental value of the heat capacity for  $H_2S$ . The term  $\xi_v^{(e)}$  can be approximated by the expression:

$$\xi_v^{(e)} = \frac{1}{2} n_H(t) \sum_{i=1}^3 \xi_v^{(i)} \approx (5 \div 8). \quad (13)$$

proportional to the number of H-bonds per molecule. Here it is also taken into account that the vibration energy for the irreducible constituent of H-bond should be divided between two molecules (multiplier 1/2) and maximum value for each vibration contribution equals to 2.

The agreement between  $\zeta_w$  calculated according to (11) – (13) and experimental data is practically full.

## 5. DISCUSSION OF THE RESULTS OBTAINED

From our consideration it follows that the most characteristic properties of water are naturally explained by its cluster structure as well as thermal excitations of clusters. The lasts play the determinative role in the formation of entropy, heat capacity and dielectric permittivity of water. Unfortunately this circumstance is not always taking into account [1]. It is necessary to note that thermal excitations of clusters in water play the same role as internal vibration degrees of freedom in alcohols belonging to the methanol series. The excitation of internal degrees of freedom is also observed for water molecules however this effect becomes essential only for temperatures comparative with the critical one and for higher ones. In contrast to this the excitation of water clusters is observed for all liquid states.

In order to explain successfully water properties we should consider H-bonds as complicated objects consisting from two

different constituents. The first of them is caused by electrostatic interactions between several modeled charges [15-18] or multipole moments of water molecules [19]. This part of interparticle interaction is mainly responsible for the clusterization in water, its tetrahedral structure and its EoS. Moreover from the requirement of minimal value for the electrostatic interaction energy it follows the dominating role of cyclic clusters, having no dipole moments in liquid states of water. The second one is formed by exchanged effects arising due to the overlapping of electronic shells for water molecules. Although their contribution to the H-bonding energy is relatively small ( $\varepsilon_b \leq 0.2\varepsilon_e$ ), namely they form the important contributions to caloric and dielectric properties of liquid water and are absent for those in liquid states of  $H_2S$ . At that, the polarization properties of water are formed by fluctuation dipole moments of cyclic clusters.

The EoS for water as well as other liquids is formed by sum of pair interparticle contributions [21]. Since water molecules are strongly clustered the change of molecular configurations takes place only on times exceeding the average life time of clusters. Moreover arbitrary pairs molecules belonging to different clusters differ from each other by their relative spatial orientations. It means that the EoS is determined by the averaged (on angular variables) interparticle potentials. If a water state is moved off the triple point the typical size of clusters is reduced and its rotation tends to be quasi-free. Due to this the character of thermal motion in water tends to that in argon and its properties – to argon-like ones.

## REFERENCES

1. Eisenberg D and Kauzmann V. *The Structure and Properties of Water*. New York, Oxford, University Press, 1969, 280 p.
2. Frenkel J. *Kinetic Theory of Liquids*. New York, Dover Publ., 1955, 592 p.
3. Samoilov OY. *Struktura vodnykh rastvorov elektrolitov i gidratatsiya ionov* [Structure of Water Solutions of Electrolytes and

- Hydration of Ions]. Moscow, 1957, Acad. Sci.USSR Publ.,183 p.
4. Bulavin LA, Malomuzh NP and Pankratov KN. Character of the thermal motion of water molecules according to the data on quasielastic incoherent scattering of slow neutrons. *J. Struct. Chem.*, 2006, 47:52-60 (in Russ.).
  5. Bulavin LA, Malomuzh NP and Pankratov KN. Specific features of self-diffusion in water. *J. Struct. Chem.*, 2006, 47:S54-S64 (in Russ.).
  6. Bulavin LA, Lokotosh TV, Malomuzh NP. Role of the collective self-diffusion in water and other liquids. *J.Mol.Liq.*, 2008, 137:1-24.
  7. Bulavin LA, Malomuzh NP. Upper temperature limit for the existence of living matter. *J.Mol.Liq. (Letter to the Editor)*, 2006, 124:136-137.
  8. Malomuzh NP, Makhlaichuk VN, Makhlaichuk PV, Pankratov KN. Cluster structure of water in accordance with the data on dielectric permittivity and heat capacity. *J. Struct. Chem.*, 2013, 54(Suppl 2):205-220 (in Russ.). <https://doi.org/10.1134/S0022476613080039> (2013).
  9. Okada K, Yao M, Hiejima Y, Kohno H, Kojihara Y. Dielectric relaxation of water and heavy water in the whole fluid phase. *J.Chem.Phys.*, 1999, 110(6):3026-3036.
  10. Pruppacher HR. Self-diffusion coefficient in supercooled water. *J.Chem.Phys.*, 1972, 56(1):101-107.
  11. Simpson K, Karr M. Diffusion and nuclear spin relaxation in water. *Phys.Rev.*, 1958, 111(5):1201-1203.
  12. Makhlaichuk PV, Makhlaichuk VN, Malomuzh NP. Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type. *J.Mol.Liq.*, 2017, 225:577-584.
  13. Malomuzh NP, Makhlaichuk VN. On the similarity of the self-diffusion and shear viscosity coefficients in low-molecular liquids. *J. Mol. Liq.*, 2019, 295:111729.
  14. Malomuzh NP, Zhyganiuk IV, Timofeev MV. Nature of H-bonds in water vapor. *J. Mol. Liq.*, 2017, 242:175-180.
  15. Berendsen HJC, Postma JPM, van Gunsteren WF, Hermans J. Interaction Models for Water in Relation to Protein Hydration, in *Intermol. Forces*, ed. by B. Pullman, Dordrecht, Springer, 1981, 331–342.
  16. Berendsen HJC, Grigera JR, Straatsma TP. The missing term in effective pair potentials. *J. Phys. Chem.*, 1987, 91:6269-6271.
  17. Jorgensen WL. Transferable Intermolecular Potential Functions for Water, Alcohols, and Ethers. Application to Liquid Water. *J. Am. Chem. Soc.*, 1981, 103:335-340.
  18. Jorgensen WL, Chandrasekhar J, Madura JD, Impey RW, Klein ML. Comparison of simple potential functions for simulating liquid water. *J. Chem. Phys.*, 1983, 79:926-935.
  19. Timofeev MV. Simulation of the Interaction Potential between Water Molecules. *Ukr. J. Phys.*, 2016, 61:893-900.
  20. Landau LD, Lifshitz EM. *Statistical Physics, 3rd Edition, Volume 5*. Butterworth-Heinemann, 2013, 544 p.
  21. Fisher IZ. *Statistical Theory of Liquids*. University of Chicago Press, 1964, 280 p.
  22. Malenkov GG. Structural and dynamical heterogeneity of stable and metastable water. *Phys. A Stat. Mech. Its Appl.*, 2002, 314:477-484.
  23. Voloshin VP, Naberukhin YI. Hydrogen bond lifetime distributions in computer-simulated water. *J. Struct. Chem.*, 2009, 50:78-89.
  24. Voloshin VP, Naberukhin YI, Malenkov GG. Percolation analysis of hydrogen bonds network in water: colouring with bond lifetime and energy. *Electron. J. "Structure Dyn. Mol. Syst."*, 2011, 10:12-25. ([http://old.kpfu.ru/sdms/sod\\_10a\\_2011.htm](http://old.kpfu.ru/sdms/sod_10a_2011.htm)).
  25. Lokotosh TV, Malomuzh NP, Zakharchenko VL. Anomalous Density and Permittivity Effects on the Structure of Water. *J. Struct. Chem.*, 2003, 44(6):1001-1010.

26. Fisenko AI, Malomuzh NP, Oleynik AV. To what extent are thermodynamic properties of water argon-like? *Chem. Phys. Lett.*, 2008, 450:297-301.
27. Chechko VE, Gotsulsky VY, Malomuzh NP. Surprising thermodynamic properties of alcohols and water on their coexistence curves. *J. Mol. Liq.*, 2018, 272:590-596.
28. Kataoka Y, Hamada H, Nose S, Yamamoto T. Study of liquid water by computer simulations. Static properties of a 3D model. *J. Chem. Phys.*, 1982, 77(8):5699-5703.
29. Krishtal S, Kiselev M. Hydrogen bonding in sub- and supercritical methanol. Molecular dynamic study. *Chemistry Preprint Archive*, 2003, 7(1). Available at SSRN: <https://ssrn.com/abstract=2979821>.
30. Kulinskii VL, Malomuzh NP. Dipole fluid as a basic model for the equation of state of ionic liquids in the vicinity of their critical point. *Phys. Rev. E*, 2003, 67:011501.
31. Makhlachuk VN, Malomuzh NP. Manifestation of cluster excitations in dielectric properties of water vapor and liquid water as well as their heat capacity. *J. Mol. Liq.*, 2018, 253:83-90.
32. Sokolov ND. H-bond. *Uspekhi Fizicheskikh Nauk*, 1955, 57(2):205-278.
33. Dolgushin MD, Pinchuk VM. Theoretical study of the nature of the hydrogen bond by comparative calculations. *Preprint ITF AN USSR*, 76-49P, Kiev, 1976, 18 p.
34. Barnes P. Machine Simulation of Water. *Progress in Liquid Physics*, Ed. by C.A.Croxtan, Chichester, Wiley, 1978, 391-428.
35. Clementi E, Popkie H. Energy Surface of a Water Molecule in the Field of a Lithium Positive Ion. *J. Chem. Phys.*, 1972, 57(3):1077-1094.
36. Fulton RL, Perhaes P. Sharing of Electrons in Molecules: Characterization of Hydrogen Bonds. *J. Phys. Chem. A*, 1998, 102:9001-9020.