Cluster structure of water and its argon-like equation of state
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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 $\tau \gg \tau_0$, 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: $\tau_{exc} << \tau_0$. 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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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. Sometimes the similar picture of displacements and rotations of molecules describes with the help of two characteristic times: $\tau_0$ and $\tau_1$ [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: $\tau_1 < \tau_0$ is carried out. Since $\tau_0$ and $\tau_1$ depend on temperature, this condition can only carried out in some temperature interval. At that with suitable accuracy $\tau_1$ can be approximated by the expression: $\tau_1 \sim a/v_T$, 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: $\tau_0/\tau_1$ 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 can see, the crystal-like representations for the description of thermal motion in water are only applicable in the narrow temperature interval: 273 K < $T$ < $T_{1p}$, $T_{1p} = 315$ K, of its normal states as well as for its supercooled ones: $T < 273$ 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 $\tau_1$ has meaning of the period for free rotation of water molecules, $\tau_1 \sim 2\pi/\omega_T$ where $\omega_T \sim \sqrt{k_B T / I}$ is the characteristic value of angular velocity, $I = m_H v_{oH}^2$ 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: $\tau_1 \sim 0.5 \cdot 10^{-12}$ s. As we can see, temperature dependences of the dipole relaxation time are different in the temperature intervals (see [7, 8]): 1) $T < T_{1p}$ where $\tau_d >> \tau_1$ and 2) $T > T_{1p}$ where $\tau_d \geq \tau_1$. 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...
molecules, obtained by different methods, is consistent with each other.

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

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

At that, the value of the activation energy for the dipole relaxation time, $\varepsilon_{ii} = E_{ii} / k_B T$, 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 $\tau_0$. 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 $\tau_0$.

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:

$$\Phi(r, \Omega_1, \Omega_2) = \Phi_{\text{disp}}(r, \Omega_1, \Omega_2) + \Phi_{\text{el}}(r, \Omega_1, \Omega_2) + \Phi_{\text{H}}(r, \Omega_1, \Omega_2),$$

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:

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

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

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

$$T_c = \frac{8a(T_c)}{27b(T_c)}. \quad (3)$$

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

$$T_c^{(SPC)} = 626K, \quad T_c^{(SPC_\mu)} = 561K. \quad (4)$$

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:

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

correct for $\varepsilon_a(k_BT) > 1$, we get the following estimates for the critical temperature:

$$T_c^{(SPC)} = 650K, \quad T_c^{(SPC_\mu)} = 604K. \quad (5)$$

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

$$T_c^{(w)} \approx \frac{\varepsilon_w^{(el)} + \varepsilon_w^{(dr)}}{\varepsilon_{r}} T_c^{(dr)} = 638K. \quad (6)$$

following from the similarity principle [20, 21].

The relative width of the temperature interval for liquid states of argon equals to $\frac{T^{(dr)} - T^{(dr)}}{T^{(dr)}} \approx 0.56$.

In the argon-like approximation the relative width of the corresponding interval $\frac{T^{(w)} - T^{(w)}}{T^{(w)}}$ for water should be the same: $\frac{T^{(w)} - T^{(w)}}{T^{(w)}} \approx 0.56$. From here we get the following estimate for the triple point temperature of water:

$$T^{(w)} = 0.44T_c^{(w)} = 280K. \quad (7)$$

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:

$$\nu_w(t) \approx \left(\frac{\sigma_w}{\sigma_{r}}\right)^3 \nu_{r}(t), \quad \nu_w(t = 1) \approx \left(\frac{\sigma_w}{\sigma_{r}}\right)^3 \nu_{r}(t = 1) = 0.56, \quad \text{SPC}, \quad 0.62, \quad \text{MP}. \quad (8)$$

Its corresponding experimental value equals to:
allows us to conclude that \( t \), i.e. its relative value does not change with approaching the water triple point. Only in the narrow vicinity of the critical point these our conclusions should be precis[20, 27].

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

\[
\tilde{\nu}_H(t) = 4(1 - \lambda t + ...), \quad \lambda = 0.85.
\]

Near the triple and critical points values of \( n_{\lambda}(t) \) are correspondingly equal to: \( n_{\lambda}(t = 0.42) \approx 0.26 \) and \( n_{\lambda}(t = 1) \approx 0.6 \), 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 \( n_{\lambda}(t) \) 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 \( T_m = 277 \text{ K} \). 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 \( \varepsilon \) can represent in the view [31]:

\[
\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \frac{\rho}{m_w} \alpha_{\text{eff}},
\]
where \( \rho \) is the mass density, \( m_w \) is the mass of a water molecule, \( \alpha_{\text{eff}} \) 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: \( \vec{d}_2 = 2\vec{d}_m \) [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:

\[
\alpha_{\text{eff}} = \alpha_m + \frac{d_m^2}{3T_t} + ... 
\]

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

\[
\alpha_{\text{eff}} = \alpha_m + \frac{c_d}{1+c_d} \alpha_{\text{v}}^{(d)}(t) + \frac{d_m^2}{3T_t} + ...
\]

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 \( \alpha_{\text{v}}^{(d)}(t) \) to the effective polarizability:

\[
\alpha_{\text{v}}^{(d)}(t) = \frac{\left\langle \delta d_d^2 \right\rangle}{3T_t} 
\]

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

In [31] it had been shown that the numerical value of \( \alpha_{\text{v}}^{(d)}(t) \) exceeds the electronic polarizability \( \alpha_m \approx 1.05 \times 10^{-24} \text{ cm}^3 \) of water monomer in several times: \( \alpha_{\text{v}}^{(d)}(t)/\alpha_m \sim 1\times10 \). It is very important that \( \alpha_{\text{v}}^{(d)}(t) \) is independent on temperature (since \( \left\langle \delta d_d^2 \right\rangle \sim T \) ).

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:

\[
\alpha_{\text{eff}}(t) = \alpha_m + \frac{c_d}{2(2-c_d)} \left( \alpha_2^{(d)} + \frac{2d_m^2}{3k_BT} \right) + \frac{(1-c_d)}{2(2-c_d)} \alpha_4^{(t)} + ...
\]

(6)

where

\[
c_d = \frac{n_d}{n_d + n_t}, \quad c_i = \frac{n_i}{n_d + n_t},
\]

are the concentrations of dimers and tetramers, and \( n_i, i = d,t \), are their densities,

\[
\alpha_2^{(d)} = \frac{\left\langle \delta d_d^2 \right\rangle}{3k_BT}, \quad \alpha_4^{(t)} = \frac{\left\langle \delta d_t^2 \right\rangle}{3k_BT},
\]

(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 \( \alpha_{\text{eff}}(t) \), determined according to \( \alpha_{\text{eff}}(t) = \frac{3}{4\pi} \frac{m_w}{\rho} \frac{\varepsilon-1}{\varepsilon+2} \), with experimental values of \( \varepsilon \) 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 another 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:

\[
\zeta_v = \zeta_m + c_d (\zeta_d - \zeta_m),
\]

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:

\[
\zeta_m = 6, \quad \zeta_d = 6 \text{ in units } 1/2k_B. \quad \text{In this case } (8) \text{ is essentially simplified:}
\]

\[
\zeta_v = \frac{6}{1 + c_d},
\]

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

\[
\zeta_v = \frac{\zeta_m + c_d \zeta_v}{1 + c_d},
\]

where $$\zeta_v$$ 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:

\[
\zeta_v = 6 \left(1 + \frac{c_d}{1 + c_d}\right).
\]

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

\[
\zeta_v = 6 \left(1 + \frac{c_d (1 + (1.6) \zeta_v^{(e)}(t))}{1 + c_d}\right),
\]

where $$\zeta_v^{(e)}(t) = \sum_{i=1}^{3} \zeta_v^{(i)}(t)$$ 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 $$\zeta_v$$ of liquid water at constant volume can be represent by the sum:

\[
\zeta_v = \zeta_v^{(0)} + \zeta_v^{(e)}.
\]

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:

$$\zeta_w^{(0)} \approx 12.$$  \hspace{1cm} (12)

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

$$\zeta_v^{(e)} = \frac{1}{2} n_{H} (1) \sum_{i=1}^{1} \zeta_v^{(i)} \approx (5 + 8).$$ \hspace{1cm} (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 ($\epsilon_1 \leq 0.2 \epsilon_{el}$), 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.

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