Surprising properties of water on its binodal as the reflection of the specificity of intermolecular interactions

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Abstract

In the paper the behavior of density (or specific volume), the heat of evaporation and entropy per molecule for normal and heavy water on their coexistence curves is discussed. The special attention is paid on the physical nature of the similarity in the behavior of density and the heat of evaporation for water and argon as well as the nearest water homolog \( H_2S \). It is shown that the appearance of this similarity is a consequence of the rotational motion of water molecules, which averages the inter-particle potential in water and leads it to the argon-like form. To describe the fine distinctions in the behavior of the binodals for water, \( H_2S \) and argon the dependence of the proper molecular volume on pressure is taken into account. In accordance with this often used the van der Waals and Carnahan-Starling equations of states are modified. The very surprising behavior of the entropy diameter for water is analyzed. It is shown that the nontrivial details of the temperature dependence for the entropy diameter is directly connected with the peculiarities of the rotational motion of molecules in water. The effect of strong dimerization of water molecules in the fluctuation region near the critical point is studied in details.

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I. INTRODUCTION

The surprising properties of water, as it is well known [1, 2], are caused by H-bonds. The character of their spatial organization and time dynamics depends essentially on temperature and pressure. As a result, the peculiarities of the translational and rotational motion of water molecules are very different near the triple and critical points. There are several key facts which allow to make the important conclusions about the behavior of the H-bond network in water and the character of the thermal motion of water molecules, in particular, near its critical point. One of them is presented in Fig. 1, where the comparison of the specific volume per molecule $v(i)$ for water and argon ($i = w; Ar$) is given. The dimensionless temperature $t = T/T_c(i)$, where $T_c(i)$ is the critical temperature of liquids, is used. As seen, the behavior of the specific volume of water is very surprising. Practically in the whole region it is argon-like. Only in the narrow vicinity of the critical point ($0.95 < t < 1$) the deviation of $v(w)(t)$ from the argon-like dependence is essential. Outside of this region ($t_m < t < 0.95$), where $t_m = 0.42$ is the melting point, the deviation from the argon-like dependence does not exceed $3 \div 4\%$. The minimum of the specific volume of water at $T \approx 277K$ corresponds to the weak increase of the ratio $R_v(t) = v(w)(t)/v(Ar)(t)$ at approaching the melting point. In accordance with Fig. 1, the temperature dependence of $R_v(t)$ can be represented in the form:

$$R_v(t) = \kappa + r_H(t),$$

where $r_H(t)$ is the contribution caused by H-bonds in water: $r_H(t) \ll \kappa$.

To describe the temperature dependence of $r_H(t)$ seems to be natural to apply to the Hilbert’s principle [? ? ], which was formulated for the first time in the algebraic invariant theory and having the numerous applications in the statistical hydrodynamic [5]. According to this principle, an arbitrary complicated function can be expanded in the series with respect to independent primitive functions, which have the same properties of symmetry:

$$r_H(t) = \sum_k r_k^{(H)} \cdot S_k(t, p), \quad (1)$$

where $r_k^{(H)}$ are the coefficients, which are functions of temperature $t$ and the dimensionless pressure $p = P/P_c$, $P_c$ is the critical pressure. The independent structural characteristics of the H-bond network, so-called structural functions [? ? ], play a role of primitive functions $\{S_i\}$. 

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The most important characteristics of the H-bond network are the average number \( n_H \) of H-bonds per molecule and the parameter of tetrahedricity \( \chi(T) \) (see \[3, 4\]). Therefore, the first two structural functions can be chosen as: \( S_1 = n_H(t, p) \) and \( S_2 = \chi_H(t, p) \). The structural functions of a higher order are assumed to be responsible for the finer details of the H-bond network and here they will be ignored. In \[5\] it was shown, that with good accuracy \( (1) \) can approximated as

\[
r_H(t) = r_H^{(0)} \cdot n_H(t), \quad n_H(t) = 4(1 - \lambda t + ...).
\]

Fitting the experimental data on \( R_v(t) \) with the help of \( (2) \) one can get: \( \kappa = 0.63, r_H^{(0)} = 0.015; \lambda = 0.85. \) The value and the temperature dependence of \( n_H(t) \), given by Eq. \( (2) \), are in good agreement with the results obtained in \[5, 6, 7\].

Below we will show, that the temperature dependence of the heat of evaporation in water is also similar to that for argon. The estimate for \( n_H(t) \), following from the analysis of the heat of evaporation, practically coincides with Eq. \( (2) \).

To explain the similarity in the behavior of the specific volume and the heat of evaporation in water and argon we should conclude that the mentioned quantities and some other thermodynamic characteristics of water are determined by the averaged intermolecular potential, which takes the argon-like behavior.
From Eq. (4) it follows that near the critical point the average number of H-bonds per molecule takes value \( n_H(1) \approx 0.7 \). It means, that in the fluctuation region, \( 0.85 < t < 1 \), water can be considered as the ensemble of dimers. This conjecture is supported by the results obtained in [? ]. Besides, it becomes to be self-evident if we take into account that in this region the volume of cavity \( (v_{cav} = 2v_m) \) occupied by two water molecules are greater than that volume, which is created by a rotating dimer \( (v_{cav} > v_d) \). Qualitatively, almost full dimerization of water molecules allows us to explain naturally the sharp enough increment of the ratio \( R_v \) near the critical point (see Fig. [4]).

The present paper is devoted to the careful analysis of the density, entropy and the heat of evaporation on the coexistence curve of water in the wide temperature range from the melting to the critical points. The special attention is paid to the dimerization effects of water molecules in the fluctuation region.

To describe the fine details in the behavior of the density, diameter of entropy and the heat of evaporation on the binodal we take into account the rotation of water molecules. Due to this the proper molecular volume becomes to be dependent on the temperature and density. The last circumstance is proved to be essential not only for water but also for all liquids with non-spherical molecules and even for the noble gases, although in smaller extent.

The comparative analysis of thermodynamic properties of the normal and heavy water is performed. It notices that the isotopic effect manifests itself not only in the shifts of the critical and melting points. In the considerably more extent it is manifested in the behavior of their diameters of entropy and their specific heats.

It is taken into account that in the fluctuation region the volume, occupied by two water molecules, is greater than that volume, which is created by a rotating dimer. As a result the strong dimerization in water is stimulated. Using the methods of chemical equilibrium, we study the degree of dimerization. Applying the van der Waals equation of state, we show that the location of the critical point in water is mainly determined by the ensemble of dimers. It is established that different values of the specific heats for normal and heavy water in their fluctuation regions, \( 0.85 < t < 0.98 \), are connected with the inner rotation of monomers, entering the dimers \( (D_2O)_2 \) in the heavy water.
II. THE DIMERIZATION OF WATER IN THE NEAR CRITICAL REGION

In this section in accordance with [? ] we use the vdW based model with the account of dimerization. We calculate the average number of $H$-bonds per molecule along the coexistence curve. Note that for completely dimerized water $n_H = 1$. In accordance with said in Introduction we assume that water near critical point is fully dimerized. Thus water dimer $(H_2O)_2$ plays the role of a “particle”. According to the quantum chemistry calculations [? ] the diameter of a dimer $\sigma_d \approx 3.5 \text{Å}$ and the dipole moment $d_d \approx 2.6 D$.

The idea that the dimers are predominant in near critical region has been put forward before (see [? ] and references therein). Though the inference was made from the analysis of structural data (Raman scattering) which did not led to the firm conclusion. Lately, the results of MD simulations [? ] favored the picture that in near critical region water behaves more like associative fluid as opposed to the assumptions about peculiar (fractal) structure of hydrogen bonded network [14, 15].

Therefore we can expect that in near critical region water can be reasonably described by the vdW EOS for the system of dimers. The basis for the use the van der Waals like EOS in near critical region is due to low density and thus intensive rotation. Indeed, the average spacing between dimers at the critical density is about $3.5 \text{Å}$ and is more than the size of dimer. However at removing of the critical point along liquid branch the character of the dimer rotation changes: the quasi-free rotation of a dimer discontinues at $v_{cav} \to v_d$. When $v_{cav}(t) \leq v_d$, the dimers breaks and linear molecular chains are formed. A molecule entering in some chain can change its spatial orientation in consequence of two mechanisms: 1) the rotation around two H-bonds connecting it with other molecules in this chain and 2) the break of these H-bonds. passes to the rotation around the H-bond connecting dimer molecules. At the further removing of the critical point linear molecular chains begin to cooperate in spatial clusters. Here a molecule can change its orientation only because of the break of H-bonds connecting it with the nearest neighbors.

The comparison of the heat of evaporation data gives the additional support for the picture of rotating molecular dipoles. It is known that the heat of evaporation of water is very big in comparison with other homologs like $H_2S$ or nonpolar simple liquids like $Ar$. This ratio for a number of the liquids is shown on Fig. 2 with $H_2S$ chosen as the reference fluid. Note that water and methanol have the same ratio.
Note that the ratio of the heat of evaporation per molecule is almost constant for different fluids along the whole coexistence curve. The same constancy of the ratio of specific volume takes place for water and argon (see [16]). This fact seems to be quite surprising because the interparticle interaction differs for different liquids. As we see, the ratio of the densities for water and its nearest homologue linearly increases within 10%. This increment is slightly larger than for corresponding ratio for water and argon (see Introduction and [17]). This fact means that the rotational motion of the weakly asymmetric molecules of liquid influences its EOS. This effect, as it follows from Fig. 2(b) has similar character for other liquids. Below it will be connected with the softness of the molecular volume entering the vdW EOS and close ones.

To explain the constancy of the ratio $R_H(i) = \frac{H(i)}{H^{(H)}}$ as well as $R_n(i) = \frac{n(i)}{n^{(H)}}$, we are forced to suggest that the simplest thermodynamic quantities are determined by the averaged inter-particle potentials. In fact this averaged potential appear to be of the van der Waals character. At that time, such quantities as heat capacity, the density, the entropy diameters and dielectric permittivity are determined by the deviation from the averaged interactions. These quantities strongly depend on the short range correlations.

To explain the numerical values of the ratio $R_H(i)$ for different liquids, we can use the following qualitative reasons. By order of magnitude, the heat of evaporation is the work per molecule which is necessary to expand its specific volume from $v_l$ to $v_g$: $H(i) \approx P(v_l - v_g)$, where all quantities are taking on the coexistence curve. Outside the fluctuation region $v_l > (\gg) v_g$, therefore we can approximately write $H(i) \approx P v_g$ or $H(i) \approx Z_c^{(i)} T_c^{(i)} \tilde{Z}^{(i)}$, where
\[
R_H(i) = \frac{T_c(i) Z_c(i) Z^{(i)}}{T^{(H_2S)}_c Z_c^{(H_2S)} Z^{(H_2S)}}.
\]

For the rare enough vapor phases of \( i \)-th and \( H_2S \) system:

\[
\frac{Z^{(i)}}{Z^{(H_2S)}} \approx 1,
\]

so:

\[
R_H(i) \approx \frac{T_c(i) Z_c(i)}{T^{(H_2S)}_c Z_c^{(H_2S)}}.
\]

As is seen from Table I, the raw estimate Eq. (4) gives unsatisfactory prediction for liquids like water and methanol. Like water, the last is known of its associative properties [17, 18]. Note that the compressibility factor is calculated assuming that only the monomers is present in near critical region. The value of \( R_H(i) \) for water with account of dimerization degree is 2.5 (see Appendix A and Eq. (A4)). Thus it allows to conclude that the dimerization for the methanol as well as water is essential in near critical region (see below).

From our consideration it follows that the determination of the energy of H-bond for water from the heat of evaporation data is not correct. In accordance with our estimates, in the vicinity of the critical point water can be considered as the ensemble of dimers with small admixture of monomers. To determine the location of the critical point for water we apply to the van der Waals EOS:

\[
p(n, T) = \frac{nT}{1 - nb} - an^2
\]

where \( p \) is the pressure and \( a \) and \( b \) are the vdW parameters. According to [19] they are:

\[
b = \frac{2\pi}{3} \sigma_d^3, \quad a = \pi \int_{\sigma_d}^{\infty} U(r) r^2 dr,
\]

\[
\begin{array}{ccccccc}
\text{Fluid} & CH_3OH & H_2O & O_2 & Ar & N_2O & SO_2 \\
R_{H}^{(m)}(i), \text{Eq. (4)} & 0.9 & 1.4 & 0.42 & 0.41 & 0.8 & 1.1 \\
R_{H}^{(exp)}(i) & 2.0 & 2.4 & 0.37 & 0.35 & 0.9 & 1.4
\end{array}
\]

TABLE I: The comparison of \( R_H(i) \) calculated according to Eq. (4) for ensemble of monomers (subscript \( (m) \)) and with the help of experimental data [16].

\( \tilde{Z} \) is the dimensionless form for the compressibility factor \( Z = \frac{P_v}{T} \). From here it follows that \( R_H \) is estimated as:

\[
\tilde{Z}(i) \approx 1,
\]

so:

\[
R_H(i) \approx \frac{T_c(i) Z_c(i)}{T^{(H_2S)}_c Z_c^{(H_2S)}}.
\]
In [7, 8] it had been shown that the attractive part of the dimer-dimer potential is mainly determined by their dipole-dipole interactions:

\[ U_a(r) = \frac{2}{3} \frac{d_{\text{dim}}^4}{r^6}. \]  

(7)

Therefore the coefficient \( a \) becomes to be temperature dependent: \( a \rightarrow \frac{a}{T} \), and the van der Waals EOS transforms to Bertlo EOS:

\[ p(n, T) = \frac{nT}{1 - nb} - \frac{a}{T} n^2. \]  

(8)

The coordinates of the critical point is determined by the standard conditions:

\[ \frac{\partial p}{\partial n} = 0, \quad \frac{\partial^2 p}{\partial n^2} = 0. \]

The coordinates of the critical point for the Bertlo EOS (8) are determined by equations:

\[ n_c^{(d)} = \frac{1}{3b_d} = \frac{1}{2\pi \sigma_d^3}, \quad T_c^{(d)} = \sqrt{\frac{8a_d}{27b_d}} = \frac{2\lambda^2 \sqrt{2}}{9} \frac{e^2}{\sigma_d}, \quad p_c^{(d)} = \frac{3}{8} n_c T_c = \frac{\lambda^2}{12\pi \sqrt{2}} \frac{e^2}{\sigma_d^4}, \]  

(9)

where \( \lambda \) is the parameter which determines the dipole moment \( d_{\text{dim}} \) of the dimer and \( d_{\text{dim}} = \lambda e \sigma_d \). We choose the value of \( \lambda \) so that to get the best fit for the coordinates of the vdW critical point which are:

\[ T_c^{(d)} \approx 647 \, K, \quad P_c^{(d)} \approx 18.0 \, MPa, \quad \rho_c^{(d)} \approx 322 \, kg/m^3. \]  

(10)

The fitting gives the value \( \lambda \approx 0.19 \) and the dipole moment of a dimer is \( d_{\text{dim}} \approx 2.9D \), which is in good agreement with the value for dimer dipole moment \( d_{\text{dim}} = 2.6D \) [7, 8]. Sure total dimerization is an approximation but above estimates show that it is consistent. Thus the difference in the compressibility factor \( Z_c \) is due to the deviation from vdW EOS since the influence of free monomers was neglected.

Now we refine the estimate for the location of the critical point taking into account that water near the critical point is the mixture of dimers and small quantity of monomers. Let us introduce the degree of the dimerization as following:

\[ n_1 = (1 - A) n_0, \quad n_2 = \frac{A}{2} n_0, \]  

(11)

where \( n_0 = n_1 + 2n_2 \) is the number density of water molecules both free and dimerized, \( n = n_1 + n_2 \) is the number density of particles (both the dimers and the monomers). The coefficients \( a \) and \( b \) are the vdW parameters [22]:

\[ b = c_1 b_1 + c_2 b_2, \quad a = c_1^2 a_{11} + 2 c_1 c_2 a_{12} + c_2^2 a_{22}. \]  

(12)
where
\[ b_i = \frac{2\pi}{3} \sigma_i^3, \quad a_{ij} = \pi \int_0^\infty U_{ij}(r) r^2 dr, \] (13)

and \( c_i = \frac{n_i}{n_1+n_2} \) are the concentrations of the monomers and dimers correspondingly with \( n_i \) being the number density of \( i \)-th species respectively, \( \sigma_i \) are the diameters of the particles and \( U_{ij} \) is the potential of the interaction between particles of \( i \)-th and \( j \)-th kinds. In [7] it was shown that the interaction between monomers and dimers is determined mainly by the dipole-dipole forces. The corresponding potentials have the form:
\[ U_{ij} = \beta \frac{2}{3} \langle d_i^2 \rangle \langle d_j^2 \rangle \frac{1}{r^6} \]

In general the virial coefficient \( a_{ij} \) is the sum of the vdW term which does not depend on the temperature and the temperature dependent dipole-dipole term. The chemical potential for monomers is:
\[ \mu_1 = -T \ln (1 - nb) + \frac{T nb_1}{1 - nb} - 2n (c_1 a_{11} + c_2 a_{12}) \]

The chemical potential of the dimers is obtained by the change \( 1 \to 2 \). To construct the binodal for the mixture of dimers and monomers we use common condition of equilibrium the equality of the chemical potentials and the pressures of the coexisting phases:
\[ \mu_{\text{liq}} = \mu_{\text{vap}}, \quad p_{\text{liq}} = p_{\text{vap}}. \] (14)

together with the chemical equilibrium equation Eq. (A1) to determine the equilibrium number densities of the species in coexistence phases.

Let us discuss the compressibility factor as a function of the degree of dimerization. For water considered as an ensemble of monomers and described by the vdW EOS is expected to be
\[ Z_{m}^{(\text{vdW})} = 3/8. \] (15)

If water is completely dimerized:
\[ Z_{d}^{(\text{vdW})} = 3/16. \] (16)

This value is close to the experimental one \( Z^{(\text{exp})} = 0.23 \) near the critical point of water and it can be considered as one of evidences in the favor of high degree of dimerization near the CP. The values of \( Z_c \) corresponding to \( n_c = \rho_c / m_a \), where \( \rho_c \) is the critical mass density and \( m_a \) is the atomic mass, for different fluids considered as the monomeric ones are in Table [I].
As seen from Table I the compressibility factor for methanol practically coincides with that estimate for water which is obtained for the ensemble of dimers. This fact also points to the high degree of dimerization in methanol near its critical point \[23, 24\], that is natural since the intermolecular interaction in methanol is determined by H-bonds, similar to that in water. For several other liquids in Table I do not forming H-bonds the values of the compressibility factor near their critical points are noticeably higher than for water and methanol. This difference is probably connected with 1) the essentially less degree of dimerization in them, even for Ar (see \[\text{?}\]), and 2) the approximate character of the vdW EOS.

![Compressibility factor](image)

**FIG. 3**: Compressibility factor as the function of dimensionless volume of the monomer \(\tilde{b}_1\) and dimensionless monomer-dimer virial coefficient \(\tilde{a}_{12}\) (see Eq. (A3)) at the energy of dissociation \(E_d/T_c = 3.5\).

The influence of the interparticle interactions on the behavior of the compressibility factor is presented in Fig. 3. As for the locus of the CP, the most strong dependence is observed on \(\tilde{a}_{12}\).

Ending this Section let us briefly discuss the interaction between molecules outside the fluctuation region. Here, as was noted above, the equation of state for water is determined by the averaged inter-particle potential. Besides the hard-core part it includes the contributions of the dispersive forces, the dipole-dipole and H-bond interactions between monomers:

\[
\langle U(1, 2) \rangle \approx U_{hc}(r_{12}) + U_{\text{dis}}(r_{12}) + U_{mm}(r_{12}) + U_H(r_{12}).
\]
The term $U_{mm}(r_{12})$ is similar to Eq. (7):

$$U_{mm}(r) = \frac{2}{3} \frac{1}{T} \frac{d_{mon}^4}{r^6},$$

but $\left(\frac{d_{mon}}{d_{dim}}\right)^4 < 0.1$. Therefore we conclude that outside the fluctuation region $U_{mm}(r_{12}) \ll U_{dis}(r_{12})$, while inside it $U_{dis}(r_{12}) \ll U_a(r)$. The term $U_H(r_{12})$ plays the noticeable role only on small distances between monomers. In fact, it leads to some renormalization of the hard-core diameter. Due to this we expect that the behavior of the specific volume per molecule, the heat of evaporation and some other thermodynamic quantities outside the fluctuation region are determined by the potential:

$$\langle U(1, 2) \rangle \approx U_{hc}(r_{12}) + U_{dis}(r_{12}).$$

The vdW EOS (5) with the coefficient $a$ do not depending on temperature can serve as quite satisfactory zero approximation for the EOS of water.

### III. THE ROTATION OF MOLECULES AND THE BEHAVIOR OF THE ENTROPY DIAMETER.

The character of the molecular motion differs in liquid and gaseous phases. The number density (or specific volume) is the natural order parameter for the liquid-vapor critical point. However, it is one-particle characteristics of a system and therefore it describes only crude enough behavior of a system. From this point of view the choice of the entropy as the order parameter seems to be more informative since the entropy is determined by correlation effects of all orders [26]. Besides the part, reducible to density, this order parameter includes also the contributions reflecting the more fine details of the molecular motion. Such discrepancy is reflected in the asymmetry of the binodal. The degree of the asymmetry of the coexistence curve is described by the diameter of density:

$$\bar{n}_d = \frac{1}{2} \left( \bar{n}_l + \bar{n}_g \right) - 1,$$

TABLE II: The compressibility factor $Z_c$ for fluids.

| Fluid | $CH_3OH$ | $H_2O$ | $H_2S$ | $Ar$ | $C_6H_6$ |
|-------|----------|--------|--------|------|--------|
| $Z_c$ | 0.19     | **0.23** | 0.28   | 0.29 | 0.27   |
FIG. 4: The diameters of the entropy (a) and the density (b) for $H_2O$ and $D_2O$ according to experimental data [16].

FIG. 5: The diameters of the entropy for different liquids according to experimental data [16].

where $\tilde{n}_i = n_i / n_c$, $i = l, g$, $n_l, n_g, n_c$ are the number densities of the liquid, gas branches of the binodal and at the critical point correspondingly. The analogous quantity can be defined for the entropy. The temperature dependence of the entropy diameter:

$$S_d = \frac{S_l + S_g}{2} - S_c$$

for normal and heavy waters is presented in Fig. 4. The difference in the values of $S_d$ is caused by the isotopic effect (see also Section V). The comparison of $S_d$ for water with those for $H_2S, O_2$ and $Ar$, which has the spherical molecules, shows that non-monotone temperature dependence of the entropy diameter arises only for non-spherical molecules for which the rotational degrees of freedom should be taken into account.

For all systems with non-spherical molecules there are two characteristic temperatures $T_l$ and $T_u$ at which $S_d = 0$. In particular, for normal and heavy waters $T_l$ and $T_u$ take the
following values (see Fig. 4(a)):

\[
\begin{align*}
H_2O &: \quad T_l = 316 \, K, \quad T_u = 499 \, K, \\
D_2O &: \quad T_l = 280 \, K, \quad T_u = 531 \, K.
\end{align*}
\]

The nontrivial temperature dependence of \( S_d(t) \) for water and substances of type \( H_2S \) and \( O_2 \) is connected with the change of the rotational motion of molecules when density of a system increases. In normal and heavy waters H-bonds play additional important role. If the average number of H-bonds per molecule is close to three or more, a molecule can only oscillate about temporary equilibrium position. Let \( \tau_0 \) be the average time for such oscillations, so called the residence time. In \([? ? ? ]\) it was shown that the value of \( \tau_0 \) is essentially more than the characteristic time of the rotational motion \( \tau_r \sim (I/k_B T)^{1/2} \), where \( I \) is the inertia moment, only for \( T < T_H \), where \( T_H \approx 315 K \). It is very surprising that the diameter of entropy changes its sign namely at this temperature \( (T_l = 316K) \). At \( T > T_H \) the residence time of the local molecular configurations is comparable with \( \tau_r \), therefore the rotational motion of water molecules will influence on the behavior of \( S_d \) analogously to that in liquid \( H_2S \) or \( O_2 \).

The character of the temperature dependence becomes partly clearer when we pass to the excess entropy

\[
S^{(ex)} = S - S^{(id)},
\]

where

\[
S^{(id)}(T) = c_v^{(id)} \ln \frac{T}{T_c} - \ln \frac{n}{n_c}, \quad c_v^{(id)} = \frac{k}{2},
\]

is the entropy of ideal gas, \( k \) is the number of thermalized degrees of freedom which are treated classically. As it follows from Fig. 6 the most essential difference between the behavior of \( S_d \) for normal and heavy water as well as \( H_2S \) is observed in the fluctuation region, where the both kind of water are close to be fully dimerized state.

As has been said above the behavior of the diameter of the entropy reflects the change of the rotational motions of the molecules with the density. One can see that (heavy)water differs in this respect from other homologs. The situation looks like there is some deficit (see Fig. 6) of the order in liquid phase of water especially near the critical point. From the point of of the dimerization picture such a fact acquires natural explanation. The interaction between water molecules is converted into formation of bound states, the dimers,
FIG. 6: The diameter for residual (excess) entropy.

which rotate freely in liquid phase in lower density near critical region. Note that the effect of lowering the entropy of the liquid phase due to nonspherical shape of the repulsive molecular cores was investigated by \cite{30} within generalized vdW EOS model in low pressure region. Here we show that the entropy diameter is the fine characteristic which is very sensitive to such effect and can be described within the model EOS where the softness of the particle core is taken into account (see Section \textbf{[V]}). To explain the behavior of the diameter of the entropy we use the basic thermodynamical representation of the entropy in dimensionless units (in units of the Boltzmann constant $k_B$):

$$S = S_c + c_v \ln \frac{T}{T_c} + f(n) - f(n_c),$$ \hspace{1cm} (21)

where $S_c$ is the entropy at the CP, $c_v$ is the dimensionless specific heat, $f(n)$ is some function describing the density dependence of the entropy. From Eq. (21) one can conclude that:

$$S_d = \frac{c_v^{(l)} + c_v^{(g)}}{2} \ln \frac{T}{T_c} + \frac{f(n_l) + f(n_g)}{2} - f(n_c).$$ \hspace{1cm} (22)

As it follows from Eq. (22), the behavior of the diameter essentially depends on the specific form of the equation of state, which determines the function $f(n)$. In its turn, the EOS is sensitive to the effective proper molecular volume corresponding to the rotating nonspherical molecules in liquid and vapor phases. The detailed analysis of this question will be given in the following Section.

Here we restrict ourselves only by the consideration of $S_d(T)$, for which $f(n)$ is taking in the ideal gas approximation. The branches of the binodal are taken in the mean field approximation:

$$\tilde{n}_l - \tilde{n}_g = 2b|\tau|^{1/2} + o(\tau), \quad \tau = \frac{T - T_c}{T_c},$$ \hspace{1cm} (23)
\[ \tilde{n}_d = a|\tau| + o(\tau). \]  

(24)

From here it follows that

\[ \tilde{n}_{l,g} = 1 \pm b|\tau|^{1/2} + a|\tau| + \ldots \]  

(25)

Supposing that outside the fluctuation region the specific heat capacities of liquid and gas phases take the constant values \( c_v^{(g)} = \frac{k}{2} \) and \( c_v^{(l)} = c_v^{(g)} + \Delta c_v \), from Eqs. (22) and (25) we get the following approximate expression for \( S_d \):

\[ S_d^{(app)}(T) = \left( \frac{\Delta c_v}{2} + c_v^{(id)} \right) \ln \frac{T_l}{T_c} - \ln \left( 1 - \lambda \left( 1 - \frac{T_l}{T_c} \right) \right), \]  

(26)

As it follows from [16] for \( Ar \) the value of \( \Delta c_v \) is 1, for \( H_2S \) \( \Delta c_v \approx 2 \) and for water (both normal and heavy) \( \Delta c_v \approx 5 \). The parameter \( \lambda \) depends on the specific EOS and

\[ \lambda = b^2 - 2a. \]

For example, for the vDW EOS \( a = 0.4, b = 2 \), for CS EOS \( a = 1.2, b \approx 2.5 \). The behavior of \( S_d^{(app)}(T) \) for different values of \( \lambda \) is presented in Fig. [7]. Here it is necessary to note that \( S_d^{(app)}(T) \) becomes to be the non-monotone function of temperature for \( k > 3 \), i.e. this peculiarity can be caused by both the rotational and vibration degrees of freedom. Of course, far away from the critical point, the contributions of the rotational degrees of freedom are determinative. However, already in a crude approximation described above we are able to estimate the position of the lesser root \( T_l \) of the equation \( S_d(T) = 0 \). We see that despite the crudeness of the approximation Eq. (25) for the binodal at suitable values of \( \lambda \) the reasonable values for the root \( T_l \) are obtained.

In the Section [15] it will be shown that the behavior of \( S_d(T) \) is noticeably changed if \( f(n) \) is taking in the Carnahan-Starling form with modified proper molecular volume.

We want to finish this Section by the brief discussion of physical cause which leads to the appearance of the upper root \( T_u \) for the equation \( S_d(T) = 0 \). The definition Eq. (18) of the entropy diameter includes the value of entropy \( S_c \) at the critical point. It is known that the value of \( S_c^{(mf)} \) calculated in the mean field approximation (for example in the vDW or CS approximations) is higher than the experimental value \( S_c^{(exp)} \). It is a result of the neglecting by the mode-mode interaction in the mean field approximation. Therefore for the correct comparison of \( S_d(T) \) calculated on the basis of experimental data with its mean field analog
FIG. 7: $S_d^{(app)}$ according to Eq. (26) as a function of $\lambda$ (a), (b) the comparison of Eq. (26) (solid line) with the parameters $\Delta c_v = 5$ and $k = 6$, $a \approx 0.73$, $b \approx 2.3$, $\lambda \approx 3$ corresponding for water with the data (dots) for $S_d$ [14].

$S_d^{(mf)}(T)$ it is necessary to pass to the modified entropy diameter $S_d^{(M)} = S_d^{(mf)} + \Delta S_c$, where $\Delta S_c = S_c^{(mf)} - S_c$. It is clear that the equation $S_d^{(M)}(T) = 0$ will take two roots: the value of $T_l$ is shifted and the additional root $T_u$ appears. This situation will be considered in more details in separated work.

IV. THE “SOFT“ CORE EOS MODEL

In this Section we discuss the nature of the non-monotone temperature dependence of the diameter of entropy. We will show that the region of negative values of $S_d$ is mainly caused by the variation of the molecular volume in dependence of pressure. The appearance of such dependence is natural for liquids with non-spherical molecules. Indeed, the proper molecular volume for them is determined as the volume of cavity formed by arbitrary rotating molecule. If the rotation of molecules becomes restricted, the corresponding cavity volume diminishes. Obviously, such an effect should take place with increasing of density. In water the considerable additional influence on the value of the effective molecular volume is generated by H-bonds. To describe the influence of the effective molecular volume on the behavior of the diameter of entropy, we start from some EOS, in which the dependence of the molecular volume on pressure is taken into account. Then we reconstruct the free energy and after this we find entropy in vapor and liquid phases and also the diameter of entropy.
The EOS for simple molecular fluids is usually taken in the form [22]:

\[ p = p_+(n, T) + p_-(n, T), \tag{27} \]

where \( p_+ \) is the pressure contribution due to hard core repulsive interactions and \( p_- \) is the contribution of the attractive long range part of the potential. For simple fluids it is taken in the standard form:

\[ p_- = -a n^2. \tag{28} \]

From what has been said above it is clear that one can model the influence of the density on the rotation as the restriction of the angular configuration space available for the molecule in a cage formed by its neighbors. The change in the available space for free rotation of the molecule can be described by the dependence of the volume parameter \( b \) on the density and the temperature. In accordance with said above we suppose that the density and temperature dependencies of the effective molecular volume \( b \) can be modeled by the relation:

\[ b = \frac{b_0}{1 + \gamma p^{(id)}}, \quad p^{(id)} = \tilde{n} \tilde{T}. \tag{29} \]

This parameter is included in the corresponding pressure term which describes the short range interaction (the hard core). The modified vdW EOS approximation for the free energy due to the interaction:

\[ \tilde{p} = \frac{\tilde{n}^2 \tilde{T}}{(1 + \gamma \tilde{n} \tilde{T})(3(1 + \gamma \tilde{n} \tilde{T}) - \tilde{n})} - \frac{9 \tilde{n}^2}{8} + \tilde{n} \tilde{T}. \tag{30} \]

For small \( \gamma \) the coordinates of the critical point are:

\[ \frac{T_c(\gamma)}{T_c(0)} = 1 + \frac{19}{9} \gamma + o(\gamma), \quad \frac{n_c(\gamma)}{n_c(0)} = 1 + 3 \gamma + o(\gamma). \]

The analogous relations for EOS corresponding to the following model of the free energy:

\[ F^{(CS)} = F_{id} + T \frac{b n (4 - b n)}{(1 - b n)^2} - a n, \tag{31} \]

where \( F_{id} \) is the ideal gas term are:

\[ \frac{T_c(\gamma)}{T_c(0)} = 1 + t_1 \gamma + o(\gamma), \quad \frac{n_c(\gamma)}{n_c(0)} = 1 + n_1 \gamma + o(\gamma), \quad t_1 \approx 4.5, \quad n_1 \approx 8.1 \]

The modification of the binodal for the Carnahan-Starling EOS at \( \gamma \neq 0 \) is shown on Fig. 8(b). As we see that the width of the binodal decreases with \( \gamma \). This naturally reflects
the diminishing of the phase asymmetry due to bigger compressibility of the effective volume, which in its turn means that the asymmetry between particle and the cavity (hole) decreases. From such point of view the most symmetrical is the binodal for liquid helium \[?\]. The calculation of the entropy diameter \(S_d\) supports this conclusion (see Fig. 9).

Entropy of the system, corresponding to the Carnahan-Starling EOS, is determined in the standard way:

\[
S = -\frac{\partial F^{(CS)}}{\partial T} \tag{32}
\]

The corresponding diameter of the entropy is presented in Fig. 11(b). Note that for water we neglected the temperature dependence of the coefficient \(a\) in Eq. (28) in accordance with the discussion in Section III. Thus the EOS with the soft core forms the adequate basis for the successful description of the binodal and fine nontrivial details in the behavior of the entropy diameter.

V. MANIFESTATION OF ISOTOPIC EFFECT

In this Section we want to complete our results presented above by the brief discussion of some distinctions in the behavior of the normal and heavy water. We focus our attention on the following characteristic manifestation of the isotopic effect: 1) small differences in the locations of the triple and critical points; 2) essentially more noticeable differences in the locations of the roots \(t_l\) and \(t_u\) of equations \(S_d(t) = 0\) \((t_k = T_k/T_c^{(k)}, k = l, u)\) and 3) the nontrivial difference in the behavior of the specific heats. In these cases we observe different
FIG. 9: The dependence of $S_d$ on $\gamma$ for Eq. (31).

(a) monoatomic, $C_{v}^{(id)} = 3/2$

(b) diatomic, $C_{v}^{(id)} = 5/2$

FIG. 10: The calculated binodal (solid) for the model Eq. (31) with $\gamma \approx 0.03$ and the binodal for $H_2O$ and $H_2S$ (dots)

FIG. 11: The entropy diameter $S_d$ for the model Eq. (31) with $\gamma \approx 0.03$ (solid line) and the data for $H_2O$ and $H_2S$ (dots). The shifted entropy diameter curve (see Section III) is shown by the dashed line.
manifestations of the isotopic effect.

The critical temperature of normal water, $T_c(H_2O) = 647K$, is rather higher than one, $T_c(D_2O) = 644K$, for heavy water. It means, that the position of the critical point in heavy water is determined by the ensemble of dimers doped by small quantity of monomers, i.e. similarly to that for normal water. The small lowering of the critical temperature for heavy water is probably connected with 1) slightly different values of parameter $\lambda^2/\sigma_d$ for $H_2O$ and $D_2O$(see Eq. (9) and 2) some distinction of the dispersive interactions between molecules. Note, that in Eq. (4) the contribution of the dispersive forces is at all ignored.

The difference in the locations of the triple points is also insignificant: $T_{tr}(H_2O) = 273K$ and $T_{tr}(D_2O) = 277K$. From here it follows that normal and heavy water belong to the same class of corresponding states. For them $T_{tr}(H_2O)/T_c(H_2O) = 0.42$, $T_{tr}(D_2O)/T_c(D_2O) = 0.43$, that essentially differs from the ratios for the water homologue $H_2S$ and benzene: $T_{tr}(H_2S)/T_c(H_2S) = 0.50$, $T_{tr}(C_6H_6)/T_c(C_6H_6) = 0.50$. Such significant discrepancy is connected with the considerable influence of the dimerization on the location of the critical point. From Fig. 1 it follows that due to dimerization the specific volume per molecule increases approximately on 15%. Assuming that the temperature shift has the analogous value: $\Delta T_c/T_c \sim \Delta v_c/v_c$, we obtain the following estimate for the critical temperature of non-dimerized water ($T_c^{(nd)} \approx T_c - \Delta T_c$): $T_c^{(nd)}(H_2O) = 550K$. It leads to the estimate: $T_{tr}(H_2O)/T_c^{(nd)}(H_2O) \approx 0.50$. This fact can be considered as an indirect evidence for the dimerization near the critical point.

The locations of the roots $t_l$ and $t_u$ of equations $S_d(t) = 0$ for normal and heavy water satisfy the following relations:

$$t_l(H_2O) - t_l(D_2O) \approx 0.053,$$

$$t_u(D_2O) - t_u(H_2O) \approx 0.054.$$

Their surprising closeness is not occasional. In the Section 4 it was stressed that the non-monotone temperature dependencies of the entropy diameter $S_d^{(k)}(t)$, $k = H_2O, D_2O$, is connected with the rotational motion of molecules. Therefore the comparison of the differences $|\Delta t_l| \approx |\Delta t_u| \approx 0.053$ with the characteristic parameter $\mu = \omega_r(H_2O) - \omega_r(D_2O)$ of the rotational motion is quite relevant. In principle, molecules can change their relative orientations by many ways; 1) each molecule rotates independently of others; 2) two nearest molecules change their orientations in concord, while all other neighbors retain in initial po-
FIG. 12: The relative value of the difference of the specific heats for normal and heavy water according to \[16\].

sitions and so on. Note, that the dimerization in vapor phase of water leads to the natural lowering of entropy and negative values of \(S_d(t)\). In liquid phase the existence of strong orientation correlations makes improbable the first way. At the same time, the corresponding pair in the second case can be identified with a dimer, for which we find an estimate:

\[
\mu \approx 1 - \frac{m_{\text{H}_2\text{O}}}{m_{\text{D}_2\text{O}}} \approx 0.05.
\]

It is necessary to emphasize that we do not speak about the rotation of pairs (dimers) in liquid phase. Hence, the very close values of two dimensionless parameters is a strong argument in the favor of the second scenario of reorientations in vapor and liquid phases of normal and heavy water.

It seems to be natural to suppose that similar character of the rotational motion in normal and heavy water will also lead to the following estimate for the ratio of their specific heats:

\[
\frac{|C_v^{(\text{H}_2\text{O})}(t) - C_v^{(\text{D}_2\text{O})}(t)|}{C_v^{(\text{H}_2\text{O})}(t)} \approx \mu.
\]

This ratio is really in correspondence with experimental data, presented in Fig. 12. However, here we would like to focus our attention on the practically constant value of the difference \(C_v^{(\text{D}_2\text{O})}(t) - C_v^{(\text{H}_2\text{O})}(t)\) in the temperature interval \(0.8 < t < 0.95\). It corresponds to the fluctuation region, in which the normal and heavy waters are strongly dimerized. As we see, in this region \(C_v^{(\text{D}_2\text{O})}(t) - C_v^{(\text{H}_2\text{O})}(t) \approx \frac{1}{2}\). This effect finds the natural explanation if we assume that the inner rotation in dimers \((\text{D}_2\text{O})_2\) is possible (see Fig. 13). The activation of this type of thermal motion in heavy water is justified by greater length of D-bonds in
FIG. 13: The relative rotation of the monomers entering a dimer. The parameters of water dimer are taken from www1.lsbu.ac.uk/water/

FIG. 14: Temperature dependence of the ratio $R_v(t) = v^{(D_2O)}(t)/v^{(H_2O)}(t)$ on the coexistence curves of the normal and heavy water [16].

The values of $R_v(t)$ near the triple points, $t_{tr} \approx 0.42$, are mainly caused by different lengths of H- and D-bonds, since the numbers of them per molecule in normal and heavy water are practically the same [? ]. From Fig. 14 it follows that the length of a D-bond is greater than one for an H-bond approximately 1.5%.

VI. CONCLUSION

The main attention in this paper is focused on the physical nature of the temperature dependence of main thermodynamic properties of water: density, heat of evaporation and
entropy as well as specific heat everywhere on the coexistence curve. All temperature interval of the two-phase vapor-liquid states is considered.

Analyzing the behavior of the density and the heat of evaporation of water we have established that these quantities have argon-like behavior everywhere excepting the fluctuation region near the critical point. It means that such a character of the temperature dependence is formed by averaged argon-like inter-particle potential, which arises in consequence of the rotation of water molecules. H-bonds bring in the specificity in the rotational motion of molecules, however their influence is not crucial. This circumstance is justified by that fact that the shear viscosities of water and argon have the same order of magnitude. The situation is considerably changed only for supercooled states of water and near its critical point. In the present paper we touch some details only for the near critical behavior.

Here the volume occupied by two water molecules becomes greater than that volume, which corresponds to a rotating dimer. As a result, the favorable conditions for the dimerization are created. Applying the method of chemical equilibrium it is shown that the degree of dimerization exceeds 0.9. Due to dimerization the characteristic ratio \( R_\nu(t) \) for specific volumes of water and argon increments approximately 15% in the vicinity of their critical points. It shown that the ensemble of dimers with small admixture of monomers allows to reproduce successfully the location of the critical point of water. It is also responsible for the correct relations between critical amplitudes.

At elongation from the fluctuation region dimers destroy and short-living linear chains of water molecules are formed. Here the thermodynamic properties of water are determined by rotating monomers (of course, the rotation of monomers is not free). Due to formation of short living H-bonds the effective proper volume, corresponding a monomer, becomes to be dependent on the temperature and density, or pressure. Including the dependence of the proper molecular volume on the pressure to the van der Waals or Carnahan-Starling equations of state leads to the very nontrivial consequences. Among them we mark out 1) the non-monotone temperature dependence of the diameter of entropy and 2) the differences in the values of the specific heats for vapor and liquid phases, calculated with the help of the modified van der Waals or Carnahan-Starling equations of states. Here it is appropriate to note that the specific heats for coexisting phases are identical if the proper molecular volume is constant. Besides, the change of the sign of the entropy diameter at the lower limit for the fluctuation region \( t_u \approx 0.8 \) is not also occasional. It is a strong argument in the
favor that this root of the entropy diameter is connected with the discrepancy of the mean
field and experimental values of entropy at the critical point.

The diameter of entropy changes also its sign at the lower temperature $t_l \approx 0.5$. The
physical prerequisite for this root of the entropy diameter is the following: near $t_l$ the ensemble
of linear molecular chains begins to form the spatially arranged the H-bond network. The rotation
of molecules becomes more difficult and the character of the density dependence of the proper molecular volume essentially changes.

The very nontrivial manifestation of the isotopic effects is observed at the comparison of
the temperature dependencies for the diameter of entropy and the specific heat of the normal and heavy water. Here we pay attention on the characteristic values of differences in the positions of the upper and lower dimensionless temperature for the normal and heavy water. These differences are close to each other and they practically coincide with dimensionless parameter describing the discrepancy in the rotations of dimers arising in vapor and liquid phases of normal and heavy water. Another remarkable fact is the difference of the specific heats for the normal and heavy waters in the fluctuation temperature interval $0.85 < t < 0.98$. In accordance with our reasons it arises owing to switching on the internal rotation for dimers in the heavy water.

The small differences in the values of the crystallization and critical temperatures for them is connected with some distinction of their averaged intermolecular potentials. In consequence of the strong dimerization near the critical point the normal and heavy water form the separated class from the point of view of the principle of corresponding states. Besides water, many alcohols belong probably to this class of corresponding states.

**APPENDIX A: THE DEGREE OF DIMERIZATION OF WATER NEAR THE CRITICAL REGION (MEAN FIELD ANALYSIS)**

The equation for the chemical equilibrium between dimers and monomers is:

$$\frac{A}{(1 - A)^2} = 2n_0 K(T) \exp \left( \frac{2\mu_1^{(ex)} - \mu_2^{(ex)}}{T} \right),$$  \hspace{1cm} (A1)

where $\mu_i^{(ex)}$ are the excess chemical potentials (with respect to the ideal gas term) of the monomers and dimers correspondingly which are determined from the excessive part of the free energy corresponding to the EOS [8]. The quantity $K(T)$ is the constant of chemical
equilibrium we can approximate it by simple expression [19]:

$$K(T) = \exp \left( \frac{E_d}{T} \right).$$  \hspace{1cm} (A2)

The dissociation energy $E_d$ corresponds to the energy of H-bond which in $k_B T_c$ units is of order $E_H = 3 \div 4 k_B T_c$ [34, 35]. Such a large value of the H-bond energy allows us to conclude that near critical water is dimerized to a great extent [? ? ]. In particular it agrees with the results of the numerical simulations [37].

In order to calculate the dimerization degree at the critical point we use the model Eq. (8) with the dissociation considered as the perturbation to the completely dimerized state. In this way we obtain the critical temperature in the linear approximation on $e^{-E_d/2} < 1$:

$$T_c = 1 + \frac{\tilde{b}_1^2 - 6 \tilde{b}_1 \tilde{a}_{12} - 4 \tilde{a}_{12}^2 + 9 \tilde{a}_{12}^2 e^{-E_d/2}}{12} e^{-E_d/2} \tilde{b}_1 \tilde{a}_{12}^2 + \ldots. $$

where

$$\tilde{b}_1 = \left( \frac{\sigma_1}{\sigma_2} \right)^3, \quad \tilde{a}_{12} = 8 \lambda \frac{(\sigma_1/\sigma_2)^2}{(1 + \frac{\sigma_1}{\sigma_2})^3},$$  \hspace{1cm} (A3)

The corresponding value for $Z_c$ is:

$$Z_c = Z_c^{(0)} \left( 1 - A_c/2 \right).$$  \hspace{1cm} (A4)

The dependence of $Z_c$ on the relevant parameters is shown on Fig. 3. E.g. at $\tilde{a}_{12} \approx 0.2$, $\tilde{b}_1 = 0.2$ and $E_d/T_c = 3.5$ it takes the value $Z_c \approx 0.2$. In the vicinity of the critical point assuming that $e^{-E_d/2} \ll 1$, from (A1) we get the degree of the dimerization:

$$A_c = 1 - \frac{1}{3} e^{-E_d/2 - \frac{1}{2} \tilde{b}_1 + \frac{3}{2} \tilde{a}_{12} - \frac{7}{8}} + O \left( \epsilon^2 \right),$$  \hspace{1cm} (A5)

where $\lambda = \left( \frac{d_1 \sigma_2}{d_2 \sigma_1} \right)^2$ is the parameter which determines the difference in charge distribution in the monomer and the dimer. The dependence of the dimerization factor on the parameters of the monomer-dimerization interaction is shown on Fig. 15.

Thus in the critical region the degree of dimerization $A$ at $\tilde{a}_{12} \approx 0.4$, which corresponds to $d_1/d_2 \approx 0.5$, $\sigma_1/\sigma_2 \approx 0.7$, is approximately 0.9. This conforms with the thermodynamic estimates given in Section 1 and the results of works [? ? ].
FIG. 15: Dimerization degree as the function of the parameters of monomer-dimerization interaction

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