

Physical Nature of The Density Maximum for Water at 4°C

Vladimir Y. Gotsulsky

Odessa I. I. Mechnikov National University

Salvatore Magazù (✉ smagazu@unime.it)

Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra Università di Messina

Nikolay P. Malomuzh

Odessa I. I. Mechnikov National University

Research Article

Keywords: water density, ordinary and heavy water, role of H-bonds (D-bonds).

Posted Date: July 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-729447/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Physical nature of the density maximum for water at 4°C

Vladimir Ya. Gotsulsky¹, Salvatore Magazu², Nikolay P. Malomuzh³

¹Dept.of General Physics

Odessa I.I. Mechnikov National University, 2 Dvoryanskaja Street, 65082 Odessa, Ukraine, vygot@onu.edu.ua

²Dipartimento di Fisica dell'Università degli Studi di Messina

Viale S. D'Alcontres 31, 98166, Messina, Italy, smagazu@unime.it*

³Dept.of Theoretical Physics and Astronomy and

Odessa I.I. Mechnikov National University, 2 Dvoryanskaja Street, 65082 Odessa, Ukrain, mnp@onu.edu.ua

(Dated: June 25, 2021)

A new approach to the physical nature of the water density maximum at 4°C is proposed. The main attention is focused on the role of H -bonds in the formation of the specific volume and thermal expansion coefficients for ordinary and heavy water. It is shown that the minimum of the specific volume for water is connected with the amplification of H -bonds (D -bonds) role at approaching their triple points.

Key words: water density, ordinary and heavy water, role of H -bonds (D -bonds).

I. INTRODUCTION

There are many attempts to explain the appearance of the density maximum for ordinary water at $T_m = 4^\circ\text{C}$ and for heavy water at $T_m = 11^\circ\text{C}$ (Fig.1). Practically all of them are based either on peculiarities of the water structure (see [4-10]) or the argon-like basis for water perturbed by H -bonds [11-13].

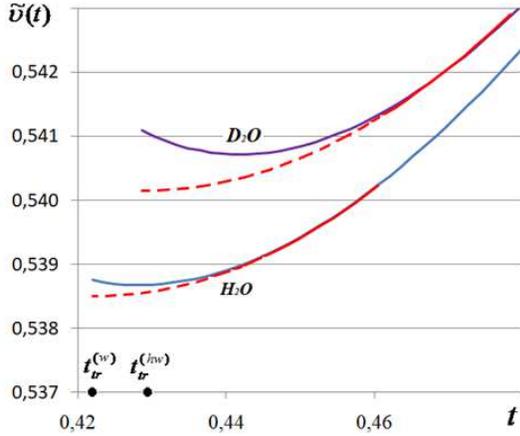


FIG. 1. Normalized specific volumes \tilde{v} per molecule for ordinary and heavy water vs. dimensionless temperature (solid lines) according to [1-3]. The dashed lines, $\tilde{v} = h + a(t - t_{tr})^2$, present the parabolic extrapolations of $\tilde{v}(t)$ starting from the conjugation point t_0 (see below).

Here we use the dimensionless variables determined by the similarity principle [14,15]: $t = T/T_c$, $t_{tr} = T_{tr}/T_c$, where T_{tr} is the triple point temperature, and T_c is the critical temperature. Similarly, $\tilde{v} = v/v_R$, where $v_R = v(T_G)$ is the regularized value of the specific volume at the Ginsburg temperature T_G [16]. The coefficient a

and values h, t_0 , where t_0 is the conjugation point for curves $\bar{v}(t)$ and $\tilde{v}(t)$, are determined from the conditions: $\bar{v}(t_0) = \tilde{v}(t_0)$, $\bar{v}'(t_0) = \tilde{v}'(t_0)$, and $\bar{v}''(t_0) = \tilde{v}''(t_0)$. They lead to the explicit equations

$$t_0 - \frac{\tilde{v}'(t_0)}{\tilde{v}''(t_0)} = t_{tr}, a = \frac{1}{2}\tilde{v}''(t_0), h = \tilde{v}(t_0) - a(t - t_0)^2,$$

which allow us to determine consecutively all parameters:

$$H_2O : t_0 = 0.456, a = 1.159, h = 0.5385;$$

$$D_2O : t_0 = 0.480, a = 1.114, h = 0.5402.$$

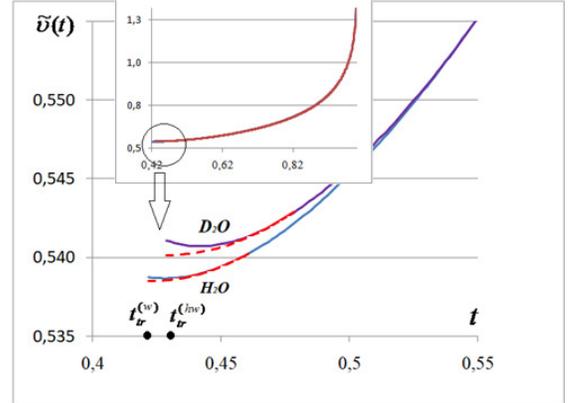


FIG. 2. Normalized specific volumes \tilde{v} per molecule for ordinary and heavy water vs. dimensionless temperature on two different scales.

The minimum of $\bar{v}(t) = h - a(t_0 - t_{tr})^2$ is located at t_{tr} , so $\bar{v}(t)$ takes the meaning of separatrix for extrapolation curves conjugating with curve $\tilde{v}(t)$ at temperatures i) $t < t_0$ and ii) $t > t_0$. In the first case, all possible extrapolated curves have minima before the triple temperature ($t_m > t_{tr}$), in the second one a similar minima take place to the left of t_{tr} . Thus, the appearance of minima for $\tilde{v}_w(t)$

* smagazu@unime.it

and $\tilde{v}_{hw}(t)$ are caused by interactions different from those determining the behavior of $\tilde{v}_w(t)$ and $\tilde{v}_{hw}(t)$ for $t > t_0$.

The curves $\tilde{v}(t)$ take also the parabolic shape near their minima: $T_m = 4^\circ\text{C}$ for ordinary water and $T_m = 11.2^\circ\text{C}$ for heavy water. Fig.2 gives us the more full representation of the relative disposition of the coexistence curves (*CCs*) for ordinary and heavy water. Here we only note, that the noticeable division of the confluent *CC* into two curves is observed for $t < t_d \approx 0.55$. Since the confluent *CC* takes the argon-like shape (see below), more essential deviation of \tilde{v}_{D_2O} from argon-like dependence compared with \tilde{v}_{H_2O} testifies that *D*-bonds are stronger than *H*-bonds. This conclusion is consistent with the spectroscopic data [1].

For $t < t_0$ and $t > t_0$ the real behavior of $\tilde{v}(t)$ deviates upward from the separatrix $\bar{v}(t)$, i.e. $\Delta(t) \geq 0$. $\Delta(t) = \tilde{v}(t) - \bar{v}(t)$. We show below, that the analysis of difference $\Delta(t)$ gives us a deeper understanding of the *H*- and *D*-bonds role in the formation of temperature dependences of $\tilde{v}(t)$ near their minima for ordinary and heavy water.

In order to explain the appearance of minimum for \tilde{v} at 4°C , many attempts (see [4-8]), carried out in the last decades, were focused on the specific structure of liquid water. It is assumed that near the triple point and in supercooled states, the determinative role belongs to clusters of two types: similar to those in hexagonal ice and ice II, arising only for pressures $p < 10^3 \text{ atm}$. The inter-particle spacing in the hexagonal ice and ice II is equal to 4.5\AA and 3.4\AA correspondingly. The positions of first two peaks for the radial distribution function in water are in quite satisfactory agreement with this assumption. Following [4-8], clusters of the first type dominate in supercooled states. The role of clusters of the second type is assumed to be noticeable only at the temperature higher than the triple point. Unfortunately, the carrying out of the last assumption raises doubts, since the formation of these clusters is improbable at atmospheric pressure and should diminish as the temperature increases. Moreover, the cogent explanation of the water density maximum requires knowledge of the temperature dependences of density and clusters' size.

The approach presented in [9], rests upon the assumption that water molecules can fill up "voids" of the water structure close to one in hexagonal ice. However, these "voids" have too small volume and displacement of molecules in them is impossible (see some details in [17]).

In [9], thermodynamic properties of water are described within the approach reminding the Landau theory [14,16] with two order parameters φ_p and φ_s , identified with density and energy density correspondingly. The last one is related to the number of *H*-bonds per molecule. Unusual properties of water – maximum of density and minimum of isothermal compressibility as well as its heat capacity – are explained with the help of some assumptions about the temperature dependence of coefficients entering to the free energy modeling. However, the last step is not reliably substantiated and it, in reality, pre-

ciates this approach.

The present work is devoted to the careful analysis of the *H*- and *D*-bonds influence on the temperature dependences of the specific volumes and thermal expansion coefficients

$$\gamma(t) = \frac{1}{v(t)} \left. \frac{\partial v(t)}{\partial T_c} \right|_{CC} = \left. \frac{\partial \ln v(t)}{\partial T_c} \right|_{CC} \quad (1)$$

near t_m . We show that values of $\gamma(t)$ for hexagonal ice and liquid water for $t_{tr} < t < 2t_m - t_{tr}$ have the same order of magnitude and they both are one order less than values of $\gamma(t)$ far away from t_m . Thus, we conclude that the volume minimum for water is caused by *H*-bond influence.

II. THE TEMPERATURE DEPENDENCE FOR THE THERMAL EXPANSION COEFFICIENT

The temperature dependences of $\tilde{\gamma}(t) = T_c \gamma(t)$ for argon, hydrogen sulphide, as well as water, methanol and ethanol on their coexistence curves are presented in Fig.3.

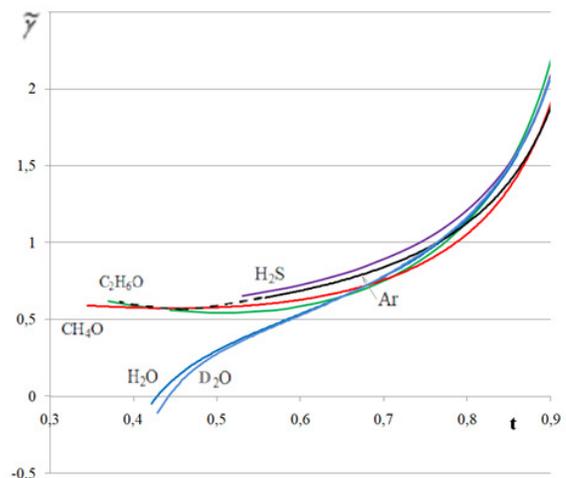


FIG. 3. Temperature dependences for the thermal expansion coefficients $\tilde{\gamma}(t)$ for ordinary and heavy water, hydrogen sulphide, methanol, ethanol, and argon according to [13]. The dashed line presents the quadratic extrapolation of argon curve on the interval: $0.3 < t < 0.56$: $\tilde{\gamma}_{Ar}^{(extr)}(t) = 1.226 - 2.978t + 3.467t^2$.

From the Fig.3, it follows that the temperature dependence of the thermal expansion coefficient is the most characteristic peculiarity of water near its triple point. If $t \rightarrow t_{tr}$, the coefficient $\tilde{\gamma}_w(t)$ demonstrates the following surprising properties: $\tilde{\gamma}_w(t)$ deviates from $\tilde{\gamma}_{Ar}(t)$ the most essentially;

- i) $\tilde{\gamma}_w(t)$ becomes negative in the narrow temperature interval near $t_{tr}^{(w)}$,
- ii) within the temperature interval $t_{tr} < t < t_0$, $\tilde{\gamma}_w(t)$ have the order of magnitude 10^{-4} , which is characteristic for the hexagonal ice ($\tilde{\gamma}_I(t)$). The thermal expansion

coefficients for other liquids are more than one order of magnitude.

The behavior of $\tilde{v}_{hw}(t)$ and $\tilde{\gamma}_{hw}(t)$ practically coincides with one for ordinary water within the temperature interval: $0.55 < t < 0.95$. At the same time, the curves $\tilde{v}_{hw}(t)$, $\tilde{\gamma}_{hw}(t)$ and $\tilde{v}_w(t)$, $\tilde{\gamma}_w(t)$ noticeably diverge from each other for $t_{tr} < 0.55$.

Surprisingly, the values of $\tilde{\gamma}_w(t)$ and $\tilde{\gamma}_I(t)$ near the triple point are equal to $\tilde{\gamma}_I(t_{tr}^-) = 0.046$ and $\tilde{\gamma}_w(t_{tr}^+) = -0.046$ (see [17, 18]), i.e. i) they have the same numerical values (!) but different signs, and ii) $\tilde{\gamma}_w(t)$ becomes comparable with $\tilde{\gamma}_{Ar}(t)$ and $\tilde{\gamma}_{H_2S}(t)$ only starting from $t \approx 0.6$ (see Fig.3).

In order to understand such a considerable distinction of $\tilde{\gamma}_w(t)$ and $\tilde{\gamma}_{hw}(t)$ from $\tilde{\gamma}_i(t)$, $i = Ar, H_2S, et, met$ in the temperature interval: $0.42 \leq t \leq 0.6$, let us consider the specificity of molecular rotations as a function of temperature. Such information can be taken from the behavior of the dipole relaxation time.

A. Dipole relaxation time for water

We consider the temperature dependence of the dimensionless dipole relaxation time $\tilde{\tau}_d = \tau_d/\tau_r$, where τ_r is the characteristic time for a full turn of an isolated water molecule, that is $\tau_r = 2\pi/(k_B T/I)^{1/2} \sim 5 \cdot 10^{-13}$ s. Its behavior in accordance with [19] is presented in Fig.4.

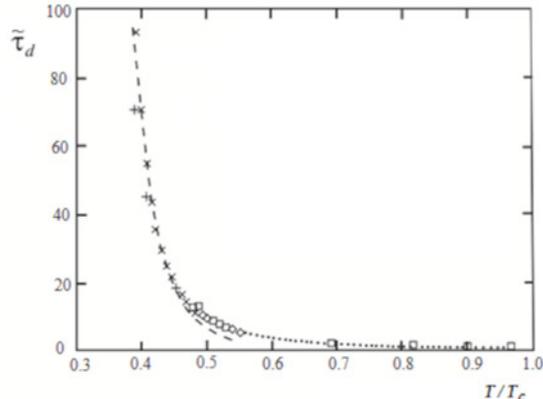


FIG. 4. Temperature dependence of the dimensionless dipole relaxation time $\tilde{\tau}_d(t)$. Dots present extrapolation values of $\tilde{\tau}_d(t)$.

As we can see from Fig.4, the behavior of is essentially different within the temperature intervals i) $0.42 < t < 0.6$ where $\tilde{\tau}_d(t) > (>>)1$, and ii) $0.6 < t < 0.95$, where $\tilde{\tau}_d(t) \approx 1$. For the first one, the behavior of $\tilde{\tau}_d(t)$ is satisfactorily described by the exponential function:

$$\tilde{\tau}_d = \tilde{\tau}_d^{(0)} \exp(\varepsilon_H/t), \tau_d^{(0)} = 5.1 * 10^{-4}, \varepsilon_H = 4.71, \quad (2)$$

where $\varepsilon_H = E_H/k_B T_c$, and the activation energy E_H practically coincides with the H -bonding energy [1, 19,

20] (this contribution is presented by the dashed line in the Fig.4).

Thus, temperature dependence of $\tilde{\tau}_d(t)$ allows us to conclude that i) the rotation of water molecules is quasi-free within the temperature interval $0.6 < t < 0.97$ and ii) their rotation essentially decelerates within the temperature interval $0.42 < t < 0.6$ and especially for $0.42 < t < 0.46$. Accordingly, the equation of state (EoS) of water and its thermal expansion within the temperature interval $0.6 < t < 0.97$ - are determined by the averaged interparticle potentials [22]. At the same time, their behavior within the temperature interval $0.42 < t < 0.46$ is mainly determined by the long-living H -bonds exactly as it takes place in hexagonal ice.

It is necessary to note that the shear viscosity of water also changes its behavior near $t \sim 0.6$ (see [23]).

The degree of similarity in the behavior of specific volumes and thermal expansion coefficients for ordinary and heavy water is expressed considerably stronger. Discrepancies between their CCs become noticeable only approaching their triple points. Evidently, these discrepancies are caused by slower rotation of heavy water molecules, i.e. by the stronger influence of D -bonds on the EoS of a system.

B. Temperature interval: $0.6 \leq t < 0.97$

Within this interval, the period of quasi-free rotation of molecules is essentially less than the life time for typical molecular configurations determining the EoS for water. Therefore, the last one is mainly determined by the averaged interparticle potentials having the argon-like structure [19]. This fact, in particular, explains the possibility to apply the Van der Waals equation for description of the EoS and in particular its vapor-liquid coexistence curve.

This reasoning remain correct for hydrogen sulfide as well as for methanol and ethanol. In correspondence with [11,13,21], the specific volumes $\tilde{v}_i(t)$ for water within the interval: $0.6 < t < 0.97$ as well as for methanol and ethanol can be approximated by the expression:

$$\tilde{v}(t) = k_i \tilde{v}_{Ar}(t) + \tilde{v}_H^{(i)} n_H^{(i)}(t), i = w, met, et, \quad (3)$$

where $n_H^{(i)}(t)$ is the averaged value of H -bonds per molecule, $\tilde{v}_H^{(i)}$ is the increment of $\tilde{v}_i(t)$ caused by H -bond formation. The contribution $\tilde{v}_H(t) n_H^{(i)}(t)$ reflects the weak influence of H -bonds on the EoS corresponding to the argon-like potential. In [13,21] it has been shown that $k_w \approx 0.82$ and $\tilde{v}_H^{(i)} < 0.05 \tilde{v}_{Ar}(t)$.

In the case of water, the temperature dependence of $n_H^{(i)}(t)$ is determined by the simplest polynomial [11,13,21]:

$$\tilde{n}_H^{(i)}(t) = 4(1 - \lambda_w t + \dots), \lambda_w = 0.85. \quad (4)$$

The thermal expansion coefficient can be approximated by the expression

$$\tilde{\gamma}_w(t) = \tilde{\gamma}_{Ar}(t) \left[1 - \tilde{n}_H^{(w)}(t) \frac{v_H^{(w)}}{v_0(t)} + \dots \right] - 4\lambda_w \frac{v_H^{(w)}}{v_0(t)}. \quad (5)$$

where $v_0(t) = k_{Ar} v_{Ar}(t)$. Fig. 5 presents the comparative behavior of $\tilde{\gamma}_w(t)$, calculated according to (5), and $\tilde{\gamma}_w(t)^{(exp)}$, obtained from the experimental data. As we can see, the agreement between experimental and predicted curves is quite satisfactory, which argues for our approach.

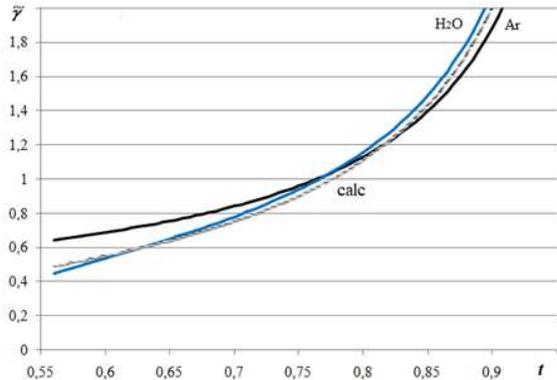


FIG. 5. Temperature dependence of $\tilde{\gamma}_w(t)$ calculated according to (5) and $\tilde{\gamma}_w(t)^{(exp)}$.

As we can see from Fig.3, the thermal expansion coefficients for ordinary and heavy water are practically coinciding in the temperature interval $0.6 < t < 0.97$. The similar behavior is also characteristic for their specific volumes (Fig.2 and [25]). In this work it had been also shown that the influence of the D -bonds differs insignificantly from those for the H -bonds only near triple points of water isotopes. This fact is naturally explained by lesser velocity of the molecular rotation, in consequence of D -bonds influence on the EoS of heavy water more strongly in comparison with corresponding influence of H -bonds on the EoS of ordinary water.

C. Temperature interval: $0.42 \leq t < 0.6$

Within the first temperature interval $0.42 < t < 0.6$, the thermal expansion coefficient of water demonstrates the most surprising properties: i) $\tilde{\gamma}_w(t)$ deviates essentially stronger from those for argon and other liquids ii) $\tilde{\gamma}_w(t)$ becomes negative in the narrow temperature interval near $t_{tr}^{(w)}$.

The temperature dependence of the dimensionless thermal expansion coefficient near the triple point is described by the polynomials with respect to $u = t - t_{tr}$:

$$\tilde{\gamma}_w(t) = \begin{cases} 0.114 + 2.357u, & 0.08 < u < 0.2, \\ -0.046 + 5.897u - 20.11u^2, & 0 < u < 0.08. \end{cases} \quad (6)$$

The second thempolynomial leads to the non-monotonic temperature dependence of the specific volume near its minimum at $T_m = 277K$.

Now we will present some arguments showing that the fall of $\tilde{\gamma}_w(t)$ from 0.046 at $t_{tr}^{(-)}$ to -0.046 at $t_{tr}^{(+)}$ is related with the suitable change of H -bond network at the hexagonal ice fusion. During this change, the number of H -bonds per molecule remains constant, $n_H^{(I)} = 4$, for all ice states.

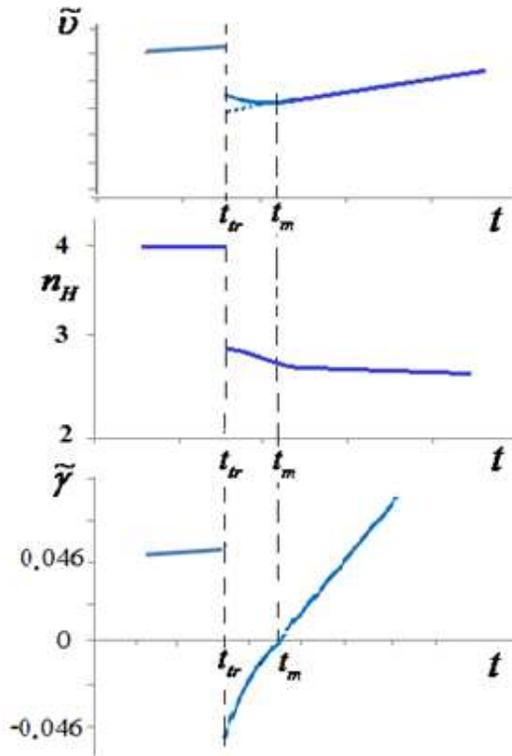


FIG. 6. The schematic behavior of \tilde{v} , n_H , $\tilde{\gamma}_w(t)$ near t_m .

The number $n_H^{(w)}$ for $t > t_0$ satisfies the inequality $n_H^{(w)} < 2.7$, and for $t > 0.55$ it is practically a linear function of temperature (see (3) and (4)). The specific volume for these temperatures as well as the thermal expansion coefficient increase similarly to the case of argon. This suggests that $\tilde{v}_w(t)$ and $\tilde{\gamma}_w(t)$ are mainly caused by the averaged intermolecular potential having for these temperatures the argon-like structure.

To the left of t_m , the situation is different: the specific volume also increases when temperature tends to t_{tr} , while the thermal expansion coefficient continues to decrease monotonously. It means that $\tilde{v}_w(t)$ and $\tilde{\gamma}_w(t)$ have not the argon-like nature and we can assume that H -bond interactions start playing the crucial role. The increase of $\Delta(t)$ for $t \rightarrow t_{tr}$ indicates that the character of H -bonds influence on the EoS differs from one for $t > 0.55$ (see the formulas (3) and (4)). Here, some increase of $n_H^{(w)}(t)$ provokes the increase of the specific volume similarly to one for the hexagonal ice. For $t \leq t_0$,

the influence of H -bonds becomes more and more weak and the argon-like effects begin to dominate. As a result, the thermal expansion coefficient becomes positive. These facts are schematically reflected in Fig.6 too.

It is very important to stress that the curves $\tilde{v}_{H_2O}(t)$ and $\tilde{v}_{D_2O}(t)$ are practically identical for $0.6 < t < 0.97$, which leads to the conclusion that their behavior is determined by the same averaged interparticle potentials. Different angular velocities of their molecular rotations are only manifested near their triple points, where their rotations decelerate considerably.

Let us complete our qualitative arguments by the estimate of $\Delta(t)$ for ordinary water. We assume that the deviation of $\tilde{v}(t)$ from the corresponding separatrix is caused by H -bonds analogously to that for $\tilde{v}(t) - k\tilde{v}_{Ar}(t)$ far away from the triple point. In accordance with this (see the subsection B)), we can write:

$$\Delta_{H_2O}(t) \approx \tilde{v}_H^{(tr)}(t) \left(n_H^{(w)}(t_{tr}) - n_H^{(w)}(t_0/2) \right).$$

Estimating $n_H^{(w)}(t)$ similarly to (4) we obtain:

$$\Delta_{H_2O}(t) \approx -4\lambda_w \tilde{v}_H^{(w)}(t_{tr} - t_0/2).$$

where we had additionally put: $\tilde{v}_H^{(tr)} \approx \tilde{v}_H^{(w)} = 0.008$ [12]. As a result, $\Delta_{H_2O}(t_{tr}) = 0.0005$. From Fig.1 it follows that the experimental value of $\Delta_{H_2O}(t_{tr})$ is quite close, $\Delta_{H_2O}(t_{tr}) = 0.00035$. The analogous agreement takes the place for heavy water too.

III. DISCUSSION

The argon-like behavior of specific volumes and thermal expansion coefficients outside of the terminate points – triple and critical ones – for all considered liquids on their coexistence curves is naturally explained by similar form of their averaged interparticle potentials [22].

This circumstance explains also the applicability of the Van der Waals EqS for low molecular liquids, including water.

Although the main contribution to the EqS for water is caused by the averaged interparticle potentials, the small deviations of its specific volume from that one for argon are caused by H -bonds or D -bonds. These deviations can be expended in a series with respect to all thermodynamic characteristics of H -bond or D -bond networks (see [11-13]), first of all to the average number of H -bonds per molecule. In our work, we restrict ourselves by that particular approximation.

Such approach is not applicable only near the terminal points: triple and critical ones. In the narrow vicinity of the critical point, the considerable expansion of a system provokes the dimerization of water molecules [26]. Near the triple point ($0.42 < t < 0.6$), the life-time of H -bonds increases similarly to the dipole relaxation time. In this situation, the thermal expansion of a system is determined by H -bonds exactly as it is for the case of hexagonal ice.

The thermal expansion coefficient at $T_m = 4^\circ C$, corresponding to the maximal density of water, is characterized by quasi-linear temperature dependence changing its sign at $T_m = 277K$. For higher temperatures, one observes the smooth transition to the argon-like region $0.6 < t < 1$.

The thermal expansion coefficient for ethanol has another peculiarity: it takes the minimal value at $T_{et} = 269K$ [13]. Assuming that it is connected with the influence of H -bonds, we should conclude that the closeness of T_m and T_{et} cannot be occasional.

ACKNOWLEDGMENTS

We express our cordial gratitude to Prof. G. Maisano, Prof. G. G. Malenkov, Prof. F. Migliardo and Dr. A. Ogulenko for detailed discussion of the obtained results.

-
- [1] D. Eisenberg, W. Kauzmann, The Structure and Properties of Water, Oxford University Press, Oxford, 2005. [ISBN-13: 9780198570264] doi:10.1093/acprof:oso/9780198570264.001.0001.
- [2] E.W. Lemmon, M.O. McLinden and D.G. Friend, "Thermophysical Properties of Fluid Systems" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303, (retrieved September 26, 2019).
- [3] S. Herrig, M. Thol, A. H. Harvey, E. W. Lemmon, A Reference Equation of State for Heavy Water, Journal of Physical and Chemical Reference Data 47 (2018) 043102; <https://doi.org/10.1063/1.5053993>
- [4] S.H. Yao, J. Lee, G.W. Robinson, Water Structure Affected by a Weak Base, J. Am. Chem. Soc. **112** (1990) 5698–5700. doi:10.1021/ja00171a003.
- [5] J. Urquidi, S. Singh, C.H. Cho, G.W. Robinson, Origin of temperature and pressure effects on the radial distribution function of water, Phys. Rev. Lett. **83** (1999) 2348–2350. doi:10.1103/PhysRevLett.83.2348.
- [6] C.H. Cho, S. Singh, G.W. Robinson, An explanation of the density maximum in water, Phys. Rev. Lett. **76** (1996) 1651–1654. doi:10.1103/PhysRevLett.76.1651.
- [7] C.H. Cho, S. Singh, G. Wilse Robinson, Understanding all of water's anomalies with a nonlocal potential, J. Chem. Phys. **107** (1997) 7979–7988. doi:10.1063/1.475060.
- [8] H. Okajima, M. Ando, H. Hamaguchi, Formation of "Nano-Ice" and Density Maximum Anomaly of

- Water, *Bull. Chem. Soc. Jpn.* **91** (2018) 991–997. doi:10.1246/bcsj.20180052.
- [9] I.Z. Fisher, I.S. Andrianova, The degree of filling of the voids in the quasicrystalline structure of water, *J. Struct. Chem.* **7** (1966) 326–331. doi:10.1007/BF00744419.
- [10] H. Tanaka, Simple physical explanation of the unusual thermodynamic behavior of liquid water, *Phys. Rev. Lett.* **80** (1998) 5750–5753. doi:10.1103/PhysRevLett.80.5750.
- [11] T. V. Lokotsh, N.P. Malomuzh, V.L. Zakharchenko, Anomalous density and permittivity effects on the structure of water, *J. Struct. Chem.* **44** (2003) 1001–1010. doi:10.1023/B:JORY.0000034807.32927.58.
- [12] A.I. Fisenko, N.P. Malomuzh, A.V. Oleynik, To what extent are thermodynamic properties of water argon-like?, *Chem. Phys. Lett.* **450** (2008) 297–301. doi:10.1016/J.CPLETT.2007.11.036.
- [13] V. E. Chechko, V. Ya. Gotsulsky, N. P. Malomuzh. On similarity degree between argon, water, hydrogen sulphide and alcohols of methanol series, *J. Mol. Liq.* **317** (2020) 11, 113941. doi: 10.1016/j.molliq.2020.113941.
- [14] L.D. Landau, E.M. Lifshitz, *Statistical Physics, Part 1*, Pergamon Press, Oxford, 1980. [ISBN: 9780750633727]
- [15] I.Z. Fisher, *Statistical Theory of Liquids*, Chicago University Press, 1964. [ISBN: 981-270-052-0]
- [16] A.Z. Patashinskii, V.L. Pokrovskii, *Fluctuation Theory of Phase Transitions*, Pergamon Press, Oxford, 1979. [ISBN: 9780080216645]
- [17] CRC Revival: *Handbook of Physical Properties of Rocks, Volume III*, Edited by Robert S. Carmichael, CRC Press 2019. [ISBN 9781138560161].
- [18] G.S. Kell, Precise representation of volume properties of water at one atmosphere, *Journal of Chemical Engineering Data* **12** (1967) 1, 66–69. https://doi:10.1021/je60032a018.
- [19] N.P. Malomuzh, V.N. Makhlaichuk. On the similarity of the self-diffusion and shear viscosity coefficients in low molecular liquids, *J. Mol. Liq.* **295** (2019) 111729. https://doi.org/10.1016/j.molliq.2019.111729
- [20] N.P. Malomuzh, I. V. Zhyganiuk, M. V. Timofeev, Nature of H-bonds in water vapor, *J. Mol. Liq.* **242** (2017) 175–180. doi:10.1016/j.molliq.2017.06.127.
- [21] Chechko V.E., Gotsulsky V.Ya., Malomuzh N.P. Surprising thermodynamic properties of alcohols and water on their coexistence curves, *J. Mol. Liq.* **272** (2018) 590–596, https://doi.org/10.1016/j.molliq.2018.09.126.
- [22] P.V. Makhlaichuk, V.N. Makhlaichuk, N.P. Malomuzh. Nature of the kinematic shear viscosity of low-molecular liquids with averaged potential of Lennard-Jones type, *J. Mol. Liq.* **225** (2017) 577–584. https://doi.org/10.1016/j.molliq.2016.11.101
- [23] V. M. Makhlaichuk, Kinematic Shear Viscosity of Water, Aqueous Solutions of Electrolytes and Ethanol, *Ukr. J. Phys.* **60** (2015) 9, 855–861. https://doi.org/10.15407/ujpe60.09.0854
- [24] N. P. Malomuzh, Cluster structure of water and its argon-like equation of state. *RENSIT.* **12** (2020) 1, 39–48. DOI: 10.17725/rensit.2020.12.03
- [25] S.V. Lishchuk, N.P. Malomuzh, P.V. Makhlaichuk, Why thermodynamic properties of normal and heavy water are similar to those of argon-like liquids?, *Phys. Lett. A* **374** (2010) 19–20, 2084 – 2088. https://doi.org/10.1016/j.physleta.2010.02.070
- [26] V.L. Kulinskii, N.P. Malomuzh, Dipole fluid as a basic model for the equation of state of ionic liquids in the vicinity of their critical point *Phys. Rev. E* **67** (2003) 011501. https://doi.org/10.1103/PhysRevE.67.011501.