# LIQUIDS AND LIQUID CRYSTALS

# HOW SUBSTANTIAL IS THE ROLE OF THE H-BOND NETWORK IN WATER?

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Analyzing the behavior of the shear viscosity and the average number of H-bonds per molecule, a similarity of molecular thermal motions in water and argon is discussed. It is shown that the shear viscosity of water demonstrates the argon-like temperature dependence on the coexistence line at $T > T_\nu$, $T_\nu \approx 320$ K. Since the average number of H-bonds per molecule is less than two in the same region, it is concluded that the contribution to the shear viscosity caused by the H-bond network is noticeably different from zero only at $T < T_\nu$. The temperature dependence of this contribution is exponential with good accuracy, and the corresponding activation energy is equal to the energy of formation or disruption of an H-bond. These and other facts allows us to conclude that the crystal-like type of the thermal motion in water takes place only at $T < T_\nu$.

## 1. Introduction

The anomalous behavior of many thermodynamic and kinetic properties of water is generally recognized [1—3]. It is supposed that, unlike simple liquids, the temperature dependences of the density of water, its isothermal compressibility, thermoconductivity, and several other values are non-monotonous. The density and thermal conductivity of water reach their maximum values at $T_n = 277$ K and $T_\lambda = 404.5$ K, respectively, and the isothermal compressibility reaches its minimum at $T_\beta = 314$ K. The origin of peculiarities of this type is connected with the existence of the H-bond network and is caused by the specific local structure of water [1—3]. To take into account the influence of H-bonds, numerous theoretical approaches have been developed

(see [4—10]). However, a clear interpretation of all the facts remains absent. In this case, an important role is played by the fact that the properties of water do not remain unchanged throughout the whole interval of its existence: from the crystallization point to the critical point, and in the supercooled metastable region. Since the number of H-bonds per molecule should diminish with increase in temperature, one should expect that the temperature dependences of different characteristics of water approach asymptotically those of argon and other simple liquids.

Such kinetic characteristics as the shear viscosity, relaxation time of shear tension, self-diffusion coefficient, and others are also worthy of a more detailed attention.

In the behavior of these characteristics, the existence of H-bonds manifests itself slightly differently: the effective activation energy exceed those for simple liquids and one-component liquids without H-bonds almost by a factor of 10 [11—13]. However, here it is very important to exclude accurately the effects of thermal expansion which make a considerable contribution to the effective activation energy (see [14—16]).

From this point of view, a thorough comparison of the temperature dependences of different values for water and argon seems to be especially important. According to the principle of corresponding states, these characteristics should be normalized with respect to their values at the critical point, and temperature should be measured in reduced units $t = T/T_c$, where $T_c$ is the critical temperature.
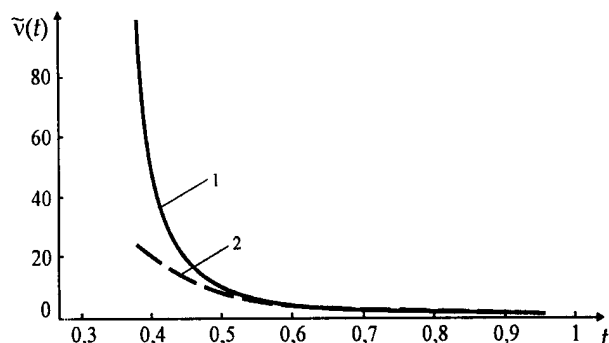
Fig. 1. Temperature dependences of the normalized shear viscosities for: *1* — water, according to [12], and *2* — argon ([12])
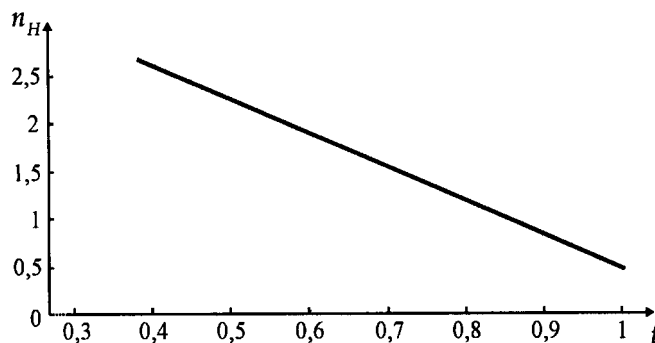


Fig. 2. Temperature dependence of the average number of H-bonds per molecule according to [10]

The choice of argon as a reference liquid was made for the following reasons. From the point of view of the molecular structure, the water homologues, in the first instance its nearest homologue $H_2S$, are more suitable. In comparison with water, the H-bonds in $H_2S$ are weaker. Their bond energy has the same order of magnitude as the dispersive (van der Waals) forces. A molecule $H_2S$, like a water molecule, has a comparatively small moment of inertia (see its estimate below). Therefore, the characteristic value of its rotation period is less than the time $\tau_t \sim a/V_T$ ($a$ is the interparticle distance, and $V_T$ is the velocity of thermal motion), which characterizes a variation of the position of its center of mass. Because of this, the averaging over rotational degrees of freedom can be performed and we expect that the equation of state of $H_2S$ will be similar to that of argon. The strong H-bonds in water hinder the free rotation of its molecules. However, the average number of H-bonds per molecule decreases as the temperature grows [10,17,18], and the conditions for the almost free rotation of water molecules are created in a wide temperature range adjacent to the critical point. Thus in this case, one can also speak of argon as a reference liquid which allows the separation of the van der Waals contribution to the intermolecular interaction, as well as the effects of thermal expansion.

In the present paper, our attention will be focused on the comparative analysis of the temperature dependences of the shear viscosities and the isothermal compressibilities of water and argon, and also on their comparison with the temperature dependence of the average number of H-bonds per molecule. In this way, it is possible to obtain an answer to the question of to what degree water is like to argon.

## 2. Behavior of the Shear Viscosities of Water and Argon on the Liquid–Gas Coexistence Line

Let us compare the temperature dependences of the shear viscosities for water and argon normalized with respect to their regular values at the critical point: $\nu_R^{(\text{Ar})}$ and $\nu_R^{(W)}$. The behavior of the functions $\tilde{\nu}^{(\text{Ar})}\left(\frac{T}{T_c^{(\text{Ar})}}\right) = \frac{\nu^{(\text{Ar})}(T)}{\nu_R^{(\text{Ar})}}$ and $\tilde{\nu}^{(W)}\left(\frac{T}{T_c^{(W)}}\right) = \frac{\nu^{(W)}(T)}{\nu_R^{(W)}}$, where $T_c^{(\text{Ar})} = 150.8$ K and $T_c^{(W)} = 647.15$ K are the critical temperatures for argon and water, respectively, is represented in Fig. 1. From here, it follows that the normalized shear viscosity of water has the argon-like character above the temperature $T_\nu \approx 320$ K. This indicates that, at $T > T_\nu$, the integrity of the H-bond network is broken and it does not play the essential role in the formation of shear viscosity. From Fig. 2, it follows that the average number of H-bonds per molecule is lesser than two at $T > T_\nu$: $n_\text{H}(T_\nu) \approx 2$. At a further increase of the temperature $t > t_\nu$, where $t = T/T_c^{(W)}$, $n_\text{H}(T)$ decreases practically linearly. This means that, in the temperature interval $(t_\nu, 1)$, the translational motion of molecules in water is in many respects analogous to that in argon. More exactly, in the interval $(t_\nu, 1)$, the formation of H-bonds results in the formation of linear chains: dimers, trimers, and so on, thus influencing the density and local structure of water. At the same time, the argon-like behavior of the shear viscosity indicates that it is less sensitive to the formation of small clusters.

It is very important that the temperature dependence of the shear viscosity for liquid argon everywhere on the coexistence line, from the crystallization point $T_m$ to the

critical one $T_c$, has the same character and is described by the polynomial

$$\nu^{(\text{Ar})}(T) = \nu_R^{(\text{Ar})} g(T), \quad g(T) = \sum_{n=1}^{m} a_n^{(m)} \left(\frac{T}{T_c^{(\text{Ar})}}\right)^n. \quad (1)$$

The coefficients $a_n^{(m)}$ depend on $m = 5 \div 10$ (see Table 1).

We should note that the specific form of a function $g(t)$ for argon has nothing in common with the exponential dependence

$$\nu^{(\text{Ar})} = \nu_0 \exp\left(\frac{E_a}{k_\text{B} T}\right) \quad (2)$$

that corresponds to the activation theory of shear viscosity [14]. Indeed, the activation energy $E_a$ determined along isochoric lines [20] is lesser than the thermal noise energy $k_\text{B} T_m$ at the melting point (see Table 2).

This fact allows us to conclude that the character of the thermal motion in argon is barrier-free. At the same time, the application of formula (2) to the description of the shear viscosity on the coexistence line leads, on the one hand, to the inequality $E_a/k_\text{B} T > 1$ consistent with the initial assumptions of the activation theory, and, on the other hand, to the dependence of the activation energy on temperature, $E_a = E_a(T)$, that contradicts this theory. A similar situation arises due to the influence of thermal expansion effects (see [14,15]) and is also observed in liquid nitrogen [16] and other liquids.

A similar character of the temperature dependences of the shear viscosities for water and argon in the temperature interval $(t_\nu, 1)$ indicates that the molecular motion in water does not have the activation nature. In other words, the model of crystal-like thermal motion in water is inapplicable in the temperature interval $(t_\nu, 1)$.

The specific mechanism of the formation of viscosity in water caused by the H-bond network can be considered only at $t < t_\nu$.

**T a b l e 1**

| $a_n^{(5)}$ | $n$ | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| | $a_n$ | 255.45 | 1114 | 1885 | −1445 | 419.775 |
| $a_n^{(10)}$ | $n$ | 1 | 2 | 3 | 4 | 5 |
| | $a_n$ | 272.1 | −1193 | 1974.94 | −1449 | 418.3 |
| | $n$ | 6 | 7 | 8 | 9 | 10 |
| | $a_n$ | 1253 | −5153 | 7838 | −5315 | 1359 |

**T a b l e 2**

| $\rho$, g/sm$^3$ | 1.192 | 1.240 | 1.340 | 1.384 |
|---|---|---|---|---|
| $E_a/k_b T$ | 0.812 | 0.89 | 0.913 | 0.967 |

As noted in Introduction, for a more adequate separation of different contributions to the shear viscosity, the comparison of values of $\nu^{(W)}(T)$ with those for water homologues $H_2S$, $H_2Se$, and so on, in which the H-bonds are noticeably weaker, would be more expedient. However, the destruction of the H-bond network integrity at $t > t_\nu$ leads to the quasi-free rotation of molecules, so that the averaging over the rotational degrees of freedom can be performed. Indeed, the ratio of the characteristic times of the rotational $\tau_r$ and translational $\tau_{\text{tr}}$ motions of a molecule, determined as

$$\tau_r \sim \sqrt{\frac{I}{k_\text{B} T}} \text{and} \quad \tau_r \sim \frac{a}{v_r}, \quad v_r \sim \sqrt{\frac{k_\text{B} T}{m}},$$

where $m$ and $I$ are the molecular mass and the moment of inertia, is equal to

$$\frac{\tau_{tr}}{\tau_r} \sim 10. \quad (3)$$

Such a ratio between $\tau_{\text{tr}}$ and $\tau_r$ allows us to introduce the effective pair potential which depends only on the interparticle distance. One can show that the averaging of multipole-multipole interactions over the rotational degrees of freedom leads to contributions of the same type as the van der Waals contributions for spherically symmetric molecules [21]. In particular, the long-range behavior of the effective potential is represented by the asymptotic expansion

$$U_{\text{eff}}(r) = -\frac{\varepsilon_6}{r^6} + \frac{\varepsilon_8}{r^8} + ..., \quad r > r_*. \quad (4)$$

## 3. Temperature Dependence of the Shear Viscosity in Water

It follows from the comparative analysis of the shear viscosities in argon and water undertaken in the previous section that

$$\nu^{(W)} = \nu_I(T) + \nu_\text{H}(T), \quad (5)$$

where

$$\nu_I(T) = \nu_R^{(W)} g(T), \quad (6)$$

is the term with the argon-like temperature dependence and $\nu_H(T)$ is the term caused by H-bonds (Fig. 3). It was shown in [10] that such a representation can be also used for the specific volume occupied by water molecules.

In the interval $t < t_\nu$, the role of the H-bond network grows with decrease in temperature. In accordance with
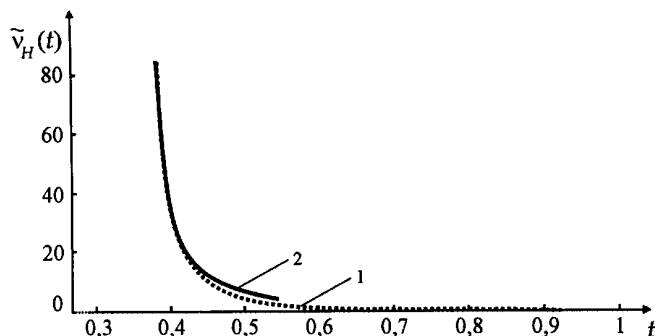
Fig. 3. Temperature dependences of the normalized contribution $\tilde{\nu}_H(T)$ to the shear viscosity of water: 1 corresponds to $\tilde{\nu}_H(t) = \tilde{\nu}_H^W(t) - \tilde{\nu}_H^{Ar}(t)$, and 2 is calculated according to (10)

[10], its equilibrium properties are described by the so-called structural functions $S_i(P,T)$ which are the structural characteristics of the H-bond network. The most important structural functions $S_1$ and $S_2$ are identified with the average number of H-bonds per molecule and the tetrahedricity parameter [22,23]:

$$S_1(P,T) = n_H(P,T)$$

$$S_2(P,T) = \chi_H(P,T). \tag{7}$$

Under non-equilibrium conditions, their role passes, seemingly, to the corresponding relaxation times. It is natural to suppose that the disruptions of H-bonds and the displacements of molecules caused by them play the main role in the formation of the contribution $\nu_H(T)$. Therefore, we can restrict ourselves to $\tau_H$ only, which is the characteristic time for the variations of $n_H$. Then the application of the Hilbert–Curie's principle (see [24]) leads to the relation

$$\nu_H(T) = c_t^2 \tau_H(T) + ..., \tag{8}$$

where the parameter

$$c_t^2 = \frac{\nu_H(T)}{\tau_H(T)} \tag{9}$$

has the dimensionality of sound velocity and should be practically constant in the temperature interval, in which $\nu_H(T)$ is noticeably different from zero. From the physical point of view, $c_t^2$ is the contribution of H-bonds to the transversal sound velocity. Note that the relation between $\nu_H(T)$ and $\tau_H(T)$ of type (20) also arises in the phenomenological relaxation theories [25]. Although, in the narrow temperature interval $t \in (0.38, 0.5)$, the values of $\nu_H(T)$ and $\tau_H(T)$ (see Figs. 1 and 4) change by
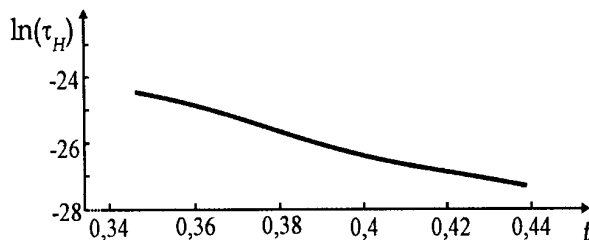


Fig. 4. Temperature dependence of the relaxation time $\tau_H$ corresponds to the data [26,27] obtained by computer simulations

one order of magnitude, their ratio, as seen from Fig. 4, remains almost constant.

At $t < t_\nu$, the displacements and rotations of molecules are closely related to the break of H-bonds. The character of these processes is naturally described by the activation theory which becomes more adequate to the picture of the thermal motion with decrease in temperature. In this case,

$$\nu_H(T) = \nu_H^{(l)} e^{\frac{E_H}{k_B T}}, \tag{10}$$

where it is expedient to determine the values of the amplitude $\nu_H^{(l)}$ and the activation energy $E_H$ from the values of the shear viscosity in the supercooled region, in which $2 < n_H \leq 3$. In such a way, we obtain

$$\nu_H^{(l)} = 1.79 \times 10^{-5}, \quad E_H = 2723 \text{ K}. \tag{11}$$

It follows from physical considerations, that the value of $E_H$ should be a multiple of the break energy $\varepsilon_H^{(1)}$ of an H-bond. The value $\frac{E_H}{k_B T_m} \approx 10$ is, actually, in the interval of permissible values of the ratio $\frac{\varepsilon_H^{(1)}}{k_B T_m} \in (7, 10)$ [1—3, 28]. The activation energy $E_\tau = 2812K$ for the relaxation time $\tau_H$, in accordance with our reasons, appears to be close to $E_H$ and $\varepsilon_H^{(1)}$.

This circumstance can be interpreted in the following way. In the temperature interval $0.38 < t < 0.42$ or, equivalently, $245 \text{ K} < T < 273 \text{ K}$, the majority of molecules form three H-bonds, as follows from Fig. 2. Due to the break of one of them and the bending of two other H bonds a molecule can move by the distance of the order of $(0.3 \div 0.5)$ Å. At that, the broken H-bond can be restored, or a new H-bond with one of the nearest neighbors can be formed. The second case corresponds to the transport of the center of mass of a molecule and its momentum. Thus, a new mechanism of the formation of the self-diffusion coefficient and the shear viscosity is realized in such a way. This mechanism is applicable only to water in the supercooled or normal state that is
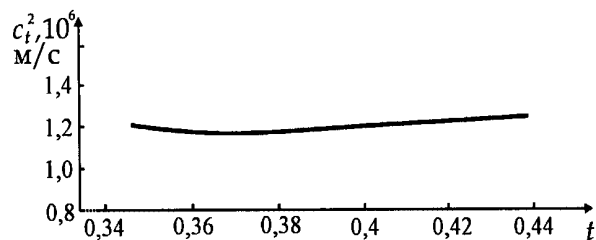
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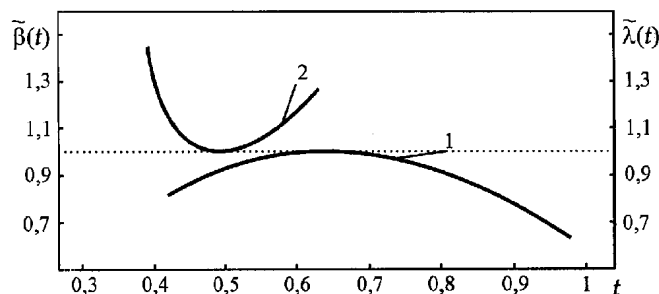Fig. 5. Temperature dependence of the square of the transversal sound velocity in water estimated by (9)



Fig. 6. Temperature dependences of the normalized: $1$ — thermoconductivity coefficient $\tilde{\lambda}(t) = \lambda(t)/\lambda_{\max}$ [12] and $2$ — isothermal compressibility $\tilde{\beta}(t) = \beta(t)/\beta_{\min}$ [13, 30]

too far from the crystallization point, where there is the developed H-bond network.

This mechanism will be described in a separate paper in more details.

## 4. Conclusion

Let us review the results presented above and obtained in other works: 1) the temperature dependences of the shear viscosities of water and argon are the same at $T > T_\nu$, where $T_\nu \approx 320$ K, 2) the temperature $T_\nu$ is also characteristic of the isothermal compressibility $\beta_T$ of water; near it, $\beta_T$ reaches its minimum and increases after that as in simple liquids. A very flat maximum of the thermo-conductivity, as seen from Fig. 5, is situated a bit more to the right, 3) the applicability of the inequality $\tau_0 > \tau_s$, where $\tau_0$ is the residence time for water molecules determined from the incoherent neutron scattering [29] and $\tau_s = \frac{a}{V_T}$ is the characteristic time of a soft binary collision, is limited by the temperatures $T < T_\nu$, 4) at $T > T_\nu$, each water molecule forms, on the average, less than two H-bonds with its nearest neighbors. These and other results allow us to conclude the following: 1) water can be considered as a liquid with crystal-like thermal motion [14, 31] only for $T < T_\nu$, 2) the developed H-bond network in water also exists at the temperatures lesser than $T_\nu$. In the opposite case, there can exist only linear molecular chains, dimers, trimers and so on; 3) the kinetic properties of water are less sensitive to the integrity of the H-bond network compared to its structural and thermodynamic properties.

A more detailed comparative analysis of the properties of water and other liquids will be carried out in the separate paper.

1. *Water*: A Comprehensive Treatise // Ed. by F. Franks. — New York: Plenum, 1972.

2. *Eisenberg D., Kauzmann V.* Water Structure and Properties. — Leningrad: Gidrometeoizdat, 1975 (in Russian).

3. *Antonchenko V.Ya., Davydov A.S., Il'in V.V.* Bases of Water Physics. — Kyiv: Naukova Dumka, 1991 (in Russian).

4. *Frank H.S., Wen W.J.* // Disc. Faraday Soc. — 1957. — **24.** — P. 133—140.

5. *Nemethy G., Sheraga H.A.* // J. Chem. Phys. — 1962. — **36.** — P. 9382—9387.

6. *Fisher I.Z., Andrianova I.S.* // J.Struct.Chem. — 1966. — **7**, N 3. — P. 337—344.

7. *Andrianova I.S., Fisher I.Z.* // Ibid. — 1968. — **9**, N 4. — P. 592—598.

8. *Stanley H.E., Teixeira J.* // J. Chem. Phys. — 1980. — **73.** — P. 3404—3421.

9. *Svishchev I.M.* // DAN USSR — 1991. — **320.** — P. 140—143.

10. *Lokotosh T.V., Malomozh N.P., Zakharchenko V.L.* // J. Struct. Chem. — 2003. — **44**, N 6. — P. 1101—1010.

11. *Handbook*: Tables of Physical Values. / Ed. by I.K. Kikoin. — Moscow: Atomizdat, 1976. (in Russian).

12. *Vargaftik N.B.* Handbook of Thermophysical Properties of Liquids and Gases — Moscow: Nauka, 1972 (in Russian); *Vargaftik N.B.* Handbook of Thermoconductivity of Liquids and Gases. — Moscow: Nauka, 1990 (in Russian).

13. *CRS Handbook* of Chemistry and Physics: a Ready-Reference Book of Chemical and Physical Data / Ed. by R.C. West. — Boca Raton: CRS Press, 1996.

14. *Frenkel J.* Kinetic Theory of Liquids. — New York: Dover, 1955.

15. *Malomuzh N.P., Fisher I.Z.* // Transactions "Physics of Liquid State" (Kyiv University Publ.) —1973. — **1.** — P. 33—38.

16. *Blazhnov V.V., Malomuzh N.P., Lishchuk S.V.* // J. Chem. Phys. — 2004. — **121.** — N 13. — P. 6435—6441.

17. *Lisichkin Yu.V., Novikov A.G., Fomichev N.K.* // J. Phys. Chem. — 1989. — **63.** — P. 833—835.

18. *Kataoka Y., Hamada H., Nose S.* // J. Chem. Phys. — 1982. — **77**. — P. 5699—5703.

19. *Sorensen C.M.* / Proc. of 12th Intern. Conf. on the Properties of Water and Steam. — New York: Begell House, 1995.— P. 308.

20. *Slyusar V.P., Rudenko N.S., Tretjakov V.M.* // Ukr. Fiz. Zh. — 1972. — **17**. — N 8. — P. 1257-1263.

21. *Kulinskii V.L., Malomuzh N.P.* // Phys. Rev. E. — 2003. — **67**. — P. 011(501-510).

22. *Naberukhin Yu.I., Luchnikov V.A., Malenkov G.G., Zheligovsky E.A.* // Zh. Strukt. Khim. — 1997. — **38**. — N 4. — P. 713—722.

23. *Paschek D., Geiger A.A.* // J. Phys. Chem. B. — 1999. — **103**. — N 20 — P. 4139—4146.

24. *Monin A.S., Yaglom A.M.* Statistical Hydrodynamics. Turbulence Mechanics. Pt.2. — Moscow: Nauka, 1967 (in Russian).

25. *Fabelinsky I.L.* Molecular Light Scattering. — Moscow: Nauka, 1965 (in Russian).

26. *Gallo P., Sciortino F., Tartaglia P., Chen S.-H.* // Phys. Rev. Lett. — 1996. — **76**. — P. 2730—2733.

27. *Lokotosh T.V., Magazu S., Maisano G., Malomuzh N.P.* // Phys. Rev. E. — 2000. — **62**. — N 3. — P. 3572—3580.

28. *Malenkov G.G., Tytik D.L.* / "Molecular Dynamics Method in Physical Chemistry" — Moscow: Nauka, 1996 (in Russian).

29. *Bulavin L.A., Malomuzh N.P., Pankratov K.N.* // J. Struct. Chem. — 2005. — In Press.

30. *International* Critical Tables of Numerical Data, Physics, Chemistry and Technology (http://www.knovel.com).

31. *Samoilov O.Ya.* Structure of Water Solutions and Hydration of Ions. — Moscow: AN USSR Publ., 1957 (in Russian).

НАСКІЛЬКИ ВАЖЛИВА РОЛЬ
ВОДНЕВИХ ЗВ'ЯЗКІВ У ВОДІ?

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Р е з ю м е

Проведено порівняльний аналіз температурних залежностей зсувної в'язкості води й аргону. Показано, що при $T > T_\nu$, де $T_\nu \approx 320$ K, в'язкість води має аргоноподібний характер. Це дозволяє в'язкість води записати у вигляді $\nu^{(W)}(T) = \nu_W(t) + \nu_H(t)$, де перший доданок залежить від $t = T/T_c$ ($T_c$ — критична температура) поліноміальним чином, як і в рідкому аргоні, а $\nu_H(t)$ має експоненціальну залежність, характерну для активаційних теорій. Оскільки при $T > T_\nu$ середнє число $n_H(t)$ водневих зв'язків, що припадають на одну молекулу, задовольняє нерівність $n_H(t) < 2$, зроблено висновок, що в цій області температур цілісність сітки водневих зв'язків порушується. З цього, а також з аналізу експериментальних результатів некогерентного розсіяння теплових нейтронів випливає, що квазікристалічна модель теплового руху у воді є придатною тільки в області температур $T < T_\nu$.