

## NATURE OF THE KINEMATIC SHEAR VISCOSITY OF WATER

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Nature of the kinematic shear viscosity of water  $\nu$  is discussed in the work. Dependences of  $\nu$  on temperature  $t$ , reduced volume  $\tilde{v}$ , and the average number of hydrogen bonds per one molecule  $n_H$  ( $t = T/T_c$ ,  $\tilde{v} = v/v_c$ ,  $T_c$  and  $v_c$  are critical values of temperature and reduced volume) are analyzed in detail on a liquid-vapor coexistence curve. It is shown that at  $T < T_H$  ( $T_H \approx 310$  K is the characteristic temperature of water) the formation of the kinematic shear viscosity is induced by activation. At  $T > T_H$ , the shear viscosity of water is the sum of two contributions. One of them is of the same nature as in simple liquids, and another is caused by effects of hydrogen bonds. The temperature dependence of  $\nu$  in this temperature region has nothing in common with exponential formulas of activation theory. The explicit form of the functional dependence of the kinematic shear viscosity on  $t$ ,  $\tilde{v}$ , and  $n_H$  is found and substantiated. It is shown that the value and temperature dependence of  $n_H$  resulting in the experimental values of the kinematic shear viscosity of water agree well with the values corresponding to density and evaporation heat data.

**Keywords:** water, argon, kinematic shear viscosity, hydrogen bonds, structural functions.

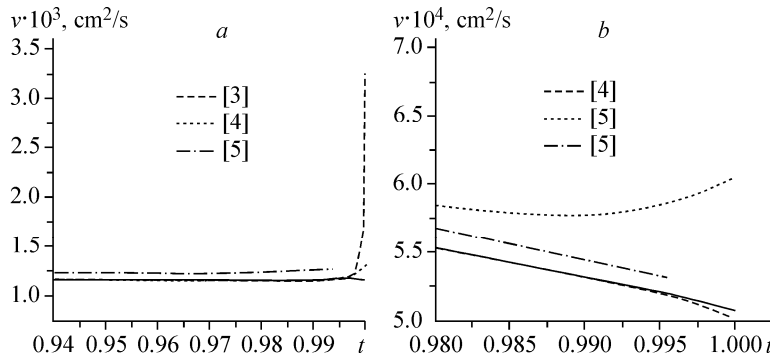
### INTRODUCTION

Nature of the shear viscosity of water has been a subject of numerous theoretical and experimental investigations [1-6]. However, a satisfactory description of its dependence on temperature and pressure, especially in wide ranges of their values, is still absent. This is related to serious difficulties caused by the existence of hydrogen bonds in water. The latter significantly affect the local structure of water and the character of thermal motion therein. Their role, however, does not remain unchanged as temperature and pressure vary, which is not always properly taken into account. So, the temperature dependence of the shear viscosity of water on the saturation line is often described by formulas such as [7, 8]

$$\eta(T) = \eta_1 \exp(\varepsilon_1 / T) + \eta_2 \exp(\varepsilon_2 / T) + \dots, \quad (1)$$

that are characteristic of activation theory of viscosity [9, 10]. Using the sufficient number of exponents it is always possible to fit experimental data to any previously given accuracy. At the same time, it is rather a serious problem to give physical sense to activation energies  $\varepsilon_i$  and pre-exponential factors  $\eta_i$  in (1). In particular, the use of contributions for which  $\varepsilon_i/T < 1$  is generally inadmissible because the activation energy should not be lower than the thermal noise energy [10]. A description of the temperature dependence of viscosity of non-hydrogen bonded liquids also meets this requirement. In the case of argon, as shown in [11-13], the formally defined activation energy is 2-3 times smaller than the energy of thermal noise.

Relations between  $\varepsilon_i$  and  $\eta_i$  and the most important characteristics of the hydrogen bond network such as the hydrogen bond energy and the number of bonds per one molecule remain still unclear.



**Fig. 1.** Temperature dependence of the kinematic shear viscosity of water (*a*) and argon (*b*) around their critical points according to experimental data. Solid lines correspond to the behavior of the regularized component  $\nu_R(t)$ .

In order to solve this major problem the following approach is proposed in [14]. The temperature dependence of the kinematic shear viscosity of water  $\nu$  on the saturation line is represented as a sum

$$\nu^{(w)}(T) = \nu_R^{(w)} \tilde{\nu}(t) + \nu_H(t), \quad (2)$$

where  $\tilde{\nu}(t)$  is the dimensionless function determining the behavior of argon viscosity

$$\nu^{(Ar)}(t) = \nu_R^{(Ar)} \tilde{\nu}(t), \quad (3)$$

$\nu_H(t)$  is the excess contribution arising from hydrogen bonds. The dimensional factor  $\nu_R$  corresponds to the regular component of the kinematic shear viscosity in a critical point [15, 16]. Similar character of the temperature dependence is typical of the law of corresponding states [17].

The contribution  $\nu_H(t)$  arising from the existence of hydrogen bonds plays a dominant role in water at  $T < T_v$ ,  $\sim 310$  K, as shown in [14]. It has been also supposed in [14] that at  $T > T_v$  the temperature dependence of the kinematic shear viscosity of water is close to that observed in argon. This conclusion quite naturally followed from the results of works [18, 19], where it was shown that at  $T > T_v$  thermal motion in water is of the argon type. However, the analysis of later experimental data (as compared to those used in [14]) has allowed to ascertain that a small but regular deviation of the shear viscosity from the argon type dependence is observed in the region of  $T > T_v$ .

The purpose of the present paper is to analyze in detail these deviations and to find their relations with features of the hydrogen bond network behavior in water.

## REGULAR COMPONENTS OF THE KINEMATIC VISCOSITY OF ARGON AND WATER IN A CRITICAL POINT

The behavior of the kinematic viscosity  $\nu$  of water and argon on the saturation lines around critical points are presented in Fig. 1. Their values were determined in the standard way using the experimental values of the dynamic shear viscosity  $\eta$  and mass density  $\rho$ :  $\nu = \eta/\rho$ . As seen from Fig. 1a, the values of  $\nu$  reconstructed with the help of [3] and [4] practically coincide with each other up to  $t = 0.998$ . A closer approach to the critical point leads to an increase in  $\nu$ , according to the data of [3], which corresponds to the results of fluctuation theory of critical phenomena. Values of  $\nu$  listed in [4] remain finite. The shear viscosity value of water obtained by parabolic extrapolation from the region of  $t \leq 0.998$  to the point  $t = 1$ , we call the regularized value. Extrapolating by the formula

$$\nu^{(w)}(t) = (1.460t^2 - 2.828t + 1.484) \cdot 10^{-2} \text{ cm}^2/\text{s},$$

we find

$$v_R^{(w)} = 1.159 \cdot 10^{-3} \text{ cm}^2 / \text{s}. \quad (4)$$

Fig. 1b shows that in the case of argon, the discrepancy between  $v$  values taken from different sources is somewhat larger in the temperature region  $0.95 \leq t \leq 1$ . Here we prefer the later data [4]. The value of the regularized component of the shear viscosity of argon  $v_R^{(Ar)}$  is also found by parabolic extrapolation

$$v^{(Ar)}(t) = (-1.564t^2 + 2.870t - 1.255) \cdot 10^{-2} \text{ cm}^2 / \text{s}$$

and proves to be equal to

$$v_R^{(Ar)} = 5.07 \cdot 10^{-4} \text{ cm}^2 / \text{s}. \quad (5)$$

## ANALYSIS OF DIFFERENT CONTRIBUTIONS TO THE KINEMATIC SHEAR VISCOSITY OF WATER

The kinematic shear viscosity of liquids is one of their basic kinetic characteristics. It is formed by various components of the thermal motion of molecules in liquids, first and foremost, translational and rotational. In the case of water, hydrogen bonds should significantly affect the character of these movements. Indeed, if the water molecule is bonded to the nearest neighbors by three or four hydrogen bonds, then it can only oscillate. If only one or two hydrogen bonds are formed, displacements and rotations of molecules remain restricted though their character significantly changes in comparison with the previous situation.

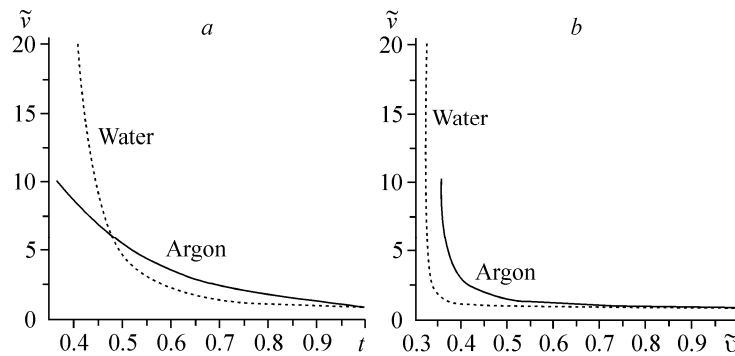
To isolate the translation contributions generated by displacements comparable in value with the average distance between molecules, we present the kinematic viscosity of water in the form of (2). The behavior of the function

$$\tilde{v}(t) = \frac{v^{(Ar)}(t)}{v_R^{(Ar)}}, \quad (7)$$

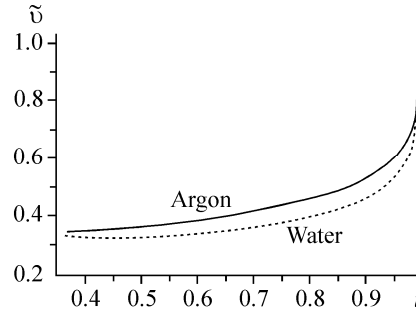
and also of  $\tilde{v}^{(w)}(t) = v^{(w)}(t)/v_R^{(w)}$  is displayed in Fig. 2a. It is necessary to note here that values of  $\tilde{v}(t)$  for supercooled argon, i.e. at  $t < t_m^{(Ar)} = 0.56$  are obtained by parabolic extrapolation

$$\tilde{v}_{\text{ext}}(t) = 32.296 - 81.67t + 55.297t^2.$$

Numerical values of coefficients at  $t$  degrees are found using the values of argon viscosity in the range of  $0.56 \leq t \leq 0.7$ . The corresponding values of water viscosity  $\tilde{v}^{(w)}(t)$  at  $t < t_m^{(w)} = 0.42$  are taken from [2] (see also [20]).



**Fig. 2.** Comparative behavior of normalized kinematic shear viscosities of argon (solid line) and water (dashed line) depending on temperature (a) and reduced volume (b). Experimental data are taken from [4].



**Fig. 3.** Temperature dependence of reduced volumes of water and argon on the saturation line.

The cross point  $t_v$  of temperature dependence curves for the kinematic shear viscosity of water and argon is one of the characteristic points of water, as it will be clear from the further discussion. It follows from the equation

$$\tilde{v}^{(w)}(t_v) = \tilde{v}_{\text{ext}}(t_v) \quad (8)$$

that  $t_v \approx 0.4778$ , which corresponds to  $T_v \approx 309.19$  K.

Note that the temperature  $T_v$  almost coincides with the characteristic temperature  $T_n \approx 315$  K found in [18] based on the analysis of experimental data on incoherent scattering of thermal neutrons. It follows from the results of [21, 22] that in the temperature region  $T < T_n$  each water molecule is bonded to the nearest neighbors by approximately three bonds. Therefore, during the lifetime  $\tau_0$  of this configuration a molecule oscillates around its temporary equilibrium position. The breaking of only one H-bond leads to a shift of the molecule and the formation of a new triplet of hydrogen bonds in another position. Then this process repeats. Its similarity to thermal motion in crystals is obviously the larger, the stronger is the inequality  $\tau_1 \ll \tau_0$ , where  $\tau_1$  is the characteristic time of a displacement from one temporary equilibrium position to another.

The number of hydrogen bonds per one molecule decreases with increasing temperature, which is accompanied by a change in the character of thermal motion of molecules. At the temperature  $T_n \approx 315$  K, the characteristic times  $\tau_0$  and  $\tau_1$  are compared, and hence,  $T_n$  is interpreted as the upper limit of applicability of quasi-crystalline representations. At  $T > T_n$  the character of molecular motion in water becomes more and more similar to that in non-hydrogen bonded liquids, in particular, in argon [23, 24]. Its major feature is the absence of vibrations around temporary equilibrium positions.

These facts give us grounds to assume that at  $T_H \approx T_v \approx T_n$  a dynamic phase transition [25] occurs in water caused, first of all, by the hydrogen bond network effect.

Hydrogen bonds arising in the region of  $T > T_n$  lead to a decrease in the reduced volume  $\tilde{v} = v/v_c$  occupied by one molecule in comparison with its value in argon, where  $\tilde{v}$  is formed only by van der Waals interaction forces (Fig. 3). As the kinematic shear viscosity depends not only on temperature but also on reduced volume, it is useful to compare the behavior of  $\tilde{v}$  on the water / argon coexistence curves and to consider it as the function of  $\tilde{v}$ . Fig. 2b shows that  $\tilde{v}^{(w)}(\tilde{v})$  and  $\tilde{v}^{(Ar)}(\tilde{v})$  coincide in a rather wide range of  $0.6 < \tilde{v} < 1$ . However, it follows from Fig. 3 that this corresponds to only a narrow vicinity of the critical point:  $0.9 < t < 1$ .

Hence, let us note that the kinematic shear viscosities of argon  $\tilde{v}^{(Ar)}(\tilde{v}, t)$  and benzene  $\tilde{v}^{(B)}(\tilde{v}, t)$  that significantly differ from each other on the coexistence curve in  $(\tilde{v}, t)$  coordinates become identical in  $(\tilde{v}, \tilde{v})$  coordinates. This fact along with a number of other reasons allow a conclusion to be drawn in [26] that  $\tilde{v}^{(Ar)}(\tilde{v}, t)$  and  $\tilde{v}^{(B)}(\tilde{v}, t)$  satisfy the dynamic version of the principle of corresponding states.

The kinematic viscosity of water, on the contrary, demonstrates another type of behavior. Thus, our main attention should be paid to its dependence on the number of hydrogen bonds  $n_H$  formed by one molecule.

## DIRECT INFLUENCE OF HYDROGEN BONDING ON THE SHEAR VISCOSITY OF WATER

In general, the static kinematic shear viscosity of water should be considered as the function of  $t$ ,  $\tilde{v}$ , and  $n_H$

$$\tilde{v}^{(w)} = \tilde{v}^{(w)}(t, \tilde{v}, n_H). \quad (9)$$

Of course, in the equilibrium state  $n_H$  is not an independent variable:  $n_H = n_H(t, \tilde{v})$ . However, hydrogen bonding results in a new mechanism of viscosity formation, and therefore, it is expedient to extract the dependence of  $\tilde{v}$  on  $n_H$  in (9).

The temperature dependence of the contribution  $\tilde{v}_H(t) = v_H(t)/v_R^{(w)}$  formed by hydrogen bonding and defined as  $\tilde{v}_H(t) = \tilde{v}^{(w)}(t) - \tilde{v}(t)$  according to (2), is presented in Fig. 4a. It is the point  $t_v$  where  $\tilde{v}_H(t)$  vanishes.

The degree of influence of hydrogen bonding depends on the region of  $t$  and  $\tilde{v}$  values. In particular, on a liquid-vapor coexistence line and near it we should distinguish between  $T < T_v$  and  $T > T_v$  regions. In the first of them, thermal motion of water molecules is completely determined by the influence of hydrogen bond network, as noted above, and has a crystal-like character. Then, in order to describe the temperature dependence of viscosity, it is possible to use activation theory [10]. In Fig. 4a the dotted line represents the curve

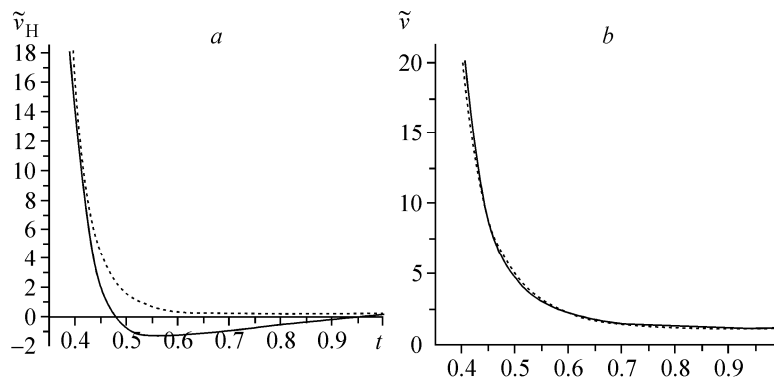
$$\tilde{v}_H(t) = \tilde{v}_0 \exp(\varepsilon/t), \quad (10)$$

whose parameters ( $\tilde{v}_0 = 1.29 \times 10^{-4} \text{ cm}^2/\text{s}$  and  $\varepsilon = 4.705$ ) are selected by the condition of the best approximation of  $\tilde{v}_H(t)$  in the supercooled region.

The following value of the activation energy of viscosity  $\varepsilon_H$  per one molecule corresponds to the dimensionless parameter  $\varepsilon = 4.705$ :

$$\varepsilon_H = \varepsilon k_B T_c \approx 3044 \text{ K}.$$

This value is of the same order of magnitude as the hydrogen bond energy  $\varepsilon_H^{(1)}$  [1, 27], and it can be considered as an independent evaluation of  $\varepsilon_H^{(1)}$ . The similarity of  $\varepsilon$  and  $\varepsilon_H^{(1)}$  values can be interpreted as follows. In the temperature range of  $0.38 < t < 0.42$  or  $245 \text{ K} < T < 273 \text{ K}$ , the majority of molecules form three or four hydrogen bonds [21, 22]. If the molecule is bonded to the nearest neighbors by three H-bonds, then the breaking of one of them allows it to move at a distance of about  $0.3\text{--}0.5 \text{ \AA}$ . This is the shift value compatible with bending of hydrogen bonds. Moving this way, the molecule in question either restores the broken H-bond or forms a new one, thus fixing itself in a new temporary equilibrium position. Mass and momentum space transfer that determines the processes of self-diffusion and shear viscosity in water corresponds just to the latter case. It is clear that the mechanism of such a transfer is peculiar only to hydrogen-bonded systems. In particular,



**Fig. 4.** Temperature dependence of  $\tilde{v}_H(t)$  (a) and  $\tilde{v}^{(w)}(t)$  (b) (solid lines). Dashed lines depict  $\tilde{v}_H(t) = \tilde{v}_0 \exp(\varepsilon/t)$  (a) and  $\tilde{v}^{(w)}(t)$  curves (b), the latter corresponding to formula (22).

in water it can occur only in that temperature range where  $n_H$  is substantially larger than two, i.e. in supercooled water and its normal states for which  $T > T_H$ . It is the region of states of water where a developed network of hydrogen bonds exists.

In the region of higher temperatures  $T < T_H$ , hydrogen bonds do not crucially affect the character of thermal motion of water molecules anymore; therefore their contribution to the kinematic shear viscosity can be described in terms of perturbation theory. The item  $\tilde{\nu}_H$  in the formula

$$\tilde{\nu}^{(w)}(t, \tilde{\nu}, n_H) = \tilde{\nu}(t, \tilde{\nu}) + \tilde{\nu}_H(t, n_H) \quad (11)$$

can be represented with suitable accuracy in the form of expansion in series using structural functions  $S_i$  of the hydrogen bond network [21]

$$\tilde{\nu}_H(t, n_H) = \kappa_1 S_1 + \kappa_2 S_2 + \dots \Rightarrow \kappa_1 n_H + \kappa_2 \chi_H + \dots, \quad (12)$$

where  $\chi_H$  is the tetrahedrality parameter [28, 29]. As quasi-static shear flows do not result in a regular distortion of the network of hydrogen bonds, the coefficient  $\kappa_2$  has to be zero. It is shown in [21] that on the liquid–vapor coexistence line the values of  $n_H(t)$  are described by a linear dependence of the form

$$n_H(t) = 4(1 - 0.88t + \dots). \quad (13)$$

It follows from Fig. 4a that the almost linear character of the temperature dependence is also inherent to the shear viscosity in the region of  $T > T_H$ . It gives grounds to write

$$\tilde{\nu}_H(t, n_H) = -\kappa n_H + \dots \Rightarrow -4\kappa(1 - \gamma t + \dots), \quad \kappa > 0. \quad (14)$$

The negative sign in formula (14) can be naturally explained by that the formation of hydrogen bonds between water molecules reduces their translation mobility that plays the main role in the formation of viscosity in the region where the developed network of hydrogen bonds is absent. In turn, this should be accompanied by decreasing momentum transfer rate and water viscosity. Such a situation should be maintained until hydrogen bonds form the developed spatial network. In this case, both molecular displacements and momentum transfer become possible only as a result of overcoming potential barriers, i.e. the viscosity should be of the activation character. As we see, this obviously occurs at  $T < T_v$ . Note also that otherwise, at  $T > T_v$ , when the developed network of hydrogen bonds is not formed, their bending insignificantly affects the character of transfer processes.

Assuming that  $\tilde{\nu}_H \rightarrow 0$  at  $t \rightarrow 1$ , the proportionality coefficient  $\gamma$  has to be 1, which leads to the value of  $\kappa \approx 1$ . Note that the corresponding expression

$$n_H^{(v)}(t) \approx 4(1 - t + \dots) \quad (15)$$

for the average number of hydrogen bonds per one molecule coincides with that reconstructed by the behavior of the evaporation heat [30] and agrees well with (13). The temperature dependence  $\tilde{\nu}_H(t, n_H)$  can thus be approximated everywhere on the line of phase coexistence by the formula

$$\tilde{\nu}(t, n_H) \approx \tilde{\nu}_0 \exp(\varepsilon/t) - 4(1 - t) + \dots \quad (16)$$

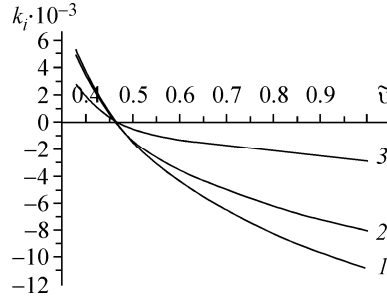
If the number of hydrogen bonds per one molecule in the critical point does not tend to zero, as it follows from (13), the contribution  $\tilde{\nu}_H$  of hydrogen bonds to the kinematic shear viscosity at  $t = 1$  also should be non-zero. In this case, it is useful to represent the temperature dependence  $\tilde{\nu}^{(w)}(t)$  in the form of

$$\tilde{\nu}^{(w)}(t) = (1 - \xi)\tilde{\nu}(t) + \tilde{\nu}_H(t), \quad (17)$$

where  $\xi = \tilde{\nu}_H(1)$ . As above, we approximate  $\tilde{\nu}_H(t)$  by linear dependence (14) that leads to the interrelation equation:  $\xi = -4\kappa(1 - \gamma)$ . Let us find the two remaining constants  $\kappa_1$  and  $\gamma$  by fitting (17) to experimental data in the temperature range of  $T > T_v$ . Thus,

$$\kappa \approx 1.07 \quad \text{and} \quad \gamma \approx 0.98. \quad (18)$$

The relative contribution of hydrogen bonds  $\xi$  to the kinematic shear viscosity of water in the critical point does not exceed  $-0.08$ .



**Fig. 5.** Numerical values of  $k_i$  coefficients,  $i = 1, 2, 3$  as functions of the reduced volume.

## KINEMATIC SHEAR VISCOSITY OF ARGON

The importance of this question for our work is explained by that the kinematic shear viscosity of argon is formed only by translational degrees of freedom. Therefore, a comparison of the behavior of  $\tilde{\nu}^{(w)}(t)$  and  $\tilde{\nu}^{(Ar)}(t)$  on the line of phase coexistence allows a natural separation of contributions of all other components of thermal motion of molecules, first of all, those that are related to hydrogen bonds. The nature of  $\tilde{\nu}^{(Ar)}(t)$  was the subject of a detailed analysis in [26]. Here we limit ourselves only by final results and brief discussion.

It was shown in [26] that in the region of states of liquid argon  $0 < t < 1$  and  $0 < p < 2$ , where  $p = P/P_c$  is the normalized pressure, the behavior of its kinematic shear viscosity on the coexistence line, isochors, and isobars [3, 4, 31, 32] can be described by the expression

$$\tilde{\nu}(\tilde{v}, t) \approx \frac{\zeta_0}{(\tilde{v} - 0.36)^{1/3}} [1 + k_1(\tilde{v})\tau + k_2(\tilde{v})\tau^2 + k_3(\tilde{v})\tau^3 + \dots], \quad (19)$$

where  $\varepsilon_0 \approx 0.68$ ,  $\tau = t - 1$ , and values of coefficients  $k_i$  are specified in Fig. 5. We see that the kinematic viscosity values of argon are mainly determined by its reduced volume, more precisely, by its excess above own molecular volume  $v_0 \approx 0.36$ . This fact was noted in [33] long ago.

Let us discuss now the character of the dependence  $\tilde{\nu}^{(Ar)}$  on  $\tilde{v}$  and  $t$  from the viewpoint of dimensional reasons. The kinematic shear viscosity has the dimension  $[\nu] = L^2/T$ . The ratio  $l^2/\tau_s$  is the simplest combination of molecular parameters with this dimension, where  $l \sim n^{1/3}$  is the average interparticle distance,  $n$  is the density of the system,  $\tau_s \sim l/v_T$  is the characteristic time of soft collisions [34],  $v_T$  is the thermal velocity of a molecule. However, with increasing density the combination  $l^2/\tau_s \sim v_T/n^{1/3}$  decreases, which is characteristic of the self-diffusion coefficient that has the same dimension.

The simplest combination that decreases with increasing density is  $v_T^2 \tau_v \frac{\sigma}{l}$ . Here  $\sigma$  is the molecular diameter, and  $\tau_v$  is the characteristic time of molecular vibrations ( $\tau_v \sim \sigma(m/\varepsilon)^{1/2}$ , where  $\varepsilon$  is the interaction energy as a part of the intermolecular potential. Note that due to the transition from  $\sigma$  and  $\tau_v$  to  $l$  and  $\tau_s$  we have excluded the undesirable dependence on density and temperature. Thus, we obtain

$$\nu(v, t) \sim \frac{T_c \sigma^2}{(m\varepsilon)^{1/2} v_c^{1/3}} \frac{t}{\tilde{v}^{1/3}}. \quad (20)$$

Since  $\varepsilon \sim T_c$  and  $v_c \sim \frac{2\pi}{3} \sigma^3$  as supposed in the theory of van der Waals equation of state [17], then

$$\nu(v_c, t = 1) \sim \sigma v_T(T_c) \sim 10^{-3} \text{ cm}^2/\text{s}$$

which coincides by the order of magnitude with the experimental value of the kinematic shear viscosity in the critical point.

Using the same arguments about the role of own volume as in deriving the van der Waals equation of state, equation (20) can be generalized as follows:

$$v(v, t) \approx \frac{T_c \sigma^2}{(m\varepsilon)^{1/2} v_c^{1/3}} \frac{t}{(\tilde{v} - \tilde{v}_0)^{1/3}} \Rightarrow \frac{\zeta_0}{(\tilde{v} - \tilde{v}_0)^{1/3}} (1 + f(\tau)). \quad (21)$$

Formula (19) shows that the value of  $v_0 \approx 0.36$  is 1.5 times larger than its value corresponding to van der Waals theory ( $v_0 \approx 0.25$ ). Owing to this fact, the details of the intermolecular potential more substantially affect the equation of state rather than the behavior of the shear viscosity.

## RESULTS AND DISCUSSION

According to the results of our study, the kinematic shear viscosity of water can be described on the liquid-vapor coexistence line and in its vicinity by the formula of the form

$$\tilde{v}^{(w)}(\tilde{v}, t) \approx \frac{\zeta_0}{(\tilde{v} - \tilde{v}_0)^{1/3}} \mu(\tau, \tilde{v}) + \tilde{v}_0 \exp(\varepsilon/t) - 4\kappa(1 - \gamma t) + \dots, \quad (22)$$

where  $\mu(\tau, \tilde{v}) = [1 + k_1(\tilde{v})\tau + k_2(\tilde{v})\tau^2 + k_3(\tilde{v})\tau^3 + \dots]$ . Parameters  $\zeta_0$ ,  $\tilde{v}_0$ , and  $k_i$  ( $i = 1, 2, 3$ ) have the same values as in argon. The optimal agreement of (22) with experimental data takes place at

$$\tilde{v}_0 = 1.29 \cdot 10^{-4}, \varepsilon = 4.705, \kappa = 1.07 \text{ and } \gamma = 0.98.$$

Hydrogen bonding significantly affects the behavior of the viscosity of liquid water in the whole temperature range of its existence. In supercooled water their contribution to  $\tilde{v}(\tilde{v}, t)$  is dominant and can be described by the second item in (22) with good accuracy. This contribution prevails also for normal water in a temperature interval of  $273 \leq T < T_H$ . The developed network of hydrogen bonds with a distinct global structure specifies thermal motion of molecules in this region of states.

At  $T > T_H$ , the viscosity of water is determined by the first and third items in (22) that reflect the effect of the finite molecular volume and hydrogen bonds. Fig. 2a shows that the role of the first item is slightly more important. In this temperature region, and actually starting from the melting point, the temperature dependence of viscosity is not exponential, i.e. is not of activation type. Here hydrogen bonds do not form a network with a well-pronounced spatial structure, but associating molecules in clusters, they significantly affect the momentum transfer in the system.

It is very important that the number of hydrogen bonds per one molecule  $n_H^{(v)}(t) \approx 4(1 - t + \dots)$  obtained from the analysis of the kinematic shear viscosity is rather close to the values that follow from the analysis of density [21], heat capacity [22], and evaporation heat [30]. The values of  $n_H(t)$  obtained in computer experiments [35-37] are larger, which, in our opinion, is caused by a substantial dependence of  $n_H(t)$  values on the hydrogen bond determination (see [36]).

The obtained results, of course, have to be supplemented with a qualitative model that explains how hydrogen bonding affects momentum transfer in a system and the formation of viscosity therein.

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## REFERENCES

1. F. Franks (ed.), *Water: A Comprehensive Treatise*, Plenum, New York (1972).
2. R. C. West (ed.), *CRS Handbook of Chemistry and Physics: a Ready-Reference Book of Chemical and Physical Data*, 67th ed. Boca Raton: CRS Press (1996).
3. *TPP Program* ("Thermophysical Properties of Water and Water Vapor," <http://www.prowas3.narod.ru>).
4. Data from NIST Standard Reference Database **69**, June 2005 Release: NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/fluid/>).



5. N. B. Vargaftik, *Handbook on Thermophysical Properties of Gases and Liquids* [in Russian], Nauka, Moscow (1972); N. B. Vargaftik, *Handbook on Thermophysical Properties of Gases and Liquids* [in Russian], Energoatomizdat, Moscow (1990).
6. T. V. Lokotosh, S. Magazu, G. Maisano, and N. P. Malomuzh, *Phys. Rev.*, **62E**, 3572-3580 (2000).
7. T. Litovitz, and K. Davis, in: *Physical Acoustics. Principles and Methods*, W. P. Mason (ed.), Vol. IIA, Properties of Gases, Liquids and Solutions, Academic Press, New York (1965).
8. I. G. Mikhailov, V. A. Solov'ev, and Yu. P. Syrnikov, *Fundamentals of Molecular Acoustics* [in Russian], Nauka, Moscow (1964).
9. H. Eyring, *J. Chem. Phys.*, **4**, 283-291 (1936).
10. Ya. I. Frenkel, *Kinetic Theory of Liquids* [in Russian], Nauka, Leningrad (1975).
11. N. P. Malomuzh and I. Z. Fisher, *FZhS*, **1**, 34-39 (1973).
12. I. V. Blazhnov, N. P. Malomuzh, and S. V. Lishchuk, *J. Chem. Phys.*, **121**, 6435-6443 (2004).
13. I. V. Blazhnov, S. Magazu, G. Maisano, et al., *Phys. Rev.*, **73E**, No. 3, 031 (201-208) (2006).
14. L. A. Bulavin, N. P. Malomuzh, and K. S. Shakun, *UJP*, **50**, 653-658 (2005).
15. M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* [in Russian], Nauka, Moscow (1987).
16. A. Z. Patashinskii and V. L. Pokrovskii, *Fluctuation Theory of Phase Transitions* [in Russian], Nauka, Moscow (1982).
17. L. D. Landau and E. M. Lifshits, *Statistical Physics*. [in Russian], part 1, Nauka, Moscow (1976).
18. L. A. Bulavin, N. P. Malomuzh, and K. N. Pankratov, *J. Struct. Chem.*, **47**, No. 1, 48-55 (2006).
19. L. A. Bulavin, N. P. Malomuzh, and K. N. Pankratov, *ibid.*, Supplement, S50-S60.
20. M. F. Chaplin, *Water Structure and Behavior* (<http://www.lsbu.ac.uk/water/index.html>).
21. T. V. Lokotosh, N. P. Malomuzh, and V. L. Zakharchenko, *J. Struct. Chem.*, **44**, No. 6, 1001-1010 (2003).
22. Yu. V. Lisichkin, A. G. Novikov, and N. K. Fomichev, *Zh. Fiz. Khim.*, **63**, 833-835 (1989).
23. A. Rahman, *Phys. Rev.*, **136A**, 405-412 (1964); *J. Chem. Phys.*, **45**, 2585-2592 (1966).
24. M. A. van der Hoef and D. Frenkel, *Phys. Rev. Lett.*, **66**, 1591-1594 (1991).
25. W. Doster, S. Cusack, and W. Petry, *Nature*, **337**, 754-756 (1989).
26. N. P. Malomuzh, A. V. Oleynik, O. P. Rudenko, and A. M. Khlopov, *UJP*, in press (2007).
27. D. Éizenberg and W. Kautzman, *Structure and Properties of Water* [in Russian], Gidrometeoizdat, Leningrad (1975).
28. Yu. I. Naberukhin, V. A. Luchnikov, G. G. Malenkov, and E. A. Zheligovskaya, *J. Struct. Chem.*, **38**, No. 3, 593-600 (1997).
29. D. Paschek and A. A. Geiger, *J. Phys. Chem.*, **103B**, 4139-4146 (1999).
30. N. P. Malomuzh and A. V. Oleynik, *UJP*, in press (2007).
31. V. P. Slyusar, N. S. Rudenko, and V. M. Tret'yakov, *UFZh*, **17**, No. 8, 1257-1263 (1972).
32. B. A. Younglove and H. J. M. Hanley, *J. Phys. Chem. Ref. Data*, **15**, No. 4, 1323-1337 (1986).
33. A. Batchiski, *Z. Phys. Chem.*, **84**, 643-706 (1913).
34. V. Yu. Bardic, N. P. Malomuzh, and V. M. Sysoev, *JML*, **120**, 27-30 (2005).
35. Y. Kataoka, H. Hamada, S. Nose, and T. J. Yamamoto, *Chem. Phys.*, **77**, 5699-5706 (1982).
36. G. G. Malenkov and D. L. Tytik, *Dynamics of Networks of Hydrogen Bonds in Liquid Water By Computer Experiment*. (in: *Method of Molecular Dynamics in Physical Chemistry*) [in Russian], Nauka, Moscow (1996) pp. 204-233.
37. G. G. Malenkov, *J. Struct. Chem.*, **47**, Supplement, S1-S31 (2006).