PHYSICAL REVIEW E VOLUME 62, NUMBER 3 SEPTEMBER 2000

Nature of self-diffusion and viscosity in supercooled liquid water

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(Received 5 January 1999)

The nature of the simplest transport processes in water, namely, self-diffusion and shear viscosity, is analyzed on the basis of a version of the microinhomogeneous structure model. The study predicts the existence of locally ordered groups of molecules, taking into account considerations of acoustic properties, light scattering, and computer simulation findings. In particular, it is shown that the anomalous properties of water in supercooled states are mainly connected with the existence of quasiordered regions, which we call clusters. Furthermore, the spatial sizes and evolution times of the crystal-like clusters, as well as the temperature dependence of their fraction volume, are established. Special invariants of the characteristic parameters of molecular motion are pointed out. Finally, it is shown that the self-diffusion in supercooled water is caused by the processes of formation and destruction of crystal-like clusters, while the processes of internal partial reconstruction give the main contribution to the shear viscosity coefficient.

PACS number(s): 61.20.−p, 66.30.Fq, 62.10.+s, 62.20.−x

I. INTRODUCTION

In comparison with the majority of one-component liquids, water shows many unusual properties in its normal and supercooled states. The connection of these water anomalies with subsystems of strong H bonds becomes evident by comparing water with its homologue H_2S. It is sufficient to note here that, for example, the melting temperatures of H_2S and H_2O differ from each other by about 100 K, and that, in certain temperature ranges, the temperature expansion coefficients and the temperature derivatives of thermoconductivity even have different signs, etc. [1,2].

To explain the observed peculiarities of water properties, different approaches have been proposed [3–15]. Many efforts have been made toward a more adequate account of the crystal-like structure of water. In [3–6] the existence of finite size microregions with icelike structure and with irregularity in their dispositions was hypothesized. In these publications an important role was attributed to the water molecules that fill the cages of icelike patches. Although this model allowed the authors [3–6] to explain qualitatively the behavior of the thermoconductivity, thermal expansion coefficients, and some other physical quantities, it is not self-consistent: the attempts to reproduce numerically the different thermodynamic characteristics and to furnish reliable values of the key parameters of the model failed. Besides this, ignoring the time evolution of the icelike framework does not allow an adequate description of the viscoelastic properties of water. And what is more, the nature of self-diffusion, as the simplest transport process, remains unclear within this approach.

Another approach to the structure and thermodynamic and kinetic properties of water was developed in [7–15], initiated by H. E. Stanley. According to this approach, the structure of water is inhomogeneous: small ‘‘icebergs’’ of nanosizes are imbedded in a highly connected network. These small compact groups of strongly bonded molecules, forming three or four hydrogen bonds (so called patches) were supposed in [7–9] to be spatially separated from weakly bonded molecules with no or one H bond. General arguments about the appearance of the ordered regions in the continuous H-bond network were given in [7]. On the basis of such a picture the negative sign of the thermal expansion coefficient in the supercooled region and in the normal one near the melting point, the increase of isothermal compressibility κ_T and of heat capacity C_P on cooling, and also the anomalies of other thermodynamic properties of water get a natural and consistent explanation. The estimate of patch size obtained in experiments on x-ray scattering [8] is approximately 8–10 Å.

In [10–15] the details of water microstructure were specified step by step and corresponding mathematical models were formulated. A classification of the supercooled states was proposed. While liquid or amorphous water have never been observed experimentally in the region below the line of homogeneous nucleation $T_H(P)$ down to the line $T_X(P)$ above which amorphous ice crystallizes, numerous computer simulations of noncrystalline water in this region [16–21] have been very successful and give much information for theoretical discussion. There are reasons to assume [12–14] that a new unusual point, close to the critical one, exists in ‘‘no man's land.’’ It is evident that its existence influences the properties of water in the supercooled and even in the normal state.

Unfortunately, many important questions concerning the fine details of patch microstructure and also the specificity of the relaxation processes in a system containing nanosize formations were discussed in [7] only briefly. The time of rotational relaxation τ_R was the only kinetic characteristic studied in [7] within a special one-particle model, for which the applicability should be more carefully motivated. Also, the nature of the surprising empirical relation $D\tau \simeq 2 \times 10^{-16}$ cm^2, D being the diffusion coefficient, holding in a wide temperature interval [23] was not quite understood in [7].

To describe the crossover in the density of states $\rho(\omega)$ obtained in experiments on depolarized light scattering [24] and also to explain the temperature dependence of the crossover frequency ω_c, a fractal structure of locally ordered microregions of strongly bonded molecules was hypothesized

[24,25]. But, unfortunately, a clear physical idea about the possible nature of the fractal ordering in water has not been presented.

In recent years the properties of water in its supercooled states have been studied in great detail by light scattering [22,24,26,27], x-ray and neutron scattering [28–30], computer simulations [16–21], etc. The results of these experiments testify unambigiously to the existence of several different spatial and time scales in supercooled water structure and dynamics. But no theoretical attempts have been made to classify and explain the whole set of available experimental data.

The present work addresses an investigation of the nature of self-diffusion and viscosity in the supercooled states of water. In Sec. II we deal with the microinhomogeneous structure of water and introduce the concept of a quasiordered cluster characterized by a space-time structural hierarchy. Interpretation of the results obtained in computer and molecular light scattering experiments within this cluster model is carried out in Sec. III. In Secs. IV and V we present an analysis of the mechanisms of self-diffusion and shear viscosity.

II. CLUSTERS AS THE ELEMENTS OF SUBSTRUCTURE

The most important structural element of water in its normal, supercooled, and crystal states is the H bond. The specificity of the latter is connected with the noticeable energy of its formation, its sharply directed character, and strong correlations in the coordination of the relative directions of H bonds formed by one molecule. Linear H bonds have a tetrahedral coordination, i.e., the angles between H bonds are close to those between the lines connecting the center of a tetrahedron with its vertices. Because of these properties, hydrogen bonds strongly influence the local structure, and, as a consequence, the thermodynamic and kinetic properties of water. To reveal the mechanism of this influence the interrelation between the H-bond structure and features of the water molecule must be taken into account.

The simplest and most important characteristic of the H-bond network is the average number of H bonds, ψ, formed by some molecule, $\psi=\langle\psi_i\rangle$. At equilibrium ψ is a function of temperature and pressure only:

$$\psi=\psi(P,T). \tag{1}$$

On increasing the temperature, ψ decreases smoothly from its value $\psi_m=2.6$ at the melting temperature to the value $\psi_b=1.8$ at the boiling temperature [31]. Upon supercooling ψ increases, approaching the value $\psi_h=4$, inherent to ice, crystal or amorphous. While the possible values of ψ_i are not very large, the deviations $\psi_i-\psi$ will be of the same order of magnitude as ψ. They are smaller the greater $\psi(P,T)$ is. All the molecules of the system can be partitioned into three subsets for which $\psi_i>\mathrm{int}[\psi]$, $\psi_i=\mathrm{int}[\psi]$, and $\psi_i<\mathrm{int}[\psi]$, where $\mathrm{int}[\cdots]$ denotes the integer part of a number. Compact groups of molecules of the first or third type will be called clusters.

Clusters essentially influence the properties of a liquid if (1) they have mesoscopic sizes, i.e., each cluster contains not less than 20–30 molecules; (2) their lifetimes are much greater than the typical time scale $\tau\sim l/V_T$, where l is the intermolecular spacing, and V_T the velocity of the thermal motion. The number of molecules forming a cluster (or, in other words, its size $D\simeq 9-10$ Å) as will be shown below, follows from the demand of its stability. The same estimates have been obtained in experiments on x-ray scattering [7] and in computer simulations [18–20]. The fact that the results obtained in different ways are in perfect agreement with each other testifies to the reliability of the cluster size estimate. Further consideration confirms that both the conditions (1) and (2) occur in the supercooled region.

The number of H bonds per molecule is not the only important characteristic of molecular order in the system. To take into account the spatial orientations of the H bonds we must introduce an additional parameter χ, which is defined as

$$\chi(N)=\frac{1}{N}\sum_{i=1}^{N}\Theta_i^2, \tag{2}$$

where the summation is carried out over a compact group of N molecules and

$$\Theta_i=(\vec{n}_1^{(i)}\times\vec{n}_2^{(i)})\cdot(\vec{n}_3^{(i)}\times\vec{n}_4^{(i)})+(\vec{n}_1^{(i)}\times\vec{n}_3^{(i)})\cdot(\vec{n}_2^{(i)}\times\vec{n}_4^{(i)})$$
$$+(\vec{n}_1^{(i)}\times\vec{n}_4^{(i)})\cdot(\vec{n}_2^{(i)}\times\vec{n}_3^{(i)}). \tag{3}$$

$\vec{n}_1^{(i)},\ldots,\vec{n}_4^{(i)}$ are the unit vectors along the lines connecting the oxygen atom of the ith molecule with its two protons and to the two maxima of the effective negative charge density. For hexagonal ice $\chi=0$, since multipliers of the type $(\vec{n}_1^{(i)}\times\vec{n}_2^{(i)})$ and $(\vec{n}_3^{(i)}\times\vec{n}_4^{(i)})$ are orthogonal to each other (we neglect thermal fluctuations). For liquid water the parameter χ can serve as a measure of H-bond bendings. It is naturally to expect that χ has essentially different values for clusters of different types.

Now we want to mention that the time evolution of clusters can be essentially different from the time evolution of the surroundings. In particular, let us consider a cluster of the first type for which $\langle\psi\rangle_c\simeq 4$ and $\chi_c\simeq 0$ (the symbol c indicates that the averaging is carried out over cluster molecules). If the size of such a cluster is large enough, its structure is close to that of hexagonal ice I_h. The main elements of the ice structure, as is well known, are hexagonal rings of H bonds. The hexagonal rings correspond to the most energetically preferable and stable H-bond configuration [32]. As a result, the lifetime of such a cluster, a crystal-like cluster (CLC), should be essentially greater in comparison with the time evolution of the H-bond configurations outside it. In other words, the CLC can be treated as an element of a substructure, which reveals itself as a formation on the supermolecular level.

The minimal size of a CLC is strongly connected to its stability. To provide stability, the CLC must contain several rings of H bonds oriented in different planes. One can verify that this condition is satisfied for clusters with size $r_c\geqslant 2r_h$, r_h being the diameter of the hexagonal ring in ice I_h. Therefore, the minimal size of a long-living crystal-like cluster estimated in such a way is about 10 Å. Experiments [18,19] reveal the existence of qualitative changes in water structure exactly on such space scales. In our opinion, the results of computer simulations [18,19] can be viewed as being in favor of the cluster concept of water structure. It is also reasonable to expect that the average size of a CLC will smoothly increase as the temperature is lowered.

Clusters with binding energy and number of H bonds smaller than their average values will be called gaslike clusters (GLCs). The structure of these clusters, in contrast to that of CLCs, is determined, to a great extent, by bifurcated hydrogen bonds which spoil the tetrahedral nature of the H-bond coordination.

It is important to note that the notion of CLCs does not coincide with that of the nucleus of a new phase. In fact, nuclei of hexagonal ice can form only a subset of CLCs with the mean value $\langle\psi\rangle_c$ close to 4 and the parameter $\langle\chi\rangle_c$ near to zero. The accumulation of structural defects in small clusters is responsible for the growth of the expectation time of the critical nuclei at a particular temperature in comparison with the case of simple liquids.

It is evident that at different values of temperature and pressure the relative role of clusters of the two types is not the same. Near and above the boiling temperature the dominating role is played GLCs. On the contrary, the clusters of crystal-like type determine the peculiarities of water near the melting point and in the supercooled region.

Let ϕ be the relative volume occupied by CLCs. To estimate the magnitude and the temperature dependence of ϕ, the following arguments can be used. The densities of the system inside and outside crystal-like clusters differ noticeably from each other. Therefore, the average density ρ of a system can be approximated by the expression

$$\rho(T)=\langle\rho_{(\mathrm{CLC})}(T)\rangle\phi(T)+\langle\rho_{(out)}\rangle[1-\phi(T)]. \tag{4}$$

The average value of the density $\langle\rho_{(\mathrm{CLC})}\rangle$ inside CLCs can be put with suitable accuracy equal to ρ_{ice} for hexagonal ice. On the other hand, the density $\langle\rho_{(out)}\rangle$ outside CLCs is due to molecules that belong to GLCs and to intercluster boundaries. It can be estimated with the help of extrapolation of the water density $\rho_*\equiv\rho(T_*)$ from a temperature T_* far above the melting point (where water exhibits normal behavior) to supercooled region. Applying linear extrapolation we get

$$\phi(T)=\frac{\rho(T)-\rho_{ext}(T)}{\rho_{ice}(T)-\rho_{ext}(T)}, \tag{5}$$

where

$$\rho_{ext}(T)=\rho_*+(T-T_*)\frac{\partial\rho}{\partial T}\bigg|_{T_*}. \tag{6}$$

For T_* we use the value $T_*=350$ K [the corresponding value $\rho_*\equiv\rho(T_*)=0.954$ g/cm^3 and the temperature expansion coefficient is $(\partial\rho/\partial T)|_{T_*}=-8\times10^{-4}$ g/cm^3 K [33]]. The temperature dependence of ρ_{ice} is also described by a linear extrapolation:

$$\rho_{ice}(T)=\rho_m+(T-T_m)\frac{\partial\rho_{ice}}{\partial T}\bigg|_{T_m}, \tag{7}$$

where T_m is the melting temperature, $\rho_m=0.902$ g/cm^3, and $(\partial\rho_{ice}/\partial T)|_{T_m}=-4\times10^{-4}$ g/cm^3 K [1].

The numerical values of $\phi(T)$ obtained with the help of formula (5) for several temperatures are $\phi(273\text{ K})=0.11$; $\phi(253\text{ K})=0.31$; $\phi(243\text{ K})=0.41$. The estimates [3] of the relative number of molecules that belong to crystal-like frame are essentially greater. So in [3] near the melting point $\phi\simeq0.86$.

The role of the crystal-like structure seems to be especially important at the temperature $T\leqslant T_h$, where T_h is defined by the equation

$$|\Delta\Phi(r_h)|\sim k_BT_h, \tag{8}$$

where $\Delta\Phi(r_h)$ is the volume contribution to the formation energy of an icelike nucleus of size $r\simeq r_h$. The value $\Delta\Phi$ can be estimated by using the formula $\Delta\Phi\sim r_h^3\rho L\tau_m$, where L is the heat of melting and $\tau_M=(T-T_M)/T_M$ [note that we neglect the surface energy in Eq. (8) since it is not connected with structurization effects]. Using Eq. (8) we obtain for τ_M $\tau_M\sim k_BT_M/r_h^3L\rho\simeq(0.01\text{–}0.1)$. The correspoinding value of T_h is $T_h\sim260$ K. In this temperature range the specific volume ϕ occupied by CLCs, becomes essentially different from zero. The lower limiting value of ϕ can also be estimated with the help of nucleation theory. In accordance with [34,35],

$$\phi\geqslant\exp\left(-\frac{4\pi}{3}\frac{r_n^2\sigma}{k_BT}\right), \tag{9}$$

where r_n is the averaged size of the nucleus and σ is the surface tension. Since $r_n\geqslant r_h\sim3$ Å, we obtain $\phi(T)\geqslant\exp[-(T_m/T)(\sigma/\sigma_m)]$, where $\sigma_m\sim10$ ergs/cm^2. The surface tension σ has the same order of magnitude as σ_m [34]. The values of $\phi(T)$ calculated in such a way are consistent with our estimates given above.

Let us consider now the dynamical properties of supercooled water. The slowest evolution process in the system is connected with the largest scale formations in it and thus will be determined by the rebuilding of CLCs. Therefore, the average lifetime τ_c is one of the characteristic times of the system. The destruction of a CLC occurs in several steps due to some sequences of reconstruction of H-bond microconfigurations. These reconstructions, inside the CLC and outside it, are due essentially to the same mechanisms that are responsible for the dielectric properties of water and ice. For this reason we introduce a second characteristic time τ_l, during which the microconfigurations of hydrogen bonds remain practically unchanged. For molecules inside and outside CLCs the time τ_l can be interpreted as a residence time for the molecules. On the time scale τ_l the processes are partially irreversible, while on the time scale τ_c they are completely irreversible. It is natural to expect that τ_l and τ_c satisfy the inequality

$$\tau_c>(\gg)\quad\tau_l>\tau_0,\qquad T<T_*, \tag{10}$$

where $\tau_0\sim a/v_\mathrm{T}$, a being the interparticle spacing and v_T the average velocity of the thermal motion. The inequality (10) is greater the deeper the supercooling is. The ratio τ_c/τ_l depends in the main on the average size of the clusters. As long as this size changes insignificantly, the ratio will be almost constant. For deep supercooling and $T > T_m$ the correlation between τ_l and τ_c is violated.

The times τ_c and τ_l do not represent the full set of characteristic times for water in its supercooled states. First of all, we must consider also the time $\tau_{\rm H}$ during which the H bonds of molecules remain practically invariable. In the whole supercooled temperature range $\tau_H \simeq 0.1$–0.2 ps.

One more characteristic time τ_m is connected with the relaxation of transverse excitations in the system. The specificity of these excitations is caused by the microinhomogeneous structure of water for $|\vec{k}| \sim 1/r_c$ and will be considered in more detail below.

III. TIME EVOLUTION OF THE CURRENT-CURRENT AUTOCORRELATION FUNCTION

The analysis of cluster-formation phenomena in supercooled water and of the corresponding set of characteristic times enables us to make certain predictions about the character of the time evolution of correlation functions for different physical quantities. The simplest, but also the most important, is the current-current correlation function $\langle \vec{J}_{\vec{k}}(t) \vec{J}_{-\vec{k}}(0) \rangle$, where $\vec{J}_{\vec{k}} = (1/\sqrt{N}) \Sigma_{i=1}^{N} \vec{V}_i \exp(i\vec{k} \cdot \vec{r}_i)$. The time evolution of the transverse $\Phi_{\vec{k}}(t)$ and longitudinal $F_{\vec{k}}(t)$ parts of this autocorrelation function is determined by different mechanisms, but both these quantities depend essentially on the value of the wave vector. More precisely, the microinhomogeneity of the supercooled states in water initiates the k dependence of the respective relaxation times for wave vectors $1/r_c \leqslant |\vec{k}| \leqslant 1/a$, where a is the interparticle spacing and r_c is the cluster size.

First of all, we must take into account that the transverse modes are not directly connected with variations of density, the last being dependent mainly on the relative volume of CLCs, ϕ. Therefore the characteristic time τ_c, describing the slowest evolution in the system, will not affect the behavior of $\Phi_{\vec{k}}(t)$. In contrast, the reconstruction of H-bond microconfigurations in the time interval $[\tau_H, \tau_l]$ will influence both the transverse and the longitudinal modes. With the help of the unit vectors $\vec{n}_1, \ldots, \vec{n}_4$ [see Eq. (10)] we can construct the following tensor parameter:

$$\hat{T}^{(2)} = \sum_{i=1}^{N} [(\vec{n}_1^{(i)} + \vec{n}_2^{(i)}) \otimes (\vec{n}_3^{(i)} + \vec{n}_4^{(i)}) + (\vec{n}_1^{(i)} + \vec{n}_3^{(i)}) \otimes (\vec{n}_2^{(i)} + \vec{n}_4^{(i)}) + (\vec{n}_1^{(i)} + \vec{n}_4^{(i)}) \otimes (\vec{n}_3^{(i)} + \vec{n}_2^{(i)})]. \tag{11}$$

Here $\otimes$ designates the direct product of vectors. Tensor $\hat{T}^{(2)}$ appears to be the sum of two irreducible parts: scalar and tensor ones. The tensor part vanishes in the case of tetrahedrally coordinated H bonds. Both parts of $\hat{T}$ change considerably on the time scale τ_l on which H bonds undergo substantial distortions that lead to their rupture and to the formation of new microconfigurations. From here it follows that the time evolution of the transverse part of the current-current autocorrelation function will be determined by the expression

$$\Phi_{\vec{k}}(t) = \Phi\left(\frac{t}{\tau_M(k)}\right), \tag{12}$$

where

$$\tau_M(k) = \tau_M + \tau_t(k). \tag{13}$$

The time τ_M has the same nature and the same order of magnitude as in simple liquids; it tends to the relaxation time $\tau_{\rm H}$ for large values of the wave vector, $|\vec{k}| \geqslant 1/r_h$. The additional term $\tau_t(k)$ is connected with the tensor part of $\hat{T}^{(2)}$.

The longitudinal part of the autocorrelation function $F_k(t)$ should have a more complex structure, because the local density depends both on the volume fraction of CLCs, ϕ, and on the scalar parameters $\chi, \hat{T}^{(2)}_{scal}$. As noted above, both these have an identical time behavior. Thus, $F_{\vec{k}}(t)$ is expected to depend at least on two characteristic times of different physical nature. In the simplest case,

$$F_{\vec{k}} \simeq F_1\left(\frac{t}{\tau_1}\right) + F_2\left(\frac{t}{\tau_2}\right). \tag{14}$$

Of the two relaxation times τ_1, τ_2 only the first one is connected with the oscillation motion of molecules, and must have a strong spatial dispersion:

$$\tau_1 = \begin{cases} \tau_{\rm H} & \text{if } |\vec{k}| \simeq 1/r_h \\ \tau_l & \text{if } 0 < |\vec{k}| < 1/r_h . \end{cases} \tag{15}$$

The value of the second relaxation time appears to be close to τ_c for all values of $|\vec{k}|$,

$$\tau_2(\vec{k}) = \tau_c + \gamma_2(k), \quad \gamma_2 \ll \tau_c . \tag{16}$$

The weak k dependence of τ_2 is caused by the mutual influence of the relaxation process and acoustic wave spreading.

On the basis of our approach let us discuss the results of a detailed quantitative analysis of the current-current autocorrelation function for the supercooled states of water, performed in [18,19] by molecular dynamics (MD) simulations. The different transverse and longitudinal contributions to this autocorrelation function were approximated by simple exponents. It was shown that the transverse part of the autocorrelation function can be approximated with sufficient accuracy by one exponent with k-dependent relaxation time. The dependence of the latter on wave vector is significant only for $|\vec{k}| \geqslant 0.1$ Å^{-1}, which is in good agreement with the estimations of the smallest size of the CLC. The comparison of the expected and observed values of relaxation times also supports our assumptions.

For the description of the longitudinal component of the current-current autocorrelation function the authors [19] considered two exponents with relaxation times $\tau_1(\vec{k})$ and $\tau_2(\vec{k})$ which differ in order of magnitude and also in their k dependence. The order of magnitude and the position of the spatial dispersion region allow us to identify the smaller time τ_1 with that described by Eq. (15). The strong temperature dependence of $\tau_1(\vec{k})$ is an additional argument in favor of such an assumption. The spatial dispersion of the second relaxation time is weak. On lowering the temperature from the

TABLE I. The characteristic times τ_c and τ_l, as well as their ratio τ_c/τ_l at different temperatures, according to [16].

T (K)	284	258	238	224	213	209	206
τ_l (ps)	1.4	3.7	12	24	86	147	500
τ_c (ps)	8.5	21.6	74.5	243	1220	2980	7500
$\frac{\tau_c}{\tau_1}$	6.1	5.8	6.1	10.1	14.2	20.7	15.3

melting point down to the spinodal (more specifically, the characteristic temperature that in the majority of work is interpreted as a point on the spinodal), τ_2 changes by several orders of magnitude. These properties of the time τ_2 suggest identifying it with the mean lifetime of a CLC.

The experimental data reported in [16] can be used for an independent accurate determination of the residence time τ_l of a molecule. In fact, in the cited work in addition to the current-current autocorrelation function, the time dependences of the mean-square displacement of the molecules $\langle \Delta \vec{r}^2(t) \rangle$ and the non-Gaussian parameter $\alpha_2(t) = 5\langle \delta \vec{r}^4(t) \rangle / 3(\langle \delta \vec{r}^2 \rangle^2) - 1$ were carefully studied. Since in the time interval $(0,\tau_{\mathrm{H}})$ the motion of a molecule is quasidetermined and at $t > (\gg)\ \tau_c$ it has a simple diffusional nature, it is natural to expect that the function $\alpha_2(t)$ will reach its maximum value at $t \simeq \tau_l$. In other words, at $t \sim \tau_l$, the features of irreversibility become noticeable. The formula

$$\alpha_2(t) = \alpha_2\left(\frac{t}{\tau_l}\right), \qquad \tau_{\mathrm{H}} \leqslant t_l \leqslant \tau_c, \tag{17}$$

which follows for reasons of dimensionality, fits the experimental data [16] with good accuracy. It is necessary to note that $\alpha_2(t)$ reaches its maximum value exactly at $t = \tau_l$.

The values of τ_l, and also the values of τ_c, the last being identified by us with the relaxation time τ_2 of the longitudinal component of the current-current autocorrelation function, taken from [16], are given in Table I. It is worth noting that the ratio τ_c/τ_l remains nearly constant within a large enough temperature interval, including the supercooled region.

The results of computer simulations [21] can also be considered as confirmation of the proposed picture. The thermal motion of one water molecule and also the time behavior of the interparticle spacing between two molecules that were nearest neighbors at $t=0$ have been studied in [21]. The following characteristic possibilities were investigated: two molecules belong at $t=0$ to groups of (1) hydrogen-bonded (HB) molecules and (2) not-H-bonded (NB) ones. It was shown that the mobility of the NB molecules at the early stages of motion is much greater in comparison with that of the HB molecules. But for the time $t \geqslant t_m$ a complete loss of the memory effects is observed. The value of t_m is close to the lifetime of the CLCs: $t_m \simeq 20$ ps at $T = 245$ K [21], $\tau_c(245\ \mathrm{K}) \simeq 30$–$40$ ps (see Table I). To reflect more strongly the difference in the relative thermal motion in the pairs of HB and NB molecules, it is expedient to consider the difference in the mean-square interparticle spacings for HB and NB molecules,

$$S(t) \equiv \langle \Delta \vec{r}^{\,2}_{12}(t) \rangle_{\mathrm{HB}} - \langle \Delta \vec{r}^{\,2}_{12}(t) \rangle_{\mathrm{NB}},$$

where $\Delta \vec{r}_{12}(t) = \vec{r}_{12}(t) - \vec{r}_{12}(0)$ is the change in the relative distance between two molecules that were nearest neighbors at $t=0$ and $\langle \cdots \rangle_{\mathrm{HB}}$ and $\langle \cdots \rangle_{\mathrm{NB}}$ denote the averaging over the subsets of HB and NB molecules. This function allows us to give a precise description of the memory effects as well as to characterize the processes of microconfiguration rebuilding. The value $S(t)$ reaches its maximum at a moment t_l that is 4–5 times smaller than t_m. So again we meet with the manifestation of at least two different time scales describing the molecular processes in water.

Important information on relaxational processes in water can be obtained by using light and neutron scattering, etc. The frequency dispersion of the longitudinal sound velocity and absorption coefficient in supercooled water have been carefully investigated in experiments on polarized Brillouin light scattering [27]. It was shown that the dispersion curves for hypersonic velocity and absorption coefficient can be approximated with good accuracy by one-Lorenzian functions. Calculations of the structural relaxational time τ_v have been made for the cases of two limiting assumptions: (1) the shear relaxation time τ_s is considerably smaller than τ_v ($\tau_s \ll \tau_v$); (2) τ_s and τ_v are equal ($\tau_s = \tau_v$). The values of τ_v obtained in these two cases differ by a factor of 1.5 and are smaller than those obtained in computer experiments [16] (by about three times). Here it is worth noting, that direct comparison of the results obtained in experiments and computer simulations is not always correct because of the strong dependence of MD simulation results on the chosen potential. But what is more important is that the temperature dependence of τ_v falls off from the Arrhenius one approximately at the same temperature at which the ratio τ_c/τ_l begins to grow rapidly. This fact finds a simple explanation within our representation: the value of the activation energy, as well as the ratio τ_c/τ_l, remains almost constant until the cluster average size changes significantly (see Table I).

A more detailed analysis of the time dependences of the mean-square displacements of molecules obtained in [16] for different temperatures allows us to point out the invariants

$$\langle \Delta \vec{r}^2(\tau_{\mathrm{H}}(T)) \rangle \simeq I_1 \simeq 0.3\ \text{Å}^2,$$

$$\langle \Delta \vec{r}^2(\tau_l(T)) \rangle \simeq I_2 \simeq 0.8\ \text{Å}^2,$$

$$\langle \Delta \vec{r}^2(\tau_c(T)) \rangle \simeq I_3 \simeq 8\ \text{Å}^2$$

in the whole temperature interval of the supercooled states. Note that in the same temperature interval the values of the relaxation time τ_c, self-diffusion coefficient, and viscosity change by more than three orders of magnitude (see Table I).

The above relations can be considered as independent principles for determination of the characteristic times τ_{H}, τ_l, and τ_c. Thus, the value $\sqrt{0.3\ \text{Å}^2} \simeq 0.5$ Å has the meaning of the mean-square amplitude of translational oscillations of water molecules in the vicinity of the temporary quasi-equilibrium positions. Another value is $\sqrt{0.8\ \text{Å}^2} \simeq 0.9$ Å; it is close to the well-known value of the maximum deformation of a linear H bond (usually, one speaks about H-bond formation if the O-O distance is in the interval 2.6–3.4 Å.

TABLE II. The values of the displacement $\sqrt{\langle a^2\rangle}$ of the water molecule calculated with the help of the formula (18) at different temperatures. The self-diffusion coefficient D and τ_c are taken from [16] (see also Table I).

T (K)	284	258	238	224	213	209	206
D (10^{-5} cm^2/s)	1.3 ± 0.1	5.2×10^{-1}	1.4×10^{-1}	4.4×10^{-2}	1.1×10^{-2}	5×10^{-3}	1.8×10^{-3}
$\sqrt{\langle a^2\rangle}$ Å	2.58	2.59	2.51	2.53	2.83	3.01	2.85

Larger deformations lead to the rupture of H bonds. And, finally, $\sqrt{8\ \text{Å}^2}\simeq 2.75$ Å is nothing but the mean distance between the molecules.

Taking these results as a basis, we pass to a detailed analysis of the self-diffusion process and viscosity in supercooled water.

IV. SELF-DIFFUSION PROCESS IN SUPERCOOLED WATER

Cluster formation by molecules in supercooled water imposes essential constraints on their thermal motion. Due to the H-bond network, a molecule that belongs to the CLCs can perform mainly vibrational motion. Rebuilding of the H-bond network, taking place at $t\simeq\tau_l$, is accompanied by small displacements of some molecules inside the cluster, which are strongly connected with each other. Therefore, the elementary diffusion act will be connected with the destruction of the cluster as a whole. This corresponds to the radical rebuilding of the H-bond configuration inside the cluster. The typical displacement of the molecule can be identified with the interparticle spacing $a_0\simeq n^{-1/3}$, where n is the number of particles per unit volume.

The contribution of nonclustered molecules can be ignored. This is because the motion of nonclustered molecules that are inside crystal-like clusters (cluster defects) and those forming intercluster boundaries is restricted by clusters. As a result, the self-diffusion coefficient of water in the supercooled state can be approximated by the formula

$$D_s=\frac{\langle a^2\rangle}{6\tau_c}, \tag{18}$$

where $\langle a^2\rangle$ is expected to be approximately equal to $a_0^2=n^{-2/3}$. The numerical values of $\sqrt{\langle a^2\rangle}$ calculated on the basis of data on D_s and τ_c taken from [16] are collected in Table II.

The almost constant values of $\sqrt{\langle a^2\rangle}$ in the temperature range investigated, in which the parameters τ_c and D_s vary by a factor of 10^3, is a very convincing argument in favor of the proposed representation. From this point of view, the origin of formula (18) becomes quite clear. It is interesting that the numerical value of the combination $\sqrt{6D_s\tau}$ again appears to be approximately equal to the interparticle spacing (2.8 Å).

Usually, D is expected to be in inverse proportion to the shear viscosity and the size of a particle, which follows from dimensionality arguments. In particular, such a dependence is inherent in Einstein's formula

$$D=\frac{k_BT}{6\pi\eta r_M}, \tag{19}$$

where r_M is the radius of the particle. Rewriting Eq. (18) in the form of Eq. (19), we get the following estimate for the effective (hydrodynamic) radius r_* of a molecule:

$$r_*=\frac{k_BT\tau_c}{\pi\langle a^2\rangle\eta}. \tag{20}$$

It is not difficult to check that the numerical value of r_* is almost independent of temperature and is close to 1 Å for the temperatures accessible in experiments ($t>-25\,°\text{C}$) [1,36]. Such a magnitude of r_* reflects the inadequacy of the assumptions used in deriving Einstein's formula. Indeed, the Fokker-Planck equation for the one-particle distribution function is not applicable for systems with strong H bonds. Moreover, due to strong binary correlations, there is a considerable difference between the real and the mean forces applied to the molecule. The formula

$$\vec{V}_i=\mu(-\vec{\nabla}_iU), \tag{21}$$

where V is the drift velocity of the particle in the potential field U (μ is the mobility), playing the key role in deriving Eq. (19), should be corrected by the factor $\tilde{g}$:

$$\vec{V}_i=\mu\tilde{g}(-\vec{\nabla}_iU), \tag{22}$$

which is analogous with the Kirkwood factor in the theory of dielectric permeability of water [37]. In accordance with this, one can propose the following modification for D:

$$D=\frac{k_BT\tilde{g}}{6\pi\eta r_M}. \tag{23}$$

The experimental data on the self-diffusion coefficient [16] and shear viscosity [1,36] at low temperatures can be correctly reproduced by the formula (23) with $r_M=1.45$ Å and $\tilde{g}\approx0.75$.

The mechanism of self-diffusion described above is characteristic for supercooled water. Nevertheless, it makes sense to estimate the value and the temperature dependence of the so called collective part of the diffusion coefficient. This contribution is caused by collective long-living hydrodynamic modes and was considered for the first time by Fisher [38]. In accordance with [38,39] the velocity $\vec{V}$ of a molecule can be represented as the sum

$$\vec{V}(t)=\vec{V}_r(t)+\vec{V}_c(t), \tag{24}$$

where the first term describes the motion of the molecule with respect to its nearest surroundings and the second the collective drift of the molecular group in the field of thermal hydrodynamic fluctuations. Since $\vec{V}_r$ and $\vec{V}_c$ describe inde-

TABLE III. The effective radius r_{eff} for a Lagrange particle in water, calculated according to Eq. (28), and the parameter $(1-\sigma)$.

T (K)	284	273	263	248
$1-\sigma$ (%)	6.7	4.8	2.2	0.4
r_{eff} (Å)	16.5	22	31.5	74

pendent types of molecular motion, the self-diffusion coefficient should be represented in the form of the sum

$$D=D_r+D_c\,, \tag{25}$$

where

$$D_c=\tfrac{1}{3}\int_0^\infty\langle\vec{V}_c(t)\vec{V}_c(0)\rangle dt. \tag{26}$$

Following the Lagrange approach to the theory of thermal hydrodynamic fluctuations the authors of [39] showed that

$$D_c=\frac{k_BT}{6\pi\nu r_{eff}}, \tag{27}$$

where

$$r_{eff}=\sqrt{\pi}\,\frac{\nu}{c_t}, \tag{28}$$

has the meaning of the hydrodynamic radius of a liquid particle (ν is the kinematic shear viscosity and c_t is the transverse sound velocity). Since the intensity of hydrodynamic fluctuations decreases on lowering the temperature, the ratio D_c/D will diminish too. From this point of view the value

$$\sigma=1-\frac{D_c}{D} \tag{29}$$

can be considered as a dynamical measure of the cooperativity in water. Numerical values of $(1-\sigma)$ and r_{eff} are shown in Table III. From Table III it follows that the role of the collective diffusion in supercooled water remains small up to the melting temperature. At the same time, the relative values of D_c/D for simple liquids near their melting points are not less than 20%. Thus, cluster formation in water leads to a considerable suppression of the fluctuations of hydrodynamic microflows.

V. SHEAR VISCOSITY OF WATER

The relaxation processes associated with the shear viscosity are mainly of the same origin as self-diffusion, so the relation between η and D is described by the formula (19) with satisfactory accuracy. At the same time, it is very important to clarify the role of each relaxation process. For this purpose we will use a method equivalent to the mean-field approximation.

Let the velocity field of the system be given by the formula

$$\vec{u}=\lambda z\vec{i}, \tag{30}$$

where $\vec{i}$ is the unit vector along the X axis. The relative velocity of two nearest molecular layers in accordance with Eq. (30) is given by

$$\Delta\vec{u}=\lambda a\vec{i}, \tag{31}$$

where $a=n^{-1/3}$. In the mean-field approximation this difference in the velocity arises as a result of the action of an average force $\vec{f}$,

$$\Delta\vec{u}=\mu\vec{f}, \tag{32}$$

which is connected with the shear viscosity by the relation

$$\vec{f}=\lambda\,\eta a^2\vec{i}. \tag{33}$$

The mobility of the molecule, μ, can be written with satisfactory accuracy as

$$\mu=\mu_l+\mu_c\,, \tag{34}$$

where the symbols l and c denote the types of relaxation processes. The oscillations of a molecule near a quasiequilibrium position do not lead to the displacement of the molecule, so they do not contribute to its mobility.

It is necessary to note that the representation of the viscosity as a sum of different contributions [Eq. (34)] is possible only in the case when the time and space scales of the corresponding molecular processes are well separated. Since the motion of a molecule at $t\geqslant\tau_c$ is irreversible, we can estimate μ_c by the formula

$$\mu_c=\frac{D}{k_BT},$$

where

$$D=\frac{\langle\Delta\vec{r}^{\,2}(t_c)\rangle}{6\tau_c}. \tag{35}$$

Unfortunately, we cannot use a similar formula for μ_l, since the thermal motion at $t\sim\tau_l$ has essentially collective character and is not fully irreversible. The displacements of molecules involved in the rebuilding of local H-bond configurations on the time scale τ_l are not responsible immediately for the self-diffusion process. At the same time, they provide the effective transport of momentum. The existence of an l mechanism is the characteristic difference between water and simple liquids. To obtain the effective mobility of a molecule in the l process we apply the relation

$$\langle\Delta\vec{r}^{\,2}(\tau_l)\rangle\simeq(\mu_l\tau_l)^2\langle\vec{f}^{\,2}\rangle, \tag{36}$$

where $\langle\vec{f}^{\,2}\rangle$ is the mean-square force acting on a molecule. The magnitude $\langle\vec{f}^{\,2}\rangle$ is determined by the static parameters of water, mainly by the density. Since the value $\langle\Delta\vec{r}^{\,2}(\tau_l)\rangle$ is independent of temperature, we obtain from Eq. (35)

$$\mu_l(T)=\mu_l(T_m)\frac{\tau_l(T_m)}{\tau_l(T)}. \tag{37}$$

Combining Eqs. (34), (35), and (37) we arrive at

$$\eta = \frac{1}{a[\langle \Delta \vec{r}^2(\tau_c)\rangle / 6\pi k_B T \tau_c + \mu_l(T_m)\tau_l(T_m)/\tau_l(T)]}. \tag{38}$$

Thus, the shear viscosity coefficient in Eq. (38) depends on two characteristic times of the system, the third spatial invariant $[\langle \Delta \vec{r}^2(\tau_c)\rangle]$, and the mobility μ_l of the molecule at the melting point. Since the value $\mu_m(T_m)$ remains unknown, the temperature dependence of shear viscosity is not completely described. Taking into account that in a wide temperature interval $\tau_c \simeq 6\tau_l$, we obtain the following relationship:

$$\frac{\eta}{\tau_l} \simeq \text{const.} \tag{39}$$

This relation is confirmed by the experimental data on η [1,36] in the interval $(+25\,°\mathrm{C}, -25\,°\mathrm{C})$. We are not aware of experimental data for lower temperatures. The value of the adjustable parameter $\mu_l(T_m)$ is: $\mu_l(T_m) = 1.5 \times 10^9$ cm/s dyn.

VI. CONCLUSION

The main attention in this paper was devoted to the nature of the simplest transport processes—self-diffusion and viscosity—in supercooled water. The study was carried out on the basis of a cluster representation. After a definition of the cluster, its properties were formulated and the mechanisms of self-diffusion and viscosity proposed. The values of kinetic coefficients obtained agree well with the experimental data. It is necessary to note that we analyze in this paper only the most general properties of crystal-like clusters, as well as their simplest manifestation in the dynamical behavior of water. From this point of view we ignore the detailed structure of the clusters and of surrounding media (gaslike clusters), the character of transient layers between them, the interactions between clusters, etc. The applicability region of the picture developed for molecular motion essentially coincides with the metastable region of the supercooled states of water. Above the melting point the relative volume ϕ occupied by crystal-like clusters becomes small. Thus, clusters in practice do not restrict the spatial displacements of nonclustered molecules. To describe the transport properties in weakly clustered water another approach has to be developed.

Many important problems in the physics of supercooled water still remain unsolved. First of all, it is necessary to construct adequate kinetic equations for the description of the time evolution of crystal-like clusters. Furthermore, the growth of the number of long-lived crystal-like clusters on lowering the temperature leads to the possibility of formation of a percolation cluster. As a consequence, on approaching the spinodal, water can pass into a glasslike state. Such a possibility hads already been discussed in the literature [13]. The proper mathematical models, able to describe the short range correlations in the states of molecules (formation of clusters) and long range correlations between the clusters, will be of great benefit in constructing the equation of state for supercooled water and for water at low temperatures.

We are confident that the representation developed in this paper will allow us to explain the behavior of density, thermal expansion coefficient, and heat capacity, the negative sign of the thermoconductivity coefficient, the anomaly of thermal behavior of the Landau-Placzek ratio, and other peculiarities of water. These questions will be considered in detail in further papers.

ACKNOWLEDGMENTS

We cordially thank Professor S. Bratos, Professor A. K. Lyashchenko, Professor G. Malenkov, Professor Yu. Naberuchin, Professor G. A. Puchkovskaya, Professor H. E. Stanley, Professor J. Teixeira, and Professor B. Veytsman for very fruitful discussions of the results.

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[1] *CRS Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*, 67th ed., edited by R. C. Weast (CRC Press, Boca Raton, 1996).

[2] *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1972).

[3] I.Z. Fisher and I.S. Andrianova, J. Struct. Chem. **7**, 326 (1966).

[4] I.S. Andrianova and I.Z. Fisher, J. Struct. Chem. **9**, 517 (1968).

[5] I.Z. Fisher, J. Struct. Chem. **3**, 313 (1962).

[6] I.S. Andrianova, O.Ya. Samoilov, I.Z. Fisher, J. Struct. Chem. **8**, 736 (1967).

[7] H.E. Stanley and J. Teixeira, J. Chem. Phys. **73**, 3404 (1980).

[8] L. Bosio, J. Teixeira, and H.E. Stanley, Phys. Rev. Lett. **46**, 597 (1981).

[9] A. Geiger and H.E. Stanley, Phys. Rev. Lett. **49**, 1749 (1982).

[10] S. Sastry, F. Sciortino, and H.E. Stanley, J. Chem. Phys. **98**, 9863 (1993).

[11] S. Sastry, F. Sciortino, H.E. Stanley, S.S. Borick, and P.G. Debenedetti, in *Proceedings of 12th International Conference on the Properties of Water and Steam*, edited by H.J. White, J.V. Sengers, D.B. Neumann, and J.C. Bellows (Begell House, New York, 1995), p. 363.

[12] F. Sciortino, U. Essmann, P.H. Poole, and H.E. Stanley, in *Proceedings of 12th International Conference on the Properties of Water and Steam* (Ref. [11]), 355.

[13] S.T. Harrington, R. Zhang, P.H. Poole, F. Sciortino, and H.E. Stanley, Phys. Rev. Lett. **78**, 2409 (1997).

[14] O. Mishima and H.E. Stanley, Nature (London) **396**, 329 (1998).

[15] H.E. Stanley, S.V. Buldyrev, M. Canpolat, M. Meyer, O. Mishima, M.R. Sadr-Lahijany, A. Scala, and F.W. Starr, Physica A **257**, 213 (1998).

[16] P. Gallo, F. Sciortino, P. Tartaglia, and S.-H. Chen, Phys. Rev. Lett. **76**, 2730 (1996).

[17] M. Diraison, J.-Cl. Leicknam, G. Tarjus, and S. Bratos, Phys. Rev. E **50**, 2689 (1994).

[18] F. Sciortino and S. Sastry, J. Chem. Phys. **100**, 3881 (1994).

[19] U. Balucani, G. Ruocco, M. Sampoli, A. Torcini, and R. Vallauri, Nuovo Cimento D **16**, 817 (1994).

[20] I. Ohmine, H. Tonaka, and P.G. Wolynes, J. Chem. Phys. **89**, 5852 (1988).

[21] A. De Santis, A. Ercoli, and D. Rocca, Phys. Rev. E **57**, 4871 (1998).

[22] F. Aliotta, C. Vasi, G. Maisano, D. Majolino, F. Mallamace, and P. Migliardo, J. Chem. Phys. **84**, 4731 (1986).

[23] H. Pruppacher, J. Chem. Phys. **56**, 101 (1972).

[24] D. Majolino, F. Mallamace, P. Migliardo, F. Aliotta, N. Micali, and C. Vasi, Phys. Rev. E **47**, 2669 (1993).

[25] J. Teixeira, Atti Accad. Pericolanti Cl. Sci. Fis. Mat. Nat. **71**, 187 (1995).

[26] G. Maisano, D. Majolino, F. Mallamace, P. Migliardo, F. Aliotta, and C. Vasi, Mol. Phys. **57**, 1083 (1986).

[27] S. Magazu, G. Maisano, D. Majolino, F. Mallamace, P. Migliardo, F. Aliotta, and C. Vasi, J. Phys. Chem. **93**, 942 (1989).

[28] S.-H.Chen, *Quasielastic and Inelastic Neutron Scattering and Molecular Dynamics of Water at Supercooled Temperatures* (Kluwer Academic Publishers, Dordrecht, 1991), p. 289.

[29] M.-C. Bellissent-Funel, J. Teixeira, L. Bosio, and J.C. Dore, J. Phys.: Condens. Matter **1**, 7123 (1989).

[30] F.J. Bermejo, M. Alvarez, S.M. Bennington, and R. Vallauri, Phys. Rev. E **51**, 2250 (1995).

[31] Yu.V. Lisichkin, A.G. Novikov, and N.K. Fomichev, Russ. J. Phys. Chem. **59**, 987 (1985).

[32] A. Vegiri and S.C. Farantos, J. Chem. Phys. **98**, 4059 (1993).

[33] R.J. Speedy, J. Chem. Phys. **91**, 3354 (1987).

[34] J. Frenkel, *Kinetic Theory of Liquids* (Dover Publ., New York, 1955).

[35] E.F. Abraham, *Homogeneous Nucleation Theory* (Academic Press, New York, 1974).

[36] C.M. Sorensen, in *Proceedings of 12th International Conference on the Properties of Water and Steam* (Ref. [11]), p. 308.

[37] J.G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).

[38] I.Z. Fisher, Zh. Éksp. Teor. Fiz. **61**, 1647 (1972) [Sov. Phys. JETP **34**, 878 (1972)].

[39] N.P. Malomuzh and I.Z. Fisher, J. Struct. Chem. **14**, 1302 (1973).