Coherent Molecular Motion in Aquatic Environment. Extraction of Correlation from Noise

G. G. Malenkov[a], Yu. I. Naberukhin[b], and V. P. Voloshin[b]

[a] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
e-mail: egor38@mail.ru*

[b] *Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences,
ul. Institutskaya 3, Novosibirsk, 630090 Russia
e-mail: naber@kinetics.nsc.ru, voloshin@kinetics.nsc.ru*

Abstract—Molecular dynamics simulation of liquid water and system "argon–thin water film" has been performed. In was shown that time dependence of distances between oxygen atoms of water molecules, connected by hydrogen bonds, looks like random noise and these molecules are doomed to move concertedly. The average distance between the argon atoms dissolved in water is retained for some time, so the argon atoms included in the hydrogen bond networks, but not capable to participate in hydrogen bonds are involved in concerted motions. The problem of revealing the correlations in the motion of molecules and atoms is discussed.

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The concept of liquid water as continuous endless network of hydrogen bonds that bound its molecules was apparently for the first time expressed in the well known article of J. Bernal and R. Fowler published in 1933 [1]. At that time the idea of water as the mixture of molecular associates called at that time hydrols was dominating. The revolutionary idea of Bernal and Fowler was not immediately accepted by scientific society although its most advanced representatives appreciated this idea. "Ocean is one big molecule" – this phrase Langmuir [2] liked to repeat. The idea of water as a mixture of hydrols is not outdated till nowadays but now hydrols are called clusters. But most of researches studying water systems agree with the fact that the structure of liquid water is the continuous three-dimensional network of hydrogen bonds. Moreover, nowadays it is normal to mark out liquids where molecules are united into a spacial network to a special class which is different from usual associated liquids. This point of view was expressed and proved by M.N. Rodnikova ([3], see also [4]). There is a question: why liquid water existing in continuous associated condition has such low viscosity (~1 mPa s at room temperature) and self-diffusion coefficient is so big (~3×10^{-5} cm^2 s^{-1})? The answer is very simple: because the lifetime of a hydrogen bond is not long, molecules continuously change hydrogen bond partners.

All works of computer simulation of structural condition of liquid water, as well as the results presented in this article confirm the existence of continuous three-dimensional network of hydrogen bonds in water and nicely describe the experimental data of self-diffusion coefficient in a wide range of temperatures [5, 6] (Fig. 1).

Computer water flows as good as real despite the presence of structural network. The distribution of lifetime of hydrogen bonds in water is very wide [9, 10]. It is shown [11, 12] that long living hydrogen bonds form groups creating branching three dimensional clusters (Fig. 2).

During coloring of the network of hydrogen bonds by their lifetime it was found that the life time conformable to percolation threshold is close to average time of life of bonds.
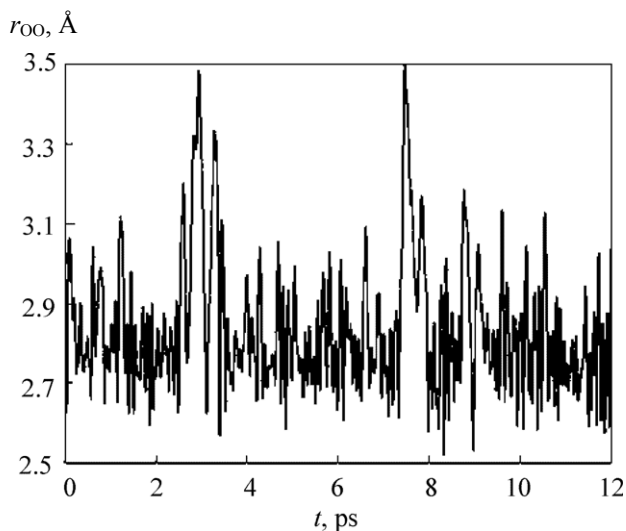
Motion of molecules connected by hydrogen bonds cannot be incoherent. If these bonds live quite long time then the same long living molecules realize their coherent motion. Clusters formed due to long living
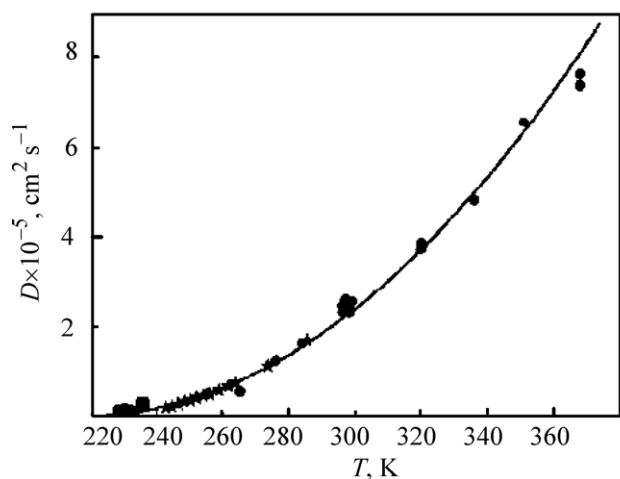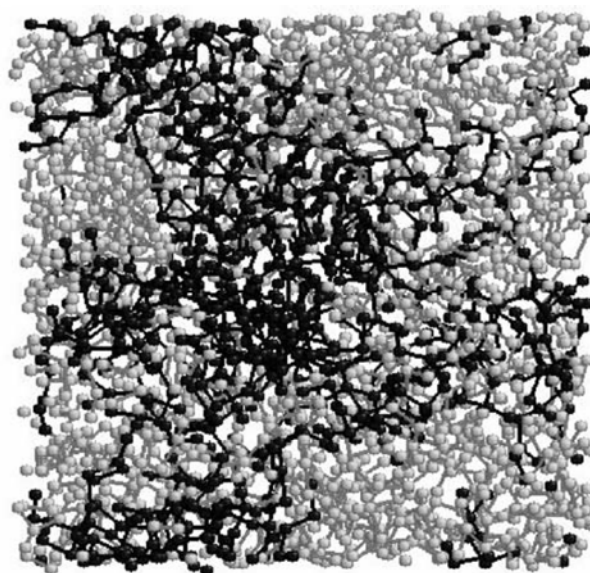
Fig. 1. Dependence of self-diffusion coefficient of water molecules on temperature at atmospheric pressure. The line is extrapolation of the most reliable experimental data [7], stars are experimental data for supercooled water [8], dark circles are self-diffusion coefficients determined in numerical experiment.

Fig. 2. Coloring of network of hydrogen bonds in supercooled water by the time of their life. The virtual temperature is 261 K. 3456 molecules in cubic cell with periodical boundary conditions. Bonds living more than 19 ps are colored. Percolation threshold of given model is 18 ps. Consequently, at such coloring the endless cluster does not exist. The biggest cluster containing 885 molecules is shown.

bonds renew all the time: some molecules leave bonds, others join them.

All numerical experiments with results which are discussed in this article relate to the system containing 3456 molecules of water in independent periodical cell (in case of modeling of modification of ice III the

Fig. 3. The change of the distance between molecules of liquid water in time. During 12 ps molecules were bound by hydrogen bond.

independent cell contained 768 molecules). If it is not specially expressed the virtual temperature of modeled system is equal to room temperature (297–300 K). The procedure of making calculations is described in many of our works (see, for example, [5, 6]).

The Phenomenology of Molecular Motion in Aquatic Environment

Dynamics of Water Molecules Bonded by Hydrogen Bonds

Time dependence of the distance between molecules of liquid water (atoms of oxygen) bonded by hydrogen bond looks like chaotic signal or noise (Fig. 3). Many examples of such signals it is possible to find in works of S.F. Timashev who names dependences of that kind as Flicker Noise (see, for example, [13]).

We will not discuss here the problems of criteria of hydrogen bonds on the basis of which it is possible to determine these bonds in computer models of water (this problem is considered in [5, 9, 11, 14]); we will take into account the fact that if during some time the distance between atoms of oxygen r_{OO} is within 2.5–3.6 Å and its average value is constant and close to

(a) (b)
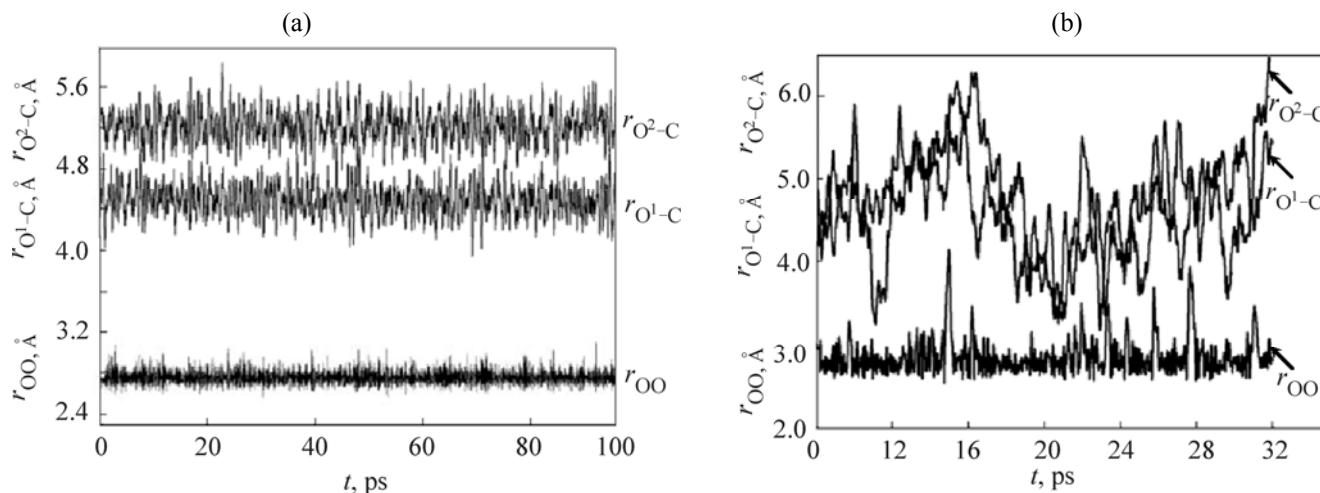
Fig. 4. Dynamics of molecules of water in (a) ice III and (b) in liquid water. Virtual temperature, K: (a) 130 and (b) is 297; $r_{O^1–C}$, $r_{O^2–C}$, r_{OO} is the distance from atoms of oxygen to the origin and the distance between atoms of oxygen; molecules of liquid water move, in the same time the hydrogen bond between them remains.

2.8 Å then there is a hydrogen bond between molecules of water. Molecules of water bound by hydrogen bonds, obviously, move in space. If in solid systems their average position stays in the same place (Fig. 4a) then in liquid it migrates (Figs. 4b and 5).

The migration of molecules bound by hydrogen bond is often equated to collective diffusion or collective component of self-diffusion (the discussion of problems connected with collective diffusion see, for instance, in [15]). But the main contribution in the self-diffusion is connected with jumps of molecules accompanied with the break of hydrogen bonds. But this is not absolutely correct [11, 12]. The molecules bound with hydrogen bond can make combined jumps without the break of bonds (Fig. 5); at the same time the other bonds where these molecules participate can, obviously, break.

As it was mentioned above, molecules bound by hydrogen bond should move coherently. We use term "coherent" which does not have numerical value, and we are not trying to estimate the degree of this coherence. Such coherence is reflected by the dependences which are shown in Figs. 4b and 5 and which show at the same time the distances between atoms of oxygen and their motion from initial position (see Fig. 5) or distances from the origin (see Fig. 4b).

Coherent Motion of Molecules which are not Bound by Hydrogen Bonds

As molecules bound by long-living hydrogen bonds form big clusters, it is possible to expect that the

coherence will be observed also in the motion of distant from each other molecules. In Fig. 6 there are several examples of time dependences $r_{OO}(t)$. As it is seen in Fig. 6 during some time the distance between molecules of water fluctuates not only close to values corresponding to the length of hydrogen bond but also significantly exceeding the length of bonds; in the same time molecules during that time move, and their motion cannot be incoherent. It is noticeable that
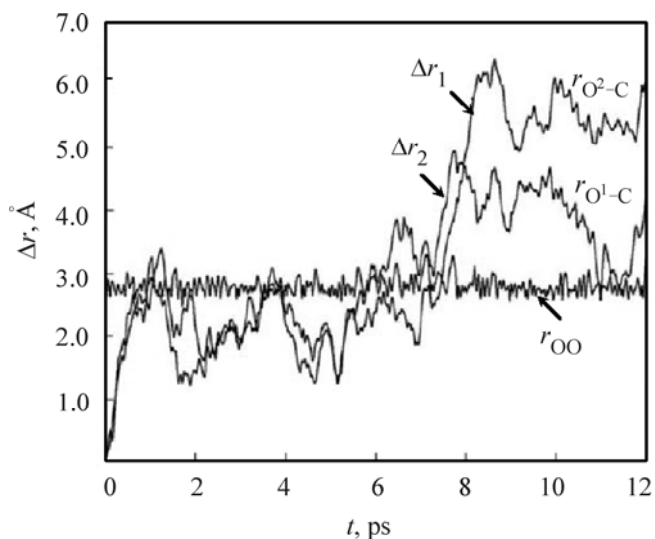
Fig. 5. The movement of two molecules of water Δr from their location of the initial configuration and the distance between them. The hydrogen bond existed between molecules for 12 ps. Approximately on 7th picosecond both molecules made combined jump but hydrogen bond did not break.
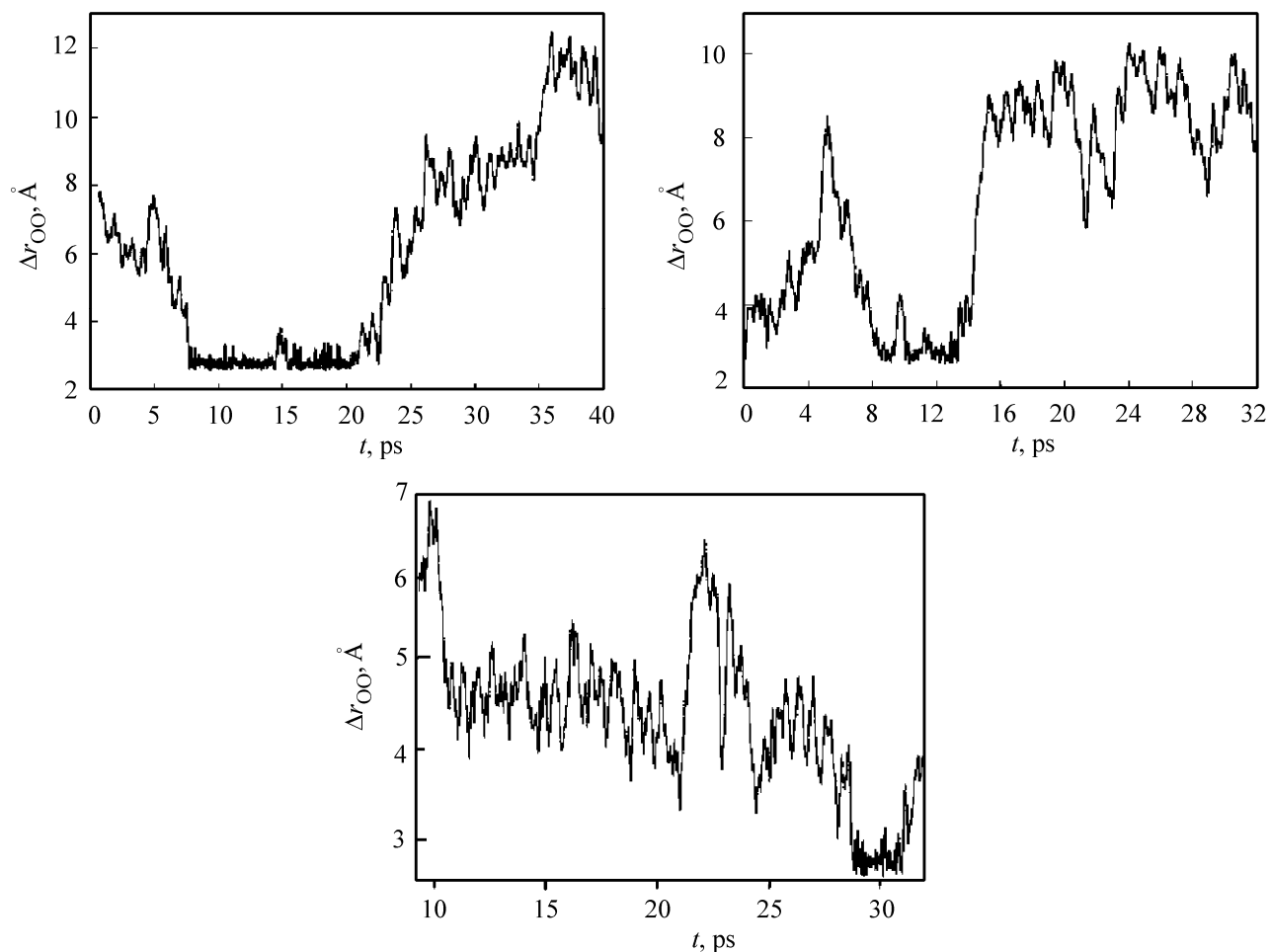
Fig. 6. Examples of dependences r_{OO} on time for liquid water (at 297 K).

amplitudes of fluctuation of values r_{OO} for distant from each other molecules are bigger than for molecules which are bound by hydrogen bond.

Obviously, parts with approximately the same value r_{OO} can be seen not on each recorded dependence $r_{OO}(t)$. Usually distances r_{OO} grow monotonically. It is necessary to mention that the vibration frequency $r_{OO}(t)$ for molecules which are not connected by a hydrogen bond is approximately four times lower than in case of molecules bound by a hydrogen bond. Frequencies of vibrations can be roughly estimated by the calculation of the number of peaks of this function within certain time interval (for example, 10 ps). We will not discuss here the problems which are connected with frequencies of these vibrations because their periods are too small; we are interested not in the correlation of high frequency vibrations but in the large scale correlation. Let us mention only the fact that appropriate frequencies can be seen in densities of vibration conditions obtained with the use of Fourier

transformation of autocorrelation function of the speed of motion of atoms of oxygen and calculated during the numerical experiment (see, for example [16]). It is a question of translational vibrations with frequencies within 50 and 200 cm^{-1}.

Coherent Motion of Hydrophobic Particles Introduced into the Network of Hydrogen Bonds

During modeling of thin water films in atmosphere of argon it was found that on both time dependences $r_{Ar-Ar}(t)$ and $r_{OO}(t)$ there are areas where the distance between atoms of argon is approximately constant, i.e. r_{Ar-Ar} fluctuates at some average value (Fig. 7).

Due to the fact that the interaction energy of argon atoms is more than 20 times less than energy of hydrogen bond, the only reason which makes atoms of argon to stay on the certain distance from each other is that these atoms are built in into the network of hydrogen bonds in water films. Atoms of argon are
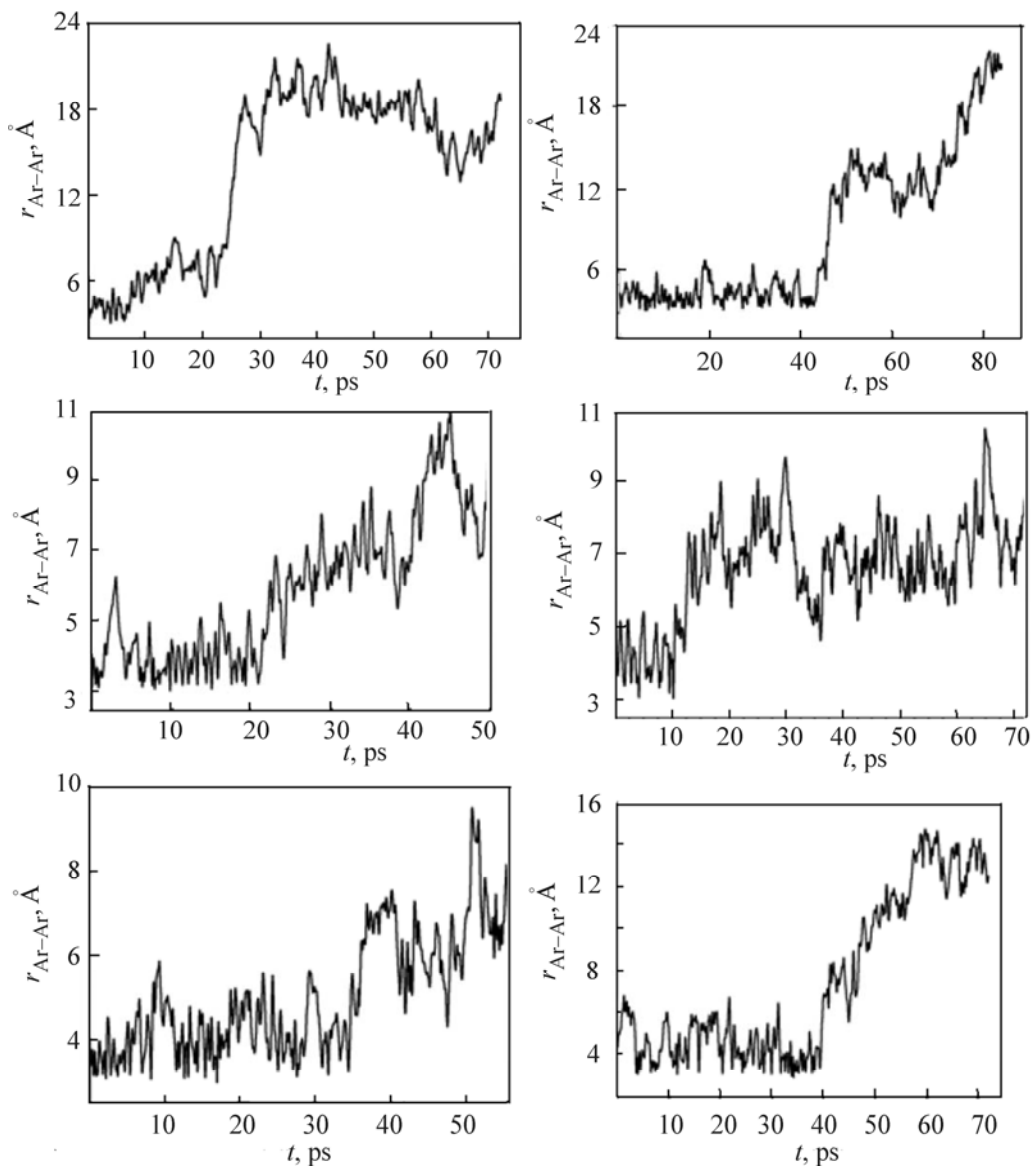
Fig. 7. Examples of time dependences of distances between atoms of argon in water film. Argon atoms are "dissolved" in central areas of the film.

able to occupy empty places of crystal net of hydrogen bonds. Four modifications of argon hydrates are known [17].

Argon hydrate is stable at low pressure; molecules of water create three-dimensional network which consist of voids of two types where atoms of argon can locate. Two atoms of argon can locate in bigger voids. The simulation of the dynamics of this hydrate carried out by us [18] showed that the average distance between atoms of argon is 3.35 Å (see Fig. 8a) and the amplitude of vibration of this distance is strongly dependent on the temperature.

At modeling of the crystalline argon hydrate we did not succeed to observe either the diffusion of molecules of water or atoms of argon. Two atoms of argon located in one cavity of the hydrate move only inside it. They have two favorite positions and often exchange these positions (see Fig. 8b). This motion is not reflected in the function $r_{Ar-Ar}(t)$.

Liquid films of water where atoms of argon were "dissolved" were simulated in our experiments. Molecules of water moved inside the film as intensive (and in surface layers more intensive) as in the volume of water. It is seen in Fig. 8 that the behavior of
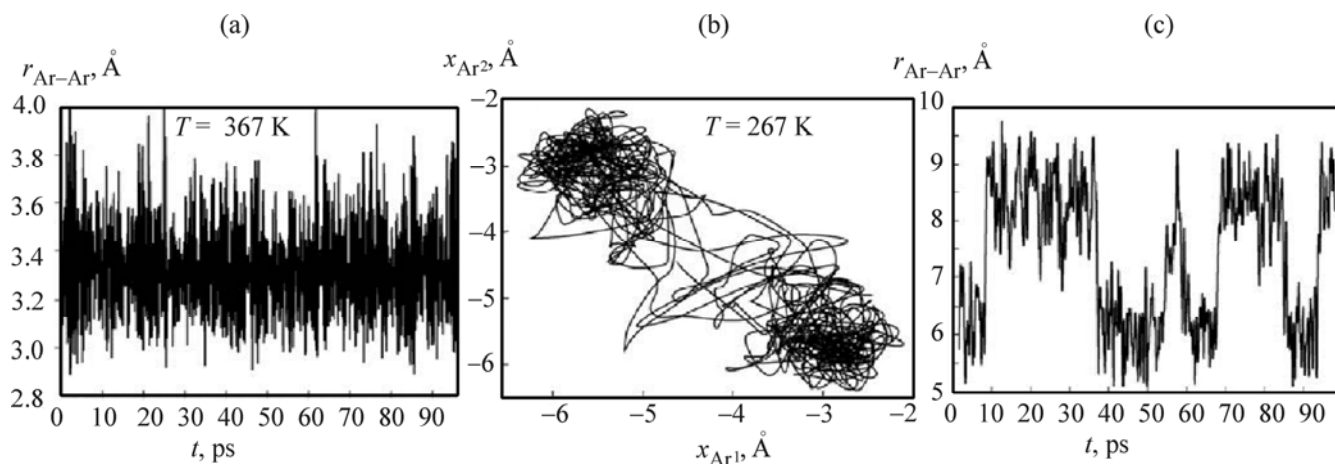
Fig. 8. The dynamics of two atoms of argon in hydrate: (a) is the change of the distance between atoms of argon located in one cavity of the hydrate, in time; (b) is the dependence of coordinate of one atom x_{Ar2} on coordinate of another atom x_{Ar1}. There are "favorite" positions of argon atoms in the cavity of the hydrate and they often exchange these positions: (c) is the change of the distance between two atoms of argon located in neighboring cavities of the hydrate, in time.
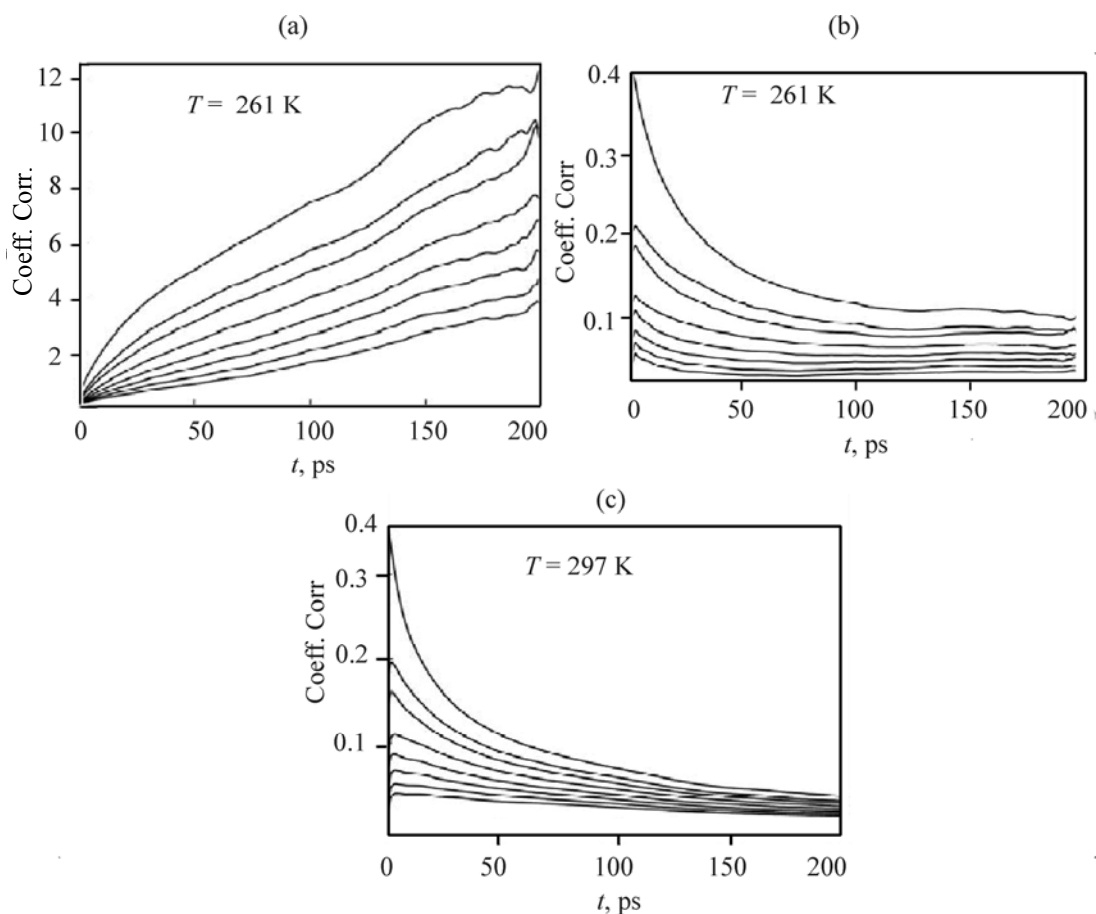
Fig. 9. Correlator of displacement vectors of two molecules of water where initial distance between them is in (a) given limits and (b, c) the change of the correlation coefficient of the displacement of two molecules in time at virtual temperature 261 and 297 K. Curves relate to different initial distances between molecules; top-down, Å: 2.15–3.15; 3.15–4.15; 4.14–5.15; 5.15–6.15; 6.15–7.15; 7.15–8.15; 8.15–9.15; 9.15–10.15.
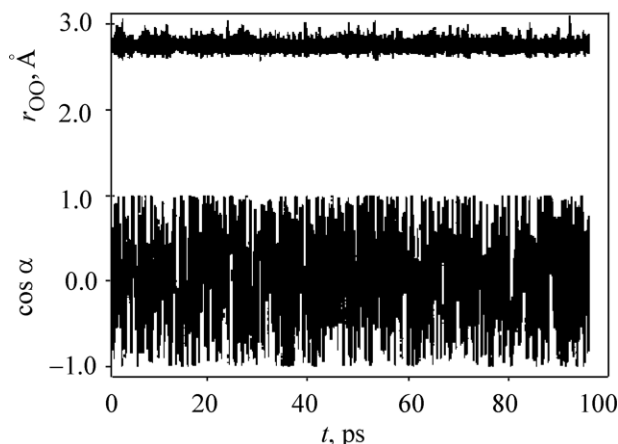
Fig. 10. Time dependences of distances between two molecules of water in ice III and cosine of displacement vectors of these molecules.

function $r_{Ar-Ar}(t)$ is very similar to the behavior of function $r_{OO}(t)$ that describes the dynamics of molecules of water.

Vibration frequencies of distances r_{Ar-Ar} in liquid argon are approximately two times lower than those of argon atoms which are in one big cavity of clathrate crystalline hydrate. But vibration frequencies of distances of atoms r_{Ar-Ar} of argon which are in different cavities of crystalline hydrate (see Fig. 8c) are close to vibration frequencies in case of hydrate in liquid water. Although atoms of argon do not create hydrogen bonds neither with each other nor with molecules of water they being included into the network of hydrogen bonds are involved into coherent motion where molecules of water participate.

Neither atoms of argon nor molecules of water diffuse in argon crystalline hydrate. Hydrogen bonds do not break. The distance between atoms of argon which are in the same or different cavities fluctuate at constant values. The distance between atoms of argon in liquid water also within some time remains constant but at the same time they move together with molecules of water.

### Correlation in Motion of Molecules of Water

As it was said before, molecules of water bound by hydrogen bonds should move coherently. It is even more correct in case of long-lasting bonds. Moreover, it is possible to expect coherence also in motion of molecules distant from each other in clusters because molecules bound by long living bonds unite in extensive clusters. This was confirmed by the
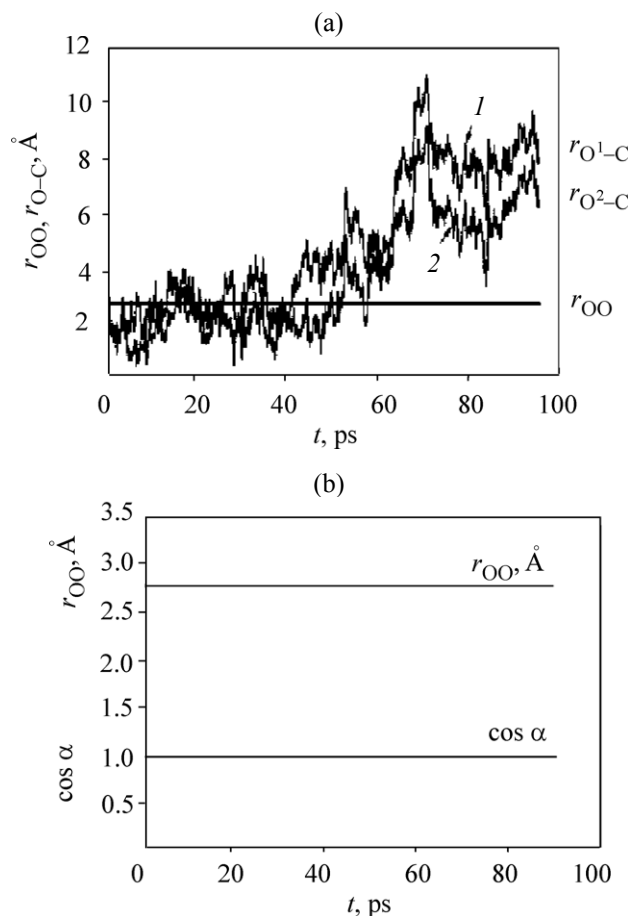
Fig. 11. Time dependences of the distance between atom of oxygen and the origin in liquid water and cosine of displacement vectors of molecules. (a): (*1*) is the real dependence obtained in numerical experiment, (*2*) is the same curve moved to 2.77 Å (average length of hydrogen bond) and (b): distances r_{OO} and cos a do not depend on time.

observation of the behavior of individual molecules. But in order to find correlation in the motion of molecules it is necessary to obtain numerical characteristic of this coherence. The trajectory of the system composed of 3456 molecules of water and length to which these molecules move within several hundreds of picoseconds was recorded. For each configuration of set of molecules pairs of molecules were selected where values r_{OO} are within: 2.15–3.15; 3.15–4.15; 4.14–5.15; 5.15–6.15; 6.15–7.15; 7.15–8.15; 8.15–9.15; 9.15–10.15 Å.

Configurations in 50 ps of virtual time were selected as initial ones. Therefore the amount of configurations used for averaging decreased during the numerical experiment. The behavior of each pair with
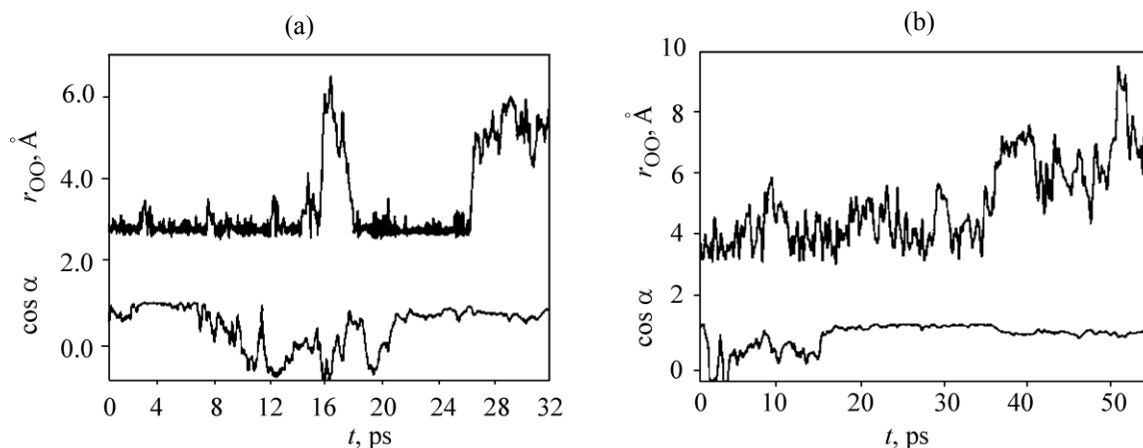
Fig. 12. Time dependencies of cosine of (a) real pairs of molecules of water and (b) pairs of atoms of argon in water film, and distances between these molecules (atoms).

given value r_{OO} was observed during the whole time till the end of numerical experiment. Several functions of the average distance between molecules which changed with the virtual time were calculated.

We make clear once again that at further consideration of the value of the displacement of water molecules, we mean the displacement of atoms of oxygen. The mean-square displacement of one (any) molecule is equal to:

$$<\Delta \mathbf{r^2}>(t) = <[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2>.$$

The function $<\Delta \mathbf{r^2}>(t)$ after short time interval (approximately 2 ps) goes to diffusive asymptote:

$$<\Delta \mathbf{r^2}>(t) = 6Dt,$$

where D is the self-diffusion coefficient of molecules in liquid water.

Exactly in this way the self-diffusion coefficients were determined in numerical experiments; results of these experiments are illustrated in Fig. 1 (dark circles). If we are interested in mean displacement of two molecules where the distance between them stays within certain narrow limits then it is necessary to calculate the value $<[\Delta \mathbf{r}_{ij}(t)]^2>$ which is the mean square of the length of vector of the displacement of two molecules:

$$<[\Delta \mathbf{r}_{ij}(t)]^2> = <[\mathbf{r}_{ij}(t) - \mathbf{r}_{ij}(0)]^2> = <[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2>$$
$$+ <[\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2> - 2\text{Corr} = 2<\Delta \mathbf{r^2}> - 2\text{DP},$$

where DP is the average product of the displacement of pair of atoms where the initial distance between them is within given limits. In fact, DP is the correlator of the displacement vectors of two atoms of oxygen:

$$\text{DP} = \text{Corr} = <[\mathbf{r}_i(t) - \mathbf{r}_i(0)]\cdot[\mathbf{r}_j(t) - \mathbf{r}_j(0)]>.$$

Value $<[\Delta \mathbf{r}_{ij}(t)]^2>$ is different from diffusive asymptote $<[\Delta \mathbf{r}_{ij}(t)]^2>_{as} = 12Dt$ by the correlator Corr. The change of the correlator in time for different initial distances between molecules of water is shown in Fig. 9a. The correlator increases with the time because displacements of molecules increase.

The measure of correlation is the correlation coefficient obtained from correlator by rating on length of displacement vectors:

$$\text{Coef. Corr.} = <[\mathbf{r}_i(t) - \mathbf{r}_i(0)]\cdot[\mathbf{r}_j(t) - \mathbf{r}_j(0)]/|\mathbf{r}_i(t) - \mathbf{r}_i(0)|$$
$$\cdot|\mathbf{r}_j(t) - \mathbf{r}_j(0)|>.$$

The correlator used here is the scalar product of displacement vectors of molecules, and the correlation coefficient is the cosine between vectors.

Initial values of correlation coefficients for molecules where the distance between them in initial configurations are within 2.15–3.15 Å (i.e. there is hydrogen bond between them) for two temperatures 261 and 297 K are almost similar, around 0.4 (Figs. 9b, 9c). The decrease in the correlation coefficient with the time for such pair of molecules is very well described by the sum of two exponents. For $T = 261$ K the typical time of the first exponent is 8 ps, for the second one it is 36 ps. For $T = 297$ K these timings are 13 and 119 ps, respectively. The correlation coefficient decreases with the time due to two reasons: the average distance between molecules increases, the correlation degree decreases with the time. It is not a surprise that correlation decreases more slowly at low temperatures. The average lifetime of the hydrogen bond (and, respectively, the average percolation

threshold at coloring of the network of hydrogen bonds by lifetime) is approximately 20 ps at 261 K and approximately 8 ps at 297 K. These lifetimes do not show up on time dependences of correlation coefficients. No wonder as well that the correlation coefficients also for molecules which are removed on 10 Å from each other are different from zero in small times. We observed coherent moving molecules which were even 20 Å distant from each other. But it is astonishing that correlation coefficients do not turn to zero even after hundreds of picoseconds. The phenomenon of long living correlations in molecules motion should be subjected to further deep investigation.

Cosines of Displacement Vectors of Molecules

Under consideration of time dependences of average cosines of displacement vectors of molecules it was found that these cosines do not turn to zero even after long time intervals.

For better understanding of real meaning of cosines of displacement vectors of molecules in time we will come back to consideration of the behavior of individual molecules. In order to see correlation in displacements of molecules it is necessary not only that the distances between molecules changed only a bit within certain time but also that molecules themselves displaced. As it was noticed above we do not show the interest in possible correlations of high frequency vibrations of molecules in the context of this work. In the numerical experiment carried out by us there was hydrogen bond between molecules of water within all the time of its duration; the distance between molecules fluctuated in narrow limits and on the average remained constant, and the correlation coefficient (cosine of displacement vectors) fluctuated within –1 and 1 on the average round zero, notably 0.067 (Fig. 10). Another situation is illustrated in Fig. 11: the distance r_{OO} is constant and equal to 2.77 Å, cosine of displacement angle is also constant and equal to one.

These are two extreme cases: the distance r_{OO} and position of atoms fluctuate around average position, the average cosine is close to zero; molecules move but the distance between them is definitely constant, cosine is equal to one. Real situations are between these extremes. In Fig. 12 there are examples of time dependences of cosines of displacement vectors of real pairs of molecules of water, and pairs of atoms of argon in water film, as well as changes of distances between atoms.

It follows from the comparison of time dependences of distances between particles and behavior of cosines of their displacement vectors that the search of new approaches to the description of correlation in motion of molecules in water is needed.

REFERENCES

1. Bernal, J.D. and Fowler, R.H., *J. Chem. Phys.*, 1933, vol. 1, pp. 515–548.
2. Gorbunova, K.M., *Private Message*.
3. Rodnikova, M.N., *J. Phys. Chem.*, 1991, vol. 67, no. 2, pp. 275–280.
4. Rodnikova, M.N. and Chumaevskii, N.A., *J. Struct. Chem.*, 2006, pp. 154–160.
5. Malenkov, G.G., *Ibid.*, 2006, vol. 47, pp. 5–35.
6. Malenkov, G.G., Tytik, D.L., and Zheligovskaya, E.A., *J. Mol. Liquids*, 2003, vol. 106, nos. 2–3, pp. 179–198.
7. Holz, M. and Heil, S.R., *Sacco A. Phys. Chem. Chem. Phys.*, 2000, vol. 2, pp. 4740–4742.
8. *Voda i vodnye rastvory pri temperaturakh ne nizhe 0°C* (Water and Water Solutions at Temperature Lower than 0°C), Frank, F., Ed., Kiev: Naukova Dumka, 1985.
9. Malenkov, G.G., Tytik, D.L, Zand heligovskaya, E.A., *J. Mol. Liquids*, 1999, vol. 82, no. 1, pp. 27–38.
10. Voloshin, V.P. and Naberukhin, Yu.I., *J. Struct. Chem.*, 2009, vol. 50, no. 1.
11. Voloshin, V.P., Malenkov, G.G., and Naberukhin, Yu.I., *Ibid.*, 2007, vol. 48, no. 6, pp. 1133–1138.
12. Malenkov, G., Naberukhin, Yu., and Voloshin, V., *Struct. Chem.*, 2009, in press.
13. Timashev, S.F., *Flikker-shumovaya spektroskopiya: informatsiya v khaoticheskikh signalakh* (Flicker Noice Spectroscopy: Information about Chaotic Signals), Moscow: Fizmatlit, 2007.
14. Malenkov, G.G. and Titik, D.L., *Izv. Ross. Akad. Nauk, Ser. Fiz.*, 2000, vol. 64, no. 8, pp. 1469–1474.
15. Bulavin, L.A., Lokotosh, T.V., and Malomuzh, N.P., *J. Liquids*, 2008, vol. 137, no. 1, pp. 1–24.
16. Voloshin, V.P., Zheligovskaya, E.A., Malenkov, G.G., Naberukhin, Yu.I., and Titik, D.L, *Ross. Khim. Zh. (Zh. Ross. Khim. O–va im. Mendeleeva)*, 2001, vol. 45, no. 3, pp. 31–37.
17. Manakov, A.Yu. and Dyadin, Yu.A., *Ibid.*, 2003, vol. 47, no. 3, pp. 28–41.
18. Malenkov, G.G. and Zheligovskaya, E.A., *J. Inclusion Phenomena and Macrocyclic Chem.*, 2004, vol. 48, no. 1, pp. 45–54.