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Collective Effects in Molecular Motions in Liquids

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

[a] Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia
[b] Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia
E-mail: egor38@mail.ru
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Abstract—The collective effects in water were studied by investigating the spatial distribution of long-living hydrogen bonds and revealing correlations in molecular motions. The existence of extended clusters, whose molecules are linked by long-living bonds, suggests the existence of correlations between the motions of its molecules. The mean scalar products of the shift vectors of two molecules were calculated using the narrow ranges (DP) of intermolecular distances in the initial configuration. The average correlation coefficients (the cosines of angles between the shift vectors of two molecules) were also calculated. The DP and cosine values were averaged over all pairs with this intermolecular distance. The DP values increased with time and formed a plateau after a few hundred picoseconds. The plateau was attributed to the existence of molecular vortices that cover large (several nanometers) volumes of the liquid. The conclusion was drawn that hydrophobic species, for example, noble gas atoms incorporated in the water net could be involved in collective motions.

Keywords: water systems, mobility of molecules, collective effects, computer simulation.

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INTRODUCTION

The collective effects in the diffusion motion of molecules in liquids have attracted the attention of researchers. Many publications, however, considered surface diffusion [1–4], colloid systems [5, 6], and polymer solutions [7]. There were no systematic studies of collective effects in the molecular motions in liquids, including water. The possibility of these effects was discussed by Larsson [8], who studied the dynamics of a lead melt by neutron scattering and molecular dynamics. The collective effects in the atomic motion in a model binary alloy were reported in [9], where the average cosines between the shift vectors (more precisely, between the directions of the jumps) of atoms were used. The positions of molecules in their structures obtained by quenching instant configurations separated by several picoseconds were compared and collective (cooperative according to the terminology of [10]) motions of molecules were found. The results are certainly qualitative, but the approach used is interesting. The authors of [11] calculated the interspecies correlation functions, which were also indicative of collective motions.

The collective motions are often discussed in connection with interpretation of the dependence of the half-width of the incoherent peak of quasielastic neutron scattering on the square of the wave vector. This dependence was used to calculate the self-diffusion coefficient [12]. The diffusion coefficient is generally calculated using the Oskotskii model [13] or its vari-

ants. Models of this type suggest that molecules oscillate, for a certain period of time, around the transient equilibrium position and then jump. The equilibrium position itself is slowly shifted. The self-diffusion coefficient calculated using this model contains two contributions: one from jumps and the other from the drift of the transient position. The second term is just the one that was identified with collective diffusion (see, e.g., [14]). However, this is not justified. Earlier, we showed that hydrogen-bonded molecules can jump simultaneously [15, 16] and hence cannot avoid collective motions. The wide distribution of the lifetimes of hydrogen bonds led us to conclude that the presence of molecular groups involved in long-living hydrogen bonds was directly related to the collective motion [17–19] because hydrogen-bonded molecules have to move in a concerted way (i.e., are involved in a collective motion). In this connection we studied the distribution of long-living hydrogen bonds in space [15, 16, 20, 21]. (See the discussion below.)

A very interesting approach to collective motions in liquid was proposed by Fisher [22]. He assumed that the collective components of the velocity of molecular motion in liquids were identical to the velocity of Lagrangian particles. This idea was elaborated by his followers. The modern state of this original approach in the context of the general problem of collective motions is described in review [23], which considered two our approaches to the collective motions (the spa-

tial distribution of long-living hydrogen bonds and correlations in molecular motions).

METHODS

The structure and dynamics of aqueous systems were studied by the molecular dynamics method. The calculations were mostly performed in a microcanonical ensemble (NVE) using a computer program, whose kernel was developed by E.A. Zheligovskaya. The equations of motion were integrated using an algorithm suggested by Grivtsov and Balabaev [24]. The intermolecular interactions were calculated with atom−atom potential functions described in [25]. Details of the calculation procedure were given elsewhere (e.g., [17, 19, 20] and references therein). The program was improved by G.G. Malenkov and V.P. Voloshin. The dynamics of systems of 10000 molecules was modeled with GROMAX software. The intermolecular interactions in these systems were calculated with TIP4P potential functions. The net of hydrogen bonds was constructed and colored according to lifetimes using the special programs developed by Voloshin (see also [15, 16, 20, 21]). The time dependences of the functions considered below and describing the shift of two water molecules were calculated using the computer programs written by V.P. Voloshin. Trajectories of up to 5 ns in length were obtained. Instant configurations were recorded after a certain number of steps (at least 1000). These configurations contained all molecular pairs with intermolecular distances within certain ranges. They were considered initial. The correlation functions at the start of the trajectory, therefore, are more reliable than those at its end.

The water−argon systems were modeled with the programs described in [26]. The argon−argon and argon−water interactions were described in the same publication. The system contained 103 argon atoms and 3353 water molecules in the cubic cell.

Spatial Distribution of Long-Living Hydrogen Bonds in Water

The ideas of percolation theory as applied to description of the net of hydrogen bonds in liquid water [27−30] played a key role in the development of our concept about the structure of this substance [31, 32]. In their pioneering studies [27−30], Stanley, Teixeira, Geiger, and Rahman colored the instant configurations of the net of hydrogen bonds according to pair interaction energies. To study the spatial distribution of long-living bonds it is necessary to know the lifetime of each bond in a given instant configuration, which requires the information about its past and its future fate. Details of these studies are found in [15, 20, 21].

The main characteristic of the net (the three-dimensional net of hydrogen bonds in water in our case) from the viewpoint of percolation theory is the

**Table 1.** Coloring of bonds according to their lifetimes

Characteristic	297 K	261 K
Mean percolation threshold	7.96 ps	20.49 ps
Mean fraction of colored nodes	0.851	0.749
Mean fraction of colored bonds	0.428	0.275
Mean number of finite clusters	312.33	394.24
Mean number of nodes in finite clusters	1377.76	1747.52
Mean number of bonds in finite clusters	1073.90	1366.03
Number of infinite clusters	1	1
Mean number of nodes in infinite clusters	1563.44	842.28
Mean number of bonds in infinite clusters	1637.46	874.74

Note: Those bonds were colored whose lifetime exceeded the time corresponding to the percolation threshold. Mean values of 501 configurations are reported [20]; the cubic periodic cell contains 3456 molecules.

percolation threshold [33, 34]. The bonds that live longer than the time corresponding to the percolation threshold form an infinite cluster. This does not mean that all molecules are part of this infinite cluster. As an example we show the results of a percolation analysis of hydrogen bond nets at 261 (overcooled water) and 297 K (Table 1).

It can be seen that the coloring of the net according to lifetimes equal to or exceeding the percolation threshold time leads to more than 300 clusters of different sizes. The single molecules were neglected. Earlier, we showed [19] that the coloring of bonds according to lifetimes exceeding by far the percolation threshold time led to reasonably large clusters in the net. The composition of these clusters constantly changes because the coloring according to the lifetimes of bonds neglects their formation and cleavage times. The lifetimes of clusters can be characterized by their half-life (the time within which they lose 50% of their molecules). Figure 1 shows the fate of some clusters. The range of half-lives is narrow. It is smaller on average than the percolation threshold time, but close to it or even higher for many clusters.

It was concluded [15] that the coloring of a net according to lifetimes near the percolation threshold gave the results close to the results of random coloring, although the statistics on percolation analysis of the nets colored according to the lifetimes of hydrogen bonds was yet insufficient at that time. This is confirmed by a detailed percolation analysis (Table 2). As mentioned in [15], this indicates that hydrogen bonds do not show cooperativity any longer at times higher than 5 ps; that is, we can evidently create a theory of collective motions that is based on combinatorial analysis alone. The coloring according to life-
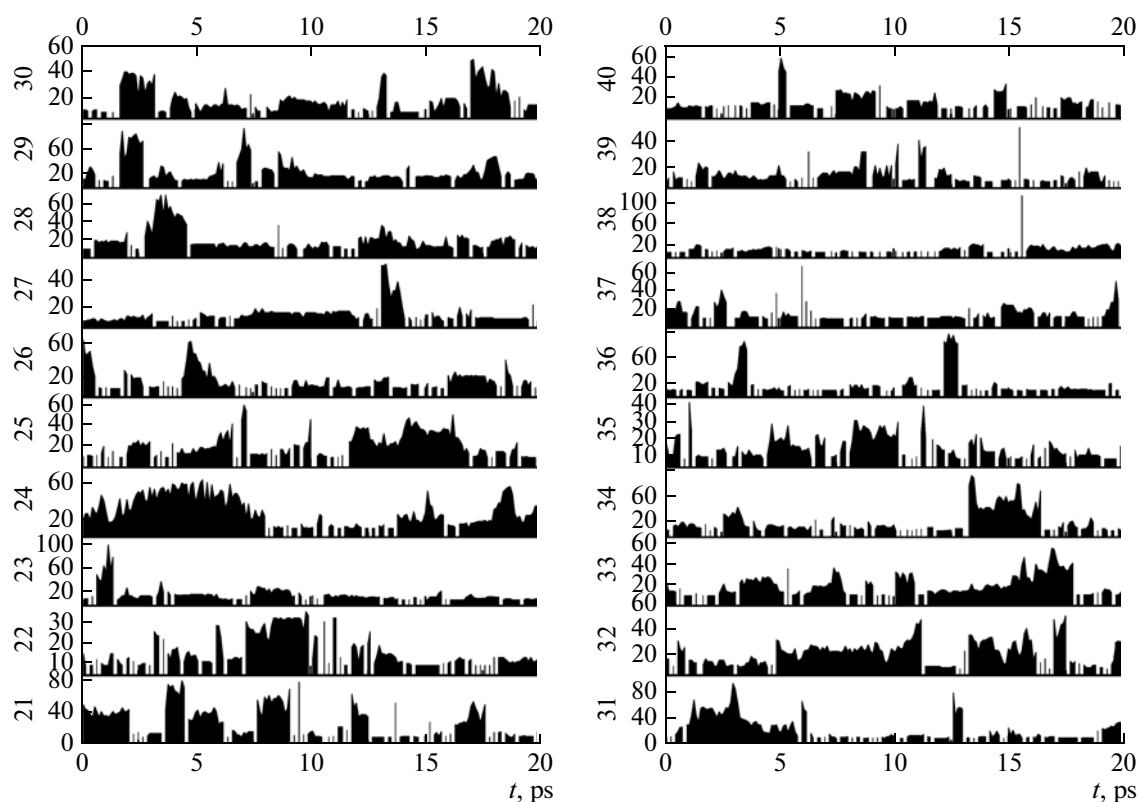
Fig. 1. Time dependences of the number of molecules in clusters (their conventional numbers are given on the ordinate). The region without gaps represents one cluster. The gap denotes the "death" of the given cluster (it lost more than 50% of its molecules). After the gap, the number belongs to another cluster containing other molecules. The temperature was 310 K. The bonds with lifetimes larger than 8.9 ps (above the percolation threshold) were colored.

times, nevertheless, gives percolation thresholds that are steadily smaller than the thresholds obtained in the random coloring of bonds in the same net. This suggests a weak tendency toward unification of long-liv-

Table 2. Percolation coloring of the net of hydrogen bonds according to lifetimes above the percolation threshold (I); random coloring of the same nets (II); $T = 310$ K

Characteristic	I	II
Percolation threshold, ps	7.452 ± 0.264	–
Mean fraction of colored bonds	0.392 ± 0.018	0.418 ± 0.014
Mean number of finite clusters	943 ± 104	798 ± 81
Mean number of nodes in finite clusters	2428 ± 391	2299 ± 393
Mean number of bonds in finite clusters	1498 ± 316	1530 ± 348
Mean number of nodes in infinite clusters	1028 ± 391	1157 ± 393
Mean number of bonds in infinite clusters	1064 ± 498	1202 ± 412

ing bonds with each other (statistically more significant data on percolation analysis of nets are given in [21]). Recall that in the random coloring of bonds in the ideal net of diamond (cubic ice), the percolation threshold is 0.3893 ps [35].

It is noteworthy that the times corresponding to the percolation thresholds are close to the mean lifetimes of hydrogen bonds determined using the dynamic criterion [36, 37] (see [31, 32] for the dynamic criterion). Note also that the times found in the numerical experiment (percolation threshold and average lifetime) are close to the experimental dielectric relaxation times, especially at moderately low temperatures (Table 3).

The percolation characteristics of clusters obtained by coloring hydrogen bonds according to their lifetimes indicate that these are moderately branched clusters containing few rings. This is indicated by the numbers of units (molecules) and bonds in the clusters in which molecules are linked by long-living bonds. These clusters can contain molecules not involved in long-living bonds. They constantly change in composition, losing or acquiring molecules.

Correlations in the Diffusion Motion of Molecules

To reveal correlations in the motions of water molecules, we studied the behavior of two-particle functions that describe the simultaneous motion of two particles lying a certain distance apart from each other at the initial moment. Here, we are not concerned with the rotational motions of molecules and consider below only the shifts of oxygen atoms and the distances (r_{OO}) between them. As is known, the mean square of the shift of oxygen atoms $\langle r^2 \rangle = \langle [r_i(t) - r_i(0)]^2 \rangle$ in the diffusion limit (at $t > 2$ ps) is a linear function of time and is proportional to the diffusion coefficient:

$$\langle r^2 \rangle = 6Dt.$$

Similarly, the mean square of the length of the shift vector of two molecules, the initial distance between which lies in a certain range

$$\langle [\Delta \mathbf{r}_{ij}(t)]^2 \rangle = \langle [\mathbf{r}_{ij}(t) - \mathbf{r}_{ij}(0)]^2 \rangle$$

should tend toward $2\langle r^2 \rangle$:

$$\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle + \langle [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \rangle$$

$$\to 2\langle r^2 \rangle = 12Dt.$$

If the motion of these molecules is correlated, the time dependence of the function $\langle [\Delta \mathbf{r}_{ij}(t)]^2 \rangle$ should differ from $2\langle r^2 \rangle$ by 2DP, where DP is the mean scalar product of the shift vectors of two atoms, the initial distance between which lies in the given range.

DP is actually a correlator of the shift vectors of two oxygen atoms:

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

The correlator increases with time because the molecular displacements increase. The measure of the coherence of the molecular motion can be the correlation coefficient K obtained from the correlator by normalizing it to the values of the shift vectors

$$K = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] / |\mathbf{r}_i(t) - \mathbf{r}_i(0)|$$

$$\cdot |\mathbf{r}_j(t) - \mathbf{r}_j(0)| \rangle.$$

Table 3. Mean lifetimes of hydrogen bonds (t_1), mean lifetimes corresponding to percolation thresholds (t_2), and experimental dielectric relaxation times (t_3), ps

| T, K	t_1	t_2	t_3
250	26.56	33.29	46.5 [38]
261		20.49	27.9 [38]
280	12.03	14.28	13.9 [38]
297	~7 [15]	7.96	8.22*
310	6.84	7.99	7.05*

* Interpolation of the best experimental data [31].

The correlation coefficient equals the mean cosine between the shift vectors of two molecules:

$$K = \cos\alpha.$$

The time dependences of the cosines between the shift vectors of two individual molecules were considered in [16]. These dependences are nontrivial and the fact that the distance between the molecules (r_{OO}) fluctuates around a certain constant value within a certain period of time does not ensure that $\cos\alpha$ approaches unity. Some examples of the dependences $r_{OO}(t)$ and $\cos\alpha(t)$ are shown in Fig. 2.

The preliminary results of calculations of the DP correlators and correlation coefficient $K(\cos\alpha)$ were discussed in [16, 20]. It was shown that DP increased and K decreased with time within the first 200 ps. K did not reach zero even for relatively long initial distances. This means that the correlations in molecular motions remained.

We also studied the behavior of several functions of interatomic distances. The curves that show how the average modulus of variation of the distance between two atoms changes with time for different initial distances intersect in a narrow range of times; i.e., the sequence of these curves changed to the opposite (Fig. 2 in [20]). The region of intersections of the curves is 8−10 ps for $T = 297$ K and 22−26 ps for $T = 261$ K. Note that the indicated times are close to the mean lifetime of the hydrogen bond, the time corre-
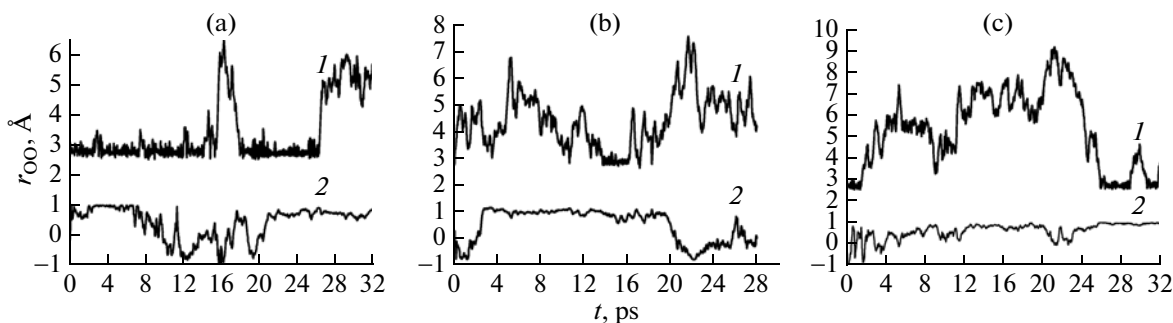

Fig. 2. Time dependences of the distances between the oxygen atoms of two water molecules; (*1*) and (*2*) are the time dependences of the cosine of the angle between their displacement vectors.
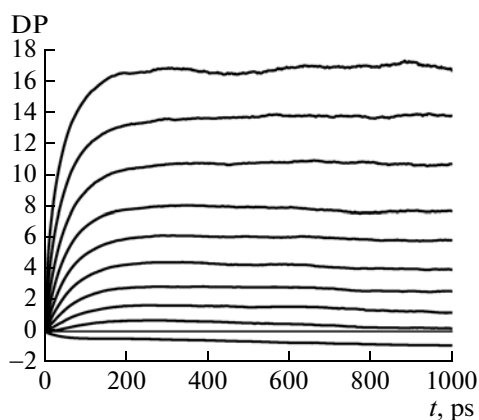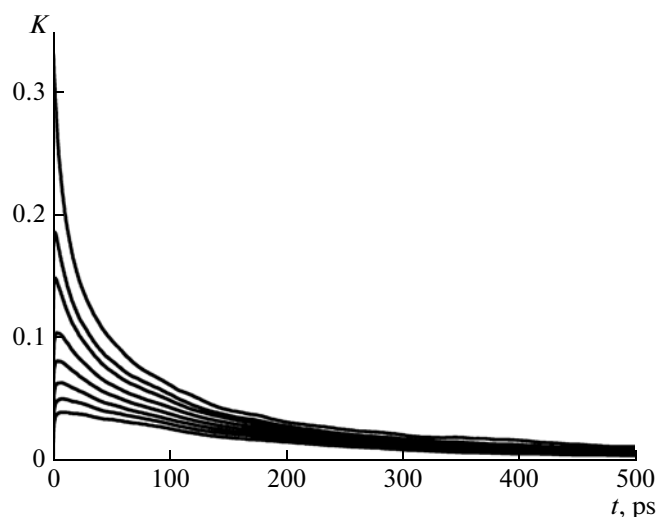
Fig. 3. Time dependences of the DP correlator at 310 K for 3456 molecules in the independent cell and different distances r_{OO} (from top to bottom) are 2–3, 4–5, 6–7, 8–9, 10–11, 12–13, 14–15, 16–17, 18–19, and 20–26 Å.
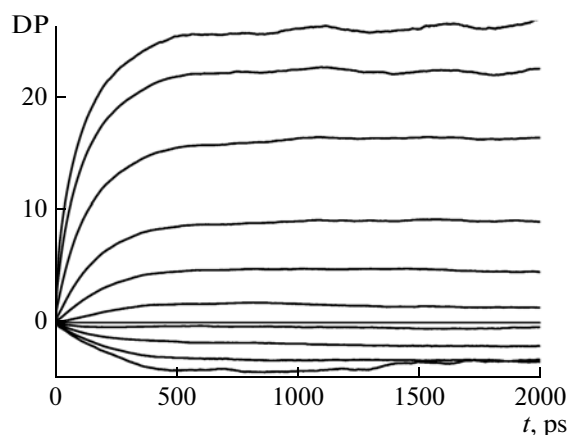
Fig. 4. Time dependences of the DP correlator; $T = 280$ K, 10 000 water molecules in the cell. The distances r_{OO} (from top to bottom) are 2–4, 4–6, 8–10, 14.5–15.5, 1.7–20.3, 24.8–25.2, 29.9–30.1, 34.1–35.1, 39.9–40.1, and 53–55 Å.
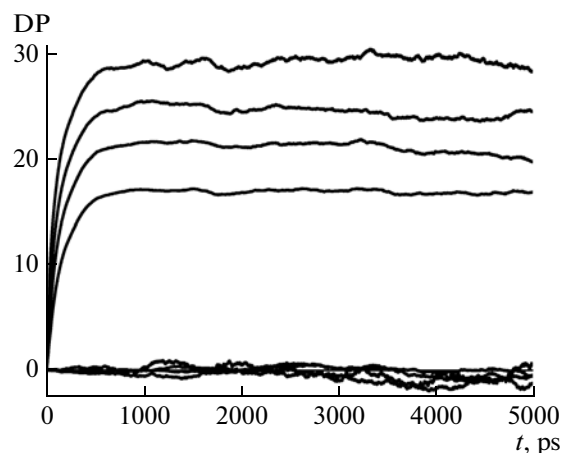
Fig. 5. Time dependences of the DP correlator. The upper four curves are the result of a computer simulation of water dynamics (10 000 molecules in the independent cell) at 280 K. The lower four curves that fluctuate around zero refer to the random wandering of 10000 noninteracting particles. The distances r_{OO} (from top to bottom) are 2–3, 4–5, 6–7, and 9–10 Å.

Fig. 6. Time dependences of the correlation coefficient $K(\langle \cos\alpha \rangle)$; 3456 molecules in the independent cell, $T = 310$ K; the distances r_{OO}^{init} (from top to bottom) are 2–3, 3–4, 4–5, 5–6, 6–7, 7–8, 8–9, and 9–10 Å.

sponding to the percolation threshold, and the experimental dielectric relaxation time. These times evidently play a very important role in the dynamics of liquid water.

A more detailed and thorough study of the behavior of DP(t) led to an astounding result. After growing for hundreds of picoseconds, the function formed a plateau and was almost time-independent till the end of the numerical experiment (the longest experiments lasted for 5 ns of virtual time). This is well illustrated by Figs. 3 and 4.

For random wandering of particles, this function fluctuated around zero, as would be expected for all initial interatomic distances (Fig. 5).

In the model of the real dynamics of water, the higher the initial r_{OO}, the smaller the height of the plateau. Since the shift vector length grows monotonously and the cosine of the angle between them decreases monotonously (Fig. 6), the plateau near DP(t) requires fine mutual compensation of the two effects.

Regarding the dependence of the plateau height on the initial r_{OO} values (r_{OO}^{init}), we noticed that the height became zero at r_{OO}^{init} that was slightly smaller than half of the cubic cell parameter ($a/2$); r_{OO}^{init} was ≈ 21 Å ($a/2 = 23/5$ Å) for a system of 3456 molecules and
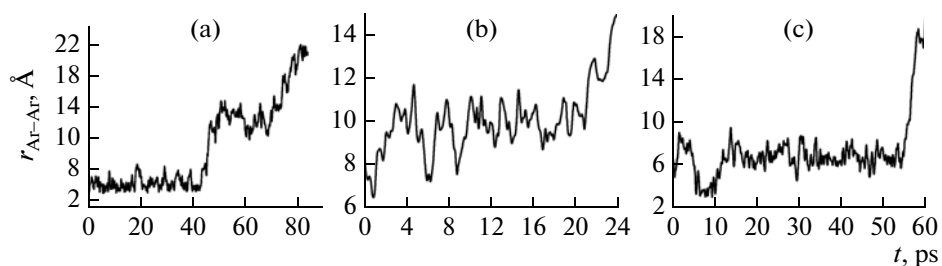
Fig. 7. Time dependences of the distance between argon atoms: (a) the atoms were in close contact until the 45th ps; (b) the interatomic distance fluctuated around 7 Å between the 15th to 55th ps; (c) the distance fluctuated around 9 Å until the 21st ps.
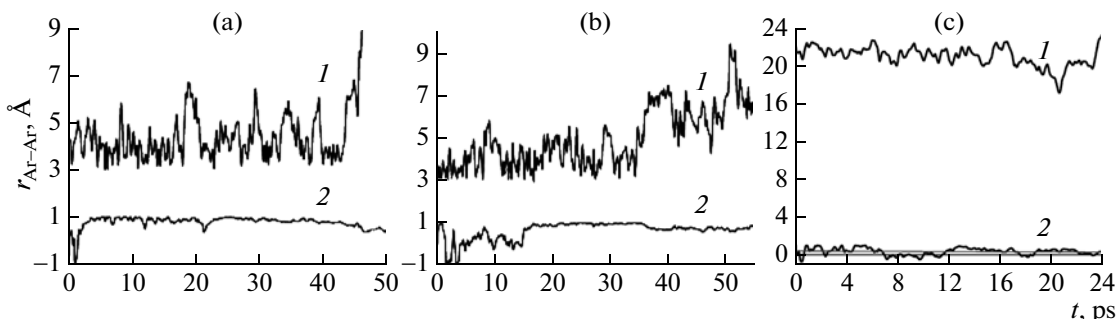
Fig. 8. (*1*) Distances between argon atoms and (*2*) cosine of the angle between them.

≈ 30 Å ($a/2 = 23.44$ Å) for a system of 10 000 molecules. This led us to conclude that the unusual behavior of DP(t) was explained by vortex motions, which covered regions of space larger than the unit cells used in our study. Vortex motions in the model liquid (in a two-dimensional system) were discovered in 1970 by one of the "fathers" of molecular dynamics Alder (Fig. 1 in [39]). They were also observed by Kotelyanskii et al. in a two-dimensional system [40]. In three-dimensional systems, vortices are certainly much more difficult to observe than in two-dimensional ones. The vortex hypothesis relates to the same set of ideas as the concept about the Lagrangian particles of Fischer and his disciples. The idea is that the laws of hydrodynamics work at molecular scales and times.

Collective Motions of Argon Atoms in Aqueous Solutions

We did not perform a percolation analysis of the system of points formed by the atoms of noble gases dissolved in water and did not calculate the mean correlation functions that describe the concerted character of their motion. When incorporated in the net of hydrogen bonds formed by water molecules, however, these atoms should be involved in the collective motions of water molecules. Earlier [16], we presented the plots of the time dependences of the Ar–Ar distance (r_{Ar-Ar}) and the cosine of the angle between the shift vectors in water films. Here we show these dependences for argon and helium atoms in bulk water. Figure 7 presents the time dependences of r_{Ar-Ar}.

The argon atoms can stay near one another for prolonged times ($r_{Ar-Ar} \approx 4$ Å is the analog of the hydrogen bond). The distance between them sometimes fluctuates, for a long time, near a certain value, markedly exceeding the sum of the van der Waals radii of argon. Figure 8 shows several examples of the dependences of $\cos \alpha(t)$ and the corresponding dependences $r_{Ar-Ar}(t)$.

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