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Structural and dynamical heterogeneity of liquids

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Abstract. Brief review of the development of the ideas about the heterogeneity is given. In our works it is meant that structural heterogeneity is the non-uniform space distribution of the particles (atoms or molecules) with similar values of the parameters which characterize their surroundings. Volumes of the Voronoi polyhedra (VVP) built around the particular particle, tetrahedrality index T (for water) and potential energy (E_p) of the molecules or atoms were chosen as such parameters. It was shown that molecules the similar (large or small) values of T , VVP and E_p group together often forming ramifying clusters. Structural heterogeneity – grouping of the atoms with similar values of VVP was found for computer models of liquid argon. Dynamical heterogeneity is manifested in different mobility of the molecules with different values of the parameters which characterize their environment. The less trivial dynamical heterogeneity is connected with the fact that the molecules joint by the long-living hydrogen bonds form the clusters which move as single entities. The study of such clusters led us to the investigation of the collective motions in liquids. We found in the course of these works that in liquids there are regions of the space in which the molecules on the average move in the same direction. The size of these regions is more than ten nanometers and they are well manifested if we follow the system during time interval of the order of 100 ps. This also can be regarded as a peculiar dynamical heterogeneity of liquids.

Keywords: Voronoi polyhedron, tetrahedrality index, clusters, hydrogen bonds, argon, computer simulation

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1. INTRODUCTION

This paper is mostly devoted to water, though some material about liquid argon is also presented. It has turned out that peculiarities of structural and dynamical heterogeneity of these two liquids are very similar in spite of the great difference in intermolecular interactions. The idea that water is not homogeneous has been put forward as early as in 1883 by Harold Whiting in

his rather confusing publication "A New Theory of Cohesion Applied to the Thermodynamics of Liquids and Solids" [1]. Nine years later a paper by W.C. Röntgen "Über die Constitution des flüssigen Wassers" [2] appeared, which was shorter and much more clear and lucid than [1]. In these two papers the idea that later was called the two-state model of water was proposed. Röntgen's ideas about the structure of water are discussed by Yu.I. Naberukhin in the paper [3] published on the occasion of the centennial of the Röntgen's paper. Many two-state models of water have been proposed. They are discussed in the well-known book by D. Eisenberg and W. Kauzmann "The structure and properties of water" [4]. A different approach to structure

of water was put forward in the famous paper by J.D. Bernal, R.H. Fowler "Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions" [5]. The concept of a continuous three-dimensional tetrahedral network in water was proposed in this paper. This concept was developed by J. A. Pople [6], by J.D. Bernal himself [7, 8] and then by M.G. Sceats and his co-workers [9, 10]. Classical two-state models imply that there are no hydrogen bonds between the molecules in the denser state [4]. In the middle of the 60-th the two-state models of water have been proposed in which molecules in both states are involved in hydrogen bonds [11, 12]. In other words, such models imply that continuous hydrogen network exists in water but density and structure varies from one region to another. It means that this network is not homogenous. All these two-state models were mental, speculative pictures. Their era was coming to the end. The era of computer simulation began [13-15]. One of the first papers in which on computer simulation attention to structural inhomogeneity of water was given was the publication by Alfons Geiger and H. Eugene Stanley "Low density "patches" in hydrogen bond networks of liquid water" [16]. But, as far as I know, no systematic study of this inhomogeneity was performed before the publication of our first paper dedicated to this problem [17].

2. STRUCTURAL HETEROGENEITY

The structural heterogeneity of liquid water is discussed in many publications on the structure of this substance. Some aspects of this problem are treated and corresponding references are given in the review papers [18, 19]. Rather unusual approach to water inhomogeneity can be found in [20].

In our works structural inhomogeneity of the network of computer simulated water was revealed as a non-uniform space arrangement of molecules whose local environment characteristics lied within certain limits. The local

environment of the molecule was characterized by following parameters.

1. The tetrahedrity index (T). It shows a degree of deviation of the nearest surroundings of the molecule from the ideal tetrahedral one. T for ideal tetrahedron is zero.
2. The volume of the Voronoi polyhedron (VVP) build around centre of an oxygen atom. It shows local density around a particular molecule. Figuratively speaking, the inverse of the VVP is the density of a single molecule [18]. See about Voronoi polyhedral the book by N.N. Medvedev [21].
3. Potential energy E_p (the energy of interaction of this molecule with all other molecules of the system). The principal contribution to E_0 is the interaction with the nearest molecules.

The tetrahedrity index T was calculated by the equation

$$T = \sum_{i=1}^5 \sum_{j=i+1}^6 (l_i - l_j)^2 / (15 \langle l \rangle^2), \quad i = 1, j = i+1,$$

where l_{ij} is the length of each of the six edges of the tetrahedron whose vertices are occupied by the oxygen atoms of the four nearest water molecules; $\langle l \rangle$ is the arithmetic mean of the lengths of all its six edges.

The volumes of the Voronoi polyhedra were calculated with the help of the program developed and kindly provided by V.P. Voloshin.

The molecular dynamics simulation of liquid water showed that molecules with high or low values of these parameters group together forming ramifying clusters, piercing the volume of the system. Correlation between values of different characteristics of local environment is feeble, if any [18, 19, 22-24].

In order to reveal structural heterogeneity of water we chose a certain number of molecules with highest and the same number of molecules with the lowest values of VVP , T , E_p and depicted their distribution in space (**Figs 1-4**). We have found that at room temperature approximately half of the molecule are participated in four hydrogen bonds, in two of as donors and in two as acceptors [18, 19]. We call such type of

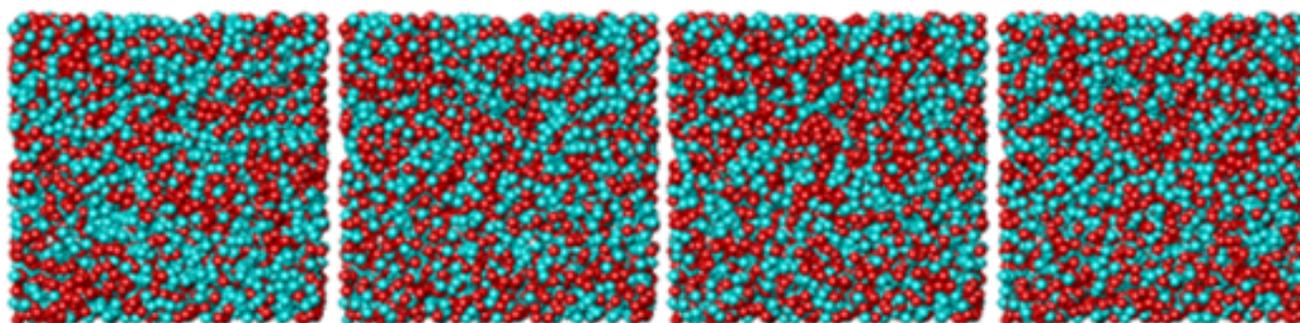


Fig. 1. Heterogeneous spatial distribution of molecules with different values of parameters that describe their local environment. An instantaneous structure for the system of 3456 molecules with periodic boundary conditions is shown. In the first three figures, dark (red) molecules are those whose parameters are smaller than the critical value that divides all molecules into two equal classes. Light (blue) molecules are those whose parameters exceed the critical value. Left to right: partition according to the volume of Voronoi polyhedra, tetrahedrality index, and potential energy. In the extreme right figure, dark molecules are those whose type of coordination is a_2d_2 . The given configuration contains about 49.5% molecules of this type. All other molecules are shown as light balls.

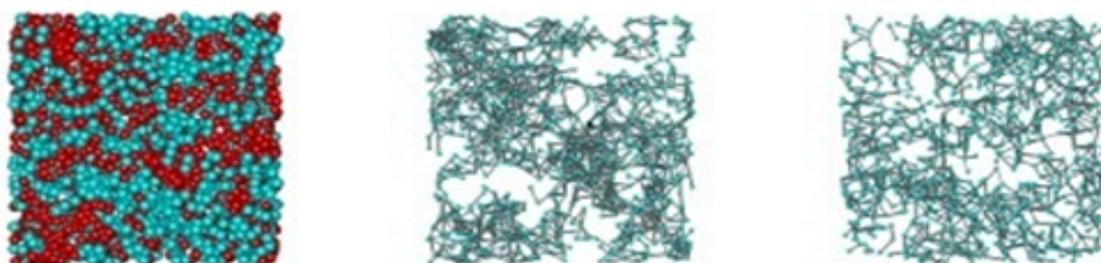


Fig. 2. Coloring of molecules according to the volume of Voronoi polyhedra. One third of molecules are selected from each group of molecules with the largest and smallest values of VVP. Left: dark spheres — molecules with $VVP < 28.157 \text{ \AA}^3$ (1152 molecules from the total number 3456), light spheres — molecules with $VVP > 31.1 \text{ \AA}^3$ (also 1152 molecules). Middle: spatial arrangement of molecules with $VVP < 28.157 \text{ \AA}^3$. Only molecules with neighbors separated by less than 4 \AA are shown. These molecules are connected by bonds, their number is 1100. Right: spatial arrangement of molecules with $VVP > 31.11 \text{ \AA}^3$. Molecules having neighbors at distances of less than 4 \AA are shown. These molecules are connected by bonds, their number is 1061.

coordination a_2d_2 . That is why we can study space distribution of molecules with a_2d_2 coordination and all the others and compare these distributions with distributions of the molecules with high and low values of VVP, T, E_p , when all the molecules are divided into two equal classes (Figs 1, 4). In **Fig. 1** pictures when 50% molecules with low

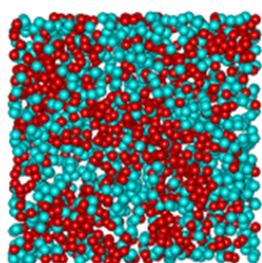


Fig. 3. Colouring according to VVP values. A configuration of 3456 molecules is shown, $T = 298 \text{ K}$, $d = 0.998 \text{ g/cm}^3$. 25% of the the molecules with the smallest and 25% molecules with the largest VVP values are chosen Red spheres- molecules with small VVP values ($< 28.33 \text{ \AA}^3$). Blue spheres – molecules with large VVP values ($> 34.10 \text{ \AA}^3$ 864). 864 molecules of each kind.

and 50% molecules with high values of VVP, T and E_p are shown. Distribution of molecules with a_2d_2 coordination and all others is show in the right picture of **Fig. 1**. Pictures when one third of molecules have been selected from each group of molecules with the largest and smallest values of VVP are shown in **Fig. 2**. The case, when 25% molecules with high and low VVP values have been chosen is shown in **Fig. 3**.

Details of distribution of the molecules with different types of coordination are shown in **Fig. 4**. It is seen that in all the cases molecules with high and low of VVP, T and E_p values or with similar type of coordination strive to group together forming ramifying clusters. It is a good reason to recall the English proverb "birds of a feather flock together". As it was shown in our paper "Quantitative characteristics of structure inhomogeneity of water" [24] this tendency

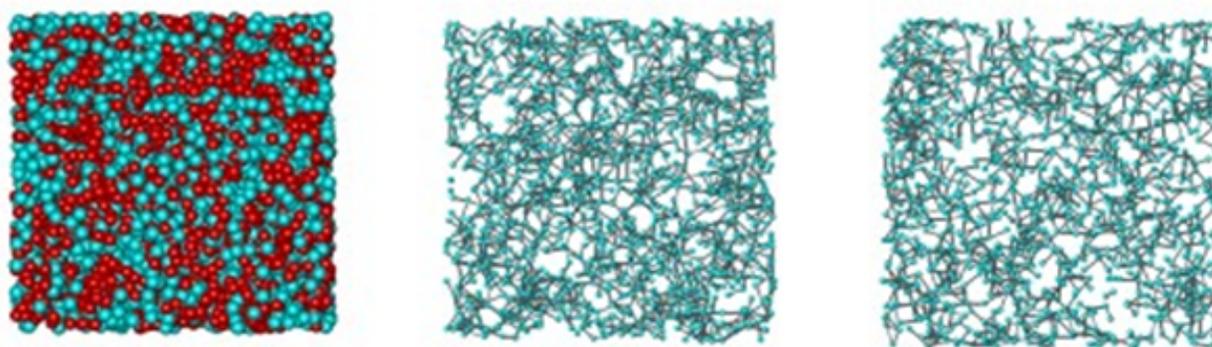


Fig. 4. Colouring according to types of coordination. A configuration of 3456 molecules is shown, $T = 298$ K, $d = 0.998$ g/cm³. Left: red spheres — molecules with a_2d_2 coordination (1758 or 50.87%), blue spheres — all other molecules. Middle: molecules with a_2d_2 coordination form a network. Right: molecules with coordination other than a_2d_2 also form a network. There are 1369 molecules connected by bonds.

is most pronounced in the case of the space distribution of the molecules with high or low values of VVP . Inhomogeneity with respect to local density revealed in our simulations turned out to be much subtler and more interesting than it was implied in primitive two-state models.

Structural heterogeneities of liquid argon and of liquid water were compared in the paper "Argon and water" [25]. As it can be seen in **Figs 5** (argon) and **6** (water), the character of the distribution of molecules with high and low VVP values is quite similar in these two liquids.

3. DYNAMICAL HETEROGENEITY

There are several kinds of dynamic heterogeneity. The most trivial one lies in the fact that dynamic properties of the molecules with different surroundings are different. This

was demonstrated for the crystalline ices [19, 26] and for amorphous ice [19]. It is quite natural that the amplitude of oscillations of molecules with greater values of VVP (less local density around them) is greater than that of molecules with smaller values of VVP (denser local surroundings). It seems to be quite natural as well that the slope of the temporal dependence of the mean square displacement $\langle r^2 \rangle(t)$ (proportional to the diffusion coefficient) of the molecules in the denser regions of the water network (with smaller VVP values) is smaller than that of the molecules in the looser regions (with large VVP volumes) [18, 19]. It is not easy to determine diffusion coefficients of molecules from the low and high density regions (by means of computer simulation), because the

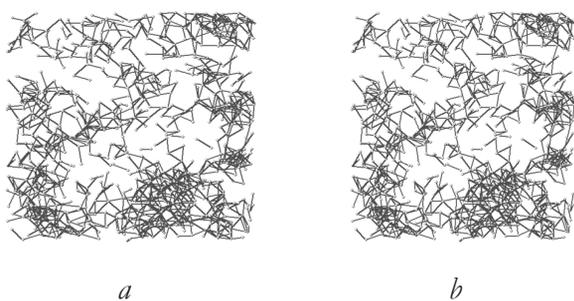


Fig. 5. Argon 110 K, $d = 1.513$ g/cm³. 4000 atoms in the periodic box. 25% with highest and lowest VVP values are chosen. a) There are 1000 atoms, whose $VVP < 41.97$ Å³. 942 from them have neighbors which are nearer than 4.4 Å. They are linked by conventional bonds. b) There are 1000 atoms whose $VVP > 45.97$ Å³. 0-6 from them have neighbors which are nearer than 4.4 Å. They are linked by conventional bonds.

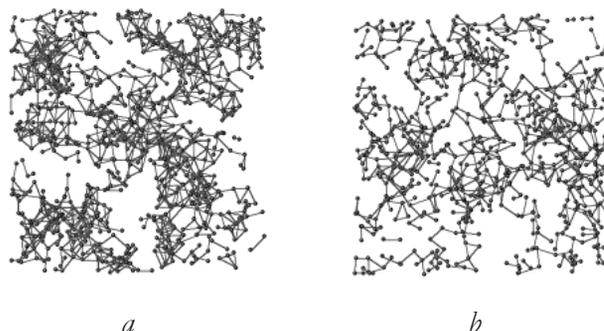


Fig. 6. Colouring of the water molecules according to VVP values. Instantaneous configuration contains 3456 molecules. 25% of the molecules with the smallest VVP values ($VVP < 27.32$ Å³) and 25% molecules with the largest VVP values. a) Molecules whose $VVP < 27.32$ Å³ are connected by conventional bonds ($R_{max} = 4$ Å). There are 808 such molecules. b) Molecules whose $VVP > 32.03$ Å³ are connected by conventional ($R_{max} = 4$ Å). There are 717 such molecules.

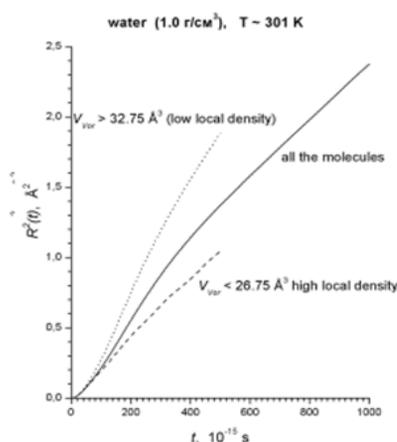


Fig. 7. Time dependence of centre of mass mean square displacement for molecules with high and low values of the Voronoi polyhedron volumes (V_{vor}). Liquid water at ambient conditions. See Fig. 18 in [18] or Fig. 21 in [19].

molecules do not maintain their VVP values for a long time. The mean square displacement function reaches the diffusion regime ($\langle r^2 \rangle(t) = 6Dt$, D is the self-diffusion coefficient) at $t > 1$ ps. We managed to follow $\langle r^2 \rangle = f(t)$ for the molecules with high and low VVP values only for about 0.5 ps (Fig. 7). But there is no doubt that, according to computer simulation, the diffusion coefficient of molecules in the regions with high local density is smaller than that of the molecules with low local density. Meanwhile, one of the best known and bright ‘anomalies’ of water is the increase of diffusion coefficient with increase of density (this anomaly is observed at $T < 310$ K). D reaches a maximum at a pressure of about 2 kb (Fig. 8), which corresponds to a density $\sim 1.08 \text{ g/cm}^3$ at ambient temperature. In our works a non-monotonic dependence of D (calculated for all molecules) on density was found [18, 19]. It is pertinent to note that our molecular dynamics simulation excellently reproduces experimental data on the dependence of diffusion coefficients on temperature at ambient pressure [27]. Dependence of diffusion coefficient on local density leads to a non-trivial situation. A paradox arises: if we compress the whole system, the diffusion coefficient increases, but the diffusion coefficient in the regions with high local density is lower than in the regions with low local density and in the system as a

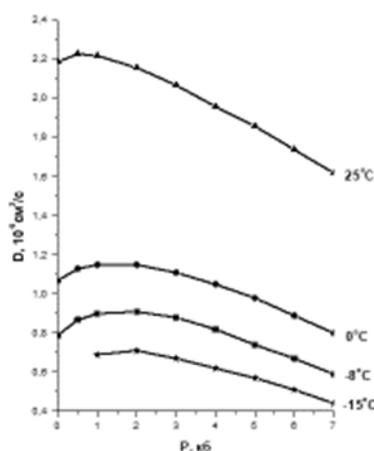


Fig. 8. Pressure dependence of the self-diffusion coefficient of water. Experimental data obtained (NMR, spin echo). See Fig. 12 in [18].

whole. This means that this ‘anomaly’ cannot be explained by a primitive two-state model, which implies that water is a composite of high density regions and low density regions. This paradox was discussed in [18, 19] but no satisfactory explanation was found.

Another, less trivial dynamic heterogeneity of liquid water is the result of the broad distribution of the hydrogen-bond lifetimes [28]. A certain number of long-living bonds exists. This means that associates incorporating two or more molecules exist in liquid water and move as a unified complex for rather a long time [22, 23]. Such associates could not be revealed by the analysis of the separate instantaneous structures. It is necessary to colour the hydrogen-bonded network with respect to lifetimes of hydrogen bonds. To this end molecular dynamics trajectory 50 ps long was obtained (3456 molecules, 298 K, 0.998 g/cm^3) [22, 30]. Coordinates of the molecules in the configurations, separated by 1 ps were recorded. Lists of hydrogen bonds (geometric criterion, $r_{\text{OO}}^{\text{max}} = 3.3 \text{ Å}$) were compiled for each configuration. The configuration obtained at 25th ps was chosen as a reference one and its list of hydrogen bonds was compared with hydrogen bond lists of 24 previous and 25 following configurations. This is a rather rough procedure for estimation of hydrogen bond lifetimes but it may be quite adequate for revealing associates of molecules

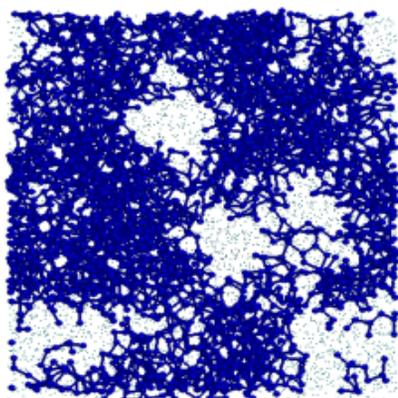


Fig. 9. Colouring according to hydrogen bond lifetimes. Water 10240 molecules in the cubic periodic cell. $T=310$ K. Hydrogen bonds whose lifetime is longer than 6 ps are coloured. Percolation threshold is 6.8 ps. Infinite cluster is shown.

connected by long-living bonds. If we colour in the reference configuration the bonds with lifetimes longer than 7 ps they will form an infinite ramifying cluster, resembling clusters formed by molecules with high or low values of VVP . Infinite percolating cluster is shown in **Fig. 9**. It was obtained in the other computer experiment. System containing 10240 molecules in the cubic periodic cell was simulated. Temperature was 310 K. Of course not all the bonds living longer than percolation threshold belong to this cluster. In the case system containing 3456 molecules in the cell, the bonds living longer than 8 ps do not form an infinite cluster, but clusters containing several dozens or hundreds of molecules can be found (**Figs 10a, 10b**). This means that the percolation threshold with respect to hydrogen-bond lifetimes (determined in such a rough way) lies between 7 and 8 ps in the case of this particular molecular dynamics trajectory. The average value of the percolation threshold is 7.96 ps at room temperature (**Table 1**). About 20% of bonds have lifetimes longer than 7 ps. It should be stressed that molecules participating in long-living bonds do not form compact complexes but rather loose branching clusters. There are many molecules which do not participate in long-living bonds and frequently exchange their neighbours inside these clusters. Bonds with lifetimes longer than 20 ps are



Fig. 10a. Colouring according to hydrogen bond lifetimes. System contains 3456 water molecules in the periodic cell. Bonds whose lifetimes are longer than 15 ps are shown.

united into small clusters containing one bond (two molecules), two bonds (three molecules) and very rarely three bonds (four molecules). This is a vivid illustration of collective diffusion. Molecules connected by long-living hydrogen bonds are doomed to move concertedly.

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 [31] (see [18, 19] 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 1**). The percolation characteristics of clusters obtained by colouring hydrogen bonds according to their lifetimes indicate that these

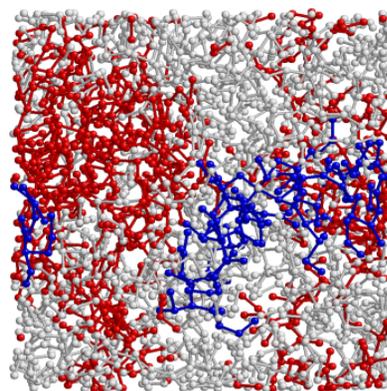


Fig. 10b. Colouring according to hydrogen bond lifetimes $T = 262$ K. System contains 3456 water molecules in the periodic cell. Molecules whose lifetimes are longer than 19 ps are shown ($t \geq 19$ ps). They do not form infinite cluster. The largest cluster formed by the molecules bonds between whom live longer than 19 ps contains 885 molecules.

Table 1
Mean lifetimes of hydrogen bonds (t_1), mean lifetimes corresponding to percolation thresholds (t_2), and experimental dielectric relaxation times (t_3)

Temperature, K	Mean lifetime of hydrogen bonds $\langle t_1 \rangle$, ps	Percolation threshold (t_2), ps	Dielectric relaxation time (t_3), ps ¹
250	26.56	33.29	46.51
261		20.49	27.9
280	12.03	14.28	13.9
297	~7	7.96	8.22
310	6.84	7.99	7.05

¹The sources of information about experimental dielectric relaxation times see in [30].

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 longliving bonds. These clusters can contain molecules not involved in long-living bonds. They constantly change its composition, losing or acquiring molecules.

Study of collective motions in water with the help of two-particle correlation functions [31] led us to conclusion that the unusual behaviour of these functions could be explained by vortex motions, which covered regions of space larger than the periodic cells used in our study. But, of course, the correlation functions give only indirect evidence of the existence of the vortex-like motions in liquids. In order to prove that such motions really exist in MD models of liquids, it is necessary to visualize them. To this end it was necessary to study large systems containing several dozens or even hundreds of thousands particles and obtain long MD trajectories [32].

Displacements of single particles are chaotic. In order to reveal the regularities in this chaos, it

is necessary to pass from the description of the of individual particles to the groups of particles and follow their displacements during long time intervals. It means that it is necessary to go to the higher level of the description of the motions in this chaos. Usually such a procedure is called coarse graining. The goal of coarse graining is to develop quantitative measure of collectivity in particle motion.

Let us construct a sphere with the radius R_{sph} in some point in the space of our model. This sphere should contain a considerable number of particles. Having calculated the trajectories of all the particles, which have been inside the sphere in the initial moment t_0 , during a succeeding time interval Δt , we can calculate a vector of average displacement $\langle \Delta R \rangle$ of these particles. If the motion of all the atoms were not correlated, the vector of their average displacement $\langle \Delta R \rangle$ would be close to zero. If their motion is correlated, this vector will be long enough. The more correlated the motion of the particles is, the longer will be the vector $\langle \Delta R \rangle$. So the length of $\langle \Delta R \rangle$ could be chosen as the measure of the correlation of motion of atoms inside the sphere. We can pin the vector of mean displacement of atoms $\langle \Delta R \rangle$ to the centre of the sphere and consider it to be the characteristic of the collective motion of the particles which initially have been inside the sphere. We place the centres of the spheres in the nodes of the grid which divides each of the edges of our cubic box into several equal parts of length. In our case the edges were divided into

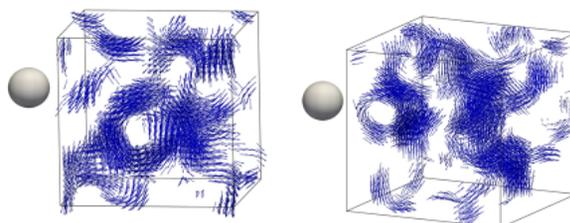


Fig. 11. Fields of average displacement vectors ΔR of argon atoms. 15% of the longest vectors are shown. 500 000 argon atoms in the periodic cell. 27000 spheres have been placed in the cell. Their centres have been put in the nodes of the cubic lattice build inside the cell. We calculated the displacement vectors for each atom, which have been inside the sphere in the initial moment displacement vector has been calculated. Average displacement vector were calculated for each sphere during the period $dt = 100$ ps. The size of the sphere in comparison with the size of the cell is shown in the left.

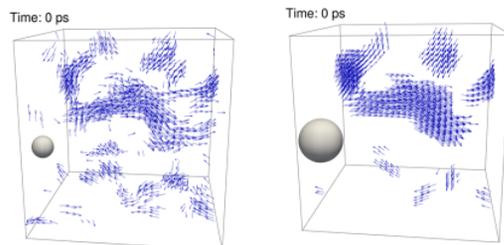


Fig. 12. Fields of average displacement vectors ΔR of argon atoms. 50 000 argon atoms in the periodic cell. 5 % of the longest vectors are shown. The size of the sphere in comparison with the size of the cell is shown. Left: $R_{sph} = 2.5\sigma$; right: $R_{sph} = 5.0\sigma$, $\sigma = 0.3405$ nm.

30 parts and as a result 27000 nodes appeared in which we placed the centres of the spheres and to which we pinned the $\langle \Delta R \rangle$ vectors. The described procedure allows us to observe mutual disposition of the vectors of average displacement of the atoms in all the space of the model and to build the field of the vectors of mean displacements of the atom groups. While scrutinizing this field, we can follow how the measure of collectivity of the motions changes from one place to another. We can build the field of $\langle \Delta R \rangle$ vectors for any initial moment t_0 , that is, for any instantaneous configuration (snapshot) along the MD trajectory. If we chose the spheres with the longest $\langle \Delta R \rangle$ vectors we shall reveal the regions in our model system, in which atoms or molecules move approximately in the same direction. In such regions the long $\langle \Delta R \rangle$ vectors group together and form the local flows with the lengths of several nanometers. These flows are bent. Sometimes whirl-like structures

arise (**Fig. 11**). In the other regions of the system motion of the particles is more chaotic. The examples of obtained pictures are shown in Figs. 11-13. The picture depends on time interval Δt and radius R_{sph} . It is very interesting that pictures obtained for argon and water are rather similar (**Figs. 12** and **13**).

The study of whirl-like motions allowed to reveal dynamic heterogeneity of much larger scale than described in other sections of this article. It is another manifestation of heterogeneity of liquids. This large scale heterogeneity is displayed very similarly in such different liquids as argon and water [32]. The same we observed when we compared small scale structural inhomogeneity of these two liquids [25].

4. CONCLUSION

Structural heterogeneity of liquids is the tendency of their molecules (or atoms in the case of liquid noble gases) with similar values of the parameters which characterize their local environment. Dynamical heterogeneity is different character of motion of the molecules or atoms in different regions of the space. Peculiarities of these kinds of heterogeneity for such different kinds of liquids as water and argon are very similar.

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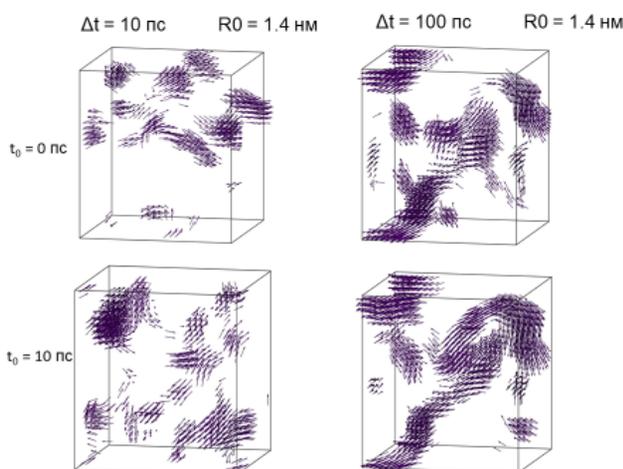


Fig. 13. Fields of average displacement vectors ΔR of argon atoms for different Δt . 50000 molecules in the periodic cell. 5% of the longest vectors are shown. R_0 is radius of the sphere

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