Structural and dynamical heterogeneity of liquids

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Received January 22, 2020; peer reviewed February 05, 2020; accepted February 10, 2020

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, tetrahedricity 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, tetrahedricity index, clusters, hydrogen bonds, argon, computer simulation

UDC: 538.91

For citation: George G. Malenkov. Structural and dynamical heterogeneity of liquids. RENSIT, 2020, 12(1):29-38; DOI: 10.17725/rensit.2020.12.029.
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. Scents and his co-workers [9, 10]. Classical two-state models imply that there are no hydrogen bonds between the molecules in he 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 tetrahedricity 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 ($V\forall P$) build around centre of an oxygen atom. It shows local density around a particular molecule. Figuratively speaking, the inverse of the $V\forall P$ 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 $E_p$ is the interaction with the nearest molecules. The tetrahedricity index $T$ was calculated by the equation

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

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; $\langle \rangle$ 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 $V\forall P, T, E_p$ 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
coordination $a_{d_2}$. That is why we can study space distribution of molecules with $a_{d_2}$ 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 and 50% molecules with high values of $VVP$, $T$ and $E_p$ are shown. Distribution of molecules with $a_{d_2}$ 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...
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 $\langle r^2(t) \rangle$ (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

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**Fig. 4.** Colouring according to types of coordination. A configuration of 3456 molecules is shown, $T = 298 K$, $d = 0.998$ g/cm$^3$. Left: red spheres — molecules with a $\sigma_2$ coordination (1758 or 50.87%), blue spheres — all other molecules. Middle: molecules with a $\sigma_3$ coordination form a network. Right: molecules with coordination other than a $\sigma_3$ also form a network. There are 1369 molecules connected by bonds.

**Fig. 5.** Argon 110 K, $d = 1.513$ g/cm$^3$. 4000 atoms in the periodic box. 25% with highest and lowest $VVP$ values are chosen. a) There are 1000 atoms, whose $VVP < 41.97$ Å$^3$. 942 from them have neighbors which are nearer than 4.4 Å. They are linked by conventional bonds. b) There are 1000 atoms whose $VVP > 45.97$ Å$^3$. 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 ($VVP < 27.32$ Å$^3$) and 25% molecules with the largest $VVP$ values. a) Molecules whose $VVP < 27.32$ Å$^3$ are connected by conventional bonds ($R_{\text{max}} = 4$ Å). There are 808 such molecules. b) Molecules whose $VVP > 32.03$ Å$^3$. are connected by conventional ($R_{\text{max}} = 4$ Å). There are 717 such molecules.
molecules do not maintain their $V/V_P$ values for a long time. The mean square displacement function reaches the diffusion regime ($<r^2>(t) = 6Dt$, $D$ is the self-diffusion coefficient) at $t > 1$ ps. We managed to follow $<r^2> = f(t)$ for the molecules with high and low $V/V_P$ 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 $\sim 1.08$ 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 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, $r_{OO}^{\text{max}} = 3.3$ 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.
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 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 concertedy.

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
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 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 $R_{\text{sph}}$ 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 $\Delta t$, 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

| Temperature, K | Mean lifetime of hydrogen bonds ($t_1$), ps | Percolation threshold ($t_2$), ps | Dielectric relaxation time ($t_3$), ps |
|---------------|-------------------------------------------|---------------------------------|----------------------------------|
| 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                             |

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

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

**Fig. 11.** Fields of average displacement vectors $\Delta R$ 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.
30 parts and as a result 27000 nodes appeared in which we placed the centres of the spheres and to which we pinned the \(<\Delta R>\) 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 \(<\Delta R>\) 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 \(<\Delta R>\) 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 \(<\Delta R>\) 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 \(\Delta t\) 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 is 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.

REFERENCES

1. Harold Whiting H. A New Theory of Cohesion Applied to the Thermodynamics of Liquids and Solids. Proceedings of the American Academy of Arts and Sciences, 1884, 19:353-431.
2. Röntgen WC. Über die Constitution des flüssigen Wassers. Ann. Phys. Chem. N.F., 1892, 45:91-97.
3. Naberukhin YuI. Centennial of the Röntgen's paper on the structure of water. *J. Struct. Chem.*, 1993, 33(6):772-774.

4. Eisenberg D, Kauzmann W. *The structure and properties of water*. Oxford Clarendon Press, 1969.

5. Bernal JD, Fowler RH. Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions. *J. Chem. Phys.*, 1933, 1:515-548.

6. Pople JA. Molecular association in liquids. II. A theory of the structure of water. *Proc. R. Soc. A*, 1951, 205:163-178.

7. Naberukhin YuI, Luchnikov VA, Malenkov GG, Zheligovskaya EA. Spatial localization and dynamics of water molecules with good tetrahedral surroundings. *Journal of Structural Chemistry*, 1997, 38(4):593-600.

8. Malenkov GG. Structure and dynamics of liquid water. *Journal of Structural Chemistry*, 2006, 47, Supplement, pp. S1-S31.

9. Malenkov G. Liquid water and ices: understanding the structure and physical properties. Topical Review. *Journal of Physics. Condensed Matter*, 2009, 21(28):283101-283136.

10. Stanley HE, Buldyrev SV, Franzese G, Giovambattista N, Starr W. Static and Dynamic Heterogeneities in Liquid Water. *Phil. Trans. R. Soc. A*, 2005, 363:509-523.

11. Medvedev NN. *Metod Voronogo-Delone v izuchenii struktury nekristallicheskikh sistem* [Voronoi-Delaunay method in the study of non-crystalline systems]. Novosibirsk, 2000, SO RAN Publ., 209 p.

12. Malenkov GG. Structural and dynamical heterogeneity of stable and metastable water. *Physica A*, 2002, 314(1-4):477-484.

13. Malenkov GG, Tytik DL, Zheligovskaya EA. Structural and dynamic heterogeneity of computer simulated water: ordinary, supercooled, stretched and compressed. *J. Molec. Liquids*, 2003, 106(2-3):179-198.

14. Davis CM, Litovitz TA. Two-State Theory of the Structure of Water. *J. Chem. Phys.*, 1965, 42(7):2563-2576.

15. Mu Shik Jhon, Grosh J, Ree T, Eyring H. Significant-Structure Theory Applied to Water and Heavy Water. *J Chem. Phys.*, 1966, 44(4):1465-1471.

16. Barker JA, Watts RO. Structure of water: A Monte Carlo calculation. *Chem. Phys. Lett.*, 1969, 3(3):144-150.

17. Rahman A, Stillinger FH. Molecular Dynamics Study of Liquid Water. *J. Chem. Phys.*, 1971, 55:3336.

18. Sarks G, Malenkov GG, Dashevskii VG. A study of the structure of water by the Monte Carlo method. *Journal of Structural Chemistry*, 1973, 14(1):4-8.

19. Geiger A, Stanley HE. Low density “patches” in hydrogen bond networks of liquid water. *Phys. Rev. Lett.*, 1982, 49(24):1749-1952.

20. Naberukhin YuI, Luchnikov VA, Malenkov GG, Zheligovskaya EA. Hydrogen bonds in computer simulated water. *J. Molec. Liquids*, 1999, 82(1):27-38.
29. Voloshin VP, Malenkov GG, Naberukhin YuI. Description of collective effects in computer models of water. *J. Struct. Chem.*, 2007, 48(6):1066.

30. Malenkov GG, Yu. I. Naberukhin YuI, Voloshin VP. Collective Effects in Molecular Motions in Liquids. *Russian Journal of Physical Chemistry A*, 2012, 86(9):1378-1384.

31. Voloshin VP, Malenkov GG, Naberukhin YuI. Collective motions in computer models of water. *Journal of Structural Chemistry*, 2013, 54, Supplement 2:233-251.

32. Anikeenko AV, Malenkov GG, Naberukhin YuI. Visualization of the collective vortex-like motions in liquid argon and water: Molecular dynamics simulation. *The Journal of Chemical Physics*, 2018, 148:094508-094518.