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ORIGINAL RESEARCH

Collective effects in diffusional motion of water molecules: computer simulation

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Abstract Molecular dynamics simulation of the system containing 3,456 water molecules in the cubic periodic box was performed. Virtual temperatures were 261 and 297 K. Hydrogen bond networks of water computer models were coloured with respect to hydrogen bond lifetimes. Percolation thresholds τ_c were found. Hydrogen bonds whose lifetimes are longer than τ_c form infinite cluster. Values of τ_c are: 8 ps for 297 K and 20.5 ps for 261 K. Along with this infinite cluster many finite clusters connected by long-living hydrogen bonds are formed. They may contain several dozens or even hundreds of molecules. Molecules connected by long-living bonds are doomed to move concertedly. Correlation of displacement vectors for the pairs of water molecules whose oxygen–oxygen distances in the initial configurations (R^0_{OO}) lay within certain limits was studied. Initial values of correlation coefficients only slightly depend on temperature but decrease notably as R^0_{OO} increases. It is about 0.4 for R^0_{OO} lying in the 2.15–3.15 Å interval and about 0.05 for R^0_{OO} lying in the 9.15–10.15 Å interval. Values of correlation coefficients decrease with time, but do not reach zero even after several hundreds of picoseconds.

Keywords Water · Computer simulation · Hydrogen bond life times · Correlation coefficients · Collective motions

Introduction

Structure and dynamics of liquids are intimately related. It is a matter of common knowledge. But different viewpoints on the character of this relation exist. Samoilov [1] used to say that the structure of a liquid is dictated by its dynamics. On the other hand, Bernal [2] formulated paradoxical idea: “fluidity of a liquid is consequence of a molecular irregularity rather than the inverse”. Both statements emphasise close relation between structure and dynamics, but they reflect the difference in the understanding of what the structure of a liquid is. Samoilov most likely understood it as “a crystal structure disturbed by thermal motion”. Bernal insisted that different principles underlie the structure of these two aggregate states. Bernal’s viewpoint is closer to the viewpoint of the authors of this article. In any case, no one denies that such relation exists. For more details, see the review paper by one of the authors [3]. Nanoscale structural inhomogeneity was shown to exist in water [3–7]. This inhomogeneity is connected with the nonuniform spatial distribution of molecules with close values of the parameters which characterise their surrounding. For instance, molecules with large values of Voronoï polyhedra volume (VVP, measure of local density of the system) group together forming ramifying infinite clusters. The same can be said about the molecules with small VVP values and about the molecules with high and low values of tetrahedricity (measure of the nearest regularity of the surrounding of the molecules). The molecules behave according to the proverb “birds of a feather flock together”. This structural inhomogeneity leads to the trivial dynamic inhomogeneity: dynamic characteristics, such as frequencies of vibration and diffusion coefficients are different for the molecules with high and low values of the parameters characterising their local surrounding. Less

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trivial dynamic inhomogeneity of water is connected with broad distribution of the hydrogen bond life-times [3, 6, 8, 9]. Molecules connected by long-living bonds are doomed to move concertedly. We have shown that bonds living longer than some critical value (percolation threshold) form infinite ramifying cluster similar to the clusters formed by, e.g. molecules with small VVP values [10]. Percolation threshold for computer model of water with virtual temperature about 297 K was found to be close to 7 ps which is close in turn to average value of hydrogen bond life-time for this temperature. The results published in [10] are based on the analysis of the small number of configurations and should be regarded as preliminary ones. The results of more thorough and detailed study of room temperature model will be given in this article. New results on the supercooled water model will be also presented.

As it has been already said, molecules connected by long-living hydrogen bonds have nothing to do but to move in a concerted way. It means that the problem of the space distribution of long-living hydrogen bond is intimately related with the problem of collective motions of the molecules. The latter problem has been discussed by many authors. Historical review and modern state of art can be found in the survey [11]. It is commonly thought that collective diffusion is related to the contribution of displacement of the temporal equilibrium positions of the molecules between the jumps implied in the models of molecular motions used for the interpretation of the results quasielastic neutron scattering [12]. The first model of such kind was proposed by Oskotskii [13]. The idea that collective motions are pertinent to the drift of the temporary equilibrium position is based on the intuitive considerations and has never been proved. We have demonstrated in [10] that two molecules connected by a hydrogen bond can jump simultaneously without rupture of this bond, not to mention that actual motion of water molecules is far more complicated than it is implied in the primitive models of Oskotskii's type [13]. No systematic study of collective motions in water has been done by computer simulation. Ohmine et al. [14] compared positions of molecules in the inherent structures obtained by quenching the instantaneous configurations separated by several picoseconds and found collective, or as they called it, cooperative displacements of molecules. Bertolini et al. [15] calculated the interparticle correlation functions, indicating that collective motions were present. Existence of such motions is a trivial fact, however. As indicated above, the occurrence of long-living hydrogen bonds and their grouping together in ramifying clusters lead inevitably to the collective motions. Formation of such clusters provides reason to cherish hope that distances between water molecules would oscillate around some average value for a long time not only when these molecules are connected by hydrogen bonds. Indeed, it was found that average distance between molecules maintained practically constant for some time when it was much longer than 3 Å (up to 20 Å) [10]. It means that groups containing many water molecules are involved in collective motions.

These findings are pertinent to the original approach to the problem of collective motions in liquids proposed by Fisher [16, 17] and developed by his followers [11, 18–20]. According to this approach, collective component in the self-diffusion coefficient is regarded as self-diffusion coefficient of the Lagrange particle of the appropriate radius. It was shown that contribution of collective component in self-diffusion at temperature close to the melting point of water is about 10% and radius of Lagrange particle at this temperature is about 20 Å [20]. Computer simulation can be a powerful tool for verification of these theoretical results and for creation of a vivid picture of the molecular motions in liquids.

Methods

All the results presented in this article were obtained in the course of molecular dynamics simulation of the system containing 3,456 water molecules with periodic boundary conditions. Interactions between rigid water molecules were described by the atom–atom potential functions, proposed in [21]. The equations of motion were integrated using the Verlet algorithm and Grivtsov–Balabayev method of treating constraint equations for bonds of fixed lengths [22] was used. Different systems were simulated using this interaction model and computer programme by one of the authors and his colleagues (see, for instance, [23] and references therein). Special programmes for search of the hydrogen bonds, for colouring of the hydrogen bond network in respect to the life times and for calculation of time dependences of different functions related to the displacement of molecules were created by the authors.

Colouring of the hydrogen bond network with respect to hydrogen bond life-times

Molecular dynamics trajectories for virtual temperatures 297 and 261 K were obtained. Instantaneous configurations after each 0.1 ps were recorded. Lists of hydrogen bonds for each recorded configuration were made (geometric criterion was used; two molecules were assumed to be connected by hydrogen bond if $r_{OO} < 3.3$ Å, $r_{OH} < 2.5$ Å). 86 configurations were selected from the 297 K trajectory and 100 configurations were selected from the 261 K trajectory. Lists of hydrogen bonds in the selected configurations were compared with corresponding lists in previous and succeeding ones. In such a way hydrogen bond life-times were estimated. For each selected configuration, percolation thresholds τ_c were determined. If we colour the bonds whose life-times are longer than τ_c, one infinite cluster of hydrogen-bonded molecules and many finite clusters are revealed in a selected configuration. If we colour the bonds whose life-times are longer than some τ value greater than τ_c, no infinite clusters can be found in the selected configuration. Average results for percolation analysis of hydrogen-bonded networks for two temperatures are given in Table 1.

It is seen that 85% of molecules at room temperature and ¾ of molecules in supercooled water participate at least in one bond which lives longer than percolation threshold. It is remarkable that average size of infinite clusters at room temperature is twice as great as average size of infinite clusters at low temperature. Numbers of molecules and of bonds in the infinite clusters are close to each other. It means that degree of ramification of these clusters is rather low: number of molecules which participate in three bonds is close to the number of molecules which are located at the dead ends of the branches. One of the finite large clusters is shown in Fig. 1. In this case, bonds which live longer than 19 ps are coloured. As for this particular model percolation threshold is 18 ps, there are no infinite clusters under such colouring.

It should be pointed out that the networks were coloured according to the total life-times of hydrogen bonds (see [9] for details). Some of these bonds have just arose, some of them will be broken soon. These clusters continuously change their composition. Some molecules leave them, others join them. The clusters are very loose and contain molecules which do not participate in long-living bonds.

Correlations in motions of molecules in water

Mean square displacement of molecules is: $\langle \Delta \mathbf{r}^2 \rangle (t) = \langle [\mathbf{r}_i(t - \mathbf{r}_i(0)]^2 \rangle$. After short period of time (~2 ps), $\langle \Delta \mathbf{r}^2 \rangle (t)$ approaches very closely diffusional asymptote $\langle \Delta \mathbf{r}^2 \rangle = 6Dt$.

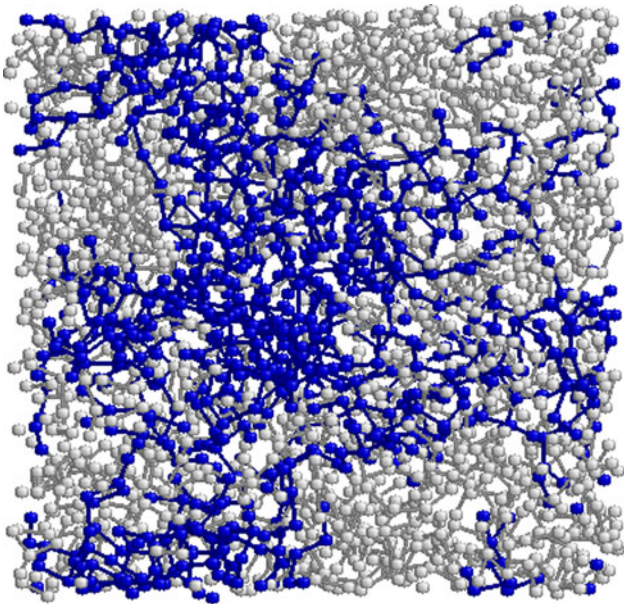

Fig. 1 Instantaneous structure of water. $T = 261$ K. 3456 molecules in the cubic cell with periodic conditions. Bonds which live longer than 19 ps are coloured. Threshold for this particular configuration is 18 ps. *Coloured bonds* do not form an infinite cluster. The largest cluster contains 885 molecules. They and bonds between them are shown in *blue* (*black* in printed edition). The other clusters are shown in *gray*. Single nodes are not shown. Fraction of coloured nods (molecules) is 0.79. Fraction of coloured bonds is 0.36. Number of finite clusters is 402. They contain 2,729 nods and 2,379 bonds

Mean square of the length of vectors of displacement of two water molecules i and j in which oxygen–oxygen distance in the initial configurations laid within certain limits is:

$\langle [\Delta \mathbf{r}_{ij}(t)]^2 \rangle = \langle [\mathbf{r}_{ij}(t) - \mathbf{r}_{ij}(0)]^2 \rangle = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle + \langle [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \rangle - 2\mathrm{Corr} = 2\langle \Delta \mathbf{r}^2 \rangle - 2\mathrm{Corr}$, where Corr is the correlator of vectors of displacement of two water molecules (scalar product of these vectors): $\mathrm{Corr} = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \rangle$.

Table 1 Colouring of the bonds according to their life-times

Characteristic	Temperature	
	297 K	261 K
Average percolation threshold, ps	7.96 ± 0.39	20.49 ± 1.16
Average fraction of coloured nods (molecules)	0.851	0.749
Average fraction of coloured bonds	0.428	0.275
Average number of finite clusters	312.33	394.24
Average number of nods in finite clusters	1377.76	1747.52
Average number of bonds in finite clusters	1073.90	1366.03
Number of infinite clusters	1	1
Average number of nods in the infinite cluster	1563.44	842.28
Average number of bonds in the infinite cluster	1637.46	874.74

The bonds whose life-times exceeded the life-time corresponding to the percolation threshold were coloured

Dependence of $\langle[\Delta\mathbf{r}_{ij}(t)]^2\rangle$ on time differs from the diffusional asymptote: $\langle[\Delta\mathbf{r}_{ij}(t)]^2\rangle$ asympt $= 12Dt$ by the value of the correlator (Corr).

Correlator increases with time because displacement of molecules increases.

Coefficient of correlation is the measure of the correlation:

$$\text{Coef. Corr.} = \langle[\mathbf{r}_i(t) - \mathbf{r}_i(0)] \times [\mathbf{r}_j(t) - \mathbf{r}_j(0)] \big/ |\mathbf{r}_i(t) - \mathbf{r}_i(0)| \times |\mathbf{r}_j(t) - \mathbf{r}_j(0)|\rangle$$

Coefficient of correlation is actually cosine of the angle between the vectors of displacement of the two molecules. If the vectors are parallel coefficient of correlation is unity.

We performed several molecular dynamics simulations of the same system containing 3,456 water molecules for the same two virtual temperatures 297 and 261 K. Here, we present the results obtained from analysis of trajectories: 200 ps long for 261 and 500 ps for 297 K. 200 configurations separated by 1 ps were saved from the first trajectory and 500 configurations were saved from the second trajectory. In each of the saved configurations pairs of molecules in which initial r_{OO} distance laid within certain limits were chosen and their fate was traced during the successive part of the trajectory. The following values of r_{OO} intervals were chosen: 2.15–3.15, 3.15–4.15, 4.15–5.15, 5.15–6.15, 6.15–7.15, 7.15–8.15, 8.15–9.15, 9.15–10.15 Å. Along with mean square of the length of vectors of displacement of two water molecules, correlator of vectors of displacement of two water molecules and correlation coefficient, temporal dependence of some other functions relating to the displacement of the pair of molecules have been calculated. These functions were: mean change of the distance, mean modulus of the change of distance, mean length of the vector of relative atomic position change, mean distance (without subtraction of the initial distance). Temporal behaviour of most part of these functions is rather inexpressive and trivial. Only dependence of change of the modulus of the distance between oxygen atoms on time is somewhat unexpected. It is shown in Fig. 2. The curves which display graphically temporal dependences of this function for different initial r_{OO} values intersect at some time value τ_x (about 10 ps at room temperature and about 25 ps at low temperature). This time τ_x can be relevant to some important but yet unknown processes occurring in liquid water.

As to coefficient of correlation, its behaviour is also rather unexpected (Fig. 3). Initial values of this coefficient are almost the same for both temperatures. There are detectable correlations in the displacements of the pairs of molecules during several dozens of ps even for the molecules separated by 10 Å in the initial configuration. It is quite natural that coefficients of correlation decrease faster at higher temperatures. It is not trivial that even after hundreds of ps these coefficients reliably are not zero. This finding need further more thorough investigation.

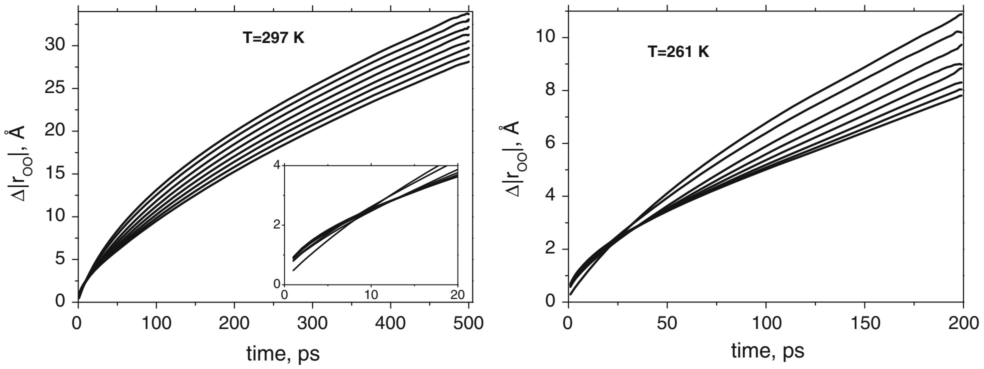

Fig. 2 Change of the modulus of the distance between oxygen atoms. Pay attention at the intersection points (about 10 ps at 297 K and 25 ps at 261 K). Values of r_{OO} in the initial configurations were (from *top to bottom* in the *right part* of the figure): 2.15–3.15, 3.15–4.15, 4.15–5.15, 5.15–6.15, 6.15–7.15, 7.15–8.15, 8.15–9.15, 9.15–10.15 Å

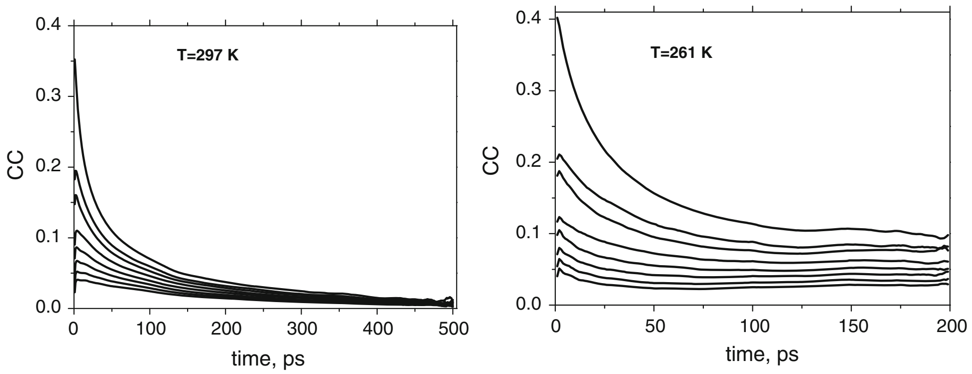

Fig. 3 Mean correlation coefficient of the displacement of oxygen atoms in the pair of molecules. Order of initial r_{OO} values is the same as in Fig. 2

Conclusions

Molecules connected by hydrogen bonds living longer than 8 ps at 297 K and longer than 20 ps 261 K form infinite ramifying cluster. They have no other possibility but to move concertedly. The cluster is not very compact. Molecules which do not participate in long-living hydrogen bonds can be inside the cluster. The clusters formed by long-living hydrogen bonds persistently change their composition: some molecules leave, some join them. The molecules can migrate inside the cluster, but continue to participate in the collective motion.

Correlation between displacements of molecules retains for a long time even if distance between them is 10 Å. The nearer are the molecules to each other the greater is correlation in their motions.

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