

DESCRIPTION OF COLLECTIVE EFFECTS IN COMPUTER MODELS OF WATER

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The dynamics of a system containing 3456 water molecules in a cubic cell with periodic boundary conditions at 297 K was simulated. The time dependence of distances between oxygen atoms was examined for many pairs of molecules. These distances often oscillate around a certain average value over long periods of time (10 ps and longer). These average values can be about 2.8 Å (hydrogen bond) or much larger, up to 12-13 Å and more. This suggests that big groups of molecules are involved in a concerted motion. Lists of hydrogen bonds in 50 configurations divided by an interval of about 1 ps are compared. The average lifetime of a hydrogen bond is about 7 ps. The network of hydrogen bonds is colored according to their lifetimes for one of the configurations. The bonds that live longer than 7 ps form an infinite cluster. The bonds that live longer than 8 ps join to form a great number of finite clusters including several hundreds of nodes (molecules). These clusters contain few closed cycles. Even the bonds that live longer than 20 ps are united into clusters each containing two or three nodes (molecules). The self-diffusion coefficient for molecules involved in long-lived bonds is likely to be slightly smaller than that for molecules which do not participate in these bonds.

Keywords: water, self-diffusion, collective effects, computer simulation.

INTRODUCTION

All three approaches accepted in modern fundamental science, i.e., theory, experiment, and computer simulation, are used to investigate the self-diffusion mechanism of molecules in liquids, including the role of collective effects. NMR spectroscopy provides the most reliable data on the self-diffusion coefficients of molecules in water (spin-echo; see, for example [1]), but, like the radioactive tracers method, they fail to give information about the mechanisms of molecular motions. Quasielastic neutron scattering is more informative in this respect [2]. To determine the self-diffusion coefficient, it is necessary to calculate the dependence of the half-width of the incoherent peak γ on the squared wave vector k^2 based on a certain model of molecular motion set *a priori*. These models are based on a quasicrystalline picture of molecular motions in liquids suggested by Ya. I. Frenkel in his classic book [3]. Different versions of this picture used to interpret the data of quasielastic neutron scattering are presented in the fifth chapter of the monograph [2] (pp. 148-167; studies of water are discussed on pp. 167-176). In all of these versions, molecules are assumed to oscillate around some temporary equilibrium position for some period of time τ_0 and then move rapidly to the neighboring equilibrium position. The model of Oskotskii

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[4] takes into account the possibility for the temporary equilibrium position also to move during this period of time τ_0 . This displacement is described by the self-diffusion coefficient D_0 . It is commonly thought that the D_0 coefficient corresponds to the contribution of collective effects to the self-diffusion process [5, 6]. However, this statement is based on intuitive considerations and has never been rigorously proved. Estimations of the τ_0 and D_0 parameters depend on both the assumption about the mechanism of the molecule transition from one equilibrium state to another and the experimental data used. In the original work of Oskotskii, based on the experimental data available at that time, $\tau_0 = 1.7$ ps and $D_0 = 0.7 \cdot 10^{-5}$ cm²/s. Novikov, Sobolev, and Rodnikova [7] obtained the values of $\tau_0 = 3.1$ ps and $D_0 = 0.8 \cdot 10^{-5}$ cm²/s in their calculation of these parameters. Bulavin, Malomuzh, and Pankratov [6] considered and improved the mobility models of water molecules and the methods for calculating $\gamma(k^2)$ in detail. The assumption about an abrupt transition of a molecule from one equilibrium position to another leads to absolutely different values of τ_0 and D_0 than the assumption about the free travel of the molecule. The latter assumption is a development of the idea of Fisher, Samoilov, and Andrianova [8]. The authors of [6] apparently interpreted the most reliable experimental data [9] obtained in a wide range of temperatures, including the data for overcooled water. It was also shown [6] that quasicrystalline approaches were absolutely inapplicable to description of molecular motions in water above 315 K.

Apart from the interpretation of experimental data, the methods of theoretical physics are employed to build proper models of molecular motions that take into account the collective motions. Fisher proposed the most promising and fruitful idea [10], later developed by his followers [11-13]. He supposed that the collective components of self-diffusion of molecules in liquids were determined by the motion of the so-called Lagrange particle (i.e., an aggregate of molecules moving as an entity). He estimated the percent of the collective component in the self-diffusion coefficients of simple liquids, including liquid metals, and showed that it was about 10% near the melting point and increased with temperature. These estimations were refined in [11-13], where other liquids were also considered. It was shown, in particular, that the collective component of the self-diffusion coefficient for slightly overcooled water was about 50% and decreased with increasing temperature. The Lagrange particle radius for water was estimated at ~ 4 Å.

As for computer experiments, there were no systematic investigations of collective molecular motions in water. Ohmine et al. [14] compared the 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. Although the results are qualitative, this is an interesting approach. Bertolini et al. [15] calculated the interparticle correlation functions, also indicating that collective motions were present. Generally, the existence of these motions is a trivial and undoubtful fact. Water molecules are hydrogen-bonded, and the average lifetime of these bonds is several picoseconds. The problem is evaluation of the contribution of the collective motions to the total self-diffusion coefficient and determination of the temperature dependence of this contribution. Other questions are: How many molecules are involved in these motions? What is the lifetime of the groups of molecules participating in collective motions? All these questions remain unanswered.

MODEL AND METHODS

A system containing 3456 molecules in an independent cubic cell with periodic boundary conditions was simulated by the molecular dynamics method at 297 K. The atom-atom potential functions proposed in [16] were used to describe the intermolecular interactions. The water molecule is represented as a rigid system of three force centers coinciding with oxygen and hydrogen atoms. The algorithms and programs used for molecular dynamic simulations were the same as in our previous works (see, for example, [17]).

The initial configuration was obtained from the structure of a hypothetical modification of ice that was isostructural with the silicon (SiIII) and germanium (GeIV) modifications (the so-called BC8 structure [18] containing 16 atoms in a body-centered cubic unit cell). This hypothetical modification turned out to be unstable in the simulation with our potentials

proposed in [16] and was destroyed even at very low temperatures. We simulated a system containing 432 molecules in an independent cubic cell and obtained by tripling each of the edges of the initial body-centered unit. The starting configurations used in the present work were obtained by doubling each of the cell edges and reproducing the content of these unit cells. In other words, the working periodic cell of the models studied in this work contained 216 crystallographic unit cells of the BC8 structure.

This configuration was substantially relaxed. Hundreds of virtual picoseconds of the molecular dynamic simulations preceded the initial configuration used here. The lists of hydrogen bonds were compared, the lifetimes calculated, and the hydrogen bond networks colored (according to the lifetimes) with special computer programs.

RESULTS AND DISCUSSION

The fate of many individual molecules was traced using their biographical maps (or “life maps”) that showed when and with which molecules the given molecule formed hydrogen bonds [19, 20]. Figure 1 displays one of these maps.

Also, the time dependences of the distances between the oxygen atoms and the unit center and/or their displacements from the initial positions were analyzed (Fig. 2). For many molecular pairs, the time dependences of the distances between their oxygen atoms were found (Fig. 3). These observations of the behavior of the individual molecules showed that many molecules were often involved in hydrogen bonds with long lifetimes (up to 30 ps and sometimes even longer), sometimes in two or three long-lived bonds simultaneously. Complexes of three or four molecules evidently move as an entity in a concerted way. Sometimes two hydrogen-bonded molecules make a joint “slow jump” at a distance of 3.5 Å, which lasts for 0.5-1 ps (Fig. 2). This shows that the question about the role of jumps and collective motion is much more complicated than it is usually considered to be.

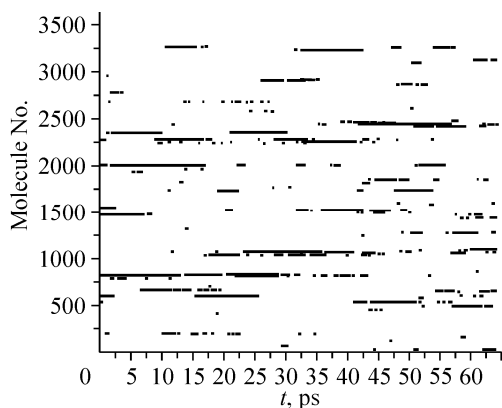


Fig. 1. Example of a “life map” of one molecule during 64 ps. The line segments correspond to the time periods during which a hydrogen bond with another molecule existed. A simplified geometric criterion of an H bond is used, $r_{OO} < 3.3 \text{ \AA}$. The numbers of these molecules are shown on the ordinate axis. It can be seen that there were periods when the molecule participated in several relatively long-lived bonds. It was also often involved in very short-lived bonds (for many of these, the lifetime is shorter than the dynamic criterion [21, 22]; i.e., these are not bonds).

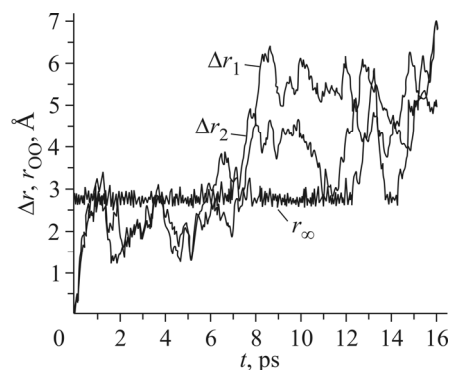


Fig. 2. Concerted motion of two water molecules. Their shift relative to the initial position (Δr_1 , Δr_2) and the distance from each other (r_{OO}) are shown. A hydrogen bond existed between them for 12.6 ps from the start of observation. After ~ 7 ps, both molecules made a jump without breaking the bond.

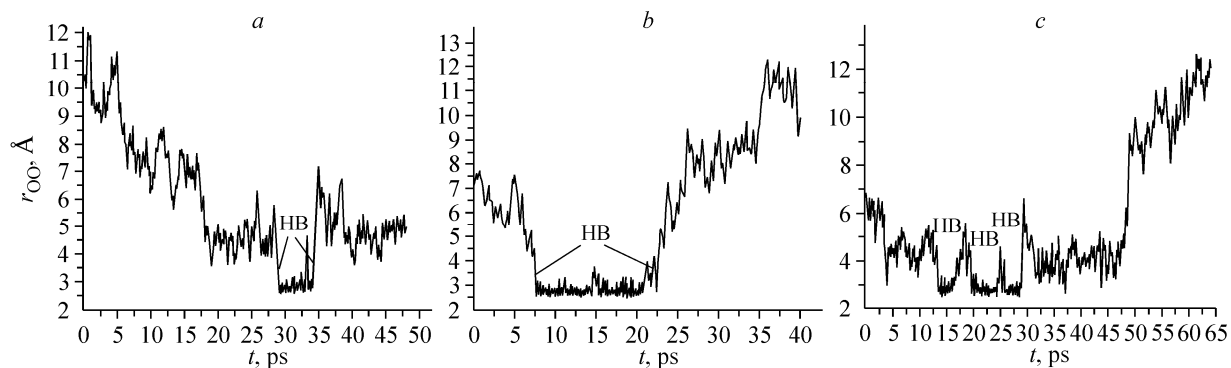


Fig. 3. Time dependence of the distance between oxygen atoms (r_{OO}) in different pairs of water molecules. (a) Within the time interval from 6 ps to 17 ps, r_{OO} was 6-8 Å, and then the water molecules approached each other to 4-5 Å (this r_{OO} corresponds to the second peak of the radial distribution function g_{OO}); after 28 ps, a hydrogen bond formed between them. It broke after 34 ps. After this, molecules stayed at a distance of 5-7 Å for some time and then approached to 4-5 Å. (b) At first, r_{OO} was 6-8 Å, then a hydrogen bond formed, which existed for about 20 ps. The molecules moved away, but r_{OO} stayed within the range 8-9 Å for ~10 ps and 12-15 Å for the last 5 ps. (c) At first, r_{OO} was about 6 Å, then it decreased to 4-5 Å, and a hydrogen bond formed. It existed with short interruptions for longer than 10 ps. Then for about 15 ps r_{OO} was 4-5 Å, after which it greatly increased, and the molecules started to move away from each other.

Molecules often stayed, for sufficiently long times, at almost constant distances from one another, which noticeably exceeded the typical hydrogen bond length (Fig. 3).

Several hundreds of dependences such as those shown in Figs. 2 and 3 were considered. The distances between oxygen atoms can stay nearly constant for long periods of time (10 ps and longer) and fluctuate around average values of 5 Å, 10 Å, 12-13 Å and larger. However, shorter distances between molecules may not be constant. This suggests that clusters of molecules that move in a concerted way are branched rather than compact ensembles. This conflicts with the theory developed by I. Z. Fisher and his followers. According to it, the collective motion of molecules in liquids is represented as a motion of the Lagrange particle, i.e., a compact “solid” ensemble [10-13].

In order to examine this in detail, we obtained a 50 ps long molecular dynamic trajectory and recorded 50 configurations separated by one virtual picosecond. Lists of hydrogen bonds were composed for all configurations and then compared. Hydrogen bonds were found using a simplified geometric criterion, $r_{OO} < 3.3$ Å. The 25th configuration was chosen as the basic one. The lifetimes of its hydrogen bonds were determined by comparing its list of hydrogen bonds with the lists of 25 previous and 25 subsequent configurations. This is a rather rough estimation. If a bond between two molecules was revealed in two configurations separated by one picosecond, it was assumed that it had not been broken. From the viewpoint of a collective motion study, it is not really important whether the bond was broken or not during this picosecond. The molecules could not drift far from each other and none of them could leave the collective ensemble. A more thorough investigation of lifetimes using a more realistic dynamic criterion of hydrogen bonds [21, 22] should lead to increased lifetimes in comparison with those roughly determined by us. The distribution of H-bond lifetimes (Fig. 4) and the average lifetime of 6.8 ps, therefore, correspond to a picture painted with rough strokes (in 1 ps). The average lifetime of a hydrogen bond determined more correctly must be shorter.

The software system created by us allows the hydrogen bond network (for example, of the 25th configuration) to be colored according to hydrogen bond lifetimes. We can color the bonds whose lifetimes fall in a particular range. It was found that bonds living longer than 7 ps form an infinite cluster. Of course, not all bonds enter into it. The bonds living longer than 8 ps do not form an infinite cluster. This means that the percolation threshold for the lifetime is between 7 ps and 8 ps. It is interesting that the average hydrogen bond lifetime determined by our rough method (6.8 ps, Fig. 4) is very close to the percolation threshold. The bonds living longer than 8 ps form large branching clusters, some of which include hundreds of bonds (Fig. 5c). The network in which the bonds living longer than 15 ps are colored breaks up into a variety of small clusters

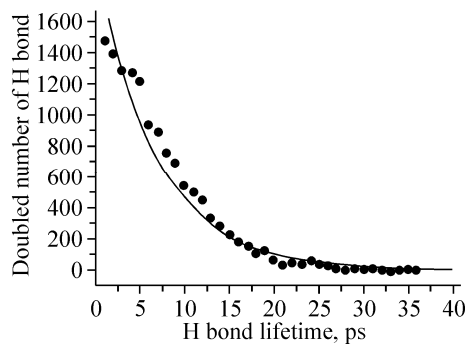


Fig. 4. Lifetime distribution of hydrogen bonds. 50 configurations of a system of 3456 water molecules are considered. The average lifetime of H bonds is 6.8 ps. The line is the exponential $y = 2000 \exp(-t/6.8)$.

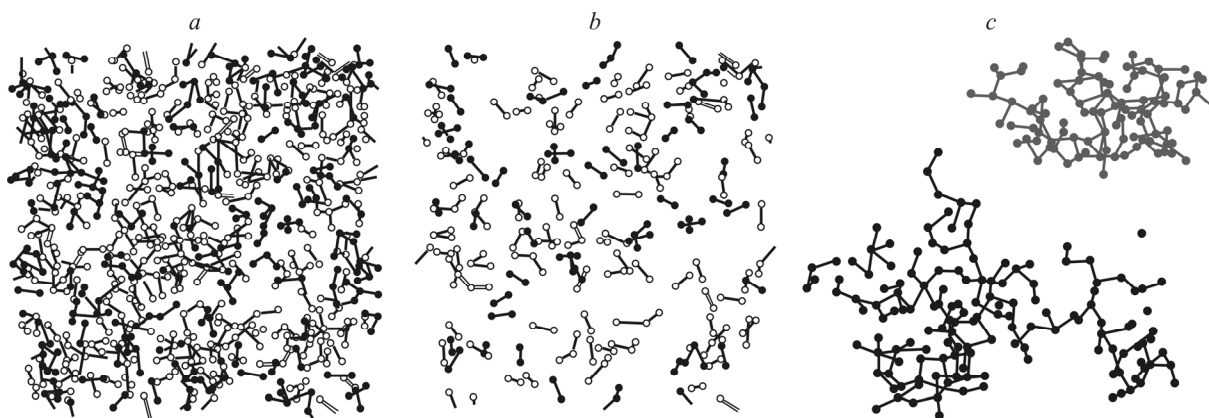


Fig. 5. Coloring of hydrogen bonds according to their lifetimes. Clusters of molecules involved in bonds living longer than the time period t are shown. The single bonds are omitted. (a) $t = 15$ ps; (b) $t = 20$ ps. Molecules group in small clusters. (c) $t = 9$ ps. Clusters of more than 100 particles are shown, namely, clusters of 152 (bottom) and 104 (top) molecules. Molecules do not form an infinite cluster but are united into large branching clusters. At $t < 8$ ps, molecules form an infinite cluster (but not all of them enter into it).

including 2, 3, 4, rarely 5 nodes (molecules). Typically, cycles are seldom met in these clusters. These are linear clusters, as a rule. Thus, there are many complexes in which molecules are bound to move in a concerted way. This implies that collective motions play an important role in self-diffusion of molecules in water. However, quantitative determination of this role remains a challenge.

It seems interesting that the coloring of the network according to H bond lifetimes is practically identical to random coloring, corresponding to the fraction of colored bonds with the given lifetime. This means that cooperativity of hydrogen bonds is not revealed at periods of time longer than 5 ps, and it is possible to create a theory of collective motions based only on combinatorial analysis.

We tried to determine the dependence of the self-diffusion coefficient for water molecules on the lifetime of hydrogen bonds in which they are involved. For this purpose, we found the dependences of the mean square shift of oxygen atoms separately for molecules involved in at least one hydrogen bond that lived longer than some period of time t and for all other molecules (Fig. 6). It was revealed that the slope of this dependence (on the part of the curve corresponding to time periods longer than 2 ps) is smaller for molecules participating in long-lived bonds.

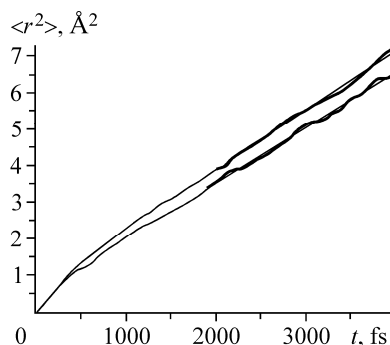


Fig. 6. Time dependence of the mean square shift of molecules involved in at least one hydrogen bond that lives longer than 8 ps (lower curve) and all the others (upper curve). Linear approximation was performed for the part of the curves at $2 < t < 4$ ps. The slope of the curve (and hence, the self-diffusion coefficients) for molecules participating in long-lived bonds is slightly smaller than that of the others. The calculated self-diffusion coefficient is $2.5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ for the lower curve and $2.7 \cdot 10^{-5} \text{ cm}^2/\text{s}$ for the upper curve.

CONCLUSIONS

The dynamic simulation (at room temperature) of a system of several thousands of water molecules with periodic boundary conditions revealed many pairs of molecules involved in a concerted motion. The latter shows itself as the distances between molecules that remain constant for long periods of time (10 ps and longer). The distance may be comparable to or larger than the hydrogen bond length. The pairs of molecules involved in the concerted motion can make joint jumps. A particular molecule has in its surroundings both molecules separated from it by constant distances (staying constant for long periods of time) and molecules quickly moving away. Thus, it is difficult to isolate a Lagrange particle that moves as an entity in water. Molecules involved in long-lived bonds with one another certainly move as an entity. However, they form branching but not compact clusters. Molecules involved in H bonds that exist longer than 7 ps form an infinite branching cluster. But inside these clusters are molecules that participate only in short-lived bonds and quickly move in space. The self-diffusion coefficient of the molecules involved in long-lived bonds is slightly smaller than the self-diffusion coefficient of the molecules that do not participate in these bonds. However, this difference is not large and probably unreliable.

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