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(2, Pirogova Str., Novosibirsk 630090, Russia; e-mail: naber@ngs.ru)**LONG-TERM CORRELATIONS IN DIFFUSIVE
MOTION OF WATER MOLECULES AND RARE GAS
ATOMS IN HELIUM AND ARGON AQUEOUS SOLUTIONS**

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Collective effects in the diffusive motion of aqueous systems consisting of 10,000 particles (pure water, He and Ar aqueous solutions) are studied, by using the molecular dynamics simulation. The two-particle correlation function $DP(t)$, which is the average scalar product of the displacement vectors of two molecules initially separated by distances lying in certain narrow intervals, is calculated. The calculations were carried out for water molecules and for atoms of rare gases. The presence of He and Ar atoms in 3%-solutions is shown to weakly affect the form of the $DP(t)$ function for water molecules. For He and Ar atoms in aqueous solutions, as well as in the cases of water molecules and Ar atoms in pure liquids, the corresponding correlation functions are found to have a plateau. For a system composed of 1,000 Ar atoms and 9,000 water molecules, no homogeneous liquid solution is obtained even at high pressures.

Keywords: molecular dynamics, diffusive motion, collective effects, He and Ar aqueous solutions.

1. Introduction

Diffusive motion in liquids is not one-particle by character, but always contains plenty of collective components that are different by magnitude and lifetime. While studying them, it is very useful to use two-particle correlation functions. However, it is very difficult to obtain those functions in the course of a real physical experiment. Therefore, we proposed to study the collective character of diffusive motion on the basis of molecular dynamics models for liquids and solutions, when the coordinates and velocities of all atoms are known at any moment. In order to study collective effects in liquid, we used two-particle correlation functions of various forms, which were described in our work [1] in detail. The most interesting among them seems to be the behavior of the function designated in our publications as $DP(t)$,

$$DP(t) = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)] \cdot [\mathbf{r}_k(t) - \mathbf{r}_k(0)] \rangle_{R0}.$$

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This is the average scalar product of the displacement vectors of two molecules initially located at the given distance $R0$ from each other. This function first grows and then forms a plateau. The altitude of the latter diminishes, as the initial distance $R0$ increases, and becomes negative at large $R0$ (see Fig. 1). This typical form of the correlator $DP(t)$ is observed in both the water [1] and liquid argon [2] models. Such a behavior may probably reflect the common property of all dense liquids, which is presumably associated with the existence of mesoscopic vortex-like collective motions in them [1, 3]. In this work, we intend to clarify whether the function $DP(t)$ has a similar behavior for atoms of rare gases dissolved in water.

We simulated aqueous solutions of helium and argon. Those atoms strongly differ by mass: the argon atom is 10 times heavier than the helium one. They interact with water quite differently. At room temperature and under atmospheric pressure, argon dissolves in water almost four times better than helium does. The solubility of helium has a minimum at a temperature of about 35 °C, whereas the solu-

bility of argon monotonously decreases in the temperature interval from 0 °C to 100 °C (see Tables 32 and 33 in work [4]). Argon forms four different hydrates [5], three of which can be called clathrate. Helium does not form classical clathrate hydrates, i.e. when its atoms occupy polyhedral voids in the water frame. Instead, it forms interstitial solid solutions with ice modifications ice Ih [6, 7] and ice II [8–11]. Since the solubility of helium and argon is very low at atmospheric pressure (at 25 °C, the solubility of helium equals 7×10^{-6} mole fraction, and that of argon 2.52×10^{-5} mole fraction), the correlations in the motion of their atoms should be studied by performing a simulation for elevated pressures. At atmospheric pressure, the solubility of helium in ice Ih and liquid water is approximately identical. As the pressure grows, the ratio between the solubility in ice to the solubility in water grows and reaches a value of 2 at a pressure of 80 atm [7]. At a pressure of about 2 kbar, ice Ih transforms into ice II. The structure of the latter contains three times less voids than the structure of ice Ih, but those voids are larger. Under the helium pressure, the composition of interstitial solid solutions in ice II can reach $\text{He} \cdot 6\text{H}_2\text{O}$ [8, 9, 11]. The dependence of the helium solubility in liquid water on the pressure was also studied in works [12] (to a pressure of 1000 atm) and [13] (to 600 atm). The pressure dependence of the helium solubility was discussed in work [14]. At the same time, the dependence of the argon solubility on the pressure was studied much less thoroughly. In work [15], the argon solubility at a temperature of 25 °C was studied in a pressure interval of 25–101 atm, and the corresponding value of Henry constant was quoted. The values of Henry constants for the helium solubility in water are presented in work [16]. These data can suggest that solubility of argon at high pressures is higher than that of helium.

2. Methods

The simulation was carried out, by using the molecular dynamics method on the basis of software package LAMMPS. The parameters of the Lennard-Jones interaction potential between identical atoms were selected as follows: for H atoms, $\varepsilon = 0.046$ kcal/mol and $\sigma = 0.40$ Å; for O atoms, $\varepsilon = 0.1521$ kcal/mol and $\sigma = 3.150574$ Å; for Ar atoms, $\varepsilon = 0.23827$ kcal/mol and $\sigma = 3.405$ Å; and, for He atoms, $\varepsilon =$

$= 0.020296$ kcal/mol and $\sigma = 2.556$ Å. The parameters of the interaction between different atoms were calculated as the arithmetic (for σ) or geometric (for ε) mean of the corresponding atomic values. The interaction between water molecules was described by means of TIP3P potential. The total number of molecules in every model amounted to 10,000. The temperature was put to equal $T = 310$ K. Before the calculations of the correlation functions started, all model systems were relaxed for 2 to 10 ns in order to obtain quasistable configurations.

The following models were analyzed:

- 1) pure water; the edge of a cubic cell $a = 66.9665$ Å and $P \approx 0$;
- 2) the mixture water (9,700 molecules) + argon (300 atoms, 3%); $a = 67.5701$ Å and $P \approx 0$;
- 3) the mixture water (9,700 molecules) + helium (300 atoms, 3%); $a = 66.9477$ Å and $P \approx 0$;
- 4) the mixture water (9000 molecules) + argon (1,000 atoms, 10%); $a = 69.5764$ Å, and the pressure was raised, until a homogeneous solution was formed;
- 5) the mixture water (9,000 molecules) + helium (1,000 atoms, 10%); $a = 65.1792$ Å, and the pressure was raised until a homogeneous solution was formed.

At the initial moment, the atoms of rare gases were uniformly distributed over the cell volume. While simulating the systems containing 10 mol.% of gases, a phase separation was observed at low pressures; namely, gas atoms aggregated into a droplet (Fig. 3). The pressure grew to a value, which allowed the initial homogeneous solution with the uniform distribution of gas atoms in space to be maintained.

The function $DP(t)$ was calculated for those atomic pairs, in which the initial interatomic distance fell within a narrow interval $R_0 \pm \Delta R$. The calculation procedure was described in work [1] in detail. Using the molecular dynamics method in the NVT-ensemble with a simulation step of 2 fs, the model trajectories of various lengths were calculated. The instant configurations of atoms were registered every 2 ps. Afterward, the initial distances in molecular pairs forming a certain selected configuration called “reference” were compared with their counterparts in the next 500 configurations, i.e. within the 1-ns time interval. The results were averaged over a large number of reference configurations belonging to a model trajectory section, the duration of which considerably exceeded the expected characteristic time of sought correlations. For pure water, a trajectory with the

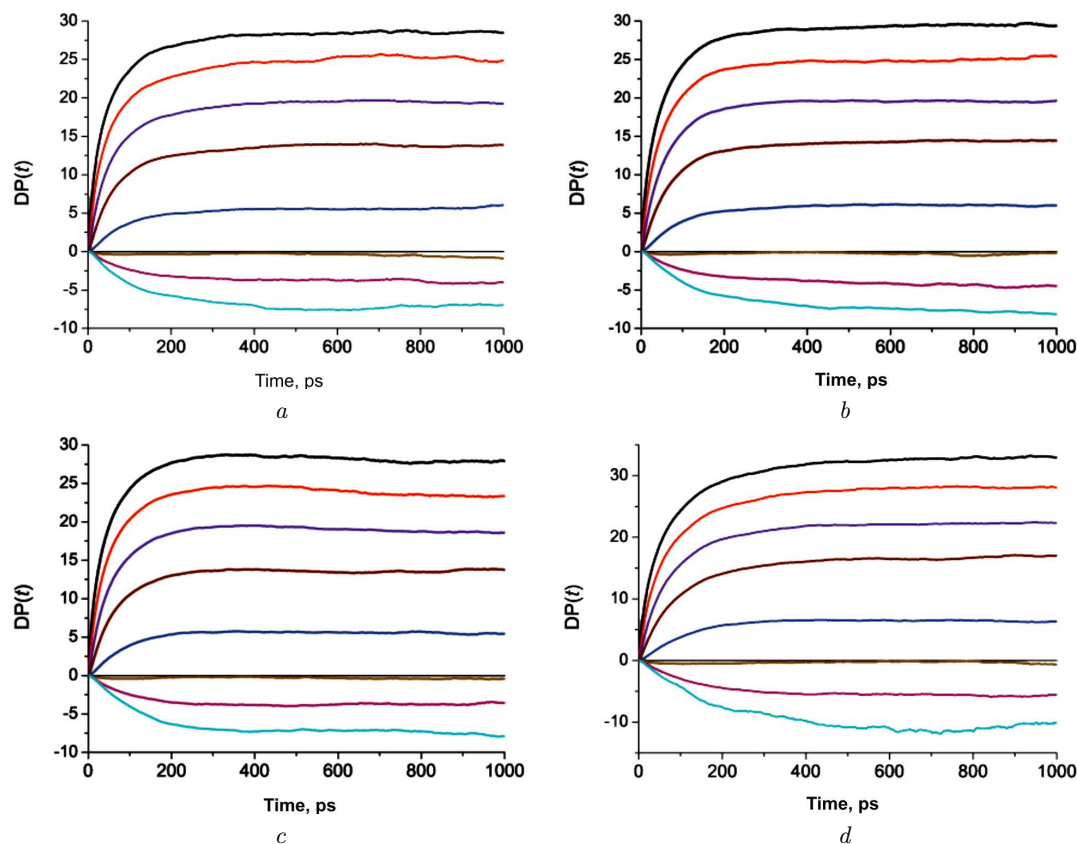


Fig. 1. Time dependences of the correlator, $DP(t)$, for oxygen atoms of water molecules in molecular-dynamic models: pure water (a), 3% solution of argon atoms in water (b), 3% solution of helium atoms in water (c), and 10% solution of helium atoms in water ($P = 5$ kbar) (d). Curves correspond to various initial distances R_0 between the particles in the pair: 3, 5, 8, 12, 20, 30, 40, and 57 Å (from top to bottom). A temperature equals 310 K

shortest length equal to 4 ns was used, in which the first 1,500 configurations from the initial 3-ns section were used as reference ones. The reduction in the number of molecular pairs or their higher diffusive mobility required a more careful averaging. Therefore, for 10% of solutions, 21-ns trajectories were used. The trajectory increased to 37 ns for the 3% solution of argon and to 101 ns for the 3% solution of helium. In the latter case, the largest number of reference configurations, 50,000, were used; nevertheless, the averaging quality left much to be desired.

3. Results Obtained and Their Discussion

The correlation functions $DP(t)$ for oxygen atoms of water molecules in the solutions concerned practically do not differ from those functions in pure water (Fig. 1). The only difference consists in that, for

the 10% helium solution (Fig. 1, d), the plateau altitude is a little higher than in other cases. The correlators $DP(t)$ for rare gas atoms in aqueous solutions also form a plateau (Fig. 2). Since the number of gas molecules in the solutions is much smaller than the number of water molecules, the fluctuations of those functions are much stronger than for oxygen atoms. This effect is the most pronounced for helium atoms in the 3% solution (Fig. 2, b), with their self-diffusion coefficient being 2.5 times higher than that of argon atoms (Table). Notwithstanding the noise background in the curves, it is evident that the plateau altitudes are much higher for argon and lower for helium, than for water (at identical R_0). This fact can be a subject of further researches.

As was mentioned above, while simulating the helium and argon solutions containing 10 mol.% of rare gas atoms, the latter aggregated into a droplet at low

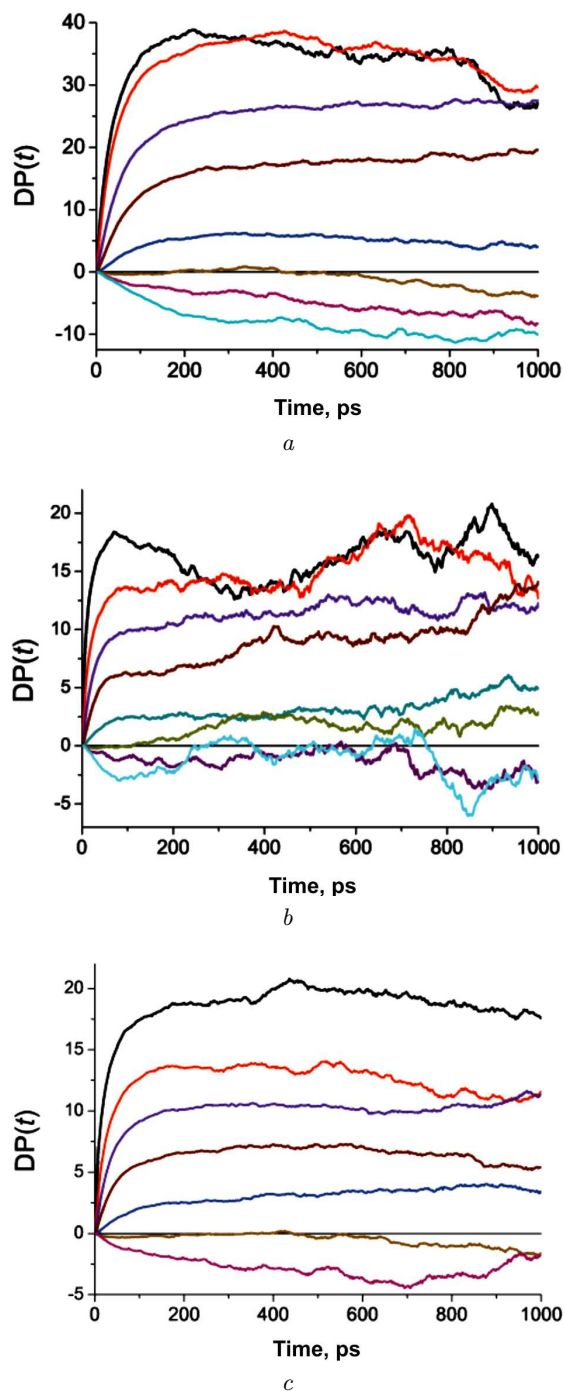


Fig. 2. Correlator $DP(t)$ for rare gas atoms in aqueous solutions: 3% solution of argon atoms in water (a), 3% solution of helium atoms in water (b), and 10% solution of helium atoms in water ($P = 5$ kbar) (c). Curves correspond to the same initial distances between the particles in the pair as in Fig. 1. The curve for $R_0 = 57$ Å in panel c is absent

pressures (Fig. 3). In the case of helium solutions, the homogeneous solution was obtained at a pressure of about 5 kbar. The argon solutions underwent the phase separation at much higher pressures. The tendency of argon atoms to form a droplet stopped only at a pressure of 50 kbar. However, the self-diffusion coefficients of argon atoms and water molecules at this pressure became so low (Table) that the solution was not a liquid anymore, but sooner a softened and vitreous medium. We recall that it is ice VII that is a stable phase of water at a temperature of 310 K and a pressure of 50 kbar. Neither nuclei of ice crystals nor nuclei of rhombic argon hydrate PCII, which is stable at those parameters, did we manage to detect in our calculations [17]. Probably, this model system is not a liquid. Therefore, we do not write its correlation functions and compare them with the previous ones. On the contrary, the 10% helium solutions at a pressure of 5 kbar are quite liquid, and the corresponding correlators $DP(t)$ for them are depicted in Figs. 1, d and 2, c.

The self-diffusion coefficients calculated for our models are summarized in Table. One can see that the water-water interaction potential used in this work results in the overestimation of the self-diffusion coefficient. Potentials SPC/E and TIP4P bring about results that are closer to those obtained experimentally. Even better agreement with experiment is given by potential PM often used by us [19] (see Fig. 1 in work [20]). But, in this work, we did not intend to reproduce all properties of simulated systems. Our aim was to show that the two-particle correlation functions for Lennard-Jones particles dissolved in a water-like solvent behave identically to those for water molecules and Lennard-Jones particles in the corresponding liquid phase. The fact that the behavior of those functions is qualitatively identical for liquid water simulated with the use of various potential functions was demonstrated by us earlier [1].

The data in Table testify that the self-diffusion coefficient of water molecules in the 3% helium solution is almost the same as in pure water and is a little lower in the 3% argon solution. The self-diffusion of argon atoms in the 3% argon solutions is slower than the self-diffusion of water molecules. Consequently, it is no wonder that the self-diffusion of water in this mixture slowed down. The self-diffusion coefficient D of helium in the 3% solutions of helium is

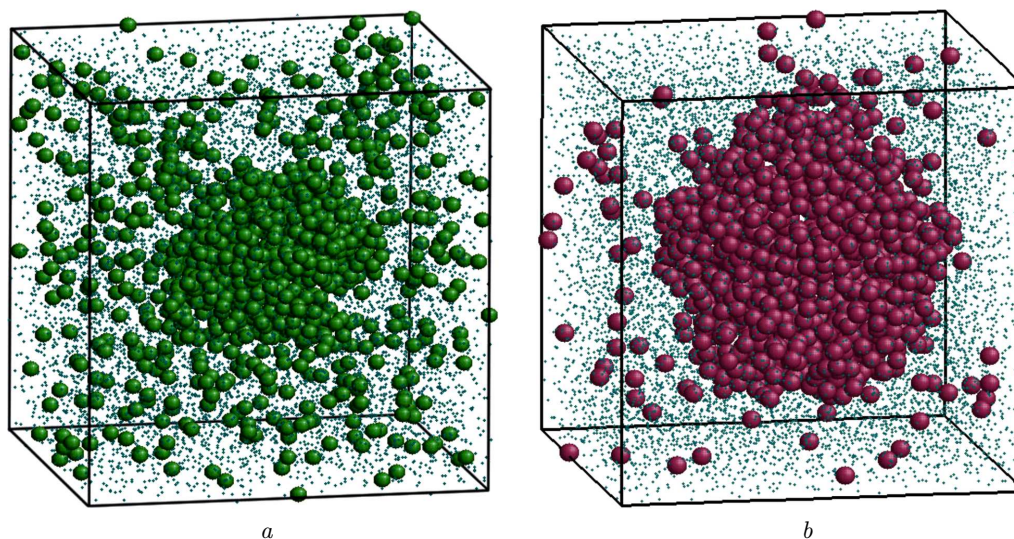


Fig. 3. Formation of droplets by noble gas atoms in the 10% solutions at low pressure: helium solution (left panel), argon solution (right panel). Balls correspond to gas atoms, and points to water molecules

much higher than the corresponding value for water. However, the self-diffusion of water got slower in this case as well, although not so strongly. Only in the 10% solutions, the characters of diffusive motion exerted by water molecules and rare gas atoms are changed substantially.

The homogenization in our model of 10% argon solution took place at much higher pressures in comparison with the model of 10% helium solution. It could be expected, because the Henry constant for helium considerably exceeds the corresponding value for argon. The ratio between the Henry constants equals 2.36 for nitrogen and argon [15], and 1.35 for helium and nitrogen [16].

Self-Diffusion Coefficients D in Simulated Systems ($10^5 \text{ cm}^2/\text{s}$)

System	Pressure, kbar	Water	Argon	Helium
Pure	~ 0	6.92*	3.33**	–
3% Ar	~ 0	6.54	6.26	–
10% Ar	~ 50	0.14	0.049	–
3% He	~ 0	6.86	–	16.4
10% He	~ 5	4.87	–	9.56

* Result were obtained with model potential TIP3P. Simulation with other potentials gives $D = 3.52 \times 10^5 \text{ cm}^2/\text{s}$ (SPC/E) and $3.39 \times 10^5 \text{ cm}^2/\text{s}$ (TIP4P). The experiment value equals $3.027 \times 10^5 \text{ cm}^2/\text{s}$ [18].

** For a system of 500000 argon atoms, $T = 132 \text{ K}$.

Among other two-particle correlators, we would like to attract attention only to the values of average cosines between the displacement vectors that appear in the formula for $DP(t)$. We will designate this parameter as AC . The AC value in the initial trajectory section, AC_0 , practically does not depend on the number of particles in the system and slightly depends on the temperature for particles that are in contact with one another at the initial time moment (for water, these are molecules linked by a hydrogen bond). The AC_0 magnitude can be a good characteristic for the correlation degree of motions for the particles of this type. For water (pure and in gas solutions), this quantity is close to 0.34, for helium atoms in the 3% and 10% aqueous solutions to 0.15, and for argon atoms in the 3% solution to 0.21. It is of interest that the AC_0 magnitude for pure liquid argon is also close to 0.21 (50,000 and 500,000 atoms in the periodic cell, a temperature of 132 K). For clear reasons, we did not simulate the dynamics of liquid helium. This phase exists at very low temperatures, when quantum-mechanical effects play a crucial role.

4. Conclusions

Hence, we have established that the time dependences of the correlator $DP(t)$ —the scalar product of displacement vectors of two particles—for helium and ar-

gon atoms dissolved in water behave identically to those for water molecules in pure water and argon atoms in liquid argon. First, they grow, and then form a plateau. The plateau altitude decreases as the initial distance between particles, R_0 , increases. The presence of rare gas atoms weakly affects the form of the correlation functions for water molecules. The magnitudes of correlation coefficients AC_0 —the average cosines of angles between the displacement vectors for pairs of particles contacting with each other at the initial time moment—are smaller for atoms of rare gases than for water molecules. The correlation coefficient AC_0 for helium is smaller than for argon. The AC_0 -values for argon atoms dissolved in water and in pure liquid are almost identical.

It is a great pleasure and honor for us to be published in the special issue of Ukrainian Journal of Physics devoted to the anniversary of L.A. Bulavin. The communication with Leonid Anatoliyovich and his team was always interesting and resulted in the generation of new ideas. In particular, the direction of researches [1], which this work belongs to, appeared owing to this communication and was stimulated by the excellent review [21].

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ДОВГОТРИВАЛІ КОРЕЛЯЦІЇ
В ДИФУЗІЙНОМУ РУСІ МОЛЕКУЛ ВОДИ
І АТОМІВ БЛАГОРОДНИХ ГАЗІВ У РОЗЧИНАХ
ГЕЛІЮ І АРГОНУ

Резюме

Методом молекулярної динаміки досліджувалися колективні ефекти дифузійного руху у водних системах з 10 000 частинок: чистої води і розчинів в ній гелію і аргону. Розраховано двочастинкову кореляційну функцію $DP(t)$ – середній скалярний добуток векторів зсуву двох молекул, початкові відстані між якими знаходяться в заданих вузьких межах. Такі розрахунки проведено для молекул води і для атомів благородних газів. У 3% розчинах присутність атомів гелію або аргону мало впливає на вид функції $DP(t)$ для молекул води. Ці функції для атомів гелію і аргону в водних розчинах виходять на плато, так само як і у випадку молекул води і атомів аргону в чистих рідинах. Для системи 1000 атомів аргону + 9000 молекул води не вдалося отримати рідкий однорідний розчин ні при яких тисках.