

HELIUM, NEON, AND WATER

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The molecular dynamics method is used to study liquid aqueous solutions of helium and neon, liquid water films and solid films with an ice II structure in helium and neon atmospheres, and solid solutions of helium and neon in ice II. Gas atoms wander randomly in water and make occasional slow jumps. The structure of the hydrate shell of the gas atoms bears little resemblance to the structure of ice II and other ice modifications. The solubility of neon in a water film is only a little higher than that of helium. Helium and neon atoms that find themselves in the channels of a thin ice II film make the same jumps along the channels as those along the channels in the structure of ice II crystals. The motions of two neon atoms in the neighboring (along the z axis) planes are correlated, whereas there is no correlation between the motions of helium atoms.

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INTRODUCTION

In [1], a comparison was made between some of the structural features of liquid water and argon and a discussion was provided on the behaviour of argon in aqueous solutions and thin water films and in the voids of CS-II clathrate hydrate, which is stable at low pressures. Some aspects of these problems were also discussed in our publications [2-4]. The relations between helium and water are completely different from those between argon and water. The water solubility of argon, as well as many other gases, decreases at atmospheric pressures in the range of existence of liquid water, whereas the solubility of helium passes through a minimum at about 30 °C [5]. The water solubility of neon, as well as argon, decreases with increasing temperature [5]. In contrast to argon, helium and neon form no clathrate hydrates in a strict sense of the word, i.e., those in which noble gas atoms are in convex polyhedra with many pentagonal faces. The crystalline substances that are sometimes called helium and neon clathrate hydrates are, in fact, interstitial solid solutions in ice Ih [6, 7], II [8-13], and Ic [14, 15]. However, helium and neon atoms can get inside the voids of “normal” clathrate hydrates formed by other substances, e.g., tetrahydrofuran (CS-II structure [16, 17]) and methane (CS-I structure [18]), and stabilize these clathrate hydrates. In this article, we discuss the results of computer simulations of helium–water and neon–water systems and investigate bulk aqueous solutions of helium and neon (with concentrations of about 3 mol.%), thin liquid water films in an equilibrium with neon or helium, solid helium and neon solutions in ice II, and thin ice II-structure water films surrounded by noble gas atoms. The latter systems were simulated to trace how gas atoms get inside the ice II channels.

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RESEARCH METHODS

All the results discussed in this article come from computer simulations (molecular dynamics method). The simulations were run with the software derived from programs used to simulate argon CS-II clathrate hydrate and a solid solution of helium and argon in ice II [19] and a liquid water film–argon and helium system [3]. The water–water interactions were described by the atom–atom potential functions proposed in [20]. Their parameters, as well as those of the Lennard-Jones helium–helium and helium–water potentials, are given in [3, 19]. Water–neon systems were simulated using atom–atom potential functions with the following parameters (in the formula $E = a/r^6 + b/r^{12}$): $a_{\text{Ne-Ne}} = -179.9$, $b_{\text{Ne-Ne}} = 78145.6$, $a_{\text{Ne-O}} = -359.34$, $b_{\text{Ne-O}} = 187351$, $a_{\text{Ne-H}} = -41.13$, and $b_{\text{NeH}} = 6735.7$. Energies were measured in kcal/mol; distances, in angstroms. The initial values of the parameters were taken from [21] and somewhat modified to consider the data in [22, 23] for neon–neon [24] and neon–water interactions.

The simulations of aqueous helium and neon solutions contained 103 noble gas atoms and 3353 water molecules. The initial configurations were obtained from the equilibrated configurations of aqueous argon solution in [1]. Argon atoms were “transformed” into helium and neon ones. The cubic periodic cell had an edge of 46.98 Å. The simulations were made in a microcanonical ensemble; the temperature of the simulated liquid systems was 300 K. Solid solutions and films were simulated at different temperatures, which are given in Results and Discussion.

The liquid water film–noble gas atoms system was simulated in the same way as in [3]. The rectangular periodic cell contained 3456 water molecules and 192 gas atoms. Its parameters were 60 Å, 60 Å, and 140 Å. In the middle of the cell, there was a 40 Å-thick water film with rough surfaces (Fig. 4), which was surrounded by gas atoms. There was an ongoing exchange of gas atoms between the gaseous phase and the film.

The simulations of the ice II–noble gas system used a cell containing 576 water molecules and a varying quantity (which cannot be more than 96) of gas atoms. The orthorhombic cell parameters were 22.486 Å, 25.9624 Å, and 25.012 Å.

In the simulations of the solid water film with an ice II structure–noble gas system, the cell parameter along the trigonal axis of ice II (the z axis of the orthorhombic simulation cell) was increased to 100 Å. A varying quantity of gas atoms was placed between images of a thin crystalline water film.

RESULTS AND DISCUSSION

Liquid helium and neon solutions. Simulations of aqueous helium and neon solutions were discussed in [25-27]. In this article, we consider those aspects of noble gas solutions that were usually overlooked in other works. Fig. 1 shows the time dependence of the coordinates of individual helium and neon atoms and the dependence of the x coordinate on the z coordinate, i.e., the projection of the atomic trajectory onto the xz plane. Evidently, the atoms wander randomly in space, making occasional slow jumps. The motion of water molecules in liquid water follows a similar pattern [28].

Previously, we studied aqueous helium and argon solutions in [29]. This study showed that 3% and 10% helium and 3 mol.% argon solutions have long-term correlations: the average scalar products of the displacement vectors of the two atoms, which are spaced at a certain distance from each other in the initial configurations, reach a plateau. Previously, we showed that the correlation in the motions of atoms and molecules also manifests itself in that the distance between two particles remains approximately constant during a certain period [4]. In this case, the cosine between the displacement vectors of the particles ($\cos\alpha$, or the correlation coefficient) is close to unity (Fig. 2*b*).

It was shown in [29] that the average cosine between the displacement vectors of closely located helium atoms in aqueous solutions at small times is 0.15, which is less than for water molecules (0.32) and argon atoms in liquid argon and in solution (0.21). The lower correlation of the motions of helium atoms appears to be due to the mobility of helium atoms (the diffusion coefficient is $16.4 \cdot 10^{-5} \text{ cm}^2/\text{s}$ versus $2.3 \cdot 10^{-5} \text{ cm}^2/\text{s}$ for water [29]). Experimental values of the diffusion coefficients for helium and neon are $7.22 \cdot 10^{-5} \text{ cm}^2/\text{s}$ [31] and $4.16 \cdot 10^{-5} \text{ cm}^2/\text{s}$ [31, 32], respectively. According to molecular dynamic

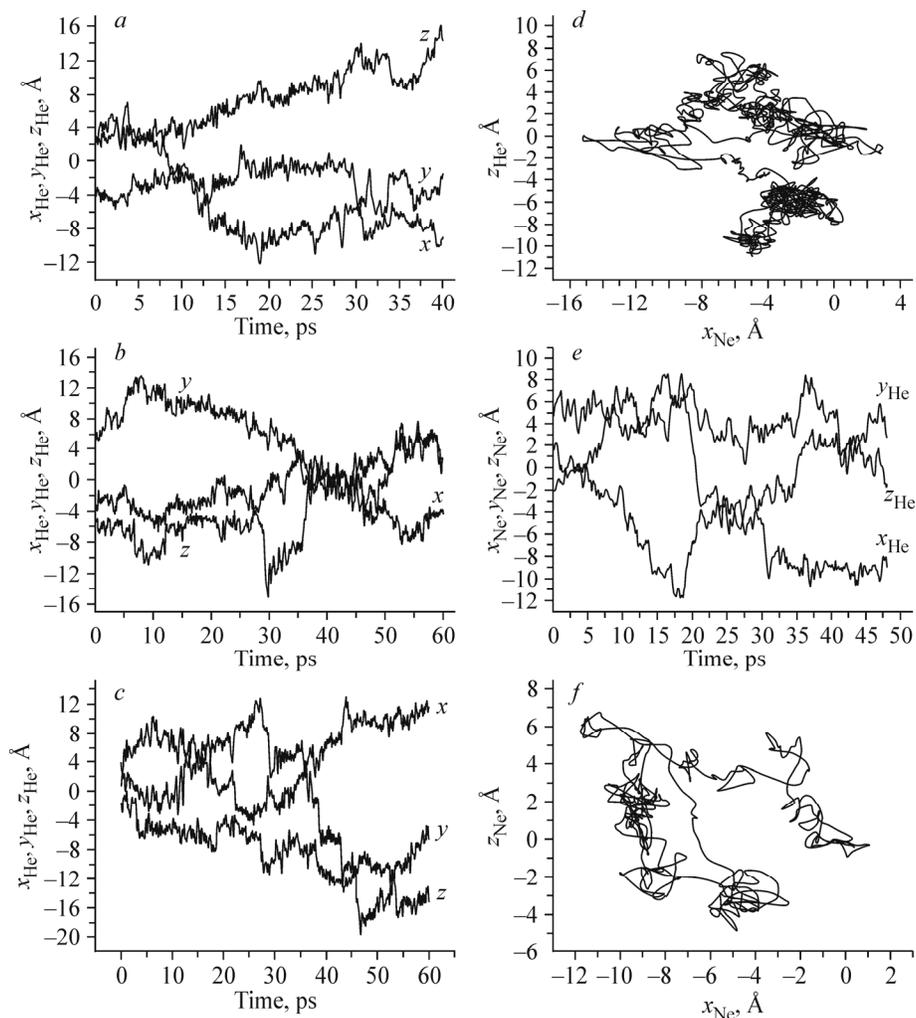


Fig. 1. Time dependences of the coordinates of helium and neon: (a), (b), (c), and (e). A projection of the trajectory of helium (d) and neon atoms (f) onto the xz plane. Aqueous solutions of helium and neon. $T = 298$ K.

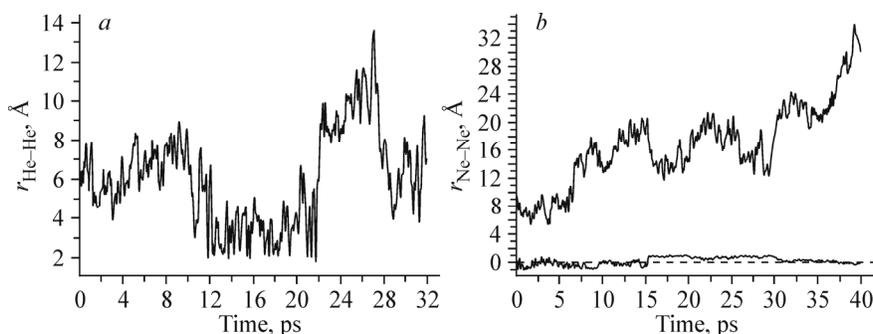


Fig. 2. Time dependence of the distance between two helium atoms in an aqueous solution (a). Between 12 ps and 22 ps, this distance was fluctuating around 3 Å. The upper curve is the time dependence of the distance between two neon atoms in an aqueous solution; the lower curve is the time dependence of the cosine of the angle between the displacement vectors of these neon atoms (b). Between 15 ps and 20 ps and between 25 ps and 30 ps, the cosine was close to unity.

calculations, the diffusion coefficient of helium is $10 \cdot 10^{-5} \text{ cm}^2/\text{s}$ [33] and $7.85 \cdot 10^{-5} \text{ cm}^2/\text{s}$ [27] and that of neon is $2.4 \cdot 10^{-5} \text{ cm}^2/\text{s}$ [33] and $2.57 \cdot 10^{-5} \text{ cm}^2/\text{s}$ [27].

The fact that the time dependences of the interatomic distances have intervals where this distance is approximately constant and that the $\cos\alpha$ dependences have intervals where the cosines are close to unity confirms the existence of a correlation in the motions of helium and neon atoms in aqueous solutions.

According to [1], the environment of noble gas atoms in argon solutions differs from their environment in clathrate hydrates. As mentioned above, it is typical of helium and neon to form solid solutions in ice Ih, II, and Ic. We considered dozens of structures associated with the nearest environment of these atoms in aqueous solutions, and we did not find a single case where their environment would resemble the structure of any ice modification. Typical structures of the hydrate shells of helium and neon are shown in Fig. 3.

Thin water films in helium and neon atmospheres. In [3], we presented some of the results obtained by studying thin water films in helium and argon atmospheres. Here, we present more accurate results obtained by a more rigorous simulation of films in a helium atmosphere and new results on films in a neon atmosphere. Fig. 4 shows a typical pattern of an instant configuration of a water film in a helium atmosphere.

The film surfaces are very rough. Fig. 5 shows the decrease in the number of molecules in a unit volume in the transition layer between the film and the gaseous phase (for more detail see [3] and [34]). Previously, we showed that the decrease in the density of water in the transition layer is largely due to the roughness rather than the local density of water: the local density of hills on the film surface is nearly the same as inside the film [3]. The thickness of the film (with the transition layer) is 36 Å. Inside the film, there are 40 to 50 helium or neon atoms. In [3], it was reported that the film contains an average of 30 helium atoms. Further studies showed that the number of helium atoms dissolved in the water film is somewhat higher. The average number of helium atoms is 42; that of neon atoms is 46. During the simulation, there is an ongoing exchange of gas atoms between the film and the gaseous phase. The dimensions of our periodic cell are 60 Å, 60 Å, and 140 Å; the film thickness is 36 Å. Consequently, if all noble gas atoms were located with the same density as on

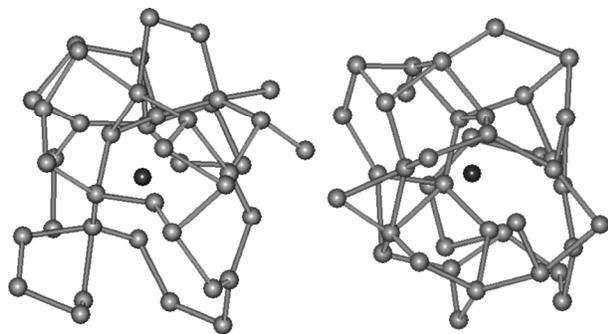


Fig. 3. Environment of noble gas atoms in water: helium on the left and neon on the right. The figure shows the oxygen atoms in water molecules at a distance of up to 6.5 Å from gas atoms. The figure also shows the hydrogen bonds.

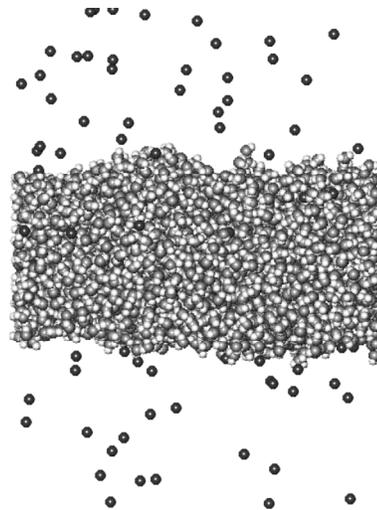


Fig. 4. An instant photograph of a water film in a helium atmosphere. The figure shows the helium atoms that are nearest to the film. In total, the independent periodic cell contains 192 helium atoms (dark balls) and 3456 water molecules (grey). View along the y axis. The z axis is perpendicular to the film surfaces. The figure shows that the surface is rough. The origin of coordinates is at the center of the film. Inside the film ($|z| < 18 \text{ Å}$), there are 41 helium atoms.

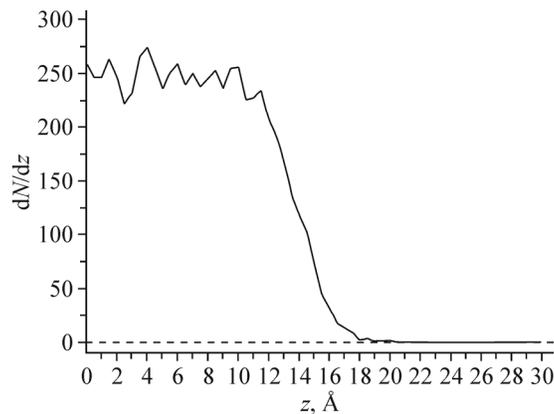


Fig. 5. Transition layer of the film shown in Fig. 4. N is the number of water molecules in a layer with a thickness of $2z$. At $z > 18$, $N = 3456$ (in this case, there are no evaporated molecules). The transition layer has a thickness of 8 \AA ($10 \text{ \AA} > |z| > 18 \text{ \AA}$).

average across the cell, the film would contain 49 atoms. Thus, the concentration of gas atoms in the film is only a little lower than in the gaseous phase. The film contains, on average, 120 argon atoms [3]; argon is approximately 2.5 times more soluble in the film than helium and neon. According to the data in [5], at an atmospheric pressure and at $25 \text{ }^\circ\text{C}$, the argon/helium and neon/helium solubility ratios are 3.6 and 1.17, respectively. It should be noted that our model systems had different pressures. Based on the quantity of gas atoms in the gaseous phase, it can be estimated at 21.3 atm for helium, 20.7 atm for neon, and 10 atm for argon. For more details on the pressure dependence of the water solubility of helium and argon, see [29].

We considered many instant photographs of the environments of helium and neon in water films. They are no different from their environments in bulk water and bear absolutely no resemblance to their environments in interstitial solid solutions.

Helium and neon in ice II. In [19], we showed that helium atoms diffuse along the channels in the structure of ice II. This diffusion is observed if some of the voids in the structure are not filled. If all the voids are filled (i.e., the composition of the solid solution is $\text{He}\cdot 6\text{H}_2\text{O}$), there is no diffusion. We observed the dynamics of individual helium and neon atoms in ice II.

Helium and neon atoms make occasional jumps along the z axis. Most of the jumps end in a neighboring void of the ice II structure. The jumps are about 3 \AA in length and about 0.3 ps in duration (Fig. 6*a*). A few jumps skip one void, i.e., end in a void next to a neighboring one. These jumps are about 6 \AA in length and about 0.6 ps in duration (Fig. 6*b*). Neon atoms make similar jumps. We discuss them below, in the section about films with an ice II structure.

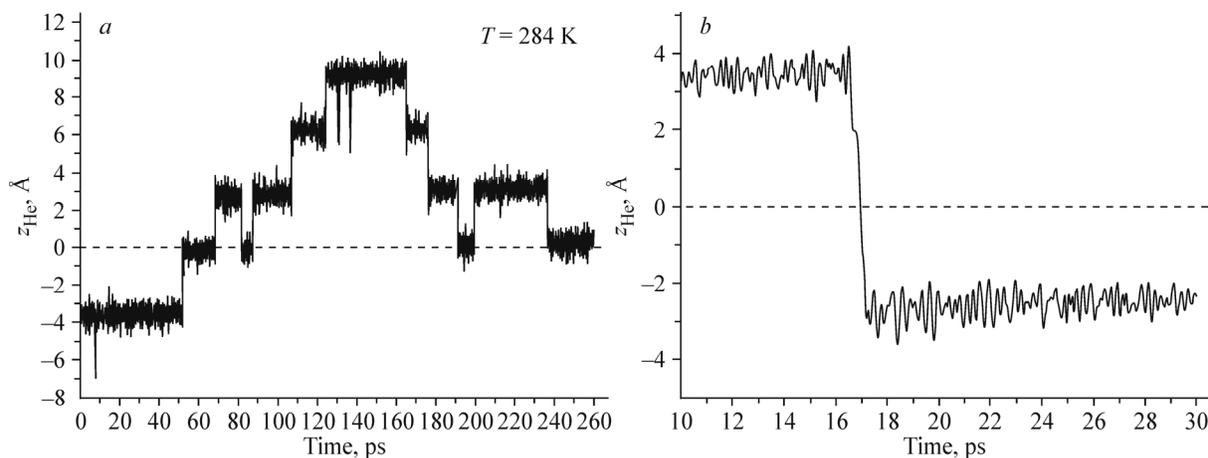


Fig. 6. Jumps of the helium atoms in the channel of the ice II structure ($T = 284 \text{ K}$).

We placed two helium atoms and two neon atoms in neighboring voids (places where the channels are wider) and calculated the cosine of the angle between their displacement vectors. The atoms made no jumps during this time. The average cosine (correlation coefficient [30]) was about zero for helium and 0.36 for neon. This indicates that the motions of the helium atoms in neighboring voids are not correlated, unlike those of the neon atoms, for which the correlation is quite high. It should also be noted that the distance between the neon atoms was modulated by amplitude (with a period of about 15 ps). We also calculated the cosines of the angles between the displacement vectors of the oxygen atoms in two H-bonded water molecules in ice II. The average cosine was 0.514 at 231 K and 0.509 at 254 K. We observed no modulation by the amplitude of the oscillations. Thus, the oscillations of water molecules proved to be more correlated than those of the neon atoms in neighboring voids of the ice II framework. The higher correlation between the motions of the neon atoms, compared with helium, appears to be due to the larger mass of neon and the stronger interaction between neon atoms.

Thin films with an ice II structure in helium and neon atmospheres. The figures show a few episodes from the life of helium (Fig. 7) and neon atoms (Figs. 8 and 9) in gas atoms–ice II film systems. Figs. 7*d* and *e* and 8*a* and *b* show their unsuccessful attempts to get into the channel. The gas atoms approach the film, wander across its surface, and fly away. Figs. 7*a* and *b* and 8*c* and *d* show the successful attempts. The gas atoms wander across the surface and get inside the channel. In this case, the helium atom makes a jump along the channel in the same way as it did in the ice II crystal (Fig. 7*a* and *b*). The neon atom is observed to make repeated jumps along the channel of the ice II film (Fig. 9), including long jumps, as in the case of the helium atom (Fig. 9*b*). The duration of the jumps of neon atoms is somewhat higher than that of helium atoms.

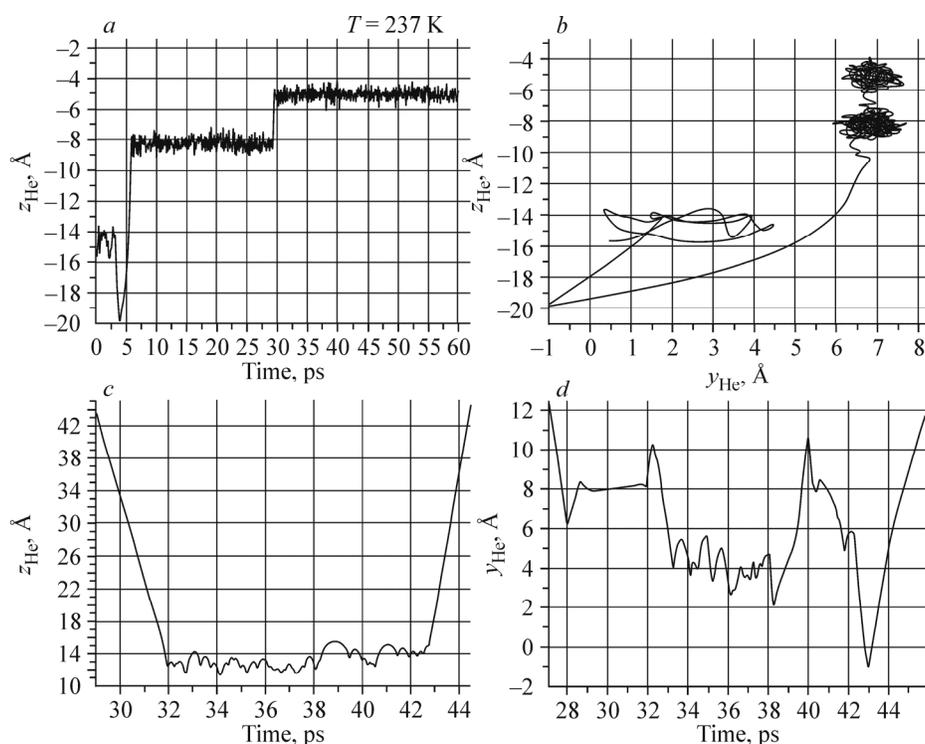


Fig. 7. Helium atoms are striking the ice II film: *a* and *b* show a successful attempt to get into the channel. *a* – a helium atom was wandering across the film surface for a while, then flew off, bumped into another helium atom, came back to the film, entered the channel, and at 29 ps made a jump into a neighboring void. *c* and *d* – unsuccessful attempts. A helium atom struck the film, kept hanging around the channel mouth from 33 ps to 38 ps, and flew away at 43 ps. The time dependence of the *z* (*c*) and *y* coordinates (*d*). $T = 240$ K.

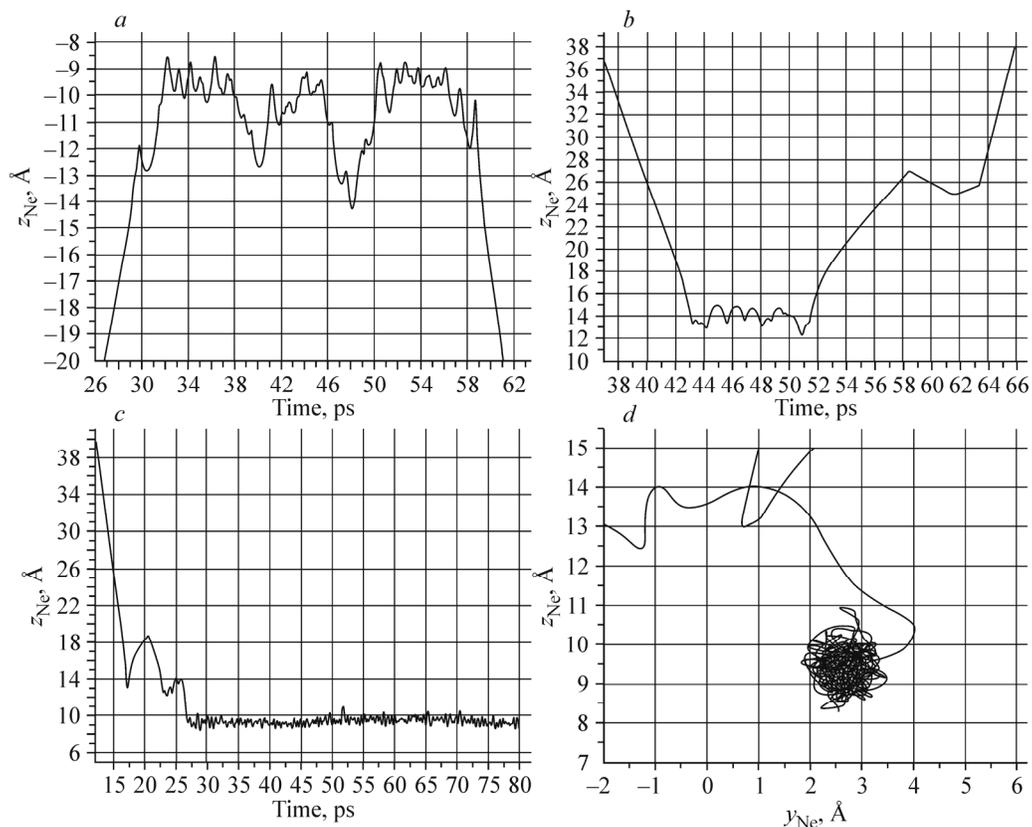


Fig. 8. *a* and *b* – an unsuccessful attempt of neon atoms to get inside the channel of ice II. The time dependence of the z coordinate. The neon atoms approach the surface. *a* – a neon atom made two unsuccessful attempts to get inside the film. *c* and *d* – a successful attempt of a neon atom to get inside the channel; *c* – the time dependence of the z coordinate; *d* – the dependence on the y coordinate. $T = 240$ K.

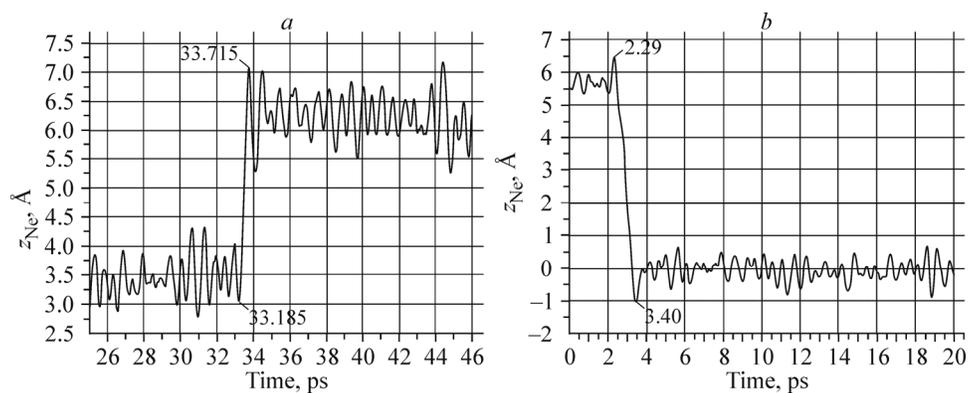


Fig. 9. A neon atom makes jumps along the channel in ice II: a jump into a neighboring void; the jump is 3 Å in length and 0.3 ps in duration (*a*); a long jump of about 6 Å in length and 1.1 ps in duration (*b*).

CONCLUSIONS

Helium and neon atoms demonstrate similar behavior in water systems. The solubility of neon is a little higher than that of helium. Atoms of the two gases wander among water molecules and make occasional slow jumps. The water molecules themselves follow the same motion pattern. Both gases form solid solutions in ices whose structure has voids that can hold atoms of these gases. When helium and neon atoms strike the surface of an ice II film, they sometimes get into the

channels and begin to make jumps along them. Moreover, they make similar jumps along the channels of crystalline ice. The duration of the jumps made by neon atoms is slightly larger than that of helium atoms. The motions of neon atoms in neighboring voids (in the same channel) are correlated. There is no correlation between the motions of helium atoms in neighboring voids.

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