INTRODUCTION

In recent years, considerable progress has been achieved in the understanding of the mechanisms of the statistical behavior of liquids in nanovoids. The behavior was found to be markedly collective. It became possible to distinguish the condensed and noncondensed phases [1]. The filling of nanovoids was found to be of threshold character, which resembles condensation in bulk systems. For nanopores of several types, the changes in the threshold values were studied in relation to the nanopore size [2, 3]. The hydrophobic or hydrophilic interaction with the walls can substantially affect the phase equilibrium in the pore, diffusing or strengthening the boundary between the condensed and noncondensed states of the system. The competition between the interactions inside the fluid and the interactions with the walls entails a diversity of phase states that are due to the surface effects of phase transformations such as layering, wetting, and capillary condensation [4–11].

Several important tendencies of molecular ordering in nanovores were found. In particular, it was found that a liquid is organized into a layered structure even in nanovores with smooth walls [12–15]. In this case, the molecular order in the first monomolecular layer in contact with the wall can radically differ from the molecular order in the inner region [16, 17]. In extremely narrow pores, the structural properties of liquids can approach the crystalline properties even at temperatures above the melting point [18–21].

The behavior of ion impurities under the conditions of nanovores was studied to a lesser extent. At the same time, the specific functions of nanostructures in crystalline minerals and biological systems often refer to impurities, but not to pure water. In particular, the selective properties of nanovores, which are critical to the understanding of the mechanisms of operation of biological membranes, can depend on the size and stability of hydration shells entrained by ions during their diffusion motion inside a cylindrical nanopore.

In porous hydrophobic materials under the conditions of capillary evaporation, liquid water does not penetrate into nanovores and water molecules can be present in the pores only in the hydration shells of ions. Therefore, the pores not completely filled with water and containing hydrated ions may be one of the most widespread states in porous media.

Here, the effect of the limited space of the nanopore on the structural properties of the hydration shell of the atomic ion was studied. The choice of the sodium ion as a prototype was dictated by its presence in natural aqueous media and by its key role in living organisms. The sodium ion has low polarizability and thus contrasts the single-charged chloride anion, which is also widespread and whose hydration in water vapors was studied by theoretical methods in more
CONDITIONS OF SIMULATION
The computations for a model planar pore with structureless walls at 298 K were performed by the Monte-Carlo method with different numbers of water molecules in the ion field. The positive single-charged sodium Na\(^+\) ion was fixed in the middle of space between the walls. The goal of this study was to reveal the main tendencies of the effect of the limited pore space on the mechanism of hydration irrespective of the specific structure of the walls. The model problem was solved for a planar pore whose walls were two parallel planes fixed at distances of 0.5 and 0.7 nm.

The free thermal motion of water molecules in the ion field was modeled. The motion of the centers of mass of molecules was limited by the region of modeling, which was a space between the pore walls in a sphere with a radius of 2 nm circumscribed around the ion. The thermal contact with the medium outside this region was modeled by the standard procedure using the distribution of the microstates of the system in accordance with the equilibrium distribution function of a canonical statistical ensemble [39]. The thermodynamic states with 1–100 molecules were modeled. Under these conditions, the molecules formed a more or less compact hydration cluster held by the ion field so that there was virtually no direct mechanical contact with the spherical boundary of the model region. The periodic boundary conditions were not imposed, which corresponds to the absence of direct interactions with adjacent hydrated ions and to the limiting low concentration of ion impurities in the pore.

All interactions of molecules with the ion and with other molecules at distances within 2 nm were explicitly summed. The interactions were described using the detailed ICP (SPC) model developed in [40, 41]. The model belongs to the last-generation models of many-body interactions in aqueous systems with ions and contains polarization interactions in the form different from that of the first term of multipole series, strong many-body interactions of covalent type, and excess charge and screening transfer effects in addition to the traditional Coulomb, exchange, and dispersion interactions. The numerical values of the model parameters were recovered on condition of consistency with the experimental free energies and enthalpies of the first reactions of attachment of vapor molecules to the ion’s hydration shell [42] and also from quantum-chemical data on the molecular coordinates and binding energies in the stable local configurations of clusters to an accuracy of tenths fractions of \(k_B T\) [43].

RESULTS AND DISCUSSION

**Ion replacement from the hydration shell.** An analysis of the images obtained by computer simulation suggests a steady effect of the ousting of the sodium ion from its own hydration shell after a sufficient number of molecules were accumulated in it (Fig. 1). The displacement effect found earlier for the chloride ion [24, 30, 32–34] and sodium ion [35, 36] under the conditions of bulk water vapors is steadily reproduced under the conditions of an extremely narrow pore. The pore walls with a width of 0.5 nm lie at distances shorter than the radius of the first hydration layer from the ion and are thus the source of strong mechanical perturbations in the shell. The effect of ion displacement to the periphery of the cluster under the pore conditions persists despite the change in the shell shape from three-dimensional to planar.

**Two stages of hydration.** The ion hydration at room temperature occurs in two stages both inside and outside the pore. At the first stage, the molecules add to the ion, forming short radial chains around the ion (Fig. 1). The chains are highly polarized. The parallel polarized chains are repulsed, due to which the hydration shell at this stage has a very loose structure and resembles a starfish in its shape.

The transition from the first to the second stage depends on the competition between the long-range Coulomb forces of repulsion between the chains and the short-range hydrogen bonds, which work against the electrostatic repulsion forces to unite adjacent molecules into a solid fabric. The second stage is char-