



Structure of water adsorbed in slit-shaped pores of silver iodide crystal



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ABSTRACT

The structure of the adsorbate formed from water vapor in flat nanoscopic pores having the width of 2.5, 1.25, and 0.625 nm is investigated in detail by Monte Carlo simulations in terms of spatial correlation functions, angle distributions and molecular configurations. The polarization energy in the interaction with the walls of the pores is included into the Hamiltonian in explicit form. The adsorption on the wall with positive ions in surface crystal layer is considerably ahead of the adsorption on the opposite wall, with negative ions on the surface. At 260 K, intensive clustering takes place on the walls at initial stage of the adsorption. Five-membered molecular cycles compete successfully with six-membered ones. Traces of five- and six-membered cycles are observable even at 400 K, though not more than a tenth part of all hydrogen bonds in the adsorbate at submonomolecular stage survives when heating to this temperature. The monomolecular film growing on the walls has a pronounced hexagonal structure resembling honey comb. On both walls, the film is retained on the surface due to the interactions not with the nearest ions, but with the ions of the second crystal layer. When heating, the probability of the formation of “bridges” between the molecular layers adsorbed on opposite walls rises noticeably. In extremely narrow pores, with the width comparable to molecular sizes, the field of the wall with positive ions on the surface determines the resulting structure of the film. The deficit of hydrogen bond donors in the first molecular layer adsorbed on the wall with positive ions on the surface is the main cause of observable poor wettability of the monolayer film. On the opposite wall, the poor wettability is the result of the deficit of hydrogen bond acceptors.

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1. Introduction

In recent past, there was an opinion that penetration of liquids into the nanoscopic pores is possible only under high pressure which was estimated within the framework of capillarity theory, similarly to the pressure under a curved surface. For instance, the penetration of water into the pores of zeolite, typically having a width from 0.2 nm to 1.5 nm, at a pressure of 100 MPa was studied in this way in [1]. A qualitatively another penetration mechanism for water in silica-based zeolite which does not fit into the continuous medium theory was reproduced in Monte Carlo simulations [2,3]. Despite quantitative disagreements, certain regularities are found to be consistent with capillary theory predictions, at least qualitatively. In particular, it was reported that the minimum of formation work, corresponding to complete filling shifts to higher pressures with decreasing width of the pore.

It was supposed in some studies [4–6] that collective effects may develop only in the conditions of an extensive network of linear pores due to strong enough interactions between individual

branches and are impossible in a single linear pore. Thus, questioned was even the very possibility of developed collective phenomena in narrow pores as such. Nevertheless, it was found in other studies that complex collective phenomena inherent in systems of large numbers of particles can take place also in nanoscopic pores: the condensation into supercooled liquid in the pores was observed in laboratory experiments [7], the spinodal for water in the pore with structureless walls was obtained in computer simulations [8].

Despite certain success achieved in theoretical study of fluids in nanoscopic cavities, the main regularities in the influence of the walls on the formation of collective behavior in the pores remain unclear. A hypothesis was proposed [3] according to which the existence of phase transition into a liquid state in the pore is a specificity only of the pores with hydrophobic walls, whereas strong attractive interaction with the walls results in suppression of collective effects.

Collective effects in nanoscopic pores can manifest themselves in the formation of specific molecular structures that are absent in bulk systems. In particular, equilibrium structure and thermodynamic characteristics of a model fluid of Lennard-Jones particles at 120 K in a slit nanoscopic pore with structureless walls were

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studied by a modified molecular dynamics method in [9]. The interaction with the walls was specified in the form of Lennard-Jones potential, and the forces between the particles corresponded to argon atoms. Obtained distributions of local density indicate a pronounced layered structure of the fluid near the walls. As the pressure increases, the layered structure is becoming more contrast. The growth of equilibrium number of particles with increasing width of the pore is accompanied by oscillations which are also a result of layered structure. Normal component of the pressure tensor also oscillates. Similar layered structure at attractive structureless wall is obtained in a model Lennard-Jones fluid with anisotropic interactions [10,11]. Though approximately 4–5 layers are clearly visible on density profiles at the surface of the wall, the dependencies of orientational order parameters demonstrate much faster attenuation with increasing distance from the wall.

Apparently, shorter characteristic length of orientational correlations as compared with positional correlations can take place for a wide range of fluids near the walls. Indeed, as it was obtained in computer simulations [12], the orientational molecular order in a slit pore filled with water molecules also strongly depends on the distance to the walls. Whereas in the contact layers located at the walls, angle distribution functions have distinct peaks corresponding to preferable orientations, the distributions in the next layers have no pronounced maxima.

Despite specific long-range order observed near the walls, all these states should be classified as liquid. As distinct from freezing, structuring of the fluid in the pore due to the presence of the walls is not accompanied by sharp changes of its transport properties such as viscosity and diffusion coefficients [13]. Thus, in pores, one can observe structuring without crystallization that may be regarded as a general distinctive feature of fluids in nanoscopic cavities.

Gas–liquid phase transitions in nanoscopic pores is of fundamental interest in view of the impact of pores on the ability of fluids to spontaneous structuring due to many-particle spatial correlations. One can expect that in narrower pores, collective effects should be attenuated and, therefore, critical density should increase and critical temperature should decrease. Indeed, critical temperature of a square-well fluid in cylindrical and slit pores is lower than that in corresponding bulk system, but, at the same time, critical density in the pore with repulsive hard walls turned out to be lower than in corresponding bulk system and is higher in the case of attractive walls [13–15]. The same result is obtained for water confined in graphite and mica slit pores [16]. These examples show that the ability of fluids to structuring may depend equally on restricted volume of the pore, and on the interaction with the walls.

Besides transitions between gas and liquid states [17], crystallization in nanopores is the object of attention in connection with its diverse manifestations in Nature and industry which include the mechanism of adsorption in porous materials and the technology of storage of combustible gases. Vapor – crystal phase equilibrium in a planar slit nanopore in the model Lennard-Jones system with force field parameters close to those in methane was studied by molecular dynamics simulations in [18]. The interaction with the walls was described in terms of “10-4-3-potential” which is the result of integration of the fields of uniformly distributed Lennard-Jones centers. The crystallization in the pore took place in the central part of periodicity cell, whereas corresponding vapor pressure was “measured” outside the pore. It has been found that sublimation pressure for Lennard-Jones system in the pore is lower than that in corresponding bulk system. Threefold change in pressure for sublimation curve and triple point was observed in [19].

Spatial heterogeneity of walls is another way for influencing thermodynamic behavior of disordered molecular systems in pores [20,21]. Specific structure of some crystals is responsible for their

anomalous properties when interacting with vapors. Surfaces having complementary crystal structure with respect to water are of particular theoretical and practical interest [22–24]. The most known example is silver iodide (AgI). Macroscopic crystals of silver iodide do not show any anomalous properties in interaction with water: they demonstrate a moderate wettability and do not dissolve in water. At the same time, AgI aerosol particles are the most efficient centers of heterogeneous nucleation of atmospheric moisture at the temperatures below zero Celsius. Though AgI aerosol is widely used on commercial basis for controlling atmospheric processes through the initialization of precipitations, molecular mechanisms providing these unique properties of silver iodide are not completely clarified. At first glance, hexagonal crystal structure of β -AgI similar to that of Ih ice could be the cause, but the poor wettability of macroscopic silver iodide crystals does not keep within such an explanation. Being exposed to vapor, silver iodide crystals are covered with water monomolecular film. The growth of the film in the direction perpendicular to the surface is hindered due to its poor wettability. The microdroplet of water molecules placed on the surface of the film does not spread and preserves its compact shape during the entire session of computer simulation [23]. The cause of poor wettability of the film formed on crystal surface complementary to the structure of water is, obviously, in the structure of hydrogen bonds within monomolecular film [24].

Silver iodide acquires its anomalous properties with respect to water vapor only in form of aerosol particles. The aerosol is prepared by combustion of acetone containing suspended microscopic crystal particles [25,26]. The evaporation of crystals in the flame of the burner is followed by rapid cooling and nucleation of AgI vapor with subsequent growth of aerosol particles which then serve as centers of heterogeneous nucleation of atmospheric moisture. To deliver the aerosol directly to the cloud, it is fired from special pyrocartridges that are suspended to the aircraft fuselage or ejected from special ground-based generators [26–29]. In all the ways of the preparation of the aerosol, it is formed in conditions of fast heating and cooling in combination of intensive mechanical impacts. As a result of this processing, the formation of numerous crystal defects on the surface of the particles can be expected. The amount and the types of the defects can vary in dependence of a concrete regime of aerosol particles formation. The scatter in the properties of the aerosol as nucleation agent in dependence of concrete technological cycle of its preparation is really observed in experiments [30,31]. These observations point to a decisive importance of crystal defects, including pores, in the formation of anomalous properties of silver iodide aerosol as nucleation agent [32–34].

What is more, due to relatively high susceptibility of iodine ions, AgI substrate in its interaction with the vapor demonstrates the effect of domain formation in adsorbed water layers. Additional forces («heteropolarization interactions» [35–37]) arise due to the disintegration into domains of spontaneous polarization. This effect results in enhanced cohesion of liquid film to the substrate. Probably, certain successful combination of different factors, including complementary crystal structure, defects and polarization forces, rather than a single one, could be a cause of anomalous properties of AgI in interaction with the vapor.

The important role of point defects on surfaces with hexagonal structure close to that of silver iodide in interaction with vapor is proved by computer simulations [34,38,39]. In particular, point defects result in destruction of poor wettability effect of the monomolecular film. As the surface density of the defects increases, the hydrophobicity of the first water layer decreases, and the first water layer on the solid surface is gradually covered by the water molecules of the irregularly shaped droplet placed on its surface [24]. The presence of point defects disrupts not only the structure and stability of the first water layer, but also its hydrophobicity.

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