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Bicanonical ensemble Monte Carlo simulation of water condensation in the field of crystal lattice defects

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ABSTRACT

The free energy, formation work and entropy dependences for water condensate formed from the vapor over the defect-free and containing surface defects basal face of β-AgI crystal at initial stage of condensation at temperatures of 260 K and 400 K are calculated using the bicanonical statistical ensemble method, with Ewald summation for long-range electrostatic and polarization interactions with the substrate. The effect of surface defects in form of rectangular “towers” as a part of regular structure on the stability of condensed phase embryos is investigated. In contrast to small-scale structures, relatively larger coarse-grained nanostructure of crystal surface demonstrates an unconditional advantage in the ability to stimulate condensation compared to defect-free surface. The formation of condensed phase embryos on the surface with multiple defects begins at vapor pressures 5–6 orders of magnitude lower than that on corresponding defect-free surface, and this effect is resistant to temperature variations. The condensate on the surface of the crystal is thermodynamically stable, both on defect-free and nanostructured surfaces, with the exception of short initial stage of the monomolecular film on the defect-free surface.

1. Introduction

Heterogeneous nucleation of vapor is the main instrument for controlling the precipitation in the atmosphere and influencing local climate [1]. Silver iodide (AgI) in the form of an aerosol is found to be the most active, though rather expensive, agent of water vapor nucleation. The aerosol is prepared by the combustion of suspension of macroscopic crystalline AgI particles in acetone, by shooting from special pyrocartridges attached to the fuselages of aircrafts, or from nozzles of special meteorological rockets. After the sublimation of AgI in high-temperature flame, the silver iodide condenses into crystalline aerosol particles, which serve as nucleation centers for water vapor in the atmosphere. High-temperature processing of AgI suspension is accompanied by a formation of AgI aerosol particles of different shape and sizes so that the surface of the particles can have different surface topography depending on the parameters of the preparation (the temperature, pressure, heating and cooling rates, the AgI vapor density etc.). Nanostructures in form of numerous surface defects can drastically influence the activity of the particles as nucleation centers.

In the last decades, considerable efforts have been directed to computer simulation studies of molecular mechanisms of water condensation on various defect-free crystalline surfaces [2–13] including AgI [14,15,16–18]. Much less work has been reported on surfaces containing single defects and nanostructured surfaces. Small sizes of crystal lattice defects, which are comparable with the radius of intermolecular correlations in liquids, do not allow the application of continuous medium as well as mean field and other approximations that do not take into account consistently the discrete molecular nature of liquids. Computer simulations represent here a most reliable source of information both of fundamental character and related to the surfaces with specific crystal structure.

A distinctive feature of water microcondensation on defect-free surfaces is its layer-by-layer mechanism which can be observed on some crystal substrates. The formation of the first molecular bilayer represents here the most important stage which determines further development of the process [19]. At the same time, the cohesion with the contact bilayer is not a single important factor. It was pointed out in [20] that changes induced by the substrate away from the interface might play an important role in the nucleation mechanism. Orientation order in the first layer at the contact of the liquid with the substrate is essentially important for the growth of next layers and condensed bulk phase as a whole [21]. The first layer of water molecules adjacent to the metal Pt(111) surface was found in [22] to display solid-like properties. The next two layers displayed ordering similar to ice-I. The structure and dynamics of water outside these layers were found to be bulk-like.

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There are only a limited number of investigations performed for water on nanostructured surfaces. In these conditions, the data obtained for the model fluids [23] including the system of Lennard-Jones (LJ) liquids [24] represent here certain compensation. Computer simulation studies for nanoscopic pores [25–28] allowed observing most general regularities accompanying the contact of liquid phase with solid surfaces containing nanoscopic structural elements [29,30]. Multiple defects localized on the surface at the distances compared to the length of intermolecular correlations make the substrate rough and can destroy molecular order in the first molecular layers completely. The LJ droplets on smooth and molecularly rough surfaces consisting of LJ particles were simulated in [31]. The roughness of the substrate was prepared by creating nanoscopic grooves. Wetting was analyzed in terms of contact angles. Despite continuum medium approximation arguments laying in the basis of Wenzel's law [32] which suggest that roughness must always amplify wetting, nanoscopic roughness in [31,33] was found to deteriorate wetting both for strongly and weakly wettable surfaces. Computer simulations of LJ droplets on flat and pillar surfaces in [34] showed that the contact angle increases with the pillar size. In addition to equilibrium state, a long-living metastable state of the droplets was observed which is characterized by incomplete penetration of the liquid into hollows between the pillars. Obviously, wetting properties of roughness are in strong dependence of its characteristic size, and roughness of nanoscopic scales exhibits qualitatively different properties in comparison with macroscopic one.

Nanostructured surfaces can display essentially different properties in interaction with liquid water in comparison with flat, defect-free ones [35,36]. It was found that the existence of a defect enhances the water molecule–and cluster–silica surface interactions, but has little effect on water thin film–silica surface interaction [37]. The origin of the weakening effect on the film–surface cohesion is the collective hydrogen bonding that imposes compromise positions of water molecules with respect to surface. This can qualitatively change the mechanism of nucleation as such. Closely located defects can produce in the contact layer collective effects which are able to speed up or slow down the growth of ice from liquid water. Thus, the roughness can have positive or negative effect on the nucleation. In [38], it was found that atomically flat carbon surfaces in contact with liquid water promote heterogeneous nucleation of ice, while molecularly rough surfaces do not.

Density function theory calculations for water molecules at step edges on rutile $TiO_2(110)$ [39,40] and anatase $TiO_2(101)$ [41–44] substrates showed higher ability of steps to hold water molecules in comparison with ideal surfaces. The calculations are done for a single water molecule in different positions close to the surface. The higher activity of steps was explained by the action of undercoordinated Ti atoms. A dramatic enhancement of adsorption properties with respect to water due to the presence of steps is also confirmed in laboratory experiments with $BaF_2(111)$ surface [45].

Molecular dynamics simulations of the deposition of model water molecules on the substrate with the structure close to the one of platinum crystal lattice with roughness composed of periodic parallel grooves [46] showed that the nucleation behavior of the supercooled water is significantly sensitive to the width of the grooves. This dependence is not monotonous: when the width of the groove matches well with the specific lengths of the ice crystal structure, the nucleation accelerates, if not, the nucleation rate is even smaller than that on the defect-free surface. A complicated character of the dependence of wettability in terms of contact angle on characteristic sizes of roughness elements is confirmed in [47]. One can differ two states of droplets on nanostructured surfaces – with incomplete penetration of a liquid into the gaps between roughness elements (Cassie-Baxter state) [48] and complete contact with the surface including the bottom of nanoscopic hollows (Wenzel state) [49]. The differences in the mechanism of adhesion to the surface in these two cases show themselves also in kinetic properties of the condensate. In particular, the droplets in Cassie-Baxter state have high mobility in their movement along the surface, do not leave traces and show a pronounced tendency to merge into large drops. This phenomenon is used by biological objects to provide strong water-repellent properties of the surfaces [50].

Nucleation of ice on water-ice interface is accelerated by a transverse local electric field that can be treated as simplest model of nanoscopic defect. Field bands exceeding a minimum size of 0.15 nm thick and 0.35 nm wide catalyze ice nucleation just as efficiently as full surface fields [51].

In general, computer studies of the interaction of water with crystal surfaces made it possible to reveal a number of regularities of a fundamental nature, the main of which are the existence of two nucleation scenarios, namely, the drop and layered nucleation, the possibility of forming a monomolecular film with a hydrophobic surface and the dependence of the contact angle on the droplet size. Optimal conditions for the formation of condensed phase nuclei do not imply the strongest adhesion of the first layer of molecules to the surface, but arise at some optimal binding force. The decisive factor here is the orientation molecular order in the contact layer of the liquid.

The situation with nanostructured surfaces is more complicated. Most of the studies of nanostructured surfaces by computer methods are related to ice formation under conditions of surface contact with a supercooled bulk liquid phase. Heterogeneous nucleation in contact with water vapor is much less investigated. The current work is an attempt toward filling this gap.

The present study is focuses mainly on the thermodynamic behavior of nuclei, primarily free energy and the work of formation, as well as their stability. To calculate the free energy at the molecular level, instead of the most popular method of thermodynamic integration [5,21] and less commonly used, but also well-known method of expanded ensembles [52], the bicanonical statistical ensemble method (BSE) is used in this work. This method makes it possible to obtain directly and with minimum expenditures the dependence of the free energy on the size of the nucleus. Until recently, computer simulation was used for studying nanostructures with a characteristic size of its elements of several molecular sizes. In the current work, the formation of condensed water embryos in the field of larger elements of inhomogeneity is simulated - with a cross section size of 13 × 13 atoms and with the distance between them of the same order of magnitude. With the increase in the spatial dimensions of nanostructure elements, one can expect an increase in collective effects and a more contrasting separation of molecules into those that are accumulated on the upper and lateral parts of the inhomogeneity elements, and also between them, on the supporting surface of the substrate, which will inevitably affect the thermodynamics of nucleation.

2. Interaction model

2.1. Elementary interactions

From considerations of continuity with the model developed in [15], pairwise water-water interaction energy U_{pair}^{w-w} was described in terms of five-center Rahman and Stillinger ST2 interaction potential [19]. The electrostatic interactions of water molecules with the ions of the crystal lattice of the substrate U_{coul}^{I-W} were represented by the sum of the Coulomb interactions of the water molecule point charges q_k contained in the ST2 potential with the ion charges Q_0^n:

$$U_{coul}^{I-W} = \sum_{i,n} \left[\sum_{k=1}^{k=4} \frac{Q_0^n}{|\mathbf{r}_k^i - \mathbf{x}_0^n|} q_k \right], \tag{1}$$

where Q_0^n is point charge of n-th ion, and $\mathbf{x}_0^n$ is its coordinates. Here and below, for brevity, the formulas for electrostatic interactions