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Research paper

Structures of surface and interface of amorphous ice

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ABSTRACT

To investigate the surface structure, we performed molecular dynamics calculations of amorphous ice. The result shows that a low density layer, which forms a few hydrogen bonds with weaker strength, exists in the surface. Furthermore, the sintering processes were simulated to investigate the structure of grain boundary formed from the adsorption of two surfaces. The result indicates that a low density region exists in a boundary between amorphous ice grains. The structures of surface and interface of amorphous ice have important implications for adsorption, diffusion, and chemical reaction in ice grains of interstellar molecular clouds.

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1. Introduction

In interstellar molecular clouds, elements such as hydrogen, oxygen, carbon, and nitrogen deposit on dust grains, and amorphous H_2O ice and other various molecules (e.g., CO_2, NH_3, CH_4, H_2CO, and so on) are formed [1]. Because the molecules undergo chemical evolutions through various processes on the surface of amorphous ice, the structure and properties of amorphous ice surface are important factors governing the chemical evolutions of organic molecules in molecular clouds.

For crystalline ice Ih, a melting layer exists on its surface even at temperatures below the bulk melting point [2]. Due to its similar properties as liquid water, the melting layer on ice surfaces is called a 'quasi-liquid' layer. The properties of the quasi-liquid layer and the consequent phenomena are relevant to questions in subjects as diverse as geophysics, astronomy, and biology [3–6]. Many studies have been performed to understand the structures and properties of the crystalline ice surface. Using X-ray diffraction, Kouchi et al. [7] showed the existence of a disordered surface structure. Studies using glancing-angle X-ray scattering have confirmed a mesoscopic structure with rotational disorder [8,9]. The thickness and critical temperature of the quasi-liquid layer have been measured using various methods such as optical ellipsometry, back scattering, and atomic force microscopy [10–14]. Molecular dynamics (MD) simulations were also performed to determine the molecular arrangements and dynamics of crystalline ice surface [15–18]. Although various studies have been performed to investigate the surface structure of ice crystals, there are only a few studies of amorphous ice surface because of its complicated structure.

Amorphous ice is formed by various procedures, for instance, pressurization of crystalline ice Ih in low temperature conditions [19], vapor deposition of water on cold substrates under vacuum [20], ultra-rapid quenching of liquid water [21], and matrix sublimation method [22]. The formation process of the deposition method is similar to the situation of amorphous ice formation in the universe. The amorphous ice is mainly classified into two types: low-density amorphous (LDA) and high-density amorphous (HDA) ice. These two types of amorphous ice were proposed by Narten et al. [20]. From their study using X-ray diffraction, they found that the density of water ice deposited at 10 K is larger than that deposited at 77 K. The densities of the LDA and HDA ice determined from their X-ray analyses were 0.94 ± 0.03 and 1.1 ± 0.1 g cm^{-3}, respectively. Using electron diffraction, Jenniskens et al. [23] found that the HDA ice has a collapsed LDA ice structure. They demonstrated that HDA ice transforms into LDA ice at temperatures above 38 K, although the collapsed structure is frozen at lower temperatures.

The transition temperature from HDA to LDA ice depends on the formation conditions and thermal history. Amann-Winkel et al. [24] showed that the transition temperature from HDA to LDA is 116 K at around 0.1 MPa. On the other hand, Kouchi [25] proposed that there are at least three types of amorphous ice in different temperature ranges. Using mass spectrometry and electron diffraction, Kouchi [25] showed that the vapor-deposited amorphous ice is transformed into different structures at 90 and 135 K with warming. At temperatures above 135 K, the ice is transformed into crystalline ice Ic at 145 K, and is transformed into crystalline ice Ih at around 157 K [25].

To investigate the molecular-level structure and properties of amorphous ice, MD simulations are effective. The first MD simulation of water-deposited amorphous ice was performed by Zhang

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and Buch [26]. Using the TIPS2 potential, they investigated formation process of amorphous ice with slow vapor deposition of water. Using the potential model, Buch [27] performed MD simulations of amorphous ice clusters from 450 water molecules. The simulations demonstrated that the clusters formed from vapor deposition at 10 K are LDA ice, and the dangling O—H bond is abundant in amorphous ice. They concluded that the cause of the uneven surface of vapor-deposited amorphous ice is the preferred attachment of new molecules to the dangling atoms on the surface. The water-deposited amorphous ice has a large surface area [3]. Wilson et al. [28] simulated the vapor deposition of water onto a water substrate and found that the resulting LDA ice has a microporous structure. The porous structures depend upon the deposition conditions.

Tse and Klein [29] modeled HDA ice by pressurization of crystalline ice Ih, and performed MD simulations using the TIP4P potential model. The result showed that the formation of HDA ice is driven by a collapse of the open lattice in ice Ih. The collapsed structure is explained by a migration of water molecules into the interstitial sites [30]. On the other hand, Jenniskens et al. [23] modeled HDA ice ($1.17\ \mathrm{g\,cm^{-3}}$) with the quenching of liquid water from 300 K, and performed MD simulations. They showed that the HDA ice is transformed into LDA ice with warming. The results showed that the most preferred coordination numbers of hydrogen bonds is four, for both HDA and LDA ices. This suggests that the HDA ice has a collapsed structure with no interstitial molecules.

Although the structure and properties of amorphous ice have been studied using various methods, there are only a few studies of its surface. In order to investigate the surface structures of amorphous ice, MD calculations of amorphous ice have been performed. Furthermore, the sintering processes between surfaces were simulated and the structure of the grain boundary formed from sintering was analyzed.

2. Computational procedure

2.1. Interatomic potential

We used an atom-atom potential model, the KAWAMURA potential model [31], which is an improvement on the KKY potential model by Kumagai et al. [32]. The potential model has two-body interactions for all atom pairs (i.e., O—O, O—H, and H—H)

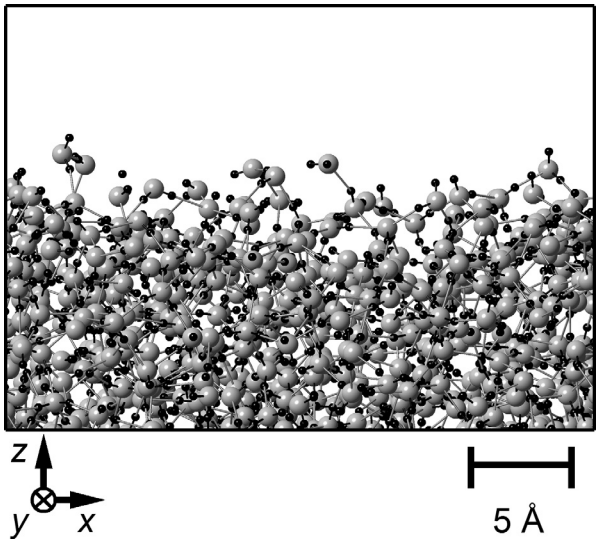

Fig. 1. Surface of amorphous ice at 10 K observed by molecular dynamics calculation. The large grey and small black circles show the oxygen and hydrogen atoms, respectively. The black and grey lines are the covalent and hydrogen bonds, respectively.

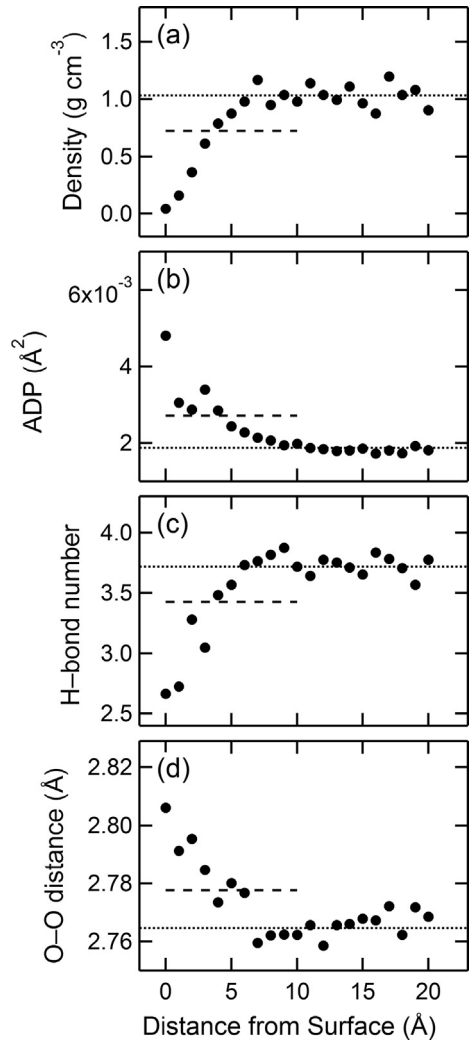

Fig. 2. Distributions of (a) density of water molecules, (b) atomic displacement parameter (ADP) of oxygen atoms, (c) number of hydrogen bonds and (d) O—O distance as a function of distance from the surface at 10 K. The dotted and dashed lines show the average values in the bulk and surface layer with a thickness of 10 Å, respectively.

and a three-body force for the H—O—H system. The two-body interactions consist of Coulomb forces, short-range repulsion, van der Waals interactions, and covalent bond potentials between oxygen and hydrogen atoms in each water molecule. The two-body interactions are given by

$$u_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{1ij}\exp\left(-\beta_{1ij} r_{ij}\right) + D_{2ij}\exp\left(-\beta_{2ij} r_{ij}\right) + D_{3ij}\exp\left\{-\beta_{3ij}\left(r_{ij} - r_{ij}^*\right)^2\right\}, \tag{1}$$

where r_{ij} is the distance between atoms i and j; f_0 is a constant for unit adaptations between the these terms; z, a, b, and c are parameters for intramolecular interactions (i.e., O—H interactions). The three-body force is used to constrain the H—O—H angle in the water molecule. The three-body force is given by

$$u_{jij}(\theta_{jij}, r_{ij}) = -f_k\left[\cos\left\{2(\theta_{jij} - \theta_0)\right\} - 1\right]\sqrt{k_1 k_2}, \tag{2}$$

where

$$k_i = \frac{1}{\exp\left\{g_r(r_{ij} - r_m) + 1\right\}}. \tag{3}$$

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