

Anisotropy in Molecular-Scaled Growth Kinetics at Ice–Water Interfaces

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Molecular dynamics simulations of ice–water interfaces at the supercooling state were performed to elucidate the anisotropic growth kinetics. The simulations were carried out for two kinds of interface orientations, namely, an ice(0001)–water and an ice(10 $\bar{1}$ 0)–water interfaces. It should be emphasized that not only the interface structures but also the growth kinetics are completely different between the interfaces. Furthermore, we analyzed the development of the translational order and the orientational order for the molecular arrangement during the growth. The results suggest that the translational order of the arrangement develops in advance of the orientational order for both interfaces.

Introduction

The ice–water interface is a current special subject in connection with such issues as the melt growth mechanism of ice crystals, the frost heaving, the freezing of water in the biological system, and so on. It is of great importance for understanding the details of such issues to elucidate the structure of the ice–water interface and the growth kinetics at the interface on a molecular scale. Up to the present, many attempts have been made to observe the ice–water interface structures by the light-scattering experiments.^{1–4} However, the scale of the structures observed in these studies was not on the order of molecular size but on the order of 0.1 μm , which was the order of the wavelength of the light used. On the other hand, Karim and Haymet⁵ investigated the ice–water interface structures using a molecular dynamics (MD) simulation for the first time and clarified the interface structures under the equilibrium state at the molecular level. However, the growth kinetics at the interface under the nonequilibrium state was not analyzed in their study. Recently, the MD simulations on the growth of ice crystal were performed by Báez and Clancy⁶ and Svishchev and Kusalik.⁷ However, these studies did not focus on the growth kinetics of ordinary hexagonal ice.

On the other hand, the anisotropy in the growth kinetics of ice crystals has attracted much attention in relation to the pattern formation of ice crystals. It is well-known that the growth forms of ice crystals grown in the supercooled water are strongly affected by the anisotropic growth kinetics at the ice–water interface.^{8,9} In recent studies,^{10,11} we investigated the anisotropic properties of ice–water interfaces using the MD simulations. As a result, the structural difference between ice(0001)–water and ice(10 $\bar{1}$ 0)–water interfaces was clarified, and the anisotropy in the growth kinetics at the ice–water interfaces was also discussed.¹¹ However, some indistinct points about the growth kinetics at the molecular level still remained, because the simulation run in the previous study was not sufficient to discuss precisely the growth kinetics of the ice–water interfaces.

In this paper, we show the new results of MD simulations for the ice–water interfaces with a much longer simulation run.

As a result, the anisotropy in the growth kinetics in conjunction with the anisotropic interface structures is elucidated at the molecular level. Finally, we discuss how the translational and orientational ordered states of the molecular arrangement advance at the interfaces during the growth of ice crystal.

Simulation Method

We used a TIP4P water molecule model¹² in order to estimate the intermolecular interactions. It is well-known that this model provides a reasonable description for the structures and dynamic properties of both ice crystal and water over a wide range of temperatures and pressures.¹³ The potential function was modified by a switching function employed by Kroes¹⁴ in the intermolecular distances from 10.45 to 10.95 Å, and the interactions beyond the intermolecular distance of 10.95 Å were ignored.

Two kinds of simulation systems were prepared to investigate the anisotropy in the growth kinetics at the ice–water interfaces. One was a system including an ice(0001)–water interface (hereafter, basal system), and the other a system including an ice(10 $\bar{1}$ 0)–water interface (prismatic system). The shape of each simulation system was a rectangular parallelepiped including 1080 TIP4P water molecules. The dimensions of the systems were 22.4 Å \times 23.3 Å \times 65.7 Å for the basal system. Periodic boundary conditions were imposed in the directions parallel to the interface (x and y directions).

Here, let us consider that the system is divided into 18 layers along the z direction, which are numbered serially from layer 1 to layer 18. The thickness of each layer corresponds to that of the molecular layer in bulk ice, which is approximately 3.65 Å for the basal system and 3.90 Å for the prismatic system. The initial position of the ice–water interface locates between layers 8 and 9. The regions of layers 1–8 and layers 9–18 correspond to the ice crystal region and the water region, respectively.

The system including an ice–water interface was constructed as follows: At the beginning of the simulation, all water molecules in the system were arranged on the ice crystal lattice points with the molecular orientations satisfying the ice rules. First, the region of layers 9–17 was heated up to 400 K for a period of 20 ps (1 ps = 10^{-12} s), with fixing the molecular positions of layers 1–8. Within this period, the molecular arrangement in layers 9–17 was completely changed to a

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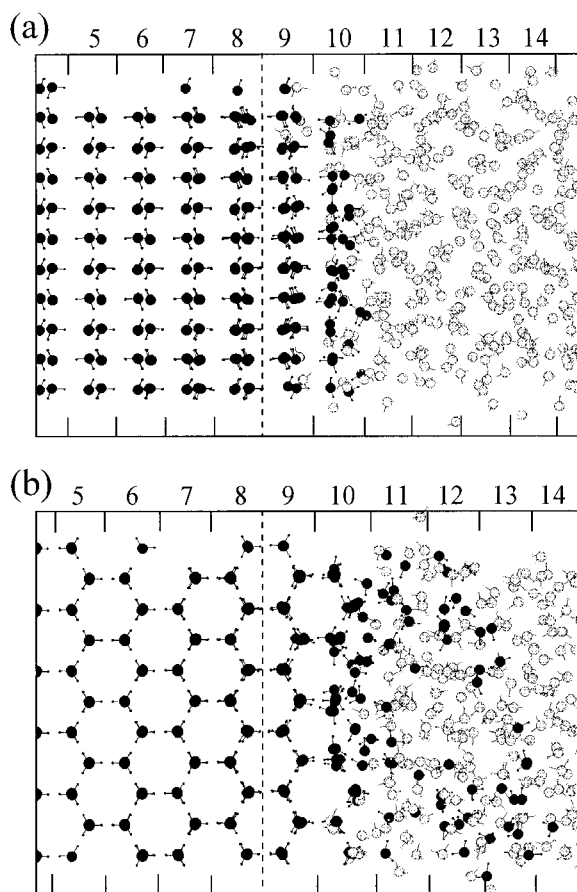


Figure 1. Snapshots of water molecules projected to the x - z plane: (a) for the basal system; (b) for the prismatic system. These are obtained by the coordinates averaged over period B (0.9–1 ns). Black-colored molecules indicate the icelike molecules. Dashed lines show the initial position of the interfaces.

random state (namely, the arrangement in bulk water). Next, the temperatures T of the region of layers 3–8 and 9–17 were approached to the simulation temperature of 230 K. After the simulation was carried out, at the constant temperature of 230 K for a period of 10 ps, the T of layers 4–17 was released from control. The T of layers 1 and 2 was always kept at 0 K during the simulation. Moreover, the T of layers 3 and 18 was also controlled at 230 K during the simulation to remove the latent heat released by the crystallization at the interface. As a result, we observed the growth processes for both systems within the total simulation run of 1 ns ($=10^{-9}$ s). The detailed method to construct the interface system is described in ref 11.

A leapfrog algorithm was used for integration of the Newton equation. The rotational motions of water molecules were also solved using the quaternion method. The time step was chosen to 2 fs ($1 \text{ fs} = 10^{-15} \text{ s}$). We analyzed the interface structures at two different periods to investigate the time dependence of the interface structures. One is a period between 0.2 and 0.3 ns, and another a period between 0.9 and 1 ns. Hereafter, they are called periods A and B, respectively.

Results and Discussion

Anisotropy in Growth Kinetics at Ice–Water Interfaces.

First of all, let us discuss the growth kinetics and the interface structures for both systems. Figure 1 shows the snapshots of water molecules projected to the x - z planes for both systems. They were obtained from the coordinates of each water molecule averaged over period B. Since the molecules in the bulk ice crystal harmonically oscillate around the ice crystal lattice points,

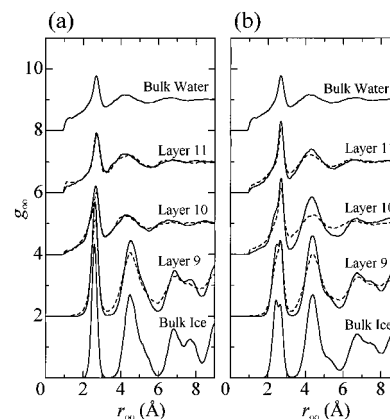


Figure 2. Two-dimensional oxygen–oxygen pair correlation functions, g_{OO} , in layers 9–11: (a) for the basal system; (b) for the prismatic system. The g_{OO} in bulk water and ice are also shown as references. Dashed and solid lines indicate the g_{OO} at periods A and B, respectively.

the time-averaged coordinates should locate on the lattice points, whereas the molecules in the water do not locate on them. Therefore, we can clearly distinguish the ice crystal structure from the water structure by using this criterion. Namely, the left-hand and the right-hand regions in the figures correspond to the ice crystal and the water, respectively. Dashed lines stand for the initial positions of the interfaces. In the snapshots, the black-colored molecules indicate the ones satisfying the following two conditions: (1) surrounded by four nearest neighbors;¹⁵ (2) connected with each nearest neighbor by a hydrogen bond.¹⁶ It goes without saying that all water molecules in the bulk ice satisfy both the conditions. Here, we define such the molecule as an “icelike” molecule.

Figure 1a shows the snapshots for the basal system. One can see that a new molecular layer was formed in layer 9 during the simulation. Namely, the growth process of ice crystal was observed for the basal system. It also can be seen that although the icelike molecules exist in layer 10, the molecular arrangement in the layer is different from that in layer 9, which is completely included in the ice crystal region. Note that since any icelike molecule does not exist in other layers of the water region, the right-hand region except for layers 9 and 10 completely holds the structure of bulk water. Therefore, we conclude that the interface structure for the basal system is smooth at the molecular level.

Figure 2a shows the two-dimensional oxygen–oxygen pair correlation functions, g_{OO} , in layers 9–11 for the basal system. Dashed and solid curves correspond to the g_{OO} at periods A and B, respectively. The g_{OO} for bulk ice and water are also shown as references. One can see that the g_{OO} in layer 9 at period B shows more distinct peaks than that at period A. This indicates that the structural order in layer 9 increased between periods A and B. The g_{OO} in layers 10 and 11, however, does not show the increase of structural order. It also can be seen that the g_{OO} in layer 9 at period B is very close to that in bulk ice, whereas that in layers 10 and 11 at period B is still close to that in bulk water. This result indicates that the rearrangement of water molecules during the growth occurs in the limited region of layer 9. Therefore, we can conclude that the growth kinetics for the basal system is in the *layer-by-layer* mode.

On the other hand, Figure 1b shows the snapshots for the prismatic system. One can see that a molecular layer with the molecular arrangement of ice crystal was formed in layer 9 as well as the basal system. Furthermore, the formation of the molecular layer partly begins in layer 10, and a large number of icelike molecules are found in layers 11–13 of the water region. This result strongly suggests that the interface structure

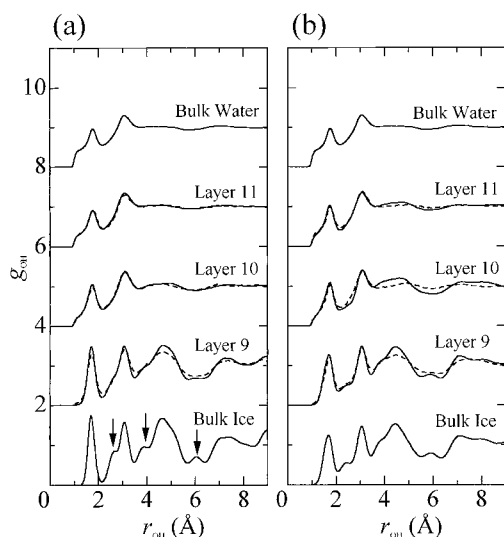


Figure 3. Two-dimensional oxygen–oxygen pair correlation functions, g_{OH} , in layers 9–11: (a) for the basal system; (b) for the prismatic system. The g_{OH} in bulk water and ice are also shown as references. Dashed and solid lines indicate the g_{OH} at periods A and B, respectively.

for the prismatic system is geometrically rough, in contrast to the smooth interface structure for the basal system and that the structure in the water region for the prismatic system has a higher ordered structure than that in the bulk water. We also should pay attention to the result that the icelike molecules gather locally at the upper and the lower regions in the water region. It means that the rearrangement of water molecules from the waterlike to icelike structures locally occurs in these regions.

Figure 2b shows the g_{OO} in layers 9–11 for the prismatic system. Not only in layer 9 but also in layer 10, the g_{OO} peaks become distinct with the increase of the simulation run from periods A to B. Furthermore, the increases of second and third peaks in the g_{OO} for layers 9 and 10 are fairly larger than that of the first peak. This result suggests that the long-range order in the structure preferably increased between periods A and B. Since the increase of long-range order must originate from the cooperative interactions among the water molecules, we conclude that the growth for the prismatic system occurs by such a kinetics as the molecules in the water region are collectively incorporated into the ice crystal lattice. In other words, the growth is dominated not in the “molecule by molecule” process but in the “collected molecule” process. It should be emphasized that the growth kinetics for the prismatic system is completely different from that for the basal system and that the anisotropy in the growth kinetics was elucidated at the molecular level.

Relationship between Translational Order and Orientational Order in Molecular Rearrangement. Next, let us discuss how the rearrangement of water molecules develops at the interface during the growth. Since the water molecule has an asymmetric geometry, both the translational and the orientational orders must be coordinately considered. In Figure 2, we showed the g_{OO} for both systems. Since the center of mass of each water molecule locates in the vicinity of the oxygen atom, we can regard the g_{OO} as a measure of the translational order of molecular arrangement. On the other hand, Figures 3a and 3b show the two-dimensional oxygen–hydrogen pair correlation functions, g_{OH} , for the basal and the prismatic systems, respectively. In contrast to the g_{OO} , the g_{OH} gives a measure of the orientational order of the arrangement.

First, let us discuss the relationship between the orders for the basal system. In Figure 3a, although the orientational order of layer 9 increases between periods A and B, the small peaks which appear in the g_{OH} of bulk ice (see the arrows in Figure

3a) are not observed in the g_{OH} for layer 9. This indicates that the orientational order of layer 9 has not reached the complete state of bulk ice, whereas the translational order has completely reached that of bulk ice as shown in Figure 2a. This situation can also be seen in Figure 1a. That is to say, although the arrangement of oxygen atoms in layer 9 resembles very much that in the bulk ice, the hydrogen atoms are arranged in the partly disordered state. Therefore, it is concluded that the development of the translational order and the rotational order occurs in the different way from each other, and that the translational order develops in advance of the orientational order at the interface of the basal system.

Next, let us consider for the prismatic system. In Figure 3b, the orientational orders of layers 9 and 10 increase with increasing the simulation run, as well as the translational order as shown in Figure 2b. Specially, the g_{OH} in layer 9 at period B is completely identical with that of bulk ice. Consequently, both the translational and orientational orders in layer 9 are considered to be in the same measure as the bulk ice. On the other hand, we can see from the comparison between Figures 2b and 3b that the orientational order in layer 10 is in the lower measure than that of the translational order. This indicates that the translational order for the prismatic system also advantageously develops more than the orientational order, as well as the case for the basal system. We also examined the hydrogen–hydrogen pair correlation functions, g_{HH} , which indicate the measure of orientational order among the hydrogen atoms. Although we do not show the results in this paper, we obtained that the g_{HH} shows the similar results as the g_{OH} .

Conclusions

We investigated the anisotropy in the molecular-scaled growth kinetics at the ice–water interfaces using the MD simulations. The growth processes were clearly observed for both the basal and the prismatic systems. It should be emphasized that the growth kinetics was completely different for both systems; that is, the growth kinetics for the basal system was in the *layer-by-layer* process, but that for the prismatic system was in the *collected molecule* process. Moreover, the interface structure was also elucidated at the molecular level; namely, the interface structure was smooth for the basal system, but rough for the prismatic system.

We also analyzed how the translational order and the orientational order for the molecular arrangement develop at the interface when the ice crystal is growing. As a result, it was found that the translational order develops in advance of the orientational order for both systems. We emphasize that the relationship between the translational and orientational orders for the molecular rearrangement during the growth was indicated for the first time.

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