



A clear observation of crystal growth of ice from water in a molecular dynamics simulation with a six-site potential model of H₂O

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Abstract

We demonstrate that a six-site potential model of H₂O, which we proposed recently, is suitable for simulation works on the crystal growth of ice from water. Using the model, a molecular dynamics simulation of a system including interfaces between the prismatic face of the proton-disordered hexagonal ice and water is carried out at a supercooled state and a pressure of 1 atm. The results clearly indicate that the ice grows at the interfaces continuously during the simulation. Moreover, the growth kinetics at the interfaces is analyzed on a molecular scale.

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1. Introduction

Studies of the growth kinetics of a crystal from its melt using a computer simulation, such as molecular dynamics (MD) and Monte Carlo (MC), largely contributes to an understanding of it on a molecular scale. Owing to the increase of the computer power, the simulation has become a powerful tool to study the growth kinetics not only for simple atomic crystals but also for molecular crystals that have a complicated structure.

Recently, simulation works on the growth kinetics of ice from water have attracted a great

deal of interest in connection with such issues as the pattern formation of snow and ice [1], and the freezing of water in biological systems [2]. However, when a simulation is applied to investigate the growth kinetics of ice from water, it is necessary to use a potential model of H₂O that is suitable for simulation works of ice and water near the melting point, T_m . Note, however, that most of the potential models proposed till now have been developed only for simulation works of water.

In the real system, the stable ice near T_m at a pressure, P , of 1 atm is the proton-disordered hexagonal ice, I_h^d [3]. Therefore, a potential model that is suitable to simulate real ice should provide I_h^d as the free energy minimum near T_m at $P = 1$ atm. Until now, the TIP4P [4] and the

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SPC/E [5] models have often been used for simulation works on the growth of ice from water [6–10]. However, recent free energy calculations demonstrated that these models are not suitable to simulate real ice, because I_h^d does not correspond to the free energy minimum near T_m at $P = 1$ atm [7,11–13]. Recently, Matsumoto et al. observed the nucleation of an ice crystal from water in a very long run of a MD simulation at a much lower temperature, T , than the real T_m , using the TIP4P model [10]. However, they observed the nucleation only at an extraordinary low negative P , but did not observe the nucleation at $P = 1$ atm. As far as we know, no simulation work has succeeded to observe the growth of I_h^d from water near the real T_m at $P = 1$ atm.

Very recently, we proposed a new potential model (a six-site model) for simulation works of ice and water near T_m [13]. In contrast to the TIP4P and the SPC/E models, our six-site model provides I_h^d as the free energy minimum near T_m at $P = 1$ atm. Moreover, T_m of I_h^d in our model is very close to the T_m of it in the real system. Therefore, our model should be much more suitable for simulation works on the growth of I_h^d from water than the TIP4P and the SPC/E models. In this paper, using our six-site model, we carry out a MD simulation of a system including interfaces between the prismatic face of I_h^d and water near T_m at $P = 1$ atm. It is clearly shown that I_h^d grows at the interfaces continuously during the simulation. Moreover, the growth kinetics at the interfaces is analyzed on a molecular scale.

2. A six-site model of H₂O [13]

The molecule in our model has six interactive sites, which are an oxygen atom (O), two hydrogen atoms (H), two lone-pair sites (L) and a site M located on the bisector of \angle HOH. A positive charge is placed on H, and a negative charge on L and M. The intermolecular interaction is represented by the sum of the Coulomb potentials acting among the charged sites, and the Lennard–Jones potentials acting on O and H.

The structures and the thermodynamic properties of ice and water in the model are summarized

as follows. (1) I_h^d corresponds to the free energy minimum near T_m of the model. (2) T_m of I_h^d at $P = 1$ atm in the model is 271 ± 9 K, which is in good agreement with the real T_m of 273.15 K. (3) Density curves of I_h^d and water near T_m at $P = 1$ atm are reproduced. In summary, the model is suitable for simulation works of I_h^d and water near the real T_m at $P = 1$ atm. Thus, it is expected that the model is also suitable for simulation works of the growth of I_h^d from water near the real T_m at $P = 1$ atm.

3. Simulation method

We prepared a simulation system of a rectangular parallelepiped, which includes two interfaces between the prismatic face of I_h^d and water (Fig. 1). The system was created using the same method as that used in past works [14,15]. First, a sample of bulk I_h^d and that of bulk water were prepared separately. The bulk I_h^d and water samples contained 720 H₂O and 360 H₂O, respectively. The structure in each bulk sample was determined by a MD simulation of the NPT ensemble at $P = 1$ atm. Then, the system including two interfaces was constructed by sandwiching the bulk I_h^d sample by two copies of the bulk water sample.

The method to create the system used in this study, however, may yield extremely large stresses at the interfaces, which cause violent molecular motions near the interfaces at the beginning of the MD simulation. Therefore, in order to relax the stresses at the interfaces, we carried out a short MC simulation of the system at $T = T_m$, before the MD simulation was carried out. The reason for the use of a MC simulation is that the stresses can

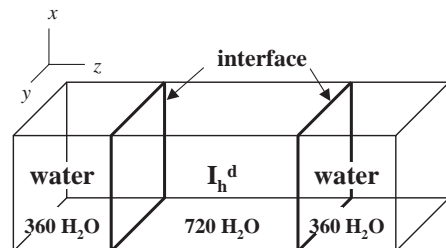


Fig. 1. Schematic illustration of the simulation system.

successfully be relaxed by trial molecular movements in the MC simulation without yielding the violent molecular motions. In the MC simulation, 1.44×10^8 trial molecular movements were performed using a standard Metropolis sampling method. We checked that the initial stresses at the interfaces were relaxed during the MC simulation, by monitoring the potential energy of the system. Then, we carried out the MD simulation at $T < T_m$ using the structure of the system at the end of the MC simulation as the initial state. Note that the switch from MC to MD simulations did not significantly influence the structure of the system.

Computation was carried out using an implicit leapfrog algorithm proposed by Fincham [16], with a time step of 1 fs. T and P of the system were kept constant at 265.58 K ($=0.98T_m$) and 1 atm, respectively, during the total run of 2.7 ns by using the method proposed by Berendsen et al. [17]. In this study, the control of P was carried out only by changing the dimension of the system for the direction normal to the interfaces (z direction), while the dimensions for the directions parallel to the interfaces (x and y directions) were kept constant during the simulation. Periodic boundary conditions were imposed in x , y and z directions. Following a previous study [13], the intermolecular interaction was modified using a switching function in the intermolecular distance from 0.95 to 1 nm [11].

4. Results and discussion

4.1. Observation of crystal growth of ice

Fig. 2(a) shows a time-sequence of the number density profile of oxygen atoms near one of the interfaces in the system along the z direction. Time-sequences of the potential energy and the density in the system are also given in Fig. 2(b). The results clearly indicate that I_h^d grew at the interface continuously as time passes. It should be emphasized that, for the first time, the growth of I_h^d near the real T_m at $P = 1$ atm was reproduced in the present simulation.

As shown in Fig. 2(a), more than four double-molecular layers of I_h^d (hereafter, we will call the

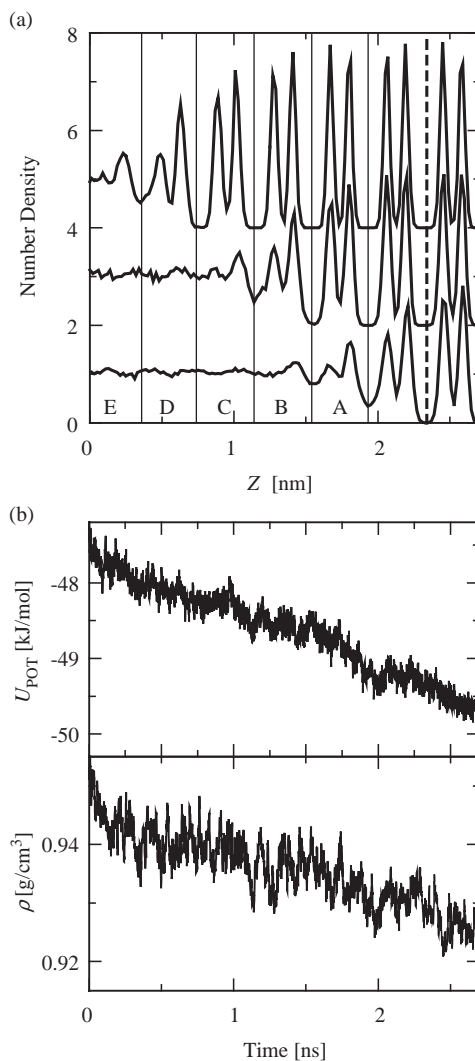


Fig. 2. (a) Number density profiles of oxygen atoms along the z direction near one of the interfaces in the system. The lower, middle and upper profiles are the ones averaged over periods between 0.3 and 0.4 ns, between 1.3 and 1.4 ns, and between 2.2 and 2.3 ns, respectively. The dotted line indicates the initial position of the interface. (b) The potential energy, U_{POT} , and the density, ρ , of the system as functions of time.

double-molecular layer “ice layer”) grew at the interface during the simulation. In addition, we also observed the growth of two ice layers at the other interface in the system. The observation of different numbers of ice layers, which grew during the simulation, between the interfaces reflects that

the growth of each ice layer is a “stochastic” phenomenon. Therefore, we expect that the numbers of ice layers, which grew at the interfaces, would be the same, if a much longer run than in the present work was carried out. We also observed the growth in a MD simulation of a system including interfaces between a $\{11\bar{2}0\}$ face of I_h^d and water at $T = 0.98T_m$. Moreover, the melting of I_h^d was observed at $T > T_m$, which supports the reliability of T_m of the model that was determined by free energy calculations of I_h^d and water [13]. Consequently, we confirmed that our model is suitable to simulate the growth of I_h^d near the real T_m at $P = 1$ atm.

Moreover, it can also be seen in Fig. 2(a) that the interface has a diffuse structure. This means that the prismatic interface has a geometrically rough structure, rather than a molecularly flat structure. Note that no significant change of the interface structure was observed during the growth. Hence, it turned out that ice layers grow at the prismatic interface with keeping the same rough structure of the interface.

The growth velocities at the interfaces, V_G , that we inferred from the present results were in the order of 10 cm/s. They are obviously larger than the experimental V_G of about 3 cm/s at $T = 0.98T_m$ in the real system ($= 267.7$ K) [3]. Even if the standard deviation of T_m in the model (± 9 K) was taken into account [13], V_G would be larger in the simulation than in experiment. The main reason for larger values of V_G in the simulation than in experiment is that latent heat, which was released at the interfaces due to the growth, was instantly removed from the system in this simulation. Namely, in this simulation, when T of the system deviated from $T = 0.98T_m$, molecular velocities in the system were instantly modified so as to approach $T = 0.98T_m$ [17]. In the real system, however, the latent heat gradually transfers from the interface to I_h^d and water phases. Generally, the transfer of the latent heat is the rate determinant factor for the growth of a crystal from its melt. Therefore, it is reasonable to observe larger V_G in the simulation than in experiment. Hence, analysis of the growth kinetics using the present simulation data, which we will describe below, should largely contribute to an under-

standing of the growth kinetics at the prismatic interface in the real system.

4.2. Growth kinetics

We analyzed the growth kinetics at the interface by estimating the fraction of molecules that are surrounded by four nearest neighbors, f_4 , as a function of time in the water phase near the interface. Since each molecule in I_h^d is surrounded by four nearest neighbors, f_4 for I_h^d , f_4^I , is unity. The number of nearest neighbors surrounding each molecule was calculated by counting the number of molecules included in a sphere of radius of 0.34 nm from each molecule. In order to analyze the growth kinetics at the interface in detail, the water phase near the interface was partitioned into six sliced regions parallel to the interface. Each region was named from region A to region E (see Fig. 2(a)). Then, we estimated f_4 as a function of time for each region.

Fig. 3 shows time-dependence of $\theta = (f_4 - f_4^W)/(f_4^I - f_4^W)$, which is a function of f_4 , for each region. Here, f_4^W is f_4 for the bulk water, which was estimated to be 0.54 ± 0.07 from a separate MD simulation of the bulk water at $T = 265.58$ K and $P = 1$ atm. θ takes unity if the structure corresponds to that of I_h^d , I_h^d , and zero if the structure corresponds to that of the bulk water. Therefore, θ can be regarded as an order parameter to describe the structure in each region.

It can be seen that θ increases from zero to unity in sequence from region A to region E, indicating the growth of an ice layer in each region. Note that, when θ for each region begins to increase from zero, θ for its underlying region has a value of 0.68 (see dotted lines and arrows in Fig. 3). This means that, whenever the growth of an ice layer occurs, the structure in its underlying region has an intermediate state between I_h^d and water, which corresponds to $\theta = 0.68$. This is consistent with the fact that the same rough structure of the interface was kept during the growth of ice layers.

Time-sequences of snapshots of water molecules in regions B and C at 1.5, 1.6, 1.7 and 1.8 ns are shown in Fig. 4. The value of θ at each moment is given in parenthesis, θ for region B reaches 0.68 at a moment between 1.5 and 1.6 ns. It can be seen

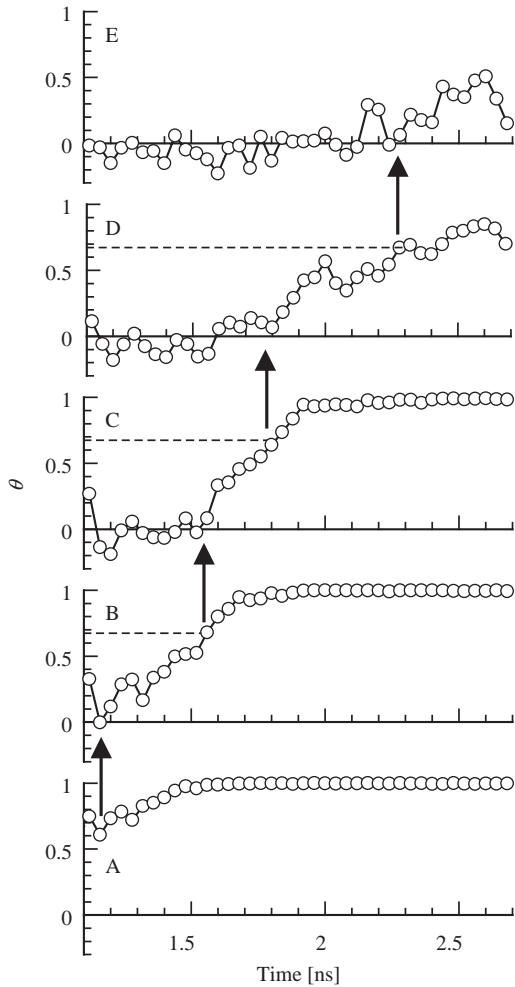


Fig. 3. $\theta = (f_4 - f_4^W)/(f_4^I - f_4^W)$ as functions of time for regions A–E.

that all molecules included in region B form a hydrogen-bonded network at 1.5 ns, though the arrangement of molecules in the network does not have long-range order. However, the molecular arrangement in the network 1.6 ns has long-range order like in I_h^d . Hence, we conclude that each ice layer grew by the reorganization of the hydrogen-bonded network, rather than by the self-diffusion of each molecule.

Note that the hydrogen-bonded network has a three-dimensional structure. This means that the network in region B is connected with that in region C. Therefore, the reorganization of the

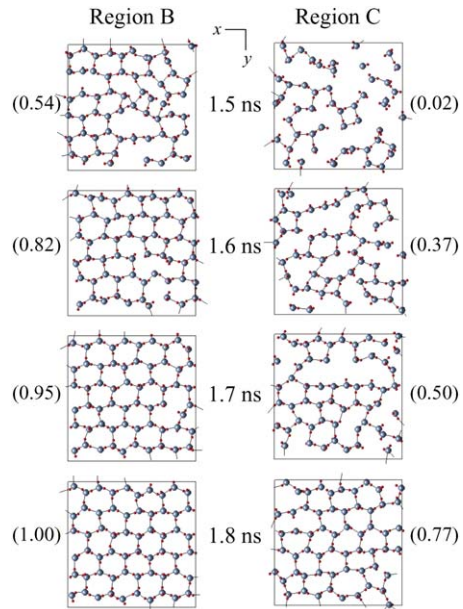


Fig. 4. Snapshots of water molecules in regions B and C at 1.5, 1.6, 1.7 and 1.8 ns. Large and small spheres in the snapshots are O and H atoms, respectively. The lines connecting two O atoms indicate hydrogen bonds, which are defined by an energetic definition [5].

network in region B induces the reorganization of it in region C simultaneously. In summary, the growth at the prismatic interface occurred by the kinetics of the reorganization of the hydrogen-bonded network, which spreads over, at least, two sliced regions. This is qualitatively consistent with the growth kinetics of collected molecule process at the prismatic interface that we speculated in previous simulation works [8,9].

Consequently, it turned out that our six-site model provides a satisfactory description of the growth of I_h^d in the real system. The strength of our model for the growth simulations is that, since T_m of the model is as high as the real T_m , mobility of molecules near T_m is enough large to yield the growth. Although the TIP4P model provides a good description of liquid water and has often been used for simulation works of the growth, T_m at $P = 1$ atm in the TIP4P model is 214 K [11], which is much lower than the real T_m . This means that mobility of molecules is too small to yield the growth near T_m . Moreover, at least at $P = 1$ atm,

the proton-ordered hexagonal structure, I_h^o , is more stable than I_h^d near T_m in the TIP4P model, unlike in the real system [13].

Finally, in order to confirm that our model is much more suitable for the growth simulations than the TIP4P model, we carried out a MD simulation for interfaces between the prismatic face of I_h^o and water at $T = 0.98T_m$ ($=210$ K) and $P = 1$ atm using the TIP4P model. However, no continuous growth of I_h^o was observed even if a slightly longer run than in the present work was carried out. For other potential models proposed till now, the most stable structure of ice and T_m of it have not been determined yet. Note, however, that, like the TIP4P model, most of those models have been developed only for simulation works of water. At present, as far as we know, our six-site model is the only one that provides the growth of I_h^d near T_m at $P = 1$ atm in a simulation work.

5. Conclusions

We applied a six-site model of H_2O [13], which we recently proposed, to a MD simulation of a system including interfaces between the prismatic face of I_h^d and water at $T = 0.98T_m$ and $P = 1$ atm. The results clearly indicated that I_h^d grows at the interfaces continuously as time passes. It should be emphasized that, for the first time, the growth of I_h^d was clearly observed near the real T_m at $P = 1$ atm in the present simulation work. Moreover, the growth kinetics at the interfaces was analyzed on a molecular scale.

In this paper, we demonstrated that our six-site model is suitable for simulation works on the crystal growth of I_h^d in the real system. In a forthcoming paper, we will discuss the growth kinetics at interfaces between I_h^d and water for different crystallographic orientations. The results will largely contribute to an understanding of the pattern formation of snow and ice crystals in the real system [1]. Moreover, use of our model for simulations of the mixture of ice (or water) and

antifreeze proteins (or antifreeze glycoproteins) will also contribute to an understanding of the inhibition mechanism of the ice growth in the biological system [2].

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