

An anisotropic behavior in crystal nucleation

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ABSTRACT

Solid/liquid phase change phenomenon of water is widely employed such as for food freezing, artificial snow and so on. In the classical theory of crystal growth, the size of an ice cluster leads to the result of either melting or solidification. In addition, the theory postulates that a crystal grows from a sphere. But in nature, we can observe the structure after the growth not to be a sphere shape. It contradicts to each other. So, it needs to be confirmed whether this theory can be applied for an anisotropic crystal or not. The critical size of ice radius is called a critical radius, which is a very small size. Therefore it is difficult to observe an atomic-scale, experimentally. And so it is necessary to carry out a simulation using molecular dynamics method. Using this simulation, it is intended to observe a solid/liquid phase change starting from sphere or ellipsoidal body of clusters. ST2 model was used for the water model. Through the observation of solid/liquid phase change, melting occurred toward a and b axes but

solidification occurred toward c axis in a case of spherical cluster. Ellipsoidal body, having a and b axes slightly bigger than that of sphere and c axis slightly smaller, was prepared. In this case, melting occurred in all three directions. So from these results, it can be said that the classical theory of crystal nucleation should consider an anisotropic behavior.

NOMENCLATURE

ΔG	Gibbs free energy	J
v_C	specific volume	m ³ /kg
γ	surface energy	J/m ²
r_C	critical radius	nm
T_m	melting point	K
l	latent heat	J/kg
ΔT	degree of supercooling	K
$\Delta\mu$	chemical potential	J

INTRODUCTION

Solid/liquid phase change phenomenon of water

is widely employed such as for food freezing, artificial snow and so on. In the classical theory of crystal growth, solid/liquid phase change occurs on the assumption that a crystal grows from a spherical crystal. That is to say, this theory postulates a crystal grows in all directions with uniformity. But as solidification phenomenon of water is an anisotropic behavior, it is thought that this theory is not applicable.

And so in this study, we tried to observe a behavior of crystal growth. It is difficult to observe an atomic-scale in the experiment. So we carried out a simulation using the molecular dynamics method.

THE CLASSICAL THEORY

The classical theory postulates that solid/liquid phase change of a crystal growth occurs as a growth from a spherical cluster. The surface energy exists at the interface between the cluster and the liquid phase. The change of free energy by increase or decrease of solid and liquid phases exists, due to solidification or melting of cluster. The sum of these energies is called as Gibbs free energy, which can be calculated as follows when a cluster of radius 'r' forms.

$$\Delta G = -\frac{4}{3}\pi r^3 \cdot \frac{1}{v_c} \cdot \Delta\mu + 4\pi r^2 \gamma \quad (1)$$

When Gibbs free energy has an extremal value, the radius can be calculated as follows

$$r_c = \frac{2v_c \gamma T_m}{l\Delta T} \quad (2)$$

When the process is phase change between liquid and solid, $\Delta\mu$ can be expressed as $\Delta\mu = l\Delta T/T_m$. This is the critical radius for nucleation of a cluster. At smaller 'r', the cluster tends to disappear because that lowers the free energy. At larger 'r',

the cluster tends to grow because that ,too, lowers the free energy. The value of the critical radius used in this study is calculated as follows.

$$r_c = 2.86nm \quad (3)$$

This is the value obtained by using the classical theory based on the surface energy and degree of supercooling to be $31.7[\text{mJ}/\text{m}^2]$ ^[1] and 15 [K], respectively.

SIMULATION METHOD

Ice structure is Ih structure which is the most common structure. Two kinds of the initial clusters were prepared. One is the spherical cluster having the size equivalent to the critical radius based on the classical theory and the other is the ellipsoidal cluster having a and b axes slightly bigger than the critical radius and slightly smaller in c axis. A method to prepare the simulation system is as follows. First of all, a sample of bulk ice is set in the cell. Then, the motion of molecules in a certain space is frozen and the temperature of other portion is raised up. So ice configuration other than the cluster portion is broken a part and becomes liquid state. Then the temperature of the cell is decreased down, and the motion of the molecules in cluster portion is released. So it becomes ice water mixture. And then the temperature of the cell is raised up to and controlled at the preset temperature, which is equivalent to the degree of supercooling, 15K in this study, and a calculation is carried out.

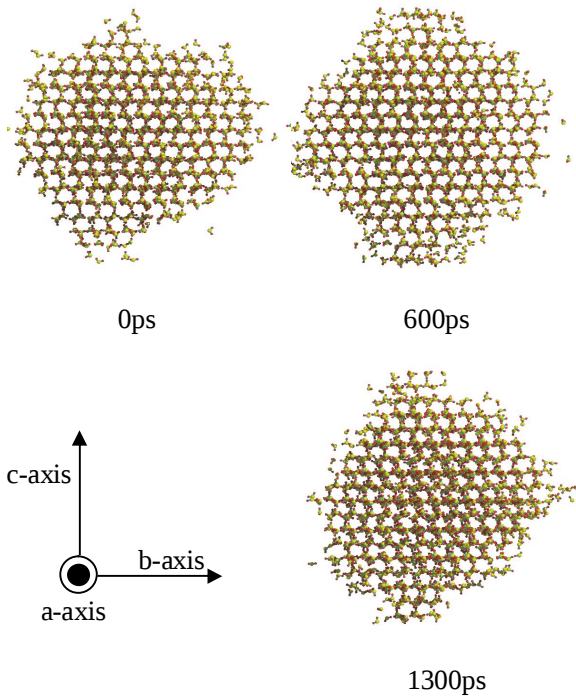
NPT ensemble was used for the governing equation where number of molecules, pressure and temperature are kept constant. The number of water molecules was set as 11664. The pressure and time span were 0.1[MPa] and 0.5[fs], respectively. Computation was carried out using the predictor-corrector method by Gear^[2]. ST2 model

was used for water molecule^[3]. This model has a structure which is similar to a tetrahedron with an oxygen atom at the center. It has two hydrogen atoms with positive charge and two negative charges without mass. Periodic boundary condition was imposed in x, y and z directions.

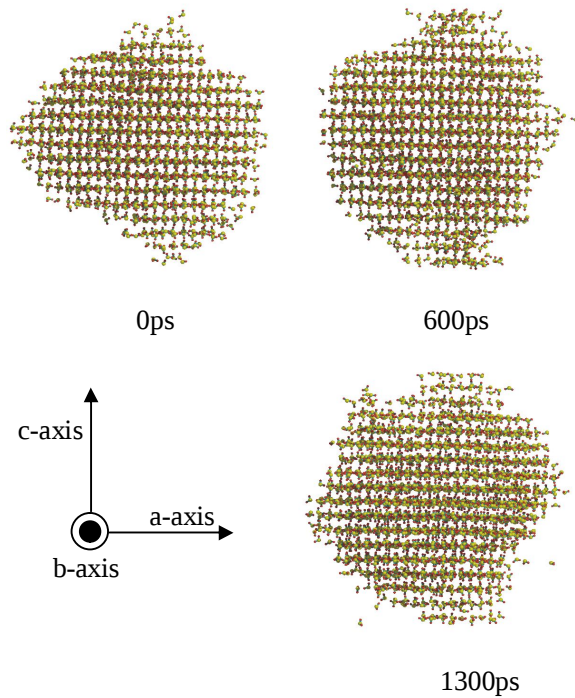
RESULTS AND DISCUSSION

First of all, the sphere cluster having the size nearly that of the critical radius was set in a cell and a behavior of crystal growth was observed.

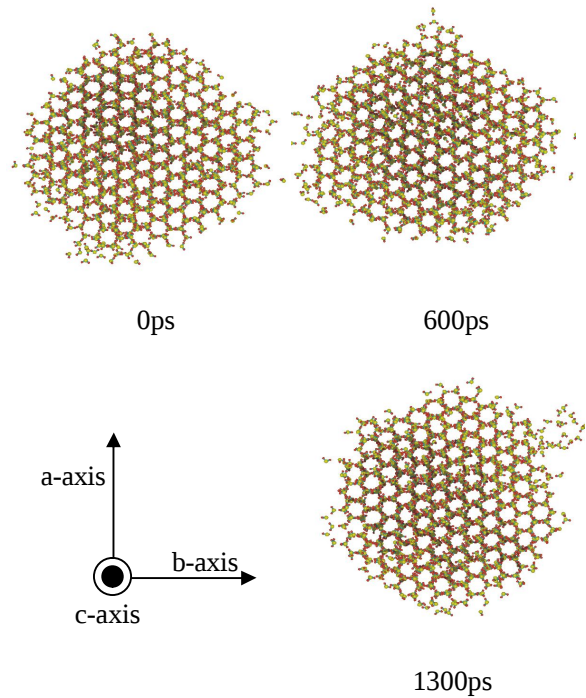
Fig.1 shows the configuration of water molecules in solid state. In order to express only water molecules in solid state, it was necessary to distinguish water molecules in solid state from those in liquid state. Difference in amplitude of vibration between solid and liquid is employed to distinguish them. Also starting time for observation was set at the time when various values were stable.



(a) Views from a-axis



(b) Views from b-axis



(c) Views from c-axis

Fig.1 The configuration of ice molecules starting from sphere shape

Fig.2 shows the time dependency of the number of ice molecules. As shown in Fig.2, it turns out that the crystal grows. In addition, as indicated in Fig.1, it seems that the crystal is melting in a and b axes direction and is solidifying in c axis. And so, in order to confirm whether the crystal grows in c axis direction, the number of ice molecules which exist at both ends in c axis direction was investigated. Fig.3 shows the distribution of the number of ice molecules at both ends in c axis. The size is increasing. From these results, it can be said that it is necessary for the classical theory to consider an anisotropic behavior in nucleation.

The reason why the cluster melted in a and b axes is due to the method to increase temperature to the preset temperature. The temperature was increased in stepwise from the temperature low enough to suppress the change in liquid/solid interface to the preset temperature. Since the temperature increment was drastic, cluster started to melt in a and b axes before the steady condition was achieved. On the other hand, the cluster did not melt in c axis while the system was kept running for a steady state. The reason for this is due to the behavior of water molecules in Ih structure. Hydrogen bonding in a and b axes are stronger than that in c axis and there is an independent structure between a, b axes and c axis. So the shape of a cluster in c axis direction was maintained.

Comparing to the phenomenon in nature, the melting with strong bonding in a axis corresponds to the Tyndall phenomenon, and the solidification corresponds to the phenomenon of growth as Frazil ice from an ice nucleus.

Next the ellipsoidal cluster having a and b axes slightly bigger than that of sphere and slightly smaller in c axis was prepared. The idea was based

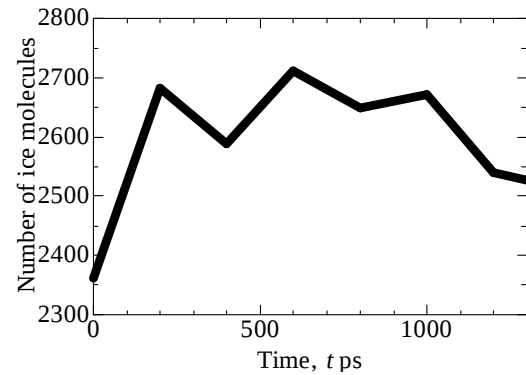
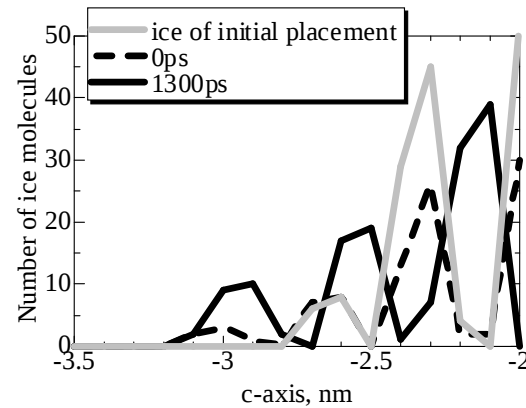
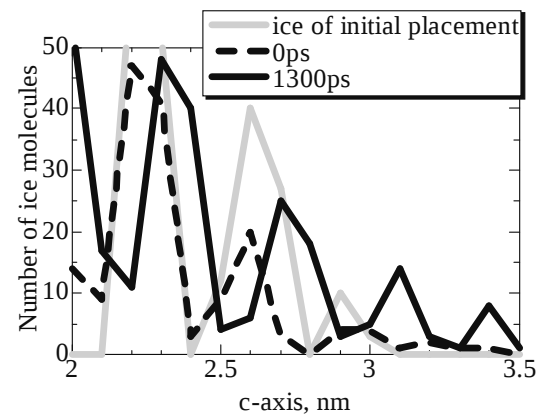


Fig.2 Time dependency of the number of ice molecules



(a) Left end



(b) Right end

Fig.3 The distribution of the number of ice molecules at both ends in c axis

on the observation starting from sphere. Fig.4 shows the time dependency of the number of ice molecules. Also Fig.5 shows the configuration of ice molecules. As shown in these figures, it turns out that the crystal melts in all axes directions.

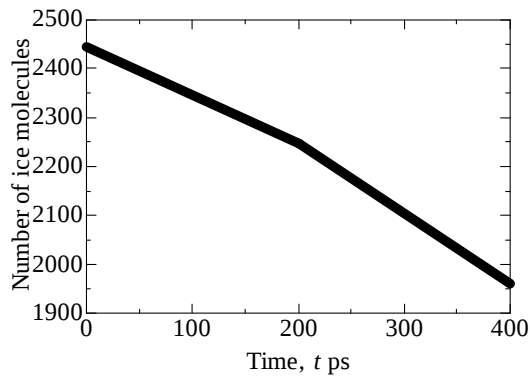


Fig.4 Time dependency of the number of ice molecules

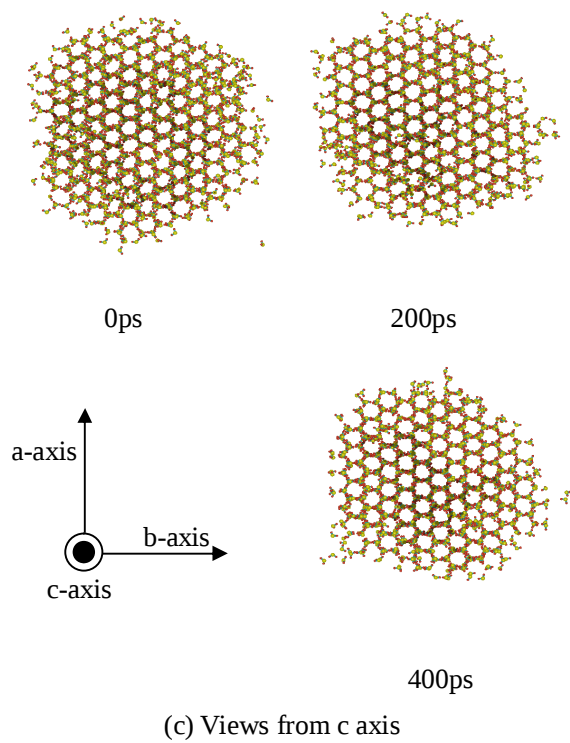
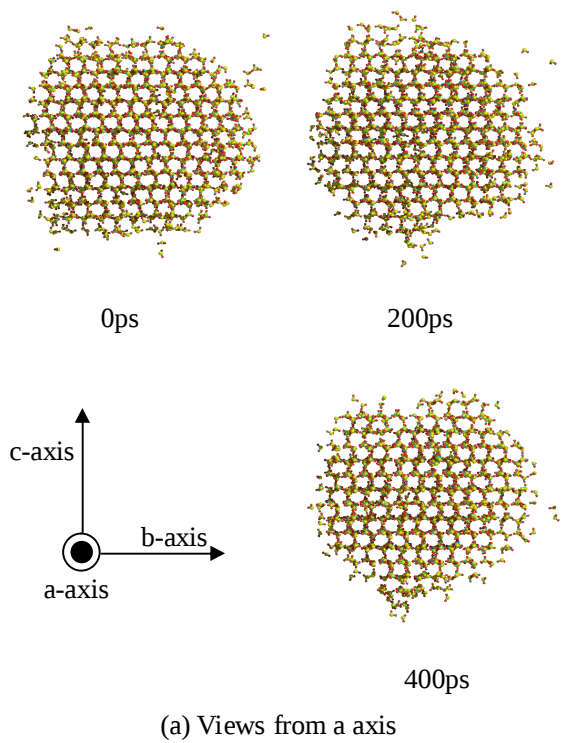
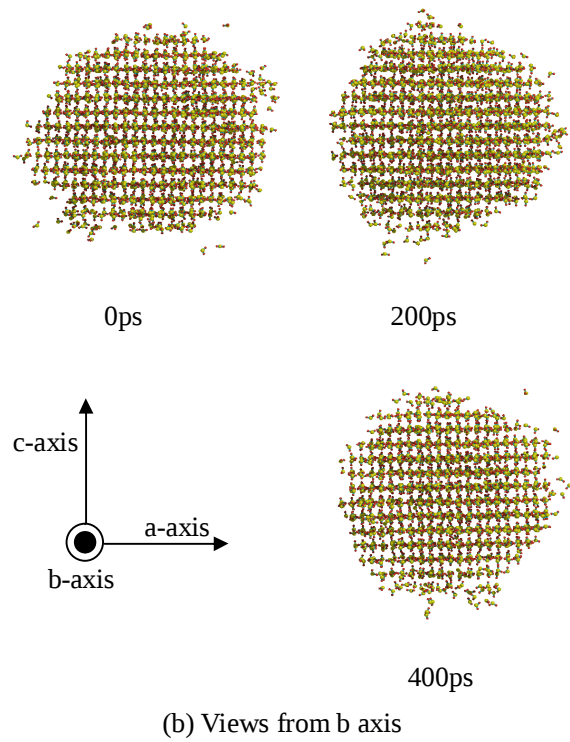


Fig.5 The configuration of ice molecules starting from ellipsoidal sphere

The reason why the crystal melted in a and b axes is similar to the reason in the case of a sphere cluster. The size was not big enough and the way to increase the temperature of the system to the preset temperature was too rapid. Also, as for in c axis, compared to the case of sphere cluster having the size of the critical radius, it turns out that the size in c axis direction was too small, this time, for solidification.

The melting of crystal due to the effect of the method of setting temperature was confirmed by observing the behavior on this crystal growth. So in order to investigate the influence of a shape and the degree of supercooling on crystal nucleation in detail, a method to raise temperature was modified and crystal growth is now investigated. The details will be reported shortly.

CONCLUSION

Solidification phenomenon of supercooled water was investigated by setting a sphere cluster in a cell. The size of the sphere was equivalent to the critical size for homogeneous nucleation in the classical theory. As a result, the crystal melted in a and b axes direction and solidified in c axis direction. From this result, it can be said that it is necessary for the classical theory to consider an anisotropic behavior of the critical nucleus. In a case of starting from the ellipsoidal cluster having a and b axes slightly bigger than that of sphere and slightly smaller in c axis, the crystal melted in all axes direction. Modification on temperature control was carried out and a simulation was performed.

ACKNOWLEDGEMENT

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