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Nucleation of supercooled water on solid surfaces

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Abstract

Heterogeneous nucleation of water was investigated using molecular dynamics simulation. Solid with fcc (111) surface was placed at the bottom of a cell consisting of 864 water molecules. ST2 model with NPT ensemble was used. The pressure and temperature were set to be 0.1 MPa and 275 K, respectively. The interaction between water and the solid was based on the equations proposed by Spohr. Exception was made on the lattice constant which was slightly modified to fit with that for ice structure. The shape of the solid surface was considered. It was found that the only one layer of water molecules was adsorbed in a case of a flat surface, whereas ice nucleation occurred by removing some of the atoms from the surface. Spohr's interaction was also modified so that the dipole moment of water became anti-ferroelectric. It was found that the modification increased the ice growth, further. The effect of lattice constant of solid on nucleation was also investigated. It was found that the variation on lattice constant with a few percent from that of ice was acceptable for nucleation, especially on shrinking side. On expanding side, however, it gave some gaps for water molecules to fit in other than that for ice structure, and it prevented the growth of ice. Hence, a guideline for the selection of ice nucleus material was obtained.

Keywords: Research; Nucleation; Water; Supercooling; Parameter; Geometry; Surface; Growth; Ice

Nucléation de l'eau en surfusion sur les surfaces solides

Mots clés : Recherche ; Nucléation ; Eau ; Surfusion ; Paramètre ; Géométrie ; Surface ; Croissance ; Glace

1. Introduction

Utilization of latent heat between water and ice became widely active. However, the existence of supercooling phenomenon makes the control difficult. There are a few methods to freeze supercooled water. One is a method to give some external forces, and the other is a method to mix some potential material with supercooled water. However, researches in an atomic level became indispensable in order to find such effective material. Congeniality of crystal structure of the material and the potential with water molecule needs to be considered.

A lot of researchers performed studies on the interaction between water and metals using molecular dynamics method. Spohr et al. [1] used BJH model [2] for water molecule, and they examined the behavior of water molecule in the vicinity of platinum (100) plane at 349 K. Raghavan et al. [3] used SPC/E model [4] for water molecule, and they examined the behavior of water at 300 K

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Nomenclature

a_c	lattice constant, Å	r	distance between atoms or charges for calculation, Å
a_h	atomic distance in three points surface, Å	R	distance between oxygen atoms, Å
a_n	atomic distance of the nearest neighbor, Å	t	time, ps
g_{oo}	oxygen–oxygen pair correlation function	x, y, z	coordinate, pm
L	size of cell, pm	ε	depth of potential, J
P_e	dipole moment, Cpm	ϕ	intermolecular potential, J
q	electric charge, C	σ	molecular size, Å

by placing them between two sheets of platinum (111) planes. Lee et al. [5] used TIP4P model [6] for water molecule, and they examined the molecular direction of the water at 25 °C near the metal surface. Three types of surfaces were prepared, namely, a smooth plane, a hydrophobic plane with the ruggedness in molecular level, and a hydrophilic plane using SiO_2. However, paper on the heterogeneous nucleation of water is few. Authors have used ice as a solid surface, and clarified the relationship between the growth rate of the solid–fluid interface and temperature, relationship between the direction of solid crystal plane and the growth rate [7,8]. Furthermore, authors selected platinum as foreign particle for nucleus since its structure is approximately similar to that of ice Ih. The behavior of the supercooled water at 250 K in the vicinity of the rugged surface was described [9].

The purpose of this study is to carry out computer simulation using molecular dynamics method, and to clarify the solidification phenomenon of water on the solid plane in order to obtain a guideline for the selection of ice nucleus material. It should be useful in various areas such as ice storage system.

2. Calculation method

NPT ensemble was used for the governing equation, where number of molecules and pressure and temperature were kept constant. ST2 model [10] was used for water molecule. 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. The potential between water molecules is shown in Eq. (1).

$$\phi_{ST\,2} = 4\varepsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right\} + S(R)\frac{1}{4\pi\varepsilon_0} \times \sum_{i=1}^{4}\sum_{i=1}^{4}\frac{q_{ei}q_{ej}}{r_{ij}} \quad (1)$$

$q_e = 0.2375e$ [C]; $\varepsilon = 5.2605\times10^{-22}$ [J], $\sigma = 3.10$ [Å].

The number of water molecules, the pressure, the temperature and a time step were set as 864, 0.1 [MPa], 275 [K] and 0.5 [fs], respectively. The rapidest solidification rate can be obtained for ST2 model at this temperature [7]. Furthermore, the predictor–corrector method by Gear [11] was used for time development.

The purpose of this research is to find an ideal material for nucleation. To begin with, platinum was selected since the crystal structure is fcc and the lattice constant gives very close bonding length to that of ice. In order to adjust the bonding length to suit with that of ice using ST2 model, the lattice constant for the solid changed slightly. Hence, the material cannot be called as platinum. However, basically, the equation for platinum, which Spohr et al. proposed [12], was used for the potential function between solid atom and water molecule. The potential energy is shown in Eq. (2).

$$\phi_{H_2O\text{–}W} = \phi_{O\text{–}W}(r_{O\text{–}W}, \rho_{O\text{–}W}) + \phi_{H\text{–}W}(r_{H\text{–}W}) + \phi_{H\text{–}W}(r_{N\text{–}W}) \quad (2)$$

$$\phi_{O\text{–}W} = \{A\exp(-ar) - B\exp(-br)\}f(\rho) + C\exp(-cr)\{1 - f(\rho)\}$$

$$\phi_{H\text{–}W} = A'\exp(-a'r)$$

$$f(\rho) = \exp(-d\rho^2)$$

$$\rho = \sqrt{(\Delta x)^2 + (\Delta y)^2}$$

Δx, Δy are the projection distance between oxygen atom and solid atom.

A, B, C, A', a, b, c, d, a' are the potential parameters as follows:

$A = 1894.2$, $B = 1886.3$, $C = 10^6$, $A' = 1.7142$ [10^{-19} J]; $a = 1.1004$, $b = 1.0966$, $c = 5.3568$, $a' = 1.2777$ [Å^{-1}]; $d = 0.5208$ [Å^{-2}].

The interaction between solid atom and oxygen atom consists of repulsive force and attractive force terms. According to the effect of $f(\rho)$, the projection distance, the influence of the solid atom becomes large when $f(\rho)$ is small, and it expressed the adsorption of the water molecule to the solid atom. In the meantime, the repulsive force always works on the hydrogen atom from the solid atom. This effect gives a configuration in which the hydrogen atom always