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Anisotropy in structural phase transitions at ice surfaces: a molecular dynamics study

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Abstract

Molecular dynamics simulations of ice surfaces at temperatures below the melting point were carried out. As a result, thin liquid-like layers (that is, quasi-liquid layers, QLL) were detected on both ice{0001}- and ice$\{10\bar{1}0\}$-faces. We emphasize that the anisotropy in the QLL thickness obtained in this MD simulations qualitatively coincides with that obtained by the experiment. © 1997 Elsevier Science B.V.

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1. Introduction

A crystal surface may start to melt at temperatures below its bulk melting point, and is covered with a thin liquid-like layer (quasi-liquid layer, QLL) [1]. This phenomenon is well known as surface melting, which plays an important role in surface phenomena as surface diffusion, surface reconstruction of crystals, crystal growth and so on.

The ice crystal is known as one of the materials which show surface melting [2–4]. The surfaces of ice crystals are important not only for surface science, but also for recent environmental problems [5,6]. On the other hand, the anisotropic surface melting of ice has received much attention in relation to the pattern formation of ice and snow crystals [7]. Although several experimental studies about the anisotropy have been performed [2–4], much ambiguity has been remained yet. Recently Kroes investigated the ice surface structure using the molecular dynamics (MD) simulation method [8], and proved the surface melting on the ice{0001}-face. However, he did not pay attention to the anisotropic properties of ice surfaces.

The purpose of this study is to elucidate the anisotropic surface melting of ice crystals at the molecular level using MD simulations.

2. Simulation method

We prepared two kinds of simulation systems. One was a system including an ice{0001}-face ({0001} system), and the other a system including an ice$\{10\bar{1}0\}$-face ($\{10\bar{1}0\}$ system). The shape of each

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system was a rectangular parallelepiped consisted of 720 water molecules. The dimensions of the systems were approximately 22.4 Å × 23.3 Å × 43.8 Å for the former and 22.4 Å × 21.9 Å × 46.6 Å for the latter. A TIP4P model [9] was used for estimation of the intermolecular interaction, and the potential curve in the intermolecular distance between 10.45 Å and 10.95 Å was modified using a switching function [8].

The computational procedure is much the same as that described in Ref. [8], except for the length of the total simulation run; namely, the total run of our study is about three times longer than that described in Ref. [8]. At the beginning of the simulations, all water molecules were arranged to make an ice crystal structure. Periodic boundary conditions were imposed in the directions parallel to the surfaces (x and y directions), and the free boundary condition was imposed in the z direction. This procedure creates two free surfaces in the system. Then, the molecules at one side of the two free surfaces were fixed on the lattice points of perfect ice crystal to preserve the property of bulk ice in the system. The time step of the computations was chosen as 2 fs. A leap-frog algorithm was used for solving the motion equation of water molecules, taking with the quarternion method for the rotational motions.

The exact melting point T_m of TIP4P ice is not known. In this study, we assumed that T_m is around 250 K just as in the MD study by Kroes [8], and performed MD simulations with every 5 K at temperatures between 220 and 250 K. The temperature was kept constant during the simulation by the scaling method [10]. As a result, the QLL was detected on both faces within the total simulation run of 1 ns. We note that the thickness of the QLL, d_{QLL}, did not change during a period between 0.5 and 1 ns. Consequently, we confirm that the surfaces of the systems reached the equilibrium state during the simulation run.

3. Results and discussion

Fig. 1 shows the snapshots of water molecules, projected to the plane normal to the surfaces for both systems at 250 K. One can see that the water molecules in the surface regions for both systems are arranged in the disordered state, in contrast to the crystalline arrangement in deeper regions. This clearly indicates that the surface melting occurs on both faces and that the disordered layers correspond to the QLL. Specially, it should be emphasized that the thickness of the QLL apparently differs between the systems. We claim that anisotropic surface melting was observed at the molecular level by this MD study.

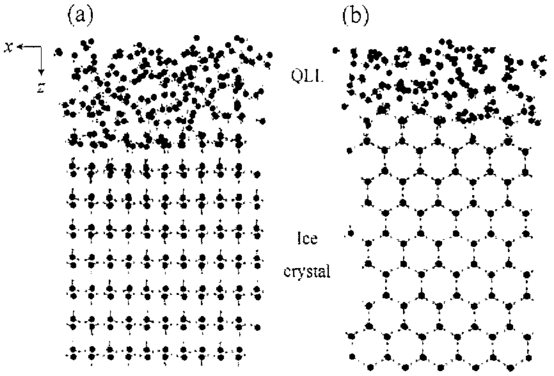

Fig. 1. Snapshots of water molecules: (a) for the ice{0001}-face system and (b) for the ice{10$\bar{1}$0}-face system. The positions of the water molecules were determined by the coordinates averaged over a period from 0.9 to 1 ns.

To estimate d_{QLL} exactly, we calculated the profiles of root mean square fluctuations in the oxygen–oxygen length between two water molecules, δ [11]. It is defined as

$$\delta = \frac{2}{n(n-1)} \sum_{i<j}^{n} \frac{\sqrt{\langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2}}{\langle r_{ij} \rangle}.$$

Here, n denotes the number of water molecules, and r_{ij} the distance between the oxygen atoms of molecules i and j. $\langle\ \rangle$ means the time average. In this study, let us introduce the criterion for the QLL as follows: if there exists a region satisfying $\delta \geq 0.1$ (that is, the Lindemann criterion [11]), then the region is regarded as the QLL. Fig. 2 shows an example of δ profiles as a function of the z component at 250 K. Solid and open circles denote δ for the {0001} and the {10$\bar{1}$0} systems, respectively. Using the criterion of δ, we can estimate d_{QLL} as 11.5 Å for the {0001} system and 9 Å for the {10$\bar{1}$0} system (see the arrows in Fig. 2).

In Fig. 3, we show the relationship between d_{QLL} and the temperature for both systems. At temperatures below 235 K, d_{QLL} for the {10$\bar{1}$0} system is larger than that for the {0001} system. However, the

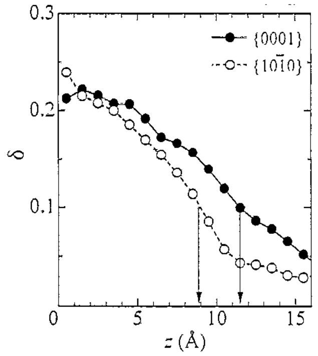

Fig. 2. Root mean square fluctuations in oxygen–oxygen length between two water molecules, δ, as a function of the z component. The initial positions of the surfaces were set to the z component of zero. Solid and open circles indicate δ for the {0001} and the $\{10\bar{1}0\}$ systems, respectively.

relationship of d_{QLL} between the systems completely reverses at higher temperatures. Note that a similar relation of d_{QLL} has been obtained by an ellipsometric study [3]. Moreover, other experimental studies have also indicated that d_{QLL} for the {0001} system is larger than that for the $\{10\bar{1}0\}$ system at temperatures close to the actual melting point [2,4]. This indicates that the anisotropy obtained in this study qualitatively coincides with the experiments. This anisotropy must be due to the anisotropic structures of interfaces between the QLL and underneath ice crystal [3,12]. Besides, we note that our results for the {0001} system are roughly consistent with the results in Ref. [8].

On the other hand, the absolute values of d_{QLL} are two or three orders of magnitude smaller than the experimental values. One of the reasons might be the difference in the condition around the surfaces [4]. For example, the surfaces used in the experiments were exposed on the air, in contrast to this simulation study. It should be mentioned specially that, in spite of the difference in the condition, both the MD study and the experiments show the same anisotropic relation. Again, we emphasize that the anisotropic surface melting obtained by this MD study qualitatively coincides with the experiments.

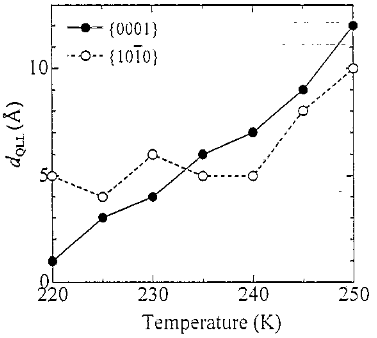

Fig. 3. Thickness of the QLL, d_{QLL}, as a function of temperature. Solid and open circles indicate d_{QLL} for the {0001} and the $\{10\bar{1}0\}$ systems, respectively.

4. Conclusions

We performed the MD simulations of both ice{0001}- and ice$\{10\bar{1}0\}$-faces. The surface melting phenomena were confirmed on both faces at the molecular level. We conclude that the anisotropy in the QLL thickness obtained in this study qualitatively coincides with that obtained by the experiment.

Acknowledgements

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