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Probing ice growth from vapor phase: A molecular dynamics simulation approach

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ABSTRACT

We demonstrate a molecular dynamics simulation approach that can be used to investigate ice growth from water vapor. Using this approach, we explore ice/vapor interfacial systems focusing on the behavior of the quasi-liquid layer (QLL) which forms on the ice surface near its melting point. The dependence of the QLL on temperature, ice face and the flux of gas-phase water molecules are examined. We find that the thickness of the QLL increases by increasing temperature, and that the prismatic QLL is thinner than the QLL on the basal face. Both observations are consistent with previous investigations. In addition, variation in the gas densities show that an increase in the flux of water molecules in the gas vapor phase, associated with higher growth rates, results in an increased thickness of the QLL.

1. Introduction

Ice plays crucial roles in many environmental and atmospheric phenomena [1,2,3]. For example, various properties of clouds are controlled by formation and growth of atmospheric ice crystals. A better microscopic-level understanding of ice growth from the vapor phase can help to provide insights into factors, for example, influencing climate processes [3]. Also, it is well known that the apparent slippery nature of ice surfaces is due to the presence of a premelted layer on its surface [1]. The properties of this premelted layer are different from those of liquid water and consequently it is commonly referred to as the quasi-liquid layer (QLL). As the characteristics of this QLL often play a decisive role in properties of the surface of ice, they have been parts of a variety of studies in chemistry, geophysics and astronomy [1,4,5,6]. The behavior of the QLL is also expected to influence ice growth from water vapor [7].

Ice growth from vapor is governed by various factors. Experiments have probed the effects of transport phenomena (of heat and particles) in addition to attachment kinetics [7,8,9], where the latter looks to account for the arrangement of incident water molecules in relation to the ice crystal. Experiments have demonstrated that the growth of ice depends on the temperature and supersaturation at the ice surface [8]. It is also acknowledged that the rates of growth (at a particular supersaturation) are apparently different on various ice faces [10,11]. Different morphological measurements of ice crystal growth from the vapor phase are in general agreement on the temperature and supersaturation dependence of ice crystal morphologies (see the work of Bailey and Hallett [12] and references within). There have also been various experimental studies aimed at probing the underlying molecular attachment mechanism at the ice-vapor interface [8,9,13,14]. However, there are significant inconsistencies among the reported results. Libbrecht and coworkers have explored possible sources of systematic errors [7,8,9] and have identified that the discrepancies among the measurements are mainly due to particle and latent heat diffusion effects and substrate interactions. A molecular simulation approach could aid on understanding the underlying physical processes that control the ice growth dynamics by providing molecular-level insight into the surface structure of ice, including the premelted layer, and how incident water molecules incorporate into the ice surface.

The QLL that forms on the surface of ice at temperatures just below its melting point has been the subject of many studies in the literature [1,5,6,7,15,16,17]. Various experimental techniques have been used to measure the thickness of the QLL [15,16,17,18,19,20,21,22] (for a more comprehensive review of the literature, see [15,16]). All of these investigations have confirmed that the QLL exists and that its thickness increases considerably as the temperature increases. However, there are discrepancies of as much as two orders of magnitude in the actual values at specific temperatures. This variation has been described as arising from different experimental techniques used to measure the thickness, differences in the ice sample preparation procedure, and existence of impurities in the experimental environment [15].

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The QLL behavior at temperatures close to the melting point has been the subject of various molecular dynamics (MD) simulation studies. Kroes [23] showed that by increasing the temperature, the disruption of the hydrogen bonding network at the surface results in disordering of the QLL. Nada and Furukawa [24] investigated the anisotropy in structural transitions on principle faces of ice at different temperatures and showed that QLL thickness on the basal face is greater than the prism face. The temperature dependence of the thickness of the QLL was also examined in the MD simulations carried out by Conde et al. [25]. In this previous work, the QLL thickness was compared on the basal, prism and secondary prism faces of ice and it was observed that for a given temperature, the QLL is thickest on the basal face and thinnest for the secondary prism face. In another MD study, Pfalzgraff et al. [26] explored the characteristics of the QLL and found a similar trend for the variation of the QLL thickness on the different faces of ice Ih. Using MD simulations, Fukazawa and Kawamura [27] showed that the peaks in the density profile from the first two layers of the surface of ice Ih are broader and lower in comparison to those of other layers; this was interpreted as indicating that the QLL consists of two sublayers of water molecules. Similar behavior in the density profiles was observed elsewhere in literature [17,28].

To the best of our knowledge, there has been no previous molecular simulation study reported in the literature that explores ice growth from water vapor. Here, we develop an approach that utilizes steady-state molecular dynamics simulations that is appropriate for investigation of ice growth from the vapor. We then demonstrate that this approach can be used to probe this phenomenon microscopically, where we have explored the dependence of the QLL behavior on temperature, ice face and flux of particles in the gas phase.

The structure of the remainder of this paper is organized as follows. The details of the simulations and the methods used in this work along with a description of the system preparation are described in Section 2. The results and discussion of simulations demonstrating ice growth from the vapor phase are provided in Section 3. Finally, our conclusions and suggestions for future work are given in Section 4.

2. Methodology and simulation details

In order to produce a steady-state flux of water molecules in the gas phase, we adapted an approach that has been successfully employed [29,30] to examine steady-state ice growth from liquid water. In this previous approach, the system consisted of a simulation cell containing ice and liquid slabs sharing two interfaces in periodic boundary conditions. The temperature was significantly elevated in a specific region of the system close to one surface of the ice slab resulting in melting, while the rest of the system was kept at the target temperature. For the present ice/vapor systems, that approach is mimicked except the liquid slab is replaced by a water vapor slab. The hot region then serves to evaporate molecules from the surface, which results in a flux of water molecules into the gap between the ice surfaces and moving towards the opposing ice surface.

For generating an initial system configuration, an ice crystal was first produced [31] by locating the oxygen atoms on lattice points based on the crystallographic parameters of ice Ih and assigning hydrogen atoms to them following the ice rules [32]. The orientations of the molecules were then adjusted to minimize the total dipole moment of the crystal. In the preparation of all systems, the temperature of the initial crystal was first increased from 0 K in a stepwise process to the target temperature. At each step the system was equilibrated at 1 bar for 50 ps to remove stress from the crystal. Once the target temperature was achieved, the initial ice slab was split equally and the two parts were displaced to generate a roughly 60 Å gap representing the vapor phase. The systems were subsequently equilibrated in the NVT ensemble for at least 2 ns. The subsequent production simulation times ranged between 60 and 200 ns, where values varied depending on the growth rate and the behavior of each system (see Table 1).

The choice of appropriate parameters for the temperature pulse (including its height, width and location) is crucial for providing an appropriate steady-state flux of gas particles that avoids formation of clusters of molecules in the vapor and gives rise to consistent ice growth. We found that a Gaussian-like temperature pulse, consisting of a Gaussian shape with a broaden peak with a maximum of 450 K and a width of 17 Å at its half height, works well to ensure complete vaporization of molecules. Temperature control was achieved with separate Nosé-Hoover 4-element chain thermostats [33] applied to each water molecule with all four time constants equal to 0.5 ps. The position of the temperature pulse was maintained at a fixed distance from the growing ice surface, where this value was determined for each system. Thus, in a steady-state simulation this temperature pulse moves into one of the ice surfaces at the same rate as the ice grows on the other surface. After performing several trial simulations, it was found that steady-state ice growth was achieved with relative distances between the center of the temperature pulse and the evaporating surface in the range of approximately $14-20$ Å.

Both the prism and basal faces of ice Ih were investigated in this work. The X, Y and Z dimensions of the simulation box of the equilibrated basal (containing 2208 molecules) and prism (containing 2464 molecules) face systems were roughly $27 \times 31 \times 150$ Å^3 and $29 \times 32 \times 150$ Å^3, respectively. Previous studies [29,31] of ice growth from liquid water have demonstrated that systems of this

Table 1
The key parameters and results for the simulations carried out in this work. ρ is the gas density (determined by averaging over the appropriate region of the gas phase density profile), σ is the QLL thickness, R_{vapor} is the measured rate of growth from water vapor, and R_{liquid} is the rate of growth from liquid water at that temperature taken from [29]. The vapor pressures were determined from the density and temperature using the ideal gas law. Specific error estimates are provided for R_{vapor}, while the relative errors for ρ and σ are estimated to be 10% and 5%, respectively.

Label	Face	Temperature (K)	ρ (mol/m^3)	Vapor Pressure (atm)	σ (Å)	R_{vapor} (Å/ns)	R_{liquid} (Å/ns)	Simulation time (ns)
b220	Basal	220	10	0.18	8.8	0.16 ± 0.02	0.18	200
b235	Basal	235	30	0.58	9.1	0.53 ± 0.07	0.60	80
b245-1	Basal	245	25	0.50	12.4	0.40 ± 0.08	0.56	145
b245-2	Basal	245	9	0.18	9.8	0.12 ± 0.04	0.56	80
b245-3	Basal	245	6	0.12	8.8	0.08 ± 0.01	0.56	65
p220	Prism	220	20	0.36	7.6	0.32 ± 0.11	0.34	135
p235	Prism	235	45	0.87	8.4	0.75 ± 0.27	0.88	100
p245-1	Prism	245	25	0.50	10.2	0.45 ± 0.03	0.85	60
p245-2	Prism	245	18	0.36	9.0	0.32 ± 0.03	0.85	90
p245-3	Prism	245	7	0.14	8.6	0.13 ± 0.01	0.85	110