Note: Heterogeneous ice nucleation on silver-iodide-like surfaces

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Ice nucleation is an important phenomenon influencing many aspects of our environment, from climate[1] to biological systems. Indeed, understanding "how ice forms" has recently been identified as one of the top ten open questions in ice science.[2] Almost all ice nucleation occurs heterogeneously, the process being initiated by an external nucleation agent like a crystalline dust particle or organic matter. However, we have relatively little knowledge about the microscopic mechanisms of this transformation, because the infrequent but rapid nature of the ice nucleation events and the small size of critical nuclei make these details hard to probe experimentally. Indeed, even for crystals that are good ice nucleants, little is known about which surfaces, steps, or defects may be the active nucleation sites.

Computer simulations can potentially help by providing insights into the microscopic mechanisms. However, ice nucleation is hard to simulate with all-atom models of water, as the natural dynamics of ice growth is very slow at temperatures where the critical nucleus is of a size that is reasonable to simulate.[3] Nevertheless, heterogeneous ice nucleation has recently become increasingly probed by computer simulations,[4–8] for example, on kaolinite[5] and graphitic[6] surfaces.

Silver iodide (AgI) is an excellent ice nucleant that is widely used in cloud seeding. Its nucleation ability was discovered in 1947 by Vonnegut[9] based on the structural similarity between β-AgI and ice I_h—both are based on the hexagonal diamond lattice and have a close lattice match ($\sim$3%). In this paper, we consider ice nucleation at model AgI-like surfaces with the aim of improving our fundamental understanding of how ionic crystal surfaces can potentially initiate ice nucleation. Previous modelling of the AgI-water system has focussed on the preferred water adsorption sites,[10,11] the structure of surface water clusters[12] and layers,[13] and nucleation of liquid water on AgI particles.[14]

To model this system we use the TIP4P/2005[15] potential for water, the Parrinello, Rahman, and Vashishta (PRV) potential for AgI,[16] and a potential with a Lennard-Jones term and a Coulombic term for the AgI-water interactions where the parameters were taken from Ref. 11. However with this setup, we found that, in contrast to real AgI, the crystal began to quickly dissolve in water, and therefore, we constrained the Ag^+ and I^- ions with a harmonic potential to their equilibrium positions in a perfect AgI crystal, with the spring con-

stant set to $k = 1000\,\mathrm{kcal\,mol^{-1}\,\mathring{A}^{-2}}$ instead of using the PRV potential.

Simulations were carried out at $T = 242$ K which represents a supercooling of approximately 10 K for TIP4P/2005. An AgI crystal slab of the correct orientation was placed in the middle of the box, so as to expose the basal, prismatic, or normal faces, with water on both sides. We ran molecular dynamics simulations at constant volume and temperature with repulsive walls at the top and the bottom of the box and periodic boundary conditions in x and y, with the position of the walls chosen so that there was $\sim$20 Å of empty space at both ends of the box. Further details of the simulations can be found in the supplementary material.[17]

We found that relatively facile ice nucleation and growth occurred on the Ag^+-terminated basal plane, but no ice formation was seen for any of the other faces on our simulation time scales. The ice formation occurs via a two-step mechanism. First, there is the fast formation of a hexagonal layer of strongly adsorbed water molecules on the surface.[14] This initial ice-like bilayer, illustrated in Figure 1(c), forms in less than 3 ps. Then, after a certain lag time (of the order of 40 ns), a nucleation event occurs and ice starts to grow on the top of this layer (typically 1 layer per 10–15 ns). After sufficient time, as illustrated in Fig. 1(d), most of the water above the Ag^+-teminated face forms ice, and the corresponding density profile (Fig. 1(e)) shows a series of clear double peaks only at the silver-terminated side, their split structure reflecting the "chair" conformations of the hexagons in these bilayers.

Interestingly, although a somewhat similar adsorbed layer formed on the I^--terminated side (see Fig. 1(b)),[13] this layer was unable to initiate ice growth. On the Ag^+-terminated basal face, the strong interaction between the Ag^+ ions and the oxygens strongly constrains the positions of the water molecules in the adsorbed layer, whereas the I^--hydrogen interaction provides a weaker constraint on the adsorbed water on the I^- face. The greater disorder and flatter, less bilayer-like character of the layer is evident from Figs. 1(a) and 1(b) and underlies its inability to template ice growth. Similarly, although water molecules strongly adsorbed on the other faces (prism and normal) that we considered, these layers are less obviously ice-like and are unable to act as templates for ice growth on our simulation time scales.

The current report provides one of the first systems where heterogeneous ice nucleation has been observed for an
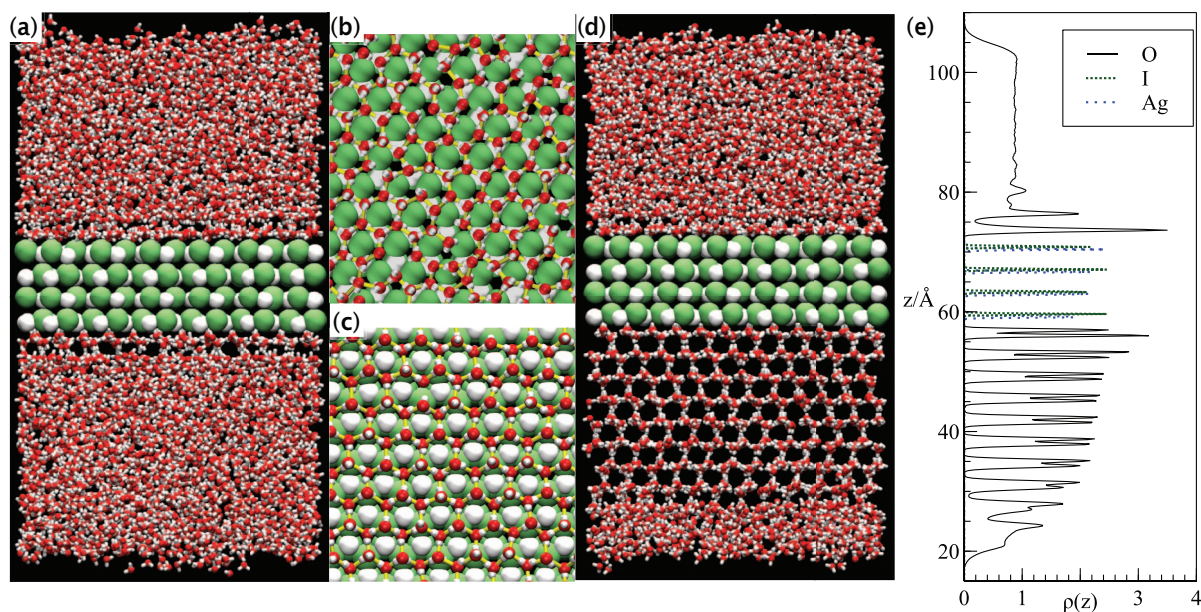
FIG. 1. Ice nucleation on the basal faces of AgI. Snapshots after $t = 3$ ps of (a) the whole simulation box, and the adsorbed layers on the (b) I^--terminated and (c) Ag^+-terminated faces. (d) Snapshot of the whole box and (e) local density variation along z at $t = 160$ ns. The box contains 4914 water molecules and 960 ions in the AgI crystal.

all-atom model of water in the absence of an imposed electric field and shows how an ionic surface can efficiently initiate ice nucleation *via* a two-step mechanism. The surface must be capable of templating the formation of a sufficiently ordered ice-like layer, which will template further ice growth. A very similar mechanism has previously been reported in Ref. 8 for a monatomic water model on model surfaces. We also note that while this report was being considered for publication, simulations of a very similar water/AgI model have been reported that observed ice crystallization in a manner very much consistent with the current work.[18]

Although our results provide interesting fundamental insights into a potential mechanism of heterogeneous nucleation on ionic surfaces, there are two important caveats concerning its application to real silver iodide. First, the spring constant used to constrain the position of the ions in the crystal is unrealistically large. For example, a value $k = 70$ kcal mol^{-1} Å^{-2} is needed to reproduce the width of the peaks in the radial distribution function obtained with the PRV potential. However, nucleation was never seen on the time scale (up to 260 ns) of our simulations with smaller k. Interestingly, this indicates that restricted thermal motion is important for templating a sufficiently ordered layer that will allow further ice growth. We note that most previous simulations of heterogeneous ice nucleation have typically used a fixed substrate with no thermal motion.[6–8,18]

Second, the basal plane of silver iodide has a non-zero surface dipole, and it is well established that such surfaces are unstable in vacuum and should reconstruct.[19] Indeed, when we simulate such an AgI slab in vacuum using the PRV potential, it undergoes a surface and bulk reconstruction (see the supplementary material for further details[17]). Hence, there is

considerable uncertainty concerning the structure of AgI basal planes in water. To probe this, a more realistic description of the water-AgI system is needed.

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