Supporting Information for "The Microscopic Features of Heterogeneous Ice Nucleation May Affect the Macroscopic Morphology of Atmospheric Ice Crystals"

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S-I. MOVIES OF HETEROGENEOUS ICE NUCLEATION

A. Movie 1

In this movie we show the nucleation event shown in Figs. 3 and 4(b) in the main article. In this trajectory, the structuring of the second layer before the first can clearly be seen.

B. Movie 2

This movie shows the nucleation event shown in Fig 4(d) in the main article. In this instance, the structuring of the first and second layers happens in a more concerted fashion than for the trajectory presented in Movie 1. In Section S-IV, however, we see that the density changes occurring away from the surface in Fig 4(d) in the main article are part of the nucleation mechanism and are not merely indicative of growth.

S-II. MOVIES SHOWING HOW THE DENSITY NORMAL TO THE SURFACE CHANGES DURING NUCLEATION

A. Movie 3

This movie shows how the density profile changes in time for the trajectory shown in Movie 1. The densities are shown as running averages over a 2.5 ns interval. The density changes away from the surface clearly occur before those occurring at the surface.

B. Movie 4

Here we show how the density profile changes in time for the trajectory shown in Movie 2. At approx. 278 ns there is a concerted change in the density in the first, second and third layers. Structuring of the layers then appears to occur first in the first layer, followed very quickly by the second layer. The densities are shown as running averages over a 2.5 ns interval.

S-III. DENSITY PROFILES AT AMBIENT TEMPERATURE

The high density of liquid water at the hydroxyl-terminated (001) face of kaolinite is in fact a feature at ambient temperatures and not a consequence of the water being supercooled. This is shown in Fig. S1, where the density of water perpendicular to the kaolinite surface at 220 K and 300 K is shown (averaged over 1 ns time interval). The water density perpendicular to the kaolinite surface has also been calculated using the PBE density functional¹ with 132 water molecules over a 15 ps time interval at 330 K, and also shows a high density peak at the surface. The DFT simulations were performed by Dr. Xiaoliang Hu using the CP2K simulation package.² Orbitals were described by an atom centred Gaussiantype basis set while an auxiliary plane wave basis set was used to re-expand the electron density.³ Analytic Goedecker-Teter-Hutter pseudopotentials^{4,5} were employed to represent the core electrons. For the valence electrons the basis sets used consisted of short ranged quadruple- ζ (hydrogen and oxygen atoms), triple- ζ (aluminium) and double- ζ (silicon) basis functions with two sets of polarization functions, except for silicon, where only one set of polarization functions was used. The plane wave cutoff for the electron density was set to 280 Ry. The Brillioun zone was sampled at the Γ -point only. The convergence criterion for the wavefunction optimization was set to 1.0×10^{-7} Ha between final self-consistent field iterations. The mass of the hydrogen atoms was set to that of deuterium and a 1 fs timestep was used to propagate the dynamics, with a Nosé-Hoover chain of length 4 used to maintain the target temperature of 330 K.

S-IV. COMMITTOR ANALYSIS FOR TRAJECTORY 'D' OF FIG. 4 IN THE MAIN ARTICLE

In Fig. S3 we present the preliminary results from a committor analysis for trajectory 'd' of Fig. 4 in the main article, using the same method as described in the main text. Here we have used configurations from two times, 281.5 ns and 284.0 ns, of the original trajectory as initial configurations for the analysis. According to this analysis, neither of the configurations can be deemed post-critical. As the density profile in Fig. 4(d) of the main paper is measured at 282.5 ns of the main trajectory, we are confident that the observed density changes are happening during the nucleation event itself, and are not a indicative of



FIG. S1. Comparison of water densities perpendicular to the kaolinite slab at 220 K and 300 K. The profiles shown are averages over a 1 ns time interval. Although the supercooled liquid is overall more structured than at 300 K, the high density peak at the surface is still features at the higher temperature.

growth of the ice crystal.

S-V. ADSORPTION ENERGIES OF THE PRISM AND BASAL FACES OF ICE TO KAOLINITE (001)

Structures for the prism face of ice bound to kaolinite were taken directly from a snapshot of one of the ice forming trajectories. For the basal face bound to kaolinite, structures were built based on the results obtained for the fist contact layer in Ref. 6, using the same size cell as those used in the MD simulations. The DFT geometry optimisations were performed using the same initial structures as the force field calculations. The definition of the adsorption



FIG. S2. Density profile of water perpendicular to the kaolinite slab using the PBE density functional at 330 K. The profile is an average over 15 ps with 132 water molecules. The density is overall more structured than that obtained from the 300 K force field simulation, but the high density at the surface relative to the rest of the system is still observed. Courtesy of Dr. Xiaoliang Hu.

energy per water molecule is:

$$E_{\rm ads} = \frac{\left(E_{\rm water/slab} - E_{\rm slab} - N_{\rm water}E_{\rm water}\right)}{N_{\rm water}} \tag{1}$$

where $E_{\text{water/slab}}$ is the total energy of the water molecules adsorbed at the surface, E_{slab} is the energy of the bare slab, E_{water} is the energy of the isolated water monomer and N_{water} is the number of water molecules. As the structures for the prism face were extracted from a finite temperature MD simulation, the energy of the bare slab was calculated separately for each structure. The DFT calculations were performed using the CP2K simulation package with the PBE density functional. Orbitals were described by an atom centred Gaussian-type



FIG. S3. Committor analysis from one of the heterogeneous ice nucleation trajectories. Results here are shown for initial configurations sampled at 281.5 ns and 284.0 ns from the initial ice forming trajectory. It is clear that by 284.0 ns the initial trajectory has not entered a post-critical regime.

basis set while an auxiliary plane wave basis set was used to re-expand the electron density. Analytic Goedecker-Teter-Hutter pseudopotentials were employed to represent the core electrons. For the valence electrons the basis sets used consisted of short ranged molecularly optimised double- ζ basis functions with a single set of polarization functions (DZVP). It has been shown that such basis set functions greatly reduce the effects of basis set superposition error.⁷ The plane wave cutoff for the electron density was set to 400 Ry. The Brillioun zone was sampled at the Γ -point only. The convergence criterion for the wavefunction optimization was set to 1.0×10^{-6} Ha between final self-consistent field iterations. Geometries were converged when the forces on all atoms were below 5.0×10^{-5} Ha/Bohr. For all calculations a minimum vacuum gap of 15 Å between periodic images was used throughout. The calculations were also performed using a regular DZVP basis set, which despite drastically changing the adsorption energies, produced the same trends observed with the molecularly optimised DZVP basis set. The DFT results presented in Fig. 5 of the main article were obtained with the molecularly optimised orbitals. In Fig. S4 we show results using both the DZVP and molecularly optimised DZVP basis sets.



FIG. S4. Adsorption energy of ice bound to kaolinite through its prism and basal faces. The empty symbols are results using the force field (same as Fig. 5 in the main article). The results shown by the purple filled symbols have been obtained using the molecularly optimised DZVP basis set, whereas the yellow filled symbols show results obtained with the regular DZVP basis set. Although there is a large difference in adsorption energies between the two basis sets, the trend that the prism face becomes more stable upon adsorption of the second water layer is found with both.

For the liquid layer calculations, 25 configurations were randomly chosen from different trajectories. Molecules whose oxygen atom position was greater than 5 Å above the average height of the surface oxygen atoms were then subsequently removed (this corresponds to a distance from the surface that approximately in the middle between the first and second ice peaks). The remaining water molecules and surface were then allowed to relax. The error bars in Fig. 5 of the main text correspond to the standard deviation in the adsorption energy.

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