

# Diffusion and Island formation on the ice Ih basal plane surface

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## Abstract

We present theoretical calculations of the adsorption, diffusion and island formation of water admolecules on the basal plane surface of an ice Ih crystal. These are preliminary calculations based on the simple TIP4P interaction potential, a pairwise additive potential function based on point charges. At low coverage, we find that an admolecule prefers to sit at non-crystallographic sites on the surface (i.e., sites that do not fit into the ice lattice). Since ice Ih is proton disordered, no two sites are exactly the same and there is a wide range of binding energies. For some local environments the binding energy is of the order of, or even larger than, the cohesive energy. The proton disorder also results in a range of activation energies for diffusion. After mapping out a large number of diffusion barriers using the nudged elastic band method, a kinetic Monte-Carlo calculation of the diffusion at 140 K was performed. At early time, the mean squared displacement has anomalous scaling with time as is common for diffusion on random lattices. But, at longer time the scaling is normal and a diffusion coefficient can be obtained. The diffusivity is slightly larger than a recent experimental upper bound given by Brown and George. The energetics and dynamics of the formation of small islands on the ice surface have also been studied. It is found that islands up to and including pentamer are non-crystallographic, but the hexamer is crystallographic. While the formation of a crystallographic hexamer from a non-crystallographic pentamer and a new admolecule involves a complex concerted motion of all the island molecules and a large relaxation of the substrate, the activation energy for the process is estimated to be quite small, smaller than the admolecule diffusion barrier. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

It is well known that ice Ih is disordered in that even though the oxygen atoms are placed on a regular, hexagonal lattice, the protons can be pointing in various directions [1]. This results in a significant excess entropy at low temperature where the rearrangement of the orientation of the molecules is too slow to reach a perfectly ordered

crystal. The disorder also has very interesting consequences for the surface dynamics, as described below.

Computer simulation studies of ice surface dynamics necessarily require some efficient potential energy function to describe the intermolecular interactions. While it is beginning to be possible to carry out ab initio DFT calculations of ice surfaces, the size of the simulation cell and the complexity of the phenomena make ab initio calculations still far too CPU intensive. Many different empirical potential functions have been

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proposed to describe water [2–9]. Most of these have been developed mainly to reproduce liquid water properties with little attention paid to crystalline ice. But, some of these potentials do seem to reproduce crystalline ice properties quite well. We have chosen to use the TIP4P potential [6] because the properties of TIP4P ice have been characterized quite extensively, including vibrational spectra and high pressure phases [10]. The cohesive energy of TIP4P ice is 0.585 eV as compared with the experimental estimate of 0.58 eV [11]. The lattice constant is 2.723 Å as compared with the experimental value of 2.75 Å. While the long range Coulomb interaction is often truncated to reduce the CPU time needed for simulations, we have included the long range interactions by using an Ewald summation. A formulation of Ewald summation appropriate for a slab was given by Parry [12,13] and we have made use of his method.

## 2. Basal plane surface of ice Ih

A sample of ice Ih is shown in Fig. 1. This represents the simulation cell used in most of the calculations presented here. The top layer is the surface layer. This cut of the crystal gives a basal

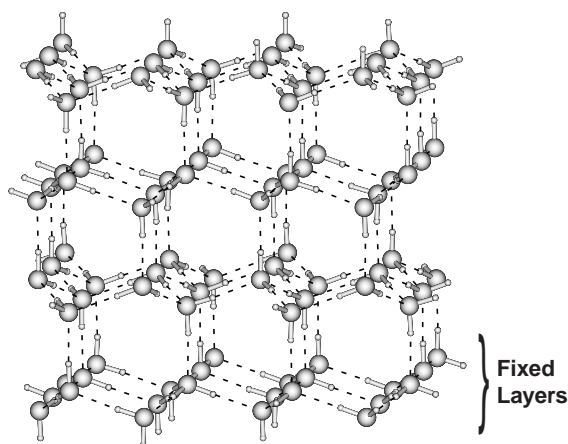


Fig. 1. A side view of a slab of four bilayers of proton disordered ice Ih used for most of the surface studies presented here. The basal plane surface is the top most layer. The bottom bilayer is held rigid. Periodic boundary conditions are used to mimic bilayers of infinite extent.

plane surface. Pairs of layers are close together, so-called bilayers, while the distance between the pairs is quite large (2.75 Å). On average 50% of the molecules have a proton pointing out of the surface. In order to mimic the attachment of this slab to a semi-infinite crystal, the bottom two layers of the slab are held fixed during the simulations.

Recent He atom scattering results have shown clearly that the ice surface at around 140 K is indeed very regular [14]. There is no sign of surface reconstruction at this low temperature. He atom scattering is very sensitive to defects so the fact that intense and narrow diffraction peaks are observed means that the abundance of defects is low (see, for example, [15,16]). LEED experiments indicate that the top layer has a large mean squared displacement, on the order of 0.25 Å, and this has been supported by dynamics simulations using the TIP4P potential [17,18].

## 3. Adsorption sites

We have identified the various adsorption sites by simulating deposition of molecules on the surface and then quenching the system to the nearest local minimum on the potential surface. The sticking coefficient was found to be unity for vapor deposition. The analysis of the sticking coefficient for various incident conditions will be presented elsewhere [19].

Due to the proton disorder, there are many different adsorption sites on the surface. While long range effects are important, mainly because of the long range electrostatic interaction, it is useful to group the sites into categories according to the local, nearest neighbor environment. In all cases, there are three molecules in the surface plane that are close to the admolecule. The binding energy strongly depends on how many of the protons in these surface molecules are pointing up from the surface. There can be at most three protons pointing up (see Fig. 2). The strongest binding is found when one proton is pointing up. Representative configurations are shown in Figs. 2(a) and 3(a). We call these sites A sites. The oxygen atom

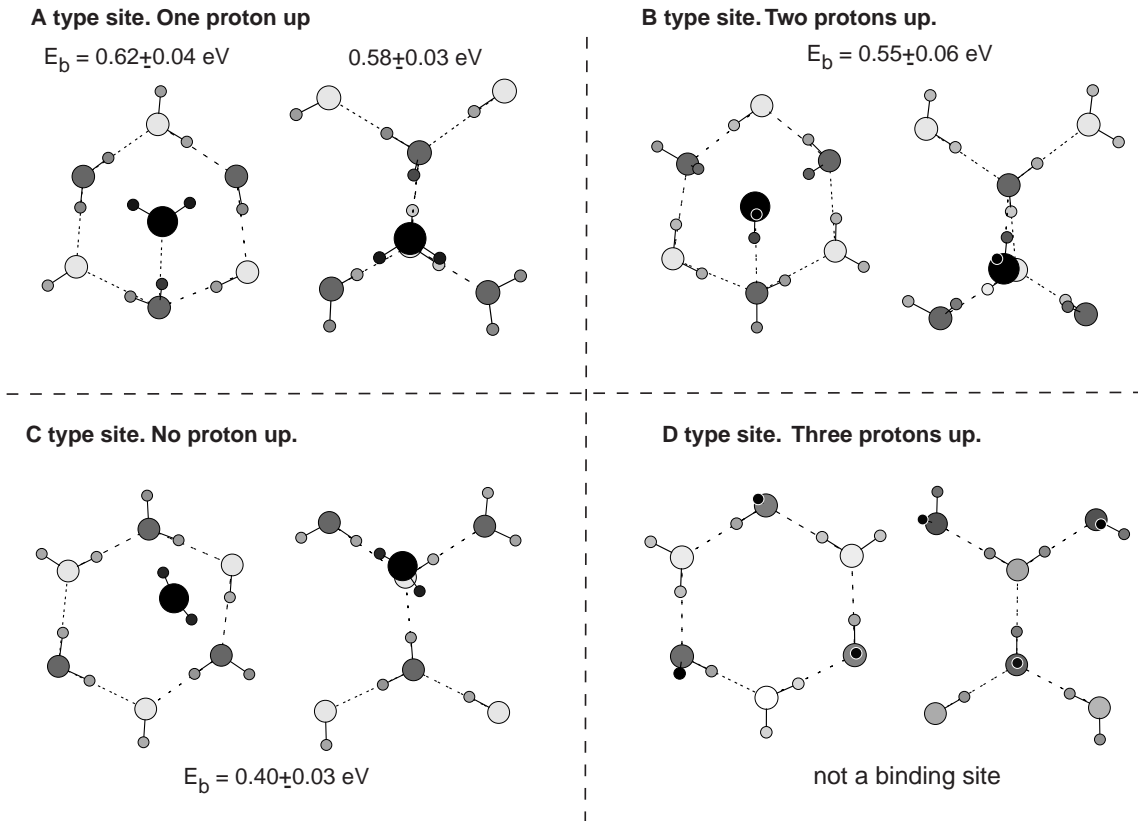


Fig. 2. Various types of binding sites for admolecules on the basal plane surface. The figure shows molecules in the top bilayer as well as the admolecule. The strongest binding is at A-type sites where one of the three neighboring surface molecules has a proton pointing up. After the admolecule binds to the site, the proton is pointing towards the admolecule. At B-type sites there are two protons pointing up, at C-type sites there are three. If none of the three neighboring surface molecules has a proton pointing up, the admolecule does not have a stable binding site (D-type). For the A-type sites it makes a significant difference whether the lower layer in the bilayer has a molecule directly underneath the admolecule or not. Surprisingly, the binding energy at A-type sites can be significantly larger than the cohesive energy. Note the large relaxation in the top layer due to the binding of the admolecule.

on the admolecule attracts the proton of the surface molecule while the two protons of the admolecule get attracted towards the oxygen atoms on the surface molecules that do not have a proton pointing away from the surface. Slightly weaker binding (on average) is found when two surface protons are pointing up towards the admolecule. One of the protons of the admolecule then ends up pointing up away from the surface. We call these B sites. Figs. 2(b) and 3(b) show a representative configuration. Much weaker binding is found when none of the three neighboring surface molecules has a proton pointing up from the surface, so-called C sites. When all three have a proton

pointing up, a stable binding site for the admolecule is not formed. When placed above and in between the three surface molecules, the admolecule slides over to an adjacent B site.

In A and B sites, the admolecule is forming three strained hydrogen bonds. The binding energy is, therefore, quite close to the cohesive energy in ice which corresponds to two hydrogen bonds per molecule. The A sites are, in fact, found to have binding energy ranging from 0.58–0.66 eV, most of them binding an adatom stronger than a kink site (where the binding energy is necessarily equal to the cohesive energy, 0.585 eV for the TIP4P potential). This is a very unusual situation.

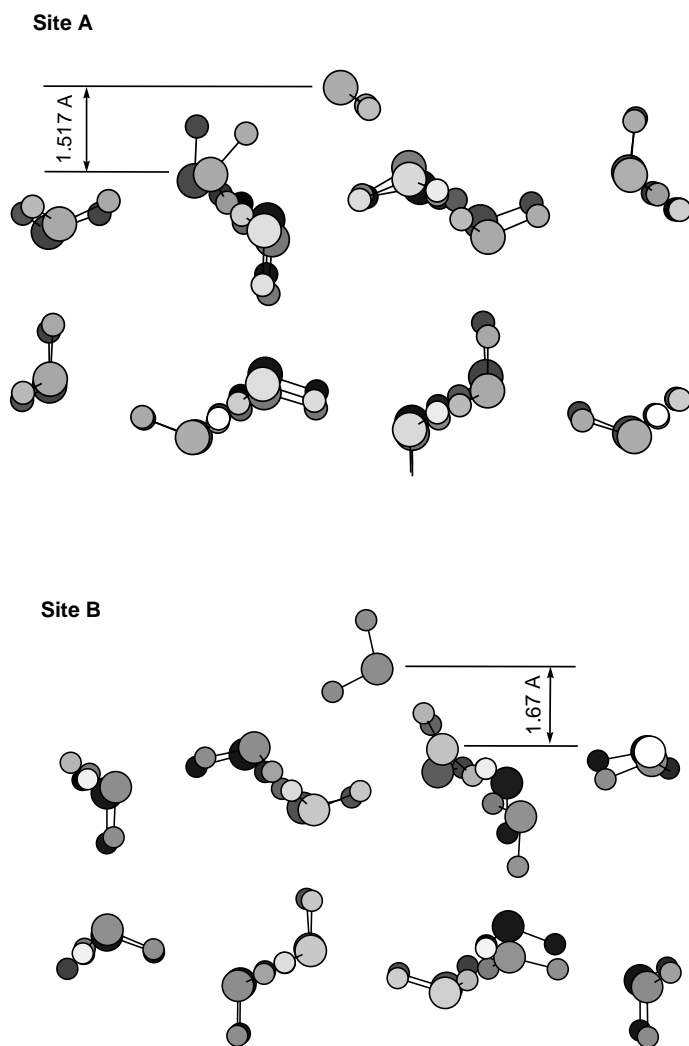


Fig. 3. A side view of the relaxed configuration of an ad molecule at an A-type site (top) and at a B-type site (bottom). At the A-type site the two protons of the ad molecule are pointing towards oxygen atoms in the surface layer, while a proton from the third neighboring surface molecule points towards the oxygen atom of the ad molecule. In this configuration, three weak hydrogen bonds form and the binding energy can be greater than the cohesive energy of the solid (which amounts to two hydrogen bonds). At the B-type site, one of the protons of the ad molecule is pointing up while the other points down towards an oxygen atom in the surface layer. Two protons from the top layer are pointed towards the oxygen atom of the ad molecule.

It can only arise because there is a large variety of binding sites on the surface. It means that ad molecules will prefer to sit at these strongly binding A sites rather than attach to kink sites. The surface will therefore tend to have a certain, low coverage of ad molecules even when the mobility is great enough for the atoms to diffuse to the kink sites. It remains to be seen whether this prediction

of the TIP4P potential holds up when the intermolecular interactions are described more accurately. It is certainly not possible to have all binding sites stronger than the cohesive energy, but since disorder is present and a range of different surface sites are formed on the surface, it is quite possible that some of them have stronger ad molecule binding than kink sites.

Some of the B sites also have binding energy larger than the cohesive energy, but only a small fraction. The binding energy ranges from 0.49–0.61 eV, overlapping to some extent with the range of binding energy for A sites. The classification of sites according to the nearest three surface molecules only gives a rough indication of the properties of the site. The fact that there are long range Coulomb interaction and the relaxation of the disordered lattice is very substantial means that any short range classification scheme is necessarily incomplete. The C sites lead to a distinctly smaller binding energy than the A and B sites, 0.37–0.43 eV. At low temperature, a diffusing admolecule will largely be confined to A and B sites, see Section 5.

The surface molecules bound to the admolecule undergo a substantial relaxation, the oxygen atoms sometimes moving by more than half an Ångström. In the absence of surface relaxation, the binding energy is typically 0.1–0.2 eV lower. An earlier study by Hale and coworkers involved a

frozen substrate and smaller binding energies were deduced than we find here [20,21]. While they used a different interaction potential, the main reason for the difference is the lack of surface relaxation in their calculations. When we freeze the surface molecules in our calculations we get results that are quite similar to the results of Hale and coworkers.

#### 4. Diffusion barriers

Calculating the activation energy barriers for diffusive hops of the admolecule is challenging because many degrees of freedom are involved, not just the coordinates of the admolecule but also those of the nearby surface molecules because of the large relaxations in the substrate. We have used the ‘Nudged Elastic Band’ method to obtain discrete representation of the minimum energy paths for various diffusion hops [22,23]. An example of such a calculation is given in Fig. 4 where

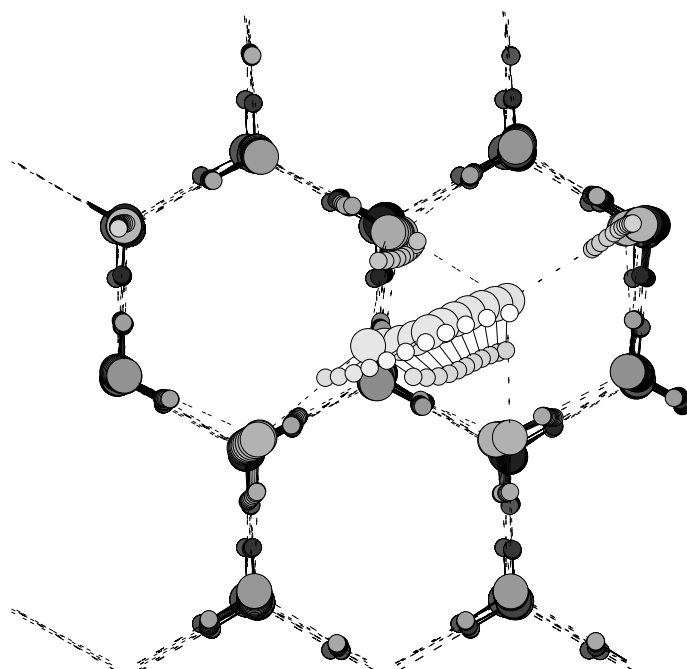


Fig. 4. The minimum energy diffusion path between an A-type site (on the left) to a B-type site (on the right). The path is discretized with 11 replicas and was found with the NEB method. One of the protons of the admolecule rotates from pointing down in the A site to pointing up in the B site. Notice the large relaxation of atoms in the surface layer. These can amount to over half an Å.

a hop from an A site to an adjacent B site is shown with 11 replicas of the system discretizing the minimum energy path. The calculation was started by first creating a straight line interpolation between the initial and final sites. The algorithm for relaxing the chain of images to the minimum energy path has been described by Mills et al. [22,23]. Sometimes more than one minimum energy path exists between a given initial and final state. Several different initial paths were therefore tried, corresponding to different orientations of the admolecule at the mid point of the path. The activation energy barrier was then extracted as the maximum potential energy along the optimal minimum energy path.

This analysis gave a range of barriers depending on the environment of the diffusing molecule. For hops between the lowest energy sites, the A and B sites, the range of barriers was 0.16–0.28 eV. Hops into C sites have larger barriers, typically larger than 0.30 eV. Again, it is very important to include the surface relaxations in the calculations. If the substrate is kept frozen the barriers are lower by about 0.1 eV.

We have carried out preliminary analysis of the prefactor,  $v$ , in the Arrhenius expression for the rate

$$k = v e^{-E_a/kT}$$

by simulating the classical dynamics of the system ('molecular dynamics' simulation [24]) and extracting vibrational frequencies from the velocity autocorrelation function. The results indicate that the prefactors are on the order of  $10^{12} \text{ s}^{-1}$ , which is typical for surface diffusion hops [25].

## 5. Simulation of long time diffusion

A direct classical dynamics simulation of the diffusion is not practical. Such simulations necessarily include the vibrational motion of the molecules and are therefore limited to timesteps that are about one order of magnitude smaller than the vibrational period. A hop over the lowest barrier, 0.16 eV, occurs on average every millisecond at 140 K. A direct classical dynamics simulation would require on the order of  $10^9$  iterations, which

would take years of CPU time. By increasing the temperature, the rate of surface diffusion hops can be increased, but in order to see a hop every hour of CPU time, the temperature would need to be raised above 400 K, which would lead to melting, a drastic example of a crossover from one mechanism to another as temperature is changed!

After the stable binding sites have been found and the activation energy barriers for hops between the sites calculated, it is possible to simulate the long time scale diffusion of an admolecule using the kinetic Monte-Carlo method [26–29]. There, a table of all possible events in the system is created and random numbers are used to select which process takes place next. The vibrational motion of the molecules is not included, and the time step in the iterative algorithm is essentially the average time interval between occurrences of the fastest process included in the table of possible events. In this case it corresponds to the hop over the lowest diffusion barrier. To simplify the calculation, all A sites are assumed to have the average binding energy of A sites, 0.62 eV and the B sites are similarly assumed to have the binding energy 0.55 eV. C sites were not included in the kinetic Monte-Carlo simulation because they are rarely visited at low temperature.

The barrier to hop among A and B type sites were assigned by drawing from the distribution of barriers calculated using the NEB method. The distribution was represented with two Gaussians, one centered at 0.16 and the other at 0.20 eV, both with a dispersion of 0.03 eV. The A and B sites form a sublattice on the ice surface, and the connected pathways between these sites form a random percolating network, as shown in Fig. 5. The prefactor was assumed to be  $10^{12} \text{ s}^{-1}$  for all diffusion hops.

The results of 50 000 repeated kinetic Monte-Carlo simulations were used to obtain the mean squared displacement of an admolecule as a function of time. For short time, when the molecules have traveled less than ca. 10 Å, the scaling is anomalous, the mean squared displacement increases nearly as the square root of time. But, at longer time the normal scaling is observed,  $\langle r^2 \rangle \sim t$  and a diffusion coefficient could be extracted from the proportionality constant. We find a diffusivity

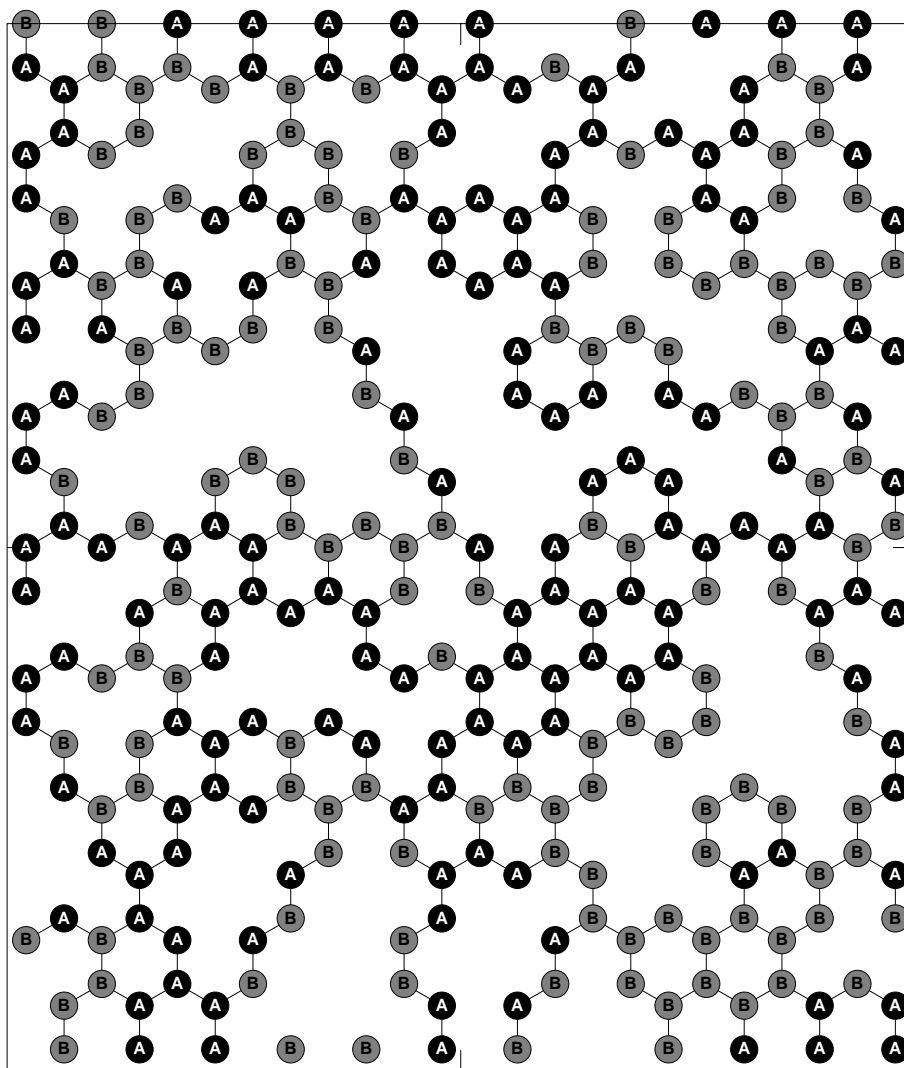


Fig. 5. Active diffusion paths on a large sample of proton disordered ice. Only the more stable sites, A and B, are shown since other sites are of too high energy to play an active role at low temperature. A line is drawn between sites where the barrier is low enough for the transition to be active at 140 K. The proton disordered surface thus creates a random lattice of sites and pathways for the diffusing admolecule. A kinetic Monte-Carlo simulation of the diffusivity on this lattice was carried out using harmonic transition state theory estimate of the hopping rate given the binding energy and barriers obtained from the structural relaxation and NEB minimum energy path calculations. The mean squared displacement at short times is anomalous due to the disorder, but at long time it increases linearly with time and a diffusion coefficient can be obtained from the slope.

of  $1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at 140 K. This is practically the same as the upper bound for the surface diffusivity found experimentally by Brown and George,  $5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  at that same temperature [30].

We repeated the kinetic Monte-Carlo simulations for a range of temperature. The calculated

diffusivity roughly follows an Arrhenius law with an effective activation barrier of 0.18 eV, slightly larger than the lowest activation barrier calculated for individual diffusion hops.

It is quite possible that the simple pairwise additive TIP4P interaction potential gives an under-

estimate of the activation barrier for diffusion. In reality, the local field at a water molecule induces a change in the molecular electric moments [4,31]. For example, an induction scheme including both dipole and quadrupole polarizability give a molecular dipole moment of 3.1 D for a molecule in ice, while the dipole moment in a hexamer water cluster is calculated to be 2.7 D [32]. The TIP4P potential function and other commonly used interaction potential functions have been parametrized to reproduce properties of liquid water and most likely do not give good enough description of a surface ad molecule, even though TIP4P seems to

describe properties of bulk ice reasonably well. We are in the process of developing a new water potential that includes dipole and quadrupole polarizability and this will be used to obtain an improved estimate of the binding energy and diffusion barriers for an ad molecule on ice surfaces.

## 6. Island formation

An important aspect of crystal growth is the formation of islands on the surface and nucleation of a new surface layer of the crystal. While the

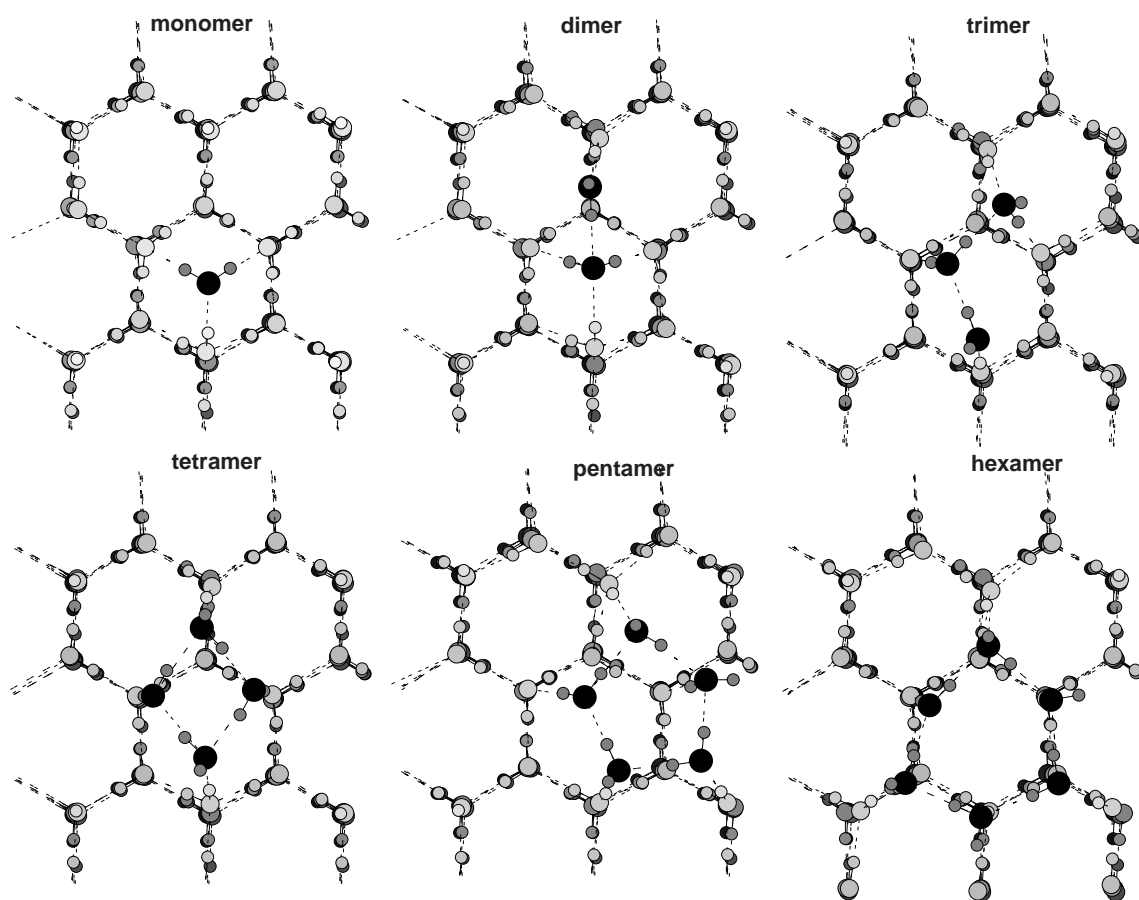


Fig. 6. Stable configurations of small islands of ad molecules on the ice Ih surface. Up to and including the pentamer the lowest energy configuration is non-crystallographic, i.e., it does not fit within the ice crystal structure. The configurations were obtained by starting with a hexamer island carved out of an ice lattice, annealing at 190 K for 3 ps and then cooling down slowly. After removing one of the molecules and annealing again the non-crystallographic configuration of the pentamer was obtained. An analogous procedure was used for the smaller clusters. Note that all these clusters are unstable with respect to dissociation into isolated adatoms at A-type binding sites.



admolecule on the basal plane of the ice Ih surface sits in a non-crystallographic site, an island that serves as a nucleus for the growth of a new surface layer must be crystallographic. The question then arises at what island size the crystallographic arrangements of the molecules becomes preferred.

In order to address this issue, we carried out simulated annealing studies of island shapes, ranging from the dimer to the hexamer. We started the simulation with a configuration obtained from the perfect crystal, heated the configuration up to 190 K for 3 ps, and then cooled it down over a

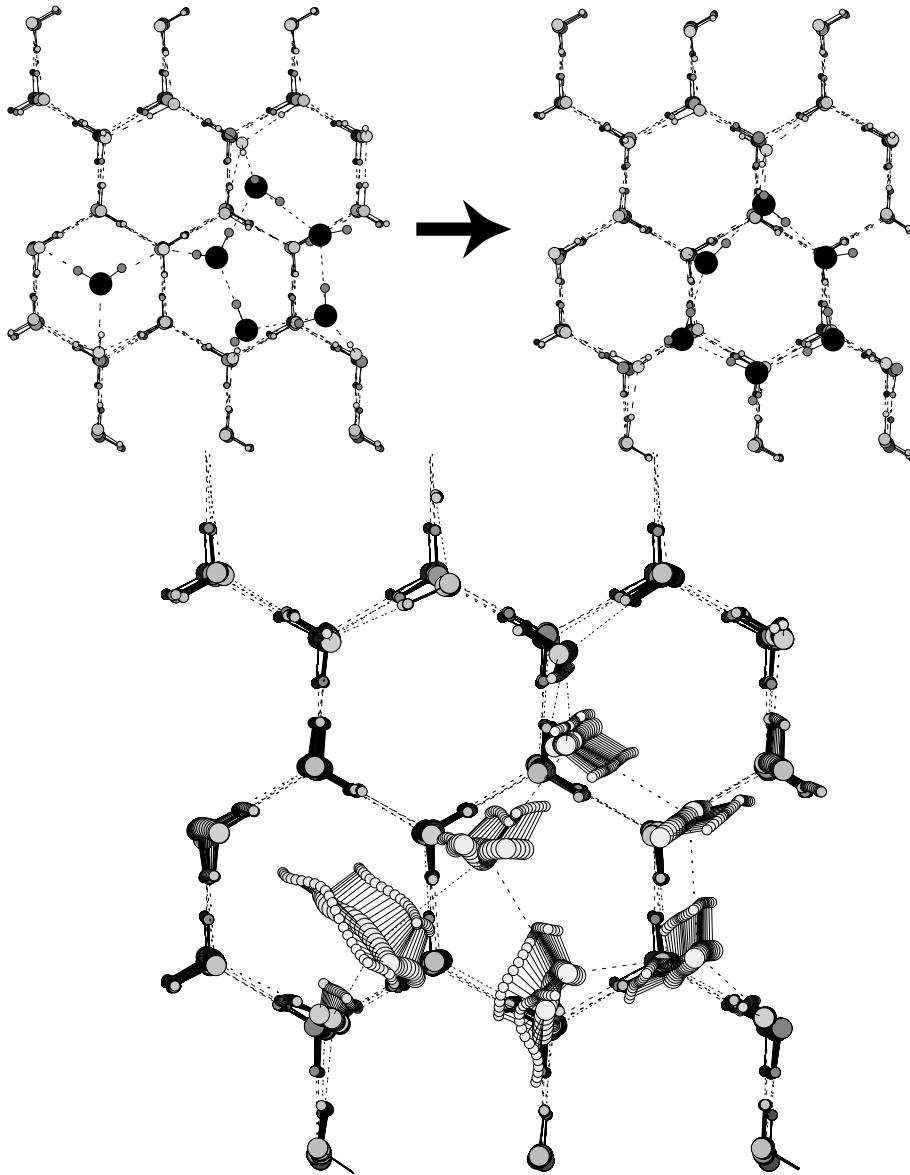


Fig. 7. Minimum energy path for the formation of a crystallographic hexamer island from a non-crystallographic pentamer and a nearby admolecule. The path was found using the NEB method. The initial state is shown in the top left part of the figure and the final state on the right. The lower part of the figure shows the path discretized with 30 replicas of the system. Note the large relaxations in the substrate molecules.

couple of ps until a potential energy minimum was reached. The results are shown in Fig. 6. The dimer and up to the pentamer are all non-crystallographic. Only when the island has grown to a hexamer is the crystallographic configuration optimal. This complexity will likely have implications for the nucleation of new surface layers during growth.

One interesting question is: What is the bottle neck for growing an ice crystal rather than an amorphous solid? That is, what is the highest activation energy in the process of assembling a crystallographic hexamer from six admolecules? We have calculated the minimum energy paths for the formation of the dimer from two admolecules, the formation of the trimer from a dimer and an admolecule, etc. The minimum energy path for forming a crystallographic hexamer from a pentamer and an admolecule is shown in Fig. 7. This is a very complex transition involving the concerted displacement of many molecules and large relaxation of the underlying molecules. Nevertheless, the activation energy for this event is not very high, only 0.1 eV. The variation of the potential energy along the minimum energy path is shown in Fig. 8. A metastable intermediate state is found from the path optimization. Note that the energy

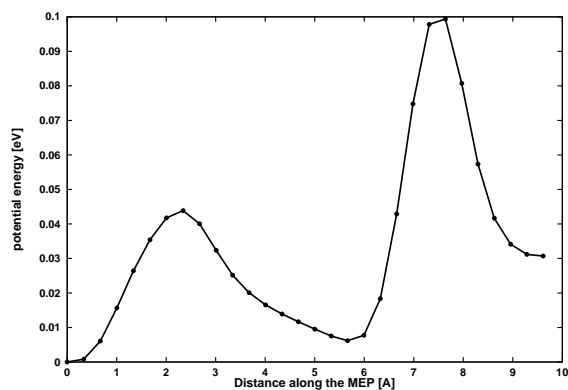


Fig. 8. Change in the potential energy along the minimum energy path for the formation of the hexamer, shown in Fig. 7. The path goes through a metastable intermediate configuration. While this is a complex transition involving concerted motion of many molecules, the activation energy is quite small, 0.1 eV, significantly smaller than the barrier for the diffusion hop of an admolecule on the flat surface.

for this event is uphill. All the islands are metastable with respect to admolecules in the very strongly binding A sites, where the binding energy is greater than the cohesive energy (and thereby, also greater than the binding energy at a kink site). Under growth conditions, the islands will form only after the very stable A sites have been filled.

## 7. Conclusions

The results presented here illustrate that dynamics at ice surfaces are quite complex. While these are preliminary simulations and have been based on a simple pairwise additive potential function, we expect that the richness will still be found when a more rigorous description of the molecular interaction is used. It is likely that the inclusion of induction effects will lead to a larger difference between the different sites on the surface, and long range effects are likely to become more important, thereby leading to even more complexity.

The presence of binding sites for admolecules with binding energy that exceeds the cohesive energy is particularly intriguing. If all binding sites were identical, this would lead to a contradiction. But, here a range of binding sites on the surface is found because of the proton disorder and then it is quite possible that *some* of the sites have such a large binding energy. The obvious question then becomes how smooth the surface is during growth and during measurements. Experiments using He atom scattering have certainly indicated that the ice Ih surface at 140 K is highly ordered [14]. According to the simulations presented here, the very stable A sites would necessarily be occupied before molecules attach to kink sites during growth. The surface will, therefore, not be perfectly flat under those conditions. However, if the surface is annealed in vacuum, some desorption will occur (the desorption rate is quite high at 150 K). The energy required to desorb a molecule from the flat surface is calculated (using TIP4P) to be 0.75 eV if a proton is pointing out of the surface, and 0.79 eV if both protons are pointed towards neighboring molecules. This is substantially larger energy than the strongest binding energy,

0.66 eV. A desorbing surface is therefore most likely going to be flat, i.e., most of the time the surface is flat. However, under growth conditions the strong binding sites will be filled before kink sites get filled, so the surface will not be flat. The results presented here based on the TIP4P potential indicate that 40% of the surface binding sites have a binding energy that is greater than the cohesive energy. It will be necessary to go to a higher level of theory to test this prediction. Calculations using a more realistic polarizable semi-empirical potential are under way [33].

The fact that clusters up to and including the pentamer are non-crystallographic can have interesting implications for nucleation of new islands on the surface during growth. The nucleation process is complex and the critical island size is likely to be large even at low temperatures. More work needs to be done to study this aspect.

We point out, finally, that the simulations presented here can only be representative of the ice surface at low temperature. At temperatures above ca. 150 K the desorption rate becomes very high. In order to have a stable surface the vapor pressure has to be appreciable and the deposition rate is high. The surface layer is very dynamic, a balance between rapid adsorption and desorption. It is an interesting open question what the surface looks like under those conditions. At still higher temperature, above ca. 240 K the surface is likely liquid-like and the diffusion mechanism is very different from the one presented here. Simulations of Kroes using the TIP4P potential show surface melting at these high temperatures and very large diffusivity in the surface layer [34], but experimental measurements are difficult and so far inconclusive.

## 8. Uncited references

[31,32].

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