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On thin ice: surface order and disorder during pre-melting


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The effect of temperature on the structure of the ice Ih (0001) surface is considered through a series of molecular dynamics simulations on an ice slab. At relatively low temperatures (200 K) a small fraction of surface self-interstitials (i.e. admolecules) appear that are formed exclusively from molecules leaving the outermost bilayer. At higher temperatures (ca. 250 K), vacancies start to appear in the inner part of the outermost bilayer exposing the underlying bilayer and providing sites with a high concentration of dangling hydrogen bonds. Around 250–260 K aggregates of molecules formed on top of the outermost bilayer from self-interstitials become more mobile and have diffusivities approaching that of liquid water. At ~270–280 K the inner bilayer of one surface noticeably destructures and it appears that at above 285 K both surfaces are melting. The observed disparity in the onset of melting between the two sides of the slab is rationalised by considering the relationship between surface energy and the spatial distribution of protons at the surface; thermodynamic stability is conferred on the surface by maximising separations between dangling protons at the crystal exterior. Local hotspots associated with a high dangling proton density are suggested to be susceptible to pre-melting and may be more efficient at trapping species at the external surface than regions with low concentrations of protons thus potentially helping ice particles to catalyse reactions. A preliminary conclusion of this work is that only about 10–20 K below the melting temperature of the particular water potential employed is major disruption of the crystalline lattice noted which could be interpreted as being “liquid”, the thickness of this film being about a nanometre.

Introduction and background

Despite the importance of ice in regulating the earth’s temperature via albedo and within atmospheric chemistry (where it serves as a catalyst for many trace gas reactions), a key unknown in these two roles is the physicochemical nature of the ice surface as a function of temperature. Faraday first mooted the idea that the surface

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of ice could have liquid-like properties, a quasi-liquid-layer (QLL), but the nature of
this layer, in particular its thickness approaching the melting temperature, is
disputed—where more than an order of magnitude separates the estimates of thick-
ness obtained using proton channelling and ellipsometry.\(^3\) A review of experimental
and computer simulation studies pertinent to the pre-melting phenomenon has
recently been compiled, which provides a useful introduction to this topic.\(^4\)
Computer modelling approaches could potentially play a role in resolving the
crystallinity of the surface as a function of temperature, and the atomic-scale mech-
anisms together with the role of defects in the pre-melting phenomenon in ice. Natu-
раllу, the verity of any such model and approach hinges upon accurately describing
the relationship between free energy and temperature. In this work we examine one
particular model, the six-site model due to Nada and van der Eerden (NvdE)\(^5\) which
was developed specifically to reproduce the melting temperature of ice Ih. In analys-
ing the surface structure we focus upon (i) the evolution of the surface structure in
the temperature regime above 200K, (ii) the identification of defects at the surface
and (iii) the spatial distribution of protons on the external surface of ice and how
this influences pre-melting and stability.

Methods

Here we use a combination of first-principles calculations adjunct to empirical
potential simulations to probe the detailed nature of structures evolving from
long-timescale pre-melting studies. Despite the incredible versatility of the TIP4P\(^6\)
model, indicated by its ability to describe large portions of the water–ice phase
diagram, a shortcoming is its ability to predict the melting temperature of water
(not withstanding recent reparameterisation of this potential due to Abascal, Vega
and co-workers\(^7\)–\(^10\)). In previous simulation work due to Kroes\(^11\) and others, the
melting of an ice slab with the TIP4P potential was considered in the temperature
range of 190–250 K. Although melting was observed, the bulk melting temperature
for TIP4P has been found to range from around 190–230 K (the most recent
estimate being 232 K\(^12\)) and hence the liquefaction mechanism at the superheated
temperatures of >230 K could be distinct from pre-melting. More recently, Ikeda-
Fukazawa\(^13\) and others have addressed pre-melting using the Kawamura potential
which has a reported melting temperature of 290 K. In their work, an ice slab was
heated to 270 K for 60 ps and the mean-square displacement of water molecules
in the outermost bilayer was noted to be very strongly enhanced in the \(c\) axis, perpen-
dicular to the crystal surface rather than the \(a\) or \(b\) axis parallel to the crystal surface.
At this temperature, only a very slight loss of structure is noted at the external
surface evidenced by a broadening of the density at the outermost layer. A very rele-
ant study is that of Carignano \textit{et al.}\(^14\) who looked at ice growth up to 275 K using
the same potential used here. Their study monitored the liquid-like layer on either
side of a slab of ice, which was in contact with both vacuum and water; comparis-
isons between our studies are drawn later. Bolton and Pettersson\(^15\) have also studied pre-
melting and their work highlighted rapid transport of water between outer bilayers
at temperatures in the region 180–210 K (TIP4P model), which was associated with
pre-melting. However, in this paper, we present the first preliminary account of our
ongoing study that attempts to shed further light on the pre-melting phenomenon,
by monitoring systematic changes in surface structure up to the melting temperature.

In this work, we use the potential due to NvdE, which is a rigid-body, six-site
model. In the original paper of NvdE the melting temperature was estimated to
be 271 ± 9 K but we note the most recent study\(^16\) with this potential puts the melting
temperature at 289 K. In addition to the oxygen and hydrogen sites, two sites repre-
sent the lone pairs, whilst a further site sits along the bisector of the two hydrogen
atoms and attempts to mimic the concentration of electron density close to the centre
of mass of the water molecule. We have used the \(6 \times 3 \times 3\) cell due to Hayward and
Reimers,\(^1\) containing 768 molecules and 8 bilayers (96 molecules per bilayer).
Hayward and Reimers developed ice cell geometries in which the protons are maximally disordered and the cell has no net dipole or quadrupole. The latter characteristics are an important pre-requisite for surface simulation; in this work we use a periodic slab approach and any significant dipole across the slab can potentially interact through the vacuum with its periodic image, which would lead to spurious artefacts. The bulk cell was initially geometry optimised at 0.1 K using NPT molecular dynamics‡ (employing the DL_POLY¹⁸ code, version 2.18) to give cell parameters of \(a = 26.92, b = 31.08, c = 29.30 \text{ Å}\), which compare favourably with the experimental geometry of \(a = 26.98, b = 31.48, c = 29.28 \text{ Å}\) taken from Röttger et al.¹⁹ at 10 K (note that these parameters relate to an ice sample which contains some fraction of ice XI. Ice XI displays small negative thermal expansion below \(\approx 70 \text{ K}\), hence the maximum error of 1.3% in \(b\) is an upper bound. At 85 K, above the Ih \(\rightarrow\) XI transition temperature, the maximum error in \(b\) reduces to 1.2%). A vacuum gap of 30 Å was introduced along the Cartesian \(z\) axis to create two (0001) surfaces and the slab was geometry-optimised. We determined that the surface energy was converged at 6 bilayers but use 8 bilayers in this work to screen interactions across the slab arising from melting at the external surface. In a contiguous series of MD runs, using a 1 fs timestep and starting at 200 K, the slab was equilibrated for 5 ps and then production runs of between 0.5 and 5 ns were conducted for 210, 220, 230, 240, 250, 255, 260, 265, 270, 273, 275, 280, 285 and 290 K. Trajectory samples were taken at 0.5 ps intervals and analysis was performed over all the configurations sampled and over sections of the longer MD runs. Conservation of kinetic energy was reasonable: at 285K the RMS fluctuation in the temperature over a 1 ns run was 2.4 K. Due care was exercised in ensuring the statistical samples taken over MD runs of unequal length were not directly compared. However, it is noteworthy that for the 285 K run, the coordination numbers extracted from 0–0.25 ns and 0.75–1.0 ns are essentially indistinguishable from one another. Additionally, the gradient of the MSD at this temperature is converged within <5 ps of the production phase.

The DFT calculations have been performed with the CP2K/Quickstep program,²⁰ which employs a hybrid Gaussian and plane-wave basis set. The Perdew, Burke and Ernzerhof (PBE)²¹ exchange–correlation functional has been used throughout and the core electrons are described with norm-conserving Goedecker, Teter and Hutter (GTH) pseudopotentials.²²,²³ The valence electrons are expanded in terms of Gaussian functions with a triple-\(\zeta\) doubly polarised basis set (TZV2P) and for the auxiliary basis set of plane waves a 340 Ry cutoff is used. Due to the larger computational demands of the DFT calculations compared to the empirical potentials, a considerably smaller (but still moderately large) unit cell with 48 water molecules per bilayer was employed. Calculations on slabs of between 2 and 6 bilayers thickness were performed and during the DFT geometry optimizations all atoms were fully relaxed. A vacuum gap of 20 Å was used throughout.

Results

In the following sections, we address the response of the thin ice slab to increasing temperature in the range 200 to 290 K. At all temperatures up to about 285 K the energies throughout the course of the MD simulations are well conserved. This can be seen for three high temperatures (275, 280 and 285 K) from Fig. 1. However at 290 K it can be seen that the total energy is no longer conserved and the crystal appears to be in a non-equilibrium melting state. Towards the later part of the simulation

‡ A timestep of 1 fs was used throughout, integration was performed using the velocity Verlet algorithm. The van der Waals cutoff used was 10.0 Å, as used by NvdE, and the Berendsen thermostat/barostat was used to control the temperature and pressure (1 atm.). The frequency of scaling was 0.005 ps which was necessary in order to minimise fluctuations in the temperature. The NVT ensemble was used for the surface simulation runs.
at 290 K, it appears that the energy is reducing and this may indicate a very long timescale restructuring process. However, we crudely infer from this that the melting temperature for the entire slab with this potential is at around 285–290 K. This is consistent with Abascal and Vega’s estimate and hence the temperatures reported here should be reduced by ~15 K to be comparable to experiment.

Firstly we examine the density across the slab to monitor the crystallinity of each bilayer in a qualitative way and then address the degree of order in each layer. We then comment on the incidence and type of defects formed and then attempt to rationalise the disparity in melting rates that are observed for the two surfaces.

(i) Density profile as a function of temperature

Fig. 2 shows a composite of the density profile, generated with 0.1 Å bins, for four-coordinated oxygen atoms across the slab taken for two temperatures, 200 and 285 K. The coordination number of each molecule was evaluated within a cutoff radius of 2.27 Å, around 0.5 Å larger than the equilibrium hydrogen-bond lengths. The number density peaks are unequal for the sub-surface slabs which is caused by the vibration and relaxation of the bilayers which leads to a broadening of the peaks that is most pronounced at the surface. The surfaces of the slab are the extrema of the coordinates plotted along the \( x \) axis. At 200 K, the outermost part of the surface bilayer is well crystalline but shows slight broadening in comparison to the inner part of the bilayer. The peak heights of the outermost peaks are noticeably smaller than the corresponding peaks of the inner bilayer because a fraction of the water molecules (the water molecules in the upper bilayer) are three-coordinated. There is evidence of surface relaxation, principally manifested in the reduced peak heights of the outer layers compared to the inner layers, which reflects a tendency to deviate from the ideal lattice position. At 200 K, the combined width of the outermost bilayer peaks are 3.00 and 2.90 Å for the lower and upper surfaces respectively, which compares to 2.40 and 2.50 Å for the central bilayers. The central bilayers are 2.70 Å apart whilst the surface layer to second bilayer distance (measured from the inner bilayer surface peak to the outer peak of the second bilayer) is 2.80 Å. For comparison, at 285 K, the central bilayers have peak widths of 2.90 and 3.0 Å. A final point upon which we comment on in more detail later is that the profile at 200 K already contains defects in the outermost layers. However,
the lifetime and incidence of these defects is extremely small and therefore the density plot is essentially unchanged from the defect-free state.

Upon increasing the temperature, the peak heights and widths for the first bilayers reduce and increase respectively. For the sake of clarity, only the 285 K plot is superimposed upon the 200 K data. Upon close inspection of Fig. 2, it can be seen that all the peaks have broadened but most noticeably at the surface. More significantly, the two surfaces on either side of the slab have disordered to different extents, the lower surface (smaller values of \(x\)) showing less structure than the upper surface. In the lower surface, there is a build-up of density between the first two bilayers indicating pre-melting or melting which is less pronounced for the upper surface. The inner part of the bilayer for the upper surface is noticeably more well-ordered than the analogous peak for the lower surface and the lower surface shows significant loss of order in the second bilayer whilst the corresponding peak in the upper part of the slab is relatively well ordered. The new overlayer on top of the original external surface has a depth of approximately 5 Å at 285 K for both the upper and lower layer.

Since the density profiles reflect the averaged position of species, the spatial relationship of species and crystallinity of each layer is open to question. Fig. 3a and 3b show a snapshot taken from the end of the dynamics run for the oxygen sub-lattice in the first three bilayers of the lower surface. In Fig. 3a, the surface is shown at 250 K and shows a vacancy in the outermost bilayer (blue), which exposes the second bilayer, but otherwise the hexagonal oxygen sub-lattice is intact. The situation at 285 K shown in Fig. 3b contrasts strongly with that at lower temperatures; all characteristic hexagonal ordering in the oxygen sub-lattice of the outer bilayer has been lost, the second layer is noticeably disordered exposing the third bilayer but the third layer is still strongly crystalline. The inferences made about ordering from the density of four-coordinated oxygen atoms in Fig. 2 appear to be supported by the visualisation of the slab. From viewing the evolution of the sub-lattice networks at 285 K, it is evident that the outermost layer depicted in blue undergoes very rapid rearrangement and from frame to frame (0.5 ps) the structure changes. Molecules furthest away (the highest molecules) from the outer bilayer are particularly mobile as they are typically one- or two-coordinated and these contribute strongly to the apparent height of the surface in the density profile as they fleetingly
leave the surface. Underlying layers have a more rigid sub-lattice although the second layer shows significant fluctuation in the 2D structure in comparison to the third layer. The external surface layer is rather rough at this temperature, from the maximum height of the external surface to the lowest exposed point in the topography of the ice surface is some $\pm 10 \text{ Å}$. From the perspective of catalysis, it is readily conceivable that these crevasses may trap or even encapsulate species which could then participate in reactions. The walls and base of the crevasse are lined with dangling hydrogen bonds which could presumably strongly bind foreign or natant water species.

(ii) Ordering and disordering in the external surface layer

We now turn to consideration of the density of under-coordinated water ice molecules, in particular the three-coordinated water molecules, to understand more of the nature of the quasi-liquid layer and its intrinsic order. In ice, each molecule is surrounded by four neighbouring molecules except at the surface where one dangling hydrogen bond is exposed. In water, using this potential model approximately half of the water molecules are three-coordinated and half are four-coordinated. Hence the proportion of four- to three-coordinate H$_2$O molecules could be used to monitor how liquid-like such a layer is. In Fig. 4a and 4b, the number of three-coordinated species on the lower and upper surfaces, respectively, are shown for selected temperatures. There is some anisotropy between the two plots. In particular, there is a qualitative change in between 230 and 260 K when three-coordinate species appear in the inner-part of the bilayer. For the upper surface inner bilayer, under-coordination is less pronounced than for the lower surface upon heating from 260 to 273 K. The number of 3-coordinate species above

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Fig. 3 Three bilayers of water ice viewed from the [001] direction, where the oxygen sub-lattice is depicted by creating bonds between oxygen atoms within 3.0 Å of one another. The external bilayer is in blue, the second bilayer is shown in red and the third bilayer towards the centre of the crystal slab is shown in green. (a) This snapshot was taken at 250 K. Only the outermost bilayer is interrupted whilst the sub-surface bilayers display a fully connected hexagonal sub-lattice. (b) This snapshot was taken at 285 K. Obvious hexagonal structure has been lost in the outermost layer and the second bilayer has also lost significant order.

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$\S$ The estimate of QLL thickness made here is slightly larger than the value of $\pm 0.6 \text{ nm}$ from Carignano et al.$^{14}$ which was obtained at a lower temperature of 275 K.
the external surface remains constant for both surfaces, potentially suggesting that these structures are in (dynamic) equilibrium. Notionally one can compare the number densities of four- and three-coordinate species and in the outer bilayers, the ratio of four- to three-coordinated species is approximately 1, suggesting this region is liquid-like. However, the structure is far from homogenous as Fig. 3 attests and hence such a measure of liquid-like nature is possibly misleading. We note that the number of one- and two-coordinated molecules increases with temperature and comprises the majority of the new overlayer. At 285 K the relative proportions of coordination are: 1-coordinate (0.1%), 2-coordinate (4.9%), 3-coordinate (12.8%), 4-coordinate (80.7%) and 5-coordinate (0.6%).

Fig. 4  Number density of three-coordinated oxygen atoms at selected temperatures for two bilayers on (a) the lower and (b) the upper part of the slab. (a) The peak at around 16 Å indicates the outer bilayer of the lower surface. (b) The peak around 43 Å indicates the upper part of the bilayer i.e. the external surface.
Another guide to the transience of the hydrogen-bond network that one attributes to water-like behaviour is exchange of hydrogen bonds. Fig. 5 shows the density of hydrogen atoms that have exchanged which oxygen they are bonded to. Again the asymmetry in the pre-melting of the ice slab is visible with slightly more exchange in the first and second bilayer for the lower surface than the upper surface. The upper surface is somewhat more resistant to the effects of increasing temperature. For both surfaces, there is evidence that both the first and second bilayer contain fractions of H$_2$O molecules that are freely exchanging hydrogen bonds in a way that is characteristic of liquid-like water rather than crystalline water. In the outermost bilayer approximately 40% of H$_2$O molecules are 3-coordinated compared to 25% in the ideal surface and around 5% are two-coordinated. One interesting feature is that at the lower temperatures (250–260 K) the upper surface has a higher concentration of waters that have changed their hydrogen-bonding neighbours than the lower surface but at much higher temperatures of circa 280 K the lower surface has a more mobile network. This observation may be explained by the upper surface somehow auto-passivating or reconstructing itself. In passing we note that provided the external water-like layer is thick enough, a radial distribution function could be generated to help establish whether it possesses long-range order and the degree of short-range order, although for the run described here we suspect the statistics are not plentiful enough for such an analysis to be unequivocal.

Interestingly, even at 280 K as displayed in Fig. 6, the ratio of H$_2$O molecules which exchange over the final 0.25 ns of a run is relatively small (9.5%) in comparison to the total number of molecules. The ratio of waters with a rigid hydrogen-bond network versus a flexible hydrogen-bond network peaks between the first and second bilayers over the lifetime of the run, with the largest ratio being found just inside the surface. This observation suggests that a proportion of the sub-surface H$_2$O molecules are more mobile than those above them, a situation analogous to a frozen lake with liquid water underneath. A potentially important observation in the context of distinguishing between melting and pre-melting is that the density and exchange plots averaged over the first 0.25 ns and final 0.25 ns (for 260–280 K) were essentially unchanged and suggest the crystal is in equilibrium i.e. not melting.
Although not reported here, we have analysed the mean-square displacement (MSD) profile of H$_2$O molecules throughout the slab. What is particularly noteworthy is that the MSD monotonically increases with temperature and by 285 K the measured diffusion coefficient is $2.37 \times 10^{-9}$ m$^2$ s$^{-1}$ for the outer layers ($0.23 \times 10^{-9}$ m$^2$ s$^{-1}$ averaged over the entire slab) which is considerably larger than the experimental values of $0.7 \times 10^{-9}$ m$^2$ s$^{-1}$ at 263.7 K (the approximate temperature this corresponds to in real terms) but close to the experimental value of $2.23 \times 10^{-9}$ m$^2$ s$^{-1}$ at 298 K. Carignano’s data$^{14}$ suggest that the NvdE potential overestimates the true diffusion of water below 298 K but not to the degree noted here. However, if the MSDs are deconvolved to show their individual diffusivities, it is clear that a small fraction of surface bound species have extraordinary diffusivity that is more than one order of magnitude faster than the QLL. The presence of these highly mobile molecules skews the apparent diffusivity considerably and highlights that collective diffusivity is not a reliable gauge of the liquid-like nature of the surface.

**Analysis of structural changes during pre-melting**

To aid interpretation of the structural changes occurring during pre-melting, the trajectories have been analysed visually to try and untangle the local events that occur which trigger the collective loss of structural order in a layer associated with melting. Three distinct temperature regimes are discussed here.

(i) **200–230 K**

According to experiments on dislocation loops in ice crystals,$^3$ evidence has been presented that interstitial defects are the dominant defect in ice. Previous simulation work by Itoh et al.$^{25}$ using the TIP4P potential produced reasonable pathways for self-interstitial migration in the crystal bulk, but the underlying energetics were deemed to be qualitative at best by the authors. More recently de Koning et al.$^{26}$ have used generalised gradient approximation (GGA) DFT approaches to examine
interstitial defect formation in the crystal bulk and arrived at a value of \( \sim 0.7 \) eV, which is considerably greater than the experimental estimate of 0.4 eV.\(^3\) The significance of the defect energies is that concentration of defects is used to rationalise the proton conductivity as well as other properties. The evidence from de Koning’s studies on these defects and other more complex defects suggests that interstitials may be less populous relative to other defects than previously thought. In the light of these insights, it is of interest to monitor the type and frequency of defect formation at the surface since the energy of formation of these species remain unknown at this time (though we note work is underway within our groups to establish surface defect energies from DFT calculations).

At 200 K self-interstitials form relatively rarely—to the extent that just one surface interstitial is seen over the duration of a 0.25 ns MD run. The mobility of the interstitials is low and migration was only noted within a radius equivalent to the next nearest neighbour at this temperature. Recent DFT calculations due to Thierfelder \textit{et al.}\(^{27}\) showed four distinct positions for surface molecular adsorption of water on the ice (0001) face, with energies ranging between 0.55 and 0.58 eV (computed using a periodic slab, plane-wave approach and the PW91 functional). Essentially Thierfelder notes two adsorption modes, one where a water molecule binds towards the centre of the hexamer ring which is the most stable site (0.58 eV), and a second where the sorbed water sits atop an ideal lattice site (0.55 eV) corresponding to the inner part of the outermost bilayer. In our simulations from above 200 K the interstitials are readily identified and it is heartening that despite the fact that a rigid dipole is used to describe the water in these pair-potential calculations, the centre site mode of adsorption is observed with increased frequency to the atop mode. Within this temperature range, the interstitials still undergo relatively slow diffusion across the surface such that probability of two interstitials being proximate is rare enough that no dimerisation of the interstitials is seen. A final observation is that in this temperature regime, only the outermost, undercoordinated molecules of the external bilayer form self-interstitials and there is no visual evidence that the lower part of the outermost bilayer is disrupted.

\textbf{(ii) 230–250 K}

Above 230 K, there is a marked increase in the number of self-interstitials formed and consequently the number of vacancies in the outermost bilayer. The interstitials begin to aggregate from around 230 K onwards, initially forming dimer pairs. We note that Thierfelder also found that dimers formed readily with an adsorption energy which is fractionally more favourable (0.576 eV per molecule) than forming two isolated interstitials (0.575 eV per molecule). However, whether DFT with the PW91 exchange–correlation functional is reliable enough to accurately compare the stability of adsorbed monomers and dimers remains open to question.\(^{28,29}\) The majority of the dimer pairs formed in our MD simulations remain as a complex which is either static or which diffuses very slowly across the surface. From around 240 to 250 K there is a qualitative change in the surface topography where molecules diffuse from the lower part of the outermost bilayer to either the outer part of the bilayer, occupying vacant lattice sites or directly above the surface as an interstitial. At around 240 K temporary holes appear in the outermost bilayers that provide access to the sub-surface bilayer but these have very short lifetimes of just a few ps and are quickly repaired by interstitial molecules and molecules from the outer part of the bilayer. Approaching 250 K, the holes become more permanent and have lifetimes of >50 ps. Over the temperature range 230–250 K, dimer clusters on the external surface begin to aggregate with one another and lone interstitials to form islands of quasi-crystalline water atop the original external surface. In this temperature regime, particularly at around 250 K the surface becomes considerably rougher as a consequence of forming vacancies in the outer bilayer and a new but incomplete quasi-crystalline layer.
Above 250 K

At temperatures above approximately 250 K, it becomes more difficult to distinguish distinct events occurring on the external surface. Analysis of the oxygen sub-lattice at $\approx 250$ K shows that the characteristic regular hexagonal structure is interrupted by defects and dynamically evolves, presumably in response to melting events on the surface and complex surface structural rearrangements. A qualitative ring analysis shows that the surface consists of largely 6-membered rings, with smaller strained 4- and 5-membered rings compensated by 7- and 8-membered rings at 260 K. However, evidently the network still retains both 2D and 3D structure and therefore appreciable long-range order is still present. At around 270 K, hexagonal order is more difficult to detect and from the disruption observed in the top two bilayers of each surface at 275–280 K the lower and upper surfaces have lost any semblance of hexagonal order. Raising the temperature to 290 K noticeably accelerates the loss of order and which is accompanied by a drift in the total energy, suggesting that over the lifetime of 1 ns the (melting) ice slab has not equilibrated.

Before leaving this qualitative assessment of structural changes we highlight two other observations, which will possibly influence the mechanism and the rate of melting at ice surfaces.

Proton disordering events

The commonly accepted mechanism of proton conduction was put forward by Bjerrum (see ref. 3 for a more complete explanation), who highlighted the role of orientational defects in proton conduction. The two so-called Bjerrum defects violate the ice rules: (i) an L-defect is formed when a molecule rotates around a water to which it donates a hydrogen bond, leaving no proton between two oxygen sites; (ii) a D-defect is created when a water rotates resulting in two protons between two oxygen atoms. Taking the instance of the D-defect, the two protons are in an unfavourable interaction and in the Bjerrum model, one of the waters rotates away forming a new D-defect and the process continues until a series of molecules change orientation and in effect a proton has migrated. Detailed analysis of the 230 K dynamics run revealed two distinct events which impact on the proton disordering and proton conduction behaviour of ice which are distinct from the Bjerrum orientational defect. We call the two mechanisms (i) relay and (ii) exchange or dosey-do. In the relay mechanism shown in Fig. 7a, water molecules rotate about their centre of mass in a process reminiscent of the Grotthus mechanism of proton transport. By contrast, in the exchange mechanism (Fig. 7b), the water molecules physically pass one another in a concerted movement. The exchange mechanism is slightly more complex than the Figure implies in that the participating molecules do not lie in the same plane during the transition. One molecule goes sub-surface whilst the other migrates via a supra-surface pathway. The two mechanisms also contrast in that in the relay mechanism the dangling proton is passed from one molecule to its next nearest neighbour via a water in the inner part of the bilayer. In the dosey-do mechanism the dangling proton is passed to its nearest neighbour from the outer bilayer to the inner bilayer. The duration of both processes differ considerably; the relay mechanism involving just concerted flipping of the water occurred over $\sim 2.5 \pm 0.5$ ps whilst the dosey-do takes considerably longer ($\sim 17.5 \pm 0.5$ ps) suggesting approximately an order of magnitude difference in the proton conduction rates. However, both mechanisms occurred just twice in a 0.5 ns 230 K run and hence more extensive sampling is needed to validate the relative rates of these processes.
General discussion

An interesting result of this paper is the observation of slightly different disordering behaviour and onset of melting for the two sides of the slab. Since each surface of our slab is representative of the (0001) surface of ice Ih being, as we mentioned, obtained with the procedure of Hayward and Reimers, it is somewhat surprising to observe two slightly different melting temperatures. However, at the outset each surfaces does not have identical proton distributions and so we looked in to this issue in detail to see if we could understand if a relation between the onset of melting and surface order existed. We sought to consider precisely how the stability of a variety of defect-free (0001) ice surfaces differs with respect to the arrangement of the surface protons. Conscious that surfaces which differ only in the spatial arrangement of the protons are likely to have very similar energies, these calculations were performed with DFT. However, the general conclusion that we reach from the DFT calculations is not altered if we use the classical water potential described here (with an additional term to better reproduce proton ordering energetics).

The intrinsic stability of the various surfaces at zero Kelvin was compared by computing their total surface energies, \( \gamma \), which is defined here per water molecule as:

\[
\gamma = \frac{E_{\text{slab}}^{\text{lab}}(n) - nE_{\text{tot}}^{\text{bulk}}}{m}
\]

where \( E_{\text{slab}}^{\text{lab}} \) is the total energy of the ice slab obtained from our first principles DFT calculations, \( n \) is the number of bilayers in the slabs, and \( m \) is the number of water molecules on the two surfaces of the slab. The bulk reference per molecular bilayer, \( E_{\text{tot}}^{\text{bulk}} \), is extracted from calculations on ice slabs from the relation:

\[
E_{\text{tot}}^{\text{bulk}} = E_{\text{lab}}^{\text{lab}}(n) - E_{\text{lab}}^{\text{lab}}(n-1)
\]

where, as before, \( n \) is the number of bilayers in the slab. The surface energy was computed for more than 20 perfect (0001) ice Ih surfaces that were identical except for the spatial arrangement of the protons in the slab. For each slab a different value of the surface energy was obtained. The fact that we do not get a unique value for ice
Ih is partly to be expected since it is already known, for example, that the cohesive energy of bulk ice depends on the degree of proton disorder within the simulation cell.\textsuperscript{30–33} However, the interesting finding here is that the variation of the surface energy (\(\sim 50\) meV per \(\text{H}_2\text{O}\)) with the degree of proton order by far exceeds the typically small range (\(\sim 4\) meV per \(\text{H}_2\text{O}\)) seen in bulk ice Ih. After exploring in detail the proton distributions at each of the surfaces, we find that the spatial distribution of the upright OH groups at the surface, those which “dangle” out of the surface, are key. In order to distinguish different distributions of these dangling OH bonds, we define an order parameter:

\[
C_{\text{OH}} = \frac{1}{N_{\text{OH}}} \sum_{i=1}^{N_{\text{OH}}} c_i
\]  

where \(N_{\text{OH}}\) is the total number of dangling OH bonds on the two surfaces of our simulation slab and \(c_i\) is the number of the next nearest-neighbour dangling OH bonds around the \(i\)th dangling OH bond. The order parameter, \(C_{\text{OH}}\), quantifies the uniformity in the distribution of the dangling OH bonds at the surface. The smaller the value of \(C_{\text{OH}}\), the more uniform the distribution. The larger the value of \(C_{\text{OH}}\), the more inhomogeneous or disordered the distribution of the dangling OH groups is, with the important consequence that on average the dangling OH groups at the surface are closer together. The smallest possible value of \(C_{\text{OH}}\) for a non-polar surface is 2, which is in accord with the structure proposed by Fletcher\textsuperscript{34} for low-temperature ice. Remarkably, we find that when all the surface energies of the many surfaces considered are plotted as a function of \(C_{\text{OH}}\) a rather clear linear correlation is observed, as shown in Fig. 8. Moreover, for certain values of \(C_{\text{OH}}\) we have computed more than one structure and despite having different proton arrangements, surfaces with the same value of \(C_{\text{OH}}\) always come within \(\sim 4\) meV per \(\text{H}_2\text{O}\).

Having observed a correlation between the intrinsic stability of a surface, measured here by means of the total surface energy, we now revisit the slab used.

![Graph](image.png)

\textbf{Fig. 8}  The surface total energy of ice (0001) as a function of the order parameter defined in the text.
in the molecular dynamics simulations, in a way anticipating that this might explain the different melting behaviour on the two sides of the slab. However, employing the order parameter defined in eqn (3) we find that the two surfaces of the slab have precisely the same value: 2.92. Thus, although we have observed a correlation between surface order and surface energy, it appears that even surfaces with the same average extent of surface order may start to melt at different temperatures.

This leads us then to examine proton ordering in more detail and consider whether local, as opposed to global, proton arrangements have an impact on the susceptibility of a surface to pre-melting. Indeed from the relation displayed in Fig. 8 we get an indication that molecules will likely be unstable, or “hot” when three or more protons surround them. It turns out that the lower surface has sixteen molecules with highly unfavourable sites with clusters of three or more adjacent dangling protons whilst the upper surface has only twelve. Thus we suggest that the greater proportion of the local hot spots with high local concentrations of dangling OHs may be responsible for the slightly lower onset of melting on the lower surface of the slab. We can imagine figuratively speaking that at the hot-spots on the real ice surface associated with clusters of protons, these regions are prone to pre-melting and form ‘puddles’, which may also act as traps for trace gases in atmospheric reactions. The previous discussion is somewhat speculative at this stage and it could be that the slightly different melting behaviour at the two surfaces is an artefact of having reasonably small surface areas with a relatively low variance in the local C\textsubscript{OH}. In future work, a systematic study of the melting temperature of various ice surfaces as a function of average and local C\textsubscript{OH} is planned. An additional point in critique of the results presented here which also acts as a word of caution for all simulations of ice-surface pre-melting relates to the rather long timescales required. Indeed, despite the structures observed at the external surface appearing to be in equilibrium at around \(\approx\)285 K, there is still the possibility that the surface has not always attained its equilibrium structure. In Carignano \textit{et al.},\textsuperscript{14} the QLL was found to equilibrate in just 200 ps at 275 K and this concurs with our observations. However, in particular, by monitoring the structure visually, it can be seen that the outermost water molecules very slowly organise themselves to form chains after 1 ns at temperatures above 275 K. Possibly, more extensive simulations are required to establish whether more ordered structures develop on a very long timescale.

The final issue worthy of note is the melting temperature; our results indicate that the surface, despite being manifestly disordered at the surface for two bilayers at the crystal surface, does not melt until 285–290 K, in agreement with the estimate of Abascal \textit{et al.}\textsuperscript{16} However, it is somewhat surprising that given the surface was in contact with free vacuum, the surface does not melt at a lower temperature. Our model of the surface does not contain any ionic defects which are known to be present in real ice samples and perhaps this prevents us from observing disordering at relatively low temperatures (observed at just above 200 K by Wei \textit{et al.}\textsuperscript{35}). We might expect ionic defects and extrinsic impurities to surface segregate which may well affect the response of the surface to temperature and perhaps the thickness of the QLL reported by experiment.

**Conclusions**

In collating the conclusions, in this section we subtract 15K from the temperatures at which we observe phenomena in order to make contact with experiment. We find that:

- The ionic defect-free pure ice (0001) surface shows anisotropy in its melting which we attribute in part to the spatial arrangement of protons on the surface.
- The outer surface is liquid-like at temperatures above \(\sim\)250 K but this lies in a crust of interrupted ice immediately below which the sub-surface H\textsubscript{2}O is rather mobile (and can diffuse to the outer surface)
Surface interstitials (ad-molecules) are seen at 200 K. These interstitials are not evidence of melting or pre-melting since they occur at temperatures well below the formation of the QLL. At temperatures of around 240–250 K, these single interstitials are extremely mobile, diffusing faster than liquid water, hence the collective diffusion coefficient should not be used to gauge the extent of water-like structures at the surface or the identification of water at the surface. When single interstitials dimerise their diffusion is markedly slower.

Large holes of width ~0.5–1.0 nm appear in the outermost bilayer at temperatures below 250 K. These ‘crevasses’ are at least 1.0 nm deep at temperatures around 10 K below the melting temperature and have the capability of trapping foreign species. The roughness of the surface is considerably larger than expected, suggesting even at temperatures typical of arctic and antarctic lower and upper atmospheres, the sticking probability of species to the surface will deviate significantly from the classic picture of the Kossel crystal ideal surface.

In current work, we are extending the timescales of the MD runs described here and we are exploring in detail how proton arrangement influences the melting of the ice surface. We are also investigating more quantitative schemes for discriminating between liquid and crystalline water, such as that of Carignano et al.\textsuperscript{14}

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