

# Surface premelting of water ice

Ben Slater<sup>a</sup> and Angelos Michaelides<sup>b</sup>

<sup>a</sup> *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom, e-mail: b.slater@ucl.ac.uk*

<sup>b</sup> *Thomas Young Centre, Department of Physics and Astronomy, and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, United Kingdom, e-mail: angelos.michaelides@ucl.ac.uk*

## Abstract

Frozen water has a quasi-liquid layer at its surface that exists even well below the bulk melting temperature; the formation of this layer is termed premelting. The nature of the premelted surface layer, its structure, thickness and how the layer changes with temperature have been debated for over 160 years, since Faraday first postulated the idea of a quasi-liquid layer on ice. Here we briefly review current opinion and evidence on premelting at ice surfaces, gathering data from experiment and computer simulations. In particular, spectroscopy, microscopy and simulation have recently made important contributions to our current understanding of this field. The identification of premelting inhomogeneities, where portions of the surface are quasi-liquid-like and other parts of the surface are decorated with liquid droplets is an intriguing recent development. Untangling the interplay of surface structure, supersaturation and surface defects is currently a major challenge. Similarly, understanding the coupling of surface structure with reactivity at the surface and crystal growth is a pressing problem in understanding the behaviour and formation of ice on Earth.

## [H1] Introduction

Surface premelting of ice influences a multitude of phenomena on Earth, such as the genesis and lifetime of clouds, the retreat of the ice packs in the Arctic and Antarctic, the electrification of thunderclouds<sup>2</sup> and on a more mundane level, potholes in roads. Premelting of ice was first publicly reported by Faraday in the 1850s<sup>1</sup> to explain his famous regelation experiment started a few years earlier. However, only a century later, the first experiments appeared that could probe and quantify surface structural changes with temperature and relatively recently there have been several profound discoveries that enrich our understanding of ice surface premelting.

Premelting occurs on the surface and proceeds into the bulk ice crystal (Figure 1) because the surface layers are more weakly bound than those in the bulk. The structure of ice surfaces depends on the morphology of ice particulates, which expose different crystal faces. The dendritic hexagonal ice crystal is one of a panoply of distinct morphologies that are summarised in Figure 2. The manifold of morphologies arises from the interplay of temperature and supersaturation, which influences the crystal growth mechanism and hence the crystal habit<sup>3-5</sup>. Seeding ice formation with, for example, AgI and kaolinite, can afford complex structural features such as gaps in the bulk crystal, which are known as hopper crystal morphologies<sup>4</sup>. Most of the crystals depicted in Figure 2 exhibit the basal (0001) and prismatic (1010) planes, although intriguingly recent studies suggest the secondary (1120) prism face may be the most stable face under laboratory conditions<sup>6</sup>. A subtle feature of all crystalline ice surfaces is that exposed interfacial H<sub>2</sub>O molecules are undercoordinated. By definition, each water molecule must accept and donate two hydrogen bonds but this is not possible at the surface unless reconstruction occurs (another possibility is that relaxation occurs and four weak hydrogen bonds are formed rather than three strong hydrogen bonds). Additionally, if the orientation of all the undercoordinated molecules is identical, this would lead to an intrinsically unstable polar surface. Hence, there is an expectation that the surface molecules will also show orientational non-random disorder under the naturally achievable temperatures and pressures on Earth.

An excellent summary of the physical and thermodynamic foundations of premelting is presented by Dash and coworkers<sup>2</sup> and Elbaum and colleagues<sup>7</sup>. As a general definition, the onset of premelting depends on the bulk melting temperature ( $T_m$ ) with an increase of the thickness of the premelting layer as  $T - T_m$  approaches 0 K. It is also important to consider whether the surface is completely wetted or whether it would be decorated with droplets. At equilibrium, the Young expression that balances the substrate (s), liquid (l) and vapour (v) surface free energies ( $\gamma$ ) is  $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$ , where  $\theta$  is the contact angle the substrate and liquid phase and an angle of  $0^\circ$  indicates complete wetting. For a comprehensive account of the thermodynamics of wetting, see refs<sup>8</sup> and <sup>9</sup>. Because water is reasonably volatile, the equilibrium of the liquid and vapour is interdependent and so the vapour pressure is a key ingredient in establishing whether the ice surface is decorated by droplets or covered by a liquid film. More generally, Stranski<sup>10</sup> made an important contribution reasoning that the surface energy of a crystal (of any composition) can be lowered by wetting the surface with its melt<sup>11</sup>. Frenken<sup>12</sup> suggested that the presence of a premelted layer can contrast nucleation near the melting temperature; a liquid requires a “nucleus” of solid to trigger freezing, which requires supercooling below the melting temperature, whilst it was argued that the presence of the premelting layer on the solid means that there is no nucleation barrier to forming the liquid from the solid.

Traditionally, the big unsolved question in ice premelting under ambient pressure is related to the temperature at which premelting occurs and the spatial extent of the premelted ice layers — the quasi-liquid layer (QLL). A range of techniques has been used to investigate the onset temperature of premelting and thickness of the premelted layer on ice and the outcome of measurements by a subset of techniques are highlighted in Figure 3. The temperature at which premelting begins has been estimated to be anywhere between  $\sim 200$  K and  $260$  K<sup>13–17</sup> and the maximal thickness of the QLL is approximately  $1–100$  nm<sup>16,18–20</sup>. Figure 3 vividly illustrates a central problem in premelting: the disparity between the onset temperature and thickness of premelting layers between different techniques. This problem leads to questions such as which technique is capturing the correct phenomenology? What are the consequences of premelting from a physicochemical point of view? We will now step through a timeline of key observations stemming from different techniques and piece the evidence together to highlight the state of the art knowledge, and the holes or fuzzy regions in our understanding of this topic. To aid navigation, a timeline with some of the key developments in the field is shown in figure 4.

In this brief review, we summarise some of the key developments in the field and highlight outstanding problems that are ripe for investigation through experimental and computer modelling approaches. We cannot summarise 160 years of work towards understanding the QLL of ice and we also note there is a substantial literature of premelting in other materials, such as metals. Indeed, theory in this area has been developed for decades<sup>11</sup>. Hence, we now discuss some important staging points in the literature, with the perspective of trying to bracket what temperature premelting initiates at and the thickness of the premelting layer at a given temperature. We start with a brief introduction to the structure of ice and then discuss developments in understanding the premelting layer in roughly chronological order. We emphasise that we focus on ice premelting in contact with the vapour phase but recognise that premelting of ice occurs with a host of substances and direct readers to the excellent review of Dash et al.<sup>2</sup> for an introduction to that aspect of premelting. We also emphasise that our aim here is for a critical review of recent work in particular rather than an exhaustively detailed and complete historical account of the literature. Several authors have reviewed work on the QLL and we encourage readers to delve into this literature for further information<sup>2,11,21–26</sup>.

## [H1] Early characterisation

Specific studies on premelting of ice started to appear in the late 1950s and here we focus on a selected set of experimental and theoretical studies that sought to pin down the basic question of what temperature the QLL originates and how thick the QLL is at a given temperature. Golecki and Jaccard<sup>13</sup> reported on proton back-scattering and channelling experiments of the (0001) surface between  $143$  and  $271.2$  K. They observed a marked increase in back scattering above  $238$  K, which was interpreted as blocking of the channels along the  $c$  axis due to strong thermal vibrations and partial disordering. The disordered layer was found to increase in thickness at  $213$  K and reach  $\sim 80$  nm at  $271$  K (which was extrapolated to be  $95$  nm at  $272$  K, corresponding to  $\sim 260$  bilayers). In stark contrast, surface conductivity measurements<sup>27</sup> only detected anomalous increases in conductance at  $262–267$  K that was presumed to signal the formation of a liquid-like layer. Presumably, this anomaly signals the complete wetting of the surface that leads to substantial mean-free path lengths that could give rise to increased conductivity on the microscopic scale.

X-ray diffraction of single and polycrystalline ice surfaces in the 263–272 K temperature regime was reported by Kouchi et al.<sup>28</sup> The ice crystals were prepared carefully using double distilled water under slow crystal growth conditions and a microtome was used to prepare the (0001) and (10 $\bar{1}$ 0) surfaces. The measurements showed an absence of long-range structure around 272 K with no appreciable difference in the ratio of the characteristic (0001) and (10 $\bar{1}$ 0) secondary peak intensities over the 9.5 K window explored. These results indicated that premelting, as measured by the X-ray penetration depth, was equivalent for both the basal and prismatic planes for both single crystal and polycrystalline samples. However, at  $\sim$ 271 K there was a marked decrease in the intensity of the first  $2\theta$  peak, which can be interpreted as pronounced melting at the surface. A more recent study by Dosch et al.<sup>15</sup> showed substantial differences in the thickness of the QLL on the (0001) and (10 $\bar{1}$ 0) surfaces but only marginal differences in the premelting onset temperature. Premelting onset was estimated to be 260 K for the (0001) surface and 261 K for the (10 $\bar{1}$ 0) surface. However, the QLL thickness was estimated to be  $\sim$ 50 nm at 272.85 K for the (0001) surface,  $\sim$ 15 nm at 272 K for the (10 $\bar{1}$ 0) facet and approximately 44 nm for {11 $\bar{2}$ 0} at 273 K. Importantly, Dosch et al.<sup>15</sup> established a logarithmic dependence of the QLL with temperature and cleverly avoided scattering from nascent or non-equilibrium vicinal surfaces arising from evaporation by using a glancing angle approach. Dosch et al.<sup>29</sup> also performed an extremely delicate study revealing hydrogen Bragg reflections at the surface. A Bjerrum defect (Box 1) rich 2–3 nm region (approximately 6–8 bilayers) with disrupted hydrogen bonding within a 25 nm sample depth was observed at 260 K. The presence of point-defect rich surface layers and their contribution to premelting behaviour is an area deserving of more study.

Furukawa et al.<sup>30</sup> performed ellipsometry experiments on a negative crystal of ice exposing (0001) and (10 $\bar{1}$ 0) surfaces. Ellipsometry detects changes in polarity to light impinging surfaces and was used in this study to measure the refractive index and QLL thickness of a single crystal of ice. The refractive index of the surface “transition” layer was found to be 1.33 for both the (0001) and (10 $\bar{1}$ 0) surfaces, which can be compared to 1.3327 for bulk water and 1.3079 for ice indicating more liquid-like than ice-like properties. The onset of premelting was reported to be 271 K and 269–272 K for the (0001) and (10 $\bar{1}$ 0) surfaces respectively and the QLL thicknesses at 272 K were approximately 20 nm and 30 nm for the (0001) and (10 $\bar{1}$ 0) surfaces respectively (estimated from the redrawn figure in <sup>31</sup>). A curiosity of this study is that the QLL on prismatic face at 273.05 K is several hundred nm thinner than the QLL observed at lower temperature. Earlier ellipsometry experiments by Beaglehole and Nason<sup>19</sup> reported an opposite trend in the estimated QLL thicknesses: 100 nm for the prismatic face at 253 K and 0 nm for basal face at the same temperature. Furukawa et al. attributed discrepancies between their observations and other studies to potential sample purity problems and other technical aspects. Elbaum et al.<sup>32</sup> estimated the QLL on the basal plane at  $\sim$ 273.05 K to be 18 nm thick (ice crystallites grown from and in water vapour) and accompanied by macroscopic and mobile droplets (that did not fully wet the surface) with a contact angle of 0.6°; when air was admitted to the sample a much thicker macroscopic QLL of  $\sim$ 200 nm was formed indicating complete wetting or surface melting. This study prefigures work by Sazaki and co-workers more than 20 years later who explored the relationship between saturation and QLL. Another AFM study, carried out with a controlled humidity of 85  $\pm$ 5% put the QLL at 11 nm at 263 K<sup>33</sup> and 32 nm at 272 K<sup>33</sup>, whereas, Volta effect measurements place the premelting onset at 243 K<sup>34</sup> with no direct estimate of the QLL depth.

Mizuno and Hanafusa reported NMR<sup>14</sup> spectra of powdered ice that was formed from droplets of diameter  $<$ 150  $\mu$ m to attain high surface-to-bulk signal ratio. In addition to provide information about sample purity and kinetic influences on crystallisation, the surface-to-bulk signal ratio in NMR spectra measurements can be in principle related to the QLL thickness, although this was not estimated in this study. The onset of the formation of the QLL was not distinct but the barriers for rotational and translation motions at  $\sim$ 220 K were found to be 0.29 eV and 0.25 eV respectively, which are larger than those in water ( $\sim$ 0.19 eV) and substantially smaller than those found for bulk ice ( $\sim$ 0.65 eV) reflecting distinct phase properties for the surface molecules at that temperature. No discontinuity in the activation barrier was detected up to 268–271.5 K indicating that no significant bulk liquid signal was detectable even in the outermost bilayer. Similarly, the self-diffusion coefficient of the water molecules on the surface was found to be about 4% of that of liquid water even up to 271.5 K.

In one of the earliest examples of conceptual modelling of ice surface structure, Weyl speculated that water molecules on the surface would be oriented with the hydrogen atoms pointing towards the bulk due to electrostatic and hydrogen bonding considerations<sup>35</sup>. He reasoned that the presence of dangling hydrogen bonds should be minimized because they would lead to an unstable arrangement. At the time Weyl’s arguments were made, water molecule orientation and arrangement in the bulk crystal were not certain, nevertheless the arguments presented helped frame the question of the surface structure of ice. Probably the most important contribution towards discriminating the surface structure of ice, especially the QLL, and its influence on

properties was due to Neville H. Fletcher<sup>36</sup>. He proposed the first quantitative model prediction of the onset of premelting to be just above 243 K based on free energy, hydrogen bonding, Bjerrum defects and electrostatic considerations, and that thickness of the QLL would diverge towards the bulk melting point  $T_m$ . A revised model<sup>37</sup> was proposed that took into account of the quadrupole moment of water. This and more sophisticated model predicted premelting temperature between 267 K and 270 K depending on the L defect formation energy, and QLL thickness of  $\sim 1$  nm at 267 K and between 3 nm and 4 nm at 272 K and . Fletcher's model substantially underestimated the QLL thickness according to the measurement reported above, but it predicted the onset temperature in fair agreement with experimental observations. This model predates computer modelling of ice but we will see that in fact these predictions of QLL thickness are in very good agreement with state-of-the-art predictions performed with classical potential based models made some 40 years later.

Fletcher made another important contribution to the field<sup>38</sup>; considering the crystal structure of the basal and prismatic plane and taking account of the hexagonal symmetry, he studied the optimal way to arrange the water molecules on a surface to minimise the number of dangling bonds in respect of the Bernal–Fowler ice rules (Box 1) and the electrostatic dipolar repulsion between molecules. Fletcher argued that an ordered, striped surface configuration, in which each molecule in the outer layer is surrounded by six nearest-neighbours with four anti-parallel and two parallel dipoles moments, would minimise electrostatic interactions on the basal plane. On the prismatic plane, pairs of anti-parallel molecules were predicted to stripe the surface. Note that both the proposed basal and prism configurations were microscopically apolar in the direction perpendicular to the surface, an important consideration in minimising the surface energy. Fletcher predicted that these ordered surface configurations would be adopted at very low temperatures: 30 K for the basal plane and 70 K for the prism plane. These models were not quantitatively tested until more than a decade later when they have been demonstrated to be favourable low energy structures<sup>39,40–42</sup>.

Elbaum and Schick<sup>43,44</sup> applied the Dzyaloshinskii, Lifshitz and Pitaevskii (DLP) dispersion model<sup>45</sup> to predict that surface melting of ice would be incomplete at the triple point. Most significantly, their model predicted the coexistence of complete wetting layers and water droplets, in line with their own experimental observations<sup>32</sup>. According to the DLP model (using the experimental data reported in Elbaum and Schick<sup>43</sup>), the liquid thickness at the free energy minimum (see the Young equation and ref. <sup>43</sup>) is between 2 and 4 nm, which is in marked contrast to the experimental thicknesses reported above. Furthermore, the model predicted that the rates of premelting at equilibrium and away from equilibrium are not equivalent<sup>46</sup>.

This selection of data present here (more extensive summaries and critique can be found elsewhere<sup>21–24</sup>) highlights considerable variation and uncertainty in the thickness of the QLL, its onset and whether particular faces of the ice crystallites are more prone to premelt at lower temperatures than others. Suffice to say, variation in these data arises from the effects of thermal vibrations on the surface structure, the potential influence of impurities (extrinsic defects), intrinsic point and line defects as well as sample preparation artefacts and vapour pressure. More fundamentally, the connection between the atomic scale structure, the ideal surface structure and surface properties under any relevant conditions was limited by the absence of local or average structure information about the surface. Furthermore, the scatter in the reported QLL onset temperatures and QLL thickness measurements is in part due to the probe depth and the intrinsic resolving power of the experimental techniques. A key issue in the experiments mentioned in this section was the control and equilibration of the vapour pressure as vividly shown in the work of Elbaum et al.<sup>32</sup>. In that case, it was reported that mobile water droplets under water vapour did not fully wet the surface, but that a  $\sim 200$  nm QLL was formed at the same temperature and ambient air pressure. Given the extreme sensitivity of the nature of the ice surface to vapour pressure, a route to disambiguation would be to eliminate vapour and perform the measurements vacuum conditions. This required progression in instrumentation through the development of surface science approaches as well as modelling approaches to resolve the structure of the QLL.

## **[H1] High vacuum and modelling studies**

A major change in the refinement of our knowledge of premelting came from the advent of ultra-high vacuum (UHV) approaches in surface science combined with the emergence of modelling. From around the 1980s onwards, UHV approaches had reached a state of maturity and widespread use in fields such as surface catalysis<sup>47</sup>. To contribute to the QLL questions of structure and premelting temperature, it was necessary to perform extremely well controlled experiments, and meticulous sample preparation to minimise the possibility of surface contamination that could affect the measurements. Additionally, atomic scale models were required to model the structure and predict the stability of liquid water and crystalline ice with sufficient accuracy. By the

1990s, surface science approaches, models (classical and quantum chemical, especially density functional theory (DFT)) and computer architecture had come of age, opening up the possibility of answering basic questions, such as what is the surface structure of pristine crystalline ice I<sub>h</sub> and what is the structure of the QLL?

A landmark demonstration of the synergic benefits of allying surface science techniques and modelling approaches was reported by Materer et al.<sup>48</sup> (see also Ref. <sup>49</sup>), who used low-energy electron diffraction (LEED), classical molecular dynamics (MD) and DFT calculations to study the (0001) ice surface. In this work, a Pt(111) substrate was used to grow an ice film at 140 K and the LEED pattern acquired at 90 K. Co-author Kroes extended their TIP4P study of 190–250 K<sup>50</sup> (see below) to simulate the (0001) surface at 90 K. According to LEED, ice I<sub>h</sub> rather than ice I<sub>c</sub> (Box 2) was resolved with reasonable confidence but the measurements did not help distinguish whether the ice surface was terminated by a full bilayer or a half-bilayer. Intuitively, the full bilayer model would be expected to be more stable because the half-bilayer or single-layer models expose twice as many dangling hydrogen bonds as the full bilayer model. Indeed, the DFT results discussed within this paper appear to confirm this speculation and the classical MD suggested that only the bilayer model is compatible with the structure and amplitudes of vibration measured. Notably, according to LEED measurements, the amplitude of vibration of the upper layer of the first bilayer (which has one dangling hydrogen bond) at a chilly 90–K is large enough that it cannot be directly discerned from the lower layer of the same bilayer. The key experimental evolution and findings in this field are summarised by Li and Somorjai<sup>25</sup>. However, LEED could shed no light on the nature of the arrangement of the protons at the surface and the structure of the premelting layer. Bluhm et al.<sup>20</sup> performed an important set of X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS) experiments. Bluhm and Salmeron developed a novel near ambient pressure XPS experiment that enables determination of atomic-level information at well-defined solid–liquid interfaces. Their study revealed that the onset of a discernible QLL was above 250 K and that at just below the melting temperature (271 K) the QLL was ~2 nm thick. Their result is notable not least because it marks the lowest experimental estimation of QLL depth just below T<sub>m</sub>.

From around the 1980s, more or less contemporaneous with developments in surface science, classical modelling approaches based on force field methods began to be relevant in water ice studies<sup>51</sup>. A key development in this field was the advent of the rigid body TIP4P<sup>52</sup> four site water potential. The three site single point charge (SPC)<sup>53</sup> and TIP3P<sup>53</sup> models had already appeared but TIP4P had proved to yield accurate reproduction of the water radial and partial radial distribution functions and the structure of ice. Another important development was due to the careful work of Hayward and Reimers<sup>54</sup> who examined the random orientation of water molecules within ice structures subject to polarity constraints to produce ice configurations that contained intrinsically apolar bilayers. It is important to include apolar bilayers if one wants to model apolar surfaces without reconstruction, despite the small energetic penalty for violating the constraint. The advent of well-behaved density functionals and availability of supercomputers are other crucial developments in quantum chemistry and computer hardware that enabled the study of water and ice at the quantum mechanical level on a tractable timescale. For a contemporary survey of the performance of DFT for water and ice the reader is referred to the review by Gillan et al.<sup>55</sup> and for a greater emphasis on classical models to the review by Cisneros et al.<sup>56</sup>.

Building on the advent of the TIP4P model, two important modelling contributions to the evolution of the ice premelting came about, the first was due to Kroes<sup>50</sup> and the second was due to Nada and Furukawa<sup>57</sup>. Kroes considered the molecular dynamics of a periodic oriented (0001) slab of ice in the 190–250K temperature range for up to 260 ps (at elevated temperatures). Below 210 K, the surface was determined to be crystalline evidenced by no self-diffusion whereas appreciable self-diffusion, rotational and translational disorder comparable with bulk water was observed above 230 K. Increased polarisation of the surface was noted as the target temperature was elevated and the protons of the water molecules at the vacuum–ice interface layer were noted to point into the surface rather than out of the surface. Kroes carefully pointed out that the non-polarisable nature of the TIP4P model and the use of fixed layers in the simulation precluded him from commenting on whether surface melting was complete. Importantly, it has subsequently been shown that the melting temperature of ice with the TIP4P model is approximately 230 K<sup>58</sup>, so it is likely that full melting was occurring at 230 K and above but that it was tempered by the fixed ice substrate. Nevertheless, the disordering observed in the regime between 210 K–230 K was evidence of premelting well below T<sub>m</sub> for this model. Similar findings were reported by Bolton and Pettersson using TIP4P<sup>59</sup>.

Nada and Furukawa<sup>57</sup> also used the TIP4P model and compared the structural response of (0001) and (10 $\bar{1}$ 0) ice–water interfaces. That study considered 100 ps molecular dynamics simulations again at 230 K, now known to be the bulk melting temperature of TIP4P ice. The important result was that the (0001) surface was shown to be more disordered than (10 $\bar{1}$ 0), with a larger disordered layer thickness on the basal plane hinting at strongly anisotropic surface properties and structural responses. Notwithstanding the uncertainty over the effects of heating model slabs beyond the bulk melting temperature of the TIP4P model, this study was interpreted as providing evidence of no major distinction in the melting response of these two surfaces.

The arrangement of protons at the ice surface was proposed by Buch et al.<sup>39</sup> building on two sets of experimental data. The first set of data was obtained from sum frequency experiments on the surface of ice, which showed orientational disordering of surface water molecules at 200 K<sup>17</sup> that was first interpreted as a proxy for premelting and later confirmed in another independent study<sup>60</sup>. The second set of data was obtained from helium scattering studies<sup>61</sup> that previously could not help discern whether the basal surface of ice showed ordered arrangements of protons, such as Fletcher’s phase<sup>38</sup>, or a disordered arrangement in which the Fletcher phase is not dominant, as it was suggested by more recent measurements<sup>62</sup>. Buch used dynamical and Monte Carlo simulations based on TIP4P-ice<sup>63</sup> to show that the Fletcher striped phase of protons was most stable and in fact this arrangement was found to be stable until surface reconstruction occurs above 180 K. Comparison of the models with previous sum frequency generation (SFG) studies<sup>64,23</sup> provided additional evidence to support the hypothesis that protons adopt ordered arrangements at the surface. Very shortly after this work was published, Pan et al.<sup>40,42,65</sup> demonstrated through a DFT assessment that ordered proton arrangements, including those proposed by Fletcher, were indeed the lowest energy arrangements of protons at the surface. In addition, the lowest energy configurations were found to be stable beyond the premelting and bulk melting temperature suggesting that there is a clear driving force for the surface of ice to display ordered hydrogen configurations rather than random distributions. The latter prediction may be important in understanding uptake and chemical reactivity on ice particles in high-altitude clouds for example, where ordering will lead to patches of the surface that are more favourable for binding electrophiles and others that are more attractive for nucleophilic centres<sup>66</sup>. It is noted that potential models such as the TIP4P family generally fail to reproduce the correct ground state bulk crystal structures for hydrogen ordered ices (such as ice XI), whilst DFT has an excellent track record of predicting ground state hydrogen ordered structures<sup>67–75</sup>. Other surface ordered configurations were also found with internal energies that were considered to be isoenergetic with the Fletcher striped phase within the uncertainties associated with DFT. Pan et al.<sup>40</sup> also discerned that the surface energies of the basal and prism faces in their optimal arrangement of protons were essentially identical within the accuracy of DFT.

Although the terminating structure of ice at low temperature seemed to have been resolved, the premelting temperature and QLL thickness remained open questions for theory. Abascal and Vega performed crucial work laying the foundation for more accurate modelling of the QLL by reparameterising TIP4P to reproduce the melting temperature of ice<sup>58,76,63</sup> and key features of the phase diagram for water for the first time. TIP4P-2005 ( $T_m = 249 \pm 3$  K) and TIP4P-ice ( $T_m = 271 \pm 3$  K) models were used by Conde et al.<sup>18</sup> to determine the thickness of the QLL and the onset temperature for premelting. Both models predicted a similar thickness of the QLL but a qualitative difference was found in the respective QLL depths of the basal plane compared with the primary and secondary prism faces. TIP4P-ice gave the largest QLL on the secondary prism face rather the primary prism or basal face, whereas TIP4P-2005 gave the smallest QLL on the secondary prism face compared with the primary prism and basal face. Focusing on the TIP4P-ice results, which reproduced the  $T_m$  more accurately, the onset of premelting was found to be  $\sim 170$  K on the basal face,  $\sim 190$  K for the primary prism face and  $\sim 200$  K for the secondary prism face. These estimates are broadly in line with helium scattering experiments of Suter et al.<sup>77</sup> who detected anomalous response from the surface at 180 K and also compatible with the expected premelting temperature according to Tammann’s postulate<sup>78</sup> ( $\sim 180$  K).

These results are also comparable with XPS and NEXAFS results of Bluhm et al.<sup>20</sup> that yielded an estimate of the QLL thickness of  $\sim 2$  nm at 271 K, just below the melting temperature. However, Bluhm’s estimate of the premelting onset was above 250 K, in marked disagreement with the study of Conde et al.. Similar QLL depths were obtained by Carignano et al.<sup>79</sup> using a six-site water model<sup>80</sup> at 275 K, at the time thought to be above  $T_m$ , but a subsequent study determined  $T_m$  for the six-site TIP6P model to be 287 K.<sup>81</sup> Simulations reported in Bishop et al.<sup>42</sup> at 285 K using TIP6P show figuratively that only the top two bilayers have liquid character, the outermost layer being disordered but the second bilayer partially ordered, structure that is qualitatively consistent with the findings of Conde et al. Note that simulated surface energies are an incredibly delicate quantities because

they measure the difference between bulk and surface stability and have been found in remarkably good accord,  $\sim 30\text{-}35\text{ mJ m}^{-2}$ , using a variety of potential models and different techniques including the capillary wave method and Mold integration<sup>82,83</sup>.

We note that for many properties of the QLL the coarse grained model<sup>84</sup> of water (mW), which has been used extensively to study homogenous<sup>85-90</sup> and heterogenous ice nucleation<sup>91-93,94</sup>, yields results that are generally consistent with those from atomistic models of water<sup>84,88,95-98</sup>. Because of its greatly reduced computational cost compared to standard atomistic models, it is possible to examine larger system sizes (see below) and perform more extensive analyses of the sensitivity of the QLL thickness to temperature. Notably, Limmer and Chandler have used mW to examine the thickness of the QLL up to  $T_m - 0.25\text{ K}$  in what is to date the most detailed and probably best converged study close to the melting temperature, finding logarithmic evolution of the QLL from approximately  $T_m - 5\text{ K}$ . The latter study was performed on cubic ice (not stacking disordered ice, Box 2), however, it remains to be identified whether the same qualitative behaviour is seen in hexagonal ice. Likewise it would be interesting to see if the same logarithmic dependence is recovered with fully atomistic water models.

We also note in passing that, in the context of Frenken and Stranski's proposal, the function of the QLL is to passivate the solid as the bulk melt temperature is approached, McBride et al.<sup>99</sup> determined that the TIP4P model of ice can be superheated to around  $80\text{ K}$ <sup>100</sup> beyond its bulk melting temperature when all the free surfaces are removed, that is just the crystal bulk is simulated under 3D periodic boundary conditions.

All of the work described thus far has focused on pristine ice surfaces but in reality intrinsic defects will be present, of which vacancies and interstitial defects being expected to be the most prevalent<sup>22</sup>. In 2011, Watkins et al.<sup>101</sup> reported a DFT study of the basal plane of the ice surface at  $0\text{ K}$  that revealed a surprising finding: the surface of perfect crystalline ice is amorphous. It was found that vacancy formation energy (in this case, the energetic cost of removing a water molecule from the crystal and placing it in a bulk vacancy) varies by up to  $\sim 0.7\text{ eV}$  depending on whether a molecule is removed from the outer layers or the crystal bulk. The outermost layer shows a remarkably large variation of  $\sim 0.35\text{ eV}$  depending on the molecular environment of the molecule that is removed, as shown in figure 5. The average vacancy formation energy in the outermost layer is very comparable to the activation energy for translation reported by Mizuno and Hanafusa using NMR<sup>14</sup> and viscosity measurements that show transport to be mediated by vacancies<sup>102</sup>. Ordinarily crystalline materials are expected to show a single value for the vacancy energy in bulk, which is the case for bulk ice. At the surface, the vacancy formation energy is expected to be less than that in the bulk and attenuation between the bulk and surface vacancy formation energy is also expected. It was found that in fact whilst the average vacancy formation energy decreases the closer to the surface the molecule is removed, a wide variation was observed especially in the lower part of the first bilayer and the upper part of the second bilayer. Upon closer investigation, it was found that the formation energies were correlated with the dipole moment of the molecules that were being removed, which varied from  $2.9\text{ D}$  to  $4.4\text{ D}$  as opposed to the bulk solid in which the dipole moment was uniform at  $3.5\text{ D}$ . By the third bilayer, the dipole moment distribution is more or less like the crystal bulk so just the two outer bilayers are qualitatively different from the underlying part of the crystal. The outer two layers of the crystal have molecules sat essentially on their ideal lattice sites but the heterogeneity of the dipole moments (which arise because of the orientational disorder at the surface) means that these layers have qualitatively distinct properties from the crystal bulk. Bizarrely, some of the water molecules in the outermost two bilayers are more strongly bound to the crystal than molecules in the crystal bulk. These computational results were corroborated in a separate study by Moreira et al.<sup>103</sup> Recent SFG measurements<sup>104,105</sup> that showed that the surface of ice has properties resembling supercooled water argue that there are two key temperatures in the premelting regime:  $\sim 245\text{ K}$ , which signals the melting of the outermost bilayer, and  $\sim 270\text{ K}$ , which signals the melting of the second bilayer. The interpretation is supported by the insight from the work of Sanchez et al.<sup>16</sup>, which showed, using molecular dynamics with a polarizable water model, that the first bilayer melts around  $235\text{ K}$  and the second around  $270\text{ K}$ . Studies by Smit et al. and Sanchez et al. suggest that around  $270\text{ K}$  only the outer two layers are melted and form a film of around  $1\text{ nm}$  in thickness. This interpretation is further supported by two IR studies by Sadchentko and Ewing in which they used a cold finger setup.<sup>106,107</sup> The study by Watkins et al.<sup>101</sup> highlights the importance of polarisation and defects that need to be considered in simulations of premelting, and an explicit heterogeneity that exists in ice surfaces that is present prior to premelting.

## [H1] Heterogeneity at the surface

A major experimental breakthrough has come from the work of Gen Sazaki and co-workers.<sup>108–111,112</sup> Over the last few years, Sazaki et al. have pioneered the use of laser confocal microscopy combined with differential interference contrast microscopy to study the surface of ice. One of the many reasons that this work is particularly important is related to the use of a direct local probe to elucidate structural features providing unprecedented insight into features of ice crystals. Sazaki et al.<sup>109</sup> reported direct visualisation of steps on the basal and prism surfaces of an ice crystal. Their work showed the time evolved structure at the surface revealing a 2D crystal growth mechanism and that the step heights on both the basal and prism faces corresponded to the height of a bilayer, thus indicating that incomplete bilayers are metastable. Images were collected at  $\sim 263$  K and showed step-bunching and regular step separations revealing that, despite various spatially and temporally averaged techniques indicate the existence of liquid-like character, the surface has crystalline, sharp features that suggest short and long range order is present at these temperatures. The same study also showed growth spirals (dislocations) that were seen to form under the conditions sampled. Growth spirals were also imaged on the basal face in an earlier ellipsometry study<sup>30</sup> and the microphotograph depicted therein may also show droplets. Sazaki et al. observed crystal growth on the prism face at  $\sim 271$  K again indicating that crystalline order is maintained at these temperatures, despite SFG measurements suggesting premelting of two bilayers at this temperature. Next, Sazaki et al.<sup>113</sup> imaged the ice surface in the range of temperature 258–272.9 K and performed a delicate investigation of the surface in the 271–272.9 K range collecting measurements every 0.1 K steps at a heating rate of 0.02 K per minute. The crucial finding was the observation of water droplets (of  $\sim \mu\text{m}$  scale), which were termed  $\alpha$ -QLLs (bulk liquid droplets), at the surface below 273 K. These droplets were found between 271.5–272.6 K depending on the particular experiment (see figure 6). The observations were consistent with previous optical reflection (interference microscopy and ellipsometry) measurements by Elbaum et al.<sup>32</sup> who also observed droplets on the surface of ice close to the melting temperature (sensitive to the vapour pressure), in line with previous predictions<sup>43</sup>.

The droplets in the Sazaki experiment were seen to coalesce until they formed a film coating the crystal. The film was determined to be considerably thicker than a bilayer but its depth could not be quantified directly or with any certainty. These droplets were seen to move on a timescale that was incompatible with crystal growth leading to the conclusion that the droplets were indeed of liquid like character. When the droplets coalesced to form a continuous film, this QLL was termed  $\beta$ . These  $\beta$ -QLLs formed around 272.5 K and they were observed to disappear, forming separated beads of water ( $\alpha$ -QLLs), at 272K.  $\beta$ -QLLs have a flatter profile than  $\alpha$ -QLLs indicating that the wettability of  $\beta$ -QLLs is higher than  $\alpha$ -QLLs and that the interaction energy of  $\beta$ -QLLs with ice is more favorable than  $\alpha$ -QLLs.  $\alpha$ -QLLs and  $\beta$ -QLLs were seen to co-exist suggesting distinct phases and be immiscible, further supporting the idea these phases are distinct. In previous experiments, these distinct heterogeneous phases were not observed perhaps due to the lower spatial resolution or kinetic artefacts. These two forms of QLL were initially observed on the basal plane of ice but then subsequently observed on the prism and other faces of an ice crystal<sup>112</sup>. In a related paper<sup>114</sup>, it was shown that  $\alpha$ -QLLs occur at screw dislocations whilst  $\beta$ -QLLs are associated with microdefects (pits on the surface) and in both cases a strain field promotes the formation of these distinct QLLs. The detailed structure of screw dislocations has been assessed<sup>115</sup> at 270 K and it was found that the dislocation core was immediately enveloped by a double bilayer, so that the hexagonal ABABAB stacking sequence is perpetuated. Similar double bilayer structures were observed on the prism and basal plane. Similar features and unambiguous signatures of cubic ice spirals were also identified by atomic force microscopy (AFM) and scanning tunneling microscopy (STM)<sup>116</sup> on an ice sample imaged at 145 K.

The thickness of the  $\beta$ -QLLs has been determined to be  $9 \pm 3\text{nm}$ <sup>117</sup> at 271.4 K, remarkably close to the values obtained by ellipsometry. The next major development came from theory, which argued that two different regimes can be identified for the formation of QLLs: one in which surface condensation is associated with supersaturation and another in which surface melting is associated with undersaturation<sup>110</sup>. Indeed the  $\alpha$ -QLLs and  $\beta$ -QLLs were shown to be triggered by supersaturation conditions<sup>108</sup> and essentially kinetically controlled. The equilibrium between wetting and coalescence had previously been predicted.<sup>7,118</sup> It has also been shown that the condition of the surface (the presence of impurities for example) may strongly affect the onset and character of the QLLs. Intriguingly, the structure of the surface has a strong effect on the wettability and also the mode of crystal growth<sup>119</sup>. A greater understanding of the molecular processes at work could lead to insights into how to control ice growth and hence anti-icing materials.



Evidence for inhomogeneities and partial crystallinity in the QLL can be found in the excellent work of Hudait et al.<sup>95</sup> and Bishop et al.<sup>42</sup>. A recent modelling study by Pickering and co-workers<sup>98</sup> provides unprecedented insight into the formation of QLLs, which potentially may help explain some of the observations from optical microscopy due to Sazaki and various colleagues. Pickering et al. have performed comprehensive grand canonical MD calculations (that is, considering the grand canonical statistical ensemble  $\mu VT$ , where  $\mu$  is the chemical potential,  $V$  is the volume of the system and  $T$  is the temperature) using the mW<sup>120</sup> potential. Simulations were performed on both the basal and prismatic planes on slabs with surfaces as large as  $\sim 26$  nm x 31 nm, making sure that the vapour pressure is equilibrated through a barostat, in light of recent experimental results. Several important findings stem from this work but perhaps the finding of greatest importance is that the QLL is composed of crystalline portions and liquid-like regions and that the QLL formation can be attributable to incomplete premelted layers. The other new insight is that the QLL is dynamic or fluxional, meaning that regions of the QLL that are solid were seen to become liquid. The connection with the homogenous nucleation of ice is clearly relevant here and merits deeper investigation. The authors argue that the definition of the thickness of the QLL becomes somewhat arbitrary because some component of the QLL is solid. At 270 K,  $\sim 70\%$  of the first bilayer is liquid water, whilst only 6-15% of the second bilayer is liquid water on both the prismatic and basal faces as shown in figure 7. The QLL thickness was also seen to be measurably sensitive to the vapour pressure. At 260 K, Pickering et al. found that 50% of the basal first bilayer is melted, in contrast to the 38% reported by Hudait; the discrepancy was suggested to arise from the settings used to determine which molecules are liquid. Notwithstanding the ambiguity associated with defining the QLL thickness, Pickering et al. report a QLL thickness of  $\sim 5$ -8 Å at 270 K, which is clearly much smaller than experiment. Conde et al.<sup>18</sup> reported a thickness in the same order of magnitude at 270 K using their TIP4P/Ice potential. These data are particularly useful as the melting temperature of the mW<sup>120</sup> and TIP4P/Ice<sup>63</sup> models are essentially in direct agreement with experiment within the uncertainty of estimating the melting temperature.

Another, hidden, heterogeneity at the ice surface has been revealed by Benet et al.<sup>121</sup> who performed MD simulations using the TIP4P/2005 model. Their work has shown that, although the QLL–vapour interface is smooth, the underlying QLL–crystal interface is extremely rough. Moreover, the fluctuations in the QLL–vapour and QLL–crystal dynamic interfaces are independent of one another. It would be interesting to see whether the magnitude of the fluctuations observed by Pickering using the mW model and those observed by Benet et al. using TIP4P/2005 are quantitatively consistent.

### [H1] Chemistry at the ice/air interface

We now turn to contemplate the consequences of premelting on atmospheric chemistry. In particular we focus on a selection of recent studies on the uptake of atmospherically relevant compounds on the surface of ice. Several recent excellent reviews on this topic exist by Abbatt<sup>122</sup>, Dash et al.<sup>2</sup>, Kang<sup>123</sup>, Bartels-Rausch et al.<sup>24</sup> to which the interested reader is referred.

Surface temperatures on Earth at the poles and vicinity vary between  $\sim 180$  K to well above the bulk transition temperature (occasionally) in Antarctica and (regularly) in the Arctic. Cloud temperatures vary tremendously between 150 K and 340 K<sup>124</sup>, the former being representative of lower bounds for polar stratospheric clouds and of particular note because these conditions are expected to foster stacking disordered ice (Box 2). Nevertheless, ice particles within large fractions of cloud cover expose a complete or incomplete premelted ice layer. Recent laboratory experiments indicate that below 160 K ( $154 \pm 5$  K as reported in<sup>126</sup>) amorphous solid water is the dominant phase<sup>125</sup> of ice rather than any crystalline form and that at 180 K conversion of cubic ice (actually stacking disordered ice<sup>127</sup>) to hexagonal ice is slow (taking longer than one hour<sup>126</sup>). Heterogenous agents such as dust and organic matter facilitate nucleation of ice at low temperatures in general<sup>128</sup>, though recently it has been demonstrated that adding ammonium salts promotes nucleation<sup>129</sup>. Notwithstanding the uncertainties associated with the phase of ice present in clouds and their interface saturation levels, cloud-bound ice and surface ice presents some fraction of premelted ice and so the question of how this changes the chemistry of the surface arises.

Changes in pH at the ice surface, which clearly can influence reactivity and uptake properties, have been measured to be rather small<sup>130</sup>. The surface of pristine ice has been argued to be acidic with a pH  $< 4.8$ <sup>131</sup> (using IR spectroscopy, isotopic labelling and combined classical and ab-initio DFT MD studies, although modelling was performed on liquid water). Watkins et al.<sup>132</sup> showed, through a comparative assessment of the surface segregation of hydronium and hydroxide in the presence of Bjerrum defects, that the trapping energy of both

species was essentially not distinguishable. However, on the basis of transport barrier arguments, it was suggested that hydronium ions were more likely to segregate to the surface than hydroxide, whereas reactive sputtering studies have detected enhanced concentrations of hydroxide at the surface.<sup>133</sup>

Uptake of alkanes on ice surface has been known to be anomalous and this was attributed to the premelting layer<sup>134</sup>. Experimental studies at 258 K (for example, in the presence of a QLL) using glancing-angle laser-induced fluorescence<sup>135</sup> and classical MD and DFT simulations<sup>136</sup> have shown that organic pollutants such as polyaromatic hydrocarbons (PAHs) accumulate on ice surfaces. According to the fluorescence studies, PAHs such as naphthalene aggregate more efficiently on ice–air interfaces than water–air interfaces. The molecular-scale interpretation for such a preference offered by the modelling studies is that the disordered and denser water layer has a stronger affinity for the delocalised electron density of naphthalene than does ice. Photolysis of naphthalene was found to be an order of magnitude faster on ice than on liquid water at 272 K and 274 K, respectively. Intriguingly, the rates of photolysis on ice at 258 K 272 K were identical (within experimental uncertainty) and the same was observed on liquid water at 274 K and 297 K. These results highlight the need to understand the nature of the QLL to rationalise why there is such a marked discrepancy in rates for a 2 K difference in the ice and water samples. One possibility is that the naphthalene aggregates on ice and these aggregates persist even on the essentially pure liquid outer layer until just above 272 K, when these become unstable with respect to separation on the entirely liquid layer.

Measurable quantities of H<sub>2</sub>O<sub>2</sub> have been detected in natural snow. Such a H<sub>2</sub>O<sub>2</sub> concentration is smaller than that detected in rainwater but large enough that its presence cannot be ignored in rationalising the properties of ice. Indeed, H<sub>2</sub>O<sub>2</sub> provides an efficient way of scavenging SO<sub>2</sub> from the atmosphere to yield H<sub>2</sub>SO<sub>4</sub><sup>137</sup> and SO<sub>2</sub> uptake has been measured for ice spheres<sup>138,139</sup>. More generally, H<sub>2</sub>O<sub>2</sub> is essential to the Fenton mechanism of hydroxyl radical formation (see for example ref <sup>140</sup>), so understanding the uptake of this and other environmentally important gases is an area which deserves more attention from the modelling community.

For sea ice, the presence of salt may be important. Ice is very hostile to any impurities and expunges salt from sea water in a superconcentrated solution as an ice boundary layer. The salt rich interfacial region causes a reduction in the freezing point<sup>2,129</sup> so the surface layer is expected to show an increased tendency to premelt. The uptake properties of these layers with trace gases under controlled, reproducible conditions remains a significant experimental challenge.

CO<sub>2</sub> uptake on ice has been shown to be significant<sup>141</sup> and comparable to SO<sub>2</sub>. Strongly enhanced gas uptake has been attributed to the onset of premelting and the adsorption of gas in the QLL. It is therefore rather surprising that no recent measurements of CO<sub>2</sub> uptake have been performed given concern over the rising levels of atmospheric CO<sub>2</sub> levels and the possible role of snow and ice in the carbon budget. Again, there is a relative dearth of modelling studies in this area and measurements of uptake over a range of temperatures of geophysical significance and in particular, approaching T<sub>m</sub>, would offer valuable cross-comparisons.

One consequence of the amorphous nature of the pristine ice surface identified by Watkins et al.<sup>142</sup> is that this is comprised of molecules that exhibit a range of polarities and binding energies even below premelting. Watkins et al.<sup>142</sup> reported that H<sub>2</sub>O molecules weakly bound at the surface of crystalline ice can be exothermally displaced by H<sub>2</sub>S, HCl and HF so that the latter molecules are trapped on the ice surface and can potentially undergo fast dissociative reactions<sup>143</sup>.

Whilst there are many examples of modelling studies of molecules on pristine crystalline ice, the role of the premelting layer in surface chemistry has yet to be addressed comprehensively. Recently Hudait et al.<sup>95</sup> have performed a very instructive set of simulations examining the influence of ions and glyoxal molecules on ice surfaces at premelting temperatures. 45 x 10<sup>9</sup> Kg of this simple dicarbonyl is released in the atmosphere on an annual basis along with 140 x 10<sup>9</sup> Kg of methylglyoxal<sup>144</sup>, quantities that simulations suggest equate to 10–100 ppt. The major conclusions from this work were that ions increase the liquidity of the surface of ice over a range of temperatures. The ions perturb their coordination shell of waters, promoting melting, however the ions aggregate and hence the effect of the correlation between ion concentration and the fraction of liquid molecules is less than unity. The ions show diffusivity that is around a third of that in bulk water. Conversely the interaction between the glyoxal and the ice surface is extremely weak. In fact, the diffusivity of the glyoxal is approximately 25 times larger than in liquid water resulting in the molecules surfing across the surface without perturbing the

solid or liquid underlying structure. Clearly this an area that deserves more attention, in particular from the modelling community to link with the findings of Sazaki et al.<sup>110</sup>

## Outlook

Over the last 5–10 years, key findings have emerged from single and aggregated experimental studies and an array of modelling approaches revealing new and fundamental aspects to the now >160 year conundrum of the nature of ice's quasi-liquid layer. Despite clear progress and in particular the watershed publications of Sazaki and co-workers and also Elbaum and co-workers<sup>7,32</sup>, many open questions remain to be answered. The following discussion describes some of the most urgent topics.

### [H2] Resolve discrepancies on QLL thickness

Despite considerable effort, differences in measured QLL thicknesses remain. There are differences between distinct experimental techniques and disparities between experiment and simulation. The former is no doubt influenced by the distinct experimental techniques probing different features and “skin” depths of the surfaces, as well as different levels of impurities and in plane inhomogeneity, such as  $\alpha$ -QLLs. The discrepancy between the simulated QLL thickness and that observed by a variety of experimental techniques is much larger than could be reasonably expected. Simply, at just below the bulk transition temperature a consistent picture comes from simulations, chiefly from classical models. Currently, it seems clear that  $\sim 2$  bilayers of water melt slightly below the transition temperature (although probably the best converged estimate at  $T_m - 0.25$  K is 1.8 nm ( $\sim 4$  bilayers) albeit calculated for cubic ice)<sup>84</sup>. The most conservative estimate from experiment comes from X-ray absorption and puts the QLL at a minimum of around 3 nm ( $>7$  bilayers). The work of Elbaum et al. and latterly of Sazaki and co-workers suggests that the vapour pressure, typically omitted in simulations, may play a strong role in conditioning the surface and the influence of saturation on measurements needs to be better understood at a molecular level. Another point which requires attention is the effect of stacking disorder on premelting. Even if experiments are conducted on a sample that is initially pure  $I_h$ , the high vapour pressure and vapour–solid phase equilibrium leave open the possibility that stacking disordered ice ( $I_{sd}$ ) can nucleate and the higher free energy of  $I_{sd}$  could lead to lower premelting temperatures. A related issue to untangle in establishing the properties of the QLL is capillary condensation, where cracks and/or step bunches can lead to an effective supercooling estimated to be 30–50 K<sup>145</sup> leading to ice or condensate formation in equilibrium with the vapour<sup>146</sup>. Given bulk  $I_{sd}$  can persist to 240 K<sup>147</sup>, its influence on the onset temperature of premelting cannot be ignored. In this context, from the experimental side, a tantalising prospect is the recent advent low kV transition electron microscopy (TEM)<sup>148</sup> which may be able to image ice if sufficiently thin samples can be prepared.

Simulation techniques have improved enormously since they were first applied to the study of the QLL in the 1990s. However, there remain clear shortcomings with the simulation approaches. These can be grouped into two broad categories. The first one is related to the approximations of intermolecular interactions. The vast majority of simulation of the QLL has involved relatively simple classical intermolecular potentials such as the atomistic TIP4P model or the coarse-grained mW model. As we have seen, work with these models has been incredibly helpful in furthering understanding of the QLL. However, they certainly do not provide an exact description of the true nature of water structure and dynamics and have various widely discussed shortcomings such as incorrect prediction of dynamics and long-range behaviour and the neglect of polarisation effects<sup>56</sup>. First principles approaches, such as DFT, provide a more sophisticated approach in which the full electronic structure of the system is taken into account and polarization effects are explicitly accounted for. As noted, DFT studies of ice surfaces have emerged and there is considerable scope for the application of DFT in this area. However, the computational cost of DFT calculations (several orders of magnitude greater than classical force fields) means that system sizes and simulation timescales are severely limited. In addition, for certain properties of pure water and ice the approximate nature of the exchange–correlation functional that underlies practical DFT calculations means that the accuracy of DFT is often not superior to well-parameterized classical potentials<sup>55</sup>. An interesting and powerful middle ground is provided by state-of-the-art intermolecular potentials fitted to high quality first principles data. The fitting can be done with traditional approaches or through machine learning. Such potentials (for example, MB-pol<sup>149</sup>, the Gaussian approximation potential water model<sup>150</sup>, neural network water<sup>151</sup>, amoeba<sup>152</sup> or the TTM potentials<sup>153</sup>) offer very high accuracy for pure water systems, come at a fraction of the cost of DFT, and offer promise for improved simulations of the QLL. An additional aspect that is generally not taken into account is the quantum nature of the nuclei. However, the light mass of the hydrogen atoms in water means that quantum nuclear effects (such as, quantum delocalisation, tunneling, and zero point

energy) can have an impact on the properties of water and ice<sup>154</sup>. Indeed, it has been suggested that quantum nuclear effects can play a role in the onset of the QLL<sup>155</sup> and this issue deserves more investigation.

The second shortcoming of simulation approaches is related to the use of simplified water models. Despite the enormous increases in computing power, improvements in algorithms and software since the 1990s, the structural models generally used to examine ice surfaces are highly idealized and simplified versions of reality. More specifically, the emerging picture of a heterogeneous QLL calls for yet larger simulation cells to be considered in simulation studies. Care should be paid to understand the size and length-scale of the structural heterogeneities in the QLL and any associated heterogeneities in the dynamical properties of the QLL. Furthermore, Bjerrum defects, vacancies, ionic, line and extrinsic defects are usually omitted. Bjerrum defects have been shown to migrate to the surface where they can potentially trap ions — either autogenitically or extrinsic ions. Vacancies are believed to be the dominant defect in the bulk but at the surface their effects are expected to be amplified. A potentially important point made by Watkins and co-workers<sup>101</sup> is that, because of the highly inhomogeneous binding energies of water bound to the outer layer of ice, the perfect bilayer surface can reconstruct where weakly bound molecules can gain energy by binding to favourable atop surface locations above the outermost bilayer. These events have been seen in simulations<sup>156,42</sup> but further insight into their importance is needed. Simulations suggest that ionic defects in the form of both hydronium and hydroxide ions have tendency to migrate to the surface. DFT approaches taking into account the likely proton arrangements at the surface suggest that these species are attracted to distinct parts of the surface — hydronium to proton depleted areas and hydroxide to proton rich areas. Line defects such as screw dislocations and step edges, known to occur with a high spatial density and potentially a source of catalytically active centres, have been repeatedly observed but few models have been reported to date. Incomplete bilayers have been analyzed in a recent DFT and STM study<sup>157</sup>. Junior and colleagues have performed the first DFT calculations on model stacking faults and partial dislocations<sup>158</sup> in the crystal bulk but further work in this area is needed, perhaps capitalising on novel 2D approaches<sup>159,160</sup> to explore what influence all of the point and line defects have upon premelting. The advent of highly accurate water models<sup>149,155,56</sup> holds promise for simulating the long length-scales needed for line dislocations in particular where electronic relaxation, mimicked through changes of polarisation, is likely to be an essential feature of capturing the dislocation core structure. Important developments have been made in the theoretical assessment of the effect of extrinsic defects, such as impurities, on premelting<sup>161</sup>. Beaglehole and Wilson demonstrated that brine, silicate and HF have a measurable influence on the onset of premelting and the QLL thickness. Understanding the influence of brine on premelting is clearly particularly important to predicting the crystallisation and melting of sea ice in water of varied salinity.

## [H2] Structure and properties of the $\alpha$ -QLL

The observation of two immiscible phases of water ( $\alpha$ -QLL and  $\beta$ -QLLs) atop a third phase of water, crystalline ice is very curious. The non-wetting nature of  $\alpha$ -QLL is mysterious and although progress on theory has been made by Sazaki in this direction<sup>108</sup>, the observation of a quadruple point, solid- $\alpha$ -QLL/ $\beta$ -QLL-vapour is clearly of fundamental interest.  $\alpha$ -QLLs have been observed at dislocation cores whilst  $\beta$ -QLLs are observed on pitted surfaces, so untangling these structural influences on the formation of QLLs is important. The  $\alpha$ -QLL presents an enormous challenge to atomistic modelling because of the length-scale of the droplets, not to mention the technical challenges of thermostating four phases. There may be benefit in revisiting premelting in notionally simpler systems such as metals<sup>162</sup> or Lennard-Jones models<sup>163</sup> to explore whether the phenomenon of two distinct QLLs is particular to water ice (noting that droplets and films of pentane have been observed to coexist on water<sup>164,8</sup> but water ice appears to be a rare if not unique example of a material that exhibits three distinct coexisting phases). An adjunct question is whether at low vapour saturation, when  $\beta$ -QLL is expected to be exclusively present, as the bulk-melting temperature is approached and the thickness of the QLL increases, does partial or complete wetting occur; is it possible to have a partial  $\beta$ -QLL?

The advent of computationally efficient and reasonably accurate models such as mW, highly accurate potentials (for example, developed through machine-learning<sup>165</sup>), as well as the ever-increasing numbers of molecules that can be tackled at the DFT level<sup>166,167</sup> open up the prospect of gaining profound insights that are of fundamental interest but also potentially important for anti-ice applications and for other materials. Efforts to achieve a closer integration of experimental studies with modelling also promise to be an effective means to progress the field<sup>168</sup>.

Finally, we reflect on the overarching questions: what is the onset temperature of premelting and what thickness is the QLL at a given temperature? For both questions, the point of reference is important. For a fictional, perfect, defect-free ice  $I_h$  basal terrace, simulations with well-validated models are unanimous; the onset temperature as determined by order parameters to distinguish between crystal and liquid is  $\sim 240$  K. The thickness of the QLL only gets larger than the equivalent of two bilayers at  $>270$  K. Bjerrum defects, ionic defects, line defects such as step and screw dislocations (that destabilise the lattice) will increase the QLL thickness but to an unknown extent. Furthermore, the composition of the QLL is dynamic, as shown beautifully by Pickering and co-workers, who observed patches of liquid ebbing and flowing within layers interposing and exchanging with crystalline regions. In reality, the experimental work of Elbaum et al. and latterly of Sazaki and co-workers has highlighted the complex relationship between vapour pressure and the QLL. The QLL is now understood to be inhomogenous and dynamic and, subject to vapour pressure, to consist of droplets and wetting layers,  $\alpha$ -QLL and  $\beta$ -QLL's respectively. The influence of vapour pressure, equilibration and  $\alpha$ -QLL and  $\beta$ -QLL's on reported QLL thickness and the temperature of premelting onset is unclear. Because different measurement techniques have different sensitivities to the presence of  $\alpha$ -QLL and  $\beta$ -QLL's, resolving discrepancies between different experimental techniques is probably not possible at a quantitative level. Moreover, characterisation experiments to examine the influence of defects, for example, on QLL development are certainly needed.

To move forward calibrating theory with experiment, X-ray absorption<sup>20</sup> and SFG<sup>16</sup> appear to be techniques that currently offer prospects of quantitative comparison and interpretation of structural changes. Beyond further elucidating the effect of vapour pressure, equilibration and defects on  $\alpha$ -QLL and  $\beta$ -QLL's, using a chemical probe, such as gases, as a means of charting structural and significant chemical changes should be an illuminating direction to pursue. For example,  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  are important trace gases in atmospheric chemistry<sup>169,170,140</sup> and uptake measurements for  $\text{SO}_2$  on ice at a range of temperatures exist<sup>169,171</sup> providing a means to calibrate theory and experiment and potentially make useful predictions for the atmospheric science community, provided experiments are reproducible and models can reproduce those experiments.

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## BOX 1

### Basic crystallography of bulk ice

Although crystalline ice has many phases, we typically only experience one form of ice: the hexagonal phase of ice known as I<sub>h</sub>. In the crystal bulk, the oxygen atoms of the molecules are arranged in the same way that silicon stacks in the tridymite mineral and carbon in lonsdaleite. Dame Kathleen Lonsdale summarised the key developments<sup>175,176</sup> in the story of the structure solution and the position of the hydrogen atoms (actually D<sub>2</sub>O) was resolved unambiguously using neutron diffraction in 1957 by Peterson and Levy<sup>177</sup> after the first

neutron study by Wollan et al.<sup>178</sup> The bulk structure is shown in the panel of Figure 1 along with the key surface structures for hexagonal ice.

The molecules are arranged in bilayers that stack in an ABABAB repeat sequence in the [0001] direction shown in Figure 1. Each molecule in an infinite crystal of ice I<sub>h</sub> obeys the Bernal–Fowler ice rules<sup>173</sup> that state each oxygen atom is bonded to two hydrogen atoms and each oxygen hydrogen bonds to two other oxygen atoms so that only one hydrogen atom is located between oxygen nearest neighbours. Each water molecule has a tetrahedral geometry but there are six possible molecular orientations that obey the ice rules, giving rise to orientational disorder. One consequence of this orientational (and hydrogen) disorder is that I<sub>h</sub> is paraelectric. Upon cooling to around 72 K<sup>179</sup>, the water molecules in principle align to adopt a distinct hydrogen ordered analogue of ice I<sub>h</sub>, the ice XI<sup>174,180,181</sup> phase that is ferroelectric.

The ice rules can be violated by the formation of orientational defects, termed Bjerrum defects<sup>182</sup>, L defects (from the German *Leere* meaning empty) have a missing hydrogen atom between two neighbouring oxygen atoms, and D defects (from the German *Doppeltbesetzte* meaning doubly occupied) where two hydrogen atoms lie along the vector connecting two neighbouring oxygen atoms. Additionally charged ionic defects can form from autoionisation for example, yielding H<sub>3</sub>O<sup>+</sup> hydronium and OH<sup>-</sup>, hydroxide. Self-interstitial defect, is another common point defect, in which a molecule displaces off its ideal lattice site (see ref <sup>22</sup> and <sup>183</sup>).

## BOX 2

### Cubic ice and stacking disorder

There are two additional, metastable phases of ice that are important in understanding the physicochemistry of ice on earth: cubic ice, I<sub>c</sub><sup>184</sup> (ABCABC stacking of the bilayers) and stacking disordered ice, I<sub>sd</sub><sup>85,185</sup>, which contains a randomly mixed and varied proportion of I<sub>c</sub> and I<sub>h</sub> sequences. At the time of writing, there is no unambiguous evidence that ideal I<sub>c</sub> crystals have been prepared in the laboratory (though scanning tunneling microscopy (STM) image of individual layers of I<sub>c</sub> has been reported<sup>116</sup>), although Nature may well have achieved this feat<sup>186</sup>. In 1629, Christophe Scheiner noted a halo around the sun at approximately 28° due to the scattering of solar rays by ice crystals in high altitude clouds. A purely cubic ice crystal could have a perfect octahedral morphology (completely distinct from documented forms, see figure 2) that would give rise to refraction at approximately 28° whilst hexagonal columnar I<sub>h</sub> ice crystals refract rays at 22°. The 28° signature of pure ideal cubic ice is incredibly rare, reported less than ten times since 1629.

Despite the dearth of evidence for the existence of ideal cubic ice, use of I<sub>c</sub> in the literature is still ubiquitous although I<sub>sd</sub> is, likely, a more accurate classification of this phase type. I<sub>sd</sub> and I<sub>c</sub> are metastable with respect I<sub>h</sub> I<sub>sd</sub> or I<sub>c</sub> transform to I<sub>h</sub> at around 150 K but detailed analysis due to Malkin et al.<sup>85,187</sup> suggest that cubic sequences are evident up to 257 K. Above ~176 K, I<sub>c</sub> or I<sub>sd</sub> transforms irreversibly to I<sub>h</sub><sup>188</sup> yielding  $-46 \pm 3 \text{ Jmol}^{-1}$  at 200 K, but the lifetime of I<sub>c</sub> and I<sub>sd</sub> is non-negligible, certainly in the context of the reactivity of ice particulates in clouds. Despite the tiny energy difference between I<sub>sd</sub> and I<sub>c</sub>, and I<sub>h</sub>, Kuhs et al.<sup>147</sup> suggest lifetimes of I<sub>sd</sub> crystals of several days (by extrapolation) at 175 K, several hours at 185–190 K and advocate the I<sub>sd</sub> phase persists up to at least 240 K.

Computer simulations by Molinero et al.<sup>189</sup> show that nucleation of  $I_{sd}$  at 230 K is three orders of magnitude faster than  $I_h$ , underlining its importance in the context of premelting and recrystallisation phenomena. Hence the role of  $I_c$  and  $I_{sd}$  in premelting needs to be considered along with the dynamics of crystallisation and surface recrystallisation under different vapour saturation conditions.

**Figure 1** The unit cell of hexagonal ice  $I_h$  (a) and side views of the surface structure of the basal face (b), primary prism face (c) and secondary prismatic face (d) of hexagonal ice  $I_h$ . The top of the surface is indicated by an eye motif and crystallographic axes labels are given to aid orientation. The bilayers for the basal face and primary prism face are highlighted in green and their heights are 0.37 nm and 0.39 nm for the basal and prism faces respectively. The unit cell depicts one possible arrangement of the water molecules possible in the  $P6_3/mmc$  space group. Pauling proposed that there are  $(3/2)^N$  possible arrangements of  $N$  water molecules in ice<sup>172</sup> that obey the Bernal–Fowler ice rules<sup>173</sup> and that these would be isoenergetic. In fact, at 72 K, a hydrogen ordering transition can in principle result in a distinct ferroelectric  $Cmc2_1$  phase<sup>174</sup>, although a fully ordered phase has yet to be produced in the laboratory. Density functional calculations have shown that the ordering transition is driven by purely electrostatic forces<sup>68,70</sup>.

**Figure 2** The varied morphologies of hexagonal ice  $I_h$ . a) A survey of the relationship between the crystal habit and supersaturation.. See also ref<sup>4</sup> for a comprehensive recent survey. The six-fold symmetry of snow crystals has been noted throughout history, a particularly early example being the poetry of Han Ying in circa 135 BCE who commented that “snow flowers have six points”<sup>191</sup>, potentially depicted in 1555<sup>192</sup> and more certainly sketched in around 1600 by Dominic Cassini<sup>193</sup>. b) Despite the dramatic variation in aspect ratio and crystal shape the morphology (for example) is dominated by the basal face (shown in blue), primary prismatic face (shown in green) and the secondary prismatic face (shown in red), see figure 1 for the atomic scale structure. Part a adapted from ref<sup>190</sup>. Part b adapted from ref<sup>194</sup>.

**Figure 3** A selective overview of estimates of approximate QLL thickness obtained from physical measurement: X-ray diffraction<sup>15</sup>, X-ray absorption<sup>20</sup>, ellipsometry<sup>30</sup> and computer simulation approaches: molecular dynamics<sup>18</sup> (using TIP4P/Ice water model) and grand-canonical Monte Carlo/molecular dynamics<sup>98</sup> (using coarse grained model of water (mW)). The dotted yellow line indicates the approximate boundaries for the QLL estimated using two different approaches, see ref. <sup>98</sup> for a detailed account. The different experimental probes produce radically different estimates of what temperature the QLL appears at and the largest depth of QLL measured. Computer simulations with well validated potential models produce a much narrower estimate of the maximum QLL thickness and the rates of premelting from the two independent simulations is in close accord. Interestingly, only photoelectron spectroscopy measurements appear to be qualitatively similar to the molecular simulations. For a more complete illustration of the disparity in the literature between techniques, see figure 7 in ref.<sup>24</sup>

**Figure 4** Timeline of some of key developments in unravelling the nature of the quasi-liquid layer of ice (QLL), as selected by the authors. For a more complete summary of the evolution of the field, readers are encouraged to refer to other reviews of the literature.<sup>2,22–24,195</sup>



**Figure 5** Inhomogeneity in the outer two bilayers of ice. **a)** The variation in the dipole moment of water molecules projected onto coloured spheres. Weakly bound water molecules with small dipole moments are represented in red, strongly bound water molecules with large molecular dipole moments are represented in blue and molecules exhibiting intermediate binding and dipole moments are in white. **b)** The orientationally partially disordered arrangement of molecules at the surface gives rise to dipolar fields (indicated in light green) that reduce (top) or increase (bottom) the dipole moment of the central water molecule. **c)** Vacancy formation energies computed using density functional theory (DFT) Watkins<sup>101</sup>. The work by Watkins and coworkers showed that the four layers in the first two bilayers of ice of the inset basal slab more weakly bound than the layers in the centre of the slab. The centre of the 6 bilayer slab exhibit uniform vacancy formation energies equating to almost degenerate binding energies. Conversely, a fraction of molecules in the first bilayer (in particular) and the second bilayer are relatively weakly bound and presumably more susceptible to premelting. The defect-free crystalline ice surface has an amorphous like quality, which may be related to the evolution of the quasi-liquid layer (QLL). Intriguingly, a sum frequency generation (SFG) and molecular dynamic (MD) study by Sanchez et al.<sup>16</sup> showed a clear melting of the first two bilayers but no clear melting of the third bilayer, which may be expected to be a consequence of the distinct polarisation character of the outer two layers of ice<sup>105</sup>. Part **a**, **b** and **c** adapted from ref. <sup>101</sup>.

**Figure 6** The emergence of two distinct and immiscible quasi-liquid layers (QLLs) over an ice surface. **a)** Bulk-water-like droplets form with diameters  $\gg 1000$  nm under supersaturated conditions on growth spirals. **b)** Optical microscopy images taken at 272.5 K of a high spatial density region festooned with screw-dislocations (growth spirals) where the droplets are seen to be located. The droplets have non-zero contact angles indicating distinct viscosities of the droplet from the underlayer<sup>114</sup>. A thin liquid-like layer wets the surface which has a different viscosity again from the droplet. The observation of these three phases is a direct visualisation of a quadruple point. Aside from the different depths probed by different experimental techniques that undoubtedly influence the range of reported QLLs, the direct observation of droplets with distinct physical properties from the wetting  $\beta$ -QLL layer places another question mark against a range of experimental measurements. Atomic force microscopy (AFM) measurements<sup>33</sup> that have reported 32 nm QLL depth at 272 K could be affected by the presence of droplets that could have led to artificial rastering of the image. Sample preparation and extrinsic defects (impurities) may also affect the emergence of these droplets. Part **a** adapted from ref.. Part **b** adapted from ref. <sup>114</sup>.

**Figure 7** Heterogeneity in the quasi-liquid layer (QLL) obtained through grand canonical molecular dynamics (MD) The large slab shows the top two bilayers of  $\sim 26$  nm x 31 nm slab obtained at 270 K with coarse grained model of water (mW) where water molecules within 3.5 Å are connected by sticks. Liquid water is shown in blue whilst ice is shown in red in the first bilayer (top right) and yellow in the second bilayer (bottom right). Even just below bulk melting temperature ( $T_m$ ), part of the outermost bilayer is still ice-like, while the second bilayer is mostly ice-like. The first bilayer corresponds to  $\beta$ -QLL but the inhomogeneous nature of the QLL raises questions about distinguishing the depth of the QLL using experimental probes. Figure adapted from ref.<sup>98</sup>