Melting the ice one layer at a time

OR

Peeling back the layers of ice

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The melting of ice is one of the most common processes on earth. Interestingly as an ice crystal is warmed from below towards its bulk melting temperature of 0°C, a thin film of water forms on it. This water film, referred to as a pre-melting layer or a quasi-liquid layer (QLL), has been known about for well over a century [1]. It is relevant not just to the melting of ice but to important associated phenomena such as the motion of glaciers, the formation of snow and clouds, winter sports and more. As such, the QLL has been widely investigated and at times controversially discussed [2, 3]. In PNAS Sánchez et al. [4] report a joint experimental and simulation study in which an interesting perspective on the early stages of QLL formation is proposed. A sharp change in the vibrational response of the ice-air interface at 257 K (-16°C) is interpreted with the help of molecular dynamics simulations as the melting of a complete bilayer at the ice surface. The suggestion is that ice melts in a bilayer by bilayer manner at the ice-air interface.

In simple terms, crystals melt upon heating because the thermal driving force towards disorder overwhelms the energy associated with chemical bonding that holds the crystal together. Atoms or molecules at the surface of a material tend to form fewer bonds with their neighbors and so are less resistant to the disordering forces of heat. Consequently the surface can start to melt at temperatures below the bulk melting temperature. Clearly this is a general explanation, not specific to ice, and indeed pre-melting layers form on the surfaces of many materials. The issues of interest when seeking to understand pre-melting relate to the temperature at which the surface of the crystal starts to melt, how it thickens as the bulk melting temperature is approached, the uniformity of the film that forms, and the implications it has for macroscopic phenomena. These might appear as simple issues, however, obtaining molecular level understanding of surfaces is far from straightforward and calls for the application of sophisticated surface sensitive techniques and extreme levels of cleanliness [5]. An impressive arsenal of surface sensitive techniques has been developed and many of these have been applied to the surface of ice. This includes scattering techniques, scanning probes, optical microscopy, spectroscopies, simulations and theory. For some relevant reviews see refs. [2, 3, 6]. Such work has considerably deepened understanding of ice surfaces but different techniques probe different properties of the surface and unfortunately in terms of the QLL there is little consensus, particularly as one gets to within a few degrees of the bulk melting temperature. This can be seen from the small selection of data on the

thickness of the QLL as a function of temperature shown in Fig. 1. Data in Fig. 1 is mostly for the basal face of ice; the face most commonly exposed on ice crystals which presents water molecules in an hexagonal bilayer arrangement.

Using vibrational sum frequency generation (SFG) spectroscopy Sánchez *et al.* [4] have probed the vibrational properties of the ice surface as a function of temperature in the 230 to 270 K temperature regime. The focus was on the vibrational frequency at the ice surface associated with intermolecular interactions, and primarily the basal face was examined. By analyzing their data they identified a sudden change in the vibrational response at 257 K which, with the help of spectra calculated from molecular dynamics simulations, they interpret as the melting of an entire bilayer of ice. Spectral calculations of the ice surface are challenging [11] and, indeed, obtaining quantitative agreement between molecular scale simulations and experiment for water and ice can be difficult [12, 13]. The level of agreement between the measured and simulated spectra is a particularly impressive aspect of this study and lends considerable support to the interpretation reached by the authors. A noticeable change at approximately 257 K appears to be consistent with earlier X-ray absorption measurements of Bluhm *et al.* [8]. It is also not inconsistent with earlier SFG measurements of QLL formation on the basal surface of ice [14]. Indeed bringing together the earlier SFG study, which went down to temperatures as low as 173 K, with that of Sánchez *et al.* the picture that emerges is that at 200 K disorder sets in within the top bilayer of ice. It is noteworthy that this is somewhat above the Tammann temperature for ice (137 K), at which surface disorder could be expected to be observable. Then at 257 K the second bilayer melts and subsequently surface melting proceeds from 257 K onwards.

It is interesting that Sánchez *et al.* find something special about 2 melted bilayers. In Watkins *et al.* [15] it was shown by detailed calculations that the molecular binding energy (the energy required to remove a water molecule from ice) can vary by 30-70 kJ/mol within the first 2 bilayers but the binding energy of molecules in the third bilayer is essentially uniform. The molecular binding energies suggest that the bonding network within the first 2 bilayers is qualitatively different from layers deeper within the crystal, so the melting behavior of the outer 2 bilayers could be different from subsequent bilayers.

The study of Sánchez *et al.* [4] does not provide insight into what happens above 257 K, so it is unclear whether melting continues in a bilayer by bilayer manner beyond the single step

postulated at 257 K. However, much closer to the bulk melting temperature a complementary series of high-resolution optical interferometry measurements has provided insight [16, 17]. (See also the recent PNAS Commentary by Limmer [18].) These measurements, typically conducted within a couple of degrees of the bulk melting temperature, paint a complex picture of the QLL; one that is spatially and temporally heterogeneous where micrometer sized water droplets sit on top of a thin liquid layer and come in and out of existence, dependent largely on the water vapor pressure. Such inhomogeneity at the meso-scale is consistent with the inherent molecular level inhomogeneity that proton disorder confers on the ice crystal and the variation in surface molecular binding energies [15]. Nonetheless, understanding the connection between the optical interferometry and SFG measurements of Sánchez et al. will make interesting work for the future.

Sánchez et al. [4] have provided compelling evidence for a QLL picture that is just two bilayers thick at 257 K. Upon going beyond 257 K there remains considerable disparity between the various experimental measurements. From a theory and simulation perspective excellent progress has been made recently [19], and predictions of QLL thickness are in good agreement (c.f. refs [10, 19, 20]). However, there are also some challenges to bridge the gap between experiment and theory. It is not clear whether the ideal, defect-free models that have generally been used in past studies of pre-melting have an influence on calculated behavior. Larger surface models are needed to better sample inhomogeneity at the surface and the effects of surface steps and point defects should also be explored. Given the delicate nature of the hydrogen bonding and van der Waals interactions that hold ice crystals and the molecules in liquid water together the accuracy of the underlying theoretical description also must be considered carefully when aiming for quantitative understanding [12, 13].

The illuminating study of Sánchez et al. builds upon previous studies and provides the clearest evidence yet that the QLL, first conceptualized by Faraday [1] over a hundred and fifty years ago, is remarkably thin even close to the melting temperature. A vibrational signature feature at just -16 °C is directly correlated with the melting of the second bilayer at the surface, evidenced by computer modelling. The evidence suggesting a layer by layer melting process is mounting but there are still significant differences in the thickness of the QLL inferred from different experimental measurements, especially close to the melting temperature. Conversely, the agreement between theoretical studies, using several different

models, is surprisingly consistent. Perhaps the most pressing challenges to the field are to rationalize the large disparity in the reported QLL and to understand how the QLL influences properties such as chemical reactivity and uptake.

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