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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The Quasi-Liquid Layer of ice revisited: the role of temperature gradients and tip chemistry in AFM studies" *by* Julián Gelman Constantin et al.

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The authors deeply thank the appreciative comments by Referee #2, Thorsten Bartels-Rausch, and his editorial decision to accept the manuscript for final publication in ACP after dealing with his comments.

Regarding the specific questions:

1. Additionally, I'd ask you to comment on the following point and modify the manuscript accordingly. It is not entirely clear to me how the AFM measurement are calibrated relative to the ice sample thickness. If I understood correctly, the distance of the solid ice

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Discussion paper

is z=0, How is that determined? In other words, measuring the force-distance how do you determine the thickness of the QLL without determining the samples topography, or thickness. It appears to me that this calibration is a central issue in AFM and I would ask you to comment on this in more detail.

Answer: Indeed, calibration is a central issue in AFM indentation experiments. We decided to give a detailed discussion of calibration in the Supplement, in order not to disturb the reading of the main article by non-AFM experts. We believe that the most original contributions in our work are the improvements regarding temperature gradients and the chemistry of the tip. We did not want to distract the attention from those aspects. Nevertheless, we do discuss in the main article some of the assumptions needed for the interpretation of force curves and calibration mistakes that would lead to overestimation of the QLL thickness (pages 8-9 of this manuscript). Regarding the specific doubts presented by the Referee, first, it must be clarified that the measured jump-in distance (and, hence, the QLL thickness) does not depend on the zero distance definition. This issue is relevant in the conversion of the force curves after contact, hence it must be taken into account for studies of indentation, viscoelastic models, etc. We added a paragraph in the Supplement which explains that the zero distance definition does not affect the QLL thicknesses determined in this work, and we also added two references that discuss these calibration issues in detail. In the same way, the ice samples thickness does not have an impact on QLL thickness determination, since AFM force-curves study the ice-QLL surface. We did find relevant to add a paragraph and a figure (Fig. S6) clarifying that we do have a lower bound of ice thicknesses, which are large enough to discard influence of the substrate and nano-confinement effects. The same is not true for results by Bluhm et al., as the Referee remarked in another comment (see below).

Changes in the manuscript: Page 7, lines 20-29: We did not observe the ice droplets mentioned by Bluhm and coworkers, (Bluhm et al., 2000), probably due to the fact that they prepared ice samples with thicknesses of few ice bilayers. In our case, ice samples thicknesses were not measured systematically (as it was not the focus of this work), but in most of the experiments ice thickness exceeded the spanned indentation depth (hundreds of nanometers to 5 μm, the maximum vertical distance that can be measured with the AFM scanner used for these experiments). In few experiments we were able to measure the ice thickness, since the AFM tip reached the infinitely hard mica substrate (Fig. S6, Supplement). Considering these macroscopic thicknesses, we can assure that we studied the ice-vapor interface without the influence of the underlying substrate or nano-confinement effects.

Supplement, page 3, lines 16-19: It must be emphasized that one of the main parameters determined in this work, the jump-in distance, is calculated as a difference between ztip distances: d_(jump-in)= z_tipˆC -z_tipˆB , where superscript B and C refer to positions of the tip at Fig. S1. Hence, the jump in distance is directly influenced by calibrations of zpiezo and Sens (from eq. S.5), but does not depend on the calibration of the spring contact or the zero distance definition.

Supplement, page 3, line 33 – page 4, lines 1-3: Figure S6 shows one of the few cases when we could measure explicitly the thickness of the ice sample. The thickness can be estimated from the difference between the end of jump-in (ztip = 0) and the infinite slope (mica substrate, ztip $\approx$ 40 nm). In most of the experiments, thicknesses were much larger, therefore the tip did not reach the mica substrate. In those cases, we can only infer a lower bound for the ice thickness (the maximum indentation depth).

2. Small comments Page 1, Line 25: melted layer -> pre-melted layer

Answer: We thank the Referee for noting this inconsistency in nomenclature. The use of the term “premelting” and “premelted layer” has been discussed, as it might suggest a direct link between the QLL and true melting. Our discussion takes that difference into account, but in some parts of the article we have been inconsistent in the language.

Changes in the manuscript: Page 1, Line 25: Slightly below the melting temperature, Tm, a disordered layer in the solid-vapor interface has been observed in many crystalline solids. This layer is commonly called in the literature "quasi-liquid layer" (QLL), since many of its properties differ from those corresponding to the bulk supercooled liquid at the same temperature.

Page 2, Line 13: The physics of the disordered surface in ice and its geophysical consequences have been reviewed by Dash et al. (Dash et al, 2006) and Bartels-Rausch et al. (Bartels-Rausch et al, 2014), who reported a comparison between calculated and measured QLL thicknesses.

3. Page 9, Line 6: Apparently, Bluhm probed nm thick ice growing on a support. I would argue that the structure of that ice does not reflect the surface of bulk ice crystals, but rather of nano-films on a support being influence on that support. So, I would suggest to highlight more specifically that this study did not probe the QLL on ice.

Answer: We thank the reviewer for the suggestion. We extended the paragraph regarding Bluhm and coworkers experiments to highlight this fact.

Changes in the manuscript: Page 9, Line 31: Results by Bluhm et al. (Bluhm and Salmeron, 1999; Bluhm et al., 2000) present an opposite trend to most of the literature values, that is, lower QLL thicknesses at higher temperatures. However, it should be noted that they measure QLL thickness over much thinner samples (0.3 nm to 3 nm), which corresponds to a few bilayers of ice-like water molecules on the substrate. It should be stressed that these experiments do not give information on the QLL of bulk ice, even if the structure of water on the substrate could be related to that of crystalline ice. Nano-films properties might show a large dependence on the thickness and the influence of the substrate.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2017-1213/acp-2017-1213-AC2-supplement.pdf

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