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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Surface roughness during depositional growth and sublimation of ice crystals" *by* Cedric Chou et al.

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Response to Referee #1

The authors describe a new laboratory setup for investigating roughness of single ice crystals grown in the apparatus. Their main result is the appearance of a ratcheting up of ice surface roughness/irregularity as crystals are subjected to cycles of growth and sublimation, a "memory effect". Motivation for the work is given in terms of the radiative properties of ice-containing clouds in Earth's atmosphere.

I found this to be a useful and interesting contribution to what seems to be a still poorly constrained topic (ice surface roughness). The experimental apparatus and analysis

methods seem to be described in sufficient detail, with a few minor exceptions (see below). The time-lapse videos provided in on-line supplement were especially valuable in aiding the interpretation of figures 10 and 11, but the manuscript stands on its own even without them.

We thank the Referee for the encouraging and insightful comments, questions and helpful suggestions. We list them below, together with our clarifications and changes to the manuscript in blue.

1. It seems that the discussion of whether ablation leads to more or less roughening should be improved in a couple of ways. Figures 10 and 11 do seem to suggest that ablation conditions tend to reduce roughness, but I think the videos of the 2-D scattering patterns tend to tell this story more clearly. And there are more interesting patterns evident in those videos: what are the bands caused by? Finally, while the literature references given by the authors seem to point in the opposite direction, it seems worth mentioning that at at least one SEM study (Butterfield et al, Quantitative three-dimensional ice roughness from scanning electron microscopy, 2016) appears to support the authors' findings that ablating crystals tend to be less rough.

We believe that most readers would find it hard to interpret the videos - that's why we rely on the quantitative measure of roughness instead. But to aid the interpretation, in addition to the existing explanation in section 3, we now provide further explanatory text at the end of section 2.3:

> "The presence of isolated bright spots or bands is an indication of flat crystal facets, while spots covering a large proportion of the pattern signify the presence of roughness or high complexity".

We have not cited the work of Butterfield et al. (2016) because in common with many

other studies (several of which we do cite) it investigated ice growth in near vacuum, which as we argue is less relevant to atmospheric processes, and because it did not control for supersaturation, which we find to be a critical factor.

2. I found the discussion of roughening mechanisms more speculative than the authors let on. In particular, the last paragraph of section 3.1: none of what is presented in that paragraph is substantiated by evidence given in the paper. I also have a problem with the attribution at the beginning of section 3.1, in which the statement "the growth rate is slow enough for the deposited molecule to diffuse on facets to well-separated attachment sites at steps, kinks, and ledges" is not really justified, even if one can find such statements in the literature. I would point the authors to numerous studies that show that the picosecond-scale sticking coefficient on the quasi-liquid layer of ice is close to 1, and conversion of quasi-liquid to ice occurs faster than horizontal diffusion permits Neshyba et al, A quasi-liquid mediated continuum model of faceted ice dynamics, 2016, offer an alternative view. In general, I found it puzzling that there was no mention of the role of the quasi-liquid layer in these sections; if they are going to speculate, at least that factor ought to be included. At the very least, the authors should flag these sections as more highly speculative than currently indicated.

We admit that our discussion is speculative, not least because this initial study focuses mainly on quantifying the phenomenology, rather than the causes, so we have insufficient information at this stage to pinpoint definite origins of the observed roughness. Nevertheless, the Reviewer's comment highlights the major issue we have already pointed out: different growth studies show differences in crystal behaviour that remain to be explained, and there are many, sometimes conflicting views reported in the literature. An attempt at clarification, also pointing out the difference between experiments in air and in near vacuum, was for example provided by an interactive comment in ACP by Kiselev (2014). To reinforce this last point we now insert additional text and references in section 3.2:

> "This distinction is known to lead to different growth rates as well as habits (Beckmann, 1982; Kuroda and Gonda, 1984;".
>
> "Furthermore, in experiments carried out under atmospherically-relevant air pressures, crystals having undergone more than one growth cycle tended to develop more faults (Beckmann, 1982)."
>
> and
>
> "[A further difference between the diffusion limited and kinetics-limited growth is that the former can lead to] increased numbers of faults (Beckmann, 1982) and"
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> "Beckmann, W.: Interface kinetics of the growth and evaporation of ice single crystals from the vapour phase: III. Measurements under partial pressures of nitrogen, J. Crystal Growth, 58, 443–451, doi:10.1016/0022-0248(82)90291-3, 1982.
>
> Kuroda, T., and Gonda, T.: Rate determining processes of growth of ice crystals from the vapour phase, Part II: investigation of surface kinetic processes, J. Meteor. Soc. Jap., 62, 563–572, doi:10.2151/jmsj1965.62.3_563, 1984."

For the atmospherically relevant case of growth and sublimation in air, we point out that the process is vapour diffusion limited, not limited by attachment kinetics. In this context, the timescale of the processes occurring on the surface is less critical, as more time is available for lateral diffusion. Moreover, the lateral diffusion lengths are reported to be high in this context (e.g. Pfalzgraf et al., 2011), justifying our qualitative description.

As for the relevance or otherwise of the quasi-liquid layer (QLL) concept itself, we have decided that this side topic was again too broad and complex to be discussed in our

paper. Nevertheless, we can say here that while QLL appear to be important at warmer temperatures, close to the melting point, they become thinner and correspondingly less important at lower temperatures. At the temperatures relevant here the thickness of the QLL is reported to be very low, below the lattice constants of ice (e.g. Conde et al., 2008). We can also point out that much of this area is subject to a similar misapprehension as ice growth in vacuum: most QLL studies are done by molecular modelling in the absence of air, making them less relevant to atmospheric processes. This is compounded by differing use of terminology: molecular-scale roughness, much discussed in the literature, is different from the roughness on the "optical" scale (i.e. on the scale of the wavelength of light or larger) that is the subject of this work. Moreover, to our knowledge, molecular dynamics modelling studies of the QLL have so far failed to replicate the surface roughness observed experimentally; it was even argued that roughness may arise due to processes at larger scale, potentially fitting the stacking disorder connection postulated here (Pfalzgraf et al., 2010). On a broader note, we think that it would be brave to try to overturn decades of evidence and crystal growth theory by claiming overriding importance for QLLs in this context. They do not yet explain many features of ice surface growth (e.g. growth inhibition and supersaturation thresholds). Conversely, some relevant features can be explained, somewhat counter-intuitively, by layered growth without the recourse to QLLs, e.g. rounding during sublimation (Nelson, 1998). Layered growth and sublimation, and the presence of well-defined elementary steps and terraces has been demonstrated in many systems, including ice; moreover, it can lead to larger step heights (relevant here) through step bunching (e.g. Nelson, 1998; Peterson et al., 2010; Sazaki et al., 2010; Misbah et al., 2010). So we are unsure what the relevance of QLLs is and how to bring this concept in without making the discussion more speculative (which the Reviewer advises against).

Lastly, the Neshyba et al. (2016) study authors admit that the modelling conditions do not make it directly applicable to atmospheric processes (p. 14049 therein) and do not even refer to roughness; we therefore fail to see its relevance.

To clarify the importance of step growth, we insert the following text and additional references in section 3.2.

> "Moreover, the bunching of elementary molecular steps, possibly due to the Schwoebel effect (Misbah et al., 2010), can result in the creation of larger, microscopic (as opposed to elementary) steps that can be seen in SEM micrographs (Cross, 1969).
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> Misbah, C., Pierre-Louis, O., and Saito, Y.: Crystal surfaces in and out of equilibrium: A modern view, Rev. Mod. Phys., 82, 981-1040, doi:10.1103/RevModPhys.82.981, 2010."

3. Mentions of “diffusion-limited” and attachment kinetics are unlikely to be understood by many ACP readers; I‘d suggest elaborating a little, or omitting these points of discussion.

At the first mention we now additionally clarify that we refer to vapour diffusion. The distinction we point out is important, as it permits an evaluation of the (ir)relevance of various laboratory experiments to the atmospheric context, and differences between their outcomes. We have already provided several relevant references to kinetics- and diffusion-limited growth at several points in the article for interested readers to follow.

> "...growth in the absence of air that takes place in a SEM chamber, instead of being limited by vapour diffusion as is the case for ice at tropospheric pressures, becomes limited by the attachment kinetics..."

4. I think it would be appropriate to point the reader to the authors own prior discussion of the possibility of roughness ratcheting-up, as in Ulanowski et al, 2014.

At the beginning of section 3.2 we now refer the readers to the prior discussion in the reference suggested.

"Ulanowski et al., 2014"

5. Some very minor points: I think the paragraph just preceding section 3.1 is misplaced; it seems to refer to figure 8, but that figure has not been introduced yet. In section 3.2, where reference is made to “small scale vertical motions” as a possible mechanism for formation of irregular crystals, it might help to clarify that those are (I presume) atmospheric vertical motions. And there are a few misspellings here and there (“closeer" in section 3.1) that I presume will be weeded out in the next round of editing.

We have placed this explanatory text where it is because it refers to several subsequent figures. Concerning vertical motions, we insert the word "atmospheric" for clarification.

References for Reply:

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