**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Liquid-like layers on ice in the environment: bridging the quasi-liquid and brine layer paradigms" *by* M. H. Kuo et al.

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This manuscript presents a mathematical model to calculate the thickness of a disordered region on ice. It combines two different approaches to calculate the thickness for very clean ice up to very highly concentrated brine solutions. The new mathematical treatment is compared to earlier approaches and applied to estimate the thickness of the disordered layers for various published lab-studies.

This is an interesting topic of high relevance for the atmospheric science community (and beyond). As such it might be well suited for publication in ACP. I encourage the authors to submit a revised version of the manuscript for publication in ACP. In its current form I had difficulties to clearly identify the benefits of this new approach compared to earlier work. The goal of models that will use this mathematical approach

will be to capture field studies. For which environmental conditions is the QLL-part of the model important? Also, I feel that the manuscript would benefit from focusing more on the mathematical treatment and less on its performance to estimate the thickness for some studies.

1 General Comments

1.1 Relevance

Currently, first modelling-approaches are being developed and discussed that try to include a detailed description of snow/ice/firn chemistry. This is an extremely innovative and interesting field of research. In those model-approaches, the chemically active phase of snow is treated as aqueous phase and an estimate of the volume of this aqueous phase or its thickness on grains in the snow a central parameter. Thus any improvement in the estimation of this parameter is per se of high relevance. The use of aqueous phase chemistry of snow is justified by the presence of a surface disorder on snow crystals. The extend of the disorder has been observed to increase with temperature and is thought to increase with solute concentration.

The manuscript proposes a new mathematical treatment for the thickness of the surface disorder that captures both the temperature and solute concentration dependence. The performance of the model is compared to the mathematical treatment that is currently used in most snow-chemistry models and to thicknesses of the disorder that were derived from measurements. The manuscript also tries to highlight the importance of the surface disorder in snow and especially how the surface layer disorder increases with solute concentration.

For me, these are two different issues and I find the discussion of both in this manuscript sometimes difficult to follow. I fell that the discussion of either topic needs to

be deeper and go more into the details. Concerning the importance of solute-induced surface disorder I wonder, which of the studies that are mentioned (for example on page 8148) hypotheses a disordered layer to explain their results, which of them actually observed the disorder, and which of them allow to conclude that this disorder is best described by a (homogeneous) layer the depth of which increases with solute concentration? Concerning the improvement of the mathematical treatment, I wonder if your model can be applied to grain boundaries and triple junctions? You mention those in the introduction, but then curvature and surface effects are not explicitly treated or discussed. Or, what do you mean by "equilibrium thermodynamics" (p 8150 l6) and why did you not derive the QLL thickness based on thermodynamics as described in Dash, J., Rempel, A. Wettlaufer, J., 2006. Reviews of Modern Physics, 78(3), p.695-741? Could you compare your approach to the one by Dash. Also, what is the main difference to the approach by Cho (2002) to which you compare your model in Fig. 1.

I kindly suggest focusing more on the mathematical treatment, comparing it to other approaches and to measurements of surface disorder thicknesses. As the estimation of this thickness is an important parameter in current snow-chemistry models, any improvement merits publication in ACP. I don't see the need to –at the same time- argue for the importance of solute-induced disordered surface layers in real snow. Also, I feel that discussing the later topic in detail would be a review by its own.

1.2 Brine, liquid-like or liquid

One new aspect of this work is that the new approach can be used for a range of solute concentrations – from very clean ice up to highly concentrated brine solutions. Could you mention the concentration of solutes in the ice phase (and in the disordered layer), or even –if appropriate- surface concentrations of adsorbed species throughout the manuscript for the various studies cited as examples of surface disorder? This might help the reader to place the specific study on the disorder scale of your unified

model (QLL – intermediate – brine / liquid). For example on p 8148 line 10: What is the concentration in chloride in the disordered layer observed by McNeill (2006, 2007) and is this closer to QLL or brine conditions? This also holds for the studies mentioned later on page 10, which have concentrations in the brine regime and which of these worked with pure ice (QLL regime). Kerbrat (2007), for example, worked mostly in the liquid regime.

1.3 Language

- It is a valuable approach to treat the liquid brine layer and the quasi-liquid layer mathematically differently. For any given sample results of either calculation are compared and one of the two is chosen to describe the thickness of the disorder. Because the model treats both aspects separately, I think the term unified model does not describe the approach well.

- For me "model" implies that the mathematical description is derived based on physical concepts that describe the system. The QLL model is very much based on a correlation of measurements results. I suggest referring to it as empirical correlation. Correlations are often used in environmental science to describe and predict, so it is a valuable approach.

- In the beginning of your manuscript (p 8146, line 5) the brine layer is introduced as being a (true) liquid. Later in the manuscript the BL is referred to as a liquid-like (or disordered) layer or even as QBL. I find this sudden switch from liquid to liquid-like confusing. Maybe the use of brine could be reserved to (true) liquids, and everything else is disordered?

PS: I do like the title.

2 More specific comment

- Figure 1 compares modelled brine layer thickness with observations. Both models capture the trend in data quite well for temperature above 250 K. At lower temperatures I find the correlation with experimental data less convincing. Your model does a better job at high temperatures, but has a larger discrepancy to measurements at lower T. Could you comment in more detail why your model "results in better agreement at low temperatures" in Figure 2 (p8151).

- Please explain the symbols also of equation 2?

- One outcome of this work is that the thickness of the disordered layer can be estimated for any lab-study. This is for example done on p 8156 where BL thicknesses of 20-163 um are given for a study by Kerbrat (2007). The authors stated that their ice films are 40 - 100 um thick, does this than imply that the whole ice film is disordered or even a true liquid? Or does your model over-predict the BL thickness?

- How do your findings on the disorder induced by nitric acid relate to Křepelová, A., Newberg, J., et al., 2010b. The nature of nitrate at the ice surface studied by XPS and NEXAFS. Physical Chemistry Chemical Physics, 12(31), pp.8870-8880? How does your ratio of water to nitrate compare to this surface sensitive study?

- What are typical concentrations of (total) solutes in cirrus clouds and polar snow pack? For which of those is the QLL-model more appropriate and for which the brine-model? I feel this is a central question; maybe the QLL-model is only needed for lab-experiments?

- What do you mean by "equilibrium thermodynamics" (p 8150 l6) and why did you not derive the QLL thickness based on thermodynamics as described in Dash, J.,

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Rempel, A. Wettlaufer, J., 2006. Reviews of Modern Physics, 78(3), p.695-741?

In summary, I really like the main intention of this manuscript: To improve the calculation of the disordered layer. Such estimates are used in current chemical models that try to parameterize snow chemistry in detail, such as Thomas, J.L. et al., 2010. Modelling chemistry in and above snow at Summit, Greenland – Part 1: Model description and results. Atmospheric Chemistry and Physics Discussions, 10(12), pp.30927-30970. I suggest this manuscript for publication in ACP once the manuscript is improved. I hope that my suggestions are helpful for this.