

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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Response to T. Bartels-Rausch (Comments in quotation marks, responses below)

"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

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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."

RESPONSE: Thank you for your valuable comments; we have taken them into consideration in our revised manuscript. We have made a number of changes to the mathematical treatment of the BL, which is now distinctly different from that of earlier studies. A more detailed description of the changes is provided below. Regarding the connection and applicability to field (as well as laboratory) studies, we have also addressed them in the revised model, which now takes as input experimentally-accessible quantities such as solute concentration in the melt solution of a snow sample.

"1 General Comments 1.1 Relevance Currently, first modeling-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

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that the discussion of either topic needs to be deeper and go more into the details."

RESPONSE: We have extensively revised the manuscript and clarified the discussion throughout. After careful consideration we decided to reduce the discussion of the QLL in the paper and focus more on the brine layer model. Specifically, after considering the reviewers' comments and offline discussions, we conclude that not enough is known at this time about the dependence of interfacial chemistry on the presence or extent of the QLL for these two models to be combined explicitly. So we have changed our approach. We have tabulated the conditions under which very little or no brine is expected to be present based on our model, but the QLL may still significantly affect interfacial chemistry, and therefore care must be taken in modeling. We revised and extended our BL modeling approach. We also go into more detail regarding the modeling approach and the analysis in the manuscript. We believe these changes have improved the overall quality and readability of the manuscript.

"Concerning the importance of solute-induced surface disorder I wonder, which of the studies that are mentioned (for example on page 8148) hypothesizes 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?"

RESPONSE: In some cases we inferred the effect of the interfacial layer, in other cases it was hypothesized or inferred but not observed by the authors, and in a few cases it was directly observed by the authors. This passage has been removed from the revised manuscript due to the shift in focus.

"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."

RESPONSE: Our model predicts the volume fraction of brine. That brine can exist at grain boundaries, triple junctions, pockets, etc. as well as at the gas-ice interface. We

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do not treat brine in these different locations differently in the model. We have used the volume fraction representation more throughout the revised manuscript and in the figures since it is more general in this respect, and also applies equally for all assumed sample geometries.

"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."

RESPONSE: The QLL is not a phase described by classical equilibrium thermodynamics (it violates Gibbs' Phase Rule). The semiempirical QLL model is now removed from the paper, as mentioned above.

"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."

RESPONSE: In our original BL model, we did not assume low solute concentration in the brine layer, as was done in the Cho model. We further have modified the BL treatment in the revised manuscript, so there are now more conceptual differences between the models. Cho et al. (2002) used the ideal solution approach to characterize the BL, noting that this treatment is valid for dilute solutions. Since the brine layer may be highly concentrated, depending on the conditions, the ideal solution assumption may not apply. The activity of ions changes as a function of temperature and concentration and can become significant especially at low temperatures. Our revised model allows

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for non-ideal solution behavior. It also accounts for partitioning of volatile solutes into the gas phase, and dissolution of solute into the bulk ice matrix.

"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?"

RESPONSE: Thank you for your suggestion. Based on your suggestion and that of Jennie Thomas, we have included more discussion of solute content in the gas, brine, and ice phases under different conditions in the revised manuscript. Comparisons to experimental studies have been included in the manuscript where applicable. McNeill et al. inferred a chloride concentration of 9.3×10^{-5} mol HCl/cm³ in the QLL at 196 K and 7×10^{-7} Torr HCl.

"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."

RESPONSE: We agree with the reviewer that Kerbrat (2007) worked in the liquid regime and we corrected this in the revised manuscript.

"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."

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RESPONSE: We appreciate the reviewer's comment. As mentioned above, we changed our approach and modified the title accordingly.

"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."

RESPONSE: The proposed QLL "model" in the original submission of this work was described as "semi-empirical" throughout the manuscript. Although the fit parameters were indeed empirically determined as you commented, the functional form of the equation actually has a theoretical basis originating in intermolecular potential functions. That being said, we recognize the lack of agreed-upon constraints that can be used in such an approach and have concluded that a thorough and detailed treatment is outside the scope of this work. Therefore, in the revised manuscript, we have refrained from in-depth discussions of the QLL phenomenon and focused mainly on the treatment of solute-containing systems.

"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 liquidlike (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."

RESPONSE: We acknowledge that the brine is a true liquid, and we have been careful to be consistent with our terminology in the revised manuscript

"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

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measurements at lower T. Could you comment in more detail why your model "results in better agreement at low temperatures" in Figure 2 (p8151)."

RESPONSE: We revised this model as described above and it now fits the experimental data of Cho et al. (2002) better at high and low temperatures. The deviation at low temperatures seen in the original manuscript likely resulted from non-ideal behavior as the interfacial solution becomes sufficiently concentrated. Cho's model treated the brine layer as an ideal solution.

"Please explain the symbols also of equation 2?"

RESPONSE: We have modified the equation and defined all the symbols in the text immediately following it.

"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 then imply that the whole ice film is disordered or even a true liquid? Or does your model over-predict the BL thickness?"

RESPONSE: The BL model is not applicable in the Kerbrat et al (2007) case since they worked in the liquid regime and we corrected this in the revised manuscript.

"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?"

RESPONSE: We ran the BL model at HNO₃ partial pressure 7.5×10^{-7} Torr (conditions similar to Křepelová et al. 2010), and brine layer formation is not predicted under those conditions, consistent with the conclusions reached by the authors. Please refer to Table 1 in the revised manuscript for a list of conditions under which very little (<10 nm surface layer) or no BL is predicted. We have included citations for these studies,

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but since the focus of our paper has shifted away from the QLL, this work is not directly relevant to the model we present in the revised manuscript, so it will not be discussed in detail.

"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?"

RESPONSE: Micromolar levels of individual solutes such as NO₃⁻ and Cl⁻ are reported in polar snowpack (see, for example, Thomas et al., *ACP*, 2011, Table 2). HNO₃/H₂O ratios of 10⁻⁵-10⁻² have been observed in cirrus ice particles (Voigt et al., *ACP*, 2007). We apply the model to these concentration regimes in the revised manuscript. In the revised model we focused on modeling the brine layer, which, as you pointed out, is of greater prevalence in environmental systems. Although completely pure ice may only exist in the laboratory, we do believe that in systems with very low solute concentration, such as pristine snow, there is the possibility that the QLL rather than a true liquid interfacial layer dominates interfacial chemistry. Please see section 4.2.2 of the revised manuscript for a specific example.

"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., C2768 Rempel, A. Wettlaufer, J., 2006. *Reviews of Modern Physics*, 78(3), p.695-741?"

RESPONSE: Please refer to the response above to a previous comment addressing the same issue.

"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-

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30970. I suggest this manuscript for publication in ACP once the manuscript is improved. I hope that my suggestions are helpful for this."

RESPONSE: We thank you again for your helpful comments. We have included a reference to the Thomas et al. manuscript in our revised paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8145, 2011.

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