

## ***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.***

**M. H. Kuo et al.**

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Response to interactive comment by J. Thomas (Comments in quotation marks, followed by the responses)

"I would like to generally express my support for this manuscript, while also noting that it needs some revisions to be published in ACP. This is the type of analysis that is needed to bridge the gap between the experimentalists and modelers involved in the snow chemistry community. It is necessary to have clear, well documented, expressions for the liquid layer thickness for inclusion in snow chemistry models, even if these expressions are currently imperfect. As the knowledge of the surface of ice increases, these expressions can be refined in the literature and snow chemistry models. There is currently no clear consensus on what should be used and this paper would help to

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provide a starting point for correct representation in models. In general, I encourage the authors to take their analysis further so that it can be published. The current version of the manuscript needs some modifications, including potentially a change in the title (as noted by the reviewer)."

RESPONSE: Thank you for your interest in the paper, and for your helpful comments. The title of the paper is now changed.

"The authors should discuss the experimental techniques used to measure the QLL on pure ice and why there is such disagreement in the results. Helping modelers to determine the best measurement for inclusion in snow chemistry models is one of the major values of this paper. Suggesting a reasonable range of error for their equations would also be helpful."

RESPONSE: The main difficulty in comparing QLL thicknesses measured by different experimental methods is that the experimental methods often probe totally different physical properties of the QLL. The QLL thickness also depends on sample impurity concentrations, which can vary from study to study. At this time very little is known about how interfacial chemistry changes with these physical properties which indicate the extent of the QLL. For all of these reasons, we decided to reduce the discussion of the QLL in the paper and focus more on the brine layer model. A detailed discussion of the QLL will be featured in one of the review articles from the 3rd Workshop on Air-Ice Chemical Interactions (AICI).

"In equation 2, this is expressed in terms of the water mole fraction. The equation would be more useful in my opinion if expressed in terms of the solute mole fraction. As noted above, it would also be helpful to discuss in detail the error associated with using this equation."

RESPONSE: We corrected this in the revised manuscript and the model is now expressed in terms of solute mole fraction.

"Given recent evidence for snow chemistry in regions without a brine layer (for example Summit, Greenland), the authors should discuss the situation for regions with lower total ion loading specifically in the paper."

RESPONSE: This point is very important, and something we had in mind when we formulated the unified model presented in the discussion manuscript. This issue is discussed specifically in the revised manuscript. We have tabulated the conditions under which very little (<10 nm surface layer) to no brine formation is predicted in the various scenarios to which we applied our model. Please see Table 1 in the revised manuscript.

"It would be helpful to discuss how to treat systems including more than one anion (HNO<sub>3</sub> and HCl or HNO<sub>3</sub> and HBr, for example) as well as how to treat systems without ions (organics)."

RESPONSE: In the revised manuscript, we used single-solute systems as examples and made suggestions of how the model may be extended to multiple solute or organic systems. Specifically, we now include solute activity coefficient in the model. Empirical expressions for this quantity are available in the literature for atmospherically relevant, multi-component systems. References for such studies have been included.

"In models, the liquid layer thickness doesn't have a lot of meaning without also defining geometry. What is the total brine volume associated with this thickness? What exactly does liquid layer thickness mean for brine layers? For the surface of snow grains, the situation is also complicated and a discussion of how to use the liquid layer thickness to calculate a liquid fraction warranted."

RESPONSE: We agree that some clarification was in order here. In addition to the brine layer thickness, the brine layer volume fraction is an output of this model. In the model, the layer thickness is related to the volume fraction via the surface area to volume ratio. Different geometries may be chosen by specifying the surface area to volume ratio. We have discussed this aspect in more detail in the revised manuscript.

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"I encourage the authors to discuss the recent work using XPS and NEXAFS to look at the surface of ice. How does this work fit into their model?"

RESPONSE: We have included citations for these recent studies. Applying our BL model to their experimental conditions we found that brine layer formation is not predicted under the conditions of those conditions, consistent with the conclusions reached by the authors. 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.

"It is somewhat confusing for me that the detection limit for the ellipsometry measurements is 80 nm. Many of the values in Figure 4 predict a thickness less than this measurement. Therefore, there is often a QLL present below the detection limit. Can this be clarified in the context of figure 3?"

RESPONSE: We agree. The 80 nm detection limit for the ellipsometer was inferred from the model, but after revising the model to include non-ideal solution behavior and enforced mass balance closure, our results for this example system have changed significantly. The observations of McNeill et al. 2006 are no longer predicted with the brine layer model, implying that the interfacial layer they detected using ellipsometry was quasi-liquid (QLL). The experimentally determined detection limit of the ellipsometer is 10 nm as reported by McNeill et al. 2006.

"A detailed discussion of all of the measurement techniques and what they measure would add significant value to this manuscript. I would encourage the authors to change the words "surface brine layer" to "brine layer". There is no reason why this is limited to the surface. There is another review on this in Physics Today called "Why is ice slippery?" (Rosenberg, 2005). I noticed this is not mentioned. This has a figure very similar to Figure 4 with all of the experimental data summarized. The authors should cite this paper and mention how their analysis adds value to what is already in the literature."

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RESPONSE: As mentioned above, detailed discussion of QLL techniques is now beyond the scope of this paper. This will be a section in one of the reviews from the AICI conference. The "surface brine layer" is called "brine layer" in the revised manuscript.

"In figure 6, the authors should clarify what is meant by NaCl concentration. Is this the concentration in a melted solution? What is the corresponding concentration in the brine layer and in the surface layer?"

RESPONSE: The NaCl concentration in the figure legend is the total concentration of NaCl in the unfrozen solution. We have made this more clear both in the text and in the figure legend. A detailed discussion of this system is presented in section 4.1 of the revised manuscript. The model also predicts solute concentrations in both the bulk ice phase (where applicable) and brine layer. Brine layer concentrations are presented and discussed in the revised manuscript.

"In snow chemistry models it's important to know both the thickness and the chemical composition of the QLL and BL. Demonstrating that the thickness and derived concentrations are reasonable are both essential points that should be made in the revised version."

RESPONSE: This is a valid point. We included comparisons of our model predictions to experimental results where available in the revised manuscript.

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