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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 Anonymous Referee #3 (Comments in quotation marks, followed by the responses)

"The paper by Kuo et al. puts together a mathematical description, or more accurately, approach or algorithm, for describing the thickness of the disordered water layer on ice, with the intention of formulating a unified “model” that describes the amount of disordered water on ice surfaces, ranging from pure ice devoid of any solutes, to environmental samples that may be rich in solutes. This paper is reasonably well written, and succinct, on a topic of considerable community interest. I applaud the intent of the paper. This is an area of inquiry that badly needs quantitative description and firm theoretical foundation, so that predictions can be made about solute/reactant concen-

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trations on the surface of environmental ice, and so that the community can continue addressing important questions such as the applicability of aqueous phase rate constants to reactions of species in this ice-surface water. I find myself, as many of us do, struggling for the proper adjectives for the water on the surface of the ice for all cases, and, indeed, the authors fall victim to this problem. It appears that everyone agrees that one call the water on the surface of pure ice the “quasi-liquid layer”. However, I believe that one can reasonably argue, as the paper implies, that the QLL may really only exist in laboratory settings, as, at least on Earth, there really isn’t any pure water-ice. This then brings us to a problem with this and many papers - since we are unsure if the “brine layer” on the surface of environmental ice is/behaves just like a real aqueous brine, we often use confusing terms like “quasi-brine layer”, because we are not sure. However, for this paper, the authors should try hard to be consistent with their terms for real environmental ice, or laboratory ice with solutes. I do believe that this paper can be made publishable, with some changes, though I am not very certain what they should be. So, I will just provide my suggestions. If they take my advise, and stick to the brine layer conditions, then this would be major revisions; however, I leave that to the authors and editor. My main concern relates to the fact that, while they aimed for a unified model, this was not achieved, in a mathematical sense. Rather, the paper presents a conditional approach, i.e. one equation when (effectively) there is a brine layer caused by solutes, and a different one when there is not. However, it appears to me that the two cases are effectively addressing two quite different scenarios, and two somewhat different sub-communities, i.e. laboratory studies of the pure water QLL, and environmental studies of real ice and snow (and/or laboratory studies of frozen aqueous solutions of solutes). Since most of the experimental data that the authors are interested in relates to the presence of a brine layer, and since there is not really a mathematically unified model presented here, the paper might be cleaner if it focused on the brine layer treatment. This feeling is also supported by my concern that the QLL best-fit equation that they provided is empirical, and intended to simply come as close as possible to fitting all the existing experimental data on the QLL, without attempt at

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discrimination. I am not sure that fitting all the available data represents a laudable goal. Specifically, I believe that some of the past studies may have been conducted under conditions in which contamination by solutes from various sources was possible, and that such contamination may have affected the results. This issue is one of the likely factors contributing to the very large (orders of magnitude!) spread in the observations. Thus, I would suggest that it would be better for the authors to dig into the experimental conditions in each case, and try, if possible, to rule out some data sets, if that can be done objectively, or focus on data sets for which there is great confidence in the purity of the water, and perhaps in the quality and detection limits for the method. However, at that level of effort, a separate paper on the QLL might be warranted, and we are back to my suggestion that this paper might best focus on the brine layer."

RESPONSE: We thank the reviewer for his or her helpful comments. We have extensively revised the manuscript. 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. 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).

"My last major concern is that the paper should be sure to compare the results of their model to that of other formulations, e.g. that of Wettlaufer et al., 1999. I have a number of minor criticisms of the detail of the content, and I list those here, in the approximate order that they appear in the manuscript."

RESPONSE: As described above we focused on the brine model now in more detail, and we compared our model to that of Cho et al (2002). The comparison is presented in section 4.1 in the revised manuscript and illustrated in Figure 2. The model presented in Wettlaufer 1999 was developed to analyze the effect of very small impurity concentrations on the extent of the quasi-liquid, whereas our model is applicable to

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systems with sufficient solute to form a true liquid layer. Therefore, a direct comparison is not very meaningful since the models address very different concentration regimes for which different thermodynamic and physical processes are dominant. In the revised manuscript, we refer the readers to Wettlaufer for systems with very low impurities.

"1. Page 8146, line 10 - I don't think it really is a unified model; it is more two distinct functional treatments of conceptually different surface conditions."

RESPONSE: We no longer discuss a unified model in the revised manuscript, as mentioned above.

"2. Page 8147, line 21 - I don't really think that this is effectively correct, in that I believe that for conditions applying to polar snow and ice that the effects of the solutes and surface adsorbates dominate the structure of the surface water, and that a "QLL" is not appropriate in this case (see line 5 of page 8154). Indeed, for -30 oC, if the dominant ions were NaCl, you might expect the surface layer salt concentration to be ~8M. This section on pages 8147 and 8148 seems to confuse and mix up the terms QLL; in the presence of "impurities", under many real world conditions, the QLL is likely insignificant, compared to the effects of solutes. Again, this confusion might be avoided by not discussing the QLL in this paper, especially since no fundamental insights about the QLL are provided here (e.g. by providing a fit to the data)."

RESPONSE: We took the reviewer's suggestion and focused our discussion on the BL.

"3. Because people are more often used to using the mole fraction of the solute in dilute solutions, it will avoid confusion if you provide the mathematical definitions of x_w and $x_{w,0}$ in the text after equation 1, e.g. $x_{w,0} = n_w/(n_w + n_s)$. But you go on to use the terminology in a confusing way, e.g. line 28 on page 8150, you refer to $x_{w,0}$ as "the total solute concentration". It would be better if equations 1 and 2 were rederived so that they were expressed in terms of the solute mole fractions and not the water mole fractions."

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RESPONSE: We have adapted your comments and in the revised manuscript, equations are written in terms of solute mole fraction and the definition of symbol made clear.

"4. Page 8153 - you refer on lines 19 and 20 to a disorder onset at -30 oC. It is not clear from Figure 4 that there is any general agreement on the "onset", which seems to vary from -20 to -100oC. Isn't this likely a function of operational definition and/or detection limit of disorder? Again, unless the paper's coverage of the QLL is expanded, these issues are treated casually here, and I think are best moved to a more QLL-focused paper."

RESPONSE: We agree. The discussion about QLL onset temperature is now more general in the revised manuscript.

"5. Page 8155, line 13 - insert "stratospheric" before "ozone"."

RESPONSE: We have made this addition in the revised manuscript

"6. Figure 6 - shouldn't there be a discontinuity at the NaCl 2H₂O eutectic pt.?"

RESPONSE: In our revised model, we take into account the effect of non-ideal behavior as the solution concentrates, but solid formation is not treated in the model. Our model reproduces the experimental data of Cho et al. (2002) well: it shows the brine volume fraction reaching a plateau once the eutectic temperature is reached. We also included a statement to advise the reader to use caution when applying model results at sub-eutectic temperatures.

"7. Page 8157, line 22 - isn't the BL model applicable to essentially all environmental ice? This sentence should say that, or something along the lines that most of the thickness for all environmental ice can be described by the BL model."

RESPONSE: In the revised manuscript, we have applied our model to three chemical systems in several different scenarios. For all the scenarios presented, we used a range of solute concentrations found in environmental ice. Based on our findings for

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the various scenarios, we provide a summary in Table 1 of conditions under which very little (<10nm surface layer) to no brine formation is predicted. For these conditions, we advise modelers to be cautious since a QLL can still be present that is able to alter interfacial chemistry.

"8. Page 8158, line 17 - it might be appropriate to comment on the extent of information available about the distribution of organic solutes between the ice and the BL."

RESPONSE: To our knowledge not much is known about the phase partitioning of organic solutes in these systems. We now mention this in the Summary and Outlook section of the revised manuscript.

"9. Re Figure 4 - there is much more data in the Sadtchenko and Ewing paper than shown in your Figure; if you are not showing all the data, why not, or, is it possible the legend is not correct and the S&E data are the circles?"

RESPONSE: Figure 4 is now removed from the manuscript.

"10. Figure 5 - I don't think it makes sense to extend the pure ice QLL line down much below a water molecule diameter, i.e. about 0.3nm. In Figure 5 it extends to considerably less than an O-H bond length!"

RESPONSE: We agree with the reviewer. This is fixed in the revised manuscript.

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

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