**Atmospheric
Chemistry
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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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Response to Anonymous Referee #1 (Comments in quotation marks, followed by the responses)

"Ice chemistry and physics are highly dependent on its surface properties, which include the presence of a disordered layer, often called the QLL (quasi-liquid layer). This QLL has been shown in previous work to thicken in the presence of impurities and some studies have suggested that it then became more similar to a liquid, and it was then sometimes called a brine layer (BL). However, neither the actual properties of this QLL or BL nor its chemical reactivities have been firmly established. In particular, snow chemistry models are weakened by the fact that (1) the thickness of this layer is not known; (2) its reactivity is not known, and authors often had to resort to assuming that

it was similar to that of liquid water. This paper attempts to address the first issue just mentioned: what is the thickness of the QLL in the absence of impurities and of the BL when impurities are present? This is a laudable goal. From the title and abstract, I expected some theoretical developments where a single theoretical viewpoint would be used to describe both the BL and the QLL. Unfortunately, this is disappointingly not the case. First of all, the QLL is only described empirically from existing data, and a best fit curve with limited theoretical basis is obtained. A completely different approach is taken for the BL, where conventional solution thermodynamics is used. The "bridge" between both concepts is in fact equation (7), where the authors simply take the higher of the values given by the BL and QLL concepts, which remain distinct and are not unified. This clearly cannot be called a bridge between 2 paradigms. This is a mere juxtaposition of curves over 2 different domains. There is therefore no added value as far as paradigms or concepts are concerned."

RESPONSE: We appreciate the reviewer's comments and the title of the paper is now changed.

"Furthermore, each approach is questionable. Taking the best fit between all the points of Figure 4 is strange. Indeed, the differing QLL thicknesses given by different methods can be due to (a) each method probes a different property; (b) the QLL thickness depends on impurity concentrations, which were different for each study. This last suggestion was developed at length by Wettlaufer (1999). It would therefore appear more justified to select the one study more suited to the current purpose and use its data only. Furthermore, eqs. (4) to (6) are not exactly the form proposed in the studies cited, where much more complex equations are in fact proposed. See e.g. eq. (7) by Wettlaufer(1999)."

RESPONSE: We agree with the reviewer's comment regarding the QLL dataset and in fact we discussed this in the manuscript. As a result of the differences in the techniques and the measured surface properties, we believe that at this time there is no unequivocal justification for choosing one (set) of studies over the others. The main

difference in QLL thicknesses given by different methods is that each experimental method probes a different physical property 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).

"Regarding the BL treatment, the concept is similar to that of Cho et al. (2002). However, I am not certain that these considerations, developed for volumes and which neglect surface energy terms, can be applied to thin films where surface energy terms may become dominant."

RESPONSE: The brine layer is a true liquid and under many environmental conditions is relatively thick, in which case surface energy terms do not dominate. However, we have mentioned this point in the manuscript: "Note that surface energy is not treated in this model. In very thin films, the surface energy term can become dominant and it was addressed by Wettlaufer (1999)"

"The authors surely are aware of this, as McNeill et al. (2006 and 2007) themselves reached the conclusion that the BL layer caused by HCl is different from a true liquid, as for example evidenced by the HCl solubility in the BL, which is intermediate between that in ice and that in a true liquid. It is surprising that in previous studies, the authors acknowledge that liquid phase thermodynamics do not apply, but nevertheless apply them here. Also, there seems to be several errors in the derivation of their equations, as detailed below. Furthermore, the BL thickness parameterization appears different from the experimental results of McNeill et al. (2006). For example, Mc Neill et al. (2006) determine that for P(HCl) = 5 x10(-7) Torr at T=213 K, the BL is 30 nm thick, while in this work, under the same conditions, they find a thickness of 80 nm. In passing, they also mention that the detection limit with their ellipsometer is 80 nm (caption Fig 2), in

contradiction to their earlier work. Unless I have misunderstood some key point, these apparent inconsistencies do not instill confidence."

RESPONSE: We agree. After revising the model to include nonideal 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, consistent with their interpretation that the interfacial layer they detected using ellipsometry was quasi-liquid (QLL). The 80 nm detection limit for the ellipsometer was inferred from the BL model prior to revision. The experimentally determined detection limit of the ellipsometer is 10 nm as reported by McNeill et al. 2006.

"In summary for the major aspects, I am forced to conclude that both treatments of QLL and BL appear to have major flaws and that the "unification" between both approaches is not real. There seems to be no strong basis demonstrating that these QLL or BL thicknesses values are reliable, and I am not certain that I would recommend their use in snow chemistry models. It may have been more convincing to develop a parameterization based on existing unified theories, by determining coefficients for those parameterizations that best apply to environmental conditions."

RESPONSE: In the revised manuscript we omit the discussion about the "unification" concept. We have revised the BL model to allow 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. Rather than a parameterization, the newly revised model provides a strong theoretical representation of the BL under a variety of environmental conditions, and represents an improvement upon existing models of the BL. We provide comparison to experimental data where available (e.g. Figure 2). As a result, we think that our model provides insight and can be of use for modelers in the snow chemistry field.

"There are also numerous minor problems, supporting my general feeling that this work was not given the attention deserved by such an important topic. These include: 1- p.

8147, l. 20-22 : I do not think that MacTaylor supports this statement. This reference presents work at T<170K and does not seem to mention the QLL."

RESPONSE: We appreciate the reviewer's comment and we corrected this mistake.

"2- p. 8148, l. 18-19. I am not certain that the interpretation of the work of Dubowski et al., as presented here, is correct. Dubowski et al. make the hypothesis that the nitrate in their experimental samples is in the QLL. They find that the photolysis quantum yield is higher than the value extrapolated from higher T. But they did not actually demonstrate that nitrate was in the QLL, and they did not perform measurements of nitrate in another environment than the QLL, which would demonstrate that the QLL actually enhances the nitrate photolysis quantum yield."

RESPONSE: This passage has been removed from the introduction section.

"3- p. 8150, l.6 and p. 8157 l; 12: the QLL has in fact been described thermodynamically, and in particular in references cited in this paper."

RESPONSE: The QLL on pure ice is not a phase described by classical equilibrium thermodynamics (it violates Gibbs' Phase Rule). We have modified the language in the revised manuscript to be clear about this.

"4- p. 8150, l. 26 and p. 8156, l. 2: The solubility of HCl in the BL is assumed independent of the HCl partial pressure and temperature, which is certainly not the case."

RESPONSE: In that example, we had used experimentally available data for the solubility of HCl in the QLL from McNeill et al. (2006, 2007), which is only known at one temperature and pressure. The reviewer is correct that the solubility of HCl in the QLL may follow a Henry's Law-type dependence on pressure and temperature, but due to the fact that solubility data are very scarce in the QLL, we assumed that it is constant. Since we are indeed modeling the BL, a true liquid, instead of the QLL, in the revised manuscript we instead use the parameterization of the Henry's Law constant for HCl in

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supercooled liquid water presented by Carslaw, Clegg, and Brimblecombe (1995)

"5- p. 8156 l. 11. A BL thickness of 0.16 mm is not realistic. Kerbrat et al. (2007) in fact worked outside of the ice thermodynamic stability domain. They were simply melting the ice. Ice thermodynamics cannot be applied to this case, as a true liquid is present."

RESPONSE: We agree with the reviewer and we corrected this in the revised manuscript.

"6- p. 8156, l. 18 and 8157 l.. 24 Is there a reference supporting that the solubility of NaCl in ice decreases with decreasing temperature? Why would the solubility of HCl increase and that of NaCl decrease ?"

RESPONSE: We have revised the language in this passage, as it seems to have been a source of confusion. We refer the reviewer to a paper by Thibert and Domine (1997) in which they studied the solubility of HCl in ice and found that it increased with decreasing temperature. As for NaCl, we do not include any partitioning of NaCl in to the ice matrix in this model. It is known from NaCl – H2O phase diagram that the solubility of NaCl in liquid water decreases until it precipitates out completely in the form of NaCl.2H2O below the eutectic point.

"7- In the supplementary material, equation S15: does not xw,0=1, since this is the mole fraction of water at the melting temperature of pure water; which is necessarily equal to 1 ? In the text, Tm is the melting temperature of (pure) ice. Note that equation S15 is used as equation (2) in the main text."

RESPONSE: Equation S15 (also eq (2) in text) is presented as a model for the brine layer. As such, it applies to solute-containing solutions, whose water mole fraction, xw,0, at 273.15K may be close to but is certainly not unity. On page 8150, lines 6-9 of the manuscript, we specifically stated that eqs (1) and (2) cannot be applied to pure ice without impurities.

"8- In equation S16, should not the ratio of the ice density over the water density be the

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other way around ? Furthermore, if the equation is corrected, the implicit approximation is that the total number of moles in the brine is the number of moles of water. Since by definition brines can be highly concentrated, this approximation can be questioned. Since S16 leads to equation (1) in the text, I am not sure that this key equation is valid."

RESPONSE: Yes, the densities should be flipped. Thank you for pointing out the typographical error. We will also mention here that we previously used the density of water to approximate the density of the brine. This approximation may introduce errors, especially at low temperatures. In our revised model, we have taken into account the effect of solutes on the density of the brine, following Clegg and Wexler (2011) . The fraction of water in the brine layer, ( ) is derived based on exact expressions in terms of the mole fraction of water, as shown in eqs S17 and S18 (i.e. eq (1) in text).

"By the way, why do not the authors compare their thickness values to those proposed by previous authors, who actually elaborated a unified theory for QLL and BL, such as Wettlaufer(1999)."

RESPONSE: We thank the reviewer for this suggestion. We discuss our model in the context of Wettlaufer (1999) in the revised manuscript, in the Summary and Outlook section.

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