

## ***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.***

### **Anonymous Referee #1**

Received and published: 29 March 2011

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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. 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).

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. 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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

of their equations, as detailed below. Furthermore, the BL thickness parameterization appears different from the experimental results of McNeill et al. (2006). For example, McNeill et al. (2006) determine that for  $P(\text{HCl}) = 5 \times 10^{-7}$  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.

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.

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  $T < 170\text{K}$  and does not seem to mention the QLL.

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.

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.

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.

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.

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 ?

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

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

In summary, my feeling is that this paper does not present significant new developments. Its main merit is to propose an equation that would be convenient to use in models, but there is in fact little justification for this equation, and above all, there is actually no bridge at all other than graphical between the BL and QLL “paradigms”, so that the title is very misleading. Previous work by other authors, on the contrary, have proposed theories that treat both the QLL on pure ice and in the presence of impurities, (e.g. Wettlaufer, 1999), so that an actual “bridge” appears possible. 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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

(1999). And I renew my suggestion to use one of these existing theories to proposed a parameterization for atmospheric ice and snow.

I therefore regret that I cannot recommend this paper for publication in ACP. I doubt that even major changes can bring it up to ACP standards, but as always, the decision lies with the editor.

---

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper