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Liquid-like layers on ice in the environment: bridging the quasi-liquid and brine layer paradigms

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Abstract

Liquid-like layers on ice significantly influence atmospheric chemistry in polar regions. In the absence of impurities a nanoscale region of surface disorder known as the "quasi-liquid layer" (QLL) may exist below the bulk melting point (down to $\sim -30\,°C$).

5   Surface and bulk impurities are known to modulate the QLL thickness. In aqueous systems containing ionic solutes, a liquid brine layer (BL) may form upon freezing due to the exclusion of impurities from the ice crystal lattice coupled with freezing point depression in the concentrated surface layer. Brine layers are conceptually distinct from the QLL, which can exist in the absence of impurities.

10   We have developed a unified model for liquid-like layers in environmental ice systems that is valid over a wide range of temperatures and solute concentrations, spanning the QLL and BL regimes. The model consists of two coupled modules describing the thickness of the BL and the QLL. The BL module is derived from fundamental equilibrium thermodynamics, whereas the QLL formulation is derived semi-empirically based on

15   statistical mechanical principles and previously published QLL thickness data. The resulting unified model has been tested against experimental data from literature and applied to several environmentally important systems, such as HCl(g)-ice, HNO_3(g)-ice, and frozen sea ice. This model can be used to improve the representation of air-ice chemical interactions in polar atmospheric chemistry models.

1   Introduction

Ice-gas interactions in the environment affect atmospheric composition and climate in a number of ways. Exchange of trace gases with snowpack and frozen halide surfaces largely control atmospheric composition in polar regions (Domine and Shepson, 2002; Grannas et al., 2007a; Simpson et al., 2007). The heterogeneous chem-

25   istry of cloud ice particles also plays critical roles in polar stratospheric ozone depletion (Solomon et al., 1986; Molina et al., 1987; McNeill et al., 2006), in tropospheric

chemistry (McConnell et al., 1992; von Kuhlmann and Lawrence, 2006; Gamblin et al., 2006, 2007), and in climate (Gao et al., 2004a,b). A quantitative physical understanding of the interactions of snow and ice with trace gases is critical for atmospheric chemistry modeling, as well as for the interpretation of records of climate and biogeochemistry obtained via ice core analysis (Domine and Shepson, 2002). Furthermore, the extent of snow and ice ground cover, sea ice, and cloud ice particle numbers are sensitive to changes in global climate (Lemke et al., 2007; Anisimov et al., 2007; Denman et al., 2007). Therefore, accurate representation of the heterogeneous chemistry of snow and ice in coupled atmospheric chemistry-Earth system models is necessary in order to predict the effects of climate change on atmospheric composition.

One factor that contributes to the reactivity of ice surfaces and their ability to catalyze chemical reactions is a liquid-like layer that exists under a wide range of environmentally relevant conditions. Liquid-like layers on ice and snow in the environment can be categorized into two regimes: a quasi-liquid layer (QLL) which exist on pure ice or a brine layer (BL) which forms on the surface of impurity-containing ice. The two regimes are conceptually distinct and are described briefly below.

The "quasi-liquid layer" (QLL) is a nanoscale region of surface disorder that exists on pure ice. The QLL has been characterized by a variety of experimental and theoretical techniques, all of which show that it is present below the bulk melting temperature, and that its thickness decreases with decreasing temperature. During sunlit months in the polar regions, when the average temperature exceeds −30 °C, the QLL is likely to exist even in pristine areas (MacTaylor et al., 1999).

A highly concentrated brine layer (BL) exists in equilibrium with pure ice in frozen aqueous systems with high solute content (e.g. sea ice, or snow with contaminants) (Cho et al., 2002; Wettlaufer et al., 1997). When water containing solutes is frozen, impurities are excluded from the ice lattice, resulting in their selective segregation and concentration at the crystal surface, grain boundaries, or triple junctions (Harrison and Raymond, 1976; Maccagnan and Duval, 1982b; Takenaka and Bandow, 2007; Takenaka et al., 1996; Takenaka et al., 1992; Robinson et al., 2006; Mulvaney et al.,

1988; Fukazawa et al., 1998; Baker et al., 2003, 2007; Cullen and Baker, 2000; Wolff et al., 1989; Huthwelker et al., 2001). Acids are believed to concentrate at the grain boundaries and triple junctions in glacier ice and polar ice sheets, existing in an aqueous solution (Harrison and Raymond, 1976; Maccagnan and Duval, 1982a; Wolff and Paren, 1984; Mulvaney et al., 1988; Fukazawa et al., 1998; Baker et al., 2003, 2007; Cullen and Baker, 2000; Wolff et al., 1989; Huthwelker et al., 2001; Bartels-Rausch et al., 2004). Brine layers are conceptually distinct from the QLL, which can exist in the absence of impurities. However, with increasing impurity loading and at long times, the QLL may become indistinguishable from a brine layer. For example, McNeill et al. (2006, 2007) have shown experimentally that a disordered layer appears on pure single crystal ice samples at a temperature of $\sim -30\,°C$. When the ice sample is exposed to HCl in the gas phase, however, the presence of a disordered layer has been detected for temperatures as low as $-80\,°C$.

The QLL and BL are likely to influence snow and ice chemistry, but more data are necessary to quantify their effects in polar regions. The presence of the QLL has been shown to enhance the heterogeneous reaction of HCl with $ClONO_2$ on ice, as well as the uptake of CH_3COOH and HCl (for ice with crystal domains on the order of $1\,cm$) (McNeill et al., 2006). In addition to this the presence of the QLL has been shown to enhance the photochemical quantum yields of NO_3^- in ice (Dubowski et al., 2002). Field and laboratory evidence also suggests that the QLL and BL are likely to enhance the uptake of HOOH (Clegg and Abbatt, 2001; Conklin et al., 1993), HCHO (Hutterli et al., 1999; Winkler et al., 2002; Couch et al., 2000; Grannas et al., 2002), HONO (Chu et al., 2000), acetone (Journet et al., 2005), and ethanol (Kerbrat et al., 2007). Freeze concentration can create pH changes in the BL and accelerate aqueous chemistry (Takenaka and Bandow, 2007; Takenaka et al., 1992, 1996; Grannas et al., 2007b).

In this study we present a unified model for describing liquid-like layers on ice under environmentally relevant conditions spanning the QLL and BL regimes. We couple a thermodynamic model for solute-containing systems with a semi-empirical model of the QLL on pure ice. This model is then compared to experimental data from the

literature, and we demonstrate its applicability for a range of temperatures and solute compositions encountered in the environment.

2   Modeling the brine layer

Surface brine layers on sea ice have been known to be chemically important and many
5 studies have been done to probe the freeze concentrations of frozen brines (Conklin and Bales, 1993; Foster et al., 2001; Michalowski et al., 2000; Cho et al., 2002). Cho et al. (2002) derived a thermodynamic model to predict the fraction of liquid water in the surface brine layer formed upon freezing of a salt-containing solution, assuming low solute concentratoin. Here we present a model which is also valid for higher solute
10 concentrations which may be encountered in the BL, and apply the model to predict the thickness of the brine layer.

Brine layer thickness, d_{BL}, can be calculated knowing the fraction of liquid water in each phase:

$$d_{BL} = \frac{x_w}{x_{w,0}} \frac{(1-x_{w,0})}{(1-x_w)} \left(\frac{\rho_w}{\rho_{ice}}\right) \left(\frac{A}{V}\right)^{-1} \tag{1}$$

15 where ρ is the density of each phase, A/V is the surface area to volume ratio for the ice sample, and $x_{w,0}$ is the mole fraction of water in the unfrozen solution. In an extended system such as a slab of sea ice, A/V could include the air-ice interface, the seawater-ice interface, and area of grain boundaries per control volume. The mole fraction of water in the liquid interfacial layer(s), x_w, can be derived based on a thermodynamic
20 model of the ice-brine equilibrium:

$$x_w = x_{w,0} \exp\left[-\frac{\Delta H_w^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \tag{2}$$

Derivations of Eqs. (1) and (2) are provided in the Supporting Information.

Cho et al. (2002) used NMR to study freeze concentration in aqueous NaCl solutions and seawater for $-44\,°C < T < 0\,°C$. Figure 1 compares our model results to the experimental data of Cho et al. (2002) as well as the thermodynamic model presented by them which assumes low solute concentration.

Unlike brine layers, the QLL can exist on ice in the absence of impurities and is not described by equilibrium thermodynamics. The model described by Eqs. (1) and (2) yields a liquid layer thickness of zero at zero impurity concentration (even at temperatures close to the melting point) and therefore will not predict the presence of the QLL on pure ice in the absence of solute. We derive a semi-empirical approach for modeling the QLL on pure ice in Sect. 3, and in Sect. 4 we combine these approaches to form a unified model of liquid-like layers on ice in the environment for a wide range of solute concentrations and temperatures.

In the following paragraphs we demonstrate that a liquid-like layer on initially pure ice may be described well by Eqs. (1) and (2) when sufficient gas-phase impurities exist, as would occur in a typical laboratory trace gas uptake experiment. For example, in the experiments of McNeill et al. (2006), clean, single crystalline ice samples were exposed to gas-phase HCl under conditions relevant to the stratosphere and upper troposphere (5×10^{-8} to 10^{-4} Torr HCl and 186 to 223 K). HCl uptake was monitored using chemical ionization mass spectrometry, and induction of a liquid-like layer was observed under a subset of conditions using ellipsometry. The experimental results from the ellipsometry experiments of McNeill et al. (2006) are summarized in Fig. 2. Our calculations demonstrate that the temperature and HCl partial pressure dependence of HCl-induced QLL formation as observed by McNeill et al. (2006) is reflected by predictions for this system made using Eqs. (1) and (2) (see Figs. 2 and 3). A 1 cm^3 cube of single-crystalline ice with a QLL on one face was assumed, with a solubility for HCl in the interfacial layer of 9.3×10^{-5} mol HCl cm^{-3}, as measured by McNeill et al. (2007). Although the HCl solubility is higher in the interfacial layer than in bulk ice, due to its small volume, the major contribution of the total solute concentration $x_{w,0}$ came from the solubility of HCl in bulk ice, which, following Thibert and Domine (1997)

increases with decreasing temperature as shown in Eq. (3), where X_{HCl} is the solubility in mole fraction, P_{HCl} is the partial pressure of HCl in Pa, and T is the temperature in K.

$$X_{HCl} = 6.13 \times 10^{-10} \exp(2806.5/T)(P_{HCl})^{1/1.73} \tag{3}$$

In Fig. 2, the model curves were produced using Eqs. (1) and (2) and assuming a limit of detection for the ellipsometer of 80 nm. Liquid layer depth was solved for iteratively as a function of P_{HCl}. The model reproduces the pattern of QLL induction observed by McNeill et al. (2006) well. The model of Cho et al. (2002) also roughly reflects this pattern, but our model results in better agreement at low temperatures, where interfacial layer thickness is small, and thus solute concentration in the layer is high. The apparent applicability of these models, which were developed for frozen aqueous solutions, to pure ice in the presence of trace amounts of HCl in the gas phase (i.e. a system with low total solute content) supports the use of a unified model for treatment of interfacial layers in environmental systems at a range of conditions.

3 Modeling the QLL

The QLL has been characterized on hexagonal ice by a variety of experimental and theoretical techniques, all of which show that it is present below the bulk melting temperature, and that its thickness increases with increasing temperature (Petrenko and Whitworth, 1999; Dash et al., 1995; Demirdjian et al., 2002; Mizuno and Hanafusa, 1987; Dosch et al., 1996; Bluhm et al., 2002; Furukawa et al., 1987; Beaglehole and Nason, 1980; Sadtchenko and Ewing, 2002; Doppenschmidt and Butt, 2000; Golecki and Jaccard, 1978; Toubin et al., 2001; Pittenger et al., 2001; Mazzega et al., 1976; Gilpin, 1980; Henson et al., 2004; Wettlaufer, 1999; Wei et al., 2002; Henson and Robinson, 2004; Hosler et al., 1957; Keyser and Leu, 1993). A summary of measured QLL thickness as a function of temperature from six experimental studies is presented in Fig. 4 (Bluhm et al., 2002; Doppenschmidt and Butt, 2000; Dosch et al., 1996; Mazzega et al., 1976; Pittenger et al., 2001; Sadtchenko and Ewing, 2002). Reported

values of the QLL onset temperature as well as its measured thickness and its temperature dependence vary widely (Petrenko and Whitworth, 1999; Dash et al., 1995; Demirdjian et al., 2002; Mizuno and Hanafusa, 1987; Dosch et al., 1996; Bluhm et al., 2002; Furukawa et al., 1987; Beaglehole and Nason, 1980; Sadtchenko and Ewing, 2002; Doppenschmidt and Butt, 2000; Golecki and Jaccard, 1978; Toubin et al., 2001; Pittenger et al., 2001; Mazzega et al., 1976; Gilpin, 1980; Henson et al., 2004; Wettlaufer, 1999; Wei et al., 2002; Henson and Robinson, 2004; Hosler et al., 1957; Keyser and Leu, 1993). Possible sources of discrepancy include the ice sample preparation method or whether the ice sample is at equilibrium with water vapor or evaporating. Furthermore, the techniques used vary in sensitivity to surface properties, and each inherently uses a different definition of "disorder".

A variety of theoretical models of the QLL on pure ice exist in the literature (Ryzhkin and Petrenko, 2002; Petrenko and Whitworth, 1999; Dash et al., 1995; Wettlaufer, 1999; Bluhm et al., 2002). The QLL has been modeled by methods of statistical mechanics, using the assumption that near-surface water molecules are oriented such that the free energy of the system is at a minimum (Wettlaufer, 1999; Dash et al., 1995). An intermolecular potential function must be postulated in order to compute the energy of the system. Several forms of the intermolecular potential have been proposed for both long-range (electrostatic and van der Waals) and short-range interactions (Wettlaufer, 1999; Dash et al., 1995). Based on these assumed potentials, various QLL thickness versus temperature relationships have been derived. The general functional forms, expressed in terms of the deviation from the bulk melting temperature, T_m, are listed in Table 1. These functional forms were compared to experimental data from the literature with the goal of developing a semi-empirical model. Experimental data of QLL thickness at various temperatures from the literature were recast in each of the forms listed in Table 1, linear plots were made for each dataset, and the corresponding linear fit parameters and correlation coefficients (R^2) were calculated.

Due to the great variability in the experimental data found in the literature (see Fig. 4), no single set of fit parameters is equally applicable to all datasets. Therefore, we have calculated the fit parameters by taking an R^2-weighted average of the slopes and intercepts obtained from all of the datasets considered. Using the inverse square root form as an example, we produced scattered plots of thickness vs. $(T_m - T)^{-1/2}$ and calculated linear fit parameters for each data set. From each linear fit we obtained a slope, an intercept, and a correlation coefficient (R^2). If the slope, intercept and R^2 values are 20, −4, and 0.8 for a hypothetical dataset A and 18, −6, and 0.9 for dataset B, the R^2-weighted average slope will be $(20 \times 0.8 + 18 \times 0.9)/(0.8 + 0.9) = 18.94$. In this manner, the following semi-empirical relationships were obtained:

Logarithmic dependence
$$d_{QLL,ln} = 4.8669 \left| \ln\left(\frac{T_m - T}{T_m}\right) \right| - 12.967 \quad (4)$$

Inverse square root dependence
$$d_{QLL,-1/2} = 20.401(T_m - T)^{-1/2} - 3.3114 \quad (5)$$

Inverse cube root dependence
$$d_{QLL,-1/3} = 24.017(T_m - T)^{-1/3} - 4.9733 \quad (6)$$

In Eqs. (4)–(6), thickness is in nm and temperature is in K. The subscripts on d_{QLL} denote the functional forms. All three models are plotted along with experimental data in Fig. 4. A table listing all the fit parameters for each experimental data set is provided in the Supporting Information.

Despite the scatter in experimental data, the general trend is that the QLL grows as the temperature approaches T_m and that the onset of surface disorder occurs near −30 °C. While all three models above exhibit the correct trend with respect to temperature, the inverse square root relationship ($d_{QLL,-1/2}$) yields a QLL onset temperature closest to observation. According to the $d_{QLL,-1/2}$ model, QLL onset occurs at −38 °C. We will incorporate the $d_{QLL,-1/2}$ model into the unified model to be presented in the next section.

Henson an coworkers recently proposed a theoretical model to predict the QLL thickness (Henson et al., 2005; Voss et al., 2005). Their model shows fair agreement with

a subset of experimental data available in the literature, but the agreement only holds well at temperatures close to the bulk melting point. Therefore their model was not considered further in the current study. For comparison, the model of Henson et al. is plotted in Fig. 4 as d_{Henson}.

Although pure ice is rarely encountered in the environment, laboratory studies investigating trace gas-ice interactions often make use of ice samples devoid of impurities. Therefore, in order to correctly interpret experimental data and make sensible assessments of their environmental implications, one must be able to predict the presence and thickness of a liquid-like layer under a given set of environmental conditions. In the next section, we introduce a model which can be used to predict the thickness of liquid-like layers on ice over the entire compositional range.

4 Modeling liquid-like layers on ice in the environment: combined model

Surface and bulk impurities are known to modulate the thickness of liquid-like layers on ice. Upon freezing of an aqueous solution (such as sea water), impurities are excluded from the ice matrix and segregated to the surface. Thus, where impurities exist, the degree of surface disorder can be expected to exceed that found on pure ice. It follows that at a given temperature, the thickness of a disordered surface layer is at a minimum when no impurities exist. In other words, in the limit of low impurity concentrations and temperatures approaching T_{m}, the predictions of the QLL model should be the lower bound of liquid layer thickness on the ice surface. In the presence of substantial amounts of impurities on the ice surface, however, the QLL model underestimates the thickness of the liquid-like layer. In order to predict the thickness of the liquid-like interfacial layer on ice over the full range of conditions found in the environment we have combined the BL and QLL models presented in Sects. 2 and 3. Based on the simple principle stated above, we proposed a unified model in which the predictions of liquid-like layer thickness calculated for a given set of conditions based on the two models are compared and the larger of the two takes precedence. To express the

unified model analytically, recall the QLL and the BL models above and let

$$d_{QLL} = d_{QLL,-1/2} = 20.401 (T_m - T)^{-1/2} - 3.3114,$$

where d_{QLL} is in nm and T and T_m are in K, and

$$d_{BL} = \frac{x_w}{x_{w,0}} \frac{(1 - x_{w,0})}{(1 - x_w)} \left(\frac{\rho_w}{\rho_{ice}} \right) \frac{V}{A}.$$

5 The unified model for predicting the thickness of the interfacial layer, d, can then be written as a conditional equation as follows:

$$d = \begin{cases} d_{QLL} & \text{if} \quad d_{QLL} \geq d_{BL} \\ d_{BL} & \text{if} \quad d_{QLL} < d_{BL} \end{cases} \tag{7}$$

This model is not limited to frozen solute-containing solutions; it can also be used to predict interfacial layer thickness induced by trace gases on the surface of pure ice.
10 Here we demonstrate the applicability of the model to the HNO_3-ice system and to frozen salt-containing solutions.

Nitric acid is known to have active roles in the heterogeneous chemistry of polar stratospheric clouds (PSC) and ozone destruction (Tisdale et al., 1999; Tolbert and Middlebrook, 1990). The photolysis of nitrate ions in the QLL or BL is also believed to
15 play a role in HONO and NO_x production in snow (Boxe et al., 2005; Boxe and Saiz-Lopez, 2008; Mack and Bolton, 1999). Figure 5 shows the application of the model to the HNO_3-ice system assuming initially solute-free ice at different HNO_3 partial pressures and a range of temperatures. The predicted interfacial layer thickness increases at high partial pressures of HNO_3. However, like the HCl-ice system described in
20 Sect. 2, the thickness of the liquid-like layer increases with decreasing temperatures due to increasing solubility of nitric acid in bulk ice at lower temperatures (Thibert and Domine, 1998). In the absence of experimental data regarding the solubility of HNO_3 in the QLL, and knowing that the solubility of HNO_3 in water is twice that of HCl (Thibert and Domine, 1998) we assume that the solubility of HNO_3 in the QLL is twice that of

HCl in the QLL. The solubility of HCl in QLL was measured by McNeill et al. (2007) to be 9.3×10^{-5} mol HCl cm^{-3}. At low partial pressures and higher temperatures, the interfacial layer thickness is dominated by the QLL model. For example, when 5×10^{-3} Torr of HNO$_3$ is present in the gas phase, the QBL model predicts a liquid layer thickness of 0.346 nm at $T = -10\,^{\circ}$C. At the same temperature, however, the QLL model predicts a thickness of 3.14 nm on pure ice. This nearly tenfold difference is potentially significant when modeling the uptake of HNO$_3$ onto ice surfaces. For instance, Kerbrat et al. (2007) showed that the uptake of ethanol on ice doped with HNO$_3$ is 60 times more than that on pure ice, which is probably due to the formation of a BL under their experimental conditions. Applying our BL model to their experimental conditions showed that the BL thickness ranged from 20–163 µm in their study.

The application of this model to frozen aqueous salt solutions shows a different profile for the predicted thickness of the brine layer as a function of temperature and salt concentration. Figure 6 shows the predicted thickness of different NaCl concentrations ranging from 4.5 µM (snow with marine influence) to 1.11 M (seawater) (Cho et al., 2002). The interfacial layer thickness increases with increasing salt concentrations and temperature and decreases at lower temperatures due to decreasing solubility of NaCl in ice at lower temperatures. The liquid-like layer thickness is primarily governed by the BL model.

The characterization of the thickness and volume of the brine layer is key to improving models of trace gas–ice interactions in snowpacks in close proximity to frozen marine areas. Boxe and Saiz-Lopez (2008) recently demonstrated the application of the model developed by Cho et al. (2002) to quantify the thickness of liquid-like layers on snowpack for use in a multiphase model to predict NO$_x$ volume fluxes in the Arctic and coastal Antarctica. In their study Boxe and Saiz-Lopez (2008) estimated the thickness of the interfacial layer assuming that the only impurities in the snowpack were NO$_3^-$ and NO$_2^-$. The presence of other impurities, whether dissolved in the interfacial layer or in the gas phase, could significantly impact the thickness of the liquid-like layer on ice and snow. Therefore, for accurate application of this model or that of Cho et al.

(2002) to environmental systems (especially in marine or coastal environments), all solutes present must be accounted for to the best of current knowledge.

5 Summary and outlook

The goal of this study was to develop a unified model for liquid-like layers on environ-
mental ice systems that is valid across the entire compositional range and for tem-
peratures relevant to the polar regions and the upper atmosphere. Our BL model is
an improvement upon an earlier model developed by Cho et al. (2002) and agrees
well with their experimental data using NMR to examine frozen sea water samples.
It also successfully modeled liquid layer thickness in a system with much lower to-
tal solute concentrations: the layer thickness calculated by our model compares well
to ellipsometry–CIMS data for HCl-induced surface disordering on pure ice (McNeill
et al., 2006). Since the QLL is not a thermodynamically allowed phase, it cannot be
modeled using equilibrium thermodynamics. It was found that a semi-empirical model
with an inverse square root dependence on the departure from the melting temper-
ature best reproduced a collection of experimental observations from the literature.
Test case studies using the unified QLL-BL model showed that both model regimes
were necessary to model interfacial layer thickness in the case of initially pure ice in-
teracting with trace gases such as HCl and HNO_3, as would be typical in laboratory
studies of trace gas-ice interactions. The BL model applies at higher partial pressures
and lower temperatures, and the QLL model dominates at higher temperatures and
lower partial pressures. However, in the case of frozen salt solutions, the BL model
alone can be used to predict the layer thickness. This difference originates from the
temperature dependence of the solubility of these different solute types in bulk ice:
the solubility of nonvolatile solutes tends to decrease monotonically with temperature,
whereas the solubility of HCl and HNO_3 in ice increases with decreasing temperature
below a given threshold. This inverse temperature dependence also holds for HCHO,
another trace gas which plays a key role in the atmospheric chemistry of polar regions

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(Barret et al., 2010).

Trace gas uptake to snow has been represented variously in models as surface adsorption (Hutterli et al., 1999), incorporation into the bulk ice matrix via codeposition (McConnell et al., 1998) or uptake to a fractional liquid water volume within the snowpack meant to represent the QLL, having the properties of an aqueous system (Michalowski et al., 2000; Boxe and Saiz-Lopez, 2008; Liao and Tan, 2008). In the environment, the composition and properties of the air-ice interface are constantly changing. Our model, because it can be applied over a wide range of temperatures and compositions, can be used to describe this dynamically evolving interface.

The parameters used here to calculate the interfacial layer thickness in each test case were based on experimental data from the literature. However, many of the physical parameters of ice in complex environmental systems have yet to be quantified experimentally. For example, the solubility of key trace gases in ice and in the QLL and BL will need to be measured in order to accurately model not just the chemistry of the air-ice interface, but the thickness of the liquid-like layer. More laboratory studies of interfacial layer thickness as a function of temperature and impurity load for different solutes are needed. Finally, complete and precise knowledge of the level of impurities in environmental systems, a key variable for determining the thickness of the liquid-like layer at the air-ice interface, is often not available. This underscores the importance of measurements of snow/ice composition, morphology and air composition for understanding air-ice chemical interactions in polar regions.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/8145/2011/ acpd-11-8145-2011-supplement.pdf.

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Table 1. Functional forms for the intermolecular potentials used to derive the QLL thickness as a function of temperature.

Logarithmic dependence	$d \propto \lvert \ln(T_m - T) \rvert$	Short-range intermolecular forces (Dash et al., 1995)
Inverse square root dependence	$d \propto (T_m - T)^{-1/2}$	Electrostatic interactions (Wettlaufer, 1999)
Inverse cube root dependence	$d \propto (T_m - T)^{-1/3}$	Dispersive, van der Waals forces (Wettlaufer, 1999)
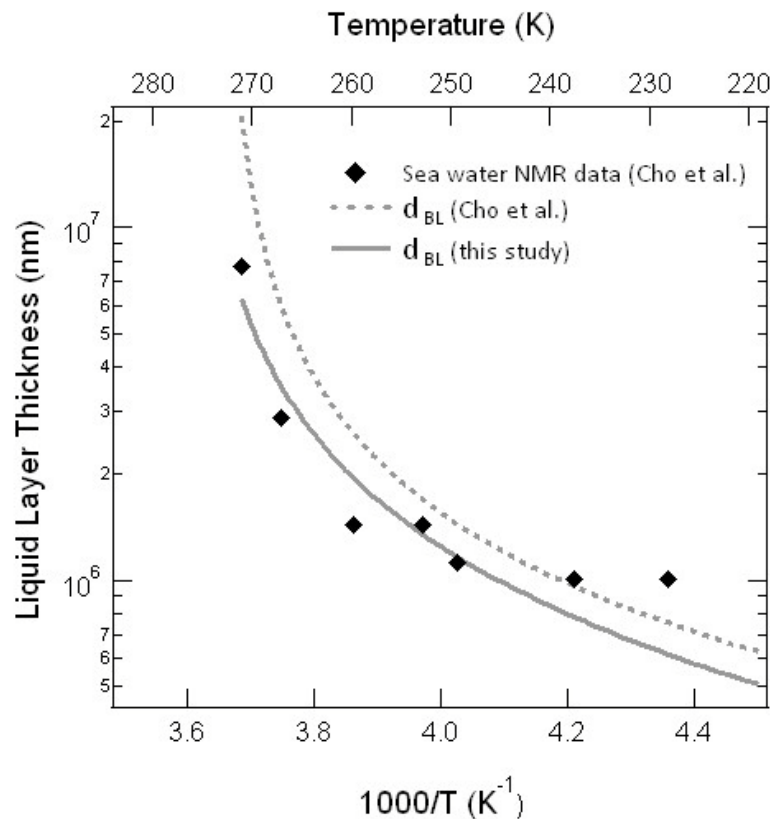
Fig. 1. Thickness of brine layer on frozen sea water extracted from NMR data by Cho et al. (2002) as a function of temperature. The dotted line represents the calculated thickness of the interfacial brine layer using Cho's model. The solid line represents the calculated thickness of the interfacial brine layer using the BL model in this study.

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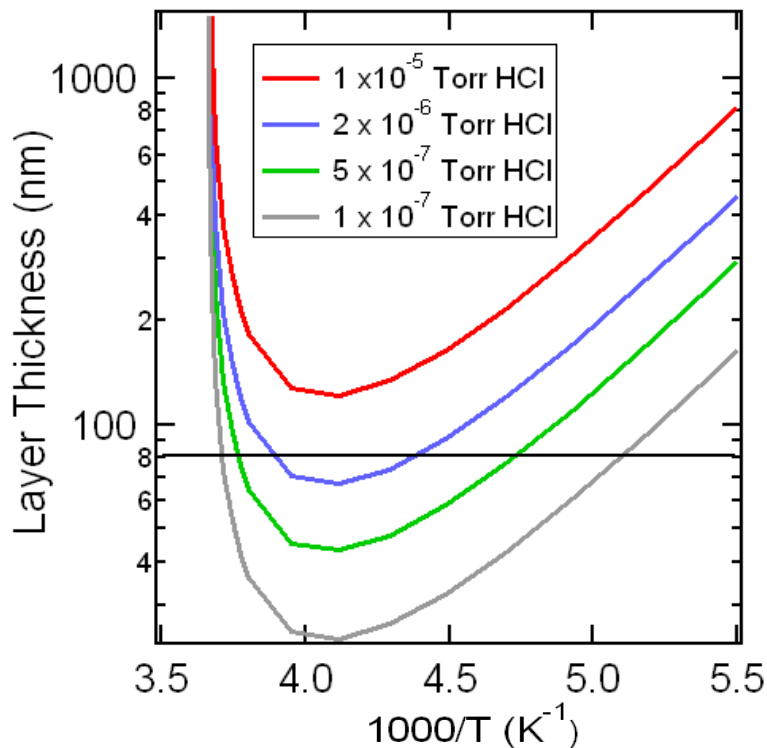
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Fig. 2. Predicted thickness of the HCl-induced QLL at different HCl partial pressures and a range of temperatures via Eq. (1). The black solid line represents the detection limit of the ellipsometer at 80 nm.
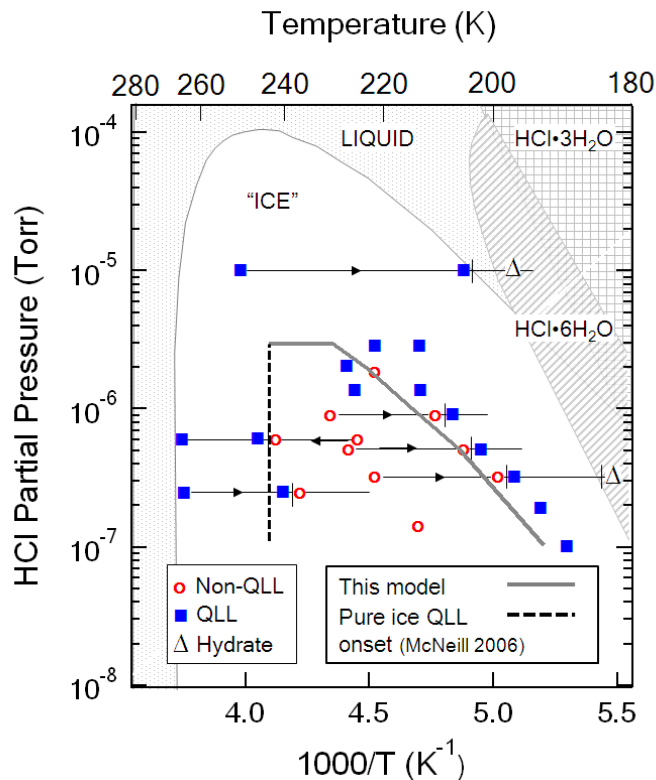
Fig. 3. Ellipsometer-CIMS study results summarized on the HCl–ice phase diagram adapted from McNeill et al. (2006). Squares indicate conditions where a change in signal consistent with formation of a disordered surface layer was observed, and circles indicate no surface change. Phase transitions are indicated by open triangles. The dotted line represents the onset temperature of the QLL formation shown by McNeill et al. (2006). The solid grey line represents the conditions at which the HCl-induced QLL formation can be detected by the ellipsometer assuming a 80 nm detection limit.

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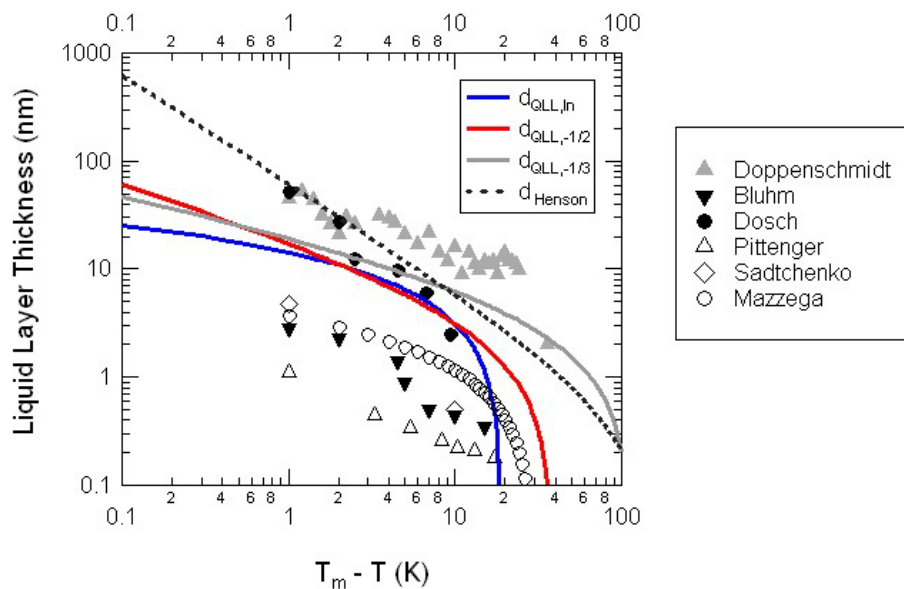
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Fig. 4. Literature summary showing QLL thickness on pure ice as a function of temperature below the melting point (0 °C). Data shown are from: Bluhm et al. (2002); Doppenschmidt and Butt (2000); Dosch et al. (1996); Mazzega et al. (1976); Pittenger et al. (2001); Sadtchenko and Ewing (2002). The $d_{QLL, \ln}$, $d_{QLL, -1/2}$ and $d_{QLL, -1/3}$ represent the semi-empirical models to fit the experimental QLL thickness on pure ice. The curve labeled d_{Henson} is the model proposed by Henson et al. (2005).

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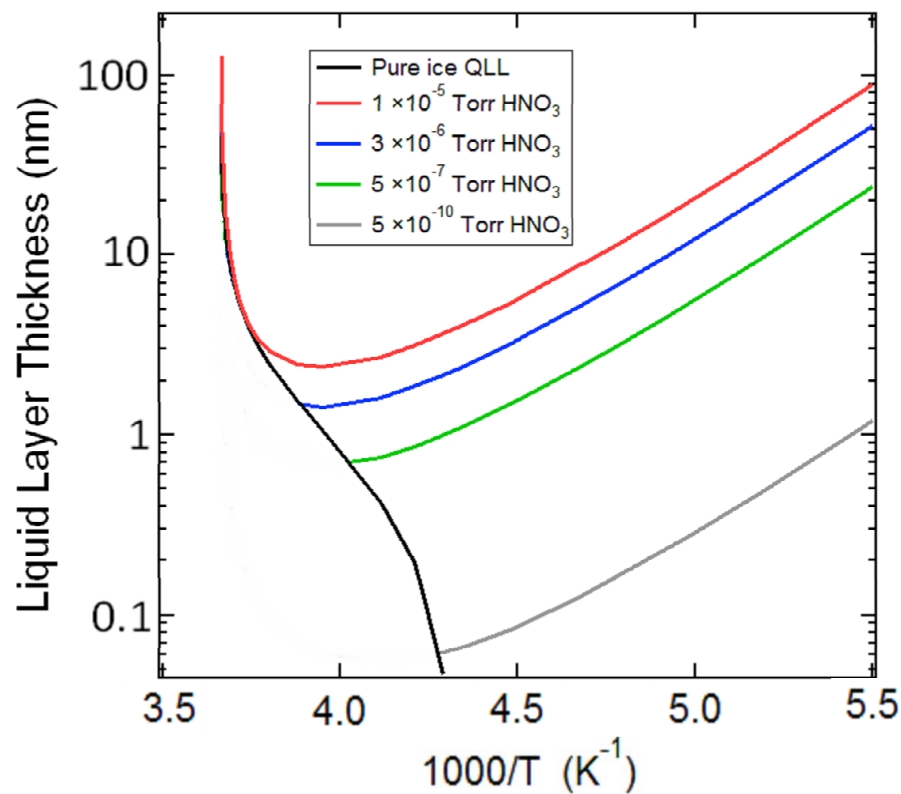Printer-friendly Version

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Fig. 5. Calculated interfacial layer thickness at different HNO_3 partial pressures and a range of temperatures. The black solid line represents the thickness of the QLL on pure ice in the absence of impurities calculated using the QLL model.

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Fig. 6. Calculated thickness of the brine layer at different NaCl concentrations and a range of temperatures. The black solid line represents the thickness of the QLL on pure ice in the absence of impurities calculated using the QLL model.
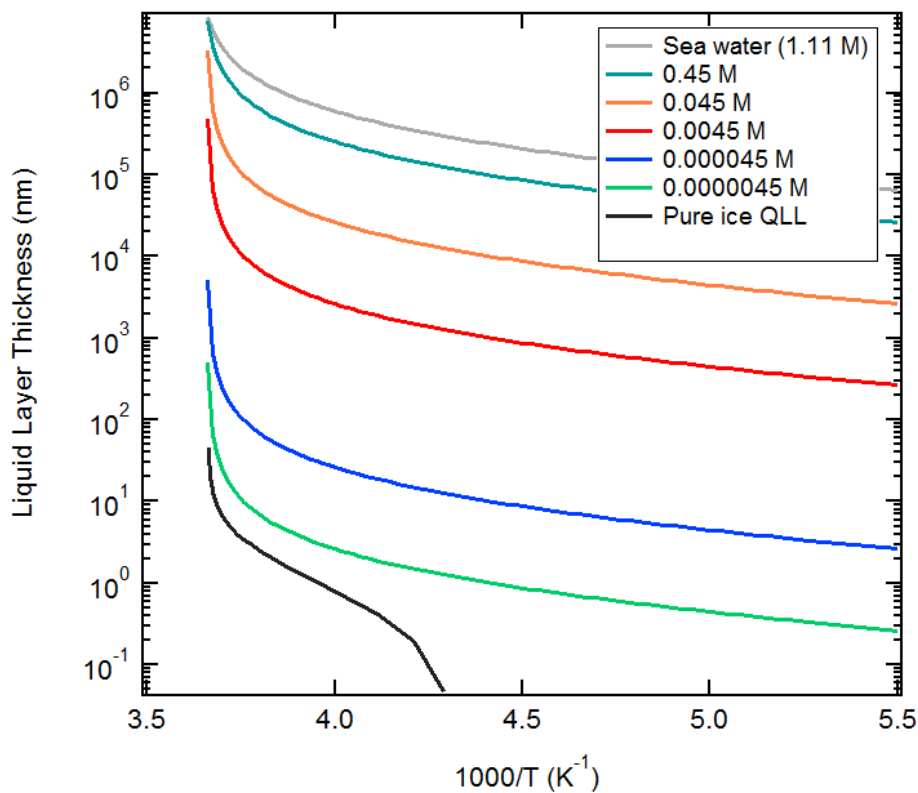
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