Mechanism of charge transfer between colliding ice particles in thunderstorms

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Abstract. We derive a theoretical mechanism for the charge transfer between colliding ice and soft hail particles, based on current ideas of surface melting. According to this theory, each of the ice surfaces is covered with a film of quasi-liquid water, whose thickness can be estimated as a function of temperature and local curvature. We show that during contact of two particles, fluid will flow from the thicker to the thinner layer, and we estimate the volume transferred in atmospherically relevant situations. We postulate a charge structure within the surface-melted layer based on observations on similar systems and show that this leads to estimated charge transfers consistent in approximate magnitude and sign with trends observed in the laboratory.

1. Introduction

Many laboratory studies [*Takahashi*, 1978; *Gaskell and Illingworth*, 1980; *Jayaratne et al.*, 1983; *Baker et al.*, 1987; *Keith and Saunders*, 1989, 1990; *Caranti et al.*, 1991] have shown that under some circumstances similar to those inside thunderclouds, originally uncharged ice particles can acquire substantial electrical charge in the absence of external electrical fields.

The laboratory experiments have been of several types, and the interpretations of the results have varied widely. The experiments in some cases involved stationary ice-covered targets bombarded with ice or sand, in some cases targets moving through laboratory clouds of ice crystals and supercooled drops. *Baker et al.* [1987] studied charge transfer to a rimed rod moving through a cloud in which liquid water, temperature, and the characteristics of the collisions were varied over ranges thought to be characteristic of the charging zone in thunderstorms. Their findings can be summarized as follows: (1) Significant charge transfer (over 10^{-15} C/collision) occurs during rebounding collisions between ice crystals and soft hail when there are supercooled drops present in the cloud. (2) Significant charge transfer occurs only when both particles are growing from the vapor. (3) The charge transferred to the riming surface tends to be positive at higher temperatures and higher liquid water contents and negative at lower temperatures and lower liquid water contents.

The authors suggest, on the basis of these results, that the sign of the charge transfer depends on the relative vapor growth rates of the colliding particles; the particle growing fastest via vapor deposition appears to acquire positive charge during the rebounding collisions. Subsequent experiments by other groups have, to some extent, quantified the trends summarized here and have slightly altered the last

conclusion, but the overall nature of these results has been confirmed in all cases.

All the laboratory experiments, which we collectively refer to as simulations, were carried out in room air under conditions that did not permit direct, microscopic observations of the small-scale surface character at the point of collision or fracture. Thus there is considerable ambiguity in definition of the thermodynamic and chemical state of the "active" surface, that tiny part of the particle surface actually responsible for its acquisition of net charge. Since riming appears to play an important role in charging, most of the simulations have been carried out as the ice surface is riming and thus may in part be sublimating, in part growing from the vapor, in part wet, and in part dry. It is therefore necessary to make assumptions about temperature and supersaturation gradients in and near the active surface during the tenth of a microsecond or so [*Buser and Aufdermaur*, 1977] during which charge separation occurs.

The mechanism, or set of physical processes producing the observed charge transfer, is not understood despite a great number of candidate mechanisms that have been proposed in the recent literature. Because of the wide variety of experimental conditions and types of simulations performed, it is not clear that the charging observed is always due to the same microscopic phenomenon.

2. Theory of Charging

We define the requirements for a satisfactory model of the charge transfer mechanism as a set of detailed answers, based on the known physics of ice and ice-vapor interfaces, to the following three questions: (1) What are the charge carriers? (2) What drives the flow of charge? (3) What are the explanations for the observed correlations between charging and cloud chamber conditions in the laboratory simulations?

A large number of mechanism studies have focused on question 3, and the mechanisms derived consist of sets of processes which might give the inferred correlations between charge transfer characteristics and cloud chamber

properties. This has often required invocation of two or more different mechanisms to describe the charging in different thermodynamic parameter regimes. In view of the uncertainties in definition of the chemical and electrical properties of the environment and the state of the active surface and in view of the large number of uncontrolled parameters in the simulations we propose instead to focus on questions 1 and 2. We suggest a mechanism for charging during collisions of ice particles, in pure vapor environments, based on established properties of ice surfaces. While eventually a successful theory must also provide answers to question 3, we argue that it is useful to begin by a consideration of the known surface properties of ice under controlled conditions. This model is not complete; there are many unanswered questions and unknown parameters in it. However, the advantage of starting from the simplest system, in which the number of variables is a minimum, is that we can pinpoint precisely what experiments are needed to test the theory and to extend it, in a systematic way, as the restrictive conditions under which it is formulated are progressively relaxed to approach that most complex of all environments, the natural atmosphere.

2.1. Surface Melting

Theoretical and experimental studies have established that for many materials at equilibrium at a range of temperatures below the bulk melting point a clean solid-vapor interface is covered by a disordered, or quasi-liquid layer (QLL). The layer wets the solid-vapor interface in the case that the vapor-QLL-solid system has lower free energy than the vapor-solid system. The existence of a QLL on ice was first suggested by *Faraday* [1860] and has subsequently been found by a variety of techniques for a range of temperatures possibly extending down to −30°C for ice in contact with pure vapor, atmospheric gases [*Golecki and Jaccard*, 1978; *Beaglehole and Nason*, 1980; *Furukawa et al.*, 1987; *Elbaum et al.*, 1992], or foreign solid walls [*Maruyama et al.*, 1992; *Kuroda and Lacmann.*, 1982; *Mizuno and Hanafusa*, 1987]. In the asymptotic limit of a very thick layer the properties of the QLL are those of a layer of bulk water, but the QLL becomes appreciably different as the thickness is reduced below 10 or so molecular layers. For a review of this subject, see, for example, *Dash* [1989].

Our charge transfer model, i.e., the answers to questions 1, 2, and 3 presented in our introduction, is based on the assumption that both of the colliding particles are covered by QLLs. We summarize the model here and support it via a brief review of the relevant physics of surface melting. Finally, we suggest experiments needed to test this model.

1. What are the charge carriers? In the case where there are no trace contaminants, these are disassociated hydronium and hydroxyl ions in the QLL. If there are dissolved impurities, there may be additional ionic charge carriers. The charge distribution inside the QLL is not uniform, because of preferential adsorption effects at both the solid-liquid and the liquid-vapor interfaces.

2. What drives the flow of charge during collisions? The charging of an ice particle in a pure vapor environment occurs when it loses or gains QLL fluid carrying net charge, i.e., the charge separation process is associated with a mass transfer process occurring (1) during collisions, when mass flows from one particle to another or (2) during fracture, as part of an ice particle breaks off. The direction of mass flow

and hence the polarity of the ensuing charge flow is determined by differences in the chemical potentials (Gibbs free energies per molecule) of the separating particles.

3. Why is charge transfer correlated with environmental thermodynamic conditions? The chemical potential inside the QLL in a given location depends on the local surface curvature and the local thermodynamic conditions; thus the mass flow direction and hence also the direction of charge flow also depend on local conditions. (In equilibrium, as we recall below, the chemical potential is everywhere constant.)

In the next paragraphs we justify and expand on these statements by means of a brief discussion of surface melting as it is currently understood [*Dash*, 1990; *Löwen*, 1989].

The theory rests on consideration of G, the Gibbs free energy of a system consisting of ice in contact with vapor. Let γ_{sl} and γ_{lv} be the equilibrium surface free energies per unit area of the solid-liquid and liquid-vapor interfaces, respectively. After equilibrium is established on a freshly cleaved surface, the surface is covered by a QLL. Let N_s, N_{QLL}, and N_v be the number of molecules in the solid, in the QLL, and in the vapor, and let μ_s, μ_{QLL}, and μ_v be the corresponding chemical potentials. The Gibbs free energy of the system is

$$G = \mu_s N_s + \mu_{QLL} N_{QLL} + \mu_v N_v + A\gamma_{sv}(h) \qquad (1)$$

where A is the area and $\gamma_{sv}(h)$ is the equilibrium surface free energy of the ice-vapor interface, a function of the QLL thickness, h; $\gamma_{sv}(h)$ has the following limiting properties:

$$\gamma_{sv}(h) \rightarrow \gamma_{lv} + \gamma_{ls} \quad as \quad h \rightarrow \infty \qquad (2a)$$

$$\gamma_{sv}(h) \rightarrow \gamma^*_{sv} \quad as \quad h \rightarrow 0 \qquad (2b)$$

where γ^*_{sv} is the effective coefficient of the dry solid-vapor interface, without a liquid layer. It is assumed to be independent of T and p over the range of surface melting. We write $\gamma_{sv}(h)$ in the following functional form, which satisfies (2a) and (2b):

$$\gamma_{sv}(h) = \gamma^*_{sv} + (\gamma_{ls} + \gamma_{lv} - \gamma^*_{sv})f(h) = \gamma^*_{sv} + \Delta\gamma f(h).$$

$$\qquad (3)$$

$f(h) \rightarrow 0$ for $h \rightarrow 0$ and $f(h) \rightarrow 1$ as h gets large. The exact form of $f(h)$ depends on the intermolecular forces assumed to predominate in the system; if these are van der Waals,

$$f(h) = 1 - \frac{a_0^2}{h^2}; \qquad \frac{df(h)}{dh} = \frac{2a_0^2}{h^3} \qquad (4)$$

where a_0 is of the order of an intermolecular spacing. For all realistic force laws, $df(h)/dh$ increases as h decreases. In the limit of very thick layers the QLL has the properties of bulk liquid water and $\mu_{QLL} \rightarrow \mu_L$, the chemical potential of bulk water. The number of molecules in the QLL is

$$N_{QLL} \rightarrow A\rho_N h \qquad (5)$$

where ρ_N is the molecular number density of bulk water. We therefore approximate the Gibbs free energy for our system for all h as follows:

$$G = N_s\mu_s + A\rho_N\mu_L h + N_v\mu_v + A\gamma^*_{sv} + A\Delta\gamma f(h) \qquad (6)$$

where we have assumed all interfaces are flat.

At equilibrium, G is a minimum with respect to transformations at constant temperature and pressure, such as transfer of a few molecules from one part of the system to another. Therefore we have that

$$\frac{\partial G}{\partial N_{QLL}} = 0 \qquad (7)$$

We now use (7) to find the equilibrium properties of the QLL.

2.1.1.   *Flat interfaces.*   Let us consider the case

$$N_s \rightarrow N_s - \delta N_{QLL}; \qquad N_{QLL} \rightarrow N_{QLL} + \delta N_{QLL}$$

We find, using (5) and (6), that

$$\frac{\partial G}{\partial N_{QLL}} = 0 = \mu_L - \mu_s + A \frac{\partial \gamma_i}{\partial N_{QLL}} = \Delta\mu + \frac{\Delta\gamma}{\rho_N} \frac{df(h)}{dh}, \qquad (8)$$

where $\Delta\mu \equiv \mu_L - \mu_s$. At temperatures $T < T_0$, $\mu_L > \mu_s$; thus the first term on the right-hand side of (8) increases G. This thermodynamic "price" to pay in thickening the layer is just redeemed at equilibrium by the diminution of the surface free energy, as represented by the second term.

At pressure p and temperature T not too far from the triple point $(T_0 p_0)$, we have

$$\Delta\mu(T, p) = \Delta\mu(T_0, p_0) + \frac{\partial \Delta\mu}{\partial T} \Delta T + \frac{\partial \Delta\mu}{\partial p} \Delta p \qquad (9)$$

where $\Delta T \equiv T - T_0$, $\Delta p \equiv p - p_0$. The first term in (9) is zero, so that (8) becomes

$$\frac{\partial G}{\partial N_{QLL}} = 0 = \frac{\partial \Delta\mu}{\partial T} \Delta T + \frac{\partial \Delta\mu}{\partial p} \Delta p + \frac{\Delta\gamma}{\rho_N} \frac{df(h)}{dh}. \qquad (10)$$

In the limiting case where h diverges, the last term is zero and we recover the Clausius Clapeyron equation:

$$\frac{\Delta p}{\Delta T_{eq}} \text{ (solid-liquid)} = -\frac{\frac{\partial \Delta\mu}{\partial T}}{\frac{\partial \Delta\mu}{\partial p}} = \frac{l_f}{T_0 \Delta v_m} \qquad (11)$$

where δv_m is the difference in molecular volume in the two phases and l_f is the latent heat of fusion per molecule.

In the case of interest, h becomes small, $df(h)/dh$ becomes large, and (as implied by the Clausius Clapeyron equation) the term in Δp on the RHS of (10) becomes very small for relevant values of ΔT. Dropping this term (which changes our answer by approximately a few parts in 10^6 [*Dash*, 1991]), we have in equilibrium that

$$\frac{df(h)}{dh} = \frac{l_f \Delta T \rho_N}{\Delta\gamma T_0} \qquad (12)$$

Since the LHS of this equation is positive and ΔT is negative, the QLL forms only on surfaces for which $\Delta\gamma \leq 0$. This is the classical condition that the surface be "wettable" by its own liquid, i.e., that a drop of the liquid placed on the surface spreads out to form a layer. It was suggested many years ago [*Ketcham and Hobbs*, 1969; *Knight*, 1971] that ice does not form a QLL because experiments at temperatures just below the triple point showed that a drop of water placed

on an ice surface did not spread out but rather maintained a small but finite contact angle. However, recent experimental [*Elbaum et al.*, 1992] and theoretical work [*Elbaum and Schick*, 1991] shows that ice differs from all other surfaces studied to date in that it is incompletely wet by its melt liquid; $\Delta\gamma$ is negative for small values of h and then becomes positive, so that formation of a thin QLL is thermodynamically favored at a range of temperatures, but the QLL on ice cannot grow beyond a certain thickness. After this limiting thickness is reached, additional fluid placed on the surface will not spread out to form a layer but will (as in the experiments of *Ketcham and Hobbs* [1969] and *Knight* [1971]) remain in the form of drops.

From (8), at equilibrium,

$$\mu_s = \mu_L + \frac{\Delta\gamma}{\rho_N} \frac{\partial f(h)}{\partial h} \equiv \mu_{QLL}(h). \qquad (13)$$

If we now set equal to 0 the change in G accompanying the transfer of a few molecules from the QLL to the vapor, we find that in equilibrium

$$\mu_{QLL}(h) = \mu_L + \frac{\Delta\gamma}{\rho_N} \frac{df(h)}{dh} = \mu_v \qquad (14)$$

so for the equilibrium system, if the vapor-ice interface is flat,

$$\mu_s = \mu_{QLL}(h) = \mu_v \qquad (15)$$

We can approximate the chemical potentials in the usual way

$$\mu_s(T) = kT \ln (e_{sat}^{ice}(T)) + \mu_0(T);$$

$$\mu_L(T) = kT \ln (e_{sat}^{liquid}(T)) + \mu_0(T); \qquad (16)$$

$$\mu_v = kT \ln (e) + \mu_0(T).$$

where e is the vapor pressure in the environment. The notations $e_{sat}^{ice}(T)$, $e_{sat}^{liquid}(T)$ refer to the equilibrium vapor pressures over bulk, planar surfaces of ice and liquid water and, of course, reduce to the same value at $T = T_0$.

Inserting these expressions for the chemical potentials and the appropriate expression for $f(h)$ in (15) yields the equilibrium value of h at equilibrium. For van der Waals forces we have

$$h(eq) \equiv h_0 = \left[\frac{-2\Delta\gamma a_0^2}{\rho_N \Delta\mu} \right]^{1/3} = \left(\frac{2a_0^2 \Delta\gamma T_0}{\rho_L l_f \Delta T} \right)^{1/3} \qquad (17)$$

We find that at equilibrium over a flat surface,

$$\ln (e) = \ln (e_{sat}^{ice}(T)) = \ln (e_{sat}^{liquid}(T)) + \frac{\Delta\gamma}{kT\rho_N} \frac{df(h)}{dh} \qquad (18)$$

Thus in equilibrium in the presence of flat interfaces the vapor pressure over the system (ice + QLL) is that predicted by the Clausius Clapeyron equation at the flat ice-vapor interface and less than that over a flat bulk liquid water surface. As the temperature increases and the equilibrium value of h increases, the magnitude of the (negative) surface term in (13) and (14) decreases and the equilibrium vapor pressure over the system approaches that predicted by the Clausius Clapeyron equation for a flat liquid water surface, reaching it only at the triple point.

2.1.2. *Effect of surface curvature.* We consider now the formation of the QLL on a curved surface. For simplicity, consider the case that the ice particle is a sphere of radius R. By algebra exactly analogous to that above, we can show that in equilibrium, assuming $h/R \ll 1$ [*Baker and Dash*, 1989, equation (4)] (however, note a misprint in (1), where the minus sign should be a plus).

$$\mu_s + \frac{2\gamma_{ls}f(h)}{\rho_N R} = \mu_L + \frac{\Delta\gamma}{\rho_N}\frac{df(h)}{dh} - \frac{\gamma_{sv}(1-f(h))}{\rho_N R} \quad (19)$$

For $h \to \infty$, we recover the usual formula for the depression of the freezing point of pure water on a curved surface:

$$\delta T = -\frac{2\gamma_{ls}T_0}{l_f\rho_N R} \quad (20)$$

For

$$\gamma_{ls} \approx .03 (\text{J m}^{-2}), \qquad l_f\rho_N = 3.3 \times 10^8 (\text{J m}^{-3})$$

and $R = 10 \ \mu\text{m}$, $\delta T = -0.003$ K, small enough that we do not have to include this factor in the following argument. However, curvature effects may be very important on surfaces covered with frost or rime-induced hillocks or pits.

We now consider the liquid-vapor equilibrium and find that the equilibrium vapor pressure over the system is given by the equation

$$\mu_v = \mu_s + \frac{2\gamma_{sv}(h)}{\rho_N R} \quad (21)$$

or

$$\ln e = \ln e_{\text{sat}}^{\text{ice}}(T) + \frac{2\gamma_{sv}(h)}{kT\rho_N R} \quad (22)$$

Thus the equilibrium vapor pressure over the system now depends on R and h as well as T. The second term on the RHS of (21) is the familiar Kelvin term. The equilibrium value of the layer thickness is (to first order in h/R)

$$h_{eq}(R) = h_0(1 + 2\gamma_{ls}/3\rho_N\Delta\mu R) \quad (23)$$

As the radius of curvature decreases, the equilibrium vapor pressure increases, the equilibrium QLL thickness increases, and μ_{QLL} increases.

2.2. Mass Transfer

We consider the approach of two particles having different chemical potentials, due to a combination of temperature and curvature effects, manifested in different vapor pressures and different QLL thicknesses. As the particles near each other, there will be a net flow of vapor tending to reduce the difference in chemical potentials, i.e., flow from the thicker to the thinner film. When the particles make contact, the liquid layers merge, rapidly equilibrating any remaining difference in the chemical potentials. Then, as the particles move away from each other, the bridging liquid narrows and breaks, leaving a fraction of the combined thickness on each particle. We expect that the fractions are subject to some statistical variation, as they depend on many parameters of the dynamical process. The average, however, should be close to an equal sharing of the merged thickness. By this argument the predicted mass transfer

tends to be from the particles with locally warmer and/or higher curvature surfaces, amounting on average to one half of the difference in the QLL quantities on the contacting surfaces.

For estimates of magnitudes we assume a collision involving contacting surfaces of radii r_1 and r_2, $r_1 \ll r_2$, bearing QLLs of thickness h_1 and h_2.

We can use the familiar Hertzian collision theory [*Tabor*, 1951] to estimate the contact area A in terms of the impact velocity U and E, the Young's modulus of "ice." (Note that the measured value of E is here assumed to apply to the surface, which we are assuming is covered with a surface-melted layer.) This gives for head-on collisions

$$A = 13.4U^{0.8}r_1^2\left(\frac{\rho_M}{E}\right)^{0.4} \quad (24)$$

where ρ_M is the average mass density of the colliding particles, here taken to be 500 kg m^{-3}. With $E = 9 \times 10^9$ N m^{-2}, $U = 5$ ms^{-1}, and $r_1 = 100 \ \mu\text{m}$, we find $A = 580 \ \mu\text{m}^2$. For $r_1 = 10 \ \mu\text{m}$, $A \approx 6 \ \mu\text{m}^2$.

The merged volume V is approximately equal to

$$V \approx A(h_1 + h_2) \quad (25)$$

An alternative estimate of the merged volume is obtained by assuming complete overlap of the two liquid layers. In this event the merged volume V is approximately equal to $\pi[r_1(h_1 + h_2)]^{3/2}$. The two estimates give similar results; for example, for

$$r_1 = 100 \ \mu\text{m}, \ h_1 + h_2 = 10^{-8} \text{ m}, \ V = 6 \times 10^{-18} \text{ m}^3$$

and for

$$r_1 = 10 \ \mu\text{m}, \ h_1 + h_2 = 10^{-9} \text{ m}, \ V = 6 \times 10^{-21} \text{ m}^3.$$

The volume transferred and thus the charge transferred depend on the impact velocity but to a weaker power than observed in the laboratory [e.g., *Jayaratne et al.*, 1983]. As pointed out by *Gaskell and Illingworth* [1980], this may reflect a velocity dependence of other parameters of the collisions.

2.3. Charge Transfer

If the transferred liquid carries net electrical charge, this mass transfer will be accompanied by charge transfer. To determine the amount of charge flow, we must know the net charge density within the flowing liquid.

In his theoretical treatment of the QLL, *Fletcher* [1968] showed that orientation of water molecules (and, consequently, their dipole moments) at the liquid-vapor interface produces an electrostatic field inside the layer. Fletcher's calculation of the equilibrium configuration implied that the surface dipole moments were oriented with the positive charges (the hydrogen atoms) pointing into the vapor and the oxygens into the layer. Based on this configuration, *Baker and Dash* [1989] showed that there would be net negative screening charge in the outer layers of the QLL. These outer layers would comprise the transferred fluid. Therefore loss of QLL fluid from a particle would result in positive charging of the remaining particle.

Subsequent theoretical work [*Wilson et al.*, 1988; *Townsend*, 1991] has cast doubt on the dipole orientation originally proposed by Fletcher. Experimental results are

ambiguous. However, much stronger segregational effects known to occur at water-mineral interfaces [*Jaycock and Parfitt*, 1981] are likely to occur in the neighborhood of ice-liquid interfaces, and they can affect charge carrier densities extending out to many molecular diameters in the adjacent liquid. Many studies have explored these electrical effects as a function of solute species and concentrations, associated with dynamic freezing and also at static interfaces [*Workman and Reynolds*, 1950; *Drost-Hansen*, 1967; *Gross*, 1965, 1971]. All these were bulk measurements; the variations are complex and depend on species and freezing rate. In the atmosphere and in the charging simulations the particles were exposed to room air, which introduces a variety of impurities, some of which are ionic species that dissolve in water, and there may be preferential absorption of ions of one or the other sign into the ice. Therefore it is not possible at this time to unambiguously determine the extent of charge segregation inside the QLL. We therefore are limited to estimates of the charge density required in order to explain the charge simulation experiments. In these the magnitude of δq, the charge transferred per collision, was generally of the order of tens of femtocoulombs, varying with experimental parameters.

Let the surface charge density at the liquid-ice interface be

$$\sigma_0^+ = \frac{\alpha |e|}{a}$$

where $|e|$ is the magnitude of the electronic charge, a is a molecular area, here taken to be 5×10^{20} m^2, and $\alpha \leq 1$, and we are assuming for concreteness that the surface charge carries a positive sign. The value $|e|/a \approx 10$ C/m^2. For charge neutrality this surface charge induces a distributed charge of opposite (i.e., negative) sign, of volume density $\rho_q^-(z)$, where

$$-\int_0^h \rho_q^-(z) \, dz = \sigma_0^+$$

The negative charge density will vary through the layer, with a characteristic relaxation distance ξ; it can be shown that [*Jaycock and Parfitt*, 1981].

$$\rho_q^-(z) \approx \rho_q(0) \exp\left(-\frac{z}{\xi}\right)$$

If $\xi \gg h$, then the average volume density of negative charge within the QLL is $\bar{\rho} \approx -\sigma_0^+/h$.

An estimate of the charge exchange can be made, based on the charged double layer model and the collisional mass transfer. Assuming that $\xi \gg (h_1 + h_2)$, the charge exchange in the case $h_1 < h_2$ is

$$\delta q \approx \frac{\sigma_0^+}{\dfrac{(h_1 + h_2)}{2}} \frac{h_2 - h_1}{2(h_1 + h_2)} V \qquad (26)$$

With the earlier estimates of V, a 1% difference in QLL thicknesses and a charge density of one electronic charge per ten surface molecules (i.e., $\alpha = 0.1$), we obtain 10^{-15} C $< \delta q$ $< 10^{-12}$ C. These values bracket the order of magnitude of charge transfers found in laboratory simulations.

Much of the discussion to this point has centered on

equilibrium properties of the QLL. Nonequilibrium effects have not been thoroughly studied; however, since charging behavior appears to depend crucially on the vapor flux to/from the ice surfaces, we briefly discuss the nonequilibrium case.

We have shown that the QLL thickness can be derived from (15) for a flat surface and (19) for a curved one in equilibrium. During growth the chemical potential of the vapor is higher than that of the QLL, which is in turn higher than that of the solid. *Kuroda and Lacmann* [1982], *Fukuta and Lu* [1992], and *Baker and Dash* [1989] assumed that for relevant growth rates the QLL is in a dynamic steady state; i.e., the vapor-liquid interface is advancing or retreating at the same rate as the solid-liquid interface, so that the QLL thickness is constant. Under these conditions, assuming the growth rate is very small, so that (15) (or equation (19)) still applies, we estimated the growth effect on the thickness of the layer. Denoting $\delta\mu$ as the increase in $\Delta\mu$ due to growth, for small $\delta\mu$,

$$\frac{\delta h}{h_0} \approx \frac{\delta\mu}{3\Delta\mu} \qquad (27)$$

While this calculation underestimates the growth effect that would be found in the high supersaturations (relative to ice) in water-saturated clouds and in most of the simulations, it shows that h must increase during growth and decrease during evaporation.

3. Discussion

The charge transfer mechanism we have outlined here provides tentative answers to questions 1 and 2 of our introduction. These must be tested by further experimental work. Our fundamental premise is that charge transfer during collisions is associated with mass transfer between ice particles. Current ideas on surface melting lead to the prediction that there is a flow of surface material from warm to cold, from regions of high surface curvature to those of smaller curvature, and from regions of high vapor growth to regions of lower growth or evaporation. If the fluid is negatively charged, this flow is consistent with the observed trends in dependence of charge transfer on environmental conditions.

A fundamental test for our charge transfer model would be an investigation of the correlation between mass and charge transfer. Irregularities on the ice surface may be involved in charge transfer. It would be desirable to observe the ice surface during riming as well as during evaporation and vapor growth, first in pure vapor environments and then under controlled concentrations of atmospheric gases. The goal would be to observe the evolution of protruberances and pits under a range of nonequilibrium conditions. Such an investigation is now being initiated at the University of Washington.

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