CHARGE TRANSFER IN THUNDERSTORMS AND THE SURFACE MELTING OF ICE

M.B. BAKER
Geophysics Program, University of Washington, Seattle, Washington 98195, USA

and

J.G. DASH
Department of Physics, University of Washington, Seattle, Washington 98195, USA

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A mechanism is proposed for the electrification of thunderclouds, whereby charge separation in ice–hail collisions is a consequence of mass transfer between the particles due to size and growth effects in surface melting. The theoretical trends and magnitudes are consistent with laboratory observations of charging.

1. Introduction

Thunderstorm electrification has been explored in considerable detail, but the microscopic mechanism of charge separation remains unexplained [1,2]. It is known that the typical active centers in clouds are negatively charged regions of rapid ice formation at temperatures between about −10 and −25°C. Laboratory simulations have shown that charging accompanies collisions between small ice particles and soft hailstones in the presence of supercooled drops [2,3]. The charges transferred are small unless the particles are growing from the vapor; during diffusional growth the magnitude is greatly increased. The sign of the charge transfer depends on the relative growth rate due to vapor diffusion: the surface that grows faster becomes positively charged [4]. It has been suggested that ice surfaces in thunderstorm conditions are probably covered by liquid like layers due to surface melting, and that these layers may be involved in the charging phenomena [5–7]. However, no mechanisms were proposed for the actual role of surface melting in the charge transfer, and the idea was not pursued. We have reconsidered the problem in the light of considerable recent progress in the understanding of surface melting as a general phenomenon of solids [16–21]. It is now generally accepted that ice does undergo surface melting at its interfaces with vapor; surface disorder in ice was predicted more than twenty years ago [8], and it has since been confirmed by a number of experimental studies [9–15]. This paper proposes a model of thunderstorm electrification with surface melting as the basis of a mechanism for charge transfer. The mechanism entails mass transport of portions of melted surface statistically favoring transfer from thicker to thinner layers. Thickness variations are due to a combination of size and growth effects. Charging accompanies the mass transfer, due to a surface excess of negative ions associated with the contact potential at the vapor interface. The model agrees with laboratory observations of the dependence of the sign of charging on relative growth. The theoretical estimate of the magnitude of the charge trans-
ferred is consistent with laboratory simulations of thunderstorm conditions, but quantitative tests require further theoretical and experimental studies.

2. Theory

2.1. Theory of surface melting of Van der Waals solids

In this section we summarize the basic equilibrium thermodynamic results for the surface melting of systems governed by Van der Waals dispersion forces [16–21]. The basic treatment neglects several effects which are important for the present theory, and which are discussed in the next two sections.

The thermodynamic motivation for surface melting is a reduction of the surface free energy, but the decrease is opposed by the free energy of conversion from solid to liquid. The equilibrium thickness of the melt liquid is established by the competition between the two contributions. For a plane interface between a Van der Waals solid and its vapor, the Gibbs free energy $G_m$ of a melted layer of area $A$ and thickness $L$ coating the solid is

$$G_m = A \left[ \rho_c L \mu_c + \gamma_{sv} - \Delta \gamma (1 - \sigma^2/L^2) \right],$$

where $\mu_c$ and $\rho_c$ are the chemical potential and the number density of the liquid, $\gamma_{sv}$ is the free energy coefficient of the unmelted solid interface, $\Delta \gamma$ is the difference between the interfacial coefficients of the melted and unmelted interface, and $\sigma$ is a length on the order of the intermolecular spacing, assumed to be much smaller than $L$. The chemical potential of the layer is

$$\mu_m(T, L) = \frac{\partial G_m}{\partial (AL\rho_c)} = \mu_s + \Delta \mu(T) + \frac{2 \Delta \gamma \sigma^2}{\rho_c L^3},$$

where $\Delta \mu(T) \equiv (\mu_c - \mu_s)(T)$ is proportional to $(T - T_t)$ if $T$ is not far below the triple point $T_t$. At equilibrium under constant $T$ and $P$, $\mu_m = \mu_s$, leading to the power law temperature dependence for the equilibrium thickness

$$L_0 = \lambda t^{-1/3},$$

where $\lambda = [2\sigma^2 \Delta \gamma / T_c \rho_c (\partial \Delta \mu / \partial T)]^{1/3}$ and $t$ is the reduced temperature $(T - T_c) / T_c$. Eq. (3) has been confirmed in experiments on adsorbed Ar and Ne multilayer films [22].

The third term on the right hand side of eq. (2), which arises from the dependence of the interfacial coefficients on the thickness of the melted layer, introduces an effective interaction between the liquid boundaries. Since the interaction is attractive it contributes an effective negative pressure term within the layer. This contribution will be seen to play an essential role in the mass transfer between ice particles and hailstones.

2.2. Size and growth effects

Size effects in first order transitions are a result of surface energy, causing an increase in the vapor pressure of small droplets [23], and a depression of the melting temperature of small solid particles [24]. Several recent papers treat some effects of surface curvature in wetting transitions [25]. In general, a dependence on surface curvature can be introduced through the explicit dependence of the free energy on area. For surface melting we modify eq. (1) for spherical particles of radius $R \gg L$,

$$G_m = \frac{4}{3} \pi \left[ R^3 - (R - L)^3 \right] \mu_c \rho_c$$

$$+ 4 \pi R^2 \left[ \gamma_{sv} + \Delta \gamma (1 - \sigma^2/L^2) \right]$$

$$+ 4 \pi \gamma_{sc} \left[ (R - L)^2 - R^2 \right] (1 - \sigma^2/L^2).$$

Equating the chemical potential of the layer to $\mu_s$, the result can be expressed as a power series in $L_0/R$:

$$L = L_0 \left[ 1 + 2 \gamma_{sc} / (3 \rho_c \Delta \mu R) \right].$$

Our results so far apply to the situation in which the solid, the melted layer, and the vapor coexist in equilibrium. We now examine changes in $L$ due to growth from the vapor or evaporation. A particle grows when the vapor is locally supersaturated, so that it condenses on the liquid–vapor interface, warming and thickening the liquid layer. The particle’s temperature will rise until it is stabilized by conduction to the vapor, and the layer thickness will grow until the solid–liquid interface advances at the same rate as the
liquid–vapor interface. The “thermal” increase due to the temperature rise is obtained from eq. (3):

\[(\delta L)_{\text{thermal}}/L_0 = (\delta T)/3(T_i - T).\]  

(6)

The increase \((\delta L)_{\text{cryst}}\) associated with the advance of the solid interface can be expressed in terms of the departure from equilibrium \((\delta \mu_m)_{\text{cryst}}\) of the layer’s chemical potential. It is this deviation that drives the crystallization, and under steady state conditions \((\delta \mu_m)_{\text{cryst}}\) is just sufficient to maintain the thickness constant at its increased value. A simple relation between the changes of thickness and chemical potential is obtained from eqs. (2) and (3):

\[(\delta L)_{\text{cryst}}/L_0 = (\delta \mu_m)_{\text{cryst}}/3 \Delta \mu.\]  

(7)

The two nonequilibrium effects will each contribute to an increase of \(L\) during growth and a decrease during evaporation: \(\delta L = \delta L_{\text{thermal}} + \delta L_{\text{cryst}}\).

2.3. Short range forces and finite crystal–melt interface width

The preceding treatment assumes long range Van der Waals forces, and ignores all other types of interactions that may exist within the melted layer. The actual situation in ice appears to be more complicated, as indicated by experiments discussed below. Since the evidence indicates appreciable contributions from short range forces, the discussion is broadened to include such terms. Two types of short range interaction have been indicated through their effects on surface melting in different systems. In metals the long range Van der Waals forces tend to be screened by the conduction electrons, exponentially attenuating the power law interaction between interfaces bounding the liquid. In the range where the screening is dominant the surface term in eq. (1) is replaced by

\[A \left[ \gamma_{\text{sv}} + \Delta \gamma \left(1 - \beta e^{-L/\xi}\right) \right],\]

where \(\xi\) is the characteristic screening length and \(\beta\) represents the magnitude of the effect. Instead of the power law eq. (3), the temperature dependence is now logarithmic:

\[L_0 = -\frac{\xi}{\kappa} \ln(t/\kappa).\]  

(8)

where \(\kappa = \beta \Delta \gamma/[\xi \partial \mu_m/\partial T]\). The surface melting of Pb(110) follows such a temperature dependence over a considerable range [20], and then gradually changes to a power law very close to the triple point, as the layer thickness becomes very large [26].

A different type of short range interaction can exist in all systems, including those with purely Van der Waals forces. The simple theory outlined above approximates the melted layer as bulk liquid, and neglects the finite width of the crystal–melt interface [27], a transitional region which, in simple molecular systems, extends over a few molecular distances. The width can be neglected when it is much less than the total thickness of the liquid, but otherwise it causes important changes in the melting behavior. Liquid close to its interface with the solid phase retains a certain degree of solid like order, so that its properties are intermediate between those of the bulk solid and liquid. The solid like order decreases with distance from the boundary; beyond the immediate region of the interface, the decrease is approximately exponential. Such solid like order makes a thin surface liquid a quasi-liquid layer (QLL), and it introduces a special thickness dependence in the surface coefficients. This variation causes a corresponding effective short range interaction between the interfaces bounding the melted layer. If the surface energy due to this effective interaction is relatively strong the temperature dependence will follow eq. (8), while \(\xi\) now stands for the coherence length of the solid order parameter. Measurements on a number of Van der Waals systems show logarithmic dependence at small \(L\), and evolve to the power law at larger thickness [21,22,28–30]. The empirical values of \(\xi\) for Ar and Ne are equal to a small number of molecular layers [22], comparable to theoretical estimates for simple molecular systems [27].

The equations for size and non equilibrium effects in systems governed by short range forces
are obtained by procedure similar to those for Van der Waals systems. The finite size effect is

\[ L = L_0 \left[ 1 + 2 \xi \gamma_{ss} / (\rho \Delta \mu L_0 R) \right]. \] (9)

Nonequilibrium effects are also modified: the counterparts to eqs. (6) and (7) are

\[ (\delta L)_{\text{thermal}} / \xi = \delta T / (T_c - T), \] (10)

\[ (\delta L)_{\text{cryst}} / L = (\delta \mu_m)_{\text{cryst}} / \Delta \mu. \] (11)

3. Mass and charge transfer in ice–hail collisions

We propose that surface melting plays two additional and essential roles in thunderstorm electrification, causing both mass transfer and charge transfer between ice particles and hail during their collisions.

When the thicknesses of the surface melted layers on two colliding particles are different at the moment of contact, the unequal effective internal pressures within the layers will tend to equalize their thicknesses. The amount of material transfer will depend on the pressure difference \( \delta P_{\text{eff}} \), which is proportional to the difference in thickness \( \delta L \). From eq. (2) we obtain

\[ \delta P_{\text{eff}} = 6 \Delta \gamma \sigma^2 \delta L / L^4. \] (12)

for flat surfaces of Van der Waals systems. A similar expression follows for short range interactions. The material transfer will also depend on the fluidity of the layer, the local shapes of the contacting regions, and details of the collision. All of these factors should introduce wide variations and statistical fluctuations. We do not attempt to calculate the details, but only bring out what appear to be the principal and consistent qualitative features, i.e. that ice–hail collisions tend to transport some surface liquid from the object with a thicker film to the object with a thinner film.

Charge transfer is a consequence of the material transfer, due to non-uniform concentrations of positive and negative charges through the thickness of the melted layer. The normal concentrations of dissociated water ions and ionic impurities in the liquid are modified in the neighborhood of the liquid–vapor interface, due to their tendency to screen the electric fields associated with dipolar ordering of the water molecules. The sign of the surface potential is positive, according to measurements of the bulk water–vapor interface [31–33]. Therefore, there is an excess concentration of negative ions near the surface. This screening mechanism for charge separation within the surface melted layer was predicted many years ago by Fletcher [8], who calculated that the water molecules at the surface are partially oriented to a depth extending several molecular diameters into the liquid. The sign of the observed potential agrees with the calculation, but the depth and extent of the dipolar ordering have not been measured. According to recent computer simulations, the orientational ordering extends several molecular distances below the surface, producing a complicated potential structure [34].

The excess concentration of negative charge near the liquid interface, combined with the tendency for surface melted liquid to be transferred from thicker to thinner films, provide a mechanism for charge transfer between colliding ice particles and hailstones. In the next section we estimate magnitudes and compare the estimates with laboratory measurements.

4. Comparisons with observations

There are many experimental measurements of temperature dependent surface effects of ice at its interface with vapor, more or less consistent with the general features of surface melting. The observations have been made by a variety of techniques, including magnetic resonance, proton backscattering, ellipsometry, surface conductivity, and adsorption isotherms [9–15]. The quantitative results vary greatly, but they generally indicate partially fluid surface layers at temperatures extending down to \(-30^\circ\text{C}\) or below [35], with a translational diffusion coefficient intermediate to the bulk phases. The partial mobility suggests surface melting with a relatively broad crystal–melt interface. In this case one would expect that the melted layer thickness should have a logarithmic temperature dependence, as eq. (8). This is
indeed what has been reported from measurements by proton channeling [10]. We will therefore calculate quantitative estimates of size and growth effects according to the appropriate equations for short range effective interactions, using parameters obtained by fitting to the proton scattering results.

For a calculation of size and growth effects we assume the conditions of an extensive series of laboratory simulations [4]: ice particles of radius $R = 40 \ \mu$m, at $T = -15^\circ$C. In one set of measurements the particles were in supersaturated vapor; condensation on the liquid–vapor surface produced calculated temperature rises of 0.1 to 1°C, and growth rates up to 1 $\mu$m/s. Additional parameters are needed for calculating $\Delta L$. The chemical potential difference $\delta \mu(T)$ is obtained from the vapor pressures of ice and supercooled water. For the size effect according to eq. (9) we use the measured interfacial coefficient $\gamma_{sl} = 29$ mJ/m$^2$ between ice and water at the triple point [36]. With these values the size effect is a fractional increase $\delta L/L = 0.04$, and the thermal increase $\Delta L/\xi$ is between 0.007 and 0.07. For the growth effect it is necessary to relate the crystallization velocity to chemical potential. We will assume that a crystallization velocity $v_c$ of the solid–liquid interface in the surface melted layer requires the same value of $\delta \mu_m$ that produces $v_c$ in supercooled bulk water. With this assumption we have access to a body of experimental results [37], although it should be noted that the rates at lower temperature are likely to be appreciably smaller than the bulk rates near 0°C due to slower diffusion. Without correcting for this change the calculated increase of thickness is quite small: for $v_c = 1 \ \mu$m/s the bulk measurements indicate a chemical potential shift of 0.14$k_B$; the corresponding change is $\delta L/\xi = 0.004$. Therefore the thermal effect tends to be greater than that due to crystallization, although it is possible that the reduced diffusivity below 0°C may produce a significant increase. Thus, according to these estimates, the combination of size and growth effects can produce appreciable changes in the thickness of the surface melted liquid; depending on the growth rate and particle size, these changes can be of either sign. If $\xi$ and $L$ are comparable (as the proton scattering measurements indicate for $T = -20^\circ$C), the combined effect in $40 \ \mu$m particles during growth is an increase $\delta L/L$ between about 5% and 10%. Size effect alone is about 4%, therefore the non-equilibrium effects can decrease and even reverse the tendency for $L$ to be thicker on small particles.

The charge concentration at the liquid–vapor interface depends on the magnitude of the surface potential. A survey of laboratory measurements lists results varying widely from positive to negative values, and concludes by suggesting a value of $+80 \pm 60$ mV [31]. The most recent values [32,33] are +50 and +25 mV. (These measurements were done at room temperature, but any temperature dependence is expected to be very small and will be ignored here.) Although the surface potential is quite small, it leads to important changes in concentration due to the Boltzmann factor, which is approximately equal to 10 for a potential of 50 mV at $T = -15^\circ$C. This will produce an excess local concentration of negative ions at the surface in pure water of 1 part in $10^6$.

The estimates above lead to a rough agreement with the quantity of charge exchange in laboratory studies. Measurements with 100 $\mu$m ice spheres showed charge transfer to growing hailstones at $-15^\circ$C was typically around +100 fC [2]. According to the screening effect estimated above, the charge transfer in the experiment corresponds to the excess ion population in one or two molecular layers. This amounts to a minor fraction of the excess thickness on small growing ice particles, according to the fractional changes estimated earlier, and the layer thickness at $-15^\circ$C determined by proton scattering [10].

5. Discussion

The theory is admittedly incomplete, but it is encouraging in that it provides a mechanism for charging that seems to agree with the general observations of electrification in thunderstorms and in laboratory studies of ice–hail collisions. The model involves surface melting in an essential way, establishing the temperature limits of the effect and the mechanism for charge transfer. The
mechanism predicts that the sign of the charge transfer depends on the relative sizes of colliding particles and on relative growth rates. The direction and magnitude of charge transfer are in rough agreement with laboratory measurements.

However, in spite of its promise, the theory is still in a preliminary stage, and it should be extended in several directions. Surface melting under non-equilibrium conditions, the effects of impurities, and the dynamics of collisions are obvious and important aspects that will have to be treated in a more complete and useful theory. A number of experimental studies are also indicated. A crucial test will be to examine whether mass transfer is associated with charge transfer. New measurements are needed of surface melting of ice, the fluidity of the surface layer, and its dependence on temperature, impurity concentrations, evaporation, and growth.

Our attempt to quantify the charge exchange predicted by the theory has made us aware of serious gaps in the understanding and characterization of the interfaces of ice and water and of the surface melting of ice. Therefore, progress in the understanding of thunderstorm electrification may be limited by the need for further study of these systems.

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References

were taken during warming, which according to the present theory reduces the thickness.

[35] A recent study [14] places the lower limit of surface melting as high as \(-5^\circ C\), which may be due to limited experimental resolution; in addition, the measurements
