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Charge induced stability of water droplets in subsaturated environment

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Abstract

Atmospheric liquid and solid water particles are stabilized if they are coated with either negative or positive electric charge. The surface charge causes an increase of the partial pressure of water vapour close to the surface of each particle, effectively allowing the particles to remain in their condensed phase even if the environmental relative humidity drops below unity. The theory, briefly presented in this paper, predicts a zero parameter relation between surface charge density and water vapour pressure. This relation was tested in a series of Electrodynamical Balance experiments. The measurements were performed by stabilizing charged droplets of pure water near an ice-surface. We observed a divergence in radius as the temperature approached the freezing point from below. We find that the measurements confirm the theory within the experimental uncertainty. In some cases this generally overlooked effect may have impact on cloud processes and on results produced by Electrodynamical Balance experiments.

1 Introduction

Recently a few field measurements performed at different locations in the tropics has lead to observations of ice particles in the lowest stratosphere (Nielsen et al., 2007; Chaboureau et al., 2007; de Reus et al., 2008; Corti et al., 2008). Occurrence of ice particles in the stratosphere is somewhat unexpected since the stratosphere is generally subsaturated with respect to ice. This is indeed the case in the measurements of Khaykin et al. (2009). These measurements must prompt speculations about which mechanisms could prevent ice from sublimating in the lowest stratosphere. A possible explanation could be influence of electric charge which may be abundant in some areas of interest. The idea is basically that charges sitting on particles perturb the gas phase water dipoles locally, by attracting water molecules close to the ice surface. While the sparseness of in situ observations leaves some room for disputing this

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concept we pursue the question from a purely experimental point of view in this paper. Our approach is to measure the size of an evaporating supercooled water droplet, with diameter in the range 10–100 µm, trapped in an Electrodynamical Balance (EDB). See Achtzehnet al. (2005) and Davis (1997) for details about the EDB. During the experiment the EDB chamber is kept in a subsaturated state, i.e. the water vapour partial pressure is kept below the saturation water vapour partial pressure over a plane liquid surface. The theory of gas phase water surrounding a charged droplet is equivalent to the theory of gas phase water surrounding a charged ice particle. So if we are able to observe that charged water droplets in a subsaturated environment are stabilized according to the theory, we take that as proof of concept. These laboratory experiments will allow us to conclude whether or not stratospheric ice particles will be stabilized if charge is present on their surface. The question of whether sufficient charge sometimes is present on stratospheric ice particles cannot be answered from these laboratory experiments, and that question is as such not addressed in this paper.

2 Theory of charged hydrometeors

2.1 Equilibrium

The water vapour pressure e at distance $r=|\boldsymbol{r}|$ from the centre of an equilibrated charged spherical particle may be calculated by requiring that the chemical potential of a gas phase water molecule located close to the charged particle

$$\mu_{\text{gas}}(r) = -\frac{q\boldsymbol{r}\cdot\boldsymbol{p}}{4\pi\varepsilon_0 r^3} + \mu_0(T) + k_{\text{B}}T\ln(\text{e}(r)) \quad (1)$$

is constant in space. Here $q=ze_u$ is the electric charge, $\boldsymbol{p}$ the water dipole moment and ε_0 the vacuum dielectric constant. The equilibrium requirement $\frac{d\mu_{\text{gas}}}{dr}=0$ leads to

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an expression for the partial pressure of water close to the particle

$$e(r) = e_\infty \exp\left(\frac{|q\boldsymbol{p}|}{4\pi r^2 \varepsilon_0 k_B T}\right) \quad (2)$$

where e_∞ is the ambient partial pressure. This relation is plotted in Fig. 1 in terms of relative increase of $e(r)$ for different ice particle radii. Also shown in Fig. 1 is the socalled Rayleigh instability radius $r_R = \left(\frac{q^2}{64\pi^2 \varepsilon_0 \sigma_{l,g}}\right)^{1/3}$, below which the Coulomb interaction dominates the mechanical stabilization caused by the surface energy ($\sigma_{l,g}$ is the surface energy density) and the droplet breaks up (Rayleigh, 1882; Duft et al., 2003). For droplet radii above 1 µm we assume that the surface energy does not influence the saturation water vapour pressure. In equilibrium the vapour pressure at the surface $e(r)$ is equal to the saturation pressure over a plane liquid water surface $e_{s,l}$, so the relation (Eq. 2) may be viewed as an depression of the environmental saturation pressure $e_{s,\infty}$ above a charged surface as a function of surface charge density σ_q.

$$e_{s,\infty} = e_{s,l} \exp\left(-\frac{|\boldsymbol{p}\sigma_q|}{\varepsilon_0 k_B T}\right). \quad (3)$$

Physically this means that one would expect to observe a depression of the relative humidity RH_w to a value below unity in an "equilibrated" charged cloud. Here "equilibrated" means that the system is in thermodynamic equilibrium under the constraint imposed by presence of surface charge, but possibly still participating in mechanical processes like coalescence and sedimentation.

$$RH_w = \exp\left(-\frac{|\boldsymbol{p}\sigma_q|}{\varepsilon_0 k_B T}\right). \quad (4)$$

In equilibrium the droplet size distribution will be determined by the charge of the single droplets, since σ_q has to be the same on all droplets. If one prefers, Eq. (4) may be viewed as an additional term in the water activity (see e.g., Koop et al., 2000).

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2.2 Non-equilibrium

The condensation/evaporation of a droplet of radius 1–50 µm in an atmosphere of relative humidity RH_w may be treated as a macroscopic diffusion problem, i.e. the mass flux to a droplet of radius r may be calculated from a steady state solution to the diffusion equation. The problem has been solved in Pruppacher and Klett (1997, Eq. 13–28), and that solution includes specifically the effects of gas diffusion, and heat diffusion which turns out to be essential. Here, in Eq. (5), we extend the Pruppacher and Klett (1997) formula with a term accounting for the charge effect. While the charge changes the ambient equilibrium water vapour partial pressure in the particle's surroundings, the surface of the particle always obeys the boundary condition $e(r)=e_s(T(r))$. This leads to the following differential equation for the particle radius. Note that symbols in Eq. (5) are defined in Table 1.

$$r\frac{dr}{dt} = \frac{(1+U_d)\mathrm{RH_w}-1}{\frac{\rho_w R T_\infty}{e_{s,l}(T_\infty)D^* M_w} + \frac{L\rho_w}{k_a^* T_\infty}\left(\frac{LM_w}{TR}-1\right)} \tag{5}$$

where

$$U_d = \frac{|q\boldsymbol{p}|}{4\pi\varepsilon_0 k_B T_\infty r^2} \tag{6}$$

3 Experimental setup

We now test the validity of the charge stabilization theory in a series of EDB experiments. In order to enable a situation where a hydrometeor is exposed to a well defined partial water vapor pressure below the saturation point, we use the following setup. The EDB chamber is prepared with an ice surface on the chamber wall which is maintained at the same temperature as the captured charged particle. A liquid water charged particle kept in the trap will be subject to a water vapor partial pressure which is in fact the

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saturation water vapor pressure above ice e_i i.e. always below saturation pressure of liquid water e_l. Under these special conditions the liquid droplet terminal radius r_q is ideally a function of only temperature and charge:

$$r^2 = \frac{|pq|}{4\pi\epsilon_0 k_B T \ln \frac{e_{s,l}}{e_{s,i}}}. \tag{7}$$

This dependency is shown in a phase diagram in Fig. 2. In the temperature range between −15 °C and 0 °C the predicted r_q can reach high measurable values without reaching the Rayleigh stability limit. Generally the particle charge and chamber humidity may be controlled to some extent, but both parameters have to be determined indirectly. The initial charge is calculated from the DC bias field required to balance the particle in the gravitational field, the mass being determined from the measured particle radius. The particle charge is unchanged once the droplet has been injected into the chamber. However, in cases where the droplets reach the Rayleigh instability limit detectable bursts of charge will escape the droplet (Duft et al., 2003), and the electric charge has to be reevaluated. The relative uncertainty on the charge becomes larger in such cases. The temperature is not completely homogeneous throughout the chamber and this results in uncertainty on the humidity, which again causes a considerable scatter on the terminal radius of the droplet. Considering the "charged droplet over ice" relation (Eq. 7) one sees that as the system approaches the triple point, the term $\ln \frac{e_{s,l}}{e_{s,i}}$ becomes "critical" because it is essentially a difference between two almost identical properties. The terminal radius becomes very sensitive to small temperature variations, which leads to a lot of experimental noise. Therefore we choose to determine the partial pressure of water vapour in the trap saddle point from the initial slope of the evaporation curve, by use of Eq. (5). Note that since the charge is determined from the droplet radius and the DC-field, the relative humidity is the only unknown variable in Eq. (5), hence we do in effect have independent measurements of charge and relative humidity for each droplet.

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4 Results

A series of 163 experiments was performed at two different temperatures (268.2 K and 270.2 K). In each experiment a new charged droplet of otherwise clean water was captured in the trap. The droplets immediately started to evaporate after they had been captured. In Fig. 3 we show an evaporation curve (surface area versus time). The diameter is measured directly from camera images obtained at 5 s time intervals. The charge is then determined from the DC bias voltage required to keep the particle floating. Basically a charged droplet in an environment of relative humidity $RH_w<1$ cannot evaporate below its terminal radius. Note that without the charge effect, the droplet would have continued to evaporate until it was completely gone. The theoretical fit is the analytical solution to Eq. (5) performed without varying the charge. Basically only the initial slope is fitted, and this slope is used to determine the relative humidity through Eq. (5).

The theoretical prediction of Eq. (4) may be seen as a unique relation between RH_w and σ_q/T, which we will now examine. In Fig. 4 we plot this relation along with the measured values of RH_w and σ_q/T. The relative accuracy of the DC voltage measurement is best while the particles are still relatively large. However, during the experiment many of the particles undergo Coulomb fission as they pass the Rayleigh instability limit. Consequently the charge has to be reevaluated in the final state, and this is the main source of the reported uncertainty on σ_q. Not all the points are within the uncertainty though. These discrepancies are attributed to other experimental uncertainties, including the effect of the electrical fields in the EDB. We do not have good estimates of these possible errors, but since the measurements are generally scattered within the uncertainty around the theoretically predicted line, with a few exceptions of biased low humidity, we assume that these sporadic low biased measurements are caused by some small unknown error in the experiment. We therefore conclude that the theory is confirmed by the experiment.

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5 Perspectives

This work was inspired by a specific problem, namely the stability of tropical stratospheric ice crystals. As stated in the introduction we are not making any claims about relevance of the charge stabilization effect in tropical stratospheric clouds. We just want to present these laboratory measurements to the atmospheric science community in order to make scientists aware of the charge stabilization mechanism. It is possible that the effect could have an influence on cloud and aerosol processes in other parts of atmospheric science. For example we speculate that the effect could be relevant in thunderclouds, the most obvious place to look for a charge effect. Inside thunderstorms charge densities ranges from 0 to 10^9 unit charges (Bateman et al., 1999). For instance, a hydrometeor of diameter 0.5 mm and a charge of about 10^9 unit charges would have a surface charge density of $2.5\times10^{-4}\,\mathrm{C\,m^{-2}}$. That would decrease the equilibrium relative humidity by 4%, and it would be sufficient to cause a preference for heavily charged hydrometeors compared to neutral hydrometeors in an ongoing condensation processes. This may be thought of as an analog to the Bergeron-Findeisen mechanism. The hydrometeors eventually approach a state of identical surface charge density. The timescale for this process, for a 0.5 mm droplet, may be estimated from Eq. (5), and is found to be around 20 h, a rather large number. But for a 10 times smaller particle of the same surface charge density the process only takes around ten minutes. So potentially the charge stabilization effect could control, or at least influence, the size distribution in thunderstorm clouds, and in this way influence precipitation. We have not pursued this idea further, and we will just leave these questions open for future research.

Finally we note that it is obvious from our results that the charge stabilization effect should be taken into account in some EDB experiments. Depending on how critical results are to relative humidity variations, one can estimate the severeness of change in water activity from Eq. (4), and include the charge effect accordingly if necessary.

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6 Conclusions

A theory has been proposed for equilibrium and transient dynamics of charged hydrometeors. The theory's prediction of terminal radius of charged water droplets in a subsaturated environment was verified in an Electrodynamical Balance experiment. The existence of the charge effect is clearly evident from the experiments, and the quantitative theoretical predictions are confirmed reasonably well. The stabilization by charge effect will influence some EDB experiments where the results are sensitive to humidity, and as such it should be taken into account for interpretation of EDB experiments.

References

Achtzehn, T.,Mueller, R.,Duft, D. and Leisner, T.: The Coulomb instability of charged microdroplets: dynamics and scaling, Eur. Phys. J., D34, 311–313, doi:10.1140/epjd/e2005-00102-1, 2005.

Bateman, M. G., Marshall, T. C., Stolzenburg, M., and Rust, W. D.: Precipitation charge and size measurements inside a New Mexico mountain thunderstorm, J. Geophys. Res.-Atmos., 104, 9643–9654, doi:10.1029/1998JD200118, 1999. 25750

Chaboureau, J.-P., Cammas, J.-P., Duron, J., Mascart, P. J., Sitnikov, N. M., and Voessing, H.-J.: A numerical study of tropical cross-tropopause transport by convective overshoots, Atmos. Chem. Phys., 7, 1731–1740, doi:10.5194/acp-7-1731-2007, 2007. 25744

Corti, T., Luo, B., Reus, M., Brunner, D., Cairo, F., Mahoney, M., Martucci, G., Matthey, R., Mitev, V., Santos, F., et al.: L10810-Unprecedented evidence for deep convection hydrating the tropical stratosphere, Geophys. Res. Lett., 35, L10810, doi:10.1029/2008GL033641, 2008. 25744

Davis, E. J.: A history of single aerosol particle levitation, Aerosol Sci. Tech., 26, 212–254, doi:10.1080/02786829708965426, 1997.

de Reus, M., Borrmann, S., Bansemer, A., Heymsfield, A. J., Weigel, R., Schiller, C., Mitev, V., Frey, W., Kunkel, D., Kürten, A., Curtius, J., Sitnikov, N. M., Ulanovsky, A., and Ravegnani, F.:

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10, 25743–25757, 2010

Evidence for ice particles in the tropical stratosphere from in-situ measurements, Atmos. Chem. Phys., 9, 6775–6792, doi:10.5194/acp-9-6775-2009, 2009. 25744
Duft, D., Achtzehn, T., Müller, R., Huber, B. A., and Leisner, T.: Rayleigh jets from leviated microdroplets, Nature, 421, p. 128, 2003. 25746, 25748
Hall, W. W. and Pruppacher, H. R.: The survival of ice particles falling from cirrus clouds in subsaturated air, J. Atmos. Sci., 33, 1995–2006, 1976. 25753
Khaykin, S., Pommereau, J.-P., Korshunov, L., Yushkov, V., Nielsen, J., Larsen, N., Christensen, T., Garnier, A., Lukyanov, A., and Williams, E.: Hydration of the lower stratosphere by ice crystal geysers over land convective systems, Atmos. Chem. Phys., 9, 2275–2287, doi:10.5194/acp-9-2275-2009, 2009. 25744
Koop, T., Luo, B., Tsias, A., and Thomas, P.: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions, Nature, 406, 611– 614, 2000. 25746
Murphy, D. M. and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, Q. J. Roy. Meteor. Soc., 131, 1539–1565, 2005. 25753
Nielsen, J. K., Larsen, N., Cairo, F., Di Donfrancesco, G., Rosen, J. M., Durry, G., Held, G., and Pommereau, J. P.: Solid particles in the tropical lowest stratosphere, Atmos. Chem. Phys., 7, 685–695, doi:10.5194/acp-7-685-2007, 2007. 25744
Pruppacher, H. and Klett, J.: Microphysics of Clouds and Precipitation, vol. 18 of Atmospheric and Oceanographic Sciences Library, second revised and enlarged edition with an introduction to cloud chemistry and cloud electricity edn., Springer, Dordrecht, The Netherlands, 1997. 25747
Rayleigh, L.: On the equilibrium of liquid conducting masses charged with electricity, Philos. Mag., 14, 184–186, 1882. 25746

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Table 1. Definition of symbols in Eq. (5).

r	Droplet radius
ρ_w	Liquid water density
R	Gas constant
T_∞	Ambient temperature
$e_{s,l}$	Saturation pressure over plane clean liquid water surface*
D^*	Diffusivity of water in gas phase (corrected for kinetic effects)**
M_w	Mole mass of water
L	Latent heat of evaporation (water)
k_a^*	Heat conductivity of air (corrected for kinetic effects below mean free path)

* Murphy and Koop (2005).
** Hall and Pruppacher (1976).

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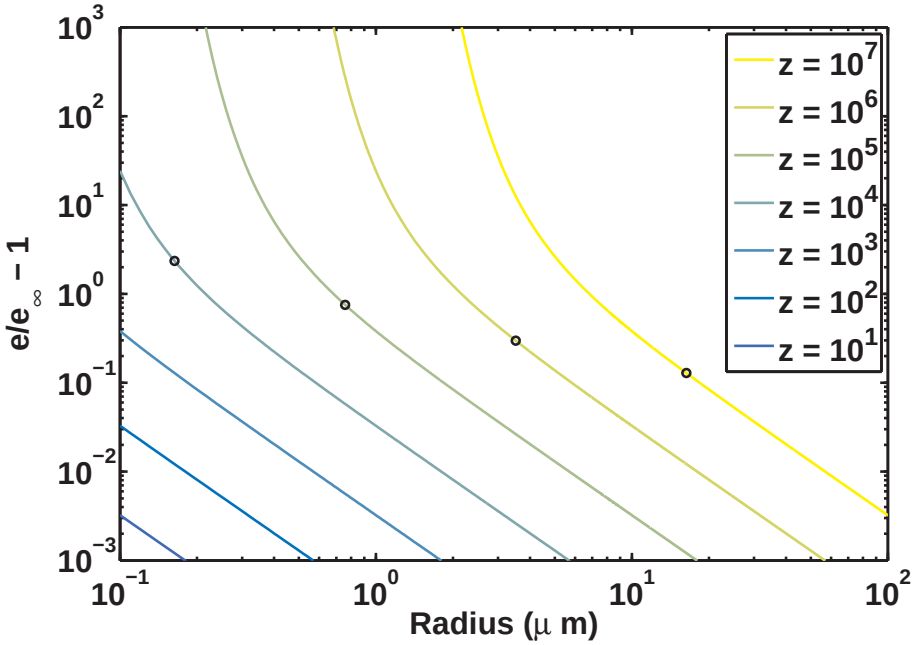

Fig. 1. Relative increase of partial pressure of water as function of distance from the centre of a spherical symmetrically charged hydrometeor for different unit charge numbers. The circles denote the radius of Rayleigh instability (see text) for a given charge.

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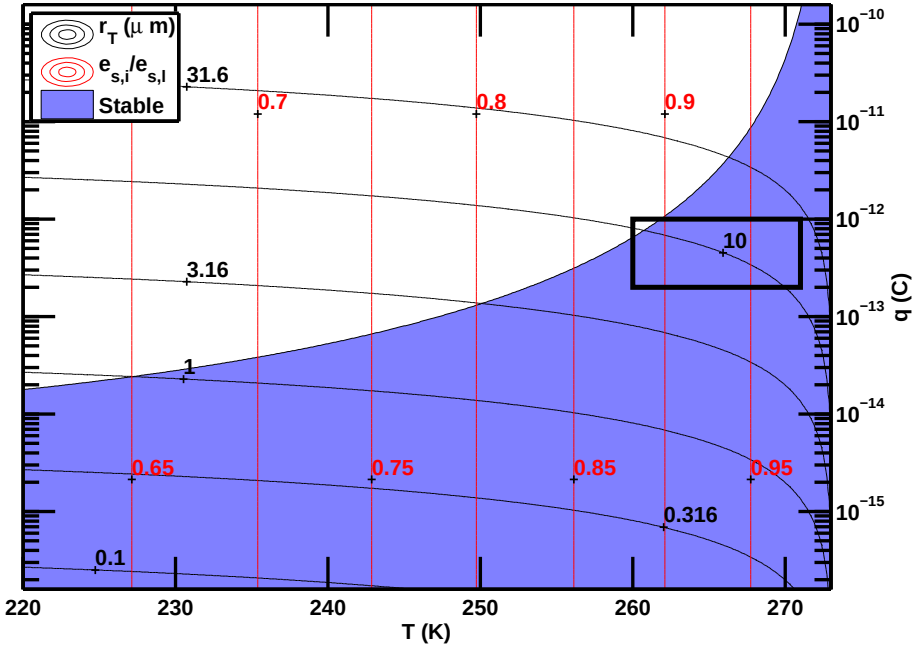

Fig. 2. Terminal radius for a charged droplet above an ice-surface. The rectangle shows the part of the phase diagram where the terminal radius is larger than the Rayleigh instability radius for a charged particle.

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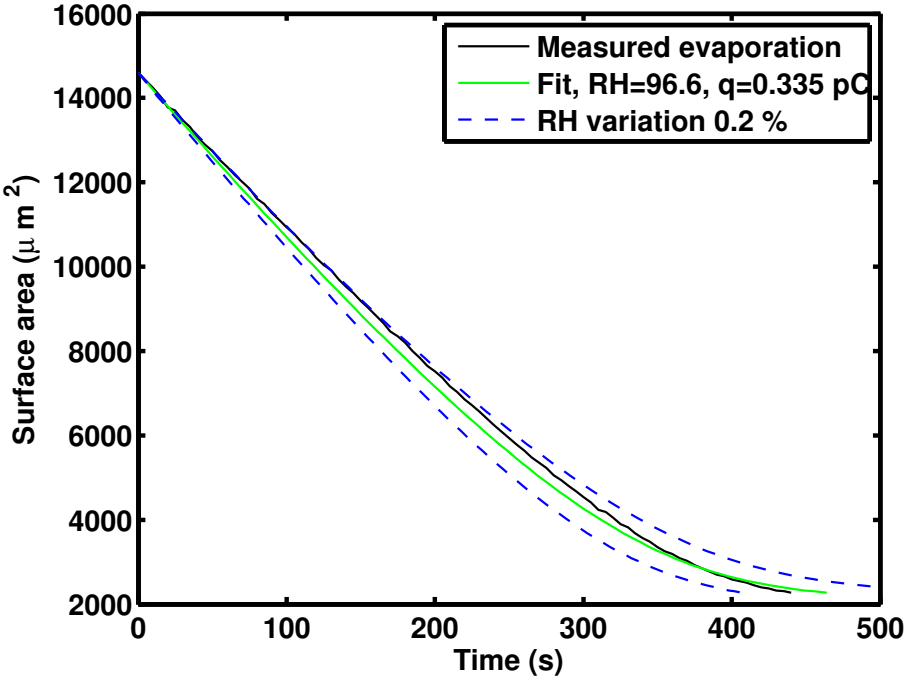

Fig. 3. Example of measured surface area of charged evaporating particle as function of time. The green curve is the analytical solution to Eq. (5). The dashed blue curves illustrate the result of varying the RH value ± 0.2%, which is the estimated uncertainty of the relative humidity.

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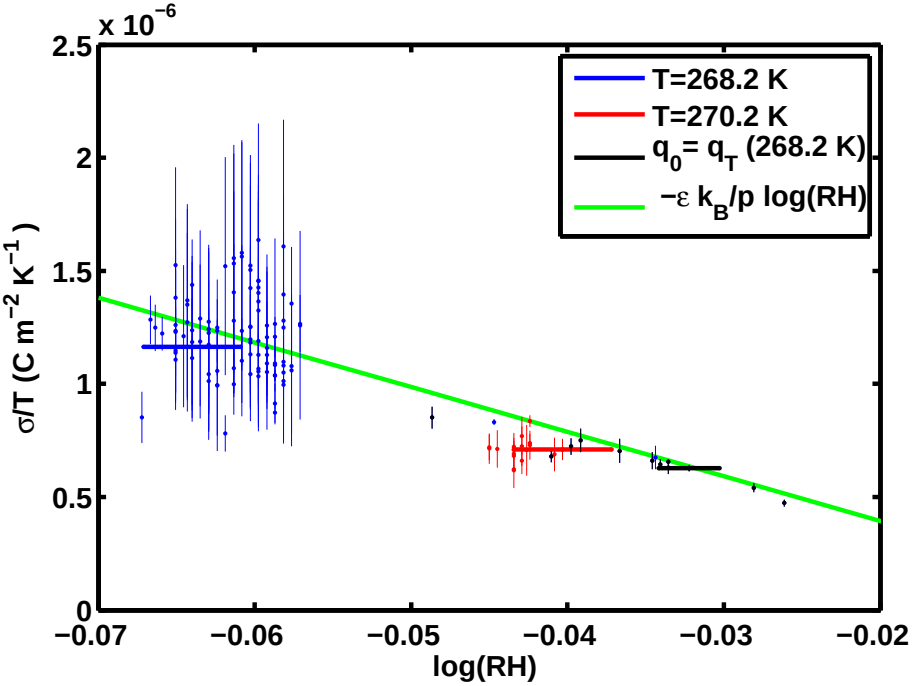

Fig. 4. Surface charge density divided by temperature versus logarithm of relative humidity, for different equilibrated droplets. The vertical lines are error bars showing the instrumental uncertainty of each measurement. Blue data: each point represents a droplet equilibrated around 268.2 K. Red data: droplets equilibrated around 270.2 K. Black data: a few droplets at 268.2 K that were not loosing charge during the experiment, hence the surface charge density is less uncertain in these measurements. The green line shows the theoretical relation between relative humidity and surface charge. Horizontal bars approximate the experimental error on the relative humidity estimated from the slope of the evaporation curves (Fig. 3).

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