Reviewer comments to the manuscript “Comparing contact and immersion freezing from continuous flow diffusion chambers” by Baban Nagare, Claudia Marcolli, André Welti, Olaf Stetzer, and Ulrike Lohmann

Alexei Kiselev and Nadine Hoffmann (contact: alexei.kiselev@kit.edu)

Karlsruhe Institute of Technology, Institut of Meteorology and Climate Research, Karlsruhe, Germany

The manuscript of Nagare et al. describes contact freezing experiments conducted with supercooled droplets freely falling through the chamber containing ice nucleating (IN) aerosol particles. At the first glance, this seems to be the ideal experimental setup to study the evasive phenomena of contact freezing. The temperature regime, humidity, droplet and particle size are all atmospheric relevant. Already the second glance reveals the difficulties in measuring the magnitudes in question (collision efficiency, CE, and freezing efficiency, FE) and interpreting the observation results. Most puzzling, the authors report no enhancement of contact freezing compared to the immersion freezing conducted with the same IN particles and in similar setup. We share the attitude of the Reviewer 1 that the manuscript should be published to provide the basis for the discussion of the presented measurements and data interpretation. There are some issues, however, that could be improved at the stage of preparation of the final manuscript that we would like to discuss here.

To our opinion, the main conclusion about the role of contact freezing made in this paper is a direct consequence of the method used to measure the CE and the approach used to compare the contact and immersion freezing behavior. We discuss these issues below followed by more specific remarks.

1. The uncertainty in interpretation of contact freezing results is obviously related to the uncertainty of determination of collision efficiency. The CE experimentally determined for 0.2 µm AgI particles (0.13) was reported being 14 times larger than calculated theoretical value. What could be the reason for such a high discrepancy? The degree of control of the experimental parameters (temperature, humidity, size and evaporation rate of the droplets, particle number concentration, droplet charge etc.) is very high, and all known interaction forces seem to be taken into account. On the other hand, the sensitivity of experimental observables to the value of the CE is very strong (see equation 19 and discussion of figure 4 in (Nagare et al., 2015), so that its knowledge is crucial for drawing a conclusion about the role of the contact freezing.

   One of the possible explanations would be the depletion of the IN particle concentration within the volume swept by the droplet train. Water droplets generated with 100 Hz frequency and falling with 0.186 m/s terminal velocity would be separated by 2 mm distance or 0.01 s time lag. The RMS diffusion displacement calculated for 0.2 µm diameter particle (Hinds, 1999, equation 7.18) is about 2e-6 m. Assuming the CE for 0.2 µm AgI particles equal to 0.13, the radius of the cylindrical volume where a falling 80 µm droplet experiences collisions with aerosol particles is

   $$r_{drop} \times (CE)^{0.5} = 4 \times 10^{-5} m \times (0.13)^{0.5} = 1.4 \times 10^{-5} m,$$

   seven times larger than the RMS Brownian displacement of the AgI particle within the droplet interarrival time. This essentially means that the particle number concentration reduced due to the scavenging by falling droplet will not return to equilibrium before the next droplet arrives. Reduced number concentration has to be compensated by higher apparent freezing efficiency (according to equation 19 from (Nagare et al., 2015) to describe the observed fraction of frozen droplets. This back-of-the-envelope calculation shows that the depletion of aerosol in the droplet train zone is quite possible and might affect the calculation of the collision efficiency. For larger aerosol particles the depletion can be even larger.

2. We share the confusion of reviewer 1 with respect to the discussion of freezing efficiency calculated with equation 1 or equation 4 (Section 4.1). In your preceding paper (Nagare et al., 2015) the CE has been calculated with equation 19, which is just equation 4 of this manuscript under assumption that FE = 1. To my understanding, with the CE defined in this way the FE should be derived using equation 4 and not with the equation 1. It is correct that the time independence of FE should indicate the contact freezing but it has nothing to do with the number of collisions required to induce the freezing, it can happen on the first collision or after several dozens of them and still have to be the dominant mechanism. Surely the choice of equation could not be helpful to decide which freezing mechanism is dominating the apparent freezing rate of the droplets.

3. Why is the freezing induced by a particle adhering to the surface of the droplet called “freezing inside-out” throughout the paper? In the original paper (Durant and Shaw, 2005) the IN particle was penetrating the surface from inside of an evaporating droplet, hence the name. In the present manuscript this name is used to describe the situation where an IN particle adheres to the surface and is only partly immersed into the droplet, as compared to the fully immersion freezing mode in IMCA/ZINC. To our understanding, partial immersion does not imply a new nucleation mechanism different. As have been shown in (Hoffmann et al., 2013a), the contact freezing efficiency of mineral dust IN particles is proportional to the surface area of the particle. We argue there that the term “contact freezing” does not imply freezing on a point contact but a considerable fraction of particle surface has to be involved into the freezing process. The term “freezing inside-out” was used to highlight the process of penetration of the droplet surface, and is not fully applicable in the present manuscript. Please consider removing this term from the paper.

4. Based on the comparison of FF and freezing onset temperatures you conclude that the contact freezing is a not dominant freezing process. This conclusion seems questionable, because to our opinion the true value of a contact FE for AgI cannot be derived from the experiment. A better way to compare the two freezing process is based on their characteristic times, as suggested in (Hoffmann et al., 2013b). There we have introduced a characteristic residence time t_{im} of a supercooled droplet experiencing collisions with the IN particles as

$$t_{im} = \frac{2 \cdot FE_{contact}}{J_{imm}},$$

where J_{imm} is the rate of freezing due to immersion freezing and can be estimated from the IMCA/ZINC measurements using the relationship between the number of unfrozen and total number of droplets:

$$\frac{N_{unfrozen}}{N_{total}} = 1 - FF = \exp(-J_{imm} \cdot t)$$

and the residence time in ZINC of $t = 3\ s$. At T = 255K the FF for the AgI 0.2 µm particles in the immersion freezing experiment (we refer to figure 1) is ≈0.95 for number concentration of 5000 cm^{-3} and therefore $J_{imm} = 1s^{-1}$. The meaning of this is that on average, droplets would freeze in immersion mode 1 second after collision with 200 µm AgI particle at this temperature. Even if we assume the $FE_{contact} = 1$ (in the figure 4 it is rather 0.3 to 0.5) the characteristic time would be $t_{im} \approx 2s$, comparable to the shortest residence time used in your experiment, and thus the condition

$$FE_{contact} \gg \frac{1}{2} J_{imm} t$$

required to observe the dominance of contact freezing is not fulfilled. This simple analysis show that at least for silver iodide particles both freezing mechanisms are competing and there is no way to derive the FE for both mechanisms separately on the time scale of the experiment.

As it is immediately follows from these considerations, the freezing on-set in purely immersion mode should be always observed at higher temperature just due to the fact, that in INCA/ZINC droplets are entering the cold zone carrying the IN particles inside, whereas time is needed in CLINCH for droplet first to collect an IN particle and then freeze due to one of the freezing mechanisms.

5. Difference or equality of FE at different reference times is discussed throughout the manuscript. However, the difference in FE for different aerosol concentrations (as seen in the figure 4) is neglected. This behavior cannot be explained by interplay of the immersion vs. contact freezing as it is done for the residence time dependence.

Specific comments

1. There is an apparent contradiction between two statements (page 6, lines 21-25).: “*Panel (a) of Fig. 4 shows that FE does not exceed 0.5 for C =5000 cm−3 because it is assumed that on average 2.35 collisions are necessary to freeze a droplet. This led us to Eq. (4) to calculate FE, which assumes that already the first collision induces droplet freezing*”. If more than one collision is needed to freeze the droplet, the freezing could occur on any of the subsequent collisions, couldn’t it?

2. (page 6, lines 25-26).: "*This reinforces the assumption that the first contact leads to droplet freezing in this temperature range and confirms the plateau condition used in Nagare et al. (2015) to derive CE.*" This is a confusing statement: in your previous paper the CE was derived from the measurements of FF under assumption that FE = 1 (in the plateau region, at T < 245K), and now you derive the FE value from essentially the same measurements under assumption of known CE? In this case you can't obtain any other value of FE but 1.

3. (page 10, line 28) Could you clarify why is the solubility of silver iodide important for the contact freezing experiments reported in this paper and what do mean by the statement "*Moreover the freezing ability depends on the surface charge on AgI particles*" (page 11 line 1).

References

Durant, A. J. and Shaw, R. A.: Evaporation freezing by contact nucleation inside-out, Geophys. Res. Lett., 32(20), 2–5, doi:10.1029/2005GL024175, 2005.

Hinds, W. C.: Aerosol technology: properties, behavior, and measurement of airborne particles, Wiley Interscience, 1999.

Hoffmann, N., Duft, D., Kiselev, A. and Leisner, T.: Contact freezing efficiency of mineral dust aerosols studied in an electrodynamic balance: quantitative size and temperature dependence for illite particles, Faraday Discuss., 165(0), 383, doi:10.1039/c3fd00033h, 2013a.

Hoffmann, N., Kiselev, A., Rzesanke, D., Duft, D. and Leisner, T.: Experimental quantification of contact freezing in an electrodynamic balance, Atmos. Meas. Tech., 6(9), 2373–2382, doi:10.5194/amt-6-2373-2013, 2013b.

Nagare, B., Marcolli, C., Stetzer, O. and Lohmann, U.: Comparison of measured and calculated collision efficiencies at low temperatures, Atmos. Chem. Phys., 15(23), 13759–13776, doi:10.5194/acp-15-13759-2015, 2015.