Reviewer comments to the manuscript: “Particle-area dependence of mineral dust in the immersion mode: Investigations with freely suspended drops in an acoustic levitator” by Diehl et al.

The manuscript presents results of heterogeneous freezing experiments with supercooled water droplets obtained in Acoustic Trap and Wind Tunnel (AT and WT, according to the abbreviations introduced by the authors of the manuscript). These two experimental approaches require levitation of the single supercooled water droplets and therefore are less popular in ice nucleation community as compared to cloud chambers, continuous flow instruments, or cold plate setups. However, the measurement data shown in the manuscript shows that single droplet techniques could be successfully used for obtaining the quantitative values of heterogeneous freezing efficiency of ice nucleating particles. The reliability of the data is confirmed by comparison with the existing data sets obtained with different experimental approaches, and also by cross comparison between the AT and WT experimental methods. In case of WT experiments, the exponential decay of the unfrozen droplet population offers a clear demonstration of the stochastic nature of heterogeneous freezing. As suggested by the authors, the advantage of the acoustic levitation of the droplet is the absence of the supporting surface, the absence of electric charge on the droplet and the absence of the suspending electric field, normally employed in electrodynamic traps. Whereas the first argument is obviously infallible, the later one requires additional clarification: the effect of charge on the freezing behavior of the levitated droplets has not been experimentally or theoretically demonstrated. All experiments, where effect of charge or electric field has been reported, involved supporting surfaces (substrates) in various form or/and external particles attracted by charged droplet. The direct influence of charge on the homogeneous freezing of electrodynamically levitated water droplets has not been experimentally confirmed (Rzesanke et al., PCCP 2012).

The authors suggest interpretation of their results based on the stochastic and singular models of heterogeneous freezing. These two approaches allows for determination of the temperature dependent nucleation rate coefficient and surface density of ice active sites. As it has been recently shown, these magnitudes are more suitable for comparison of the ice nucleation results obtained in different types of experiments.

The manuscript gives a thorough description of experimental procedure, sufficient introduction into the state of the art and detailed discussion of results and experimental accuracy, so that there are definitely no objections against the publication of the paper in the ACP. I would like to suggest several minor changes, though, that might be helpful in improving the overall quality of the paper. Some general remarks related to the interpretation of the results are formulated below, followed by more specific comments.

General remarks:

1. The title of the manuscript is somewhat misleading. It points to the acoustic levitation as a main experimental technique, although a significant part of the manuscript is dedicated to the wind tunnel experiments: 7 figures out of 21 show exclusively wind tunnel results and another four figures contain WT data alongside with the AT data. Please consider including the “wind tunnel” into the title.

   The wording of the title itself is very unfortunate, at least its first part: the key word “freezing” or “ice nucleation” is missing, so that the “immersion mode” cannot be related to the freezing process which is the subject of the manuscript. Please consider also replacing “particle area” with “particle surface area”, because it can be any other area (projection, cross section, etc.) related to the particle population.

2. On the use of specific surface area (SSA) of mineral dust particles. Throughout the manuscript, the specific surface area is used for calculation of ice nucleation rate coefficients and ice active surface site density of all mineral dust samples. I wonder if this is the reasonable approach especially if applied to such highly agglomerated clay particles as montmorillonite and illite. Although the term “specific surface area” is intuitively very clear and hardly requires explanation, the value concealed behind this convenient term is strongly dependent upon the measurement method. I assume, that the authors are referring to the BET (Brunauer - Emmet - Teller) method (Brunauer et al., 1938), which is actually done by measuring N_2 adsorption isotherm of dry outgassed (i.e., heated in vacuum up to 150°C) powder at 77K. My concern is that the value of specific surface area obtained with non-polar (nitrogen) substance is used to describe the interaction of the surface with polar water molecules (immersion freezing). It might work well for compact “rock-like” mineral dust particles (quartz, feldspar), but might pose a problem when applied to highly porous “fluffy” aggregates like illite. Besides, montmorillonite is a “swelling” phyllosilicate, meaning that water, (but not nitrogen!) is capable of penetrating the silicate layers of the montmorillonite particles increasing their “effective surface area” by a factor of 4 (maximum theoretically possible SSA in this case would be more than 800 m^2/g). Illite is not a swelling phyllosilicate but highly aggregated one (as indicated by large SSA). Do we know, what part of the inter-crystalline surface is accessible to nitrogen, and if this surface is in any way related to the surface area, accessible to liquid water during freezing?

   I understand, however, that when comparing the experimental results obtained with the *same* sample but *different* techniques the actual value of the SSA is of secondary importance. But if the ice nucleation efficiency in form of ice nucleating site density (m^{-2}) or ice nucleation rate coefficient ($s^{-1}m^{-2}$) is intended to be used in the models describing ice nucleation in atmospheric clouds (as suggested by the authors in summary section), the possible error of the simulated ice crystal concentrations could be very strong. My feeling is that BET SSA should not be used uniformly for all kinds of mineral dust particles, and extreme caution has to be exercised when describing the surface of strongly agglomerated particles as illite or montmorillonite.

3. Is that necessary to provide the same data (isothermal experiments in wind tunnel) twice, once plotted in linear coordinates, once on a logarithmic y-axis? I am referring to figures 10 and 11 vs 14 and 15. Please consider reducing the number of figures!

Specific comments:

I have very few specific comments:

Section 2.2

Line 10: "As an improvement to earlier measurements, the fractions of frozen drops were determined time-resolved."
A reference to the "earlier measurements" would be appropriate here.

Section 3.1.3

"In Fig. 12 the median freezing temperatures as determined by Broadley et al. (2012) and the present results (from acoustic levitator and wind tunnel) are shown in green and blue, respectively" and the discussion of Figure 12:

I don't exactly see the point of combining the median freezing temperatures from AT with non-linear cooling rates and isothermal experiments with WT (how is a median freezing temperature of an isothermal measurement defined anyway?). Is there any reason why would one expect exponential decay of median freezing temperature with particle surface area? You argue that if your data is extrapolated into the colder temperature region, it end up in the range of data from (Broadley et al. 2012), but it does not hold for the reverse situation: extrapolating the linear part of the Broadley-data into warm temperature range results in 4 orders of magnitude difference in terms of particle surface area needed to ensure the freezing.

I think that the figure 12 does not have any added value and should be omitted from the manuscript. Besides, the comparison with the data from (Broadley et al. 2012) in terms of nucleation rate coefficients and surface site densities (Figures 20 and 21) is present anyway and makes much more sense.

Section 3.2.1

Line 22: "*To extend the homogeneous stochastic model to heterogeneous ice nucleation by a single species it is assumed that the nucleating probability is similar for all drops of a population*".
I'm not sure that I understand the meaning of this statement. The stochastic approach considers a population of identical droplets and the probability of freezing for all of them is exactly the same, not just similar. There is no difference in stochastic description for homogeneous or heterogeneous freezing, but the classical nucleation theory (CNT) for homogeneous freezing can be adapted to heterogeneous case by introducing empirical parameters accounting for the presence of heterogeneous surface.

Section 4. Summary and Conclusions:

Line 14: "The freezing time is coupled to the freezing temperature and cannot be used to determine nucleation rate coefficients"

This sentence is very unclear. In fact, that is what you have done – calculating the nucleation rate coefficients from the incremental sections of the freezing curve.

Line 25: "The derived number densities of active sites can be used in cloud models to easily describe ice formation in the immersion mode."

I would like to stress the importance of correctly describing the particle surface area once again. In addition to the considerations suggested in my "general remarks", one have to be aware of the fact that the mineral dust particles used in the lab, even if quite representative in terms of mineral composition, could vary strongly from the atmospheric population in terms of size distribution and aggregate state of the individual particles. These two factors would strongly affect the actual effective surface area of the ice nucleating particles.

References:

Rzesanke D, Nadolny J, Duft D, Muller R, Kiselev A, Leisner T. On the role of surface charges for homogeneous freezing of supercooled water microdroplets. Phys Chem Chem Phys 14(26), 2012

Brunauer, S., Emmet, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309–319.