Responses to reviewer #2:

We thank the reviewer for his/her suggestions, which we address below in italic.

Kaufmann et al. present new heterogeneous ice nucleation data for water droplets that contain one of four substances: Hoggar Mountain dust, Arizona Test Dust, nonadeconol, and birch pollen washing water. Experiments are performed using differential scanning calorimetry. The authors use repeated freezing and thawing cycles while tracking the change in the onset freezing temperature with run number. These refreeze experiments are interpreted through the prism of classical heterogeneous nucleation theory to infer if freezing occurs quasi-deterministic on special active sites or stochastic on truly random locations on the surface.

The experimental setup has been used previously by the same authors and the experimental protocols are sound. Overall the manuscript is well written. The analysis is interesting, informative, and relevant to the ACP readers. At times the theoretical modeling seems to push against the limits on what can be in inferred in principle using the adopted methodology. If properly caveated, I recommend publication.

Comments

The concept of onset freezing isn't very clear. The manuscript states: "For the refreeze experiments, the onset of the freezing peak was evaluated. The evaluation was done using the implemented software "TA Universal Analysis" of the instrument." First, this part needs to be expanded to explain how the procedure works, what threshold is used to detect onset. Perhaps this could be illustrated with the help of Figure 1? For the Hoggar dust, the first freeze events were dominated by large droplets. I presume they are only sometimes present and the configuration may be more unstable? Do these runs coincide with the ones that are flagged by the rank correlation? Second, would it be possible to estimate how many drops or how much water volume needs to freeze to detect onset? Since this is used to repeatably probe the same active site, i.e. the most efficient nuclei in the sample, it would be important to estimate many different sites are able to compete for the "onset" detection. If it is not possible to estimate this, the authors should comment how competition from different active sites would affect the run cycle statistics and derived nucleation rates.

In Fig. 1, we show thermograms of emulsion experiments. However, we performed the refreeze experiments with single droplets of 1.8 – 2 mg weight (see Sect. 4.2). These droplets freeze immediately and completely due to the first nucleation event. The freezing is so abrupt that the sample cannot be cooled sufficiently to maintain the prescribed cooling rate and the temperature of the sample even increases instead of decreasing. The freezing onset of large droplets is therefore clearly given and taken as the nucleation temperature. To avoid confusion, we state in Sect. 4.2 of the revised manuscript: "Refreeze experiments were carried out with bulk samples which exhibit an abrupt heat release when they freeze leading in the DSC thermograms to a clear onset of the freezing peak, which was taken as the nucleation temperature."

Moreover, we improve Sect. 6.5, which presents the emulsion measurements. It now reads:

"In Fig. 1 typical thermograms of emulsion measurements with Hoggar Mountain dust (panel a), ATD (panel b) and birch pollen washing water (panel c) are shown. For ATD, Marcolli et al. (2007) showed that the observed range of heterogeneous freezing temperatures cannot be described by assuming the same contact angle for all ATD particles. Rather, the ice-nucleating sites of ATD particles are required to be of different qualities. Note, that the refreeze experiments were performed with single droplets weighing 1.8 – 2 mg which contain a high number of particles. The best nucleation sites probed in the refreeze experiments with bulk samples are active from 260 to 268 K, i.e. at distinctly higher temperatures than the average sites probed in the emulsion experiments which nucleate ice below 252 K. In contrast to the bulk measurements, no memory effect was observed for ATD emulsions. Hoggar Mountain dust is a mixture of various minerals which are nucleating ice at quite different temperatures (Pinti et al., 2012; Kaufmann et al., 2016) giving rise to the broad freezing signal starting below 257 K with the freezing of single large emulsion droplets as shown in panel (a). Again there is no overlap in freezing temperatures between the emulsion measurement and the refreeze experiments performed with large single droplets which froze from 258 to 265 K. With an onset of 255 K, the heterogeneous freezing peak of the emulsion made from the birch pollen washing water exhibits a clear overlap with the freezing temperatures observed for bulk measurements which indicates that the ice nucleation active macromolecules present in the birch pollen washing water contain quite uniform nucleation sites."

Introducing the beta factor to improve fits of j_{het} seemed like a promising approach to gain additional insight into the mechanism of freezing. However, the results show variation of beta from 10ˆ-9 to 10ˆ43, or 52 orders

of magnitude. The observable range of the universe is 10ˆ-15 to 10ˆ26 m, only 41 orders of magnitude. A physical interpretation of beta seems to stretch credulity.

As an optional suggestion. The nucleation rates for the different samples, e.g. Figure 4, could be normalized by 'active site' strength, assuming ones buys into that concept. One way to normalize the rates is to anchor rates at T0, where T0 corresponds to a nucleation rate of $10^{-3}cm^{-2}s^{-1}$ (middle panel of Figure 4). All other temperatures would be relative to T0. The actual freezing temperature could be color coded onto the symbols. Such a plot might help to highlight similarities and differences in for the different active sites probed. If the graphs collapse, then a simple parameterization for a population of particles could be reported.

If we understand correctly, this evaluation would not be based on CNT but just rely on a normalization to a selected nucleation rate coefficient. Such a presentation would have the advantage to directly disclose the differences in slopes between the experiments. However, for this normalization, an arbitrary nucleation rate coefficient (e.g. 10^{-3} $cm^{-2}s^{-1}$ as suggested by the reviewer) has to be chosen and the nucleation temperature for this rate coefficient has to be determined for each refreeze experiment by interpolating or extrapolating the nucleation rate coefficients as a function of freezing temperature. Since the increase of the nucleation rate coefficients with decreasing temperature is not linear, the choice of the fitting function would again be arbitrary. In our approach, the fitting curve has a theoretical basis because it is prescribed by CNT. Moreover, the measured increase of nucleation rate coefficients with decreasing temperature can be compared with the increase predicted by CNT. CNT predicts for the mineral dust samples a too steep and for the birch pollen washing water a too shallow increase, which is reflected by $\beta < 1$ determined for the mineral dusts and $\beta > 1$ for birch pollen washing water. We do not give too much weight to the actual value of the prefactor, rather, we use it as an indicator for a steep or a shallow increase of the nucleation rate coefficients with decreasing temperature. To make this clearer, we add the following sentence to Sect. 7.3 of the revised manuscript:

"Note that the values fitted for β range from 10^{-9} to 10^{43} for all refreeze experiments and show uncertainties of a factor of hundred for individual fits to refreeze experiments. This shows that the exact value of β is not well constrained. Nevertheless, the β-value can be used as an indicator for a steeper ($\beta > 1$) or a shallower ($\beta < 1$) increase of nucleation rate coefficients with decreasing temperature than predicted by CNT."