Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2017-31-RC3, 2017

Atmospheric Chemistry and Physics
Discussions
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Interactive comment on "Heterogeneous freezing of super cooled water droplets in micrometre range-freezing on a chip" *by* Thomas Häusler et al.

Anonymous Referee #3

Received and published: 17 March 2017

Haeusler et al. report the design and performance of a new droplet freezing cold stage system that uses a unique array of gold surface wells to produce isolated droplets of well defined sizes. As the focus of this manuscript is on the design of the experimental system, with very little discussion of the actual ice nucleation properties derived from the initial experiments, it really seems much better suited to AMT as opposed to ACP. Or perhaps it could appear as a short technical note in ACP. Regardless, if the focus remains on the performance of the new system, the manuscript requires many more details and discussion to demonstrate the new cold stage's ability to reliably measure immersion freezing properties of ice nucleating particles (INPs). Temperature control is critical in such systems, yet the accuracy and precision of the temperature control in this system was not discussed. The droplet freezing curves reported for four different types of INPs were not presented in an appropriate or sufficient manner to produce a

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meaningful evaluation of the system's ability to properly measure immersion freezing properties. These results require a deeper analysis and discussion if they are to be used to properly evaluate the system's performance. The overall quality of the results and their analysis is regrettably quite poor. I recommend major revisions, and that the paper be transferred to AMT as it fits the technical scope of AMT far better than the more scientific focus of ACP.

The most novel and significant aspect of this work is the use of a gold plated or etched gold plate to produce isolated droplets of uniform size. The low homogeneous freezing temperatures observed for pure water that come very close to that expected for homogeneous freezing of pure water are impressive. Other cold plate systems that use a hydrophobic cover slip or other substrate to place the droplets on typically experience freezing of pure water droplets at much warmer temperatures, which restricts their ability to measure the immersion freezing of less active INP systems that induce freezing close to where the pure water freezing interference is a problem.

As the use of a gold surface is the most novel aspect of this approach, it really warrants more discussion. Why was gold chosen? Was its surface already known to induce poor/zero ice nucleation properties? No discussion or references regarding this are provided. Silicon was found to strongly induce ice nucleation, so what is special about gold's surface? Might other (precious?) metals have similar desirable properties as gold? Gold is soft and easily scratched, which might present an important issue for the long term use of gold substrates for droplet freezing.

Some more details on how the pure water was prepared would also be useful. Was the water just taken directly from the commercial Milli-Q water generator, with no additional filtration etc.? I think these are important details that are often not reported by the ice nucleation community, but the quality of the water can severely limit how low in temperature the system can go before "pure" water freezing starts to interfere. If the water was taken directly from the system, this is more evidence that it is the gold substrate that allows this system to achieve freezing temperatures of pure water very close to the homogeneous limit. This would provide further important evidence to the community that it is the substrate (such as commonly used hydrophobic cover slips) that is the main cause of the higher freezing temperature of pure water commonly observed in cold stage systems, as opposed to impurities in the water itself.

I was surprised that none of Markus Petters' groups significant measurements from their cold stage were mentioned here. They have done a lot of work on validating their system, and developing protocols for analyzing the data, and have used both droplets immersed in oil and also droplets in air. The design and evaluation of other similar cold stage systems should also be discussed, as this will better convey the unique aspects of the system reported here (Budke and Koop, 2015; Mason et al., 2015; Petters and Wright, 2015; Tobo, 2016; Whale et al., 2015; Wright et al., 2013; Wright and Petters, 2013). Some important lessons regarding how to properly evaluate a cold stage system can also be learned from these other papers, and should be incorporated here to properly evaluate their system.

The temperature control system design seems to be a simple and effective one, but very little is said regarding the accuracy and precision of the temperature control. There will be some lag and offset between the setpoint temperature and what is actually produced in the substrate where the droplets reside. How significant are these, and do they vary in time during the temperature cooling cycle? There might also be a significant temperature gradient across the gold substrate droplet array. These all need to be measured and discussed. Other groups usually validate their systems by also measuring the melting points of a series of compounds to test the accuracy of the temperature control of the droplets.

Similarly, what cooling rates can this system achieve, and what cooling rate is typically used? The cooling rate can have significant effects on the observed freezing temperature, and must be accounted for (Broadley et al., 2012; Mason et al., 2015; Wright et al., 2013).

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An advantage of using isolated droplets is the ability to perform droplet refreeze experiments, which can provide important insights into the nature of the ice nucleants (Polen et al., 2016; Vali, 2008, 2014; Wright et al., 2013). It would strengthen this manuscript if its refreeze capabilities were also tested and assessed.

The analysis and discussion of the actual droplet freezing temperature curves measured is frankly very thin, and does not provide a meaningful evaluation of the system's immersion freezing measurement capabilities. The authors are aware of the important effects of INP concentration on the measured freezing temperatures, but only discuss these effects qualitatively when comparing their results to published data. A proper quantitative analysis is require here so that results from different cold stage systems that use different droplet sizes and INP concentrations can be properly compared to this new system.

The n_s framework could be used, as is commonly done in the IN community now (Hiranuma et al., 2015; Wex et al., 2015). n_s is attractive in its simplicity for accounting for how changes in total particle surface area change the observed droplet freezing temperature, but it does contain some significant issues when applied to droplet freezing measurements from a cold stage. It was recently reported that varying the INP in water concentration can cause the n_s values retrieved from cold stage measurements to change significantly (Beydoun et al., 2016). This means that n_s will not always properly normalize for changes in INP surface area, as it is intended to do. As different IN groups use different droplet volumes and INP concentrations, this may explain the persistent disagreement in n_s values obtained by different groups for the same INP system (Emersic et al., 2015; Hiranuma et al., 2015). Caution in using n_s is thus warranted, but the authors must quantitatively account for how different particle concentrations affect the measured freezing temperatures when comparing their results to literature data.

Issues of particle coagulation and sedimentation when working at high particle concentrations are another concern in cold stage systems, and high concentrations are used here (Beydoun et al., 2016; Broadley et al., 2012; Emersic et al., 2015). As this method only has an oil film at the top of the droplet perhaps the ice nucleants will always be available to induce freezing even if they settle to the bottom of the droplet. That would be a unique advantage of this approach that is worth evaluating and discussing.

The analysis and discussion of the median freezing temperatures observed for the various systems tested here needs some major attention if these results are to be used to credibly evaluate the system's performance. First, the expected homogeneous freezing temperature expected for the droplet volumes used here should actually be calculated. I suspect the authors will find that their measured temperature is very close to that expected for the droplet sizes used here, but the droplet's volume must be accounted for.

The discussion of Snomax does not reflect our current state of understanding of this widely used ice nucleant. It is known that Snomax contains at least 3 different types of ice nucleants, and that this causes at least two different freezing temperature regimes to be observed, as the concentration of Snomax is varied (Pandey et al., 2016; Turner et al., 1990, 1991). More significantly, it was recently found that the most efficient ice nucleants in Snomax that induce freezing $\sim$-3 C degrade in time, while the ice nucleants that freeze $\sim$-8 C are stable (Polen et al., 2016). So the fact that Snomax was observed to freeze around -9 C here can be explained by the degradation of the more active ice nucleants, and/or the use of low concentrations that mean most droplets do not contain the rare more active ice nucleants. Given the high concentrations used here, I suspect it is the former, but the authors can confirm this by comparing the total amount of Snomax present in their droplet volumes with the range reported by (Polen et al., 2016). Providing information about the age of their Snomax sample and how it was stored will also help to clarify this.

Note that the instability of Snomax's ice nucleation properties makes it a risky choice as an ice nucleation standard for comparison to other immersion freezing systems. The IN community really lacks good INP standards. The much higher freezing temperatures observed for microcline here might be explained by the milling of the material, but this makes the use of this system to compare to other results rather meaningless, as they are not comparing the same INP type. The authors should test their system using a better behaved type of INP that has been studied by other groups, to properly evaluate their system. Illite NX (Hiranuma et al., 2015) or Arizona test dust (A1 Ultrafine fraction) are some good possibilities. Measuring melting points of different pure compounds should also be performed.

Figure 1 doesn't really add to the paper and could be omitted.

The roughness of the gold wells and surface shown in Fig. 4 is quite notable. Based on the very low freezing temperature observed for pure water it seems that this does not create ice active surface sites on the gold, but this should be discussed as it provides further evidence of the desirable (and unique?) properties of gold as a substrate for ice nucleation measurements.

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