Reply to the Interactive Comment by Ulrich Krieger

We thank U. Krieger and his co-authors for the short comment concerning discussion of the timescales of equilibration and their effects on the ice nucleation potential of α-pinene SOA in our paper. In the revised version of the paper, we extend the discussion of the topic to include the recent studies by Lienhard et al. (2015) and Price et al. (2015). Below we reply to the concerns raised in the short comment.

We would first like to clarify why we believe that we observe heterogeneous ice nucleation. Based on instrument validation studies considering the homogeneous freezing of highly diluted ammonium sulphate droplets, as shown in Fig. 1 and 2 in the paper, we obtain the random instrumental uncertainty in temperature with a standard deviation of 0.5 K We have modelled (according to Rogers (1988)) the equilibrium maximum range in the ice saturation ratio the aerosol sample possibly is exposed to - in the vertical and horizontal dimensions - based on the temperature readings of the chamber walls. For consistency, we have plotted 10 % frozen fractions for the SOA particles in Fig. 5. All the maximum saturation ratios for the observed 10 % frozen fractions are below the depicted lines in Fig. 5 indicating where homogeneous freezing occurs. In terms of the saturation ratio with respect to water, the maximum modelled values are found in the range 0.90-0.98 and in the range 0.92-0.98 for frozen fractions of 1 and 10 % respectively. For the water saturation to reach 1 for all of these freezing conditions - a systematic wall temperature deviation of > 2 K in between the thermocouples would be required. Such a systematic wall temperature deviation is highly unlikely considering the reasonable and reproducible homogeneous freezing results presented in the paper. Hence, it is highly unlikely that the observed freezing occurring at subsaturated conditions with respect to water can be considered homogeneous freezing.

Therefore, we interpret the ice nucleation as being heterogeneous. We agree that it is possible that the heterogeneous ice nucleation we observe could be immersion freezing of partly deliquesced SOA particles having “core-shell morphology”, as suggested by Berkemeier et al. (2014) and Price et al. (2015), instead of “pure” deposition nucleation of water vapour onto insoluble ice nucleating particles. This and other possible freezing mechanisms are discussed in detail in the revised version of the paper.

The SOA measured in this study was the same as in Järvinen et al. (2015), and the observed transition from aspherical to spherical form, interpreted as a change in viscosity from semi-solid to liquid, happened at approximately RH = 80 % at T = 235 K. Thus, at RH > 80 % the SOA would be liquid in an equilibrium state. It was also observed by Järvinen et al. (2015) that the phase transition was not instantaneous, but the transition timescales from semi-solid to liquid were of the order of minutes. In order for heterogeneous ice nucleation to occur at RH = 93 % before liquefaction of the SOA, we agree that the nucleation rate needs to be sufficiently fast, and this is possible with SPIN. The nucleation times in SPIN can be of the order of tenths of seconds or even shorter.

Here, we would like to correct a misconception in the short comment: the nucleation time of a few seconds reported by Welti et al. (2012) with the ice nucleation chamber ZINC, an instrument somewhat similar to SPIN, is the residence time inside the instrument and only represents the maximum time available for ice nucleation. Actual nucleation times can be significantly shorter, and some of the particles may nucleate ice even instantaneously after entering the SPIN chamber.

In Lienhard et al. (2015), the α-pinene SOA particles were produced in a flow tube reactor at room temperature and collected onto filters, after which they were extracted and the water-soluble part of the SOA was studied as single particles levitated in electrodynamic balance to determine the diffusion coefficients of water in the SOA. The diffusion coefficients of water in α-pinene SOA at lower temperatures (T = 249.5 K and lower) were measured only up to water activities of 0.5 due to instrumental limitations. A Vignes-type parameterisation derived from model substances was applied and fitted to the SOA data, with predictions of high diffusion coefficients at the upper end of the water activity spectrum. Based on these fits and parcel model simulations it was concluded that atmospheric SOA particles are most likely in equilibrium with the surrounding relative humidity, thus making heterogeneous ice nucleation on these particles unlikely to occur above 220 K.

In the present study, we observe heterogeneous ice nucleation in the upper end of the water activity spectrum at 235 K. While the model fits shown in Fig. 2 in Lienhard et al. (2015) agree well with the measurements in the case of SOA proxies such as levoglucosan and sucrose, for α-pinene SOA the actual measurement points at T=249.5 K, T=232 K and T=209.5 K at measured water activity range (a_w < 0.5) do not indicate a clear increase in the diffusion coefficients and the agreement with the measurements and parametrization is not as obvious as for the proxies. At higher water activities where the Vignes-type parametrisation shows a drastic increase in diffusion coefficient values there are no data points. The fact that the parametrizations presented in the Lienhard et al. (2015) do not agree with the ice nucleation measurement data presented in our work – provided that the freezing we observe is either deposition nucleation on highly viscous SOA or immersion freezing of partly deliquesced SOA - brings up interesting questions and should be a topic of future studies. Interestingly, our results support the simulation results of Price et al. (2015) who suggest that core-shell morphologies could exist at moderate to high updraft speeds at 230 K and lower temperatures.

Another aspect to consider is that in our study, the SOA particles were slightly less oxidised (O:C = 0.25). Furthermore, we did the measurements using online methods, not the water extract of the SOA filter samples. Hence, the composition of the SOA particles in our study may differ significantly from that used in Lienhard et al. (2015), which could affect the properties controlling the water uptake and ice nucleation of these SOA particles.

Finally, we fully agree that the competition between liquefaction of the particle by water uptake and its ability to trigger heterogeneous ice nucleation is of crucial importance. Nevertheless, we would like to stress that much is still unknown of this topic, and as there is possibly such a significant and important difference in the atmospheric implications between the results of our paper and that of Lienhard et al. (2015), we think it is absolutely crucial that future experimental and modelling studies address this topic.

References

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