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Interactive comment on "Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene" *by* K. Ignatius et al.

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The authors observe ice formation on secondary organic aerosol in their chamber experiments and interpret the ice formation as deposition freezing of ice on semi-solid or glassy particles.

Recently, Lienhard et al. (2015) and Price et al. (2015) concluded from their measurements of water diffusivity in α-pinene secondary organic material (SOM) that aerosol particles of α-pinene SOM are homogeneous liquids under typical tropospheric temperatures above about 220 K even when rapidly humidified from dry conditions. There is some inconsistency between the interpretations of the present paper and the impli-

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cations derived from previous experiments. While the SOM is considerably different in all three experiments, this does not seem to justify the atmospheric implications suggested by Ignatius et al., as we will describe below.

Consider the key parameters of the experiment shown in Fig. 3 of the paper under discussion: SOA particles were produced from ozonolysis of α-pinene with a mean O:C ratio of 0.25±0.04 (Järvinen et al., 2015), the temperature was 235.1 K and freezing of ice was observed at a relative humidity (RH) with respect to water of about 93 %. In a separate experiment, increasing the RH very slowly from dry conditions led to a drastic decrease in depolarization, attributed by the authors to a phase transition from semi-solid to liquid. This transition occurred at a temperature of 235.1 K at 80 % RH.

Since water acts as a plasticizer in semi-solid SOA, the diffusion constant of water in the SOA changes by orders of magnitude with water content. In the following we use the numerical model described in Lienhard et al. (2014, 2015) to simulate the water uptake of the SOA in the SPIN instrument using three different assumptions for the concentration dependence of the water diffusion constant as shown in Fig. 1 (here plotted as dependence on water activity). Panel (a) of Fig. 2 shows the RH versus time we assumed in our simulations - infinitely fast transition from dry to humid - and panel (b) the resulting growth of the particle with time.

In the first scenario (black lines), we use the parametrization of Lienhard et al. (2015) which is derived from measurements of kinetic limitations of water uptake for an α-pinene SOM with an O:C ratio of 0.53. Clearly, the particle becomes a homogeneous liquid within the first 1/10 of a second; see panel (b) of Fig. 2 which shows the growth to equilibrium size). Hence, the heterogeneous nucleation rate observed by Ignatius et al. needs to be very fast. Welti et al. (2012) for example reported a nucleation time of a few seconds for immersion freezing of kaolinite particles in a very similar instrument.

In order to investigate possible causes for slower water uptake we considered keeping the shape of the Lienhard et al. (2015) parametrization but reduce the water diffusion

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constant at aw=0 by three orders of magnitude (red lines). Please note that the water diffusion constant at aw=1 is well established (Smith and Kay, 1999) and does not depend on the properties of the SOM. This yields a reduction in water diffusion constant at RH=93% relative to the reference (Lienhard et al., 2015) of about a factor of 2.4. Altogether this only extends the time for particle equilibration to less than 2/10 of a second.

To slow down the water uptake at aw $>$ 0.8, it would be more effective to reduce the water diffusion constant at aw=0.93 and not at aw=0 to shift the water uptake to higher RH. We would even expect such a shift because of the lower O:C ratio of the SOM used in this study compared with the Lienhard et al. (2015) reference. The green lines show such a shift resulting in a reduction of the water diffusion constant by one order of magnitude at aw=0.93. This reduces the time to reach a homogenous liquid particle to about 1 s. However, at aw=0.8 the diffusion constant is now close to the one at aw=0, contradicting the observations of the authors of a viscous to liquid transition at this humidity. Also, the particle still takes up water fast (at aw $>$ 0.85), so heterogeneous nucleation might be more likely to occur via immersion freezing than deposition freezing.

Finally, the step-like humidification in the SPIN instrument does not resemble atmospheric conditions. Whether or not a glassy particle may act as an INP in the atmosphere depends on the rate of atmospheric humidification, which in turn determines the competition between liquefaction of the particle by water uptake and its ability to trigger heterogeneous ice nucleation (see e.g. Berkemeier et al. (2014) and Lienhard et al. (2015). Even at extremely high humidification rates as the one shown in Fig. 3(a), a SOM particle at 235.1 K is likely to become a homogeneous liquid before reaching the saturation ratio for heterogeneous nucleation determined with the SPIN instrument, see Fig. 3(b) in which we plot the concentration profiles within the particle of initially 550 nm diameter (to compare with the ones of Fig. 3 of Ignatius et al.) at various times for the Lienhard et al. (2015) parametrization of water diffusion.

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The rate shown in Fig. 3 corresponds to an adiabatic cooling of about 5 K/s! This is an extremely high cooling rate and in most atmospheric situations cooling rates are more moderate, thus providing even more time that the case shown in Fig.3a for the liquefaction of such particles. In conclusion, we believe that heterogeneous ice nucleation is unlikely to occur at temperatures above 220 K in the atmosphere, as was suggested by Lienhard et al (2015).

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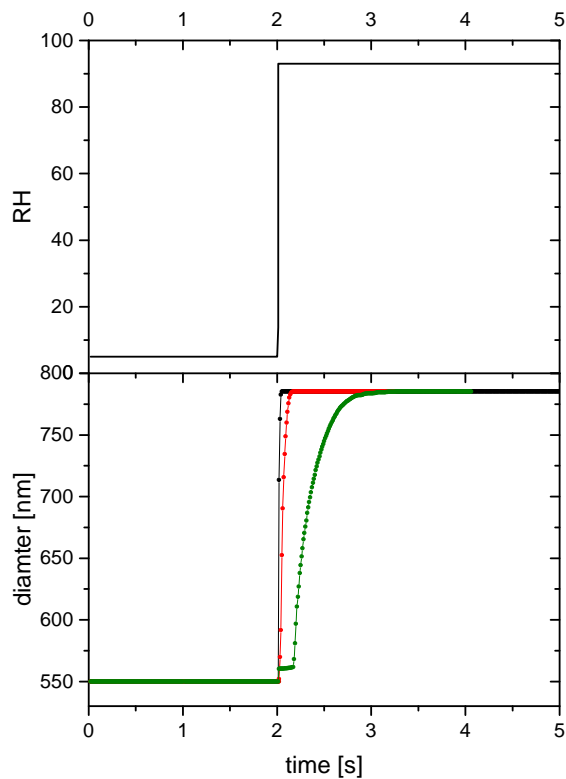Welti et al., Atmos. Chem. Phys., 12, 9893–9907 (2012).

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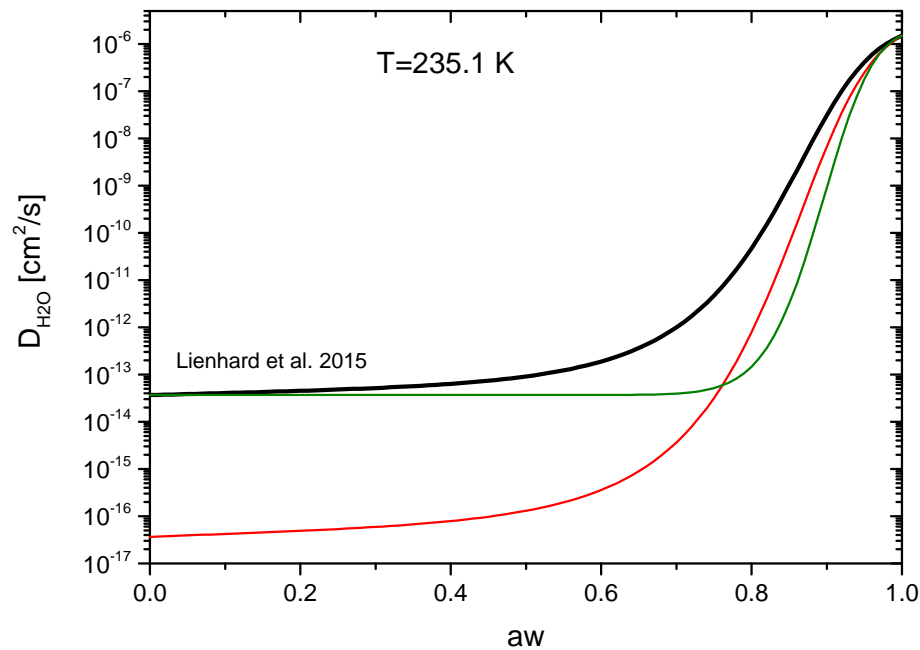
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Fig. 1. Water diffusion vs. water activity, three scenarios

Fig. 2. Panel (a): RH change with time in SPIN, panel (b): corresponding size growth to homogeneous liquid for the 3 scenarios
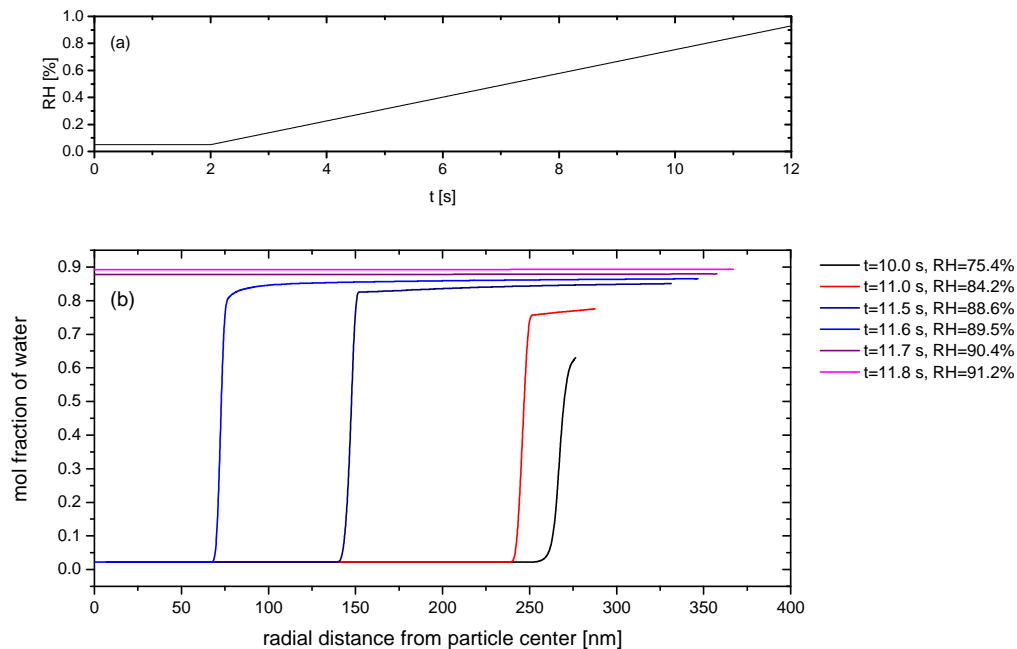
Fig. 3. Panel (a): humidification corresponding to 5 K/s adiabatic cooling, panel (b): water concentration profiles at different times during humidification