Comments on: "Ice Nucleating Properties of α-Pinene and Limonene-Derived Secondary Organic Aerosol Under Cirrus Conditions" by Rapp et al.

Summary

Rapp et al. present a study investigating the ice nucleating ability of secondary organic aerosols (SOA) derived from α-pinene and limonene precursors under cirrus-relevant conditions, for both self-nucleated and seed-particle experiments. They investigate the influence of precursor identity, SOA chemical composition, volatility, and pre-cooling on ice nucleation efficiency, and report heterogeneous ice nucleation more clearly for limonene-derived SOA. The use of glass transition temperature (T_g) as a predictor of heterogeneous ice nucleation was not supported by the results.

The manuscript is well written and appropriately organized. The figures effectively display the relevant information and the references are appropriate and comprehensive. In my opinion, this work makes a meaningful contribution to the understanding of ice nucleation properties of SOA from biogenic sources. However, the limited temperature range explored represents a notable weakness, as discussed below. I recommend publication after minor revisions, detailed in the comments that follow.

General Comments

Limited temperature range. Only two temperatures were explored (-40 and $-45\,^{\circ}$C), while cirrus clouds form down to $\sim -85\,^{\circ}$C. The authors should discuss how representative their findings are of the full cirrus regime and provide a mechanistic explanation for the absence of heterogeneous freezing at $-45\,^{\circ}$C.

Phase state is inferred, not measured. Phase state is inferred from T_g calculations rather than measured directly. The authors should state all assumed parameters explicitly and acknowledge associated uncertainties. Direct viscosity measurements (e.g., Virtanen et al. 2010) would benefit the interpretation of results.

Role of multiphase chemistry remains unresolved. The logical chain connecting seed acidity to SOA phase state and ice nucleation efficiency is central to the study's motivation but is never fully articulated. The authors should either state this chain explicitly.

Atmospheric implications need development. The section should additionally address: whether observed S_{ice} thresholds occur in the real atmosphere; whether activation fractions are sufficient to compete with homogeneous freezing; the role of updraft velocity in phase state

retention; and the source region relevance of limonene versus α-pinene.

Self-nucleated experiment conditions need clarification. It is unclear whether self-nucleated and seeded experiments were conducted under identical conditions. If generation settings were optimised to minimise self-nucleation in seeded runs, the use of the same settings for seedless runs should be justified.

Specific Comments

L11. Please clarify in what sense the contribution of BSOA to cirrus cloud formation remains unresolved. What specific aspects (formation mechanism, INP efficiency, atmospheric abundance, or radiative effect) are being referred to?

L14. The relevance of limonene as a SOA precursor should be briefly justified. Are there estimates of global or regional limonene emission fluxes that support its inclusion alongside the more widely studied α-pinene?

L65. Please briefly define subvisible cirrus clouds for the reader.

L120. Please briefly describe what multiphase reactions are in this context, as this concept is central to the study's motivation but is introduced without definition.

L124. Please provide the complete logical chain connecting seed acidity to phase state and from phase state to ice nucleation efficiency. As written, this connection is implied but not explicitly stated, making it difficult to follow for readers less familiar with the topic.

L137. Phase state is inferred from composition, volatility, and T_g in this work. Could phase state or viscosity have been measured more directly, for example, using the particle bouncing technique described in Virtanen et al. (2010)? Please discuss why such measurements were or were not feasible in this experimental setup.

L196. Is the 10 L mixing volume also applicable to self-nucleated SOA experiments where no seed particles are present? Please clarify.

L204. The paragraph describes conditions for generating seeded SOA; however, self-nucleated SOA experiments were also conducted (Table 1, Table S2). Please clarify whether the described conditions also apply to self-nucleated runs, or specify any differences in setup. In particular, if O_3 concentration and UV intensity were optimised to minimise self-nucleation, why were the same settings used for seedless runs?

L214, Figure 2. Several clarifications are needed: (i) add labels or a legend to panels to make clear which refers to PNS and which to PNS-coated particles; (ii) define and explain the NRMSE values shown in the panels; (iii) explain the different mode shifts observed for different modes in the coated PNS experiment: is this physically interpretable or an artefact of size resolution?

L244. Would it have been possible to conduct PALMS-NG analysis specifically on ice crystal residuals, targeting only particles that activated as ice, separately from the bulk aerosol population? This would have provided direct chemical characterisation of the INP-active fraction and is worth discussing even if not performed.

L245. Are there sections of the experimental setup where freshly nucleated SOA particles are at risk of changing phase state or undergoing partial volatilisation before reaching the ice nucleation measurement?

L247. It would be more physically accurate to state that the laser pulse ablates/vaporises the particle and subsequently ionises the resulting fragments, rather than "ionises the particle" directly.

L253. Please clarify the complementary roles of PALMS-NG and AMS in this study. Both provide chemical composition information. What is the added value of using both systems, and what can each measure that the other cannot?

L282. Please explicitly describe the mechanistic expectation for what happens to particles during pre-cooling at −30 °C. What change in phase state or diffusivity is anticipated, and how does this translate into the observed differences in ice nucleation onset?

L300. Were the particles injected into SPIN polydisperse? In seeded experiments where both coated seed particles and self-nucleated SOA are present, how were the ice-activating particles identified and distinguished from one another?

L304. Please clarify the difference between the machine learning classification model used in this study and the one described by Garimella et al. (2016).

L315. The statement attributed to Koop (2004) regarding temperature inhomogeneities causing earlier-than-expected homogeneous freezing cannot be located in that paper as cited. Please clarify exactly where in Koop (2004) this statement is reflected.

L316. Are the SPIN calibration measurements described here part of a published study or available elsewhere?

L324. How sensitive are the reported activation fraction values to the choice of the 100 nm threshold for separating self-nucleated from coated seed particles? How would the results change if this threshold were shifted to smaller sizes?

L340, Figure 3. It would be informative to add reference lines indicating the deliquescence relative humidity (DRH) of AS and PNS, to provide context for where phase transitions of the seed particles are expected relative to the observed freezing onsets.

L353. Would pre-cooling of pure AS or PNS seed particles (without any SOA coating) have changed their ice nucleation ability? This control experiment would help isolate the effect of pre-cooling on the seed from the effect on the coating.

L355. Please explain mechanistically how AS particles can trigger heterogeneous freezing at S_{ice} values above their deliquescence RH, given that deliquesced AS solution droplets are expected to follow the Koop homogeneous freezing line. How do these results compare with Welti et al. (2020)?

L360. Please provide a mechanistic explanation for why heterogeneous freezing was observed at −40 °C but not at −45 °C. This temperature dependence is counterintuitive given that lower

temperatures generally favour glassy phase states and should enhance heterogeneous nucleation efficiency.

L373. Please clarify how the onset of water uptake was observed experimentally.

L479, Figure 4. It would strengthen the comparison to literature if data could be presented at a common activation fraction threshold. The authors should consider contacting the original authors of referenced studies to obtain data at matching AF values.

L515, Figure 6. The lack of overlap with literature data at lower temperatures is a significant limitation. Please discuss whether it was technically possible to scan at temperatures below −45 °C with the SPIN instrument used, and whether additional temperature points between −40 °C and −45 °C could have been explored. The sparse temperature coverage limits the ability to compare and contextualise prior results.

L645. Please note that Piedehierro et al. (2021) specifically suggests that the short residence time in SPIN (∼10 s) is insufficient for particle equilibration with the surrounding RH under some conditions, which can lead to inhibition of homogeneous freezing.

L654. This statement incorrectly characterises both Piedehierro et al. (2021) and Ignatius et al. (2016). Neither study pre-cooled particles in the sense used in this manuscript. Ignatius et al. (2016) generated SOA inside the CLOUD chamber at CERN. Please correct and revise this statement accordingly.

L660. Please discuss how the different particle sizes used across studies affect the comparison of ice nucleation onset conditions, and whether it is possible to scale or normalise results to account for size effects.

L664. Please explain the mechanism proposed for pre-activation. What physical or chemical process might particles have undergone during pre-cooling that would result in them being more effective INPs?

L670. Please clarify whether the evaporation section of SPIN was active or intentionally disabled during experiments where water uptake behaviour was being evaluated. If the evaporation section was off, please provide additional information about how δ_{SPIN} during RH ramps was interpreted.

L675. An alternative mechanistic interpretation should be acknowledged: homogeneous freezing of the outer liquid shell in a core-shell morphology, where the glassy core facilitates water accumulation at the surface but does not itself act as the heterogeneous nucleating substrate.

Technical Comments

L164. The PNS abbreviation is already defined in the introduction.

L181. "detailed" → "detail".

L185. Define THC on first use.

L585. "size" → "six".

L216/Figure 2. Define D_{pg} and σ_{g} explicitly in the figure caption.

L240. Clarify whether BSOA and SOA are used interchangeably and apply terminology consistently throughout the manuscript.

L269. Define $T_{g,org}$ explicitly on first use, including the meaning of the "org" subscript.

References

Garimella, S., Kristensen, T. B., Ignatius, K., et al.: The SPectrometer for Ice Nuclei (SPIN): an instrument to investigate ice nucleation, Atmos. Meas. Tech., 9, 2781–2795, https://doi.org/10.5194/amt-9-2781-2016, 2016.

Ignatius, K., Kristensen, T. B., Järvinen, E., et al.: Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene, Atmos. Chem. Phys., 16, 6495–6509, https://doi.org/10.5194/acp-16-6495-2016, 2016.

Koop, T.: Homogeneous ice nucleation in water and aqueous solutions, Z. Phys. Chem., 218, 1231–1258, https://doi.org/10.1524/zpch.218.11.1231.50812, 2004.

Piedehierro, A. A., Welti, A., Buchholz, A., Korhonen, K., Pullinen, I., Summanen, I., Virtanen, A., and Laaksonen, A.: Ice nucleation on surrogates of boreal forest SOA particles: effect of water content and oxidative age, Atmos. Chem. Phys., 21, 11069–11078, https://doi.org/10.5194/acp-21-11069-2021, 2021.

Virtanen, A., Joutsensaari, J., Koop, T., et al.: An amorphous solid state of biogenic secondary organic aerosol particles, Nature, 467, 824–827, https://doi.org/10.1038/nature09455, 2010.

Welti, A., Korhonen, K., Miettinen, P., Piedehierro, A. A., Viisanen, Y., Virtanen, A., and Laaksonen, A.: SPIN modification for low-temperature experiments, Atmos. Meas. Tech., 13, 7059–7067, https://doi.org/10.5194/amt-13-7059-2020, 2020.