Author Response

RC2 Review of "Ice nucleating properties of α-pinene- and limonene-derived secondary organic aerosol under cirrus conditions" by Rapp et al., 2026

Anonymous Referee #2, 17 Jun 2026
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RC2: Rapp et al. present laboratory measurements of the ice nucleation (IN) ability at cirrus conditions of aerosol particles composed of self-nucleated α-pinene (AP) and limonene (LIM) secondary organic aerosol (SOA), and of ammonium sulphate (AS) or partially neutralized sulphate (PNS) particles coated with AP or LIM. The experiments probe the role of the precursors' physicochemical properties, their estimated glass transition temperature (Tg), multiphase chemistry, and precooling.

The manuscript is well organized and clear to follow. The research hypotheses are well described and addressed. IN of SOA remains a genuinely difficult topic where instrument accuracy and reproducibility are compounded by complex, hard-to-constrain aerosol systems, and this study provides novel measurements that improve our understanding of the IN ability of SOA.

I recommend publication in ACP after the authors address the comments below.

We thank the reviewer for their thorough review of our manuscript and thoughtful comments. We have addressed the comments detailed and revised the text accordingly.

General comments and questions:

1. In Section 2.6.3 you classify a freezing onset as heterogeneous when it falls below the lower bound of the homogeneous freezing region. However, at several points you note that even when the onset lies in the heterogenous regime, its uncertainty extends well into the homogeneous conditions (e.g. AP-PNS at -40°C). This makes it ambiguous whether such particles should be regarded as heterogeneous nuclei, poor heterogeneous nuclei, or effectively homogeneous. Is there additional evidence that could help resolve the freezing mode for points near the homogeneous threshold? In particular, the shape of the activation fraction spectrum may be informative: heterogeneous freezing tends to produce a gradual increase in AF with S_{ice}, whereas homogeneous freezing tends to produce a sharp, threshold-like rise. The AF spectra in Figures S3 and S4 could be examined on this basis.

   We thank the reviewer for raising this important point as these categories should be defined explicitly. We unfortunately did not find shape of the activation fraction curves to be helpful in distinguishing between heterogeneous and homogeneous onsets in these experiments. A primary factor complicating this for α-pinene-derived BSOA was the gradual growth of a water uptake mode prior to subsequent ice formation beyond the homogeneous freezing threshold of 100 nm aqueous solution droplets. Furthermore, gradual growth was observed for limonene-derived BSOA onsets that were clearly beyond the homogeneous freezing regime. As such, we would prefer to keep the qualitative definition as follows:

"Additionally, we classify a freezing onset as heterogeneous by the onset being below the lower uncertainty range in water activity (Δa_w = -2.5%) for homogeneous freezing of 100 nm aqueous droplets (Koop, 2004; Koop et al., 2000). Onsets which have error in S_{ice} with significant overlap are considered at best poor heterogeneous nuclei."

2. The methods used to estimate the glass transition temperature (Tg) need a fuller description even with references to prior work. Specifically, I think it is important to show the relations between Tg and C* and Tg and molecular composition. How do errors in C* and bulk composition propagate into the Tg estimates? The uncertainties associated with the thermogram-derived Tg (Table 2) likely don't reflect the variability of the parameterization and therefore underestimate the true error.

Are there multiple Tg parameterizations in the literature? Do they agree? What motivations brought you to use the two representations presented in the paper and not for example one based on the functional groups?

We have revised Sect 2.5 to address these points and included a detailed description in Section S1.3 of the supplement. With regards to parameterization selection, we utilized two methods: a thermogram-based volatility $T_{g,org}$ estimate (Li et al., 2020; Niu et al., 2025; Zhang et al., 2019) and a molecular-composition based $T_{g,org}$ allowing the inclusion of CHOS compounds (Li et al., 2020) which is an updated form of (DeRieux et al., 2018). We are unaware of a $T_{g,org}$ parameterization that could incorporate chemical data from Vocus-CIMS, AMS, or PALMS-NG to estimate functional group densities. A molecular dynamics simulation utilizes a functional group method (Siachouli et al., 2025); however, we cannot quantitively identify the number specific functional groups.

The estimated Tg for the pure and SOA-PNS systems are very different (Table 2), but the difference is considerably more pronounced in the bulk composition-derived parameterized Tg than for the thermogram-derived one. The bulk composition is very constant across the different systems, what then explains the difference?

We agree that the similar bulk O:C and H:C ratios do not, by themselves, explain the substantially differences between the two parameterized $T_{g,org}$. Bulk elemental ratios represent only the average oxidation state and do not uniquely constrain molecular composition, functional groups, or volatility distributions. Consequently, aerosols with similar bulk O:C and H:C ratios may still exhibit different thermal-desorption behavior and apparent volatility distributions, leading to different thermogram-derived C* and $T_{g,org}$. The larger difference obtained from the molecular-formula-based parameterization may additionally be influenced by compound-dependent Vocus-CIMS sensitivity. In our derivation, normalized ion signals were used as proxies for component abundances under the assumption of equal sensitivity among detected compounds. If the PNS and self-nucleated systems contain different molecular classes, differences in ionization efficiency or molecular coverage could alter the signal-weighted molecular-formula distribution and therefore the calculated $T_{g,org}$ difference. We have added these as potential explanations and now treat the molecular-formula-derived values as sensitivity estimates.

For AP-PNS experiments, you mention that ice nucleation onset was preceded by an onset of water uptake. How can you unambiguously assign the morphology to a core-shell type and not to a homogeneously mixed particle? This leads to two additional questions: how can you assess that the

PNS seeds had crystallized after generation? If not, shouldn't you consider a glass transition temperature for the mixture?

We cannot unambiguously assign the morphology to a core-shell type particle or confirm the phase state of the PNS seeds after passing through the PAM-OFR. However, AMS measurements of NH_4^+:SO_4^{2-} indicate some degree of neutralization had occurred, with more ammoniated character expected with time. Using E-AIM, a particle with a NH_4^+:SO_4^{2-} of 1.63 entering the PAM-OFR after exiting multiple dryers would not be thermodynamically stable as a droplet unless it experienced humidities exceeding 68%. This supports that some crystalline character is almost guaranteed, however we do not have continuous AMS measurements for each experiment.

Regarding the second point, the molecular $T_{g,org}$ parameterizations used here do not support the inclusion of inorganic sulfate. Vocus-CIMS measurements allow for the inclusion of CHOS compounds in the described parameterization that would be present if any reaction formed. To our knowledge, there is no validated parameterization of $T_{g,org}$ that explicitly allows for mixtures of inorganic and organic sulfate.

Across different parts in the manuscript I'd soften the assertion that Tg (generally) fails to predict ice nucleation. I suggest instead saying that the chosen parameterizations applied to your data do not show it (whether this generalizes to all systems and all Tg parameterizations it is not shown in the manuscript).

We appreciate this comment from the reviewer and softened the assertion that T_g more generally fails to predict ice nucleation. We are indeed constrained by the selected T_g parameterizations and precursors studied.

3. Referring to the seeds as ammonium bisulphate (ABS) in some parts of the manuscript is confusing, since by your own account only the first experiment with fresh ABS can be considered "true" ABS. For example, the coatings described in the abstract (L15) were not on ABS. Because you have AMS data, I would suggest labelling all the non-AS seeds as PNS consistently throughout and stating the neutralization degree explicitly for each experiment, including the AS, fresh ABS, and PNS cases.

We have removed all mentions of ABS unless it is in direct context with discussions on aerosol generation or the observation of purely homogeneous freezing as expected.

We note that we do not have AMS measurements for each experiment as these were conducted after the ice nucleation experiments as stated in L160 – 162 (now L225 – 227). Similarly, the VIA-Vocus-CIMS measurements were conducted during that timeframe. We have explicitly stated the timelapse between ice nucleation measurements and these physicochemical measurements similarly to the comment addressing PALMS-NG. This is also clarified when discussing the aging of the ABS to PNS in the materials part of the methods.

4. Changes in aerosol concentration and temperature can shift the gas-particle partitioning of the organic components. Can you rule out changes in chemical composition between the inlets of the different instruments, or during the precooling phase of the IN measurements? Did you try measuring the aerosol composition before and after the PCU?

We cannot rule out changes in chemical composition between inlets of the different instruments or during the pre-cooler as we did not do chemical measurements at different sections of the setup. However, multiple experimental design constraints were in place to minimize such changes. Tubing length between inlets were cut to their minimum lengths and temperature maintained nearly constant, except for the PCU. If chemical reactions were to occur in the PCU we would expect slow reaction rates given the temperature.

5. Can PALMS be used to say something about the distribution of the coating across the seed population?

PALMS-NG is unable to quantify the coating on a single particle; however, across the measured seed population we can quantify the number of spectra without any common organic ion markers. We have added the following sentence:

The number of particles without an organic coating were quantified by evaluating the intensities of common organic ion markers (see Section S2.1.1 of the SI). The fraction of uncoated particles observed ranged from 0.03% to at most 1.09%.

6. Because you compare single-component and mixed particles with different size distributions, why not adopt an INAS-density framework for the heterogeneously freezing systems, which would normalize for surface area?

Normalization such as INAS was considered for this study; however, major assumptions such as independent probabilities of initiating ice nucleation per activation site are invalid for our dataset. With the multimodal algorithm we can decompose the size distributions to retrieve modal areas (Figure S2); however, we are unable to isolate mode specific n_s due to the mixed efficiencies of our particles as shown by the self-nucleated experiments.

Please also clarify the D > 100 nm cut used in the AF denominator: how sensitive is the AF of the LIM experiments to this threshold? Given the low 0.5% AF threshold, could the small but efficient self-nucleated limonene fraction alone exceed it and account for the onset attributed to the coated seeds in the mixed experiments?

We replicated the analysis for 50 and 75 nm cut offs, with respective figures included in the supplement. Based on these figures, restricting to smaller sizes significantly effects the activation fractions of the self-nucleated limonene particles but the coated population is largely unchanged for limonene. This is supported by the observation that self-nucleated limonene rarely exceeded 100 nm when seed particles were present (Table 3). Self-nucleated particles however can grow larger and participate in ice nucleation (Figure 2c).

7. Given the high variability across IN counters, more detail on the measurement strategy is needed. Please report (i) how often filtered, particle-free air was sampled during each measurement; (ii) the background counts for each measurement; (iii) the IN activity measured on the descending S_{ice} branch (if the descending ramp returns to ice saturation, L303 should read “ice saturation” rather than “water saturation”); (iv) how often the chamber walls were re-iced or the ice layer refreshed; and (v) example ramps and ice onsets for the ammonium nitrate calibration experiments.

These points have been addressed in the text and/or supplement.

(i) Filtered, particle-free air was sampled before and after each S_{ice} ramp for 5 minutes. The background counts were interpolated across the entire dataset. The correction factor of 1.4 was also applied to the background ice.

(ii) Background counts used in correcting ice counts have been totaled for each experiment and listed in Table S5 along with relative ratios.

(iii) We specified that the IN activity on the ascending and descending branches were averaged.

(iv) Chamber walls were not re-iced or refreshed as the longest time at which SPIN operated continuously was ~ 10 hours. Background frost levels so increase with time, however they are accounted for in the background subtraction.

(v) We have also included example measurement ramps of the primary experiments (Fig. S9) and ice onsets for pre/post ammonium nitrate calibration (Fig. S10)

8. Section 4 (Experimental uncertainties) reads as a qualitative description of methodological limitations, much of which would be better integrated as concise uncertainty statements within the relevant sections.

We kindly disagree with the reviewer as we would like to summarize methodological limitations in a clear section. We prefer to leave the section as is. Furthermore, we have also included a short paragraph explaining the uncertainty in phase state as that was a key point raised during review.

Specific comments

L113: Please add Bertozzi et al. (2021) on organic coatings of seed particles (relevant also to Figure 5).

Bertozzi B, Wagner R, Song J, Höhler K, Pfeifer J, Saathoff H, et al. Ice nucleation ability of ammonium sulfate aerosol particles internally mixed with secondary organics. Atmospheric Chem Phys. 2021 Jul 16;21(13):10779–98. doi:10.5194/acp-21-10779-2021

We thank the reviewer for including this reference. The data from Figure 5 of (Bertozzi et al., 2021) has also been added to Figure 5 of this manuscript.

L136: This appears to be the only sentence describing how coating thickness was evaluated; it needs more description in the methods/aerosol-generation section. Did you compare the coating thickness for the different modes? Did you compare to the coating estimated from the AMS data assuming a core-shell morphology?

We thank the reviewer for this comment and have added a complete description of coating thickness evaluation in Section 2.3. We have since included coating thickness evaluation for all modes using the multimodal analysis where it is summarized per experiment for singlets in Table 3 and in Figure S3.

Previously, coating thickness was only evaluated for the singlet mode. This was performed by analyzing the diameter in the SEMS data corresponding to the maximum concentration ($dN/dlogD_p$). To exclude any influence from self-nucleated modes or multi-charged singlets, we only looked at particles larger than 200 nm. The

difference in maximum diameter between the SEMS scans of the seed particles and those with active BSOA formation was used to calculate coating thickness.

In the revised manuscript, coating thickness is evaluated by subtracting the initial particle diameters for each mode (excluding self-nucleated) as detailed in Section S2. An example of the modal assignment used for an experiment is included in the SI (Figure S11).

While coating estimates using AMS have been used assuming a spherical core-shell morphology (Bertozzi et al., 2021), we argue that SEMS measurements coupled with multimodal analysis provide a more accurate, real-time analysis of the particle distribution entering SPIN.

L220: From the size-distribution plots it looks like there is an additional neutralizer in front of the SEMS. If this is correct, please mention it in the description.

This is correct and has been specified in the text accordingly (L225-226)

L243: Please define "asynchronously" specifying the time elapsed between the PALMS and IN measurements.

PALMS-NG was being prepared to be shipped to Europe at the beginning of these experiments. PALMS-NG measurements were performed during the testing/refinement of stable particle generation. Generating conditions were then replicated with SPIN measurements; however, PALMS-NG was no longer available for simultaneous sampling.

Similarly, AMS and VIA-Vocus-CIMS were not simultaneously measuring during the SPIN measurements. This has been now explicitly mentioned in Sect. 2.4.2 and 2.4.3 following the same style of description (time elapsed).

L271: Citation format error.

Citations were re-indexed throughout the document with the Zotero citation management software and checked for errors.

L357: 13% of particles are doublets and your ice onset is at <1%. On what basis can you exclude that these activated particles originate from the 13% doublets, i.e., that the freezing is driven by the larger seeds?

We have included a surface area comparison of our measurements in the supplement (Figure S2) which demonstrates that the singlet mode dominates surface area in each experiment. In developing this plot, we have also improved the identification of doublet modes and their number concentrations, increasing the singlet/doublet ratios to 90- 93% across experiments. Given the above, we are confident that the singlet mode is predominantly responsible for the activated ice.

L374: How can you establish core–shell morphology rather than a homogeneously mixed particle?

Primarily due to the phase state of the ammoniated sulfate core. RH was maintained below the efflorescence point of AS prior to organic coating. Furthermore, thermodynamic testing using E-AIM as referenced in this response and the response to RC1 do not suggest a liquid core for the PNS particles.

L380: You state that no clear delineation between pre-cooling conditions was observed for the self-nucleated and LIM-PNS experiments. However, the LIM-PNS points at −45°C (Fig. 3) appear to sit very close to the homogeneous freezing region (comparable to the AP-AS experiments you classify as homogeneous) raising the same classification ambiguity discussed above. They also appear to show pre-cooling shifting the onset to higher S_{ice}, opposite to the trend in all other systems and to the summary at L734. Can you provide a suggested explanation?

We have clarified the statement and agree with the reviewer that the PNS limonene point at -45 is more like the a-pinene-AS experiments which were classified as homogeneous. The comment on L734 is attributed to the fact statistical testing on the dataset using pre-cooling showed no effect. The only instance for limonene in which the expected response of pre-cooling allows ice onsets at lower S_{ice} was for AS particles.

We have included a discussion regarding the counterintuitive nature of pre-cooling shifting ice onsets upwards in Sect. 5.2.

L390: Why did you restrict the PALMS-NG analysis to the singlet particles and exclude the larger ones that could also contribute to the IN signal?

Averaged PALMS-NG spectra shown in Figure S1 used singlets per standard data processing. Given the multimodal PSD analysis, singlets dominate total surface area (Figure S5). If doublets contributed a larger surface area fraction we would reconsider and add these into the averaged spectra but with the given results this is not warranted.

L448 / L689: You report p = 0.28 at L448 and p = 0.59 at L689 for the seed-and-precursor combination, please reconcile.

This was a typo. Given the changes detailed in the multimodal output where a higher resolution time series was used for CPC counts, some test statistics throughout the article have been updated to the most current values, however no p-values have changed above or below pre-defined significance thresholds. Furthermore, no onsets have changed to modify the conclusions of the work.

L465: Do you have AMS data to confirm the degree of neutralization?

We used the AMS to confirm the degree of neutralization of seed particles as summarized in Table 2.

L605: As written, this reads as though you measured Tg directly, please clarify.

We have removed the instance of measured T_g as this incorrectly attributes the methods applied.

L647: If LIM shows no water uptake but its glass transition is ~−70°C, what is the phase state of the particles?

We have corrected the statement that no water uptake occurred. It is more accurate to state that in comparison to a-pinene it was minimal. Regarding the phase state of the particles, we are uncertain and this should be the subject of future studies, particularly direct viscosity measurements as discussed by RC1.

L729: Please reframe specifying which Tg parameterizations fail to predict IN behaviour.

We have clarified that the volatility and molecular composition-based parameterizations failed to predict IN behavior.

L742: Please clarify why the simultaneous presence of self-nucleated particles affects the multiphase-chemistry result specifically.

We have clarified this statement in the conclusion to emphasize that the simultaneous presence of ice active seeds prevents us from solely attributing ice nucleating properties to the coated seed particles.

"Overall, heterogeneous onsets were observed more frequently for PNS seeds than for AS seeds; however, the simultaneous presence of ice active self-nucleated particles prevented us from conclusively attributing the observed ice nucleating properties to the BSOA-coated seed particles. Furthermore, uncertainties in onset S_{ice} and restricted reaction time preclude a definitive conclusion."

Figures

Figure 2: An example of size distributions from a LIM self-nucleated and LIM-coating experiment would be helpful.

This examples have been added and combined with the existing plots.

Figures 4 and 5: Figures 4–6 are cited out of numerical order and are minimally described in the main text. Please cite them in sequence and describe their content/significance in the context.

We have described these figures in more detail within the text and cited in numerical order.

Figure S1: What does "heterogeneous AF" mean? Does it cover AF for S_{ice} from 1.0 to 1.6? Are the AF values already background-subtracted? If so, how do you explain AF > 0 at S_{ice} = 1.0? Does AF > 1 indicate a miscounted ice background?

We have clarified this figure by expanding the caption accordingly. Heterogeneous AF were defined as activation fractions below the lower uncertainty limit in homogeneous freezing. Also, this is represented as % and was not clearly represented in the label. For the last several points if this is regarding Figures S3 and S4 of the original supplement, all data is background subtracted however the SPIN was set to sample at S_{ice} = 1.0 until the PCU concentrations stabilized. In this timeframe, any uncertainty in background subtraction becomes compounded. However as shown in the now included Table S5, the number of backgrounds identified is very small in comparison to the total number of ice observed in each experiment.

References

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