Response to RC2: 'Review of Tiszenkel et al, Temperature Effects on Sulfuric Acid Aerosol Nucleation and Growth: Initial Results from the TANGENT Study', Anonymous Referee #2, 14 Feb 2019

Scientific significance

New particle formation is a difficult and important problem, and there is currently a lack of diversity in the laboratory studies used to characterize it. Measurements from independent groups are to be encouraged. However, the current manuscript requires revision if it is to be suitable for ACP. At first glance, it is unclear how much new information it adds to Yu et al (2017), although the new results do become clearer with a very careful reading. The last part of the introduction should be expanded to explain how the new study differs.

Response 1: We thank the reviewer's for thoughtful comments. We agree that there was a lack of clarity in the original manuscript of the new elements of this study as it builds upon previous work, notably Yu et al 2017 which examined a similar parameter space in a similar setup. To that end, we have expanded both the introduction (Page 3, lines 8-22) and the discussion section (Section 3.2, final 2 paragraphs) to stress how this study, especially using the new TANGENT experimental setup, can contribute new findings to the literature.

The paper does not explicitly explain the point of the TANGENT apparatus, nor why it is an improvement on previous experimental setups, except via the sentence in the abstract that it allows nucleation and growth to be studied independently. This sentence should be revisited in the text with a better explanation for why this is an improvement on Yu et al (2017) where nucleation and growth rates are presented separately already. I appreciate that "separately" and "independently" are not the same, but this needs to be made more obvious in the paper text.

Response 2: We agree. In the revised manuscript, we added an expanded statement on the combination of FT-1 and FT-2 in the experimental setup section to clarify this further (Section 2.1, page 4 and 5). And in the results sections, we also included more data analysis of TANGENT results, and added discussion on the implications on the data. These TANGENT results are now presented in a separate section (Section 3.2) from FT-1 only results (now Section 3.1).

The lack of direct measurements of contaminant NH3 and amines during the experiments is a serious shortcoming, as the concentrations of contaminants could differ markedly between 2017 and 2018 measurement periods. This shortcoming limits the quantitative usefulness of the results, and places high demands on the quality of the data analysis and presentation if the paper is to meet the ACP publication criteria.

Response 3: We make several assumptions in our data analysis with regard to ammonia and amine contamination.

First, by ensuring that our experimental conditions, including using the same flow tubes, adhering to the same cleaning technique/schedule, using the same suppliers for any species added to the system, and running experiments with the same precursors, we can still be confident that the contaminant levels should not have dramatically changed between 2017 and 2018.

Second, 2017 ammonia and amine measurements were conducted both in the UD laboratory and in UAH's laboratory before transporting all instruments for the IOP, and the ammonia/amine readings in both environments were similar, showing ammonia and amine levels very close to the detection limit of

the instrument (ranging from 1 to 40 pptv depending on the species being measured). This consistency between different environments leads us to believe that ammonia/amine measurements from the 2017 IOP can give us a good idea of measurements from the 2018 IOP experiments.

In addition to explaining explicitly the benefits of their new setup, the authors should consider setting their paper apart by including in their figures a more detailed, quantitative comparison with other relevant literature, for example Duplissy et al (2016) or Dunne et al (2016). The authors could try to determine from published nucleation measurements what ammonia or amine concentration would be required to reproduce the new particle formation rates they measure.

Response 4: A quantitative comparison with CLOUD data is an important aspect of this study. We modified Figure 4 with CLOUD data from Dunne et al (2016), using data points of neutral nucleation. We believe it is now clearer where this study results stand in the current knowledge of the field.

In order to make clear the usefulness of the TANGENT setup, the authors should explain explicitly and quantitatively how they can put several different concentrations of precursors in flow tube 2, or maintain them at different temperatures, and measure different growth rates, for a constant nucleation rate in flow tube 1.

Response 5: We agree. As stated in response 2, the experimental setup section of the manuscript was expanded to specifically address the questions raised here. Specifically, we have addressed that FT-2 is kept at constant T and RH and only ozone was varied in FT-2. FT-1 was varied more diversely, with temperature, RH and SO_2 varied across experiments (Section 3.1). This had the effect of varying SO_2 in FT-2 after dilution. These experiments aimed to measure two effects in the system – the effect of changing temperature in the nucleation region as well as the effect of varying ozone in the growth region (Section 3.2).

This is exactly what is done in Figure 6 – which is excellent. However, the figure is presented in the text as describing the situation with different temperatures in the two flow tubes. While the temperatures in the flow tubes happened to be different in the measurement presented, the figure actually describes the effect of varying ozone, and no quantitative conclusion about the effect of temperature can be extracted from it.

Response 6: Yes, we address this together with the following comment.

To quantify the effect of temperature in flow tube 2, another figure is needed where the data in Figure 6 are compared to a corresponding measurement in which the two flow tubes are kept at the same temperature. More generally, the existing plots show the parameter space of nucleation rate vs sulfuric acid, temperature and humidity is quite well explored, but this could have been achieved without the second flow tube and similar measurements were already published by Yu et al (2017). It would be useful to present more measurements where the conditions in the second flow tube are varied with those in the first tube fixed.

Response 7: We agree. We have prepared an additional figure, Figure 7 in the manuscript, that shows results from an experiment that was done with FT-1 and FT-2 at the same temperature. The discussion section was expanded to discuss the implications of the comparison between the results with a temperature gradient and the results with a uniform temperature throughout the system (Section 3.2,

page 10). In short, by adding this new figure, we can see more clearly that the clusters can survive evaporation when they are transferred between different temperature regions.

Scientific quality

The measurements and calculations of nucleation rate use techniques which have been published previously. The experimental apparatus is described clearly. The quality of the data is therefore reasonably well-established, apart from the lack of measurements of contamination that I already mentioned. I have only a couple of outstanding questions. What are the temperature and RH dependences of the critical cluster size?

Response 8: The temperature dependence on critical cluster size was a linear correlation (R^2 = 0.98), going from 1.627 nm at 258 K to 1.651 nm at 297 K. However, considering an error of ±0.2 nm in these measurements, it is indeed difficult to make a definitive conclusion. The RH dependence is more difficult to surmise as RH was difficult to control in the nucleation region, but the critical cluster diameter is negatively correlated with RH across the temperature range; for example, at 268 K the critical cluster diameter was calculated at 1.50 nm at 80% RH and 1.69 nm at 23% RH. Again, the amount of error makes this fairly inconclusive.

Why is critical cluster size equal to the diameter at [H2SO4]=0 (please add reference)?

Response 9: This assumption is based on the equation for growth rate factor used in Yu et al 2017. The equation used to calculate growth rate factor (that is, enhancement of the growth rate over 1 ppt H_2SO_4 leading to 1 nm h^{-1} growth), is:

$$k_G = \frac{\Delta D_{p,tr} \times 10^7 cm^{-3}}{[H_2SO_4]_0} \frac{k_L}{1 - e^{-nk_L t_r}}$$

$\Delta D_{p,tr}$ represents the particle growth after nucleation; therefore when $\Delta D_{p,tr} = 0$, no growth has occurred past nucleation, and therefore the D_p at that point is the critical radius. In figure 3, the equation of the fit lines for each temperature is $D_p = \frac{\Delta D_{p,tr}}{\Delta [H_2SO_4]_0}([H_2SO_4]) + b$. If $\Delta D_{p,tr} = 0$ then D_p represents the critical radius, which equals the y-intercept of the line. We have now included this clarification (Section 2.2, Page 6 and 7)

The survival of the particles in the second flow tube is clearly difficult to disentangle from the strange additional growth via sulfur dioxide and ozone.

Response 10: Indeed, the growth rates in FT-2 are high. We believe there are some heterogeneous process involving SO2 and ozone are contributing to the additional nucleation and growth in FT-2. However, we do not understand these chemical mechanisms at present. Additionally, regarding to the growth, it seems that base contaminations in FT-2 are partially responsible, based on findings from Lehtipalo et al. (2018 and 2016) studies. We included this new discussion in Section 3.2

I don't have any good ideas for why this nucleation happens, beyond the obvious speculations about unmeasured contamination. Could the SO2+O3 reaction be because of a contamination by alkaline material – metallic fragments for example, or enormously high amine or ammonia concentrations – which raise the pH to something like what is seen in sea spray aerosols or cloud droplets?

Response 11: The presence of transition metals in the experimental setup could indeed serve as a source for oxidation at higher pHs (Seinfeld and Pandis p .294): The funnels at the beginning and end of FT-2 were stainless steel. It is unclear how heterogeneous reactions of our precursor gases on the surface of the flow tube could impact the nucleation. However, the particles in this experiment are likely acidic as can be seen from cluster composition of base nucleation as shown in CLOUD experiments (Kirkby 2011; Almeida 2013). Lawler et al., 2016 also showed acidic chemical composition of nanoparticles with sulfuric acid and base nucleation. We added new discussions in Section 3.2 to address acidity of the particles.

Presentation quality

The written English is generally of good quality. There are a few missing articles "a" and "the" distributed through the text. The sentence "Larger mean diameters were detected under lower temperatures for a given [h2SO4]", would imply the method used to determine the critical cluster size would give a larger critical cluster size for lower temperatures. It is clear from theory and from Figure 3 that this is not the case, so the sentence could be rephrased.

Response 12: We have fixed these errors.

Figures 3 and 4 need error bars, if possible, or at least a careful explanation of what the uncertainties are, what is in the noise and what is a real effect.

Response 13: We agree. And we added new Section 2.3 and discussed detailed error propagation analysis.

"Our results thus show that particles were observed at the end of the room temperature nucleation tube after they were initially nucleated at lower temperatures growth tube. These results can explain the presence of newly formed particles observed in Amazon forests by (Wang et al., 2016),….. " It is not clear that the second sentence follows from the first. The focus on the Amazon here and in the introduction and conclusion seems odd, since this is one of the few locations on Earth where nucleation may not be dominated by the sulfuric acid clustering that is the subject of this paper.

Response 14: We agree that those two sentences in the original manuscript did not come together as clearly as we had intended, and that focusing on the Amazon is shortsighted considering our results. We have added some clarifying contents between the two sentences in the revised manuscript. We have addressed the focus on the Amazon boundary layer by broadening the scope of our study, discussing our results in the context of the marine boundary layer, where H_2SO_4 particle formation certainly occurs, as well as polluted megacities, where NPF occurs despite high pre-existing particle loads with abundant pollutant species present such as SO_2 and O_3, as the conditions in FT-2 were during these experiments (Section 3.2).

Regardless of the composition of the particles, studies of how particles evolve once they are transferred between environmental conditions represent an area of aerosol nucleation and growth that lacks laboratory study, and this manuscript represents experiments and observations that can initiate further investigation in this area.

The demonstration that particles survive when the temperature increases is useful, however, and this enabled me to understand the reason for the TANGENT setup. The same mechanism that operates in the Amazon also operates in marine regions, where sulfuric acid nucleated in the upper troposphere

survives to make CCN at cloud level (see recent papers by Lynn Russell's group from the North Atlantic, or much earlier work by Tony Clarke and others).

Response 15: We appreciate this comment. We have added a more thorough discussion of the implications of the results from TANGENT to Section 3.2, addressing marine boundary layer aerosol distributions as well as a more detailed description of how these results can help to explain new particle formation in areas such as polluted megacities where NPF