

We thank the referee for the constructive comments, which are added in full below (in black font). Our replies are given in blue font directly after the comments; text that has been added to the manuscript is shown in red font.

Anonymous Referee #2

The study by Kürten et al. presents a revised analysis of their previous study on new particle formation of the sulfuric acid-dimethylamine-water system. The new results show that nucleation is even faster than previously thought and that the derived nucleation rates are in agreement with model simulations. Further, they show that even tiny mixing ratios of dimethylamine are sufficient to explain significant particle nucleation in the boundary layer.

The paper is well written and suitable for publication in ACP after some minor revisions. My comments are listed below:

General comments:

1) Somewhere in the paper it should be stated what the typical concentrations/mixing ratios of dimethylamine and sulfuric acid in the boundary layer are. Are the concentrations that were used in your experiment realistic?

We agree with the referee and have added the following to the end of section 1:

“The reanalyzed data cover sulfuric acid concentrations from ca. 1×10^6 to 3×10^7 cm^{-3} , which fall into the range for most observations of atmospheric boundary layer new particle formation events (e.g. Kulmala et al., 2013). The dimethylamine mixing ratio for most of the data shown in this study is ~ 40 pptv (1×10^9 cm^{-3}), which is within the rather wide range of observations (0.1 to 157 pptv, i.e., 2.5×10^6 to 4×10^9 cm^{-3}) for C2-amines to which dimethylamine belongs to (Yao et al., 2016).”

This indicates that the concentrations of the trace gases in the present study are atmospherically relevant.

2) The difference between the Almeida et al. (2013) study and your study (same holds for the Jen et al. (2016) study) becomes not really clear from the manuscript as it is written now. If I understand your study correct your experiment is the same as the one by Almeida et al. (2013) but with an improved set-up which results in a better agreement between measurement and observations. This is of course very nice, but as you write it, it sounds like “we are doing it right and Almeida et al. did it wrong” which is not correct. I am sure they did their best at the time they performed their study. Of course, with more time and more experience as well with improving knowledge previous studies can be repeated and improved. This should be discussed more clearly and fair in the paper.

The experiment in Almeida et al. (2013) and the present study is the same. The recorded data from both studies are from the CLOUD7 experiment (conducted in fall 2012). The difference between the two studies is the method that was used to analyze the new particle formation rates. In Almeida et al. (2013) the importance of self-coagulation in the small size range (here between 1.7 nm and ~ 3.2 nm) was not known yet. The fact that these small particles have a big impact on the loss rates of the growing small particles became only clear while knowledge about the

high cluster concentrations in the sulfuric acid-dimethylamine-system increased (Kürten et al., 2014) and their impact on particle growth rates was quantified (Lehtipalo et al., 2016). In parallel, the analytical method for taking into account cluster-cluster-collisions in the derivation of new particle formation rates was developed (Kürten et al., 2015a). This allowed us to revisit the previously conducted experiment (CLOUD7 from Almeida et al., 2013) and to re-calculate the formation rates with the new knowledge and analytical tools.

The reviewer is correct, that the analysis in Almeida et al. (2013) was based on the knowledge and analytical tools that were available at that time. In fact, many of the authors of the current study were involved also in the Almeida et al. (2013) study. As knowledge progressed, we are now in a position that allows us to revisit the previously published data and improve the analysis. The results of this analysis are self-consistent, i.e., they confirm what has been concluded earlier (Kürten et al., 2014; Lehtipalo et al., 2016).

In order to avoid the impression that the Almeida et al. (2013) study and the present one are based on different experiments, we have added the following to section 1:

“New particle formation rates as a function of the sulfuric acid concentration from CLOUD7 were previously published (Almeida et al., 2013). However, these data are re-analyzed in the present study using an advanced method that takes into account the effect of self-coagulation in the estimation of new particle formation rates (Kürten et al., 2015a).“

Regarding the suggestion to add further information about the Jen et al. study, we are referring to the reply to comment 12). Information about the method used by Almeida et al. (2013) is provided in the context of comment 9).

Specific comments:

3) P2, 136: add “mobility diameter” so that it reads “... at a mobility diameter of 1.7 nm...”.

Done.

4) P2, 147: The abundances of sulfuric acid and dimethylamine are given in different units (concentrations and mixing ratio, respectively). The same unit should be used for both consequently. However, I would prefer if the amounts of both species would be given as concentration and mixing ratio.

We agree that it is sometimes confusing if the units pptv and cm^{-3} are used for different trace gases. Therefore, we decided to always provide the conversion to cm^{-3} in brackets when DMA mixing ratios are mentioned.

5) P4, 197 and 1111: What the abbreviation CLOUD is standing for should be rather given in the introduction in 197 than in 1111 of the method section.

Done.

6) P5, 1144: The brackets around the reference are obsolete.

Done.

7) P5, 1152: Same here, the brackets around the reference are obsolete.

Done.

8) P5, 1169 and 1172: Is the unit really correct? If yes, why is it $\text{cm}^{-1} \text{s}^{-0.5}$?

The unit is correct. In the equation $k_w = C_w \cdot \text{sqrt}(D)$, the value of C_w is a constant that connects the square root of the diffusivity (unit $\text{cm s}^{-0.5}$) with the wall loss rate (unit s^{-1}). Therefore, C_w needs to have the unit $\text{cm}^{-1} \text{s}^{-0.5}$.

The expression in equation (2) of the manuscript originates from Crump and Seinfeld (1981). In the original publication it is shown that the wall loss rate is proportional to $\text{sqrt}(k_e \cdot D)/L$ (where k_e is the turbulent energy dissipation rate, unit s^{-1} , and L is a characteristic length, unit cm). From this expression it follows directly that the empirical constant C_w (which combines $\text{sqrt}(k_e)/L$) has the correct unit.

9) P8, 1300: Since you compare your results to Almeida et al. (2013) it would be good if you could write more about the Almeida et al. (2013) study. How were their nucleation rates derived. What are the differences between your experiment and their experiment? Were these experimentally derived or from model simulations?

As outlined in the reply to comment 2), the experiment in Almeida et al. (2013) and in the present study is identical.

The NPF rates from Almeida et al. (2013) were not derived with a model but with equations that can be found in the literature (e.g., in Kürten et al., 2016a, JGR).

The method from Almeida et al. (2013) is now summarized at the end of section 2.3:

“The method introduced here explicitly takes into account losses that occur between particles with d_{p1} and d_{p2} (self-coagulation). These losses have not been taken into account by Almeida et al. (2013). Almeida et al. (2013) derived $J_{3.2\text{nm}}$ from CPC and SMPS measurements by including the corrections for wall loss, dilution and coagulation above 3.2 nm (see also Kürten et al., 2016a). However, the extrapolation to 1.7 nm was made by using the Kerminen and Kulmala equation (Kerminen and Kulmala, 2002), which does not include the effect of self-coagulation. For the system of sulfuric acid and dimethylamine, where a significant fraction of particles reside in the small size range, this process is, however, important.”

10) P10, 1369: Please give to the concentration the corresponding mixing ratio.

We would like to keep the unit cm^{-3} for the sulfuric acid concentration, as this is the unit that is also used in the figures and in many different other publications reporting sulfuric acid concentrations (e.g., Fiedler et al., 2005; Kuang et al., 2008; Kulmala et al., 2013; Almeida et

al., 2013; Jen et al., 2014; etc.). However, related to comment 4) we have provided the numbers in units of cm^{-3} in brackets whenever a DMA mixing ratio is given.

11) P11, L402ff: Concerning the discussion on the differences between model simulation and measurements. I would say that this part could be improved. Although I agree that the agreement is very good you should also admit that the nucleation rates from the model simulation are slightly higher than the measurements which will affect the development of the size distribution. Further, it seems that the differences between the measurements and the model simulation increase with time. Furthermore, the differences are largest at in between the two modes of the size distribution. That is not discussed at all. I would assume that this is caused by an uncertainty in the model. Is the coagulation really correctly calculated? Can't you play around a little with the model and check if the differences get larger/smaller than the nucleation rate is lower/higher (assuming according lower/higher concentrations of dimethylamine and sulfuric acid)? Even larger are the difference between the aerosol volumes, but from the discussion it sounds as that the agreement is perfect which is obviously not true.

We agree with the referee that further discussion and tests regarding the sensitivity of the model would be beneficial for the manuscript. Therefore, further model calculations were performed using the following scenarios (these calculations link to the base-case simulation from Fig. 2 in the manuscript):

- Variation of the sulfuric acid concentration by $\pm 20\%$ to investigate the effect on the evolving size distribution (Fig. 2b).
- Negligence of van der Waals forces in the simulations; van der Waals forces enhance the collision rates by roughly a factor of 2.3 for the smallest particles (Fig. 2c).
- Assumption that the particles grow by the addition of building blocks consisting of 2 dimethylamine molecules and 1 sulfuric acid molecule (2:1 ratio between base and acid, Fig. 2c) rather than due to an equal amount of acid and base (1:1 ratio).

To illustrate the results, the previous version of Fig. 2 was replaced by a new version with four panels instead of two panels (see figure on the next page). In addition, the following discussion was added to section 3.4:

“In order to test the model sensitivity to certain variations quantitatively further simulations were performed (Fig. 2b and Fig. 2c). A variation of the steady-state sulfuric acid monomer concentration by $\pm 20\%$ was achieved by using different monomer production rates for the high sulfuric acid case ($P_1 = 4.17 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$) and for the low sulfuric acid case ($P_1 = 2.01 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$, Fig. 2b). This rather small variation leads to significant mismatches between the modeled and measured size distributions that is also found for the aerosol volumes (Fig. 2d).

Two further scenarios were tested with the model. First, the enhancement due to van der Waals forces were turned off. This scenario results in significantly slower growth rates and the modeled size distributions do not match the measured ones at all anymore (Fig. 2c); the same is found when comparing modeled and measured aerosol volumes (Fig. 2d). Second, the aerosol density and the molecular weight of the condensing “monomer” were changed. In the base-case simulations (Fig. 2a), the density of dimethylammonium-bisulfate is 1470 kg m^{-3} and the molecular weight is $0.143 \text{ kg mol}^{-1}$ because a one to one ratio between DMA and sulfuric acid is assumed. Since full neutralization of sulfuric acid by DMA would require a 2:1-ratio between base and acid, collision-controlled nucleation of $(\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})_2$ “monomers” instead of $(\text{H}_2\text{SO}_4)((\text{CH}_3)_2\text{NH})$ was tested. Therefore, the density was decreased by 6% to account for the density change between dimethylammonium-bisulfate and dimethylammonium-sulfate (see Qiu and

Zhang, 2011) and the molecular weight was set to $0.188 \text{ kg mol}^{-1}$. As expected, the particle growth is now slightly faster due to the additional volume added by the further DMA molecules (Fig. 2c). However, the changes are rather small and the modeled size distributions move a little further away from the measurements compared to the base case scenario (Fig. 2a).”

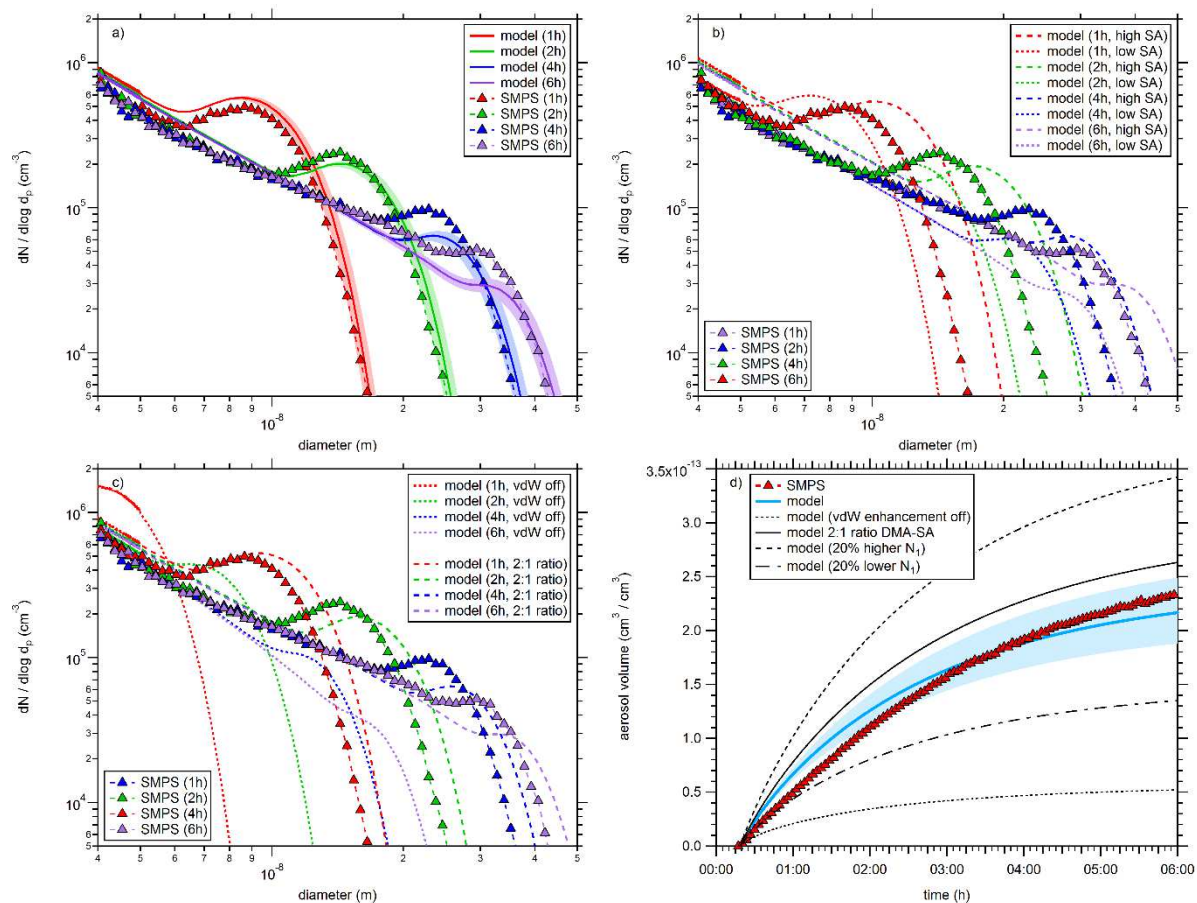


Fig 2 (replacing the previous version of Fig. 2): Comparison between modeled and measured size distributions and aerosol volumes. See text for details.

Regarding the comparison between modeled and measured aerosol volume one of the qualitative statements (“somewhat larger”) was replaced by providing the number of the actual disagreement (section 3.4):

“In the beginning of the experiment the modeled aerosol volume is up to ~40% larger than the measured one, but, towards the end of the experiment (ca. 4h after its start), the volumes agree quite well. Possibly this is because the overestimated modeled particle number density at small diameters is compensated by the underestimated particle concentration in the larger size range (see Fig. 2a).”

In addition, the statement “almost perfectly represented” is replaced by “well represented” in one of the sentences in section 3.4:

“The particle growth rate is well represented by the model given the good agreement between the positions of the local maxima in the size distribution and the intersections between the size distributions and the x -axis.”

12) P11, 1440: Same here as for the Almeida et al. (2013) study, add some more information how Jen et al. (2016) derived their nucleation rates. Was it a similar experiment as the one you performed. If no, what has been done differently etc.

The comparison between our study and the study by Jen et al. (2016a) refers to the measured and simulated clusters concentrations and not to measured new particle formation rates as these were not reported by Jen et al. (2016a, 2016b).

Jen et al. (2016) developed a model that allowed them to retrieve evaporation rates for the sulfuric acid-dimethylamine system from measured cluster signals. The signals were measured at a flow reactor after a reaction time of ~ 3 s, where the initial sulfuric acid monomer concentrations were determined prior to the mixing with the dimethylamine.

The following information was added to section 2.5:

“Within the flow tube experiments dimethylamine was mixed into a gas flow containing a known amount of sulfuric acid monomers. The products, i.e., the sulfuric acid-dimethylamine clusters were measured after a short reaction time (≤ 20 s) with a chemical ionization mass spectrometer. From the measured signals, the cluster evaporation rates were retrieved from model calculations (Jen et al., 2016a). The main differences to the CLOUD study lie within the much shorter reaction time (20 s vs. steady state in CLOUD) and in the much wider range of base to acid ratios used by Jen et al. (2016a, 2016b). This allowed them to retrieve even relatively slow evaporation rates for the sulfuric acid-dimethylamine clusters. The measured cluster/particle concentrations increased with increasing base to acid ratio, eventually approaching a plateau at a dimethylamine to acid ratio of ~ 1 . Therefore, the high dimethylamine to acid ratio used in the CLOUD7 experiment (~ 100) can probably explain why our NPF rates are compatible with collision-controlled nucleation.”

13) P11-12, 1439-478: This text part definitely belongs to the method section than to the result section.

We agree with the referee, and have moved the description of the model (that includes evaporation rates) to the methods section. Therefore, a new section (section 2.5) has been created. However, in that section only a brief overview and description of the extended model is given; the formulae are provided in Appendix A.

14) P12, 1481: The abbreviation DMA has not been introduced yet. I would suggest to keep writing dimethylamine throughout the manuscript. Otherwise, the text is quite difficult to read with all the abbreviations that are already used.

The abbreviation DMA was introduced and defined on page 7, line 230 (section 2.4). As the abbreviation DMA is also used in various other publications (Almeida et al., 2013; Jen et al., 2014; Jen et al., 2016a, etc.) we would like to keep it.

15) P14, 1529 and 1530: Please give the abundances of H₂SO₄ and dimethylamine as concentrations and mixing ratios.

See replies to comments 4) and 10).

16) P15, 1550: I would suggest to write: “This study confirms the results derived in previous studies.”

Done.

17) P14/P15, 1553, 1575, 1576: please give the according concentrations and mixing ratios.

See replies to comments 4) and 10).

18) P15, 1605: It should read “numerical model”.

Done.

19) P16, 1608-609: units for *M* and *W* missing or are these dimensionless?

These parameters are dimensionless; they were introduced by McMurry and Li (2017).

20) P30, Figure 3 caption: add DMA in brackets after dimethylamine. Give the abundances for H₂SO₄ and dimethylamine in both concentration and mixing ratio.

Done (addition of “DMA” to the figure caption). Regarding the concentration/mixing ratio values see replies to comments 4) and 10).

References

Ahlm, L., et al.: Modeling the thermodynamics and kinetics of sulfuric acid-dimethylamine-water nanoparticle growth in the CLOUD chamber, *Aerosol Sci. Technol.*, 50, 1017–1032, doi: 10.1080/02786826.2016.1223268, 2016.

Almeida, J., et al.: Molecular understanding of sulphuric acid-amine particle nucleation in the atmosphere, *Nature*, 502, 359–363, doi: 10.1038/nature12663, 2013.

Crump, J. G., and Seinfeld, J. H.: Turbulent deposition and gravitational sedimentation of an aerosol in a vessel of arbitrary shape, *J. Aerosol Sci.*, 12, 405–415, doi: 10.1016/0021-8502(81)90036-7, 1981.

Fiedler, V., et al.: The contribution of sulphuric acid to atmospheric particle formation and growth: a comparison between boundary layers in Northern and Central Europe, *Atmos. Chem. Phys.*, 5, 1773–1785, doi: 10.5194/acp-5-1773-2005, 2005.

Jen, C., et al.: Stabilization of sulfuric acid dimers by ammonia, methylamine, dimethylamine, and trimethylamine, *J. Geophys. Res.-Atmos.*, 119, 7502–7514, doi: 10.1002/2014JD021592, 2014.

Jen, C. N., et al.: Chemical ionization of clusters formed from sulfuric acid and dimethylamine or diamines, *Atmos. Chem. Phys.*, 16, 12513–12529, doi: 10.5194/acp-16-12513-2016, 2016a.

Jen, C. N., et al.: Diamine-sulfuric acid reactions are a potent source of new particle formation, *Geophys. Res. Lett.*, 43, 867–873, doi: 10.1002/2015GL066958, 2016b.

Kerminen, V.-M., and Kulmala, M.: Analytical formulae connecting the “real” and the “apparent” nucleation rate and the nuclei number concentration for atmospheric nucleation events, *J. Aerosol Sci.*, 33, 609–622, doi: 10.1016/S0021-8502(01)00194-X, 2002.

Kuang, C., et al.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J. Geophys. Res.-Atmos.*, 113, D10209, doi: 10.1029/2007JD009253, 2008.

Kulmala, M., et al.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, doi: 10.1126/science.1227385, 2013.

Kürten, A., et al.: Neutral molecular cluster formation of sulfuric acid-dimethylamine observed in real-time under atmospheric conditions, *P. Natl. Acad. Sci. USA*, 111, 15019–15024, doi: 10.1073/pnas.1404853111, 2014.

Kürten, A., et al.: On the derivation of particle nucleation rates from experimental formation rates, *Atmos. Chem. Phys.*, 15, 4063–4075, doi: 10.5194/acp-15-4063-2015, 2015a.

Kürten, A., et al.: Experimental particle formation rates spanning tropospheric sulfuric acid and ammonia abundances, ion production rates and temperatures, *J. Geophys. Res.-Atmos.*, 121, 12377–12400, doi: 10.1002/2015JD023908, 2016a.

Lehtipalo, K., et al.: The effect of acid–base clustering and ions on the growth of atmospheric nano-particles, *Nature Commun.*, 7, 11594, doi: 10.1038/ncomms11594, 2016.

McMurry, P. H., and Li, C.: The dynamic behavior of nucleating aerosols in constant reaction rate systems: Dimensional analysis and generic numerical solutions, *Aerosol Sci. Technol.*, 51, 1057–1070, doi: 10.1080/02786826.2017.1331292, 2017.

Qiu, C., and Zhang, R.: Physicochemical properties of alkylaminium sulfates: hygroscopicity, thermostability, and density, *Environ. Sci. Technol.*, 46, 4474–4480, doi: 10.1021/es3004377, 2012.

Yao, L., et al.: Detection of atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions, *Atmos. Chem. Phys.*, 16, 14527–14543, doi: 10.5194/acp-16-14527-2016, 2016.