Response to review comments on manuscript acp-2022-484

Survival probabilities of atmospheric particles: comparison based on theory, cluster population simulations, and observations in Beijing

Reviewer #1:

The authors compared the survival probabilities of atmospheric particles using theory, simulations, and observation data in Beijing. I find the the comparison with observation data especially valuable, and this work can be nice contribution to NPF studies. However, questions below need to be addressed before the manuscript can be published.

We thank the reviewer for very insightful comments and a constructive review of our manuscript. The comments have helped us to identify potential issues with our manuscript, and to considerably improve it. We have included our answers (in *italics*) to the questions (in **bold**) and marked sections from the manuscript in *blue*.

1. Line 183: 'Evaporation in the cluster formation from sulfuricacid and dimethylamine has been observed to be negligible'. This sentence is somewhat misleading and 'has been' is very vague. The evaporation rate is only close to negligible when the base concentration is very high. Jen et al. (2014) listed the nucleation rates in their Table 1. I would rather claim the simulation is a reference in the kinetic limit for comparison with the analytical formulae or observation.

We have reformulated this in the revised manuscript by removing the claim that evaporation is negligible:

(Section 2.4, Line 193): Dimethylamine effectively stabilizes sulfuric acid clusters, if its concentration is sufficient with respect to the atmospheric sulfuric acid concentration (Jen et al., 2014; Kürten et al., 2014). We assumed that the formation of clusters occurred at a kinetic limit, meaning that evaporation from clusters is negligible and cluster formation and growth are governed by kinetic collisions. Thus, in Eq. 13 E = 0.

2. Line 270: 'the loss rates of the clusters can also be considerably affected by the cluster-cluster collisions inaddition to the GRs if the background CS is small and the cluster concentrations are high'. This sentence seems to suggest growth will cause the cluster to be lost, which is incorrect.

We have reformulated this sentence as follows to not cause any misunderstanding:

(Section 3.1, Line 287): … the loss rates of the clusters can also be considerably affected by the cluster-cluster collisions if the background CS is small and cluster concentrations are high.

3. Figure 2. I would suggest adding simulated rates with cluster-cluster coagulation to the right y axis of figure 2. Since simulation with cluster-cluster coagulation is extensively shown in subsequent figures, this is important information.

We agree this would be a good idea, and have now included the values for the simulations including cluster-cluster collisions to Figure 2. We have also added discussion about them to the revised manuscript:

(Section 3.1, Line 303) For Case 2, Figure 2 shows that when the formation rates are high, and CS is low, the formation rates based on Eq. 7 are lower than those based on fluxes. This is because Eq.7 uses only one value of CoagS to approximate the coagulation losses between the upper and lower limits of the diameter range. The used CoagS underestimates these losses because in Case 2 other clusters contribute to the losses of clusters in addition to the background CS. As the observed formation rates are based on Eq. 8, which includes a more detailed description of coagulation scavenging compared to Eq. 7, we assume that the observed survival probabilities are comparable with both Case 1 and Case 2 survival probabilities.

4. I find Figure 5 challenging to read as there are too many cases presented in a single figure. I suggest reducing the number of cases presented in this figure. For instance, one fitting method can be presented while the other may go into supplemental.

This is a good suggestion to make Figure 5 clearer. We have now separated the results using linear regression to a separate figure (Supplement Figure S1).

5. The simulation is extensively compared to the observations. However, I wonder if the simulation is a good representation of atmospheric particle growth: in the simulation there is only one condensing vapor, while in the atmosphere the condensable vapor concentration increases with particle size. This is especially the case for growth between 1.5 nm to 3 nm when the Kelvin effect is very strong. For larger particles it might be alright because the 'condensable' concentration is no longer a strong function of particle size; using a single vapor to model the growth rate may coincide with the real atmosphere. Therefore, how is it justifiable that the simulation is directly comparable to atmospheric observations, especially for Figure 7? (The authors sort of discussed this matter in section 3.4.3 when the uncertainty of GR is discussed, but I wonder why the participation of other species on growth is not explicitly discussed) Overall, the role of the simulation needs to be better defined/clarified.

It is true that GR depends differently on particle size in the simulations when compared to atmospheric particle growth, which is because we have used only one condensing vapor and do not account for evaporation or Kelvin effect. However, the simulated and the observed survival probabilities are compared based on one representative GR per each diameter range (arithmetic mean for the simulations, linear regression for the observations). Based on the comparison between the analytical predictions and simulations, we know that the simulated survival probabilities are characterized well by the mean GR as the simulated survival probabilities are very close to the predictions using Lehtinen et al. (2007) formula, which assumes a constant GR. Thus, in our point of view, the main issue is how well do the observed GRs describe the actual growth of atmospheric particles, which is more of a question of uncertainties in the atmospheric GRs.

We have added the following discussion addressing this to the revised manuscript:

(Section 3.3, Line 364): We note that as ACDC Case 1 survival probabilities show only minor differences compared to L-2007 survival probabilities, the mean GR in a size range appears to represent the growth term in CS/GR well. Thus, we assume that the values of CS/GR from ACDC model simulations are comparable with the observed values of CS/GR.

In addition, we have added the following sentence to further motivate the role of the simulations in this study:

(Section 2.4, Line 176): In addition, they provide valuable information on the agreement between the survival probabilities from analytical predictions and cluster population simulations, which to our knowledge have not been published before.

6. Line 361: what is the meaning of 'median NPF event'? Median of what? The word 'median' is extensively used in section 3.4.1. I found many of them really confusing.

We have added the following to the start of Section 3.4.1 to clarify the use of median in this section:

(Section 3.4.1, Line 387) In the following, we will consider a median NPF event day in Beijing (Figure 6), by which we mean that the median diurnal variation of values was determined by calculating median values for each 10 min time-interval based on the data from all the investigated dates.

8. Line 455: I have doubts regarding uncertainty of J_5. The measurement uncertainty decreases with increasing particle size, hence I assume the uncertainly of $J_{1.5}$ is larger than that of J_3. Is it possible that $J_{1.5}$ is actually systematically underestimated, as a result of which $J_3/J_{1.5}$ is larger than reality? From what I know sub 3 nm particles often seem under detected in the observed PSD, does this have an effect?

We agree that it is possible that $J_{1.5}$ is systematically underestimated more-so than J_3 due to measurement factors such as particle charging, and that this is something we should discuss in our manuscript. We have added the following discussion to the revised manuscript:

(Section 3.4.3, Line 491): We estimate based on Kangasluoma et al. (2020) that the uncertainties in J are approximately ±50-70%, increasing with a decreasing particle diameter. At low CS/GR, a majority of the observed $J_3/J_{1.5}$ could thus be explained by uncertainties in J. The observed $J_3/J_{1.5}$ being on average larger than L-2007 predictions could be due to larger systematic uncertainties in $J_{1.5}$ compared to J_3. However, when CS/GR is larger, the observed $J_3/J_{1.5}$ are up to two magnitudes of order higher than the L-2007 predictions, and uncertainties in the observed values of J cannot explain such a discrepancy. Most of the observed values of J_6/J_3 are approximately two to four times lower than the L-2007 predictions, so that while uncertainties in J surely contribute to the variance of the observed J_6/J_3 and thus having potentially a considerable contribution to the observed discrepancy, they are unlikely to be the only explanation for the latter.

Technical corrections:

We thank the reviewer for noticing these technical issues, which we had missed.

1. **The rate constant is missing in the third term on the R.H.S. of Eqn. (8).**

   The missing rate constant has been added to Eq. 8.

2. **In the top panel of Figure 6, tick labels are missing on the left y-axis. Also, can the color scale be changed for this plot to make NPF event more visible?**

   The tick labels have been added, and the color scale adjusted to make the event more visible.

Reviewer #2:

The manuscript deals with survival properties of freshly nucleated particles while they grow and scavenge. Simple parameterizations and an aerosol dynamic model are compared against observations in Beijing, where the high survival rates have puzzled researchers because background aerosol concentrations are so high that the sink they cause should (theoretically)

result in lower survival rates than what is observed. The usefulness of the manuscript, from my point of view, lies in the uncertainty analyses presented and the discussions related to potential causes of the above-mentioned discrepancy. The manuscript is definitely suitable for publication in ACP, however, some issues have to be clarified prior to this.

We thank the reviewer for very constructive comments. They have helped us to considerably clarify some very important points, and to improve our manuscript. We have included our answers (in *italics*) to the questions (in **bold**) and marked sections from the manuscript in *blue*.

1. Several of the authors here are authors in two other papers/manuscripts, also dealing with the topic of survival rates in Beijing: Cai et al. (ACP 22, p. 11529, 2022) and Cai et al. (ACPD, acp-2022-476, 2022). In the first one of these, the authors state in the conclusions: "The low theoretical survival probabilities of new particles contrasting to the new particle formation events observed at high coagulation sinks should be caused by underestimated growth rates". In the latter one, the authors claim that experimental survival probability for 'Beijing-type' events should be determined by comparing pointwise dN/d(logdp) values and with this approach "the measured and theoretical survival probabilities are on average consistent with each other". In this manuscript, under review, the analysis is based on studying what kind of uncertainty is needed in the estimated values for GR and CS for the theory/model to match experimental findings.

We agree with the reviewer that this needs to be clarified. In the first of the papers/manuscripts, Cai et al. (ACP 22, p. 11529, 2022), it is stated that the coagulation sink of 3-10 nm particles is unlikely to be overestimated. This is in line with our results, which show that most of the survival probabilities in the 3-10 nm size range are not higher than those predicted by assuming hard-sphere coagulation. Moreover, Cai et al. (ACP 22, p. 11529, 2022) suggested that coagulation sink is ~40% higher when the contribution of van der Waals forces is accounted for. In our analysis in this manuscript we do not consider the enhancement of CoagS due to van der Waals forces and this could be one of the reasons why we observe that the survival probabilities at 3-6 nm are lower than predicted. We have briefly discussed this in our manuscript:

(Section 3.4.3, Line 518): We have neglected the enhancement of coagulation due to van der Waals forces, which can result in underestimating CoagS. The van der Waals enhancement factor of CoagS is expected to lie between 1.0 and 2.0 (Kerminen, 1994). While this alone cannot explain the majority of the differences in J_6/J_3 between observations and predictions (Figure 10), it could be a partial reason for the observed J_6/J_3 being lower than those predicted based on ACDC Case 1 and L-2007.

In Cai et al. (ACPD, acp-2022-476, 2022), it is stated that, for a growing particle number size distribution, survival probability determined as ratio of formation rates underestimates the real survival probability. Thus, it is possible that the observed survival probabilities used in our manuscript are to some extent lower than the actual survival probabilities of the particles. However, Cai et al. (ACPD, acp-2022-476, 2022) also showed that in the sub-10 nm size range in Beijing the particle size distribution can be approximated by a quasi-steady-state due to the high formation rates and coagulation sink. Thus, on average the ratio of formation rates is a relatively accurate way to determine the survival probability for sub-10 nm particles in Beijing.

We have clarified the use of formation rates to determine survival probability in the revised manuscript:

(Section 2.1, Line 108): The best method to determine the survival probability from observations depends on particle size distribution and its time evolution (Cai et al., 2022). In this study, we have

determined the survival probability as a ratio of formation rates J_1 and J_2 (Kerminen and Kulmala, 2002; Kulmala et al., 2017). This method is able to produce accurate survival probabilities for a steady-state or a quasi-steady-state size distribution, and has been shown to give relatively accurate survival probabilities in Beijing during NPF events (Cai et al., 2022).

2. As also detailed aerosol dynamics modeling has been utilized, it would be nice to see some more details about the results. With this I mean, for example, contour (or banana) plots of the growing nucleation mode for an average NPF day.

We have added the steady-state cluster distributions of the simulations to supplement (Figures S2 and S3).

3. Page 2, line 46: Here the survival probability is defined in terms of fluxes ("ratio of the formation rates of particles of diameters d1 and d2") while in the other paper by the authors (acp-2022-476) it is defined in terms of concentrations. Are these the same? If not, which one is correct?

In this manuscript we have defined the survival probability in terms of particle concentrations, and stated that it can be determined from the formation rates:

(Section 1, Line 45) …survival probability describes the fraction of particles or clusters formed at diameter d_1 that grow to a larger diameter d_2. It can be determined as the ratio of the formation rates of particles of diameters d_1 and d_2

Thus, we want to clarify that we have not defined survival probability in terms of fluxes. The justification for determination of survival probability from formation rates is discussed in the answer to comment 1.

4. Page 2, line 48: Doesn't GR also depend on particle phase chemistry?

We have now included a reference to influence of particle phase chemistry to GR in the revised manuscript:

(Section 1, Line 50) GR depends on the concentrations of condensable precursor vapors (Kulmala et al., 2005; Sihto et al., 2006; Wang et al., 2015; Stolzenburg et al., 2020) and population dynamics such as cluster-cluster collisions (Kontkanen et al., 2022). In addition, chemical reactions in the particle phase may affect GR (Apsokardu and Johnston, 2017; Kulmala et al., 2022).

5. Page 5, equation 7: What are the assumptions inherent in equation 7 if there are any? Is CoagS some kind of average in the interval? And, shouldn't the last term, if written exactly, be GR x n at the upper edge of the interval?

Both equations 7 and 8 include the assumptions that primary emissions, dilution, transportation, and other losses aside from coagulation scavenging, such as deposition, are negligible. In addition, equation 7 neglects coagulation sources and CoagS is determined based on a representative diameter, which is often, and also in this case for the results in Section 3.1, geometric mean of lower and upper limit diameters. We have now mentioned this in the revised manuscript:

(Section 2.4, Line 222) CoagS was approximated by CoagS of a cluster with geometric mean diameter of the upper and lower limits of the considered diameter range.

In equation 7 the last term is

$\frac{GR_{[d_i, d_u)}}{d_u - d_i} N_{[d_i, d_u)}$,

which is estimated based on the growth rate and number concentration (N) for the full size-range [d_i, d_u). If the size-range in question is infinitesimally small, it becomes equal to GR x n.

8. Page 8, line 203: how do you calculate the cluster flux past a certain size?

ACDC program determines the fluxes based on the cluster and monomer concentrations and the collision rates between different clusters or clusters and monomers. We have added a mention of this to the revised manuscript:

(Section 2.4, Line 219): The cluster fluxes were determined by the program based on the cluster and monomer concentrations and the collision rates between the different clusters or between the clusters and the monomers.

9. Page 10, line 250 and Fig. 1: For a single component system, If C_mon is constant, and Kevin-effect is neglected, condensation-theory tells that GR should be constant in the free-molecular regime, apart from a region at the smallest particle sizes where molecular dimensions also play a role. This means that the result in Case 1 in no surprise. In the other paper by the authors (acp-2022-476), however, the authors apply a size dependent growth rate (increases with size) in their simulations. Why these different approaches when studying essentially the same thing? One important question is also, if the current simulations with constant GR result in a narrowing size distribution when plotted in dN/d(logdp) form in log-scale.

We note that in both Cai et al. (acp-2022-476) *and this manuscript GR in simulations with constant C_{mon} has a similar size-dependency.*

Regarding GR in the simulations for this manuscript, ACDC simulates the time evolution of the cluster population based on the birth-death equations (see equation 13) and GR cannot be given to the program as an input parameter. It is true that in the simulations the size dependency of GR is different compared to how it has been observed to be in the atmosphere during NPF events. Similar size dependency could be observed in the simulations if more condensing vapors and evaporation were included in the simulations, resulting in activation for condensation at different sizes for different vapors. In this study we wanted to focus on a sulfuric acid-dimethylamine system with negligible evaporation due to the key role of sulfuric acid-amine nucleation in initiating NPF in Beijing.

In addition, the simulated and observed survival probabilities are compared based on one representative GR per each diameter range (arithmetic mean for the simulations, linear regression for the observations). Based on the comparison between the analytical predictions and the simulations, we know that the simulated survival probabilities are characterized well by the mean GR as the simulated survival probabilities are very close to predictions using Lehtinen et al. (2007) formula, which assumes a constant GR. Thus, we assume that even if the dependency of growth on cluster diameter was different in the simulations, it would not affect the results of our comparison significantly.

This has been now addressed in the revised manuscript:

(Section 3.3, Line 364): We note that as ACDC Case 1 survival probabilities show only minor differences compared to L-2007 survival probabilities, the mean GR in a size range appears to

represent the growth term in CS/GR well. Thus, we assume that the values of CS/GR from ACDC model simulations to be comparable with the observed values of CS/GR.

All the simulations were run until steady-state, i.e. the concentrations and fluxes were constant with time. Thus, the final number size distribution stayed constant with time. The steady-state cluster number size distribution are now shown in Supplement Figures S2 and S3.

10. Page 10, lines 260-263: if in the high-CS cases the clusters disappear very rapidly, is I then reasonable to assume a constant monomer concentration in the simulations?

In the simulations the monomer concentration is kept constant during the whole run by the program itself.

We have included the following note in the revised manuscript:

(Section 2.4, Line 206) We note that while the lifetime of sulfuric acid in Beijing is short due to high CS, sulfuric acid concentration can be assumed to be relatively constant during the time it takes, for example, for a 1.5 nm particle to grow to 3 nm.

11. Page 10, lines 281-282: J1.5 is almost always smaller if determined from eq. 7 than based on fluxes. Do you know why this is so?

This behavior is likely due to the fact that in Eq. 7 GR between the lower limit and upper limit is represented by one representative value, in this case the arithmetic mean GR. The mean GR appears to underestimate the growth between 1.5 nm and 10 nm slightly. We have now addressed this in the revised manuscript:

(Section 3.1, Line 298) However, the majority of the values of $J_{1.5}$ are smaller if the formation rates have been determined based on Eq. 7 compared to if they are based on the fluxes, which we assume to be caused by the mean GR between 1.5 nm and 10 nm underestimating the growth slightly.

12. Page 11, line 288 and fig. 3: Please add base-case values to figure caption.

We are unsure what this comment refers to. However, we have modified the caption of Figure 3 so that we state more clearly in the caption what different lines refer to:

(Figure 3, caption) Values with accurate CS/GR has been marked with the red line and the black lines correspond to the survival probabilities with CS/GR being 10%, 20% and 50% lower, or higher, than assumed.

13. Page 11, line 290 (and many other places): CS/GR is given as unitless? The (SI) unit of CS is 1/s and of GR m/s so how can their ratio be unitless?

The units of CS/GR have been mentioned in Section 2.3, Line 170. We have also added the units to the figures.

14. Page 13, line 361: What is a median event day? How do you determine it?

We have now added the following sentence to clarify this section and the use of median day:

(Section 3.4.1, Line 387): In the following, we will consider a median NPF event day in Beijing (Figure 6), by which we mean that the median diurnal variation of values was determined by

calculating median values for each 10 min time-interval based on the data from all the investigated dates.

15. Page 13, line 363: Should it be "…based on Eq. 13 and Eq. 14." ?

We thank the reviewer for noticing this typo, which we had missed. It should indeed be Eq. 13 and Eq. 14. We have corrected this in the revised manuscript.

16. Page 14, lines 403-405. Do van der Waals forces affect CoagS also?

Van der Waals forces may affect CoagS, which we have addressed in the answer to comment 1.

17. Page 15, lines 435-438: One thing important to mention about self-coagulation is also that as a process it also effectively decreases the number concentration. If particles of diameter 3 nm grow to 6 nm by self-coagulation alone, their volume increases by a factor of 8 so that their number concentration also would decrease by the same factor.

We agree with the reviewer. The effect of self-coagulation on number concentrations has been discussed in the manuscript:

(Section 3.3 , Line 373): In addition, Figure 5 shows $J_{10}/J_{1.5}$ for both Case 1 and Case 2. It is clear that the survival rates from 1.5 up to 10 nm are considerably decreased by cluster-cluster collisions when background CS is low. This is because when CS is low and the concentrations of clusters are high, cluster-cluster collisions reduce the cluster number concentrations more efficiently than they increase the survivability of clusters from coagulation scavenging due to enhanced growth.