Responses to Reviewers' Comments on Manuscript ID ACP-2022-262

(The effectiveness of coagulation sink of 3–10 nm atmospheric particles)

We thank the reviewers for their efforts and comments that help to improve this manuscript. The reviewers' comments are addressed in the following paragraphs and the manuscript has been revised accordingly. More details on the experiments and analysis have been provided to facilitate understanding.

The comments are shown as sans-serif blue texts and our responses are shown as serif black texts. Changes are highlighted in the revised manuscript and shown as "quoted underlined texts" in the responses. References are given at the end of the responses.

Reviewer #1

The paper by Cai et al. aims to solve one of the most confusing problems related to particle survival by quantifying coagulation coefficient. Direct experimental evidence for the effectiveness of the CoagS of new particles was provided by well controlled chamber experiments. Comparison between the measured coefficient with theoretical predictions shows that almost every coagulation leads to the scavenging of one particle, and the coagulation sink exceeds the hard-sphere kinetic limit due to van der Waals attractive force. Base on the measurement, the authors proposed high theoretical survival probabilities of new particles in NPF events observed at high coagulation sinks are caused by high growth rates. I suggest the publication of this paper. One issue should be addressed in the abstract "....the measured coagulation coefficient increases significantly with a decreasing particle size...". Please specify for what particle size this conclusion refers to. Obviously, your statement is completely wrong because coagulation coefficient with 10 nm particle decreases with the decreasing size of coagulating particles.

Response: We thank the reviewer for these comments. This sentence was revised as "… the measured coagulation sink of 3-10 nm particles increases significantly with a decreasing particle size…".

The reviewer is correct that the coagulation coefficient is a function of both particle sizes. We use the coagulation sink instead for simplicity and emphasize these particles are sub-10 nm particles to avoid confusion. Although the scavenger particles (100 nm in this study) are not given in the revised sentence, this statement should be valid for the atmosphere as the coagulation sink is majorly contributed by particles around 100 nm.

Reviewer #2

Cai et al focuses on evaluation of the coagulation rate coefficient between sub-10 nm particles and 100 nm particles in a chamber environment. In reading the manuscript, I have concerns on the manner the experiments were conducted (a large fraction of 100 nm particles remain charged after neutralization, and this is not considered in results) and analysed (equation 5 is not a valid approach in the transition regime). I have the following comments for the authors to address:

Response: We appreciate the reviewer's deep insights into the experiments and analysis. The concerns are addressed below following the comments. Briefly, we find that the concerns are related to the presentation rather than the experiments or analysis. Accordingly, we clarified that 100 nm particles remained charged after neutralization and they resemble atmospheric particles in terms of the steady-state charge fraction. The charge fraction of particles are emphasized when discussing the coagulation coefficient. For Eq. 5, we clarified that the enhancement factor therein is a function of particle size and it is valid for all regimes.

1. Figure 1. It appears that after DMA selection, the authors sent particles through a bi-polar charger (labelled neutraliser, but the authors should note the type of neutraliser in terms of source type, and strength). For the 100 nm particles, roughly 47% of them are charged at steady-state (near 20% will be +1 net charge, near 20% will be -1 net charge, and 7% multiply charged). Therefore, it seems the experiment is not between neutral particles exclusively, but between a population of charged 100 nm particles and sub 10 nm particles, as well as uncharged 100 nm particles and sub 10 nm particles. It is not clear if the charged particle-uncharged particle potential is negligible in this instance, and in comparison to the often weaker effect of van der Waals potentials, it is likely not negligible. Without directly addressing the charge influence (or clarifying that charged particles were removed), it is not clear to me that the measurements and analysis reported are sufficiently done to merit publication, as they would not necessarily be representative of the atmosphere.

Response: Thanks. We clarified that the 100 nm particles were charged at steady-state so that their charge fraction resembles the charge fraction of ambient particles. We also clarified that the interaction between a charged particle and a neutral particle may influence the coagulation coefficient, and hence the measured coagulation coefficient is an empirical value characterizing the coagulation sink of new particles scavenged by background particles at steady-state charge fraction.

We added a few sentences to the Methods section to clarify the experiments and the fact that 100 nm particles were at steady state charge distribution, representing atmospheric conditions. After the generation and DMA production, we used a bi-polar charger to neutralize both sub-10 nm particles and 100 nm particles. The neutralized particles were sent to the chamber via a Teflon tube. For sub-10 nm particles, most of these particles could be neutralized and the Teflon tube can effectively remove the remaining charged particles via electrostatic losses. For 100 nm particles, as the reviewer has pointed out, a considerable fraction of them was charged and the charged particles could pass through the Teflon tube. As a result, 100 nm particles in the chamber were charged at a steady state instead of being neutral.

We clarified that the particles with steady-state charge fractions are representative of atmospheric particles. A recent study has demonstrated the feasibility to measure the particle size distributions accurately using an SMPS without a charger because atmospheric particles are charged at a steady state (Li et al., 2022). We used neutral sub-10 nm particles in the

experiments and clarified the reason that "most (>90 %) sub-10 nm particles are neutral at a steady state charge distribution". This also minimize the influence of the Coulomb force on the CoagS. In contrast, we think that the 100 nm particles after the bi-polar charger can better characterize the coagulation sink compared to neutral particles.

We agree with the reviewer that the interaction between a charged particle and a neutral particle may influence the coagulation coefficient. In the revised Theory and Results sections, we added "Besides, the interaction between a charged particle and a neutral particle may influence the coagulation coefficient, which is also included in the experimentally determined $E(A)$ in this study." and "This enhancement is likely due to the van der Waals force and potentially the interaction between a neutral sub-10 nm particle and a charged 100 nm particle."

We also tried to compute the coagulation enhancement due to the interaction between a charged particle and a neutral particle. Using the methods in Santos et al. (2019), we found this enhancement is possibly weak: For the coagulation between one neutral 3-10 nm particle and one doubly charged 100 nm particle, the multiplicative enhancement factor is 1.00003-1.0007. Although this method was proposed for the kinetic regime only and there might be uncertainties in the results, it indicates that interaction between a charged particle and a neutral particle may be minor. Nevertheless, the intertaction between charged and neutral particles would not affect our conclusions that the coagulation sink of new particles is effective and slightly above the hard-sphere. More importantly, the charge fraction of 100 nm particles in the experiments were representative of atmospheric particles.

The type of neutralizer has been specified as "A neutralizer (Ni-63, 90 MBq)…" in the revised manuscript.

2. Section 2.1. The mixing within the chamber needs to be described in much greater detail. One concern in the experiments is that the inlet sub-10 nm particle concentration is orders of magnitude higher than the outlet concentration. The inlet flow is not diluted infinitely quickly upon entering the chamber, and there is certainly a region near the inlet where the sub 10 nm concentration is similar to the 100 nm particle concentration (their injected concentrations are similar)

Response: We added a sentence to clarify that "A low-speed fan placed near the bottom center of the chamber was used to mix particles in the chamber and its mixing ability had been experimentally validated". The experiments were to test the response of outlet particle concentration to the inlet particle concentration (similar to the experiment in Fig. 2). We found that the outlet particle concentration followed the theoretical curve, and the decay rate of 100 nm particles due to dilution and wall loss was close to the theoretical decay rate due to dilution. This indicates that the mixing time for particles is much smaller than the residence time; hence the mixing is rapid enough for this experiment.

It is true that the sub-10 nm particle concentration should be high in the inlet region of the chamber. However, we controlled the inlet particle concentration ($<10^5$ cm^{-3}) such that the self-coagulation of sub-10 nm particles was negligible. For instance, with a collision enhancement, the coagulation sink of sub-10 nm particles contributed by self-coagulation is no larger than $0.5 \times 3.3\times10^{-9}$ cm^3 s^{-1} $\times$ 10^5 cm^{-3} = 1.7×10^{-4} s^{-1}, corresponding to a residence time of ~100 min. Compared to the loss rate or the residence time of sub-10 nm particles (see Fig. 4), it is reasonable to conclude that the experiments were negligibly affected by self-coagulation.

3. Methods (General). The authors need to more explicitly state the number concentration ranges of the 100 nm particles used and the sub-10 nm particles.

Response: We stated the concentration range was 10^4-10^5 cm^{-3}. Typical concentrations of particles has also been presented in Fig. 2.

4. Equation (1). The authors neglect the influence of sub-10 nm particle self-coagulation on the differential equation governing the sub-10 nm particle concentration. From the limited data in the main text, it appears that sub-10 nm particle concentrations in the chamber were much lower than the 100 nm particle concentrations, but this needs to be discussed more directly, and brief calculations to show it is negligible.

Response: Thanks. In the revised Methods section, we added "The concentrations of 100 nm and sub-10 nm particles were controlled to be 10^4-10^5 cm^{-3} such that self-coagulation was negligible (< $0.5 \times 3.3\times10^{-9}$ cm^3 s^{-1} × 10^5 cm^{-3} = 1.7×10^{-4} s^{-1}) and the CoagS provided by the 100 nm particles were distinguishable against dilution and wall losses." As the self-coagulation of 10^5 cm^{-3} inlet particles was negligible, the self-coagulation rate of particles in the chamber would be even lower.

5. Alongside neglecting the potential influence of 100 nm particle charge on the coagulation rate, equation (5) in the manuscript is not an appropriate way to handle coagulation in the transition regime accounting for potential interactions. In the continuum limit (very small Kn), it is acceptable to write that the coagulation coefficient using the formula:

$\beta_{Cont}=2\pi\ (d_1+d_2)(D_1+D_2)E_{Cont}$ (R_1)

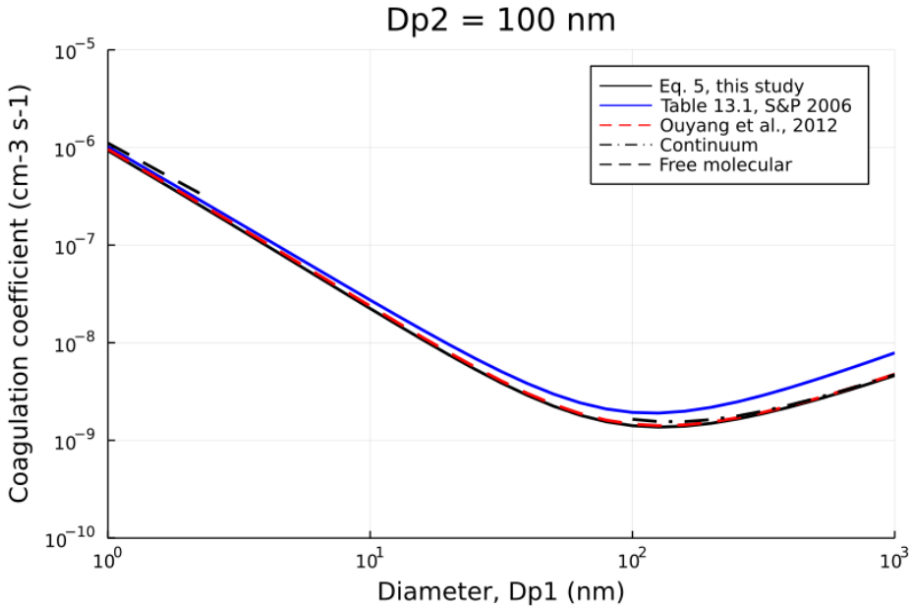
Similarly, in the free molecular limit (very large Kn), one can write:

$\beta_{FM}=(\pi kT/2m_{12})^{1/2}(d_1+d_2)_2E_{FM}$ (R_2)

where k is Boltzmann's constant and m_{12} is the reduced mass of the two particles. However, E_{Cont}, which can be calculated for spheres exactly using the approach of Fuchs for continuum collisions, and E_{FM}, which is calculated using an approach by Fuchs & Sutugin, Ouyang, or Sceats, are not one and the same, and for the van der Waals potential, usually $E_{FM}>E_{Cont}$. Because in the transition regime, the transport features controlling collision are evolving as particle diameter increases (Kn decreases), it is not correct to express equation (5) as a single enhancement factor applicable to all particles (the enhancement evolves as well). The authors should instead adopt an approach to fit E_{Cont} AND E_{FM} to results. The Ouyang (2012) reference of the manuscript attempts to do this, as does Fuch's limiting sphere approach when potentials are included and Sceats 1989 (I believe the Sceats approach is the one used in Stolzenburg 2020; see equation 3 in their paper). When the authors state they used the methods from previous studies it is not clear if they mean E_{Cont} or E_{FM}, and only considering one is not correct in the transition regime. As inference of this parameter is the central purpose of this manuscript, this issue combined with neglecting charge effects (again, unless charged particles were removed) is concerning.

Response: We would like to argue that Eq. 5 should be valid for the transition regime because the Kn term is exactly used to correct for the transition regime (and the free molecular regime). In the revised manuscript, we clarified that "The expression of the theoretical Brownian coagulation coefficient covering the free molecular, transition, and continuum regimes is given in Eq. 5…" Alternative equations for all the three regimes can be found elsewhere, e.g., in Ouyang et al.

(2012) and Table 13.1 in Seinfeld and Pandis (2006) and. As shown in the figure below, the curve for Eq. 5 with E = 1 is comparable with other formulae and it approaches the β_{Cont} and β_{FM} as Kn approaches 0 and infinite, respectively.



The reviewer is correct that E is a function of particle sizes rather than a constant. $E(A)$ in Eq.5 has been correspondingly revised as $E(A,d_1,d_2)$ to emphasize that it is "size-dependent". In this study, we compute the size-dependent $E(A)$ using the approaches in Ouyang et al. (2012) and Alam (1987). When fitting the experimental results, we fitted the empirical Hamaker constant to the measured coagulation coefficients to guarantee the size-dependency of $E(A)$. However, the E(A) was only weakly dependent on the sub-10 nm particle size, e.g., 1.33-1.39 for 3-10 nm ammonium bisulfate particles. This variation is usually smaller than typical uncertainties in atmospheric measurements. Consequently, we report a constant value in the Results and discussion section and clarified that "E was ~1.4 for particles in this size range with a weak dependence on the particle size".

We would also like to clarify that the main purpose is to investigate particle survival by measuring the effectiveness of CoagS of new particles rather than the enhancement. As discussed above, the 100 nm particles charged at the steady-state can better represent atmospheric particles. The main aim is to figure out whether the CoagS deviates from its theoretical value by orders of magnitudes. The results have convincingly shown that the CoagS was effective.

6. Equation (5), continued. The authors need to explicitly state how they are defining Kn (define lambda, the mean free path in term of other, better defined parameters, as this is not the gas mean free path). They should then discuss the Kn range examined in this study, to state whether their results apply to coagulation in the continuum limit, the free molecular limit, or a transition regime range. There is a chance Kn (which tends to be lower for particle-particle collisions) is sufficiently low that they are close to the continuum limit, such that they can simply use a continuum limit coagulation expression and $ECont$. However, as per comment 5 if the coagulation range studied is in the transition regime, then I am afraid the authors need to rethink their analysis.

Response: Thanks, we added Eq. 6-7 to the revised manuscript for Kn and the mean free path. As discussed above, Eq. 5 and the enhancement factor were for all regimes. Accordingly, we emphazied "…the theoretical Brownian coagulation

coefficient covering the free molecular, transition, and continuum regimes…" and "The Kn term is used to correct for the transition and free molecular regimes…".

Reference

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