Responses to Reviewer #2's Comments on Manuscript acp-2020-398

(Impacts of coagulation on the appearance time method for sub-3nm particle growth rate evaluation and their corrections)

We thank the anonymous referee (referred as reviewer #2 below) for the efforts and constructive comments that help to improve this manuscript. The reviewer's comments are addressed in the following paragraphs and the manuscript were revised majorly. The comments are shown as sans-serif dark red 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. Line numbers, figures, and equations quoted in the responses correspond the revised manuscript. References are given at the end of the responses.

Reviewer #2

This manuscript investigates the impact of coagulation on the particle growth rate, calculated using the appearance time method, using theoretical derivations and aerosol dynamics modeling. The topic of actual growth rate calculation is of great importance for understanding the new particle formation processes in the atmosphere. The appearance time method was originally developed by Lehtipalo et al., 2014 to calculate growth rate in the size range 1-3nm using PSM data. They highlighted that the method is robust unless coagulation process affect greatly the particles size distributions, such as a heavily polluted environment with high number concentration of preexisting particles. Although this paper is presenting a correction for coagulation on the appearance time method, the approach and the validity of the method are not adequately described. It would be more appropriate to first describe the method and its weaknesses, then present the suggested correction for coagulation impacts and then apply the method in different environment types (boreal forest and Beijing data are available for comparison).These steps, are only briefly described and definitely more examples need to be presented.

Response: We agree with the reviewer that the limitations of the appearance time method should be discussed, though the majority of this manuscript is on the derivation and validation of the correction formula for the appearance time method. The appearance time method is described in the revised Section 2.3. We added section 4.5 on the uncertainties of the appearance time method and the challenges in determining particle growth rate in the atmosphere.

However, we prefer not to extend the scope of this manuscript to applying the appearance time methods to various types of new particle formation events. The impacts of coagulation to the appearance time in the Finnish boreal forest and urban Beijing are indicated in Fig. A1. Meanwhile, as explained in section 4.5, the validation of the appearance time method and other methods in the real atmospheres needs more systematic and comprehensive investigations.

Specific comments:

Page 2, Line 19: Only few or just one application?

Response: According to our knowledge, there is only one published application (Kuang et al., 2012) and some unpublished applications. This sentence was revised as "However, few applications……(e.g., Kuang et al., 2012)" so that is does not emphasize the exact number of applications.

Page 4, Line 13 and 25 and further: Coagulation coefficient unit should be $cm^3\ s^{-1}$.

Response: Thanks. We checked the manuscript and corrected the typos.

Page 5, Line 24: As this paper describes a correction to the appearance time method it is proper to present the method.

Response: Thanks. We added a new paragraph at the beginning of this section to describe the appearance time method.

Page 6, Line 17: This section is lacking all the necessary information for the reader to understand the theoretical and experimental tools that were used to perform this study.

Response: We added a paragraph at the beginning of section 3, which introduces why the simulated and measured new particle formation events are used to test the formulae and what information can be obtained from these test.

Page 7, Line 1: What is Julia?

Response: Julia is a programming language. We replaced "Julia" with "the Julia programming language" in the revised manuscript.

Page 7, Line 20: This reference is a paper under review. More details about the experimental part should be given here.

Response: We added the environmental information on during the presented new particle formation event. The paper under review was replaced by a published paper (Deng et al., 2020b), in which the measurements are detailed.

Page 7, Line 23: This section (4.1) needs to be moved to methods, where the appearance method should be described and cited.

Response: We prefer to keep this section here because this section is mainly on the derivation of the appearance time method under an ideal condition. The derivation itself is a result. Instead, we added a paragraph in 2.3 to introduce the appearance time method and refer to readers to Section 4.1 for more details.

Page 11, Line 14: This is not shown here, we have no indication about sub-1.3nm growth rates.

Response: The reviewer mistook Fig. 5 for Fig. 4. The size range for particle growth rate in Fig. 4 covers 1.0 – 3.5 nm.

Page 11, Line 15:In Figure 4, Coags corrected seems to perform better than the Corrected total growth for particles larger than 3nm.

Response: Yes. This is because the correction term for CoagSrc is an approximation which cannot avoid potential bias. These uncertainties are discussed at the end of Section 4.2. However, considering uncertainties, Fig. 5 (instead of Fig. 4) shows that both the CoagS corrected growth rate and the corrected total growth rate agree with the theoretical growth rate.

Page 11, Line 26: This paragraph is confusing. Which formula is used, Eq 5, or some other formula from the Appendix?

Response: We added "These three impacts of coagulation source are accounted for in the corrected appearance time method (Eqs. 6 and 7)".

Page 12, Line 4: It has to be shown here that the method is described so that all limitations are discussed prior to applying the new method.

Response: The limitation of the correction formulae (Eq. 6) is that the coagulation source term is derivated based on approximation. This limitation has been clarified during the derivation and in this paragraph.

Page 12, Line 13: It is the previous study, or are there more studies?

Response: We added another reference (Olenius et al., 2014) to this sentence.

Page 12, Line 24: I would not use the expression agrees better, as it does not seem to agree, it seems to work better than the conventional method but still overestimates all particle growth rates outside the range 2-3.5 nm. These discrepancies both in absolute values but also with regard to increasing size and especially the shape of the curve have to be discussed further in the text. It has to be noted that the new curve has the same shape as the uncorrected one which suggests that there is an underlying assumption causing these deviations, it is worth providing more information.

Response: We revised this sentence as "the deviation between the corrected particle growth rate and the theoretical growth rate is smaller than the deviation between the conventional growth rate and the theoretical growth rate". The discrepancy outsize the range 2-3.5 nm has been emphasized in the next sentence: "However, for particles larger than ~5 nm and smaller than ~2 nm, the appearance time method overestimates particle growth rate even after correcting the impact of coagulation in the test case." We also added "These overestimations are caused by approximating the influence of coagulation source on particle growth with the coagulation source term in Eq. 5" to illustrate the reason for these discrepancies. In Section 4.2, we have clarified the reason why we use the approximation though it may introduce bias: "Since $CoagSrc_i$ is determined by the concentrations of all particles containing 2 to i-2 molecules, it is difficult to obtain an analytical solution of Eq. 19 without approximation. Here we provide an approximation method to correct the impact of coagulation source to the appearance time."

Page 12, Line 34: This assumption is valid for cases with clear diurnal variations of vapor concentrations as the assumed one. However what happens when condensing species exist in the afternoon as well, then the GR would be much higher. The example in 4.4 is demonstrating this weakness as in the afternoon the GR calculation is three time higher. Sensitivity tests with condensing species not vanishing in the afternoon could be useful as well.

Response: We add "To reduce this systematic bias due to a decreasing vapor concentration…" to emphasize the cause of this bias. If the vapor concentration stays relatively stable after a certain moment, the discrepancy between the theoretical growth rate and the growth rate retrieved using the appearance time method should be smaller. Fig. 5 shows a smaller discrepancy under a constant monomer concertation.

The reviewer misunderstood the example in Section 4.4. In Figs. 2-6, there is a theoretical growth rate given by the model that can be taken as a reference for the retrieved growth rate using the appearance time method. In contrast, the aerosol size distributions in Fig. 7 in Section 4.4 were measured in the real atmosphere and the true growth rate is unknown. Hence, there is no reference growth rate to justify whether the growth rate retrieved using the appearance time method in Fig. 7 is underestimated or overestimated. The condensational growth rate in Fig. 7 was estimated using the measured H_2SO_4 concentration, which is not the true growth rate. We have clarified in Section 4.4 that "Note that the sum of theoretical condensation and coagulation growth rate is not necessarily equal to the theoretical total growth rate for the measured NPF event. This is because only the condensation of sulfuric acid is considered whereas other vapors may also contribute to new particle growth." As a result, condensation of other vapors on the grown particles is more like to be the reason for that the growth rate retrieved using the appearance time method is ~3 times larger than the condensational growth rate calculated using H_2SO_4 concentration. In the main text, we have clarified that "The deviation between the measured growth and theoretical growth for particles larger than ~3 nm indicates that there are other chemical species in addition to sulfuric acid (and the bases to neutralize it) contributing to particle growth."

Page 13, Line 4: A single NPF event is not enough to demonstrate the validity of the proposed correction. Different events, under various meteorological and environmental conditions and under different environment types (and hence condensing species) are necessary to my opinion to test the new formulae.

Response: As clarified in the above response, tests using measured new particle formation events does not validate the proposed formula because the true growth rate is unknown. Instead, the validity and limitations of the proposed formula are tested using the models in the above sections. The aim of this test using a measured new particle formation event is to give an intuitive example of the impacts of coagulation to the appearance time method, though such impacts have been theoretically predicted in Fig. A1. An example using more new particle formation events is given in Deng et al. (2020a) to shown the comparison between the conventional and appearance time method, yet such a comparison is not a validation.

We added "In addition to the example given in Fig. 7, the average growth rates of 1.5-3 nm particles measured in urban Beijing retrieved using the conventional and corrected appearance time methods were reported in Deng et al. (2020a)." in section 4.4.

We also added a new section 4.5 on the uncertainties of the appearance time method in atmospheric application. As discussed therein, growth rate calculation is usually sensitive to uncertainties. A compressive study including more applications in the atmosphere, comparison between the results retrieved using different methods, and theoretical study based on simulation with uncertainties are needed to figure out a more accurate and robust method for growth rate estimation in the atmosphere.

References

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