Responses to Reviewer #3'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 editor, Dr. Radovan Krejci (referred as reviewer #3 below) for the deep insights 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. In addition to the influences of coagulation on the appearance time method and their corrections, we discuss the uncertainties of the conventional and corrected appearance time method. The potential biases of the corrected appearance time method due to vapor evaporation and the varying vapor concentration are reported and discussed. More simulation results are presented to support these discussions. Some of these simulation results are included as supplementary information. 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 #3

The manuscript presents an attempt to correct apparent nanoparticle growth rates, obtained by the so-called appearance time method, to remove errors arising from coagulation. It is true that the appearance time method may cause significant artefacts in the experimentally deduced growth rate and consequently in its interpretation and comparisons with models. The purpose of the work, i.e. to test the derived corrections against a particle dynamics model (rather than to compare the used models to measurements), is clarified in the revised manuscript. However, my main concerns are that (a) it seems that the suggested corrections do not generally work, and (b) the modeled test cases are quite limited, and for example assume that sub-3 nm particles do not evaporate which is quite a restrictive assumption.

Response: We thank the reviewer for these comments. The appearance time method was proposed to estimate the growth rate of clusters and new particles. As summarized in the Introduction, it is usually used in the sub-3 nm size range because other methods are difficult to cover this size range. 3 nm here is a rough estimation rather than a critical threshold. Previously studies have reported considerable potential uncertainties of the appearance time method (Olenius et al., 2014; Kontkanen et al., 2016; Li and McMurry, 2018), yet such potential uncertainties were usually not accounted for when using the appearance time method. The theoretical basis for the appearance time method under an ideal condition (constant vapor source, no coagulation, and no external sink) was reported quite recently (He et al., 2020). Based on derivations, this manuscript shows that coagulation has impacts on the appearance time and these impacts can be corrected using the measured aerosol size distributions. The corrections are validated by the derivations and elaborated in Figs. 1-5. However, the proposed corrections are only for the influences of coagulation. For instance, vapor evaporation and the variation of vapor concentration are not accounted for in the corrected formula. Hence, there are still uncertainties in the corrected formula. Reporting these uncertainties is one of the contributions of the revised manuscript. These revisions are illustrated and discussed in detail in the responses below.

In response to the two specific main concerns: a) The correction for influences of coagulation has been validated by derivations and illustrated using test results. In the revised manuscript, we distinguish "the correction for coagulation influence" from "the corrected appearance time method". We agree with the reviewer that there may be uncertainties in the corrected formula, yet the test results show that correcting the influences coagulation reduces these uncertainties. b) We added the discussions on vapor evaporation to the revised manuscript.

Below are the detailed comments that I would ask the authors to address:

1. Figure 6 does not look very convincing in terms of the performance of the suggested correction approaches – do other test cases exhibit similar behavior in the size-dependent errors? Rather than listing the average discrepancies in the corrected growth rates e.g. in the Abstract and Conclusions, the maximum errors should be stated, since they are up to 150 % (!) for the present test cases. In general, complex particle population dynamics cannot normally be described by simplifications, so it is not so surprising that the corrections do not work very well, or cannot be reliably applied on realistic data. This is one of the main results of the work and should be highlighted – even a negative result is a result. Instead of stating "the feasibility of the corrected method was verified" it can be said that the method was "tested", since based on the presented results it doesn't look like the method was verified. Also the title is a bit misleading since it talks about sub-3 nm particles, while later in the test it's concluded that neither the conventional nor the corrected method work reliably at sub-2 nm. I would therefore reformulate the essential parts of the text to discuss "suggestions" or "attempts" to correct, instead of "corrections".

Response: In the revised manuscript, we revised the statements such that correction and validation are only used for the influences of coagulation. Meanwhile, we emphasized that although this correction reduces the biases of the appearance time method, there are still uncertainties in the growth rate estimated using the appearance time method due to vapor evaporation and the variation of vapor concentration. These uncertainties are indicated by simulation results and reported in the abstract and conclusions.

Figure 7 (the original Fig. 6) shows the typical trend of size-dependent error of the appearance time method, whereas the amount of error varies with simulation conditions and it is indicated in Table A1. After correcting the influences of coagulation, the bias of the appearance time method is reduced.

We report the maximum errors of the size-dependent growth rate of the simulation results in the revised Abstract and Conclusions. We agree with the reviewer of 150% is a huge error; however, the uncertainties in measurements of sub-10 nm aerosol size distribution often exceeds this value (Kangasluoma et al., 2020). These uncertainties will propagate if the absolute aerosol concentration is used to estimate the growth rate, whereas the appearance time method uses only the variation of aerosol size distribution.

"Sub-3 nm particle" in the title and abstract was revised as "new particle".

In summary, the revised manuscript emphasizes more on the uncertainties of the appearance time method. We limit the correction and validation to the influences of coagulation and clarified that there are remaining uncertainties in the appearance time method. Reporting these uncertainties is a contribution of this study.

2. The omission of evaporation in the simulations limits the applicability of the results, since atmospheric small clusters and particles generally evaporate significantly. (A single test with a size-independent evaporation rate doesn't help very much, since for the smallest particles the rate may vary even by orders of magnitude with the size and composition, and the used rate is also quite low.) Therefore, I'd ask to include test cases where the smallest clusters have strongly size-dependent evaporation rates of at least around 10^{-2} s^{-1}, or even higher. For example the highest values in Schobesberger et al., Atmos. Chem. Phys. 15, 55-78, 2015 could be used for upper-limit estimates for the evaporation effects. Specifically, since often the evaporation rates of the smallest clusters exceed the vapor condensation rate, it's essential to include cases where $\beta*N_1$-E (Sect. 4.1, page 9) is negative. Stating that "the bias caused by this size dependency of evaporation is similar to that of coagulation" is odd, since evaporation and coagulation processes are very different: the former moves particles along the size axis within the studied size range, while the latter removes particles from the size

range. Can you show how their effects are similar (for arbitrary evaporation and coagulation rate constants)? In Figure 2, how would a test case with both non-zero sink and non-zero evaporation look like? The effects of evaporation may be different at sinks of different magnitude.

Response: We added discussions on the influences of vapor evaporation together with a new Fig. 6 to section 4.3. Size-dependent evaporation was assumed for the simulation in Fig. 6. The evaporation rate of the smallest cluster (dimer) was assumed to be ~0.2 s^{-1} according to the quantum chemistry results for H_2SO_4-NH_3 nucleation (Myllys et al., 2019). For sub-1.5 nm particles, the net flux for monomer condensation in the Lagrangian specification (βN_1-E) is negative. The simulation results show that in addition to changing the growth rate, evaporation may also influence the steady-state concentration of particles and hence impact the retrieved growth rate. With prior information on the size-dependent evaporation rate, this influence can be readily corrected and the corrected net condensation growth rate agrees with the theoretical value. However, since the size-dependent evaporation rate is rarely known, this correction may be not available when applying the appearance time method. Neglecting the influence of vapor evaporation on the appearance time causes an overestimation of the growth rate smaller or slightly larger than the critical size (at which βN_1-E = 0). This finding is supported by tests with different size-dependent evaporation rates. Hence, with a correction for vapor evaporation, the appearance time method is not valid to characterize net particle/cluster growth during nucleation (βN_1-E < 0). In Conclusions, we added "Further, the growth rate of vapors and clusters is recommended to be estimated based on cluster dynamics instead of their representative time."

"The bias caused by this size dependency of evaporation is similar to that of coagulation" in the original manuscript means refers to similarities in their mathematical expressions and corrections. Figure 6 shows that the correction for evaporation is similar to that for coagulation, i.e., they reduce the steady-state concentration of particles and can be corrected similarly. However, this sentence was removed to avoid confusion.

In addition to the influence of evaporation for a homo-molecular nucleation system, the supporting information includes a test with a volatile vapor and a non-volatile vapor. The appearance time method follows the theoretical growth rate in this test.

3. Sect. 4.2: it is concluded that CoagSrc does not have a major impact on the apparent growth rate. This statement could be softened, since the test cases are so limited, and also the vapor concentrations here are not extremely high. Maybe CoagSrc may still have a larger role at the higher end of atmospherically relevant vapor concentrations, e.g. at ca. 10ˆ8 cmˆ-3?

Response: This sentence was revised as "CoagSrc does not have a major impact on the apparent growth rate of sub-10 nm particles even during an intensive atmospheric NPF event in urban Beijing." We agree with the reviewer that the coagulation source may play an important role in new particle growth in some atmospheric environments. However, a high vapor concentration does not necessarily correspond to a high coagulation source because the coagulation source is determined by the concentration of new particles.

4. The particle size is mainly expressed through the diameter. The results should thus be dependent on the size of the vapor molecules: the diameters of very small nanoparticles containing equal numbers of molecules are different for e.g. large organic molecules and sulfuric acid. Also, the behavior of apparent GR with respect to diameter may be different for multi-component particle formation where the sizes of the molecular species differ significantly. Which molecular size was used in the simulations? In Sect. 4.3 it is stated that "one should be cautious about the sub-2 nm size-resolved growth rate" – could the 2-nm-limit be something else for different molecules, for example could the diameter threshold

be larger for highly oxidized organic monomers or dimers? I recommend to bring up the fact that the diameters may not be very meaningful for such small clusters.

Response: We clarify that the vapor for simulation is sulfuric acid in the revised section 3.1. A new simulation with large molecules (400 Da) was added to the supporting information. In the revised manuscript, we added "For particles close to the size of vapor molecules (sub-2 nm in these tests), the appearance time usually convolves other information (e.g., the varying vapor concentration and the size-dependent coagulation coefficient) in addition to particle growth. Figure S2 shows that with larger vapor molecules, the size range for the discrepancy between the theoretical and retrieved growth rate shifts towards larger diameters."

5. Derivation of the corrections in the Appendix: Can you elaborate how the first very first equality (GRconv = . . .) in Eq. (A9) is deduced; it is not obvious. Also, in the derivation of Eq. (A6, it is assumed that the concentration at the appearance time is 50 % of the final value. It should be noted that in the "conventional" appearance time method it is actually defined that the appearance time concentration is 50% of the maximum value (Lehtipalo et al., 2014), which is not the same as the final value in a strong clustering event. This can affect even "ideal" cases with a constant vapor concentration. In general, the correction seems to be derived for a situation where the particle distribution relaxes into a steady state (equations in the Appendix with N_i,inf). Thus I don't see a reason to believe that the appearance time method, or any "corrected" version of it, would work for realistic, dynamic atmospheric environments with varying vapor and particle concentrations, so the failure in Fig. 6 is not surprising. Why could e.g. Eq. (A8) be applied to an atmospheric non-steady-state situation?

Response: We added a sentence to illustrate the first line in Eq. S6 (original Eq.A9): "The appearance time and hence the retrieved growth rate are mainly influenced in two aspects: 1) the steady-state concentration and 2) the particle source that determines the time to reach a certain steady-state concentration."

As clarified in Section 4.1 and the recently published He et al. (2020), the appearance time should be defined with respect to the steady-state concentration, which is also equal to its maximum concentration if all the assumptions for derivation are valid. We agree with the reviewer that in the conventional appearance time method, the appearance time is usually calculated using the maximum concentration. However, this should be taken as an approximation rather than a definition. In section 4.3, we added "The 50% appearance time is herein calculated using the maximum size-resolved particle concentration because $N_{i,\infty}$ is not available, and this approximation introduces biases to the retrieved growth rate."

We also agree with the reviewer that the appearance time methods and its correction are derived based on an ideal assumption of constant vapor concentration and constant sink, which is usually not valid for the real atmosphere. Hence, we listed the assumptions for the derivations of the appearance time method at the very beginning of section 4.1. In the revised manuscript, we also add a new paragraph to emphasize the foreseeable uncertainties of the appearance time method due to the violation of these ideal assumptions: "It can be seen that none of these ideal conditions is consistent with real atmospheric environments. Since the conventional appearance time method is derived based on these conditions, violating them may cause biases in the appearance time method. We will first show brief derivations of the conventional appearance time and then discuss the correction for the influences of coagulation and other remaining potential uncertainties of the corrected appearance time method."

We disagree with the reviewer on the statement that the appearance time method does not work for the real atmosphere. It is true that due to the variation of vapor concentration, the appearance time can never be strictly accurate for new particle formation in the real atmosphere. For instance, applying Eq. S5 to an atmospheric non-steady-state situation is an approximation and it leads to uncertainties in the retrieved growth rate. Figure 7 and the data in Table A1 indicate these uncertainties caused by a varying vapor concentration. However, the appearance time method can report a growth rate close to the theoretical value (although with large uncertainties) and the correction for the influences of coagulation reduces these uncertainties. Considering the fact that other methods (representative diameter methods and the methods based on solving aerosol general dynamic equations) can rarely report a growth rate for sub-5 nm particles and the large uncertainty in determining the absolute concentration of sub-10 nm particles (up to a factor of 10, Kangasluoma et al., 2020), we think that the uncertainties of the corrected appearance time method shown in Fig. 7 are acceptable.

As clarified in the Introduction, the appearance time method is favored for sub-3 nm particles because of its above advantages over other methods. Previous studies have reported potentially huge uncertainties (Olenius et al., 2014; Kontkanen et al., 2016; Li and McMurry, 2018) in the appearance time method, yet the appearance time method, and even the maximum concentration method, are still used for the real atmosphere and the uncertainties in the estimated growth rate are usually not addressed. Instead of simply reporting uncertainties, this study aims to 1) clarify the reason for these uncertainties, e.g., how evaporation may influence the retrieved growth rate and which size range is affected instead of reporting that evaporation may cause uncertainties, and 2) provide correction formulae for the influences of coagulation which reduces the uncertainties of the appearance time method.

Minor comments:

1. After Eq. (1): “Note that Eq. 1 is expressed in the discrete form, i.e., it does not assume a continuum particle size”: one can note that it does however assume a well-defined GR typical for the continuum space, i.e. no spreading of the size distribution, and no negative average net condensation flux in the Lagrangian presentation (see comment 2).

Response: We revised the description of Eq. 1 as “When there is only one non-volatile condensing vapor……” and added “When considering particle evaporation, i.e., monomer dissociation, particle growth due to the net effect of monomer association and dissociation will be explicitly referred as net condensation growth” to address the cases with vapor evaporation. However, Eq. 1 is also valid for a spreading size distribution, as illustrated in Appendix A.

2. Sect. 4.1: Has the appearance time method actually been derived in the original paper (Lehtipalo et al., 2014), or is this something done only in the present manuscript? Is e.g. the original choice of 50 % concentration increase arbitrary?

Response: The derivation of the appearance time method under ideal conditions was reported quite recently (He et al., 2020). We include this reference in the revised manuscript. The threshold of 50 % was recommended by Lehtipalo et al. (2014) according to comparisons among simulation results. Section 4.1 does not discuss much on the usage of the appearance time method in previous studies because we think explaining the theory of the appearance time methods via derivations is more convincing than reviewing how it is used previously.

3. Table A1 and Figure 6: Would a varying coagulation sink affect the results? The growth of the boundary layer in daytime typically causes a time dependent sink.

Response: Coagulation sink influences the steady-state concentration of particles and its variation may introduce uncertainties to the retrieved growth rate. In the revised manuscript, we added “CoagS is assumed to be independent of time in the above discussions, whereas it may vary significantly during an NPF event in the atmosphere. The varying CoagS influences $N_{i,\infty}$ and hence the appearance time. Figure S3 shows that a bias of the growth rate retrieved using the appearance time method caused by a varying CoagS.” Simulation results with a varying coagulation sink are presented in Fig. S3.

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