Responses to Reviewer #1's Comments on Manuscript acp-2020-398

(Impacts of coagulation on the appearance time method for new particle growth rate evaluation and their corrections)

We appreciate the efforts of Prof. Dr. Wolfgang Junkermann (referred to as the reviewer below), in elucidating the influence of meteorological factors on the measured evolution of new particles during the case study presented in Figure 8. The reviewer provided convincing analysis to show there was a non-negligible influence of transport on the local air mass. Some concerns were raised on the validity to use a box model for new particle formation in a complex urban environment. However, these concerns are based on misinterpretations of this study because the models in this study are only used to test formulae. The meteorological analysis presented by the reviewer is not against the correction of the appearance time method. In this response, we address the reviewer's comments and again clarify the objectives and main findings of this manuscript. The comments are shown as sans-serif dark red texts and our responses are shown as serif black texts. References are given at the end of the responses.

Reviewer's comments

The paper describes a correction for the consideration of coagulation in nucleation aerosol formation modelling. This correction is changing the timing for nucleation mode particles, the time within the model until when particles have grown for example to a certain size. The title restricts this investigation to particle sizes below 3 nm where it might be especially important, however within the manuscript the appearance time is given also for other particles sizes. To illustrate the results a case study for Beijing is given for a late winter nanoparticle event.

Response: This manuscript introduces a correction for a formula to calculate the new particle growth rate, not a model to simulate new particle formation. As clarified in the manuscript and previous responses, the models are used to test the corrected formula and the case study measured in urban Beijing is used as an instance for the influence of coagulation on the appearance time in polluted atmospheric environments.

Although the first part of the model description looks reasonably for an application for chamber studies the authors fail to prove that the model is applicable for the real atmosphere. The second part, the atmospheric experimental case study is not in agreement with the particle event classification. It is clearly and temporarily out of range for a 'classical' new particle formation event according to an independent meteorological analysis which is totally missing in the manuscript.

The model and the experiment are not really directly related to each other and thus should not be published in one manuscript as related to the same process.

Response: We agree with the reviewer that the models and the measured new particle formation event in urban Beijing are not directly related to each other and the models used in this study are not directly applicable to the real atmosphere. This is because the models are used to test the formulae rather than to simulate an atmospheric new particle formation process. We have clarified in Section 3.1 that "Note that the aerosol dynamic models are only used to provide a benchmark to compare the conventional and corrected appearance time methods in this study".

This study does not investigate new particle formation mechanisms in urban Beijing by comparing modeling results with measured data. Instead, it is aimed to improve the estimation of the growth rate of new particles close to the cluster size. The new particle growth rate is a key parameter to characterize new particle formation and it is often used to indicate the growth mechanism. However, as summarized in the Introduction, it is challenging to estimate the particle growth rate down to the cluster size, especially in the real atmosphere. Representative time methods, e.g., the appearance time method and the maximum concentration method, are favored because of their feasibility to report a value (e.g., Kulmala et al., 2013; Bianchi et al., 2016; Yao et al., 2018), yet the demonstration for the relationship between this reported value and the particle growth rate needs demonstration in addition to intuition. The derivation of the appearance time method in an ideal condition with constant vapor production rate and negligible sinks was reported in a quite recent study (He et al., 2020). In this study, we show that the inevitable violation of this ideal condition may affect the appearance time and hence the estimated growth rate method. The influences of coagulation sink and their corrections are derived, tested by models, and reported in a case study in urban Beijing. The uncertainties caused by other factors, e.g., size-dependent vapor evaporation and the variation of vapor concentration are investigated are reported.

In the revised manuscript, we have emphasized in the Abstract and Conclusions that even after correcting the influence of coagulation, there may be uncertainties in the growth rate retrieved by the appearance time method due to the growth rate method. Note that these uncertainties do not indicate that the corrected appearance time method is completely not valid for atmospheric studies. Instead, when investigating particle growth mechanisms by comparing measured and simulated particle growth rates, accounting for these uncertainties helps to increase the robustness of conclusions.

The reviewer proves that the local air mass on Feb. 24, 2018 was significantly affected by transport based on a meteorological analysis. We will show below that this meteorological analysis is not against the findings of this study.

General comments

The authors miss to clarify under which environmental conditions their theory is applicable and relevant. Page 3, line 23 they promise to investigate the limitations. However, these limitations are never specified in the text. Page 15, line 18 to 20 states: uncertainties come from instrumental biases, atmospheric turbulence and omitted contributions from transport, mixing and emission to the measured aerosol size distribution.

Response: Instead of presenting environment conditions, we have stated the assumptions for the appearance time method at the beginning of Section 4.1. Violating these assumptions may cause uncertainties in the appearance time and hence limit the accuracy of the retrieved particle growth rate. In Sections 4.2 and 4.3, we discuss these limitations due to the violation of these assumptions, derive a correction formula to minimize the limitation due to the influence of coagulation, and report other potential limitations. We prefer to keep this assumption-violation-uncertainty discussion rather than specify several certain environmental conditions because it is essentially the population balance equations (e.g., Eq. 14) that determines the validity and potential uncertainty of the appearance time method. For instance, as stated in lines 18-20 on page 15, a non-negligible contribution of transport to the measured aerosol number concentration introduces uncertainties to the appearance time method because the third ideal assumption, i.e., “condensation is the only cause of the change in particle concentrations” is violated.

Summarizing the limits behind these statements mean that the theory presented is valid only for a homogeneous air-mass without any variability during the period between initialization of the model run (e.g. 00:00 until at least noon, the time given for the appearance of 4.9 nm particles (12:00), page 15, line 1). These conditions might be valid in a smog chamber (Stolzenburg et al, 2020) but are unlikely to find in the real atmosphere. Here a coupled model setup is necessary (Baklanov et al, 2008). Whether the model used in the manuscript is applicable at all for stationary ground based measurements under the conditions in the North China Plain is highly questionable.

The authors suggest by plotting model results into a graph with experimental results that the observation on February 24, 2018 can be described with their theory. However, a detailed supporting data set is missing. All available supporting data suggest that model and experiment cannot be compared as the experimental data set is not in agreement with the limitations of the model.

Response: The model used in this manuscript (e.g., in Fig. 7) is used to test the formulae for the appearance time method and it is not compared to measurement results. We have clarified this in Section 3.1.

As clarified in the caption in Fig. 8, there is no modeling result compared to the measurement results on Feb. 24, 2018. The aerosol size distribution and H_2SO_4 concentration in Fig. 8a were measured instruments, the measured growth rates in Fig. 8b were estimated from the measured evolution of aerosol size distributions using the conventional (Eq. 5) and corrected (Eq. 8) appearance time methods, and the theoretical growth rates were calculated using the measured H_2SO_4 concentration (Eq. 1) and aerosol size distributions (Eq. 2). The objective of this figure is to show that the coagulation correction for the appearance time method is necessary for sub-3 nm particles for this case study.

A three dimensional transport model including meteorological variables is available from either Flexpart of HYSPLIT. A local high resolution data set is available for example from the 320 m Beijing meteorological tower, about 7 km away from the particle observation site, close enough for a regional investigation. The data from this tower for February 24, 2018 (private communication, Prof. Fei Hu, IAP Beijing) show, that an intense vertical exchange of air masses began already a few hours before sunrise and continuing the next hours, advecting dry air from the residual layer all the way towards the ground (lowest level 8 m). This advection is reflected for example in the water vapor measurements. Starting at 2.3 g/m^3 the water vapor concentration declined to < 1.1 g/m^3 at 08:00.

This is a clear indication for a massive advection of dry air from aloft (~ 0.9 - 1 g/m3 in the residual layer between 800 and 1500 m above Beijing, HYSPLIT) and a replacement of the humid air in the planetary boundary layer. This air mass transport coincides with a concurrent doubling of the sulphur dioxide concentration between midnight and 08:00 LT. This polluted air mass contained also excess H_2SO_4, roughly doubling from nighttime levels to about 4* 10^6 /cm^3 at the time of sunrise (06:56 LT).

Response: We agree with the reviewer that a significant advection of air mass occurred before sunrise on Feb. 24, 2018. This advection is indicated by the changes in the concentrations of vapors with relatively long atmospheric residence time, e.g., H_2O and SO_2. We hold our opinions on whether the increase of H_2SO_4 concentration was mainly caused by transport of H_2SO_4 molecules or the changes of their sources and sinks due to transport or other reasons. This is because the atmospheric residence time of H_2SO_4 was short (~40 s) due to the relatively high condensation sink.

Such an increase, even before any uv-radiation would be available for photochemistry, is not at all in agreement with a photochemical production of H_2SO_4 as claimed in the manuscript (Hearth et al, 2004).

Response: We did not discuss the formation mechanism of H_2SO_4 in this study and did not state that all the H_2SO_4 molecules in urban Beijing, especially during nighttime, was formed by photochemical reactions.

The residual layer often contains large quantities of nanoparticles as shown by Quan et al, (2017) for Beijing, by Lampilahti et al, (2020) for Hyytiälä, Finland (also Hao et al, 2018) and by Junkermann and Hacker, (2018) for Germany (see there also for further examples from China and Australia).

Response: Advection indicates a potential influence of transport on the measured aerosol size distributions. This influence is affected by the size-dependent atmospheric residence time of aerosols. Aerosols close to the cluster size are thought to be formed locally because of their corresponding high coagulation sink. In Fig. 8, the particle growth rate in the sub-10 nm size range was discussed and the influence of coagulation was found to be significant for sub-3 nm particles.

The concentration of larger nanoparticles (e.g., >25 nm) with longer atmospheric residence time may be more significantly affected by transport compared to that of sub-10 nm particles. This may impact the size-dependent population balance of aerosols and hence cause uncertainties in the retrieved particle growth rate. Several studies (e.g., Cai et al., 2018; Kontkanen et al., 2020) have tried to estimate this influence from the population balance point of view. We agree with the reviewer that the influence of transport on the measured number concentrations of large nanoparticle are sometimes important in the atmosphere and have clarified that "transport, mixing, and emissions might influence the observed aerosol size distributions" when discussing the measured aerosol size distributions on Feb. 24, 2018 (line 12, page 16).

Finally: The authors present an analysis how particles might be produced in the atmosphere in a homogeneous air parcel. An admixture of air from the outside either by a replacement of the air mass by horizontal transport or a convective mixing process with air from the residual layer (Lampilahti et al, 2020) is not taken into account. Such an approach is not in agreement with highly variable ambient conditions, typical winds and diurnal cycles in the planetary boundary layer and thus not applicable for the Beijing case study.

Response: We did not discuss how particles were produced in this study.

The case study however, properly analyzed, would be a good example for a transport and convection driven nanoparticle advection, including gas to particle conversion (Gillani et al, 1979). Such a nanoparticle advection can also superpose the physical constrains of nano-particle GTP under heavily polluted conditions (Kulmala et al, 2017).

Response: We agree with the reviewer that transport may be an important source of nanoparticles with sufficiently long atmospheric residence time in the urban atmospheric environment. The different sources (e.g., vapor concentrations) and sinks (e.g., coagulation sink) at different heights may cause non-uniform vertical distribution of nanoparticles, yet more studies are needed to verify and quantify the contributions of vertical transport to the measured aerosol size distributions at the ground level. We look forward to possible collaborative researches with the reviewer to address this scientific question.

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