Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-398-RC1, 2020

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impacts of coagulation on the appearance time method for sub-3 nm particle growth rate evaluation and their corrections" *by* Runlong Cai et al.

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Received and published: 26 July 2020

Summary

The manuscript describes a numerical set of formulas that is used in an aerosol model for the calculation of the growth of aerosol particles after nucleation, especially for the range of $\sim$ 1 nm to 3 nm. This formula set is used for a calculation of the appearance time (time after cluster formation) and later for estimation of the growth rate of the larger sizes aerosols > 4 nm although the main emphasis is on the smallest size ranges, where coagulation has a major effect. Model results based on these formulas are finally compared to a nucleation mode particle event in a relative highly polluted environment

in China, in the city of Beijing in a late winter situation.

General comments

The argumentation and description of the formulas seems plausible and is according to the authors in agreement with the theory. Unfortunately this 'reference' theory, which is several times cited in the manuscript, is neither described nor referenced. Also there is no information about this general 'theory' and the underlying nucleation scheme applied. There are several nucleation schemes, binary nucleation of sulfuric acid and water (neutral and ion-assisted), ternary involving sulfuric acid, water, and ammonia; with or without organic species and sulfuric acid or charged sulfuric acid-water-ammonia (Napari et al, 2002; Riccobono et al. 2014; Dunne et al. 2016). Otherwise, the results of the subsequent calculations are at least partially contradicting previous publications that are a base for many 'new particle formation' studies within the last decade.

That discrepancy is likely due to the fact that the calculations are done only with a limited set of condensing substances, likely H2SO4. It is well known that the exclusive condensation of H2SO4 is too slow for the growth rates observed in the atmosphere and that other substances like VOC's or ELVOC's have a large share on growth rates (Ehn et al, 2014; Kuang et al, 2012; Kupc et al, 2020 and literature cited there). An overview about the problems associated with the investigation of nucleation under Chinese high pollution conditions is given by Chu et al (2019). Here also potential other compounds that might be important for NPF. Cai et al (2017) showed that H2SO4 could and should be involved but, high H2SO4 concentrations do not necessary lead to particle formation events.

The physical background besides the description of the mathematical steps is largely missing. Neither the environmental conditions for the validity of the model, nor the initial input parameters, temperatures humidity, number and size of large particles acting as a condensation sink etc. are included. 100 nm particles are mentioned in a 'certain' number.

The major difference between the new approach of the ‘appearance time method’ and the ’old’ theory, that needs to be discussed in detail is the result that, for the small particles size the growth rate due to coagulation is slowed down compared to other studies where the growth rate is continuously increasing with size (Kulmala et al, 2004, Kulmala et al, 2013, Kuang et al, 2012). The result is a longer appearance time (12 hour for 4.9 nm) than published elsewhere (Kulmala et al, 2013). For a detailed description of the current understanding of the initial steps of gas to particle conversion, and probably the ‘theory’ mentioned in the manuscript see also Kulmala et al, 2017 and Yao et al, 2018.

The model results are then compared to an event ‘typical’ for Beijing, with nucleation mode particles observed in late winter (24.2.2018). Also, in this section the authors do not give any details about the environmental conditions at the day of the particle event, nor any detailed information about the location, distance to major roads, height of the aerosol inlet above ground etc.. This information is important in a study about aerosols that may be affected by strong local sources (traffic, home emissions) and potential regional transport. Included is only a reference to a submitted, but still not yet accepted, companion paper. Also, as this is an aerosol study under conditions with a large condensational sink, it would be helpful to have data on fine particle concentration, a ‘certain number of 100 nm particles’ is way too uncertain.

The most important issue, however, is the classification of the experimental comparison data. It is the timing of the event that makes it difficult to match the event with basic atmospheric physics and chemistry and with the current observations that the mayority of NPF events are happening during daylight hours. A new particle formation event at that time of the day would require an even faster growth than shown by Kulmala (2013) and not a slower growth as indicated in this manuscript. Both, the ’old’ Kulmala 4 hours and the ’new’ 12 hours appearance time require nighttime chemistry and physics which has not been reported as a significant source for nucleation.

The data presented rather indicate a transport related change of air masses. The

H2SO4 concentration which is at background levels at sunrise peaks about one hour after sunrise and than steadily declines throughout the day (Fig. 6 of the manuscript). This behavior is contrary to the model where the peak concentration is 4 hours later at noon. This experimental diurnal pattern is neither in agreement with local emissions in a high NOx environment nor with a photochemical reaction including OH radicals and SO2.

Following Kulmala et al (2013) the appearance of 5 nm particles needs about 4 hours after initial cluster formation. This implies for the Beijing case study that cluster formation would occur before sunrise. The air mass at that time has been, according to HYSPLIT, in the area close to the city of Tangshan, not locally in Beijing. Following the results of the current study (appearance time of 4.9 nm particles $\sim$12 hours) clusters would originate even further to the east, close to the coastline at a formation time a few hours after sunset (Fig. 1). This requires a discussion of a nighttime cluster formation chemistry.

Along the backtrajectories several anthropogenic sources for sulphur compounds are located, that emit a mixture of both, particles and gas phase precursors (Fig. 1). Their emissions include sulfur dioxide, H2SO4 (Srivastava et al, 2004) and large amounts of ammonia (Li et al, 2017) and primary nanoparticles produced at elevated temperatures and with or without catalysts, Bai et al, 1992). These are than released into elevated layers of the atmosphere (Junkermann et al, 2011). Measured emission rates of such ‘new aerosol generators’ are in the order of $\sim$3*10ˆ15 s-1 MW-1. Naturally, the emitted particles undergo coagulation and further growth or shrinking (evaporation) depending on the ambient conditions (temperature, humidity) during transport under cool and dry nighttime conditions and the plume conditions favor additional gas to particle conversion (Mohnen and Lodge, 1969). The shape of the diurnal pattern of H2SO4 in Beijing is in good agreement with such an advection-convection driven transport, by far better than with a local chemistry initiated cluster formation.

The example of the early morning particle event in Beijing is probably a typical

'nanoparticle' but not a formation event. The experimental verification is looking reasonable but likely does not reflect reality.

The manuscript would need a complete revision due to the missing model and experiment description and not verified nor discussed assumptions about the classification of the particle event. It's also required to discuss the differences between the current model and the previously published growth rate versus particle sizes and the implications on the timing of the whole nucleation process (cluster formation at night versus photochemical reaction).

The authors also should make sure that the appearance of nucleation mode particles in Beijing is applied to a really local phenomena and not to a plume study.

Specific comments:

Model output

The model based on the new formula predicts initially a slow down of the growth rates of new particles within the size range from 1 to 3 nm.

The behavior of the growth rates in the 'new' model setup of the manuscript would delay the growth of newly formed particles significantly compared growth rates published elsewhere (Kulmala et al, 2004 and Kulmala et al, 2013). In these publications a continuously increasing growth rate is used. Accordingly, with the new model the growth of new particles to sizes of about 5 nm takes $\sim$ 10-12 hours compared to 4 hours in the Kulmala et al (2013) example. This is a severe difference likely due to the restriction of only one condensing vapor and has to be discussed in detail because it has strong implications for the time and location of the cluster formation process.

This difference implies several questions that are important for the model - experiment comparison (probably not for the calculation of the impact of coagulation but for the selection of a nucleation event and nocturnal chemistry) that arise, mainly related to timing:

- What is the process producing the initial clusters? At what environmental conditions temperature, rH, radiation?

- Where (locally) does cluster formation happen and, in case, H2SO4 is involved, where is it's origin?

- Are other compounds required, ammonia, water etc..?

- Why is cluster formation happening at this time and the corresponding chemical reactions are terminated after a few hours while precursors are still present?

- The model is running at least for one version with constant vapor concentration. Is this real?

- When H2SO4 is crucial for the cluster formation, why are there no more 5 nm particles appearing 12 hours after the peak of H2SO4?

- Why is the assumed H2SO4 concentration as high as measured peak values? Within the hours when nucleation mode particles grow in the model from 1 to 3 nm the H2SO4 concentration is only a smaller fraction of the model value. H2SO4 reaches model values at a time when already 10 nm particles are detected.

3D transport:

Looking into the experimental data given in Fig. 7 transport of externally produced particles and precursors is more likely to explain the observations (Cai et al 2018). Transport at night from elevated sources ($\sim$ 300 m) normally happens in clear air (low condensation sink) above the polluted nocturnal surface layer (Fig. 2). Vertical convection mixes rapidly (< 30 min) the air of residual and surface layers in the morning (Platis et al, 2016; Junkermann and Hacker, 2018). Contrary to atmospheric processes industrial nanoparticle sources run 24 hours, seven days a week and include sulphur and nitrogen chemistry as well as ammonia in large amounts (Bai et al, 1992).

A simple budget calculation with a box model similar like in Cai et al (2018) for a 300 km

plume originating at Suizhong and Quinhuangdao spreading to ∼40 km width (Rosenfeld et al, 2000), assuming a few hundred m residual layer (Platis et al, 2016, Junkermann and Hacker, 2018) and a replacement of the plume volume above Beijing with a wind speed of 25 km h-1 results, even without additional new particles, in number concentrations already in the order of magnitude finally observed in Beijing (> 80000 cm-3) and in H2SO4 concentrations ∼ 10ˆ8 cm-3, see also Junkermann and Hacker (2018). It is also in agreement with the diurnal pattern (Fig. 6) with convection beginning at ∼08:00 local time and downwards mixing of a 200 m layer of this air mass into the low nucleation mode particle concentration 600 m surface layer (HYSPLIT) (Fig. 3). Numbers are based on measured and published emission data for power stations and from HYSPLIT meteorological data along the trajectory and allow at least a rough estimate of the magnitude of concentrations. How far new particle formation plays a role during the dry, cold and dark conditions during the transport and how aerosol size distributions and H2SO4 concentrations change would be a perfect task for a complete aerosol-chemistry-transport model. Such a plume production (Mohnen and Lodge, 1969) would widen the nanoparticle size distribution and provide additional particles in the lowest size bins. Field data show, that nighttime transport in the residual layer does not really lead to a massive loss of particles (Fig. 4). The plume hypothesis above is also in agreement with the results of spatial measurements of nucleation mode particles in Germany (Ma and Birmili, 2015) at stations surrounded by several fossil fuel burning power stations using SCR or SNCR technology.

Minor comments

Who is Julia (Page 7, line 1)

A reference to a paper under review (Cai et al, 2020) still has to be considered as grey literature as long as the review process is not open access. Also, as it is not clear whether the companion manuscript passes the review process, the information in this other paper is crucial for the current manuscript but might not be available. It could be placed in a supplement.

A reference to a paper in preparation (Li and Cai, 2020) is not even grey literature!

Define the conventional method, when it is first cited, Page 5, Lethipalo, 2014? Later in the paper it is confusing, with which model the current results are compared without a reference.

The same holds for the theory when the model, which is theory as well, is compared to another theory. Within the time has to be defined in the text and figures. Is this Beijing CST?

Numbering of the tables. Why is the third table named table A1 instead of Table 3?

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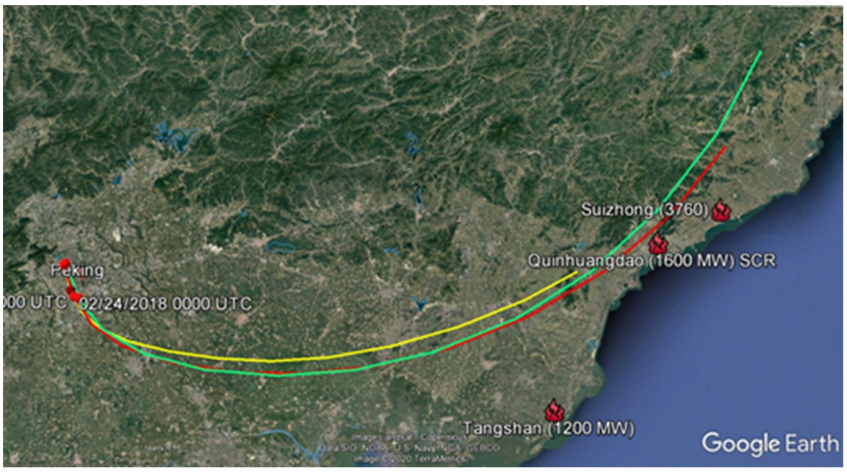

Fig. 1. Fig. 1: HYSPLIT 12 h backtrajectories for 24022018 01:00 UTC arrival in Beijing, yellow 50 m, red 250 m and green 500 m, GDAS 0.5

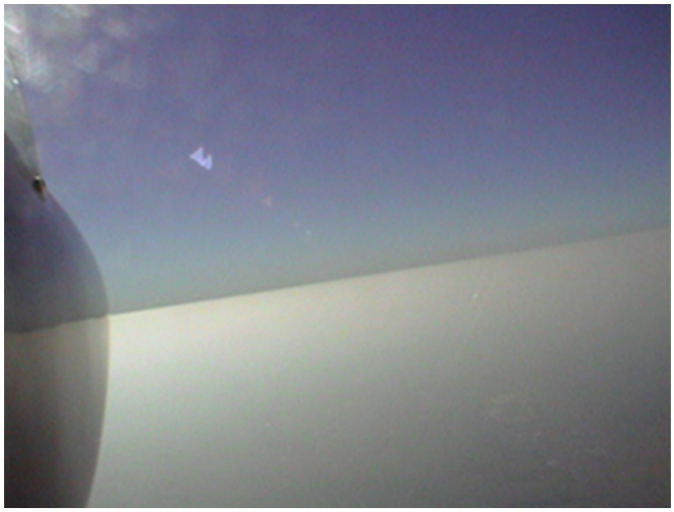

Fig. 2. Fig. 2: Febr. 19, 2002 early morning (09:00) conditions 500 m above the Po-Valley (Italy)

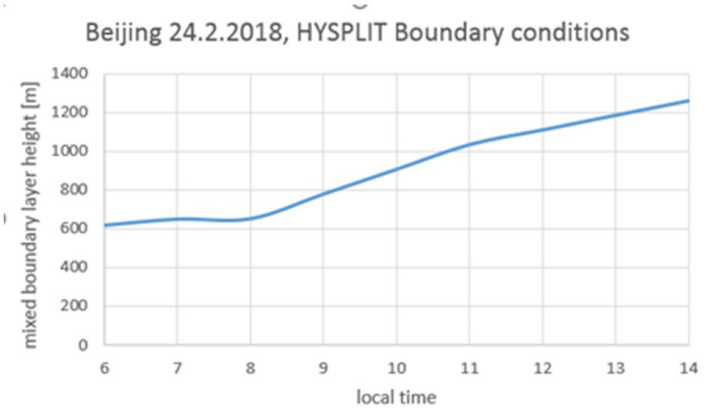

Fig. 3. Fig. 3: Boundary layer development in Beijing the morning of Febr. 24, 2018 (HYSPLIT)

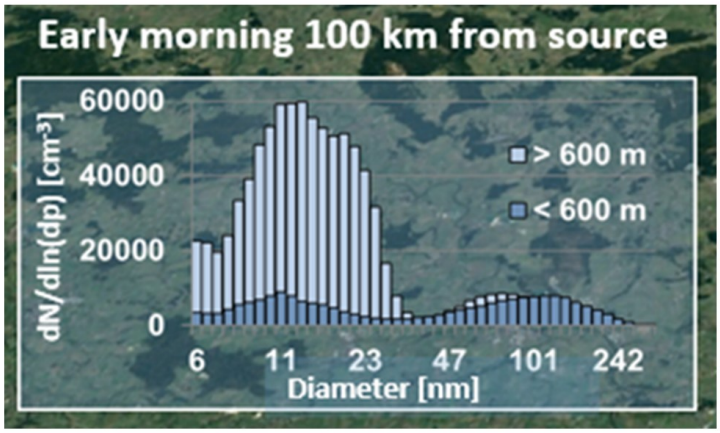

Fig. 4. Fig. 4:Size distribution above and below inversion 100 km, 10 h downwind of source (Germany, June 10, 2014, PBL 600 m), clean air in the residual layer, polluted in the PBL