

Reply to Referee #2

We thank Anonymous Referee #2 for their helpful comments. We have answered to the comments below. The bold text is quoted from the referee's comments, and the text in italics has been added to the manuscript.

GENERAL COMMENTS

In their manuscript, Kontkanen et al. present a set of numerical simulations of a one-component system, with the purpose to study the effect of cluster-cluster collisions on the growth of particles, and also the impact of different definitions and methods of the growth rate. The study is interesting, and gives a good overview of the different ways of looking at fresh particle growth, and the author's approach brings interesting new viewpoints to recent studies of nanoparticle formation in the atmosphere. The work is quite theoretical, and no comparison to actual experiments is made (as the studied one-component system would be quite difficult to produce). I think that the author's work is useful and interesting, and also in the scope of ACP. In my opinion the manuscript could be published in ACP, but I would appreciate it if some more information on the simulations and their analysis could be provided. I have listed my concerns below.

*** I did not fully follow how the simulations were performed. Were all inputs kept constant over the whole time? The authors state that there was an initial cluster distribution corresponding to a low monomer concentration. In addition, it is stated that a 'steady-state monomer concentration' is reached at some point. This suggests that the aerosol formation and growth proceeds until some kind of a steady state is reached. If it is so, this has at least the following implications for the data analysis:**

The model inputs, i.e. the monomer source rate, the external loss, temperature and the vapor properties, were kept constant during one simulation. The initial cluster distribution, corresponding to the monomer concentration of $5 \times 10^5 \text{ cm}^{-3}$, was used so that the simulations would correspond to the real situation in, for example, the atmosphere or a chamber experiment where the concentration of condensing vapor (e.g. sulfuric acid) is higher than zero already before the actual new particle formation event. As concluded by the referee, the simulations were continued until a steady state was reached.

a) from which part of the process are the various size-dependent growth rates determined? For AGR, the GR is necessarily from the start, but for the other GRs some other times could be used. Was the steady-state situation used? What was the criterion for steady state? Were the different growth rates determined at different time points within one simulation? Were the growth rates time-dependent within one simulation?

AGR was obtained by differentiating (t_{app}, D_p)-data, where the appearance time of a size bin, t_{app} , was defined as the time at which the concentration of the bin reaches 50% of the total increase in the concentration (see Sect. 2.1.2). AGR thus yields one time-independent value for each size bin in one simulation. FGR and CGR, on the other hand, were time-dependent in the simulations, as FGR depends on the time evolution of the fluxes, and CGR on the time evolution of the monomer concentration. Therefore, both FGR and CGR changed during one simulation until the steady state was reached. We determined FGR and CGR at the mean appearance times of consecutive size bins, and at the steady state. This is already mentioned on page 8, although we now slightly modified the sentence to be more exact. As the main aim of this study was to compare the different growth rates with each other, only the values obtained at the appearance times were presented in the paper. However, the steady-state results were qualitatively similar. The criterion for the steady state was that the relative changes in the concentrations of the monomer and clusters as a function of time were negligible (less than 10^{-4} %) when the integration was continued for several minutes.

b) A 'steady state' in which everything stays constant is rarely seen in nature, partly because the growing particles contribute to a growth in the sink and therefore the Q/S fraction also changes. This could, for example, introduce a coupling between the formation rate and the AGR of FGR, because high formation rate causes a fast-increasing sink quickly to the distribution. I understand that the sink in the simulations was not dynamic, and therefore this effect is omitted. Do the authors have an idea how this affects the results? In any case, it would be useful to have a description of the time-dependent developing distribution, for example using a figure. The same figure could then be used to give a graphical explanation of the derivation of the different growth rates.

The external sink, corresponding to the loss of clusters due to coagulation onto large particles in the atmosphere, was indeed kept constant in our simulations. The sink of the vapor monomer and small clusters due to collisions with the simulated larger clusters (up to the clusters containing 70 molecules), naturally increased during the simulation when the cluster concentrations were increasing. On the other hand, the clusters growing beyond the size of 70 molecules were removed from the simulation, and therefore did not contribute to the sink. This means that in our simulations the sink remained lower than if the sink due to the particles larger than 70 molecules was taken into account, and thus the concentrations of vapor monomer and clusters could increase higher. However, as we are here interested only in the beginning of a new particle formation event (when sub-3nm clusters are formed), this effect is likely not very big, as it takes several hours before the nanometer sized clusters can reach sizes large enough to contribute significantly to the total sink. Thus, the coupling between the particle formation and the sink is likely to become significant mainly in very rapid particle formation bursts, where both the initial formation and the growth occur fast. Following the referee's suggestion, we now added a figure showing the time evolution of the cluster distribution in one simulation into the Appendix (Fig. A2 in the revised manuscript).

*** A big question in particle formation research is the size dependence of growth in particle formation. From the results in this paper (Figs 1d, 2d, 3d, and 4d), it seems that for this one-component case, AGR and CGR tend to decrease with size while FGR increases with size. Is this a result that could be considered general? Is it possible that this changes in a true, multi-component case?**

CGR decreases in all cases with the increasing cluster diameter, which results directly from its definition (see Eq. (7)). The size dependencies of AGR and FGR, on the other hand, are not affected only by the substance properties, but also by the ambient conditions, as well as the size classification, i.e. the resolution of the analysis (see Eqs (3) and (4)). The results for a multi-component system with an evaporation profile similar to our one-component substance can be expected to qualitatively resemble the results presented here. However, the size-dependencies of AGR and FGR observed in our simulations cannot be generalized for arbitrary substances and environments, as they are affected by the evaporation profile of the substance, and the time evolution of the cluster distribution, determined by the time evolution of the sources and sinks. For example, in the atmosphere the monomer source rate is usually time-dependent, which may affect the size-dependence of the growth rates (see Olenius et al. (2014) where this case is discussed).

To clarify this, we added the following sentence in the Sect. 3.1 (page 9, line 24):

It needs to be noted that the size-dependencies of AGR and FGR observed here cannot be generalized for arbitrary substances and environments, because they are affected by the vapor properties as well as the ambient conditions.

*** Finally, I think that the discussion in the conclusions could be improved. In the last paragraph, (p. 14, L 23) the authors state that "conventional methods used to determine particle formation rates from growth rates may give estimates far from their true values". Based on earlier discussion, it seems that the authors bring forward the idea that not a**

single 'true' value exists (for example, the growth rate can mean the AGR, FGR or CGR). In the study of particle formation, finding the values for the formation rate J and the growth rate GR has for some time been a key objective. It would be useful if the authors could discuss here which of the given growth rates is the true value meant.

We agree that the sentence quoted by the referee was not entirely clear, and it has now been slightly changed. The aim of the statement is not to suggest that any of these growth rates would be the true growth rate of particles. Indeed, in the cases discussed in this study, where clusters grow not only by monomer collisions but also by cluster-cluster collisions, it is not possible to give one, unambiguous value for the growth rate of clusters of a specific size. With the "true value", we refer to the true value of the particle formation rate J , i.e. the flux of particles past a certain size, that is always unambiguously defined. We want to point out that determining a formation rate from a measured growth rate (here AGR) utilizing Eq. (5), as is often done, may lead to values far from the real particle flux. This issue is discussed, for example, in the end of the Sect. 3.1.

SPECIFIC COMMENTS

P7 L33: Regarding the monomer concentration ranges, I understand the limitation of the lower level. However, the upper level for the monomer concentration is less justified. This is a case of selecting a too long time step; reducing the time step in the differential equation solving would present usable results. In any case, the limits for the usability of the methods should be given.

Actually, the upper limit for the monomer concentration is not determined by the time step of the simulations, but the width of the size bins, for which the growth rates are determined. As clarified in the end of the Sect. 2.2 (page 8, line 2), if the monomer concentration was set to a too high value, concentrations of large clusters become so high that a significant fraction of the flux from a certain size bin may end up not only in the next size bin but also in the size bins larger than that. This would complicate the growth dynamics, and the method used to calculate the flux-equivalent growth rate (see Sect. 2.1.1) would not be exactly valid (see also the reply to a comment on Eq. (1) by Referee #1). Also, determining AGR from the appearance times of two consecutive bins (Eq. (4)) would not be justified if significant fractions of the flux from bin i would end up also in bins $> i+1$. As we are interested in situations where the clusters grow mainly by collisions of vapor monomer and small clusters, we have not addressed cases where the self-coagulation of the population becomes significant. We have now added a reference to Table 1 when discussing the limitations of the methods (page 8). In general, the limits for the validity of these methods are determined by the combination of all the parameters in the simulations (e.g. monomer source rate, the magnitude of the external sink, the properties of model substance) and the size bin width used in the analysis, and are thus system-specific.

P19, Table 1: For reproducibility, it is not enough to give the final monomer concentration, but also the monomer source rate is important information. I think that the monomer source rates used to obtain the final concentrations in Table 1 should be given also in Table 1.

As the referee suggests, we now added the monomer source rates used in different simulations into Table 1.