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Discussions

Interactive comment on "Errors in Nanoparticle Growth Rates Inferred from Measurements in Chemically Reacting Aerosol Systems" *by* Chenxi Li and Peter H. McMurry

Anonymous Referee #1

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The present manuscript entitled "Errors in Nanoparticle Growth Rates Inferred from Measurements in Chemically Reacting Aerosol Systems" discusses the potential errors made by applying different methods to determine growth rates (in the following referred to as GR) from measured data. The respective approaches have in common that they do not distinguish between growth by vapor uptake and other processes that change the particle size distribution (e.g.: coagulation, dilution, wall loss or losses to preexisting particles). Thus the resulting error may, depending on the significance of those processes, be considerable. The authors analyze these errors qualitatively as well as quantitatively. They describe the effect of evaporation and pre-existing particles on the evolution of the (dimensionless) particle size distributions and as a consequence on

the growth rates. The application of non-dimensional quantities is elegant in this context and allows for applying the results to a variety of cases. Further, the manuscript is clearly written. As the methods described are still frequently used by scientists in recent publications (also high impact, such as PNAS, Science or Nature) for interpreting data, it is important to show their limitations and to point towards alternatives which are available.

General comments:

The authors focus on the contribution of particle-particle interaction to growth and determine a maximum error of the growth rate for the collision controlled scenario. They do not explicitly state that this error represents a maximum overestimation of the growth rate (there are several statements mentioning this "upper limit" of the GR [page 3, line 85; page 7 line 191; p 10, line 312] or "maximum possible error" [abstract]; however, it may be interpreted by the reader as the maximum value of the error). It may also be worth mentioning the possibility of GR underestimation caused by deposition losses, dilution and losses to pre-existing particles.

The effect of pre-existing particles on GR errors is discussed as a representative case for several processes (wall loss, dilution and pre-existing particles). This, according to the authors, is justified by findings on the similarity of those processes with regard to effects on the nucleation as described in a recent study (McMurry & Li, 2017). In the present manuscript it is assumed that particle sinks of any form mainly reduce the monomer concentration. Thus, the main effect is the reduction of nucleated particles and this limits coagulation which, according to the authors reduces the error in the GRs. However, loss of particles to the wall, to preexisting particles or by dilution is not considered by the analysis methods discussed and thus potentially lowers the GR obtained from the respective methods (e.g. in a case with low particle growth where uptake of vapor by the walls is limited while the walls may represent a perfect sink for particles). This results in underestimation of the GR.

In the manuscript errors of the analyzed GRs are discussed with regard to the analysis methods applied which are not suitable to produce size and time dependent GRs. The result of those methods is rather an array giving GR for various particle sizes and different measurement times. Further, the methods have inherent errors as they attribute any change of the PSD to growth. Thus, these methods in general are not suitable to produce realistic GR. However, in some specific cases they are. The present manuscript does not provide the necessary information to distinguish between situations where the methods can safely be applied or not. The reason is the fact that possible underestimation of the GR is not discussed (e.g. low GR in a chamber with considerable wall loss and/or dilution may lead to considerable underestimation of the GR by applying one of the methods used). Thus, I suggest removing statements on situations featuring safe usage of those methods and replacing them by statements indicating where the methods cannot/should not be applied. Maybe the authors should also point out once again the possible alternative methods for data analysis which do not suffer from the errors discussed in this manuscript in the conclusion section.

Specific:

p.2, line 40 (f): "Coagulation is accounted for with the coagulation integrals in the GDE and is a relatively well understood process that can be described with reasonable confidence in models." A reference would be helpful.

p.2, line 41 (f): "Growth involves processes that are not well understood for chemically complex aerosol systems, such as the atmosphere." Reference or examples plus references would be helpful.

p.4, line 95 (f): "Our results help to inform estimates of uncertainty for complex aerosol systems, such as the atmosphere, where errors are difficult to quantify." How is this possible as the present manuscript deals with nucleation of a single molecule species which is formed at a constant rate?

p.6, line 158: "and ðİŘÿk is the particle the evaporation rate". Remove the second "the"

p.7, line 190 (ff): "We believe collision-controlled nucleation (E=0) in the absence of other particle loss mechanisms such as wall deposition (W=0) and scavenging by preexisting particles (ðİŘ£=0) provides an upper limit to errors in GRm for a constant rate system (R=constant)." The error represents a maximum overestimation of the GR. A "maximum error" would also mean that it is bigger than the maximum underestimation of the GR which may not be true. Thus this statement is too general to me.

p.7, line 199: "Most noticeably, particles grow considerably faster at early stages of simulation" Do the particles really grow faster or do they seem to grow faster? What is the reason?

p.9, line 275: "Note for the range of ðİŘ£ values examined, the presence of preexisting particles alter GRtrue/GRm values by no more than 50%." The GRtrue/GRm ratio ranges from roughly 0.35 to about 1.1 which is more than 50% (see Fig. 4b)

p.10, line 306 (f): "In practice, this means measured growth rate based on all the four representative sizes can be a reasonable substitute of the true growth rate in a similar nucleation scenario." As the possibility to underestimate the GR is not discussed, this statement does not hold true. Further, "similar nucleation scenario" is a vague statement. When would an experimental set of data be similar?

p.10. line 312: "Collision-controlled nucleation without preexisting particles results in an upper limit (up to a factor of 6) to discrepancies between true (GRtrue) and measured (e.g., GRm,mode) growth rates." It could be mentioned that this statement refers to simulated data (e.g.: Simulation showed that collision-controlled…) otherwise it is too general.

p.10, line 318 (f): "Both evaporation and preexisting particles bring GRtrue/ GRm closer to unity by decreasing the number of nucleated particles. In the case of evaporation, GRtrue/ GRm also increases as a result of elevated monomer concentration." This statement in general is not true. Evaporation and preexisting particles reduce the ratio GRtrue/GRm by reducing the overestimation caused by coagulation. In case the GR is underestimated (i.e. GRtrue/GRm < 1; caused by e.g. wall losses/dilution combined with weak particle growth) by the analysis methods, the combined effect of evaporation and preexisting particles would even increase the error.

p.10 line 324 (f): “In this case, GRm based on all representative sizes can be a good approximation of GRtrue due to negligible coagulation effects.” This statement, similar to the previous one, is too general as it considers only the possible overestimation of the GR (caused by coagulation). However, if the analysis method does not account for methods different from coagulation (e.g. dilution, wall loss, deposition), there may still be a significant difference between the measured and the “true” GR.

McMurry, P. H., & Li, C. (2017). The dynamic behavior of nucleating aerosols in constant reaction rate systems: Dimensional analysis and generic numerical solutions. Aerosol Science and Technology, 51(9), 1057-1070. doi: 10.1080/02786826.2017.1331292

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