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Referee #1

This manuscript by the CERN and Frankfurt 'CLOUD-groups' presents methods to determine
10 nucleation rates from measured particle formation rates at larger sizes. The methods presented
seem mostly valid and definitely useful but I have some serious concerns about their novelty and
how they are presented.

The paper consists basically of two parts. In the first, two simple analytical formulae are derived –
15 one for the case of small particulate scavengers, the other for scavenging dominated by wall losses.
The second part is a numerical technique that is stated as universal, i.e. should work for any
nucleation+growth+coagulation+scavenging system.

My biggest concern is related to the motivation and writing of the first part of the paper, which is
20 basically 'an attack' against the (original) Kerminen&Kulmala-equation, published in 2002. The work
on this topic by Kerminen and coworkers is actually a series of four papers, all listed as references in
the manuscript: 1. Kerminen and Kulmala (J. Aerosol Sci. 33, p. 609, 2002) 2. Lehtinen et al. (J.
Aerosol Sci. 38, p. 988, 2007) 3. Anttila et al. (J. Aerosol Sci. 41, p. 621, 2010) 4. Korhonen et al. (J.
Aerosol Sci. 69, p. 13, 2014)

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The original Kerminen and Kulmala equation is derived assuming large background particles as
scavengers (assumption 2 on page 27236 of KK, that results in the power law exponent -2 for the
sink), a size-independent growth rate and no self-coagulation. In the follow-ups this assumption was
removed and a more general equation was derived that holds for any power law dependence (2), an
30 approximate method to include self-coagulation was included (3), and analytical equations were
derived for linear and power law type size dependent growth rates (4).

Why did I repeat these here? Simply because the authors in this manuscript by Kuerten et al. have
included all of these four papers in their list of references (so they clearly know of all this work), but
35 they choose to compare their method with the oldest, original one! Furthermore, they make their
comparisons with cases for which the original KK paper was not even intended, scavenging by freshly
nucleated particles and scavenging by wall losses! Comparing to a method with a case, which even
the original authors clearly state that falls outside of their assumptions (and for which several
improvements have been made since) makes very little or no sense!!!

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The derived equations seem to be special cases of the more general ones already derived in Lehtinen
et al. (2007). Equation (12) of Kuerten et al., for the case of size-independent sink, is directly
obtained by setting $m = 0$ in equation (7) of Lehtinen et al., and, equation (19) for Kuerten et al., for
the case of wall losses by turbulence enhanced diffusion, by setting $m = -1$. (Actually this is not
45 perfectly true, since in eq. 7 of Lehtinen et al. by setting $m = -1$ one obtains 0/0. However, taking the
limit $m \rightarrow -1$ gives the 'correct' equation.). Thus, if the authors would compare their two analytical
equations with Lehtinen et al. instead of Kerminen and Kulmala, they should get identical results.

had the impressions that not all limitations – although stated in the publications – were obvious for everybody using the method. Therefore, we still feel that it is important to discuss the methods and also to formulate an expression, which can be directly applied to chamber nucleation studies.

5   In our revised manuscript section 2.1 now includes a broader overview over the series of the four papers (Kerminen and Kulmala, 2002; Lehtinen et al., 2007; Anttila et al., 2010; Korhonen et al., 2014) without deriving any of the equations. Section 2.1 only mentions the most relevant equations from Kerminen and Kulmala (2002) and Lehtinen et al. (2007), which are necessary to calculate $J(d_{p2})$ from $J(d_{p1})$, where $d_{p2} > d_{p1}$.

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The revised section 2.2 includes a relationship between $J(d_{p2})$ from $J(d_{p1})$ by taking into account two relevant loss process in chamber nucleation experiments, i.e. wall loss and dilution. We acknowledge that this relationship can also be derived from the equations presented by Lehtinen et al. (2007). However, we feel that it is important to highlight what considerations and requirements go into the previously published method and how it can be applied to chamber experiments. To our knowledge this has not been described explicitly before. While this is not a main finding of our paper, it is an important aspect that is worth explicit mentioning and brief discussion.

In summary, the first two sections of the second paragraph have been substantially revised according to the reviewers' suggestions. They will now serve as an overview for readers who are not experts regarding the Kerminen and Kulmala equation and its follow-up publications (section 2.1). The second section (2.2) formulates an easy-to-use formula for nucleation rates from chamber nucleation studies.

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The second part presents a "universal method", equation 25 on page 27244. If the method is indeed universal, it should work also for cases where self-coagulation is important. I am slightly worried that having equation (24) as a part of the derivation violates this. The justification of equation (24) is a reference to Lehtinen et al., presumably equation (3) in that paper, which states that J = GR * n. This, I believe, is true only for condensational growth, i.e. a propagating 'wave' in size space – and is incorrect when there is also self-coagulation? (In the derivation of Lehtinen et al., it is assumed that self-coagulation is negligible.) In addition, the size-discretization results in an equation (equation 25) where Nm does not depend on N_{m-1}. This seems odd, as growth is considered? Is it possible that because of this, equation (25) works better for a steady-state case and not so well for time-dependent cases?

(2a) The reviewer mentions equation (24), which was stated in the originally submitted manuscript as $J = GR*N/dd_p$. It is correct that this equation was used to describe the condensational growth by monomers (Lehtinen et al., 2007) and did not consider collisions with clusters, which can contribute to particle formation and growth if they are occurring at a substantial fraction compared to the monomer concentration.

To our knowledge no previous publication has investigated if the relationship holds also for kinetic nucleation where cluster-cluster collisions are important. However, this is a central part of the introduced method (due to changes from the first comment now introduced in section 2.3, whereas in the first submitted version it was section 2.4). Therefore, we have included a new section (section 2.4), which justifies why the assumption $J = GR*N/dd_p$ can be used also when cluster-cluster collisions are relevant. The relationship can be used if both the *GR* as well as the nucleation rate *J* are defined appropriately. In the earlier publications only growth and nucleation by monomers were considered. In this case nucleation in a certain size bin can only be due to the collision between a monomer and the cluster/particle in the next smaller bin. This means it doesn't matter whether the particle formation rate $J(d_p)$ is defined as the rate at which particles are formed at the size of d_p

exactly, or if it is defined as the rate at which particles are formed that are at or above d_p (i.e. $J(\geq d_p)$). The latter definition is useful if cluster-cluster collisions are important because in this case the collision product can "jump" into a bin, which is not just one molecule larger as it would be the case due to a monomer addition. Therefore, we are defining the particle formation rate as $J(\geq d_p)$ (see e.g. equation (13) in the revised manuscript) and also define the GR by taking into account collisions with clusters larger than the monomer (see new section 2.4, equation (16)). With these definitions it can be argued that the relationship $J(\geq d_p) = GR*N/dd_p$ also holds for situations where nucleation and growth is not completely dominated by monomer collisions. This is explained in detail in the new section 2.4 and the new Fig. 3 is used to illustrate the relevant processes.

With the addition of section 2.4 we justify why self-coagulation is taken into account in the new method. In addition, the revised version of Fig. 7 clearly demonstrates the effect of self-coagulation and it is evident that it can be adequately considered by the new method.

(2b) The second point in the previous section of the reviewers' comment refers to the question why N_m does not depend on N_{m-1} (in equation (25) in the originally submitted manuscript and equation (15) in the revised version). Additionally, the question is asked whether this can explain why the method works better for a steady-state case and not so well for the time-dependent case (referring to Fig. 6).

The fact that N_{m-1} is not included in the mentioned equation directly follows from the method and the previous equations, which we have explained in detail in section 2.4 (section 2.3 in the revised manuscript). If N_{m-1} would be included in the relevant equation the method would not work since it would contain two unknowns (N_m as well as N_{m-1}). This would make the reconstruction impossible and the essential idea is to go step by step from one size to the next smaller.

As shown in Fig. 6 the method works quite well also for the time-dependent data. In the revised version we show the reconstructed particle formation rate $J(d_{p1})$ for two different times: (1) the time at which the reconstruction is carried out from the size distribution $\geq d_{p2}$ (solid red line in Fig. 6), and (2) the time at which the particles have/had a size of d_{p1} (dash-dotted red line in Fig. 6).

Minor comments:

a) Page 27234, line 19: The definition of critical size is slightly inaccurate. It is the smallest size at which GR is on average faster than ER. Individual particles can have GR > ER even at below the critical size – otherwise nucleation would not be possible?

We have changed this. The sentence now reads as

"The critical size is the smallest size at which the growth rate of a particle is on average faster than its evaporation rate."

b) Page 27234, line 25: The reference to Kuerten et al when talking about barrierless particle formation should be replaced or supported by more original work, e.g. McMurry.

We have included the reference to McMurry (1980) at the end of this sentence.

c) Page 27235, line 4: Which diameter is the stated detection limit of 1.2 nm?

The mentioned size is referring to the mobility diameter. This is also made clear in the revised manuscript:

"However, the detection limit of newly-developed CPCs is as small as 1.2 nm in particle mobility diameter (Sgro and Fernández de la Mora, 2004; Iida et al., 2009; Vanhanen et al., 2011; Kuang et al., 2012a; Wimmer et al., 2013)."

d) Page 27236, line 20: The main reason for the 'failure' of KK when applied to chamber studies is the fact that it was not originally even designed for such cases, i.e. assumption (1).

In the context of the very first major comment made by the reviewer we have rewritten section 2.1 and removed that statement. It should now be clear that KK was not designed for chamber studies.

e) Page 27245, line 11. This "method of Lovejoy" has been used much earlier widely in the nanomaterials synthesis community, see e.g. paper by Landgrebe and Pratsinis (1990), 'A discrete sectional model for powder production by gas-phase chemical reaction and aerosol coagulation in the free molecular regime.', J. Colloid Interface Sci. 139, 63-86.

We have included the reference to Landgrebe and Pratsinis (1990) to acknowledge the earlier work that has been done regarding the modeling of coagulating particles.

f) Page 27245, line 15. What are the loss terms in the simulation (figure 4)? Is self coagulation important in this simulation, at any stage? If a case such as in figure 4 (as an experimental steady state size distribution) would be analyzed, how would one obtain the growth rate as a function of size from the data, which is needed for the analysis?

All loss terms are included when calculating the reconstructed size distribution, i.e. wall loss, dilution and coagulation including self-coagulation. From the new Fig. 7 it can be identified to what extent self-coagulation (coagulation between particles with mobility diameters from d_{p1} = 1.7 to d_{p2} = 3.2 nm) contributes to the losses for the conditions of Fig. 4 (see dashed black line in comparison to the red and green solid lines for the kinetic limit case at 6×10^6 cm^{-3} of sulfuric acid).

The growth rate for reconstructing the size distribution is obtained from equation (24) in the revised manuscript. Whereas in the originally submitted manuscript we did also simulate cases where a size-dependent GR was used (i.e. the GRs were calculated according to equation (24) for all indices between d_{p2} and d_{p1}), this has not been done anymore in the revised version. The reason for dropping this calculation is that it is unrealistic that this information is available if the size distribution is only known for sizes above d_{p2}. Therefore, the GR is calculated only once from the known size distribution according to equation (24) and this constant GR is then used throughout the whole reconstruction.

In the revised sections 2.3 and 2.4 it is now explained in more detail how the growth rate is obtained and how it is being used in the method.

g) Page 27247, line 8 (and figures 5 and 6): How is the "accurate" formation rate obtained, especially if self-coagulation is important?

The model described in section 2.5 calculates the time-dependent concentrations of clusters and particles. From this information the formation rates at and above a certain size bin can be obtained. There are two ways of doing this:

(I) From the production by looking at all possibilities how two smaller clusters (index i and j) can form a cluster, which is equal or larger than a selected size (here index $m+1$):

$$J_{\geq m+1} = 0.5 \cdot \sum_{i+j \geq m+1} \delta_{ij} \cdot K_{i,j} \cdot N_i \cdot N_j,$$

where both i and j have to be smaller than $m+1$.

(II) From the losses by using equation (11, referring to the revised manuscript):

$$J_{\geq m+1} = \frac{dN_{\geq m+1}}{dt} + \sum_{i=m+1}^{n+m} \left(k_{w,i} \cdot N_i \right) + k_{dil} \cdot N_t + \sum_{i=m+1}^{n+m} \left(\sum_{j=i}^{n+m} \delta_{i,j} \cdot K_{i,j} \cdot N_j \cdot N_i \right).$$

Both methods are implemented in the model and yield exactly the same result, which provides some verification of the model.

The calculated formation rates include by definition self-coagulation as all possible cluster collisions are included. The Js obtained in this way serve as the reference to which the reconstructed formation rates can be compared to.

The following text has been added to section 2.5 in the revised manuscript to explain this:

"Particle formation rates that have been calculated from the model serve as the reference formation rates to which the reconstructed formation rates can be compared to. We have implemented two separate procedures to calculate the NPF rates, where the first one is following the approach based on equation (11) by taking into account all loss processes, while the second one follows the production of particles from two smaller clusters (equation (20)). The two methods yield exactly the same result, which is a good verification of the model in this respect."

Additional changes

In addition to the points discussed above a few more modifications have been made to the manuscript, which are listed in the following:

(i) In the originally submitted manuscript, equation (24) was not showing the correct indices. The index on the LHS of the equation needs to be larger by one compared to the ones on the RHS since the formation rate is described from the flux of particles from the previous size bin. This has been considered in the revised version (equation (14) in section 2.3) and the subsequent equations have also been updated (equation (15)).

(ii) As part of rewriting section 2.1 and 2.2 we have removed the old Fig. 2. We feel that it is not necessary anymore to show this figure since it should be clear from the discussion that the different loss mechanisms lead to different correction factors between $J(d_{p1})$ and $J(d_{p2})$. Instead, we have added the dilution loss rate to the lower panel of Fig. 1 since this loss mechanism is now described in a bit more detail in the revised section 2.2 (see also equation (10)).

(iii) We have extended the range of the linear size bins in the model (section 2.5 and see also Fig. 4) to 100. With the reported density and molecular weight the maximum upper diameter covered by the linear size bins is now ~3.1 nm in geometric size and therefore covers both d_{p1} and d_{p2}. In the originally submitted manuscript the linear size bins ranged only up to ~2.1 nm in geometric diameter, which lead to a transition between geometric and linear bins during the reconstruction going from d_{p2} to d_{p1}. Using linear size bins throughout the relevant size range makes some formulations easier, e.g. equation (19), which includes the growth rate due to monomer and cluster collisions. The results from the reconstruction are not affected in any significant way due to this modification, however, the formulation of the equations become easier. In the same context, the index corresponding to d_{p1} has been changed from "1" to "x". Due to this change in the notation the index "1" now belongs to the bin containing only one molecule (or better a single building block for all larger clusters and particles). Based on this new definition Fig. 2 (previously Fig. 3) has also been updated.

(iv) As mentioned before the new Fig. 3 illustrates why equation (21, revised manuscript) is a good approximation also for the cases when cluster-cluster collisions are important. We feel that this is an important figure as it visualizes the complex equation (21) in an easy way.

(v) Section 3.3 (and Fig. 7) have been extended in a way that not just kinetic nucleation is used to demonstrate the capabilities of the new method. We have also included three more scenarios where we have allowed for non-zero dimer and trimer evaporation rates. In order to achieve this, the model described in section 2.5 was adjusted to include the relevant cluster evaporation rates. The results now shown in addition to the kinetic simulation in Fig. 7 demonstrate quite interesting aspects, which are relevant for chamber nucleation studies such as CLOUD where different chemical systems are tested, which can behave significantly different than kinetic nucleation.

(vi) Based on the comment by Hanna Vehkamäki we have not termed our new method "universal" anymore. However, based on the new results described above (point (v)) we have evidence that the method can be used for many different conditions. The effects of particle evaporation in the size range between d_{p1} and d_{p2} remains to be studied. Nevertheless, we want to mention that the effect of evaporation on the relatively large clusters/particles at 1.7 nm is probably small for most chemical systems relevant to the atmosphere. In addition, the study by Nieminen et al. (2010) has also neglected the effect of evaporation on the growth rates and the theory is widely used in describing aerosol growth.

(vii) Based on the implemented changes a couple of additional references have been added, which are listed in the following

New references

Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., Zhao, J., and McMurry, P. H.: Acid–base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, Proc. Natl. Acad. Sci. USA, 109, doi/10.1073/pnas.1210285109, 18713–18718, 2012.

Ehrhart, S., and Curtius, J.: Influence of aerosol lifetime on the interpretation of nucleation experiments with respect to the first nucleation theorem, Atmos. Chem. Phys., 13, 11465–11471, 2013.

Hanson, D. R., and Lovejoy, E. R.: Measurement of the Thermodynamics of the Hydrated Dimer and Trimer of Sulfuric Acid, J. Phys. Chem. A, 110, 9525–9528, 2006.

Kerminen, V.-M., Anttila, T., Lehtinen, K., and Kulmala, M.: Parameterization for Atmospheric New-Particle Formation: Application to a System Involving Sulfuric Acid and Condensable Water-Soluble Organic Vapors, Aerosol Sci. Technol., 38, 1001–1008, 2004.

5   Ku, B. K., and Fernandez de la Mora, J.: Relation between Electrical Mobility, Mass, and Size for Nanodrops 1–6.5 nm in Diameter in Air, Aerosol Sci. Technol., 43, 241–249, 2009.

Landgrebe, J. D., and Pratsinis, S. E.: A discrete-sectional model for particulate production by gas-phase chemical reaction and aerosol coagulation in the free-molecular regime, J. Colloid Interface
10 Sci., 139, 63–86, 1990.

Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, Atmos. Chem. Phys., 10, 9773–9779, 2010.

15 Olenius, T., Riipinen, I., Lehtipalo, K., and Vehkamäki, H.: Growth rates of atmospheric molecular clusters based on appearance times and collision–evaporation fluxes: Growth by monomers, J. Aerosol Sci., 78, 55–70, 2014.