

We thank the reviewer for carefully reading our manuscript and for providing constructive comments, which have improved the quality and clarity of our manuscript. The reviewers' comments are repeated in full below, with our replies indicated after each comment in blue font. Text which has been added to the manuscript is shown in red font.

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Referee #1

10 This manuscript by the CERN and Frankfurt 'CLOUD-groups' presents methods to determine 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.

15 The paper consists basically of two parts. In the first, two simple analytical formulae are derived – 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.

20 My biggest concern is related to the motivation and writing of the first part of the paper, which is 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 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).

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35 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 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 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.

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50 (1) We agree with the reviewer that our previous version of the first subsections of section 2 needed to be revised. We did not want to convey the impression of an attack against the Kerminen and Kulmala method and its subsequent publications (Lehtinen et al., 2007; Anttila et al., 2010; Korhonen et al., 2014). The method works very well for atmospheric conditions. However, from discussions we

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 $d_{p2} > d_{p1}$.

10 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.

15 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.

25 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 N_m 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?

35 (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.

40 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:

5 “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).”

10 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.

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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.

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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.

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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?

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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 $6 \times 10^6 \text{ cm}^{-3}$ of sulfuric acid).

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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 GR s 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.

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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.

50 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:

- 5 (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 $m+1$.

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

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

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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 J_s obtained in this way serve as the reference to which the reconstructed formation rates can be compared to.

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

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“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.”

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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:

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(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)).

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(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)).

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(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 Sci.*, 139, 63–86, 1990.
- 10 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.

We thank Veli-Matti Kerminen for carefully reading our manuscript and for providing constructive comments, which have improved the quality and clarity of our manuscript. His comments are repeated in full below, with our replies indicated after each comment in blue font. Text which has been added to the manuscript is shown in red font.

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V.-M. Kerminen

10 This manuscript presents an analysis on how nucleation rates should be derived from experimental particle formation rates, including those obtained from chamber experiments. Noting the increasingly important role of chamber experiments in studies of new-particle formation and growth, the topic of this paper is definitely a very important one.

15 The manuscript brings up an essential, yet not surprising, result: aerosol dynamics in an environmental chamber can be very different from that in the ambient atmosphere. Related to this, the authors 1) first demonstrate that the original method by KK2002 in deriving nucleation rates from measured particle formation rates is not applicable to chamber experiments, and 2) then introduce a revised method which is generally applicable to such experiments. I very much welcome the point 2. I also think that it is valuable to discuss the limitations of earlier approaches (point 1),
20 but such a discussion should be done in a correct way. I mainly agree with comments by the first anonymous reviewer. In addition to that, I have a few issues of my own for the authors to consider before recommending acceptance of this paper for publication.

25 The authors (K2014) spend two subsections (2.1 and 2.2 in K2014) to demonstrate why the KK2002 method does not perform well with typical chamber experiments. At the end of page 27236 (lines 19-21) and also on page 2740 (lines 2-4), K2014 give readers the impression that the failure of KK2002 method in chamber experiments is due to some other reason than violation against the assumptions 1-3 (see line 10 on page 27236) which were stated very clearly in the original manuscript by KK2002. This is not correct. K2014 shows that in chamber experiments, the main sink for small nucleated
30 clusters is either chamber walls or small (<10 nm) nuclei formed earlier during the experiment. A large chamber wall sink clearly violates the assumption 1, while a large sink by small nuclei violates either the assumption 1 or assumption 3 depending on how “pre-existing larger particles” are being defined (admittedly, this definition was a bit loose in KK2002). Most atmospheric aerosol scientists would not call 3-10 nm particles as “larger pre-existing particles”, in which case the large sink by such
35 particles would violate the assumption 1. K2014 tends to categorize these 3-10 nm particles as part of the sub-population of “larger pre-existing particles”. In this interpretation, the large sink caused by such particles violates the assumptions 3, since this subpopulation undergoes major changes during the experiment. In summary: KK2002 fails in chamber experiments because the conditions in such experiments violate the very clearly-stated assumptions in the original paper by KK2002. This is
40 definitely a valuable point to bring up in K2014, even though essentially the same information is already available in KK2002. At least some revisions of the in subsection 2.1 and 2.2 are necessary based on the arguments above.

45 (1) We have modified the first two sub-sections of section 2 substantially based on the criticism made by the reviewer. Since the first anonymous reviewer had very similar comments regarding the first part of the manuscript the following text is a copy of the reply given to reviewer #1:

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.,
50 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 $d_{p2} > d_{p1}$.

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).
5 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.

10 In summary, the first two sections of the second paragraph have been substantially revised according to Veli-Matti Kerminens' 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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K2014 introduces a new method to derive nucleation rates from measured particle formation rates which works for chamber experiments. Very good, in principle! However, I am not confident that the new method can be called universal. The method takes into account the influence of self-coagulation on the nuclei number concentration (the term $j=m$ in the r.h.s of Eq. 25), but does it take into account the influence of self-coagulation on the nuclei growth rate (Eq. 4)? The times scales over which nuclei self coagulation affects their number concentration and growth are so similar that these two processes become important under roughly the same conditions.

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25 (2) Based on the comment by Hanna Vehkamäki we have removed the word "universal" in the context of the new method. However, Hanna Vehkamäki had different reasons for requesting to remove this term.

30 In the context of the comment above, the question is addressed whether self-coagulation is taken into account not only in terms of the nuclei concentration but also regarding the nuclei growth rate.

While it was maybe not that obvious from our originally submitted manuscript that both effects are taken into account the revised version now sheds more light on this question (see also reply to comment (2) by reviewer #1). The central point is how the particle formation rate and the growth rate are defined. If they are defined in an appropriate way the relationship $J = GR * N / dd_p$ also holds when cluster-cluster collisions become important. Section 2.4 in the revised manuscript deals with the question if the relationship between J and GR is valid in such cases. Based on our arguments in this section (visualized in the new Fig. 3) we can conclude that the effect of self-coagulation on the GR is adequately taken into account by our method. The growth rate used in the reconstruction method is based on the definition in equation (24). The formation rate $J_{\geq m+2}$ in that equation is taking into account not only the contribution from monomer additions to the clusters in the next smaller size bin ($m+1$). Since all particles equal or larger than $m+2$ are considered also all cluster collisions contributing to the GR on the LHS of the equation are considered. Therefore, a method is presented, which takes into account self-coagulation both in terms of the nuclei number concentration as well as the growth rate.

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Furthermore, is it possible that J_m in Eq. 4 is independent of the nuclei number concentration in the previous size bin ($m-1$)?

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(3) The formation rate J_m is definitely affected by the number concentration J_{m-1} in the next smaller size bin. However, the formation rate can be calculated in two different ways (see also reply to comment g) by reviewer #1):

- 5 (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 $m+1$.

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

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

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We have verified with our numerical model that both ways of calculating J yield exactly the same result. Using only experimental data method (I) does not work because it would require knowledge on the concentrations of all clusters smaller than d_{p2} . Therefore, method (II) needs to be used, which obtains the formation rate from the losses of clusters/particles, which all have sizes equal or larger than d_{p2} (index $m+1$). Together with equation (14, referring to the revised manuscript) the method can be used to calculate N_m as a function of the larger clusters/particles. From the method it follows directly that N_{m-1} is not required to obtain N_m . If this would be the case the method would not work since equation (15) would need to be solved for two unknowns.

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25 One more related issue: the approach used in the new method is not entirely original either. Already K2004 (Aerosol Sci. Technol. 38, p. 1001-1008, equations 7 and 8 and the text) introduces the idea of adding extra bins below the size m shown in Fig. 3 by K2012, and then corrects the apparent particle formation rate when calculating toward the initial nucleation diameter. Of course, K2014 goes beyond K2004 in that K2004 does not take into account the effect of self-coagulation.

- 30 (4) We have added a reference to K2004 in section 2.3 of the revised manuscript:

“Also Kerminen et al. (2004) introduced extra size bins in order to increase the accuracy of their analytical formula, which connects the nucleation rate and a formation rate at a larger size similar to equation (2).”

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Other issues:

40 Since there are several pieces of work on the issue addressed in this work between K2014 and the original paper by K2002, and since most of the readers probably will not go through all the details in sections 2 and 3, I would recommend adding a brief review of the conducted work made after K2002 into the last paragraph of section 1.

45 We have added a sentence in the introduction, which briefly describes the effects that have been considered following KK2002:

“Several publications followed Kerminen and Kulmala (2002) to include additional effects, like a better description of the coagulation sink from particle size distribution measurements (Lehtinen et al., 2007), self-coagulation (Anttila et al., 2010), and a size-dependent growth rate (Korhonen et al., 2014).”

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In section 4, the authors should more explicitly bring up the limitations of the new method in determining the original nucleation rate. First, none of the methods developed so far, including the one introduced here, cannot reproduce a correct nucleation rate unless the size-dependent nuclei growth rate is known down to the size where the nucleation occurs (d_{nuc}). This is a major problem because this information is almost never available and when it is, even small uncertainties in it cause large errors (see Figure 7 by K2014 as well as in earlier works on this topic). Second, we do not really know which value of d_{nuc} to apply when estimating the nucleation rate. This definitely affects the result as well. Third, does the new method really work when self-coagulation becomes important?

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This is a very good suggestion and we have included a short discussion to section 4 addressing these issues (see added text below). (1) We agree that the size-dependency of the growth rate can be a crucial point and that it can introduce large errors especially when the GR is small and the losses are high or when there is a pronounced size-dependency. However, this is a problem all other methods have to deal with as well. Nevertheless, we will highlight in section 4 that this can be a crucial point. (2) It is correct that the critical size (d_{nuc}) is generally not known and that it is therefore not easy to choose the right d_{p1} in any method reporting nucleation rates. For this reason the CLOUD experiment has chosen a reference size of 1.7 nm in mobility diameter, which should be at or close to the critical size for most chemical systems. Regarding our manuscript we will briefly mention this challenge in section 4. (3) We believe that self-coagulation is taken into account adequately in our method both in terms of the nuclei number concentration and growth rate (see previous reply (2)).

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“One general issue with all methods, which are extrapolating formation rates towards smaller sizes, arises from the uncertainty in the growth rate. In most cases no measurement of the GR will be available down to the very small size since also the particle number concentrations are not available (otherwise no extrapolation of the formation rate would be necessary). A small size-dependency of the GR that is not taken into account can therefore lead to a big uncertainty. In addition, the critical size of the nucleating particles is generally not known. Ideally, one would choose d_{p1} to correspond with the critical size. However, since this is not possible a reasonable solution to this issue is to choose a size for d_{p1} , which is safely at or above the critical size to avoid extending the size distribution into the subcritical size regime. For this reason the CLOUD experiment has reported particle formation rates at a size of 1.7 nm in mobility diameter rather than nucleation rates (Kirkby et al., 2011).”

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40 **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:

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(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)).

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(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)).

5 (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
10 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
15 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
20 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
25 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
35 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
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New references

45 [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.](#)

50 [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.
- 5 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.
- 10 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 Sci.*, 139, 63–86, 1990.
- 15 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.
- 20 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.

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5 Kürten et al. discuss the challenges involved in extrapolating observed particle formation rates down to sizes that are below the instrumental detection limit, especially down to a "critical size where nucleation occurs" (page 2734, lines 2–3). While the topic of the manuscript is important for understanding particle formation processes, there seems to be a major confusion in the kinetic definition of the thermodynamic critical size.

10 In the beginning of the Introduction it is stated that "the critical size is the smallest size at which the growth rate of a particle is faster than its evaporation rate" (page 27234, lines 19–20). If the growth rate is understood as the collision rate, this is indeed correct for a one-component system with a smooth ΔG -curve that exhibits a single local maximum: the collision and evaporation frequencies coincide at the critical size, and above it the collision frequency exceeds the evaporation frequency. However, there is no reason to assume that there would be no evaporation above the critical size, or
15 even that evaporation would be negligible.

In the extrapolation method presented in the manuscript "the underlying assumption is that growth above this size is purely kinetic (no evaporation), which is fulfilled due to the assumption that d_{p1} is above the critical size" (page 27244, lines 6–8). This reasoning is in general not valid – on the
20 contrary, even the widely used liquid drop model gives non-zero evaporation rates for all sizes. Figure 1 shows an example for water. The collision frequencies (collision rate constant \times monomer concentration) are calculated from kinetic gas theory assuming spherical clusters, and the evaporation rates are computed from Gibbs free energies of formation using the detailed balance condition. The cluster formation energies are calculated according to classical nucleation theory. The
25 temperature is 25.0 °C, and the density, surface tension and saturation vapor pressure of water are set to $\rho = 997.0 \text{ kg/m}^3$, $\sigma = 71.68 \times 10^{-3} \text{ N/m}$ and $p_{\text{sat}} = 3.169 \times 10^3 \text{ Pa}$, respectively.

While the possibility of particle evaporation is brought up in the manuscript, the authors do not suggest how the evaporation processes would be taken into account in the extrapolation. They also
30 do not even attempt to show whether their extrapolation method gives reasonable results for cases where clusters evaporate. As long as the effect of evaporation is not taken properly into account, the method cannot be called universal.

35 We thank Hanna Vehkamäki for commenting on our manuscript. We agree, that the introduced method does not include the effect of evaporation on the clusters/particles with sizes between d_{p1} (size where the formation rate should be extrapolated to) and d_{p2} (size above which the size distribution is known). Therefore, we accept to drop the term "universal". Originally, we have used this term to express that the method can be used for any environment (ambient, chamber, or flow
40 tube) as long as the loss processes are well characterized. Since the method takes into account the effect of self-coagulation it has an additional benefit compared to other methods. However, it is true that for more general cases evaporation can be an important effect, as demonstrated by the figure provided by Hanna Vehkamäki (Fig. 1). Nevertheless, the homogenous nucleation of water vapor is not representative for tropospheric new particle formation because of the very high vapor pressure
45 of water. When applied to chemical systems, which are more relevant for the atmosphere, the particle formation rates measured at the CLOUD chamber have been reported at a particle mobility diameter of 1.7 nm. Several chemical systems have been investigated, i.e the system of sulfuric acid and water as well as sulfuric acid, water and ammonia (Kirkby et al., 2011), the ternary system of sulfuric acid, water and dimethylamine (Almeida et al., 2013) and the system involving sulfuric acid and oxidation products from α -pinene (Riccobono et al., 2014). In none of these systems significant
50 evaporation of particles above a size of 1.7 nm has been observed at the reported temperatures. Furthermore, the studies that are based on KK2002 do also neglect evaporation (Kerminen and

Kulmala, 2002; Lehtinen et al., 2007; Anttila et al., 2010; Korhonen et al., 2014). For most conditions relevant to the atmosphere evaporation for clusters with $d_p > d_{p1}$ is therefore expected to have only a small effect. However, we agree that the method should not be called “universal” anymore and have consequently removed these statements from the manuscript. In addition, we have included the following sentence at the end of section 2.3 in order to raise awareness about the possible effect of evaporation:

“However, in future studies one could examine the effect of evaporation at sizes larger than the critical diameter on the method and attempt to implement it in a similar fashion as Olenius et al. (2014) in their study about the effect of monomer collisions on the growth rates.”

Added reference:

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.

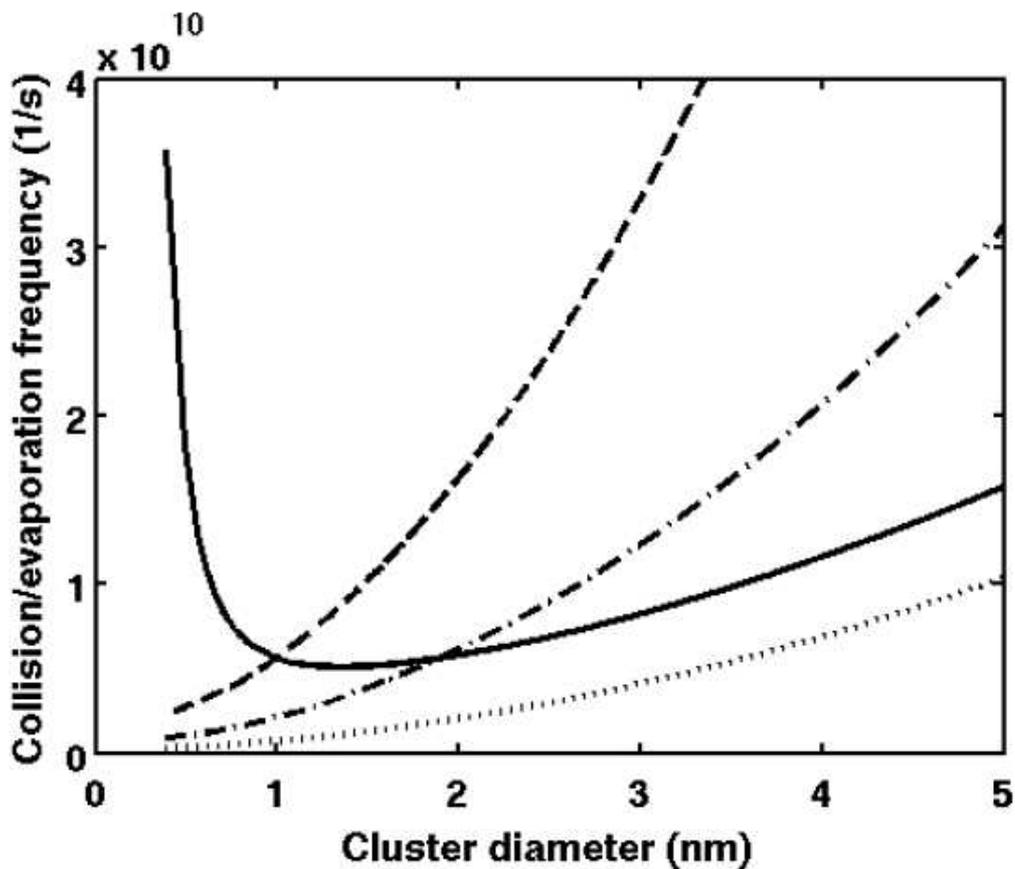


Fig. 1. Collision frequencies of water molecules with water clusters at saturation ratios $S=1$ (dotted), $S=3$ (dash-dotted) and $S=8$ (dashed), and evaporation frequencies as a function of cluster diameter.