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# On the derivation of particle nucleation rates from experimental formation rates

A. Kürten<sup>1</sup>, C. Williamson<sup>1</sup>, J. Almeida<sup>2</sup>, J. Kirkby<sup>1,2</sup>, and J. Curtius<sup>1</sup>

<sup>1</sup>Institute for Atmospheric and Environmental Sciences, Goethe University of Frankfurt, Frankfurt, Germany

<sup>2</sup>CERN, Geneva, Switzerland

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Correspondence to: A. Kürten (kuerten@iau.uni-frankfurt.de)

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## Abstract

Atmospheric particle formation rates are usually measured at sizes larger than the critical size where nucleation occurs. Due to loss of particles during their growth to the detection threshold, the measured formation rate is often substantially smaller than the nucleation rate. For this reason a correction needs to be applied in order to determine the nucleation rate from the measured formation rate. An analytical formula for the correction factor is provided by Kerminen and Kulmala (2002). Their method was derived for atmospheric nucleation measurements and we show here that it has limited applicability to chamber nucleation studies. The reason for this limitation is that the particle loss rate generally has a different dependency on particle size in other environments. Here we propose an alternative, numerical method that allows precise nucleation rates to be determined in arbitrary experimental environments. The method requires knowledge of the particle size distribution above detection threshold, the particle growth rate, and the particle loss rates as a function of particle size.

## 1 Introduction

Aerosol nucleation, or new particle formation (NPF), is an important phenomenon taking place throughout the Earth's atmosphere (Kulmala et al., 2004). The key parameter of interest is the nucleation rate, which is defined as the formation rate ( $\text{cm}^{-3} \text{s}^{-1}$ ) of new particles at the critical size. The critical size is the smallest size at which the growth rate of a particle is faster than its evaporation rate. This size depends mainly on the concentrations and other properties of the nucleating vapors, as well as on temperature. However, it is generally agreed that the critical size is somewhere below 2 nm mobility diameter under atmospheric conditions (Kulmala et al., 2013). In fact it can be as small as two molecules in the case of barrierless, kinetically-limited particle formation, where the dimer is already stable against evaporation (Kürten et al., 2014).

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Until recently the smallest mobility diameter that could be measured by a condensation particle counter (CPC) was 2.5 to 3 nm – which is substantially larger than the critical size. However, the detection limit of newly-developed CPCs is as small as 1.2 nm (Sgro and Fernández de la Mora, 2004; Iida et al., 2009; Vanhanen et al., 2011; Kuang et al., 2012a; Wimmer et al., 2013). Nevertheless, despite this progress the most widely-used CPCs have detection thresholds at 2.5 nm or above. Moreover, care is needed when interpreting data from the newly-developed CPCs since they can be sensitive to the chemical composition of the particles (Kangasluoma et al., 2014). Furthermore, CPC cut-off curves do not have the shape of a step function. Instead, detection of particles below the cut-off size (usually defined as the size  $d_{50}$ , where 50 % of the particles are detected) is occurring to some extent and, if this includes clusters below the critical size, the accuracy of the derived nucleation rates can be strongly affected. For this reason, under certain conditions, it can still be more reliable to use a conventional CPC with a nominal cut-off around 3 nm for determining NPF rates. On the other hand, in order to minimize the corrections, it is advantageous to measure the formation rates as close as possible to the critical size.

Kerminen and Kulmala (2002) have derived an analytical formula for correcting experimental particle formation rates to determine nucleation rates at a given critical size (abbreviated as the KK method in the following). This method was developed for atmospheric nucleation measurements and a similar formula was also used by the McMurry group (Weber et al., 1997; McMurry et al., 2005). In addition to atmospheric measurements, nucleation studies in aerosol chambers or flow reactors have tremendously helped the understanding of aerosol nucleation. Such experiments require an accurate method to derive the NPF rates. In this study the applicability of the KK method to chamber experiments such as CLOUD (Cosmics Leaving Outdoor Droplets) at CERN will be examined (Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014). It is shown that KK has limited applicability for chamber nucleation studies, and an alternative method is needed. We therefore present here a new method that yields accurate results for any environment – be they chamber or atmospheric data – provided the

particle size distribution above a certain threshold size is known, as well as the particle growth rate, and where all loss processes are quantified as a function of size. The new method is verified with the results from a kinetic aerosol model.

## 2 Methods

### 2.1 Review of the KK method

KK make the following assumptions in deriving their formulae (Kerminen and Kulmala, 2002):

1. the only important sink for new particles is their coagulation with larger pre-existing particles,
2. the new particles grow at a constant rate, and
3. the population of pre-existing particles remains unchanged during the new particle growth.

We will assume for now that assumption 2 is fulfilled, although the particle growth rate could be a function of size (Kuang et al., 2012b; Kulmala et al., 2013). Section 3.1 will deal with this question. Assumption 1 is generally true for the atmosphere, for which KK was derived. However, for chamber experiments, the losses due to walls and dilution are not equivalent and, as we shall see later, this introduces considerable inaccuracies. Assumption 3 is not fulfilled since self-coagulation can become important when formation rates are large (see also Anttila et al., 2010). However, the main reason for the failure of KK when applied to chamber studies is not assumption 3 but rather an approximation made that is only valid under certain conditions (see below).

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Let's start by deriving the KK formulae according to their paper. Assumption 1 can be written as:

$$\frac{dN(d_p)}{dt} = -N(d_p) \cdot \sum_j K(d_p, d_j) \cdot N_j \quad (1)$$

5 which means that the change in particle concentration  $N$  at particle size  $d_p$  can be described by the coagulation with larger particles in the size bins  $j$ , where  $K$  is the collision rate between particles of size  $d_p$  and  $d_j$ , and  $N_j$  is the concentration of particles in size bin  $j$ . Equation (1) can also be written as

$$\frac{dN(d_p)}{dt} = \frac{dN(d_p)}{dd_p} \cdot \frac{dd_p}{dt} \quad (2)$$

10 where  $dd_p/dt$  is the growth rate (GR), which is constant according to assumption 2. Therefore Eq. (1) becomes

$$\frac{dN(d_p)}{dd_p} = -\frac{N(d_p)}{GR} \cdot \sum_j K(d_p, d_j) \cdot N_j \quad (3)$$

15 Rearranging yields:

$$\frac{dN(d_p)}{N(d_p)} = -\frac{1}{GR} \cdot \sum_j K(d_p, d_j) \cdot N_j \cdot dd_p \quad (4)$$

20 The left-hand side (LHS) can be integrated from  $N(d_{p1})$  to  $N(d_{p2})$  (e.g. mobility diameters of  $d_{p1} = 1.7$  nm and  $d_{p2} = 3.2$  nm). However, the dependency of the collision rate  $K$  on  $d_p$ , on the right-hand side (RHS) of the equation, cannot be analytically integrated. Therefore, KK made the following assumption (this is actually the important approximation) that

$$K(d_p, d_j) \cdot d_p^2 = K(d_0, d_j) \cdot d_0^2 \quad (5)$$

and chose  $d_0 = 1$  nm. This last equation assumes that the collision rate decreases with particle size to the second power. Making this assumption Eq. (4) can be written as

$$\frac{dN(d_p)}{N(d_p)} = -\frac{1}{GR} \cdot \frac{d_0^2}{d_p^2} \cdot \sum_j K(d_0, d_j) \cdot N_j \cdot dd_p \quad (6)$$

5 and the RHS can now be analytically integrated from  $d_{p1}$  to  $d_{p2}$ :

$$\ln \left( \frac{N(d_{p2})}{N(d_{p1})} \right) = \frac{d_0^2}{GR} \cdot \sum_j K(d_0, d_j) \cdot N_j \cdot \left( \frac{1}{d_{p2}} - \frac{1}{d_{p1}} \right). \quad (7)$$

Rearranging and solving for  $N(d_{p1})$  yields:

$$N(d_{p1}) = N(d_{p2}) \cdot \exp \left( \frac{d_0^2}{GR} \cdot \sum_j K(d_0, d_j) \cdot N_j \cdot \left( \frac{1}{d_{p1}} - \frac{1}{d_{p2}} \right) \right) \quad (8)$$

10 or

$$N(d_{p1}) = N(d_{p2}) \cdot \exp \left( \frac{CS}{GR} \cdot d_0^2 \cdot \left( \frac{1}{d_{p1}} - \frac{1}{d_{p2}} \right) \right) \quad (9)$$

where

$$15 \quad CS = \sum_j K(1 \text{ nm}, d_j) \cdot N_j \quad (10)$$

is the condensation sink for 1 nm particles. The formation rates  $J$  can be obtained from the time-derivative of the particle number concentrations in Eq. (9). Although KK report a slightly different notation of Eq. (9), it is equivalent to their formulation.

## 2.2 Limitations of the KK method to chamber nucleation experiments

KK derived their formula for atmospheric data, where the coagulation sink is usually due to a pool of pre-existing particles with sizes around 100 nm. Figure 1 shows the calculated collision rates as a function of particle size, assuming that the size of the second particle is fixed. It is evident that Eq. (5) is a reasonable first approximation although the exponent is nearer  $-1.5$  than  $-2$  (solid black line). Realizing this, there has been a follow-up paper by Lehtinen et al. (2007) which deals with introducing the real power dependency derived from atmospheric size distribution measurements. The reported magnitude of the power dependency for pre-existing particles in the atmosphere is steeper than  $-1.5$ , in their examples.

In the case of a seedless nucleation experiment in a chamber, the particle spectra generally lie between 2 and 10 nm, because only freshly nucleated particles are involved. The collision rates for these smaller-sized particles are only weakly dependent on size (Fig. 1, colored lines, see also Seinfeld and Pandis, 2006). Therefore

$$K(d_p, d_j) = K(d_0, d_j) \quad (11)$$

should replace Eq. (5) in cases where all particle sizes are below about 5 nm. Using Eq. (11) leads to the following modified form for Eq. (9):

$$N(d_{p1}) = N(d_{p2}) \cdot \exp\left(\frac{CS}{GR} \cdot (d_{p2} - d_{p1})\right). \quad (12)$$

The correction factors from Eq. (9) (dotted red line) and Eq. (12) (dashed-dotted blue line) are shown in Fig. 2. The curves correspond to  $d_{p1} = 1.7$  nm and  $d_{p2} = 3.2$  nm (mobility diameters) because these are used in the CLOUD experiment (Kirkby et al., 2011; Almeida et al., 2013; Riccobono et al., 2014). The factor  $CS/GR$  ranges from 0.1 to  $10 \text{ nm}^{-1}$ . A typical value for  $CS/GR$  in a chamber experiment is around  $1 \text{ nm}^{-1}$ , e.g.  $CS = 0.001 \text{ s}^{-1}$  and  $GR = 3.6 \text{ nm h}^{-1}$  ( $= 0.001 \text{ nm s}^{-1}$ ). The size-independent collision rate yields a correction factor that is a factor 3.4 times that of the originally-published

KK method. The discrepancy between the two different formulations increases rapidly at higher CS/GR values. In summary, the KK method fails when applied to chamber nucleation experiments without seed aerosol because it assumes the collision rate varies as  $\sim d_p^{-2}$ , which is not valid.

### 2.3 Comparison of losses to walls and to pre-existing particles

The dominant particle loss mechanism for seedless chamber nucleation experiments is generally due to collisions with the walls of the vessel. Large (3 m) chambers such as CLOUD have wall loss rates (around  $0.001 \text{ s}^{-1}$  at 1 nm) similar to the loss rates onto pre-existing aerosols in a pristine atmospheric environment. We will address here to what extent these two environments are equivalent. The coagulation loss term in Eq. (1) can be replaced by the wall loss rate  $k_w$ :

$$\frac{dN(d_p)}{dt} = -N(d_p) \cdot k_w(d_p). \quad (13)$$

The wall loss rate in chamber experiments can be expressed by (Crump and Seinfeld, 1981; Metzger et al., 2010):

$$k_w(d_p) = C \cdot \sqrt{D(d_p)} \quad (14)$$

where  $D(d_p)$  is the diffusivity of a particle with size  $d_p$  and  $C$  is an empirical factor that depends on the chamber dimensions and turbulent mixing. The diffusivity of a particle can be calculated from the Stokes–Einstein relationship according to (Hinds, 1999)

$$D(d_p) = \frac{k_B \cdot T \cdot C_C}{3 \cdot \pi \cdot \eta \cdot d_p} \quad (15)$$

which depends on the Boltzmann constant  $k_B$ , the temperature  $T$ , gas viscosity  $\eta$  and the Cunningham correction factor  $C_C$ . The latter is a function of the gas mean free path

and the particle diameter. At small particle sizes the Cunningham correction factor is approximately proportional to  $d_p^{-1}$ , and so the wall loss rate can be approximated by

$$k_w(d_p) = \frac{C'}{d_p} \quad (16)$$

5 where  $C'$  is an empirically-determined constant. Figure 1 shows the measured wall loss rate for the CLOUD chamber as a function of  $d_p$  (dashed curve, lower panel). The wall loss rate decreases as  $\sim d_p^{-1}$ , which is weaker than the assumed power dependency of  $\sim d_p^{-2}$  for atmospheric particles (Eq. 5). Considering only wall losses an analytical solution for the correction factor can be obtained by adapting Eq. (4):

$$10 \frac{dN(d_p)}{N(d_p)} = -\frac{1}{GR} \cdot \frac{C'}{d_p} \cdot dd_p. \quad (17)$$

In this case integration yields:

$$\ln\left(\frac{N(d_{p2})}{N(d_{p1})}\right) = -\frac{C'}{GR} \cdot \ln\left(\frac{d_{p2}}{d_{p1}}\right) \quad (18)$$

15 OR

$$N(d_{p1}) = N(d_{p2}) \cdot \exp\left(\frac{C'}{GR} \cdot \ln\left(\frac{d_{p2}}{d_{p1}}\right)\right). \quad (19)$$

20 According to the example in Fig. 1, the value of  $C'$  is approximately  $0.001 \text{ nm s}^{-1}$ . Using again a growth rate of  $3.6 \text{ nm h}^{-1}$ , comparison between Eqs. (9) and (19) yields a 1.43 higher factor when wall loss is the dominant particle removal process (see also the dashed green curve in Fig. 2). However, if the growth rate becomes smaller, or for chambers with higher wall loss rates, then this factor rapidly increases, e.g. the discrepancy becomes  $\sim 35$  at  $C'/GR = 10$ . In conclusion, the KK method cannot be applied in

any environment other than one where the dominant losses are due to collisions with large pre-existing particles (i.e. atmospheric measurements and certain seed-particle chamber experiments). Furthermore, experiments and atmospheric environments with similar condensation sink rates cannot be directly compared before corrections are applied, because not only is the magnitude of the condensation sink important but also the dependency of the loss rate as function of particle size.

## 2.4 Universal method to derive the nucleation rate from the experimental formation rate

We will assume that the size distribution above a certain threshold size ( $d_{p2}$ ) is known, using a Scanning Mobility Particle Sizer (SMPS) system with  $n$  size bins. For the following discussion it is useful to add  $m$  to all bin indices, although the original size distribution contains  $n$  size bins ranging from 1 to  $n$ . In this case the size  $d_{p2}$  corresponds to the bin with the index  $m + 1$  (Fig. 3). The formation rate of particles at and above  $d_{p2}$  can then be calculated from:

$$J_{m+1} = \frac{dN_t}{dt} + \sum_{i=m+1}^{n+m} (k_w(d_{p,i}) \cdot N_i) + k_{dil} \cdot N_t + \sum_{i=m+1}^{n+m} \left( \sum_{j=i}^{n+m} \delta_{ij} \cdot K(d_{p,i}, d_{p,j}) \cdot N_j \cdot N_i \right) \quad (20)$$

where double-counting of collisions between particles in the same size bin is avoided by the factor (Seinfeld and Pandis, 2006):

$$\delta_{ij} = \begin{cases} 0.5 & \text{if } i = j \\ 1 & \text{if } i \neq j \end{cases} \quad (21)$$

The first term on the RHS takes into account non steady-state conditions, by the time derivative of the total particle number density  $N_t$  (sum of the particle concentrations from bin  $m + 1$  to  $n + m$ ). The remaining three terms on the RHS describe the loss processes of neutral particles in a chamber experiment: wall loss, loss due to dilution of

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the chamber gas (independent of particle size) and coagulation loss between particles of all size bins. Note that the index  $i$  runs from  $m + 1$  to  $n + m$  and the index  $j$  from  $i$  to  $n + m$ . In this way, the collisions between the bins  $i$  and  $j$  are not counted twice. Since we are looking at formation rates larger than a certain size, collision products will remain in the size range under consideration and therefore loss due to coagulation between bins  $i$  and  $j$  has to be taken into account only once.

Translating the formation rate from  $d_{p2}$  to a smaller size  $d_{p1}$  requires introducing  $m$  intermediate size bins, which can be defined in increments of  $\Delta d_p$  by

$$\Delta d_p = \frac{d_{p2} - d_{p1}}{m}. \quad (22)$$

The formation rate at the largest newly-introduced size bin at  $d_{p,m}$  ( $d_{p2} - \Delta d_p$ ) can be calculated from

$$J_m = J_{m+1} + \frac{dN_m}{dt} + \left( k_w(d_{p,m}) + k_{dil} + \sum_{j=m}^{n+m} \delta_{mj} \cdot K(d_{p,m}, d_{p,j}) \cdot N_j \right) \cdot N_m. \quad (23)$$

According to Lehtinen et al. (2007) the formation rate and the growth rate (GR) are connected by the following equation:

$$J_m = \text{GR}_m \cdot \frac{N_m}{\Delta d_p}. \quad (24)$$

Using Eq. (24) in Eq. (23) and assuming that the particle number density below  $d_{p2}$  is constant with time yields

$$\text{GR}_m \cdot \frac{N_m}{\Delta d_p} = J_{m+1} + \left( k_w(d_m) + k_{dil} + \sum_{j=m}^{n+m} \delta_{mj} \cdot K(d_{p,m}, d_{p,j}) \cdot N_j \right) \cdot N_m. \quad (25)$$

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In this equation all quantities are known except the value of  $N_m$ , which can be found after solving the quadratic equation (note that the last term on the RHS is quadratic in  $N_m$ ). Once  $N_m$  is found the formation rate  $J_m$  can be calculated and the process can be repeated with the next smaller size bin (index  $m - 1$ ). In this way the complete particle spectrum above  $d_{p1}$  (containing now  $n + m$  size bins) can be recreated until the final formation rate  $J_{d_{p1}}$  (at index 1) is calculated. 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.

In order to test the relative importance of coagulation – including self-coagulation – on the magnitude of the formation rate correction it is also possible to omit the last term on the RHS of Eq. (25). We will discuss in Sect. 3.3 under which circumstances this can be done without sacrificing too much accuracy.

### 2.5 Kinetic model for testing the universal method

A numerical model has been developed recently for the CLOUD chamber to simulate the formation and growth of uncharged sulfuric acid-dimethylamine particles (Kürten et al., 2014). The model assumes that particles grow from monomers by condensation and coagulation. Due to the arguments presented by Kürten et al. (2014), it has been concluded that  $\text{H}_2\text{SO}_4 \cdot (\text{CH}_3)_2\text{NH}$  clusters (abbreviated as SA · DMA) constitute the basic “monomer” for the formation of particles in a system of sulfuric acid (SA) and dimethylamine (DMA). Assuming unit sticking efficiency and zero evaporation rate, good agreement is found between the model and the experimentally-measured neutral clusters.

The kinetic model is based on McMurry (1980). The time-dependent balance equation for the monomer concentration  $N_1$  is

$$\frac{dN_1}{dt} = P_1 - \left( k_{1,w} + k_{\text{dil}} + \sum_{j=1}^N K_{1,j} \cdot N_j \right) \cdot N_1 \quad (26)$$

and, for all larger clusters ( $k \geq 2$ ),

$$\frac{dN_k}{dt} = \frac{1}{2} \cdot \sum_{i+j=k} K_{i,j} \cdot N_i \cdot N_j - \left( k_{w,k} + k_{dil} + \sum_{j=1}^N K_{k,j} \cdot N_j \right) \cdot N_k. \quad (27)$$

Here,  $P_1$  is the production rate of the monomers,  $k_w$  is the wall loss rate,  $k_{dil}$  the dilution rate, and  $K$  the coagulation coefficient.

The original model calculated concentrations of clusters ranging from dimer up to clusters of several thousand molecules. Each size bin was represented by a single cluster with a fixed number of molecules (or SA-DMA clusters, which are each treated as one molecule). The maximum particle size that can be reached with reasonable computation time is a few nm, which is too small for the current study. Therefore we adopted the method of Lovejoy et al. (2004) and incremented the size by one molecule for the first 30 bins (linear bins), and by a constant geometrical factor for the next 150 bins (geometric bins). By this method, a size of 60 nm can be reached using a geometrical factor of 1.023, which is suitable for the present study.

### 3 Discussion

Figure 4 shows the result of the kinetic model simulation for a monomer (molecular weight of  $143 \text{ g mol}^{-1}$  and density of  $1.47 \text{ g cm}^{-3}$ ) production rate of  $8.8 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ , after  $1.5 \times 10^4 \text{ s}$ . Integration of Eqs. (26) and (27) yields the displayed size distribution (grey sticks). Although the particles continue to grow, the populations at smaller sizes (below about 10 nm) are close to steady-state. Since the total particle number concentration is dominated by these smaller particles, time-dependency can be neglected in the following, but will be revisited in Sect. 3.2. The size distribution (grey sticks in Fig. 4) is obtained after normalizing the concentrations by the number of SA molecules per bin.



can be separated from the uncertainties due to size-dependent particle GR. In the absence of such measurements, a detailed error analysis is required to bracket the range of GR uncertainty and its impact on the derived nucleation rates.

When using the size-dependent growth rate in the reconstruction method, by updating the GR in Eq. (25) at each step, perfect agreement between the generated and reconstructed size distributions can be achieved (blue line in Fig. 4). A comparison between using a constant GR and a size-dependent GR is also shown in Fig. 5. Here, the formation rates are compared as function of size. The accurate solution from the kinetic model is shown by the black solid line, while the results from the reconstruction method are indicated by the symbols. Again, perfect agreement is reached when using a size-dependent GR (blue triangles), while a constant GR (red circles) leads to an over-estimation of the formation rate by  $\sim 40\%$  at the smallest size.

### 3.2 Time evolution in a simulated chamber nucleation experiment

Using the kinetic model, we show in Fig. 6 an example of the time-dependent formation rates  $J$  (black lines) for the particle sizes  $d_{p1}$  (1.4 nm geometric diameter; solid lines) and  $d_{p2}$  (2.9 nm geometric diameter; dashed lines). In addition, the rate of change of particle concentration  $dN/dt$  (blue lines) above the size thresholds  $d_{p1}$  and  $d_{p2}$  are shown. The formation rates  $J$  are directly obtained from the model using Eq. (25) and the size distribution. Interestingly, the formation rates overshoot before they reach an almost constant value. This overshoot is explained by the absence of larger particles at the beginning of the experiment. Therefore the loss rate is smaller at the beginning, which allows for faster formation rates. Once the larger particles start to form, the loss rate increases until eventually there are only small changes in particle concentrations and formation rates. This overshoot can be quite large and, in this example, reaches almost a factor of three for the maximum  $J$  compared with its steady-state value.

Using the size distribution as a function of time for particle sizes equal to or larger than  $d_{p2}$  (not shown), as well as the growth rates  $GR(d_{p2})$  (not shown) and the time

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derivative of the total ( $\geq d_{p2}$ ) number concentration of particles  $dN(d_{p2})/dt$ , the size-corrected formation rate  $J(d_{p1})$  can be derived by the method described above (red line). The derived formation rate agrees closely with the accurate solution from the kinetic model (black solid line) for conditions close to steady-state. However, when evaluating  $J$  at  $d_{p1}$  from the formation rate at  $d_{p2}$  and time  $t$  one needs to consider that the particles that appear at  $d_{p2}$  were passing the size  $d_{p1}$  at an earlier time  $t'$ . This time can be approximated by

$$t' = t - \frac{d_{p2} - d_{p1}}{\text{GR}} \quad (29)$$

if the time and size-dependency of the GR is neglected. The over-estimation (difference between the red and black lines in Fig. 6) is due to the size-dependency of the growth rate (see previous section). An accurate determination of  $J(d_{p1})$  can only be obtained after the particle formation rate at  $d_{p2}$  has reached steady-state. This is reached when the rate of change of particle concentration (dashed blue line in Fig. 6) approaches zero.

### 3.3 Formation rates as function of the sulfuric monomer concentration

In the preceding section, the universal method has only been tested for one sulfuric acid monomer concentration. Variation of the monomer production rate  $P$  in Eq. (26) will result in different sulfuric acid concentrations. The resulting size distributions ( $N$ ), growth rates (GR) and rates of change of particle concentration ( $dN/dt$ ) as a function of particle size can be used to test the reconstruction method. Figure 7 shows the results for  $5 \times 10^5$  to  $2 \times 10^7 \text{ cm}^{-3}$  sulfuric acid concentration. The accurate solution for  $d_{p2}$  is shown by the green solid line. Using a size-dependent GR the universal method (blue solid line) yields identical values as the kinetic model for  $J(d_{p1})$  (dashed magenta line). However, if a constant GR is used, corresponding to its value at  $d_{p2}$ , then  $J(d_{p1})$  (red solid line) is over-estimated since, for this system, the GR increases slightly with decreasing size.

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In practice, GR will always be subject to measurement uncertainties. In order to test the sensitivity of the universal method, the constant GR was multiplied by a factor of 1.5 (dashed red line) and 0.9 (dashed-dotted red line), respectively. The faster GR leads to an under-estimation in the reconstructed  $J(d_{p1})$  while the smaller GR leads to an over-estimation. It can be seen that the reconstructed  $J(d_{p1})$  is highly sensitive to GR, especially when the particle growth is slow. In this example a GR under-estimation of only 10 % can lead to a huge over-estimation of  $J(d_{p1})$  due to the exponential dependence on GR. Therefore, accurate growth rate measurements are essential to reliably reconstruct the particle formation rate at a smaller size.

In order to test the effect of coagulation, Eq. (25) without the last term on the RHS has been used to reconstruct formation rates at  $d_{p1}$  (blue dashed line). As long as the formation rate is below  $\sim 100 \text{ cm}^{-3} \text{ s}^{-1}$  at  $d_{p1}$  (or below  $\sim 5 \text{ cm}^{-3} \text{ s}^{-1}$  at  $d_{p2}$ ), the effect of neglecting coagulation is quite small. For larger formation rates the deviation progressively increases because coagulation becomes competitive and eventually dominant compared to wall loss and dilution. However, these numbers are relevant for the CLOUD chamber experiment and are not necessarily applicable to other chambers with other wall loss and dilution characteristics. Performing the corrections twice – once by including coagulation and a second time by neglecting it – over a range of formation rates can help to find the formation rate at which coagulation becomes important in other chambers. The advantages of neglecting coagulation are that the reconstruction is computationally much less demanding and that analytical solutions can even be used in certain cases, as described in Sect. 2.1. One major difference between most experiments and the example calculations shown in Fig. 7 is that nucleation is generally not proceeding at the kinetic limit, even though this is the case for nucleation of sulfuric acid and dimethylamine (Kürten et al., 2014). However, if there is a nucleation barrier, a much higher monomer concentration is necessary to yield the same formation rate as in a kinetically-limited system. This will result in a higher GR. Therefore, once a threshold formation rate is found where coagulation starts to become important for

a given experiment (around  $100 \text{ cm}^{-3} \text{ s}^{-1}$  in the case of CLOUD), it can be neglected for all smaller formation rates in any chemical system.

## 4 Conclusions

The Kerminen and Kulmala (2002) method is widely used in atmospheric and chamber experiments to derive nucleation rates from experimentally-measured formation rates at larger particle sizes. However, we have shown that the applicability of the KK method is limited to cases where the dominant particle losses are due to coagulation with large pre-existing particles, and that significant inaccuracies can result for most chamber experiments, where the loss rates have different size-dependencies.

We have therefore presented a new universal method that yields representative results in any general environment, provided certain quantities are known. The new method requires knowledge of the particle size spectrum above the detection threshold, the particle growth rate, and all loss processes as a function of particle size. With this information the size spectrum and the formation rate can be reconstructed in a step-wise process to a smaller size, where the nucleation rate is determined. The universal method can give accurate results and, furthermore, takes into account self-coagulation among newly-formed particles, which can be an important effect, recognized previously by Anttila et al. (2010). Additionally, if the size-dependent growth rate is available from measurements, it can be readily incorporated during the reconstruction of the size distribution.

The proposed new method allows extrapolation of the particle formation rate measured at one threshold size to a second, smaller size. In this way, a precise quantitative comparison can be made between formation rates measured simultaneously by several counters operating in the 1 to 3 nm threshold range and, where differences emerge, a deeper understanding of fundamental quantities such as cluster critical sizes, growth rates and evaporation rates can be obtained.



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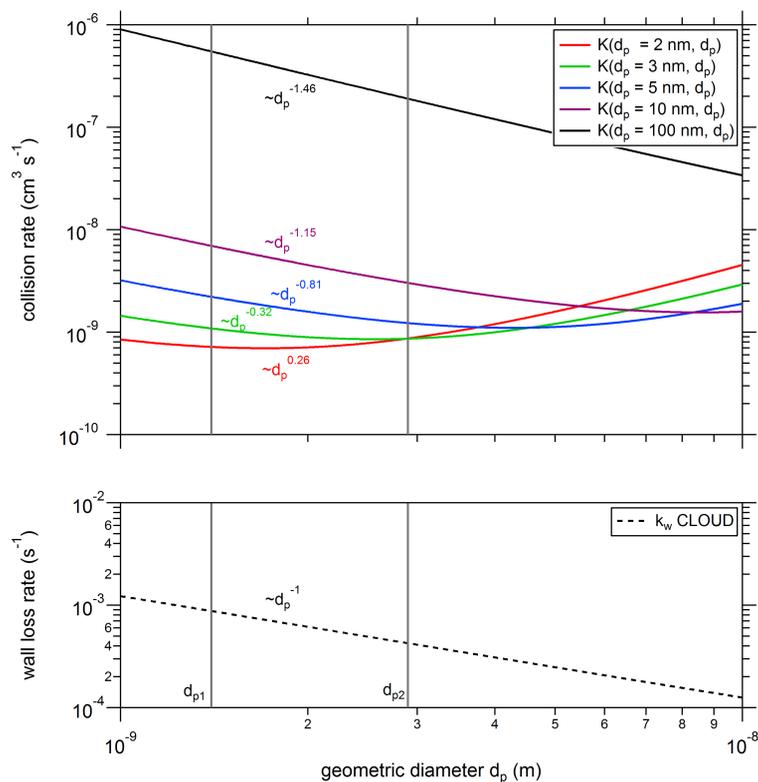
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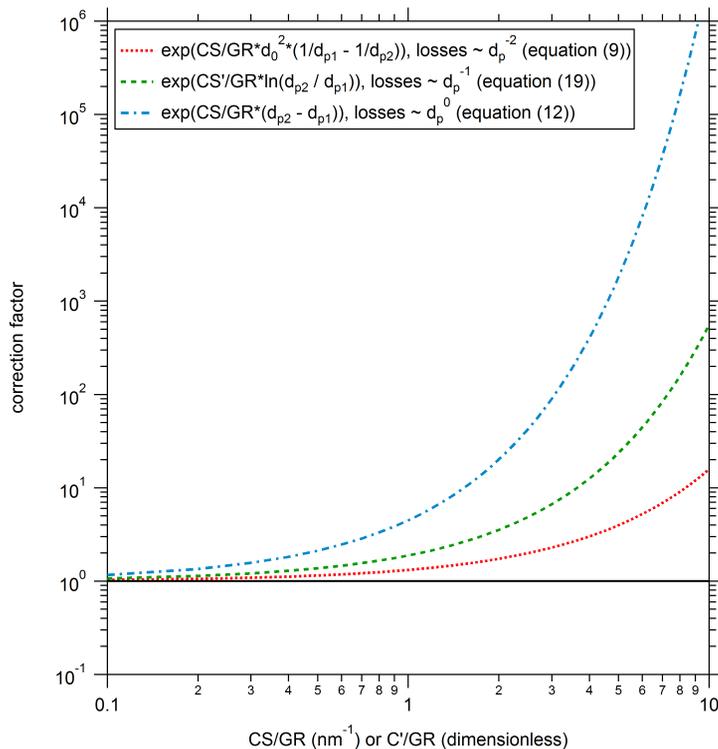
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**Figure 1.** Collision rate,  $K$ , as function of particle size,  $d_p$  (upper panel). Collision rates are calculated between two particles where one particle has a constant size (indicated in the legend of the figure) and the second particle diameter varies between 1 and 10 nm. The wall loss rate for the CLOUD chamber as function of particle size is shown by the dashed curve (lower panel). Slopes of the curves are indicated for the range between  $d_{p1}$  (1.4 nm, i.e. 1.7 nm in mobility diameter) and  $d_{p2}$  (2.9 nm, i.e. 3.2 nm in mobility diameter).

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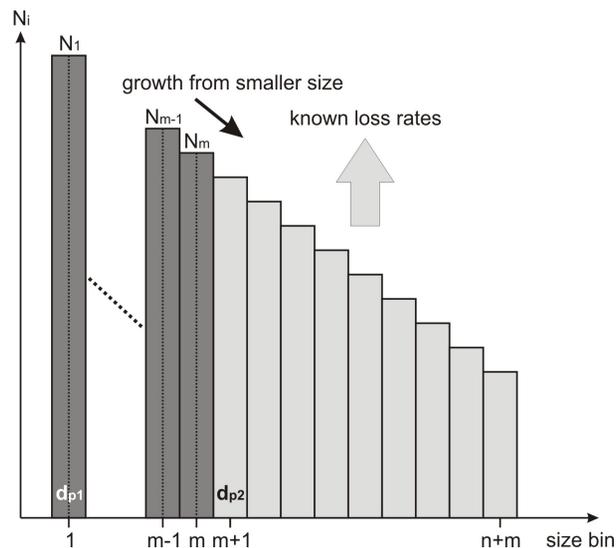
**Figure 2.** Correction factors calculated for different size-dependencies of the loss processes. The diameters used in the equations are  $d_{p1} = 1.7$  nm and  $d_{p2} = 3.2$  nm. See text for details.

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**Figure 3.** The original size distribution above the cut-off size  $d_{p2}$  (size bin  $m + 1$ ) is shown in light gray. The loss rate of particles and the rate of change of the particle concentration in this size range must be compensated by the formation rate due to smaller particles growing into the measured size range. This knowledge can be incrementally extended to bins at smaller sizes in a step-wise process, finally reaching the smaller size,  $d_{p1}$ .

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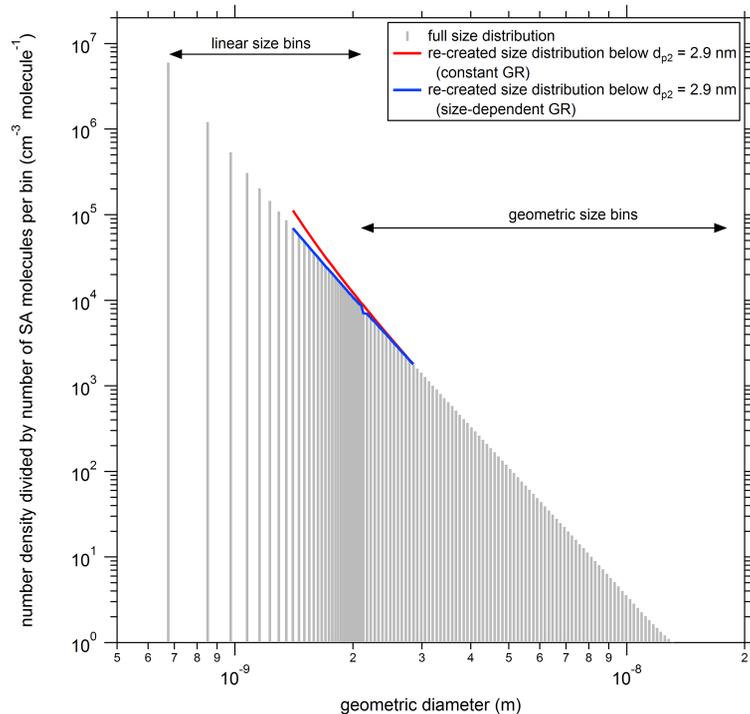
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**Figure 4.** Modeled and reconstructed particle size distribution. The model uses different definitions for the first 30 size bins (up to  $\sim 2.1$  nm) and the last 150 size bins ( $\gtrsim 2.1$  nm). In the first 30 size bins, the number of molecules in the particles increases by one between each bin, whereas in the next 150 bins the particle diameter is increased by a constant factor between each bin. Normalizing the concentration by the number of molecules per bin leads to the shown size distribution (grey sticks). The reconstructed size distribution using the new method described here is shown by the solid lines, starting from the particle distribution above 2.9 nm. The solution using a size-dependent growth rate (GR) is shown by the blue line and, for a constant GR (taken at  $d_{p2}$ ), by the red line.

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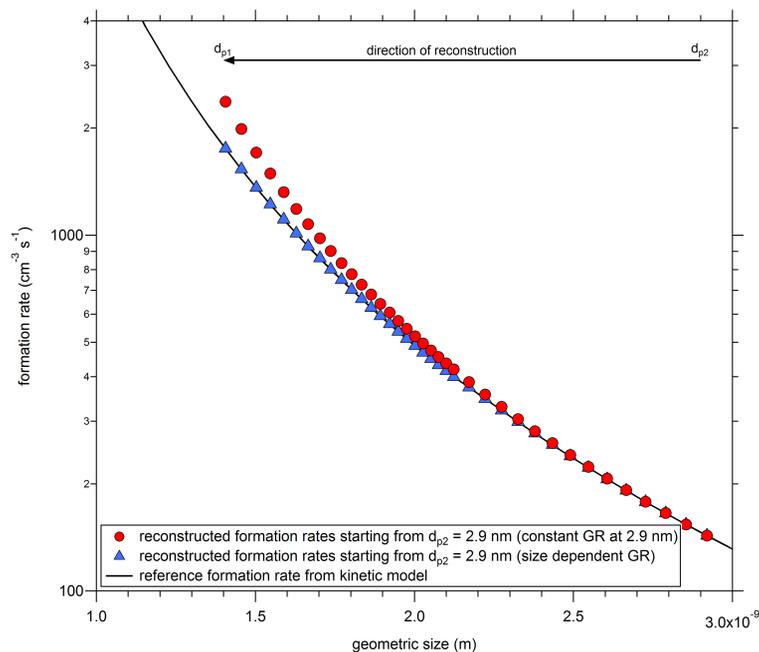
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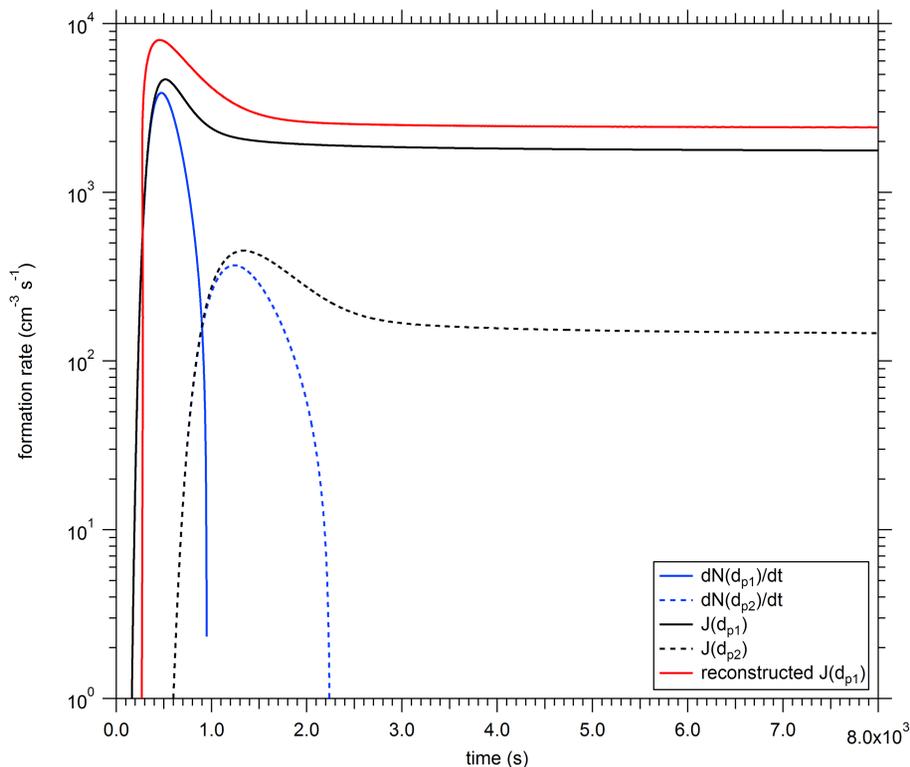
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**Figure 5.** Formation rates as function of particle size. Formation rates simulated with the kinetic model are shown by the black line. Reconstructed particle formation rates starting at  $d_{p2} = 2.9 \text{ nm}$  and ending at  $d_{p1} = 1.4 \text{ nm}$  are shown by the blue triangles for a size-dependent growth rate (GR) and by the red circles for a constant GR (taken at  $d_{p1}$ ).

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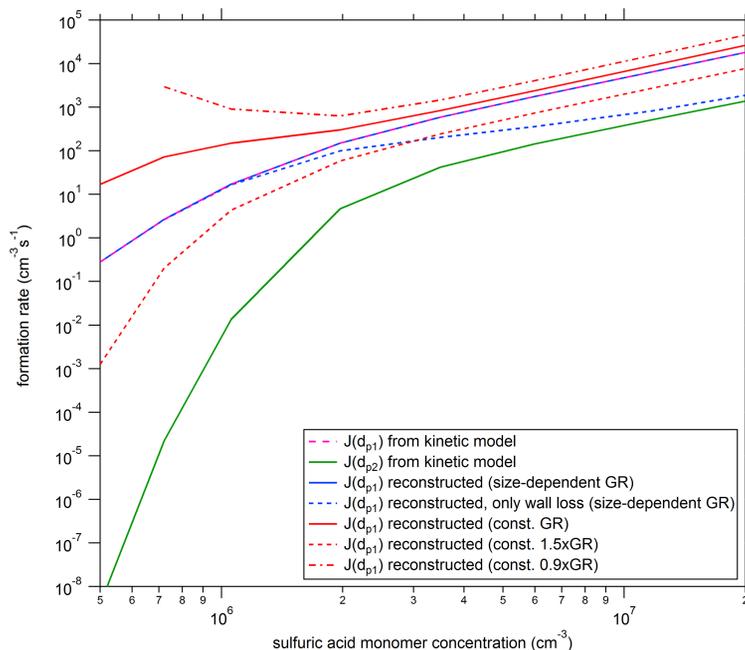


**Figure 6.** Particle formation rates  $J$  ( $\text{cm}^{-3} \text{s}^{-1}$ , black lines) and change in particle concentration  $dN/dt$  ( $\text{cm}^{-3} \text{s}^{-1}$ , blue lines) shown for two different sizes,  $d_{p1} = 1.4 \text{ nm}$  (solid lines) and  $d_{p2} = 2.9 \text{ nm}$  (dashed lines). The data are from a kinetic model calculation. The reconstructed  $J(d_{p1})$  is shown by the red solid line.

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**Figure 7.** Formation rates as function of the sulfuric acid monomer concentration. The solid green curve shows the formation rate at  $d_{p2}$  calculated from the kinetic model. The simulated formation rates  $J(d_{p1})$  from the kinetic model are indicated by the dashed magenta line. The reconstructed formation rates at  $d_{p1}$  using the size-dependent GRs are shown by the solid blue line, and agree well with the simulations. The solid red line shows the reconstructed formation rates at  $d_{p1}$  using a constant GR, evaluated at  $d_{p2}$ . Varying the constant GR by a factor of 1.5 and 0.9 results in the dashed and the dashed-dotted red curves, respectively. Neglecting coagulation but using a size-dependent GR yields the dashed blue line.

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