

# On the Limits of Köhler Activation Theory: How do Collision and Coalescence Affect the Activation of Aerosols?

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**Abstract.** Activation is necessary to form a cloud droplet from an aerosol, and it is widely accepted that it occurs as soon as a wetted aerosol grows beyond its critical radius. Traditional Köhler theory assumes that this growth is driven by the diffusion of water vapor. However, if the wetted aerosols are large enough, the coalescence of two or more particles is an additional process for accumulating sufficient water for activation. This transition from diffusional to collectional growth marks the limit of traditional Köhler theory and it is studied using a Lagrangian cloud model in which aerosols and cloud droplets are represented by individually simulated particles within large-eddy simulations of shallow cumuli. It is shown that the activation of aerosols larger than  $0.1\text{ }\mu\text{m}$  in dry radius can be affected by collision and coalescence, and its contribution increases with a power-law relation toward larger radii and becomes the only process for the activation of aerosols larger than  $0.4 - 0.8\text{ }\mu\text{m}$  depending on aerosol concentration. Due to the natural scarcity of the affected aerosols, the amount of aerosols that are activated by collection is small with a maximum of 1 in 10000 activations. The fraction increases as the aerosol concentration increases, but decreases again as the number of aerosols becomes too high and the particles too small to cause collections. Moreover, activation by collection is found to affect primarily aerosols that have been entrained above the cloud base.

## 1 Introduction

Activation is necessary for the formation of droplets from aerosols. Accordingly, activation controls the number and size of cloud droplets and hence so-called aerosol-cloud interactions, e.g., cloud albedo (Twomey, 1974) or cloud lifetime (Albrecht, 1989). In contrast to cloud droplets, which behave like bulk water, the understanding of unactivated aerosols and their activation depends fundamentally on the aerosol's physicochemical properties, which cause the so-called solute and curvature effects (Köhler, 1936). These effects enable, on the one hand, the stable existence of haze particles (also termed wetted aerosols) in subsaturated environments and inhibit, on the other hand, diffusional growth if the supersaturation does not exceed a certain threshold. This so-called critical supersaturation is associated with a critical radius, to which a wetted aerosol must grow to be considered as activated. Small aerosols activate almost immediately when the supersaturation exceeds the critical supersaturation, as it is assumed in many parameterizations of the activation process (e.g., Twomey, 1959). For larger aerosols, however, the critical radius becomes so large that the time needed for activation can be substantially increased (or prevented under certain conditions) due to the kinetically limited transport of water vapor to the particle's surface (Chuang et al., 1997). Due to their large size, however, these particles may behave like regular cloud droplets inside the environment of a cloud al-

though they are not formally activated (Nenes et al., 2001). Accordingly, Köhler activation theory is usually considered a weak concept for these particles. But where are the limits of Köhler activation theory located? An upper limit of the applicability of Köhler activation theory can be identified by the switch from predominantly diffusional to collectional (collision followed by coalescence) mass growth if the involved particles become large enough. Indeed, inactivated aerosols triggering collisions is closely related to the impact of giant and ultra-giant aerosols (dry radius  $> 1 \mu\text{m}$ ) on clouds, which are able to initiate precipitation due to their large wet radii ( $> 20 \mu\text{m}$ ) (e.g., Johnson, 1982). Moreover, recent studies indicate that collection might even affect smaller particles: by considering the effects of turbulence, the collection kernel for the interaction of small particles can be significantly increased (e.g., Devenish et al., 2012). Accordingly, the main questions of this study are: Where are the limits of traditional Köhler activation theory? At which aerosol size will collection dominate the activation process? And how much does collectional activation contribute to the activation of aerosols? To answer these questions, theoretical arguments and large-eddy simulations (LES) with particle-based cloud physics are applied. Particle-based cloud physics, so-called Lagrangian cloud models (LCMs), are especially suitable for this study because they explicitly resolve the activation process and do not rely on a parameterization of it (e.g., Andrejczuk et al., 2008; Hoffmann et al., 2015; Hoffmann, 2016). Therefore, the results will give insights on the physical processes usually not covered (or missed) by those activation parameterizations typically implemented in other cloud models.

This paper is designed as follows. The subsequent Section 2 will illuminate how collections can cause (or inhibit) activation by simple theoretical arguments. In Section 3, the LES-LCM simulation setup is introduced. Results will be presented in the Sections 4 and 5, where the former section exemplifies the applied methodology used to untangle diffusional from collectional activation and the latter section presents the results from a shallow cumulus test case. The study is summarized and discussed in Section 6. Appendix A introduces the governing equations of the applied LCM and necessary extensions carried out for this study.

## 2 Theoretical considerations

In this section, the general effects of coalescence on the activation of aerosols will be addressed. To simplify the argumentation in this part of the study, it is assumed that collections take place regardless of the physics that enable or inhibit them in reality. Moreover, all other microphysical processes, specifically diffusional growth, are neglected.

We consider one particle which grows by coalescing with other particles. Accordingly, the particle's water mass after  $n$  collections is given by

$$m_n = m_0 + \sum_{i=1}^n m_i = m_0 + n \cdot \langle m \rangle, \quad (1)$$

where  $m_0$  terms the particle's initial water mass and  $m_i$  ( $i > 0$ ) the mass of water added by each collection. The second equals sign introduces the assumption of a monodisperse ensemble of collected particles.

56 Based on Köhler theory, it can be shown that the critical radius for activation is given by

$$57 \quad r_{\text{crit}} = \sqrt{3 \frac{b \cdot m_s}{A}}, \quad (2)$$

58 where  $m_s$  is the dry aerosol mass. Curvature effects are considered by  $A = 2\sigma/(\rho_l R_v T)$ , depending on the surface tension of  
 59 water  $\sigma$ , mass density of water  $\rho_l$ , specific gas constant of water vapor  $R_v$ , and temperature  $T$ . The physicochemical aerosol  
 60 properties responsible for the solute effect are represented by  $b = 3\nu_s \rho_s \mu_l / (4\pi \rho_l \mu_s)$ , with the van't Hoff factor  $\nu_s$ , the mass  
 61 density of the aerosol  $\rho_s$ , and the molecular masses of water  $\mu_l$  and aerosol  $\mu_s$ , respectively. Accordingly, the critical mass for  
 62 activation after  $n$  collections yields

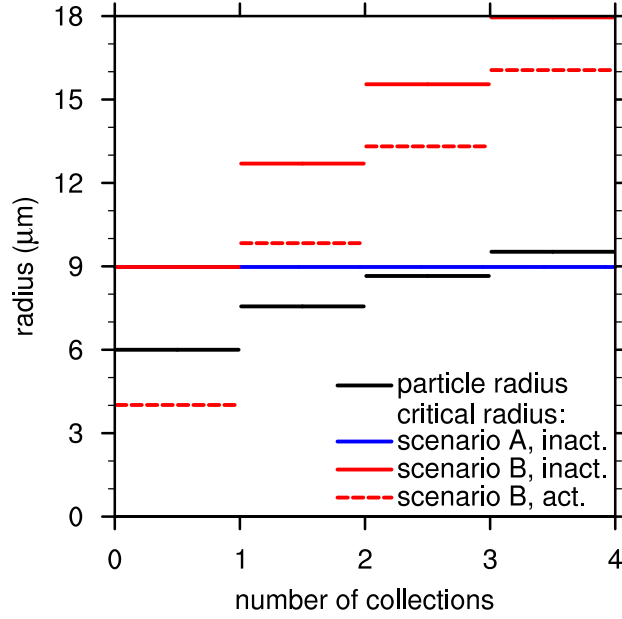
$$63 \quad m_{\text{crit},n} = \frac{4}{3} \pi \rho_l \cdot r_{\text{crit},n}^3 = \frac{4}{3} \pi \rho_l \cdot \left[ 3 \frac{b}{A} \cdot \left( m_{s,0} + \sum_{i=1}^n m_{s,i} \right) \right]^{3/2}, \quad (3)$$

64 where  $m_{s,0}$  terms the initial aerosol mass and  $m_{s,i}$  ( $i > 0$ ) the aerosol mass added by each collection. Approximating the  
 65 summation in (3) demands further assumptions on the distribution of aerosol mass within the particle spectrum. Two scenarios  
 66 are defined. Scenario A: the collected particles contain a negligible amount of aerosols. Accordingly, the aerosol mass does  
 67 not change ( $\sum_{i=1}^n m_{s,i} = 0$ ). Scenario B: each particle contains the same mass of aerosol. Correspondingly, the aerosol mass  
 68 increases proportionally to the number of collections ( $\sum_{i=1}^n m_{s,i} = n \cdot \langle m_s \rangle$ ).

69 In Fig. 1, the evolving particle radius and critical radius are displayed as a function of the number of collections (details on the  
 70 particle properties are given in the figure's caption). The simultaneous examination of particle radius and critical radius reveals  
 71 if a particle is activated (particle radius larger than critical radius) or deactivated (particle radius smaller than critical radius).  
 72 For scenario A, the initially inactivated particle (black line) grows faster than the critical radius (blue line), and the aerosol  
 73 activates after 3 collections. For scenario B, an initially inactivated particle and an initially activated particle are examined (the  
 74 critical radii are displayed in red by a continuous or dashed line, respectively). Since the critical radius for activation increases  
 75 faster than the particle radius, activation is inhibited or the deactivation of previously activated particle is caused.

76 These considerations suggest that only the collection of particles with a large amount of water and a comparably small  
 77 amount of aerosol mass (i.e., highly dilute solution droplets) might lead to activation (as shown in scenario A). This, however,  
 78 indicates that the collected particles are probably activated already. Therefore, the process of collectional activation will not  
 79 increase the total number of activated aerosols since one or more already activated aerosols need to be collected (and hence  
 80 annihilated) in the process of one collectional activation. By contrast, the collection of particles with a comparably large amount  
 81 of aerosol (i.e., less dilute solutions, as shown in scenario B) might inhibit activation since the increase of the critical radius  
 82 exceeds the increase of the wet radius.

83 The following part of the study is investigating how coalescence is able to cause aerosol activation in shallow cumulus clouds  
 84 using a detailed cloud model considering diffusional growth as well as detailed physics of collision and coalescence.



**Figure 1.** Change of particle radius (black line) and critical radius (colored lines) as a function of the number of collections for the growth scenarios A (negligible increase of aerosol mass, blue line) and B (aerosol mass increases proportional to the number of collections, red lines) as well as an initially inactivated (continuous lines) and an activated particle (dashed line). The initial wet particle radius and the wet radii of the collected particles are assumed to be  $6\text{ }\mu\text{m}$ . The initial dry aerosol mass (sodium chloride) is  $2.2 \times 10^{-16}\text{ kg}$  ( $0.29\text{ }\mu\text{m}$  dry radius) (continuous lines) and  $4.4 \times 10^{-17}\text{ kg}$  ( $0.17\text{ }\mu\text{m}$  dry radius) (dashed line). For scenario B, the collected particles contain  $2.2 \times 10^{-16}\text{ kg}$  dry aerosol mass ( $0.29\text{ }\mu\text{m}$  dry radius).

### 3 Simulation setup

The following results are derived from LES simulations applying an LCM for representing cloud microphysics. The LCM is based on a recently developed approach which simulates individual particles that represent an ensemble of identical particles and maintains, as an inherent part of this approach, the identity of droplets and their aerosols throughout the simulation (Andrejczuk et al., 2008; Shima et al., 2009; Sölch and Kärcher, 2010; Riechelmann et al., 2012; Naumann and Seifert, 2015). A summary of the governing equations and the extensions carried out for this study to treat aerosol mass change during collision and coalescence is given in the Appendix A. The underlying dynamics model, the LES model PALM (Maronga et al., 2015), solves the non-hydrostatic incompressible Boussinesq-approximated Navier-Stokes equations, and prognostic equations for water vapor mixing ratio, potential temperature, and subgrid-scale turbulence kinetic energy. For scalars, a monotonic advection scheme (Chlond, 1994) is applied to avoid spurious oscillations at the cloud edge (e.g., Grabowski and Smolarkiewicz, 1990).

The initial profiles and other forcings of the simulation follow the shallow trade wind cumuli intercomparison case by Siebesma et al. (2003), which itself is based on the measurement campaign BOMEX (Holland and Rasmusson, 1973). A

98 cyclic model domain of  $3.2 \times 3.2 \times 3.2 \text{ km}^3$  is simulated. (In comparison to Siebesma et al. (2003), the horizontal extent has  
 99 been halved in each direction due to limited computational resources.) The grid spacing is 20 m isotropically. Depending on  
 100 the prescribed aerosol concentration, a constant time step of  $\Delta t = 0.2 - 0.5 \text{ s}$  had to be used for the correct representation of  
 101 condensation and evaporation, but it is also applied to all other processes. The first 1.5 hours of simulated time are regarded as  
 102 model spin-up; only the following four hours are analyzed.

103 The simulated particles, called super-droplets following the terminology of Shima et al. (2009), are released at the beginning  
 104 of the simulation, and are randomly distributed within the model domain up to a height of 2800 m. The average distance between  
 105 the super-droplets is 4.3 m, yielding a total number of about  $360 \times 10^6$  simulated particles and about 100 super-droplets per grid  
 106 box. Initial weighting factors, i.e., the number of real particles represented by each super-droplet, are  $8 \times 10^9$ ,  $48 \times 10^9$ ,  $160 \times$   
 107  $10^9$ ,  $320 \times 10^9$ , and  $640 \times 10^9$  for each particle, representing aerosol concentrations of 100, 600, 2000, 4000, and  $8000 \text{ cm}^{-3}$ ,  
 108 respectively. These result in average droplet concentrations of about 48, 220, 550, 750, and  $1000 \text{ cm}^{-3}$ , respectively.

109 The dry aerosol radius is assigned to each super-droplet using a random generator which obeys a typical maritime aerosol  
 110 distribution represented by the sum of three lognormal distributions (Jaenicke, 1993) (Fig. 2). However, only aerosols larger  
 111 than  $0.005 \mu\text{m}$  are initialized since smaller aerosols do not activate in the current setup. The different aerosol concentrations  
 112 are created by scaling the weighting factor of each simulated particle to attain the desired concentration. The aerosols are  
 113 assumed to consist of sodium chloride (NaCl, mass density  $\rho_s = 2165 \text{ kg m}^{-3}$ , van't Hoff factor  $\nu_s = 2$ , molecular weight  $\mu_s =$   
 114  $58.44 \text{ g mol}^{-1}$ ). The initial wet radius of each super-droplet is set to its approximate equilibrium radius depending on aerosol  
 115 mass and ambient supersaturation (Eq. (14) in Khvorostyanov and Curry, 2007). The applied collection kernel includes effects  
 116 of turbulence, which have been shown to increase the collection probability of small particles significantly (e.g., Devenish  
 117 et al., 2012). See Appendix A for more details on the applied LCM.

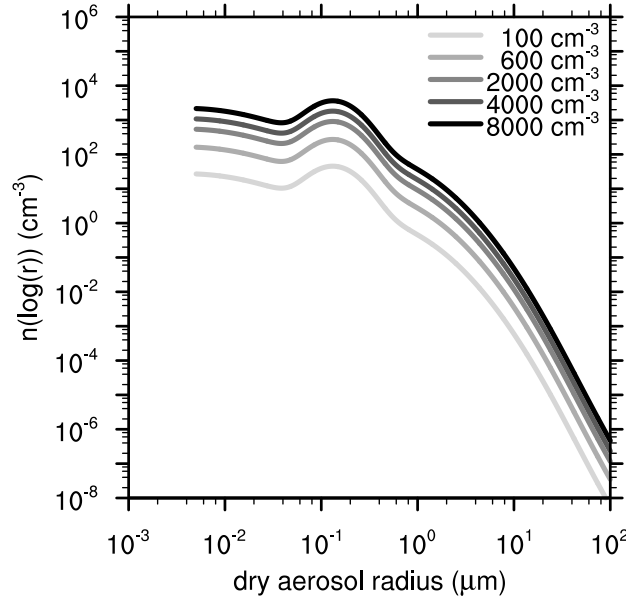
## 118 4 Methodology

119 In this section, the applied methodology for untangling the contributions of diffusion and collection to the activation of aerosols  
 120 is introduced. An aerosol becomes activated when it grows beyond its critical radius ( $r > r_{\text{crit}}$ ). Moreover, activation requires  
 121 the particle to be located in a volume of air with a sufficient supersaturation to enable unhindered diffusional growth. Depending  
 122 on the microphysical process responsible for the final crossing of  $r_{\text{crit}}$ , different supersaturation allow unhindered diffusional  
 123 growth.

124 Due to the continuous character of diffusional growth, the supersaturation has to be larger than the critical supersaturation  
 125 in the moment in which the critical radius is exceeded:

$$126 \quad S > S_{\text{crit}} = S_{\text{eq}}(r_{\text{crit}}), \quad (4)$$

127 where  $S_{\text{eq}}$  is the equilibrium supersaturation calculated according to Köhler theory (see Eq. (A3)). This condition is automat-  
 128 ically fulfilled in the case of diffusional growth due to the constraints of Köhler theory on the equilibrium supersaturation. If  
 129 the critical radius is exceeded by collection, the radius after collection might be immediately larger than  $r_{\text{crit}}$  and, hence, the



**Figure 2.** The number density distribution of dry aerosol radii for different aerosol concentrations (line brightness).

130 necessary supersaturation is allowed to be smaller to enable unhindered diffusional growth:

$$131 \quad S \geq S_{\text{eq}}(r_{\text{ac}}), \quad (5)$$

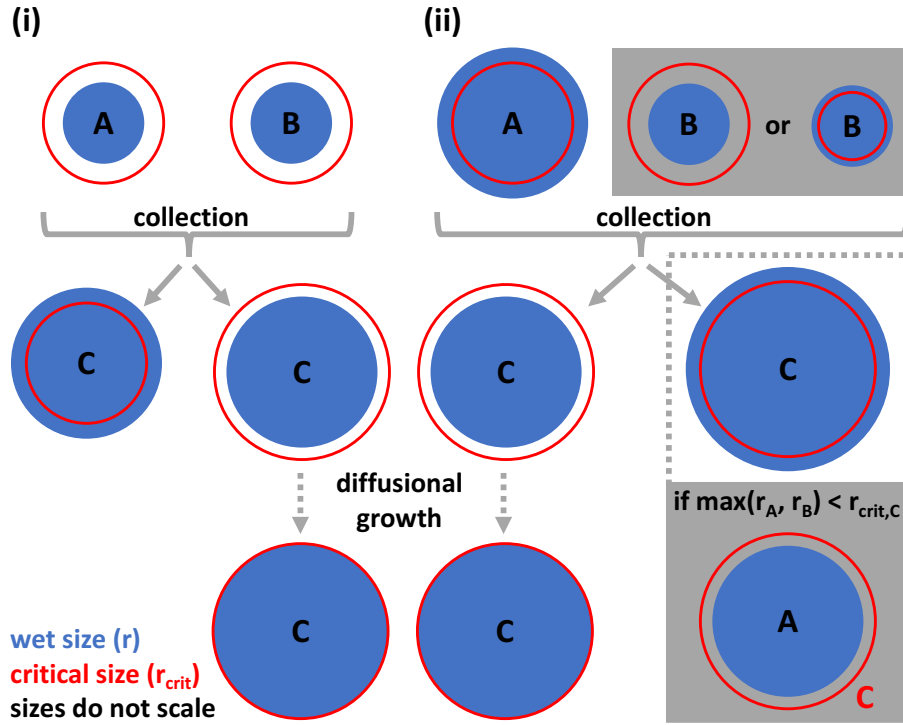
132 where  $r_{\text{ac}} \geq r_{\text{crit}}$  is the wet radius after collection. This criterion is not automatically fulfilled and checked additionally to  
 133 establish the formal equivalence of both processes, i.e., enabling unhindered diffusional growth after activation. Note that the  
 134 process of activation, i.e., the entire growth beyond  $r_{\text{crit}}$ , can be driven by diffusional growth or by accumulating liquid water  
 135 due to collection or by a combination of both.

136 To decide if an activation is primarily driven by diffusion or collection, all simulated particles have been tracked throughout  
 137 the simulation and their mass growth has been integrated from their minimum mass before activation,  $\min(m)$ , to the critical  
 138 activation mass,  $m_{\text{crit}}$ :

$$139 \quad \Delta m|_{\text{diff}} = \int_{\min(m)}^{m_{\text{crit}}} dm|_{\text{diff}}, \quad (6)$$

$$140 \quad \Delta m|_{\text{coll}} = \int_{\min(m)}^{m_{\text{crit}}} dm|_{\text{coll}}, \quad (7)$$

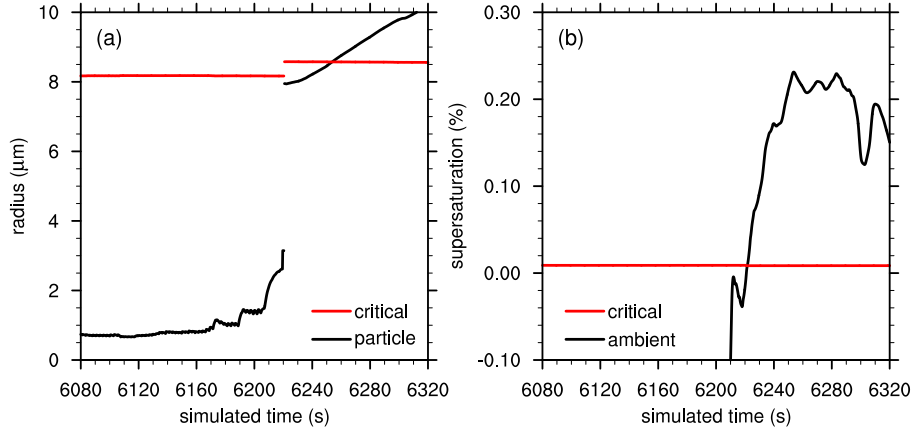
141 where  $dm|_{\text{diff}}$  and  $dm|_{\text{coll}}$  are directly derived from the LCM's model equations (A2) and (A6) – (A7), respectively. Note the  
 142 following procedures for determining  $\min(m)$ ,  $\Delta m|_{\text{diff}}$ , and  $\Delta m|_{\text{coll}}$  during the simulation: (i) If a particle shrinks below  
 143  $\min(m)$  before activation,  $\Delta m|_{\text{diff}}$  and  $\Delta m|_{\text{coll}}$  are set to zero and are re-calculated starting from this new minimum mass.



**Figure 3.** Possible microphysical processes leading to the collectional activation of particle C. Scenario (i) contains only inactivated aerosols, scenario (ii) contains at least one activated aerosol aerosol. The blue circle displays the wet size of the particle, the red circle the critical size, which has to be exceeded for activation. The displayed sizes do not scale.

144 (ii) If a particle becomes deactivated, i.e., evaporates smaller than its critical radius after being activated, the current mass is  
 145 considered the new  $\min(m)$  and  $\Delta m|_{\text{diff}}$  and  $\Delta m|_{\text{coll}}$  are set to zero. (iii) If a collection does not result in an activation and  
 146 the particle evaporates back to its equilibrium radius afterwards,  $\Delta m|_{\text{diff}}$  will be negative and  $\Delta m|_{\text{coll}}$  positive. To avoid the  
 147 potentially incorrect classification of a following activation,  $\Delta m|_{\text{diff}}$  and  $\Delta m|_{\text{coll}}$  are set to zero if  $\Delta m|_{\text{diff}}$  becomes negative  
 148 and the current mass is considered as  $\min(m)$ .

149 To identify a collectional activation, the integrated collectional mass growth  $\Delta m|_{\text{coll}}$  is compared to the diffusional  $\Delta m|_{\text{diff}}$   
 150 in the moment the particle grows beyond its critical radius. If the former exceeds the latter,  $\Delta m|_{\text{coll}} > \Delta m|_{\text{diff}}$ , this activation is  
 151 considered as collectional. There are various microphysical interactions resulting in  $\Delta m|_{\text{coll}} > \Delta m|_{\text{diff}}$ , and its basic types are  
 152 illustrated in Fig. 3. Note that also a combination or a repetition of these types is possible, i.e., multiple subsequent collections.  
 153 In a collectional activation of type (i), the water mass growth by collection dominates, i.e., the coalescence of two previously  
 154 inactivated aerosols A and B results directly or after some diffusional growth in an activated particle C. In a collectional  
 155 activations of type (ii), the critical radius increases faster than wet radius, i.e., the coalescence of an already activated particle  
 156 A with another activated or an inactivated particle B results in inactivated particle C, which activates after some diffusional  
 157 growth. If the resulting particle is directly activated, this process is only considered a collectional activation if the largest wet



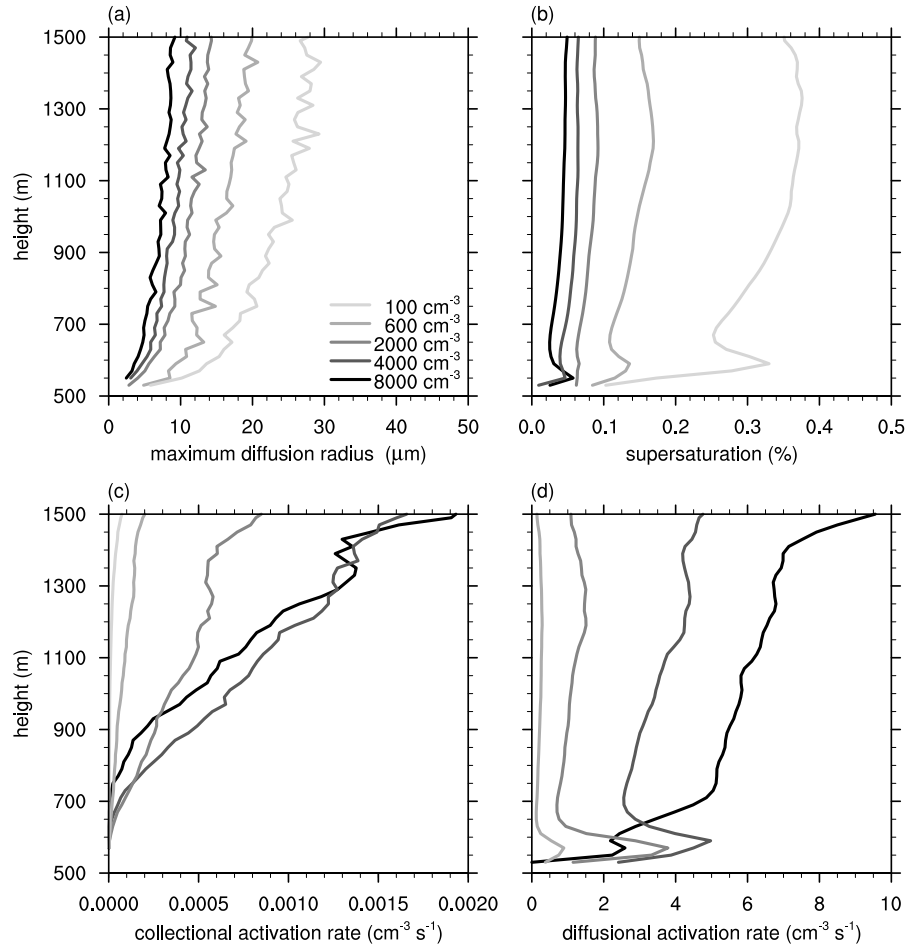
**Figure 4.** Time series of a particle which is activated by collection. Panel (a) shows its radius (black) and critical radius (red) and panel (b) depicts the ambient supersaturation experienced by that particle (black) and its critical supersaturation (red).

158 radius of the two coalescing particles A and B is smaller than the critical radius of the newly produced particle C:

$$159 \quad \max(r_A, r_B) < r_{\text{crit},C}. \quad (8)$$

160 This ensures that the combined water of particles A and B is necessary to activate particle C. If this is not the case, i.e., the  
 161 water of particle A or B is able to activate particle C on its own, the latter process is considered a regular collection of cloud  
 162 droplets or as scavenging and neglected in the following analysis. Moreover, the coalescence of two activated particles resulting  
 163 in a collectional activation is mathematically possible but not found to play a role in the analyzed simulations. Note that only  
 164 collectional activations of the first type are able to increase the number of activated aerosols, while the second type might have  
 165 no or a negative impact on the total number of activated aerosols since the coalescence of at least one activated particle results  
 166 in one activated particle.

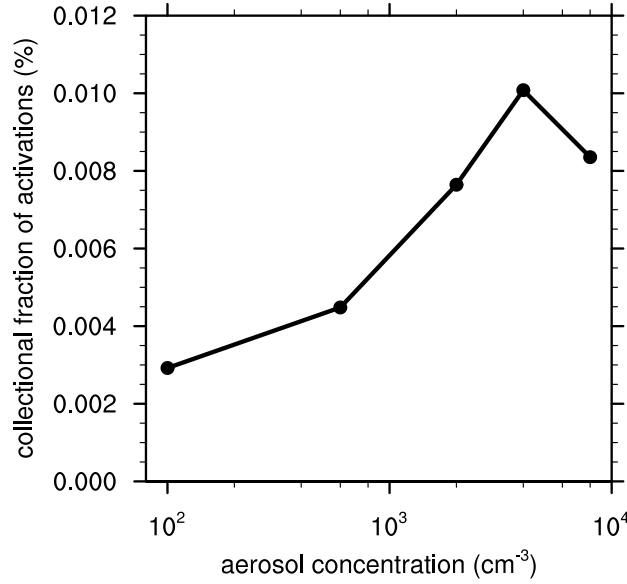
167 To exemplify this methodology, Fig. 4 shows, for an aerosol selected from the LCM simulations discussed below, the time  
 168 series of its radius and critical radius (panel a) and the ambient supersaturation and critical supersaturation (panel b). Note that  
 169 this aerosol is actually one super-droplet, representing a larger ensemble of identical aerosols, which is, however, interpreted as  
 170 one aerosol here. The initial dry radius of the aerosol is  $0.27 \mu\text{m}$ . On its way to activation, the particle experiences diffusional  
 171 growth, which can be easily identified by the continuous change of radius. One collection event, characterized by a distinct  
 172 increase in radius, is visible at 6220s simulated time. At this point in time, the inactivated aerosol (wet radius  $3.1 \mu\text{m}$ ) coalesces  
 173 with an activated particle (wet radius  $7.8 \mu\text{m}$ , aerosol dry radius  $0.13 \mu\text{m}$ ), but the product of coalescence (wet radius  $7.9 \mu\text{m}$ ,  
 174 aerosol dry radius  $0.28 \mu\text{m}$ ) remains inactivated. Due to the increased amount of aerosol mass, the critical radius (and to a lesser  
 175 extent the critical supersaturation) increases (decreases) after the coalescence. Afterwards, the particle grows by diffusion and  
 176 exceeds the critical radius at 6253s simulated time, which can be identified as the time of activation. All in all, this activation is  
 177 considered a collectional activation since  $\Delta m|_{\text{coll}} = 1.9 \times 10^{-12} \text{ kg} > \Delta m|_{\text{diff}} = 6.2 \times 10^{-13} \text{ kg}$ . Moreover, this is a collectional  
 178 activation of type (ii) since it involves the collection of an already activated aerosol.



**Figure 5.** Vertical profiles of the maximum diffusion radius (a), and the supersaturation (b), the collectional activation rate (c), and the diffusional activation rate (d) for the analyzed aerosol concentrations (line brightness).

## 179 5 Results

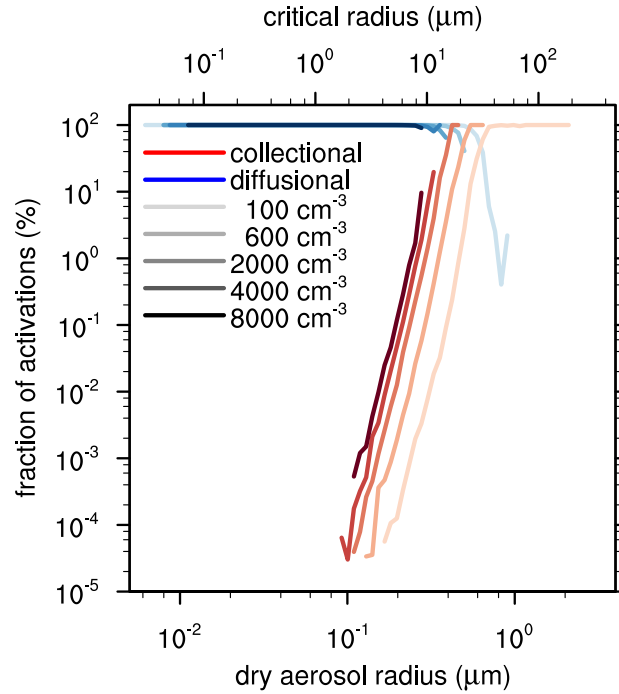
180 The last section showed that collection can contribute significantly to the mass growth leading to the activation of a single  
 181 aerosol. But how does collection contribute to the activation of aerosols in general? Figure 5 shows the vertical profiles of  
 182 (a) the maximum diffusion radius, i.e., the largest critical radius of an aerosol activated exclusively by diffusion at a certain  
 183 height, (b) the supersaturation, (c) the collectional activation rate, i.e., the number of aerosols activated by collection per unit  
 184 volume and unit time, and (d) the corresponding diffusional activation rate. Profiles (b) to (d) are conditionally averaged over  
 185 all supersaturated grid cells. Only data of the last 4 simulated hours is considered. Values above the average cloud top height  
 186 (at 1500m) are not displayed due to insufficient statistics.



**Figure 6.** The collectional fraction of all activations as a function of the aerosol concentration.

187 The maximum diffusion radius (Fig. 5 a) increases almost monotonically with height reaching maxima between  $30\mu\text{m}$  and  
 188  $9\mu\text{m}$  for aerosol concentrations of  $100\text{cm}^{-3}$  to  $8000\text{cm}^{-3}$ , respectively. The supersaturation (Fig. 5 b) exhibits a distinct peak  
 189 at the cloud base and relaxes toward its equilibrium value determined by the number of activated aerosols and vertical velocity  
 190 above (e.g., Rogers and Yau, 1989, Chap. 7). Due to the larger number of water vapor absorbers, the supersaturation as well as  
 191 the maximum diffusion radius are generally smaller in the more aerosol-laden simulations.

192 The collectional activation rate (Fig. 5 c) increases almost linearly with height. This increase can be related to the longer  
 193 lasting diffusional growth resulting in potentially larger particles at higher levels, which increases the collection kernel and  
 194 therefore the collection probability. The slope is larger in aerosol-laden environments, where more aerosols are available  
 195 for activation. Additionally, the height above cloud base, where the collectional activation starts, increases with the aerosol  
 196 concentration since the average particle radius is too small to enable collisions at lower levels. Accordingly, the collectional  
 197 activation rate in the  $8000\text{cm}^{-3}$  simulation exhibits smaller to similar values than in the  $4000\text{cm}^{-3}$  simulation although the  
 198 slope in the  $8000\text{cm}^{-3}$  simulation is larger. The shape of the collectional activation rate differs significantly from the typical  
 199 profile of the diffusional activation rate (Fig. 5 d), which exhibits as a distinct peak at cloud base where the majority of aerosols  
 200 activates after the entrainment through the cloud base in clean conditions (Slawinska et al., 2012; Hoffmann et al., 2015). In  
 201 more aerosol-laden conditions, a larger fraction of diffusional activations occurs at higher levels. In these simulations, only  
 202 larger aerosols are able to activate by diffusion due to the generally lower supersaturations. These larger aerosols, however,  
 203 need a longer time to activate. Accordingly, these aerosols are lifted to higher levels by the cloud's updraft until they grow  
 204 beyond their critical radius for activation with commensurate changes in the profile of the diffusional activation rate.



**Figure 7.** The collectional (red lines) and diffusional (blue lines) fraction of activations as a function of the dry aerosol radius (lower abscissa) and critical radius (at cloud base temperature of 294.5 K, upper abscissa) for the analyzed aerosol concentrations (line brightness).

205 The comparison of the numerical values of the activation rates in Fig. 5 c and d indicate already that the contribution of col-  
 206 lectional activation to the number of activated aerosols is significantly smaller than the contribution of diffusional activation.  
 207 Figure 6 shows that only 1 activation in 10 000 to 35 000 is caused by collection, with a greater contribution of collectional ac-  
 208 tivation in moderately aerosol-laden environments up to  $4000\text{ cm}^{-3}$ . As it will be outlined below, this increase can be attributed  
 209 to a shift of collectional activation to smaller, but more numerous aerosols. For  $8000\text{ cm}^{-3}$ , however, the fraction decreases  
 210 again since the particles are too small to trigger a larger amount of collisions.

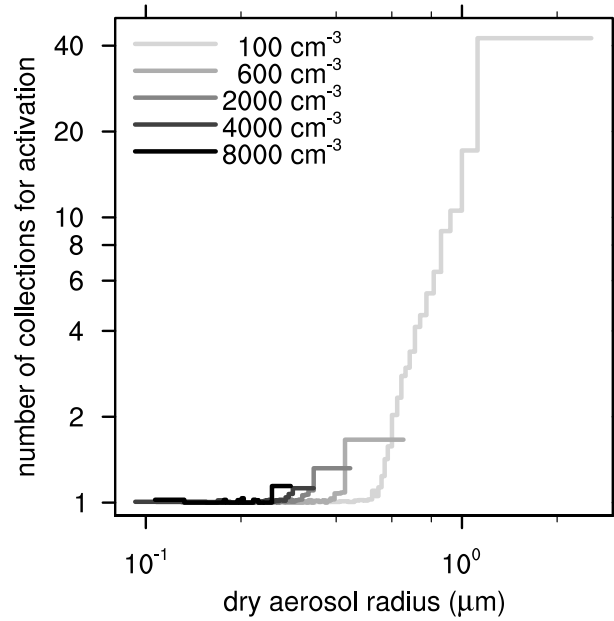
211 Figure 7 shows the collectional and diffusional fraction of activations as a function of the dry aerosol radius on the lower  
 212 abscissa and the corresponding critical radius (calculated for the cloud base temperature of approximately 294.5 K) on the  
 213 upper abscissa. As expected, diffusional activation is the dominant process for small aerosols (dry radius  $< 0.1\text{ }\mu\text{m}$ ) as long  
 214 as the dry aerosol radius is not too small and the corresponding critical supersaturation not too high to inhibit activation.  
 215 Accordingly, the left boundary of diffusional activation is shifted toward larger radii as the maximum supersaturations decrease  
 216 in more aerosol-laden environments (see Fig. 5 b). For aerosols larger than  $0.1\text{ }\mu\text{m}$ , collectional activation becomes increasingly  
 217 important affecting aerosols in the range of  $0.16 - 2.5\text{ }\mu\text{m}$ ,  $0.13 - 0.65\text{ }\mu\text{m}$ ,  $0.11 - 0.46\text{ }\mu\text{m}$ ,  $0.092 - 0.33\text{ }\mu\text{m}$ ,  $0.11 - 0.28\text{ }\mu\text{m}$   
 218 for aerosol concentrations of 100, 600, 2000, 4000, and  $8000\text{ cm}^{-3}$ , respectively. Larger aerosols do not activate at all since  
 219 their critical radius is too large to be exceeded by diffusion or collection.

220 The collectional fraction of activations increases following a power-law relation toward larger radii, reflecting the higher  
 221 collision probability of larger particles. The collectional fraction reaches up to 100 % for the 100, 600, and 2000 cm<sup>-3</sup> simula-  
 222 tions at about 0.83, 0.54, and 0.42 μm dry aerosol radius, respectively, indicating a significant effect of collectional activation  
 223 on this part of the aerosol spectrum. For higher aerosol concentrations, collectional activation does not dominate, but still con-  
 224 tributes noteworthy with fractions up to 20 % and 10 % for aerosol concentrations of 4000 and 8000 cm<sup>-3</sup>, respectively. The dry  
 225 aerosol radius at which collectional activation reaches 100 % matches the maximum radii that can be produced by diffusion. To  
 226 create any larger particles, existing particles need to be merged. Accordingly, to activate aerosols with a larger critical radius,  
 227 collection must be inherently involved. For the 100 cm<sup>-3</sup> simulation, the largest radii produced by diffusion are about 30 μm  
 228 (Fig. 5 a), corresponding to a dry aerosol radius of 0.63 μm, which is close to the first dry aerosol radii exhibiting a 100 % col-  
 229 lectional fraction of activations. A similar agreement can be found for the simulations initialized with aerosol concentrations  
 230 of 600 and 2000 cm<sup>-3</sup>.

231 In general, the range of aerosols affected by collectional activation shifts toward smaller radii as the aerosols concentration  
 232 increases. This is primarily a result of the decreasing maximum radii that can be reached by diffusion alone (Fig. 5 a). Addi-  
 233 tionally, the supersaturation decreases too (Fig. 5 b), which decelerates diffusional activation and therefore favors collectional  
 234 activation. Since small aerosols are significantly more abundant than larger ones (Fig. 2), the number of aerosols that are po-  
 235 tentially activated by collection increases as a result of this shift, resulting in the larger collectional fraction of all activations  
 236 shown in Fig. 6.

237 How many collections are necessary for the collectional activation of one aerosol? Figure 8 displays the average number  
 238 of collisions that take place during a collectional activation. For dry aerosol radii up to 0.3 – 0.5 μm (depending on aerosol  
 239 concentration), only one collection is necessary to cause activation. For larger aerosols more collections are needed: up to 42  
 240 collections for the activation of aerosols with a dry radius of more than 1.0 μm. As illustrated in Fig. 3, not all of these collec-  
 241 tions involve the coalescence of inactivated aerosols, which would result in a increase of the number of activated aerosols. In  
 242 fact, some collections involve already activated aerosols, which results in a neutral or negative impact of collectional activation  
 243 on the total number of activated particles. To quantify the influence on the number of activated aerosols, the *effective activation*  
 244 *ratio* is defined: the net increase in the number of newly activated aerosols per collectional activation. Figure 9 displays the ef-  
 245 fective activation ratio calculated from all registered collectional activations. For an aerosol concentration of 100 cm<sup>-3</sup>, where  
 246 a large portion of aerosols needs multiple collections for activations (Fig. 8), the effective activation ratio is -1.2, i.e., more  
 247 activated aerosols are annihilated than produced to enable the final activation of one aerosol by collection. But for an aerosol  
 248 concentration of 600 cm<sup>-3</sup> and more, the effective activation ratio becomes positive and is approximately constant at 0.4, in-  
 249 dicated that on average 0.4 new activated aerosols are produced per collectional activation. This ratio has to be considered in  
 250 the interpretation of the collectional fraction of all activations (Fig. 6), indicating that the net effect of collectional activation is  
 251 actually smaller (or even negative).

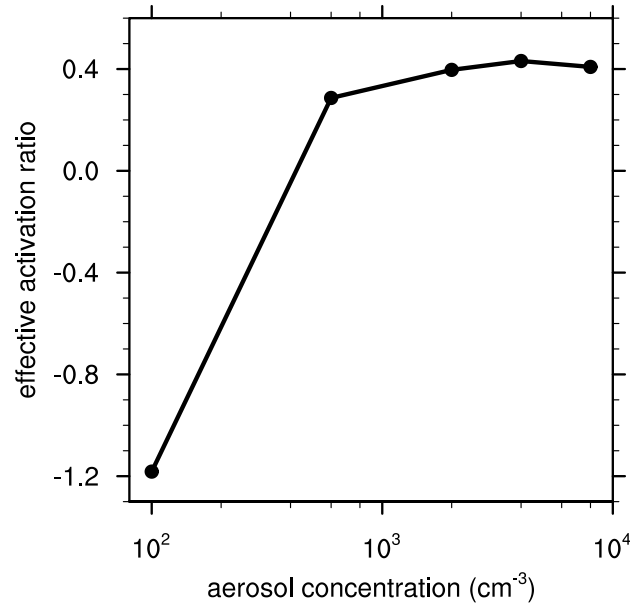
252 Although activation is dominated by collectional mass growth for larger aerosols, the growth by diffusion is still essential  
 253 to create sufficiently large particles to trigger collisions. Figure 10 a depicts the collectional fraction of mass growth needed to  
 254 grow beyond the critical mass for activation (for aerosols activated by collection). Note that the diffusional fraction of mass



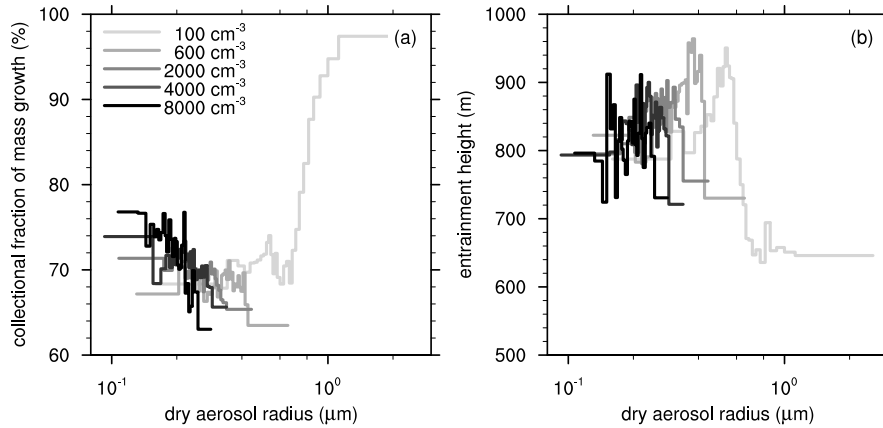
**Figure 8.** The average number of collections necessary to cause a collectional activation as a function of the dry aerosol radius for the analyzed aerosol concentrations (line brightness). The data has been binned; each bin contains at least 3 % of all registered collectional activations.

255 growth is the remaining fraction. For the smallest affected aerosols ( $\sim 0.1 \mu\text{m}$ ), the collectional fraction of mass growth is  
 256 about 75 % and decreases slightly to 65 % for aerosols of  $\sim 0.4 \mu\text{m}$ , indicating that a large contribution of diffusional growth  
 257 is necessary to produce sufficient large particles that are able to collide. The slight increase toward smaller radii indicates that  
 258 collectional activation is only possible for the smallest aerosols if they encounter a substantially larger particle. For aerosols  
 259 larger than  $1 \mu\text{m}$ , the collectional fraction increases rapidly to 97 %, which can be attributed to the large critical radii which can  
 260 be only exceeded by the collection of multiple droplets (cf. Fig. 8).

261 Figure 10 b displays the mean entrainment height of the particles involved in each collectional activation. Despite the largest  
 262 particles ( $> 0.6 \mu\text{m}$ ) in the most pristine case ( $100 \text{cm}^{-3}$ ), all collectional activations involve particles that have entered the  
 263 cloud well above the cloud base, which is located at 500 – 600 m. Accordingly, these particles miss the typical supersaturation  
 264 maximum located at cloud base (see Fig. 5 b), where the majority of aerosols activates by diffusion. Indeed, entrainment above  
 265 cloud base is generally favorable for collectional activation since these aerosols are mixed into an environment where larger  
 266 particles exist, triggering collisions among them more easily. For aerosols larger than  $0.6 \mu\text{m}$ , the average entrainment height  
 267 is located closer to the cloud base. Since multiple collections are necessary for their activation (see Fig. 8), the lower average  
 268 entrainment height is representative for the average entrainment height of all particles inside the cloud, which is the cloud base  
 269 through which most particles enter the cloud (e.g., Hoffmann et al., 2015).



**Figure 9.** The effective activation ratio (i.e., the net increase in the number of newly activated aerosols per collectional activation) as a function of aerosol concentration.



**Figure 10.** Collectional fraction of (a) the mass growth leading to collectional activation, and (b) the average entrainment height as a function of the dry aerosol radius for the analyzed aerosol concentrations (line brightness). The data has been binned; each bin contains at least 3% of all registered collectional activations.

## 270 6 Summary and discussion

271 The influence of collision and coalescence on the activation of aerosols has been studied using theoretical arguments and large-  
 272 eddy simulations (LES) with a coupled Lagrangian cloud model (LCM). The presented theory has shown that an unactivated

273 aerosol can be activated by the collection of particles with a comparably small amount of aerosol mass (i.e., particles consisting  
274 almost entirely of water), while the collection of large amounts of additional aerosol mass inhibits activation or even causes the  
275 deactivation of previously activated aerosols. The LCM simulations of shallow trade wind cumuli indicated that collectional  
276 activation becomes possible for aerosols larger than approximately  $0.1\ \mu\text{m}$  in dry radius, and its contribution increases with a  
277 power-law relation toward larger aerosols. In pristine conditions, collection is the only process for the activation of aerosols  
278 larger than  $0.83\ \mu\text{m}$  in dry radius at an aerosol concentration of  $100\text{cm}^{-3}$ . This boundary is shifted to smaller radii in more  
279 polluted environments (down to  $0.42\ \mu\text{m}$  at  $2000\text{cm}^{-3}$ ). The highest contribution of collectional activation to the total number  
280 of activated aerosols is found at an aerosol concentration of  $4000\text{cm}^{-3}$ , where 1 in 10000 activations is caused by collection.  
281 If the aerosol concentration becomes higher and hence the particles too small, collectional activation is inhibited and its contri-  
282 bution decreases again. Collectional activation frequently involves the collection of already activated aerosols reducing the net  
283 increase of newly activated aerosols per collectional activation to 0.4, while the remainder (0.6 activated aerosols) is annihilated  
284 during the activation process. Moreover, collectional activation affects predominantly particles that have been entrained above  
285 cloud base, i.e., above the region of the cloud where the highest supersaturations occur. Accordingly, these particles experience  
286 systematically lower supersaturations which prevents diffusional activation. Finally, it has been shown that the collectional  
287 activation rate increases almost linear with height, while the slope and the height, from which collectional activation starts,  
288 increase with the aerosol concentration.

289 In conclusion, this study revealed collision and coalescence as an additional process for the activation of aerosols. This  
290 process is not covered by commonly applied activation parameterizations (e.g., Twomey, 1959). But does this matter? First  
291 of all, with a maximum of 1 in 10000 activations, collectional activation can be safely neglected. But one can also argue  
292 that collectional activation is already (but implicitly) covered by standard cloud models: Activation parameterizations usually  
293 activate aerosols as soon as the critical supersaturation is exceeded, i.e., they neglect kinetic effects inhibiting the immediate  
294 activation of large aerosols, which need a certain time to grow beyond their critical radius. As pointed out by Chuang et al.  
295 (1997), this might overestimate the number of activated aerosols (or cloud droplets) since a certain fraction of the larger  
296 aerosols is falsely treated as activated. Following the argumentation of Nenes et al. (2001), these particles might act, however,  
297 as regular cloud droplets due to their large wet radii although they are not formally activated, and the estimated droplet number  
298 concentration is a valid measure for particles that behave like cloud droplets. And indeed, this study showed that a certain  
299 fraction of these formally inactivated particles are able to collide and coalesce, i.e., act as regular cloud droplets. Similarly,  
300 in standard cloud models, these falsely activated cloud droplets will experience the model's representation of collision and  
301 coalescence that might ultimately result in an implicit realization of collectional activation.

302 Accordingly, collectional activation is not of particular importance for determining the number of cloud droplets, but it  
303 indicates clearly the limits of Köhler activation theory. Without ambiguity, Köhler activation theory is only applicable to  
304 aerosols smaller than  $0.1\ \mu\text{m}$  in dry radius, while an increasing fraction of aerosols activates by collection at larger radii.  
305 Ultimately, the activation of aerosols larger than about  $1.0\ \mu\text{m}$  is entirely caused by collection (if it takes place at all). Therefore,  
306 the range between approximately  $0.1\ \mu\text{m}$  and  $1.0\ \mu\text{m}$  should be considered as a transition zone between (i) typical aerosols that  
307 need to experience sufficiently strong supersaturations to grow beyond the critical radius and (ii) so-called giant and ultra-

giant aerosols with sufficiently large wet radii to act like cloud droplets by triggering collision and coalescence without being formally activated (e.g., Johnson, 1982).

Finally, potential sources of uncertainty within this study shall be mentioned. First, the accuracy of the applied collection kernel is limited. The widely-used collision efficiencies of Hall (1980) for small particles ( $\lesssim 20 \mu\text{m}$ ) are slightly higher than other estimates (e.g., Böhm, 1992). An effect of this uncertainty might be the collectional activation of aerosols that are too small to collide in reality. Moreover, the collection kernel might not incorporate all processes relevant for collections among aerosols and droplets. For instance, Brownian diffusion might increase the collection of smaller particles (e.g., Ardouin-Dryer et al., 2015) but might not lead to collectional activation since it will predominantly add aerosol mass and only a small amount of water (cf. Section 2). Additional simulations neglecting turbulence effects on the collection kernel (not shown) have exhibited a similar spectral distribution of collectional activation, but indicated a smaller contribution to the total number of activated aerosols. Additionally, the collection algorithm itself might underestimate collisions due to the initial distribution of weighting factors (Unterstrasser et al., 2017), and the determined influence of collectional activation should be considered as a lower estimate. Second, the initialized aerosol distribution is always maritime, i.e., it includes a large fraction of large aerosols which are not part of continental air masses (e.g., Jaenicke, 1993) but are primarily affected by collectional activation as shown here. Accordingly, the collectional fraction of activations might be lower in environments which exhibit a smaller fraction of aerosols in the affected size range. Third, not all aerosols consist of (highly hygroscopic) sodium chloride although the size range affected by collectional activation is usually assumed to consist of sea salt (Jaenicke, 1993). Aerosols with a lower hygroscopicity would exhibit a smaller solution effect which is equivalent to a smaller dry radius of the sodium chloride aerosols examined here, i.e., the wet radius of these aerosols would be smaller and they would less likely cause collisions. Again, the range of aerosols affected by collectional activation would be shifted to larger dry radii.

## Appendix A: The Lagrangian cloud model

In this section, the basic framework of the Lagrangian cloud model (LCM) applied in this study as well as the extensions made to treat aerosol mass during collision and coalescence are described. One can refer to Riechelmann et al. (2012) for the original description, Hoffmann et al. (2015) for the consideration of aerosols during diffusional growth, and Hoffmann et al. (2017) for the most recent description of the LCM. This LCM, as all other available particle-based cloud physical models (Andrejczuk et al., 2008; Shima et al., 2009; Sölch and Kärcher, 2010; Naumann and Seifert, 2015), are based on the so-called *super-droplet* approach in which each simulated particle represents an ensemble of identical, real particles, growing continuously from an aerosol to a cloud droplet. The number of particles within this ensemble, the so-called *weighting factor*, is a unique feature of each particle, which is considered for a physical appropriate representation of cloud microphysics within the super-droplet approach.

The transport of a simulated particle is described by

$$\frac{dX_i}{dt} = u_i + \tilde{u}_i - \delta_{i3} w_s, \quad (\text{A1})$$

where  $X_i$  is the particle location and  $u_i$  is the LES resolved-scale velocity at the particle location determined from interpolating linearly between the 8 adjacent grid points of the LES. A turbulent velocity component  $\tilde{u}_i$  is computed from a stochastic model based on the LES sub-grid scale turbulence kinetic energy (Sölch and Kärcher, 2010). The sedimentation velocity  $w_s$  is given by an empirical relationship (Rogers et al., 1993). Equation (A1) is solved using a first-order Euler method.

As described in Hoffmann et al. (2015), the diffusional growth of each simulated particle is calculated from

$$r \frac{dr}{dt} = \frac{S - S_{\text{eq}}}{F_k + F_D} \cdot f(r, w_s), \quad (\text{A2})$$

where  $r$  is the particle's radius and  $S$  terms the supersaturation within the grid box, in which the particle is located. Curvature and solution effects are considered by the equilibrium supersaturation

$$S_{\text{eq}} = \frac{A}{r} - \frac{b \cdot m_s}{r^3}. \quad (\text{A3})$$

The factor  $f$  parameterizes the so-called ventilation effect (Rogers and Yau, 1989). The coefficients  $F_k = (L_v / (R_v T) - 1) \cdot L_v \rho_l / (T k)$  and  $F_D = \rho_l R_v T / (D_v e_s)$  represent the effects of thermal conduction and diffusion of water vapor between the particle and the surrounding air, respectively. Here,  $k$  is the coefficient of thermal conductivity in air,  $D_v$  is the molecular diffusivity of water vapor in air,  $L_v$  is the latent heat of vaporization, and  $e_s$  is the saturation vapor pressure. Equation (A2) is solved using a fourth-order Rosenbrock method.

Collision and coalescence are calculated from a statistical approach in which collections are calculated from the particle size distribution resulting from all super-droplets currently located within a grid box. These interactions affect the weighting factor  $A_n$  (i.e., the number of all particles represented by one super-droplet), the total water mass of a super-droplet  $M_n = A_n \cdot m_n$  (where  $m_n$  is the mass of one particle represented by super-droplet  $n$ ), and also the dry aerosol mass  $M_{s,n} = A_n \cdot m_{s,n}$  (where  $m_{s,n}$  is the dry aerosol mass of one particle represented by super-droplet  $n$ ). The latter interactions has been introduced for this study. The algorithm follows the *all-or-nothing* principle (Shima et al., 2009; Sölch and Kärcher, 2010), which has been rigorously evaluated by Unterstrasser et al. (2017) and has been recently implemented into this LCM by Hoffmann et al. (2017).

It is assumed that the super-droplet with the smaller weighting factor (index  $n$ ) collects  $A_n$  particles from the super-droplet with the larger weighting factor (index  $m$ ), with commensurate changes in  $M_m$ ,  $M_n$ ,  $M_{s,m}$ , and  $M_{s,n}$ . Since the weighting factor of the collecting super-droplet  $n$  does not change during this process, its wet radius

$$r_n = \left( \frac{M_n}{\frac{4}{3} \pi \rho_l A_n} \right)^{1/3} \quad (\text{A4})$$

and the dry aerosol radius

$$r_{s,n} = \left( \frac{M_{s,n}}{\frac{4}{3} \pi \rho_s A_n} \right)^{1/3} \quad (\text{A5})$$

increase. Additionally, same-size collections of the particles belonging to the same super-droplet are considered. These interactions do not change  $M_n$  and  $M_{s,n}$ , but they decrease  $A_n$  and accordingly increase  $r_n$  and  $r_{s,n}$ .

369 These two processes yield in the following description for the temporal change of  $A_n$  (assuming that the simulated particles  
370 are sorted such that  $A_n > A_{n+1}$ ):

$$371 \quad \frac{dA_n}{dt} \delta t = -\frac{1}{2} (A_n - 1) P_{nn} - \sum_{m=n+1}^{N_p} A_m P_{mn}. \quad (\text{A6})$$

372 The first term on the right-hand-side denotes the loss of  $A_n$  due to same-size collections; the second term the loss of  $A_n$  due  
373 to collisions with particles of a smaller weighting factor. The total water mass and the total aerosol mass of a super-droplet  
374 change according to

$$375 \quad \frac{dM_n}{dt} \delta t = \sum_{m=1}^{n-1} A_n m_m P_{nm} - \sum_{m=n+1}^{N_p} A_m m_n P_{mn}, \quad (\text{A7})$$

376 and

$$377 \quad \frac{dM_{s,n}}{dt} \delta t = \sum_{m=1}^{n-1} A_n m_{s,m} P_{nm} - \sum_{m=n+1}^{N_p} A_m m_{s,n} P_{mn}, \quad (\text{A8})$$

378 respectively. In both equations, the first term on the right-hand-side denotes the increase of  $M_n$  or  $M_{s,n}$  by the collection of  
379 water or dry aerosol mass from super-droplets with a larger weighting factor, while the second term describes the loss of these  
380 quantities to super-droplets with a smaller weighting factor. The function  $P_{mn}$  controls if a collection takes place:

$$381 \quad P_{mn} := P(\varphi_{mn}) = \begin{cases} 0 & \text{for } \varphi_{mn} \leq \xi, \\ 1 & \text{for } \varphi_{mn} > \xi, \end{cases} \quad (\text{A9})$$

382 where  $\xi$  is a random number uniformly chosen from the interval  $[0, 1]$  and

$$383 \quad \varphi_{mn} = K(r_m, r_n, \epsilon) A_n \delta t / \Delta V \quad (\text{A10})$$

384 is the probability that a particle with the radius  $r_m$  collects one of  $A_n$  particles with the radius  $r_n$  within a volume  $\Delta V$  during  
385 the (collection) time step  $\delta t$ . The collection kernel  $K$  is calculated from the traditional collision efficiencies as given by Hall  
386 (1980), and includes turbulence effects by an enhancement factor for the collision efficiency by Wang and Grabowski (2009)  
387 as well as parameterizations for particle relative velocities and changes in the particle radial distribution based on Ayala et al.  
388 (2008). These turbulence effects are steered by the kinetic energy dissipation rate  $\epsilon$  calculated in the LES subgrid-scale model  
389 (Riechelmann et al., 2012). The parameterizations by Ayala et al. (2008) are a direct function of  $\epsilon$ ; the tabulated values of the  
390 enhancement factor for the collision efficiency by Wang and Grabowski (2009) are interpolated to the present value of  $\epsilon$ . The  
391 equations (A6) – (A8) are solved using a first-order Euler method.

392 *Acknowledgements.* The author thanks Siegfried Raasch and Katrin Scharf (both of the Leibniz Universität Hannover) for their helpful  
393 comments on the manuscript. This work has been funded by the German Research Foundation (DFG) under grant RA 617/27-1. Simulations  
394 have been carried out on the Cray XC-40 systems of the North-German Supercomputing Alliance (HLRN). The applied LES/LCM model is  
395 freely available (revision 1954, <http://palm.muk.uni-hannover.de/trac/browser/?rev=1954>). Additional software developed for the LES/LCM  
396 model as well as the analysis is available on request.

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