Mexico City, April 4, 2017

In this document, we provide a point by point response to all referee comments and specify all changes made in the revised manuscript. The additions are marked in blue both in this document and in the revised manuscript.

Section 1: Response to Referee # 1 comments and modifications made to the manuscript (marked in blue):

Anonymous referee # 1

1. A system with five initial particles is indeed very small (Fig 2). I assume this result is shown for the purpose of demonstrating the method, it is confusing, however, because the system is too small to be of relevance.

Reply to Reviewer:

Yes, as was remarked by the reviewer, this result (with only 5 particles) is shown for the purpose of demonstrating the method. As the system in this case has only 6 possible configurations, it is much easier to explain the details of the algorithm. **In the revised version it will be emphasized that the objective of this section is to demonstrate the method.**

Changes made in the revised manuscript:

In section 2 of the revised manuscript (**"Overview of previous results: Numerical solution of the master equation"**), now it is emphasized that the objective of this simulation is to demonstrate the method.

Line 106: "The objective of this section is to present a description of the algorithm. A more detailed explanation of the method can be found in Alfonso (2015), and only a brief summary is presented here."

Line 121: "The procedure is illustrated for a system with 5 monomers in the initial state, only for the purpose of demonstrating the method. As the system in this case has only 6 possible states, it is much easier to explain the details of the algorithm."

2. The Tanaka/Nakazawa equation, which the authors use to calculate the gel mass, is not approximate. It requires, however, a trial-and-error procedure to determine the correct value of i_1 in Eqs 14 and 15. This is because Tanaka/Nakazawa depends on the mean distribution to obtain the gel fraction. If one has access to individual distributions, as the authors have, there is a simpler method: calculate the maximum mass in each individual distribution and obtain their average by weighting each value by the probability of the distribution.

Reply to Reviewer:

As a matter of fact, we follow a Monte Carlo version of the procedure detailed by the referee, in order to calculate the expected value of the gel mass from Monte Carlo simulations (see equation 16). In this case we have access to the empirical largest droplet distribution at each time. For a fixed time, this distribution is obtained by calculating the mass of the largest droplet in each realization of the Monte algorithm (the sample length is the number of realizations of the stochastic algorithm). The expected mass of the gel is the ensemble mean over all the realizations of the Monte Carlo process (See Eq. 16).
Within the master equation approach, we have access to the joint probability distribution of the random variables n_1, n_2, n_3,...,n_N, but in order to calculate the average for the largest droplet mass, we would need to calculate the distribution of the maxima. Then, the distribution of the largest droplet (before the sol-gel transition) would be a Gumbel distribution. In the current state of our model, further work is needed in order to calculate the largest droplet distribution.

3. Finite size is not necessary for gelation to occur. The solutions converge when the size of the system becomes large, though these solutions cannot be obtained by traditional

KCE and instead require the methods of Lushnikov (2004) or Matsoukas (2015). This means that finite systems, even with as few particles as 40, may be adequately described by these solutions without the need for a detailed (and costly) solution of the master equation.

Reply to Reviewer:

Yes, we agree with the reviewer that these results may be adequately described without the need for a detailed (and costly) solution of the master equation. However, the analytical techniques developed by Lushnikov (2004), and Matsoukas (2015) work only for a special type of kernels (in that case, when the probability of collision is proportional to the product of the masses). Our method (although it can be computationally expensive) works for any type of kernels.

Changes made in the revised manuscript:

The advantages of our method in compared with the analytical approaches developed by Lushnikov (2004), and Matsoukas (2015) are now briefly discussed in section 5 of the revised manuscript (Discussion and Conclusions):

Line 361: "To conclude, it is necessary to emphasize that our method (although it can be computationally expensive) works for any type of kernels, whereas the analytical techniques developed by Lushnikov (2004), and Matsoukas (2015) work only for very special cases."

4. The complete phase space of a population with N=40 monomers contains 37338 states. Do the authors solve the Master equation for all of these? Some details need to be offered regarding this calculation.

Reply to Reviewer:

Yes, we must solved the master equation for the 37338 states. For each state we have to solve the finite difference equation (5), or an equation similar to Eq. (6), but with 40-dimensional state vectors instead of 5-dimensional ones, and of course, a much more complex r.h.s. As suggested by the reviewer, our revised version will include some details of the calculations for this case.

Changes made in the revised manuscript:

In section 3 of the revised manuscript, we provide a brief explanation of the calculations for this case:

Line 196: "The complete phase space of a population with N=40 monomers contains 37338 states, and the master equation must be solved for the 37338 states. Then, for each state there is a finite difference equation (5), or an equation similar to Eq. (6), but with 40-dimensional state vectors."

Section 1: Response to Referee # 1 comments and modifications made to the manuscript (marked in yellow):

Anonymous referee # 2

General comments of the referee:

In this paper, stochastic effects in the collisional growth of cloud droplets are studied in a small volume. Solutions of master equation are shown for a system of up to 40 droplets. The results differ from the deterministic Smoluchowski equation, particularly after the sol-gel transition. This effect was studied by other authors for simplified coalescence kernels (Bayewitz et al 1974, Lushnikov 2004 from manuscript's references list). The main novelty of this paper is in comparing the deterministic and stochastic approaches for a realistic coalescence kernel. It is surprising, that it is not clearly stated if, for a realistic kernel, the deterministic equation breaks down (i.e. does not conserve mass) after the critical time, as is in the case of product kernel. Table 2 should contain results of the deterministic approach, like Tab. 1 does. From the cloud physics perspective, it is interesting to see, that for a realistic coalescence kernel, the critical time is more than 20 minutes. It is unlikely that such a small volume within a cloud would remain unmixed for that long, e.g. because of sedimentation. Therefore, using

larger simulation cells and the Smoluchowski equation seems to be vindicated. On contrary, authors suggest that the Smoluchowski equation cannot explain spectral broadening. Some additional comments on that matter would be welcome.

Reply to some aspects of the General Comments:

1) **Table 2 should contain results of the deterministic approach, like Tab. 1 does.**

   Changes made in the revised manuscript: Table 2 now contains results of the deterministic approach as suggested by the referee.

Table 2. Expected gel mass calculated from the SSA and the master equation. Simulations were performed for the hydrodynamic kernel.

Time (seconds)	Gel mass (SSA)	Gel mass (Master equation)	Gel mass (KCE)
1200 sec.	1.71×10^{-7} g	1.79×10^{-7}g	3.21×10^{-8}g
1800 sec.	3.34×10^{-7} g	3.37×10^{-7} g	3.63×10^{-7}g
2200 sec.	4.35×10^{-7} g	4.68×10^{-7} g	5.14×10^{-7} g

2) **About the critical time:**

In general, for concentrations larger than 30-40 cm^{-3}, smaller critical times must be obtained. For kernels proportional to the product of the masses, Malyshkin and Goldman (2000) demonstrated that the critical time decreases as a power of the logarithm of the initial number of particles $\tau_{\text{critical}} \sim 1/\log(N_0)$. For kernels relevant to cloud physics, we have a similar situation (a decrease in the time of occurrence of the phase transition as the number of particles in the initial distribution increases), although in this case, an analytical expression is not available such as that found by Malyshkin and Goldman (2000).

For the hydrodynamic kernel considering 40 monomers in the initial distribution (20 droplets of 17 μm in radius, and 10 droplets of 21.4 μm), the critical time was found about 1310s. Therefore, in the analyzed case the number of drops in the initial bidisperse spectrum was set equal to 30 drops. This suggests that for droplet concentrations in the range of 50-100 drops per cm^3 the sol-gel transition time will be much lower. For example, the critical time was calculated for the hydrodynamic kernel considering 50 droplets (a total of 70 monomers) in the initial distribution (30 droplets of 17 μm in radius, and 20 droplets of 21.4 μm). The critical time was estimated from Monte Carlo simulations by calculating the maximum of the standard deviation for the largest droplet mass and was found equal to 750 sec.

This problem was analyzed in detail in Alfonso et al. 2013 by using more realistic initial conditions. For example, for a turbulent cloud considering a cloud volume of 1 cm^3 and an initial bi-dispersed droplet distribution with 150 droplets of 10 μm in radius, and another 150 droplets of 12.6 μm in radius, the critical time was found equal to 1000 sec., confirming that for bidisperse initial distributions with concentrations greater than 40 cm^{-3} critical times would be obtained in the order of 1000 s.

Changes made in the revised manuscript:

Although the sol-gel transition time problem was analyzed in more detailed in Alfonso et al., (2010, 2013), a brief discussion of the topic is presented as suggested by the reviewer:

Line 270: "Although for the hydrodynamic kernel the critical time was in the order of 20 minutes, we must emphasize that, in general, for concentrations larger than 30-40 cm^{-3}, smaller critical times must be obtained. For example, for kernels proportional to the product of the masses, Malyshkin and Goldman (2000) demonstrated that for monodisperse initial distributions the critical time decreases as a power of the logarithm of the initial number of particles $\tau_{\text{critical}} \sim 1/\log(N_0)$, where N_0 is the initial number of droplets. For kernels relevant to cloud physics, we have a similar situation (a decrease in the time of occurrence of the phase transition as the number of particles in the initial distribution increases). A more detailed discussion of this problem for realistic collection kernels relevant to cloud physics can be found in Alfonso et al. (2010, 2013).”

3) On the Smoluchowski equation:

Reply to reviewer:

As discussed in the paper (see Discussion and conclusions):

1) The KCE it is not expected to be accurate when the initial numbers of particles (N_0) is small. Then, in systems of small populations the results of the kinetic deterministic equations approach may differ substantially from the stochastic means at the large end of the droplet size distribution.
2) Additionally, the KCE can fail even for $N_0 \gg 1$ if $K(i,j)$ increases sufficiently rapidly with i and j. Then, there is a transition from a continuous droplet distribution to a continuous distribution *plus* a raindrop embryo (sol-gel transition). As a results, the KCE fails to conserve the total mass of the system.

Therefore, even for larger droplet concentrations the KCE may fail if a sol-gel transition occurs. For example in Lushnikov (2004), the results of gel formation are showed for a large number of particles.

Changes made in the revised manuscript:

Line 361: “The failure of the KCE to capture the gel-formation could provide an explanation of the inability of explicit microphysics cloud models to explain the droplet spectral broadening observed in small, warm clouds. Therefore, even for large simulation cells, the use of the KCE is justified only in the absence of the sol-gel transition.

On the other hand, for the small volume approach, a model that considers the interaction between small coalescence volumes through sedimentation or other physical mechanisms for realistic collection kernels is needed. For a constant collections kernel, this theory was outlined by Merkulovich and Stepanov (1990, 1991) based on a scheme proposed by Nicolis and Prigogine (1977) for chemical reactions. Within this theory, the whole system is subdivided into spatially homogeneous sub-volumes (coalescence cells) that interact through the diffusion process, and the coalescence events are permitted only between droplets from the same sub-volume. As a result, we obtain a set of master equations for each sub-volume. Although very complex, it could be a starting point in order to consider the interactions between small coalescence volumes through different physical mechanisms."

Two new references were added:

Merkulovich,V. M.; Stepanov, A. S.: Statistical description of coagulation in finite spatially inhomogeneous systems. *Atmospheric research*, vol. 25, no 5, p. 431-444, 1990.

Merkulovich, V. M., & Stepanov, A. S.: (1991). Statistical description of coagulation in finite spatially inhomogenous systems (Part 2). *Atmospheric Research*, vol. *26,* no 4, p. 311-327, 1991.

Referee Comments:

1. Section 2 presents the numerical method used, which was already described in a previous paper. It could be removed from this manuscript, together with Figs. 1 and 2.

Yes, as the referee pointed out, the method was already described in more detailed in a previous paper. We included this section, with a simulation (with only 5 particles) for the purpose of demonstrating the method. As the system in this case has only 6 possible configurations, it is much easier to explain the details of the algorithm.

2. "Standard deviation of the mass of the largest droplet" defined by Eq. (11) is in fact standard deviation of mass divided by mean mass. It should rather be called the relative standard deviation.

Reply to Reviewer:

The corresponding modifications will be made on the revised version.

Changes made in the revised manuscript:

Line 174: “However, for a finite system (with no critical behavior), the relative standard deviation (standard deviation of mass divided by mean mass) of the mass of the largest droplet $\sigma(S_{\max})$ is expected to reach a maximum for a time close to $T_{gel} = \left[CM_2(t_0)\right]^{-1}$. “

3. Boxes with text in Fig. 3 and their respective "arrows" only blur the image. The same information is given in the caption.

Reply to reviewer:

The figure will be modified accordingly.

Changes made in the revised manuscript: The figure was modified accordingly.

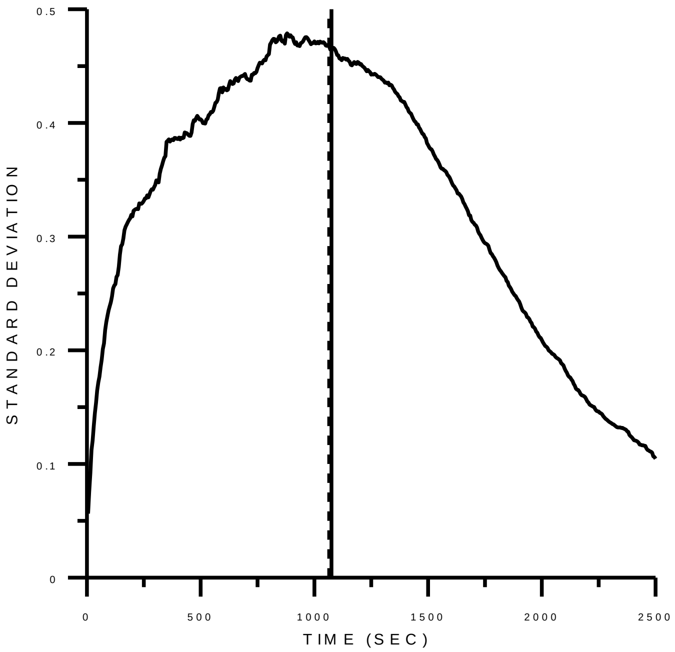


FIG 3. For the finite system, **the relative** standard deviation $\sigma(S_{\max})$ of the largest droplet mass versus time. The initial number of droplets was set equal to *N*=40 droplets of 17 μm in radius in a volume of 1 cm^3. Simulations were performed with the product kernel $K(i,j) = Cx_i x_j$ (with *C*= 5.49x10^{10} cm^3 g^{-2} s^{-1}), and N_r=2000 realizations of the stochastic algorithm were performed. The maximum value of $\sigma(S_{\max})$ is found to be 1065 sec. **(dashed vertical line),** and is very close to the sol gel transition **time (continuous vertical line)** for the infinite system (1075 sec.)

4. From my understanding, Figs. 4, 5, 8 and 9 present histograms of mass concentration of droplets within given size range (bin). Presenting them with continuous lines makes them seem like density distributions.

Reply to reviewer:

Actually, Figs. 4, 5, 8 and 9 present the expected values for each droplet mass (see Eq.7), that is, discrete droplet size distributions obtained from the master equation. In some of the figures, this distributions are compared with the equivalent size distributions obtained from the discrete kinetic collection equation (KCE).

5. Label on horizontal axes on Figs. 4 and 5 is "bin number", while on Figs. 8 and 9 it is "droplet radius". Is it the same thing?

Yes, it is the same thing. In Figures 8 and 9 we display the droplet radius for the corresponding bin-number.

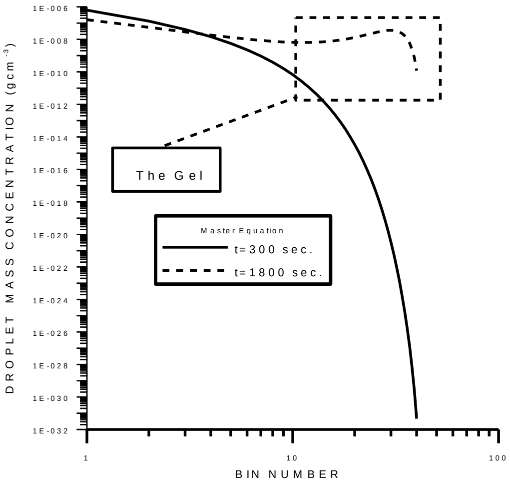
Changes made in the revised manuscript: The discrete bin grid defined in the model was briefly discussed in section 3.2.

> Line 199: "A discrete 40 bin grid was defined for our model. The mass for bin 1 is taken to be the mass of a 17 μm in radius droplet, and the mass of bin n is n times the mass of bin 1. Then, if all these 40 droplets in the initial distribution were to coalesce into a single droplet, the final droplet radius would be 58.14 μm in diameter and would belong to the mass bin 40.

6. Legend in Fig. 4(b) is titled "Master Equation", while one on Fig. 4(a) has no title. Do both figures present solutions of the master equation?

Yes, both figures present solutions of the master equation. The legend will be modified accordingly in order to avoid confusions.

Changes made in the revised manuscript: The figure was modified accordingly. Now the figure 4a is also titled "Master Equation".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1E-010
1E-012
1E-014
1E-016
1E-018
1E-020
1E-022
1E-024
1E-026
1E-028
1E-030
1E-032
DROPLET MASS CONCENTRATION (gcm $^{-3}$)
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10
100
BIN NUMBER
The Gel
Master Equation
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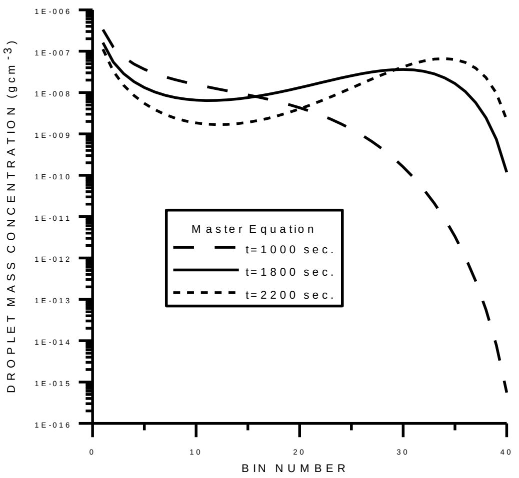
t=1800 sec.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1E-010
1E-011
1E-012
1E-013
1E-014
1E-015
1E-016
DROPLET MASS CONCENTRATION (gcm $^{-3}$)
0
10
20
30
40
BIN NUMBER
Master Equation
t=1000 sec.
t=1800 sec.
t=2200 sec.