FMs. Ref. No.: ACP-2017-269

Title: A 3D particle Monte Carlo approach to studying nucleation

We thank the referees for their careful reading and useful suggestions. Our answers are inserted into the reports in italics.

Furthermore, we have clarified a few issues in the paper, added additional material and improved language and structure of the paper.

Reviewer #1:

Köhn, Enghoff and Svensmark present a new 3-dimensional Monte-Carlo – based model for sulfuric acid clustering. Essentially, the model combines an extremely simplified parameterization for the cluster thermodynamics (and molecule-cluster or clustercluster interactions) with a sophisticated approach for simultaneously tracking a large number of molecules (and clusters) in 3-dimensional space. The authors speculate that "If each molecule could be tracked in a three dimensional space it might be possible to achieve new insights into the process of nucleation". I agree that this could indeed be possible, and was eagerly expecting to see such new insights in the results-section of the paper. Sadly, I found the paper entirely lacking in new insights, as it consisted solely of a (somewhat cursory and partially inconsistent) technical description of the model, and some (not particularly convincing) benchmarking. I'm not convinced this paper warrants publication as a stand-alone article in ACP - I would suggest the authors either submit a corrected and expanded version of technical description as a technical note somewhere, or alternatively combine it with simulations (e.g. on the proposed HSO4- clustering) that would actually provide some genuinely new insights.

We thank the referee for this estimation. Indeed, we agree that the current manuscript is a rather technical one and we have decided to withdraw it from ACP and submit it to Journal of Computational Physics.

Regardless of what the authors decide to do, I hope they take my comments below into account:

Technical comments/questions concerning the simulation details:

1) In equation 1 the motion of particles between two time steps is governed by a random step. Yet later (e.g. in discussing equations 5 & 6) the authors talk about the velocities of particles. What meaning do the velocities have if the particle motion is based on random numbers? How do the velocities from equations 5 & 6 enter into equation 1?

The referee is right. Although we have mentioned the velocities in the paper, we did not include them into our computational model. We have deleted the corresponding passages.

2)Surely the time step should be significantly *smaller* than the average time it takes for particles to diffuse the inter-particle separation? Setting the time step equal to this seems to risk numerical issues... Especially for the high-density studies where the time step used is now almost five times the average time! Sensitivity studies should definitely be performed to establish that the results are converged with respect to the time step.

The referee is right that the time step should not be too large to risk numerical issues. We have now chosen smaller time steps than $1/(2D_0 n^{2/3})$. We have specified this further in the paper.

3)What is the justification of using r=0.85 nm as the threshold for a particle being "nucleated"? This seems to be quite small for such a threshold, e.g. compared to any experimental nucleation study.

We have used this value in order to compare our nucleation rates with the ones by [Dunne et al., 2016. Global atmospheric particle formation from CERN CLOUD measurements. Science, vol. 354, pp. 1119–1124]. We have clarified this in the paper.

4)The authors cite and apparently make use of data from Yu et al 2005, which is (as the very title suggests) a sulfuric acid - WATER nucleation model. Yet they do not mention water anywhere in the paper. They are presumably following in Yu's footsteps and using a quasi-unary approach, where the effect of water is implicitly accounted for. But then they should specify this, and also give the relative or absolute humidity the simulations are (again implicitly) performed at. They might be tempted to answer that the RH is assumed to be 0% (which incidentally would leave the results atmospherically irrelevant). But then they can not use Dunne et al as comparison, because as that paper states: "For the purposes of our inorganic nucleation parameterization, we therefore assume that no nucleation occurs below 10% RH". So either the authors implicitly have water in their system, in which case A LOT of description on this is needed, or then they must abandon any comparison with the Dunne et al paper.

As in the paper by Yu et al., we have updated the model to include the water content implicitly through the molar fraction defined in the same paper. We have chosen a relative humidity of 50%. We have added all necessary information about how we have implemented the relative humidity implicitly.

5)As an additional comment to that above, the slope of the evaporation coefficient shown in Figure 1 is curiously flat compared to the original data from Yu et al 2005, (Figure 4 in that paper), especially when considering that the y-axis in the present paper is R and that in the Yu paper is number of molecules (which increases as R^3). The actual evaporation rate numbers are also curiously low especially if the intention is to model dry (RH 0%) sulfuric acid clustering, as water is well-known to stabilize the clusters (i.e. the evaporation rate for T=300K and RH 0% can hardly be LOWER than that at R=298 K and RH 50%, as given in Fig 4 of the Yu paper) .I'm also not convinced that it is even possible to obtain a completely "dry & pure" sulfuric acid vapor pressure, but I'd like to see the authors reply to the H2O issue before expanding on this further.

We have revised the calculation of the evaporation coefficient for a relative humidity of 50% and for different temperatures. We now made the mass, the radius, the surface tension of all particles as well as the concentration of sulphuric acid molecules vapor molecules a function of the mole

fraction.

Comments on the interpretation and comparison of results:

6)The authors correctly state that Monte Carlo models are well suited to capture rare events, of which nucleation certainly is an example. But are they actually capturing such rare events? In the beginning of section 3.3. the authors state that "As Fig. 3 and 5 show, the particle sizes in all considered simulations are smaller than 0.4 nm after 10 s which complicates the determination of the nucleation rate of particles with radii above 0.4 nm." I could say this more strongly: if no particles larger than 0.4 nm are formed then the nucleation rate of particles with radii larger than that is actually ZERO. So in other words the authors simulations are not actually showing nucleation (in which the particles continue growing and growing and growing after passing a critical size), just some limited initial clustering. The curve fitting of equations 8 and 9 seems to be an essentially meaningless exercise - the oscillations of the fitted rates, as well as the enormous - over 12 orders of magnitude - error bars from the fit are to me additional indications of this. Even if the curve fitting were somehow justified (for which I would like to see MUCH more justifications) the approach in my opinion destroys the original advantage of the MC method: instead of actually observing rare events, the authors are now back to the same sort of indirect fitting-based approach that plagues many other model types. Comparing to the Dunne et al parameterizations, the lack of actual nucleation observations is not actually very surprising: the simulation box size in the low-density (1E7 particles per cmˆ3) simulations is, if I understand correctly, 0.000125 cmˆ3, so with a run time of 10 s the nucleation rate would need to be on the order of 800 new particles per cm3 and s to (on average) see one nucleation event per simulation. I would suggest the authors redo their benchmarking simulations with conditions that should (e.g. based on the Dunne et al parameterization) actually lead to mutiple events per simulation, and then re-analyze their results using actual particle formation rates, not indirect fits - then there would actually be some genuine advantages to using a Monte-Carlo model.

With the updated model on the relative humidity and the corrected evaporation coefficients, we have not seen any large clusters for a temperature of 300 K, as expected. However, for temperatures of 200 K (see Figure 1 of the reply) and 238 K, there is a substantial number of clusters above 0.85 nm. We will include this into the new version of the paper. Hence, we now also calculate the nucleation rate for clusters above 0.85 nm.

7)Details should be given on exactly how the Dunne et al comparison numbers were obtained, this is currently not at all clear.

This is indeed a very good suggestion. We have added the parametrizations used by Dunne et al. into the manuscript.

8)The authors claim that "the implemented physics is sufficient enough to study the nucleation of neutral sulphuric acid clusters in order to benchmark our model". This may or may not be true, but given the issues described above, and the 13 orders of magnitude uncertainty in the fits even according to the authors own estimate, the claim is far from proven.

Actually, since we now observe nucleation for 200 K and 238 K, we calculate the nucleation rate by

actually counting clusters above 0.85 nm. This minimizes the many orders of magnitude uncertainty; for 300 K we conclude to have a nucleation rate of 0.

Figure 1: The size distribution of all particles after 50 s for n=10^7 cm^{-3} and T = 200 K.