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 #3:

Review on the manuscript “A 3D particle Monte Carlo approach to studying nucleation” by Christoph Köhn, Martin Bødker Enghoff, and Henrik Svensmark. The present manuscript deals with simulation on growth of sulphuric acid clusters. The authors call the modelling method Monte Carlo. I would avoid using such name in this context. Technically, method employs random number generator, so it can be called Monte Carlo method. However it does not give any hint on details of modeling. Furthermore, in molecular physics the term Monte Carlo simulations is reserved for the group of methods modelling equilibrium distribution functions of particular variables. In the manuscript such examples are given: Kusaka et al.(1998), and Kathmann and Hale (2001). I would call the employed method: simulation of random walk governed by diffusion equation. This remark is just a suggestion and has no influence on the referee’s decision.

We thank the referee for this suggestion. However, in other scientific areas, Monte Carlo codes refer to particle codes involving the random walk of electrons. One example, also mentioned in the introduction, is the motion of electrons in streamer discharges, e.g. in [C. Köhn and U. Ebert, 2014. The structure of ionizations showers in air generated by electrons with 1 MeV energy or less. Plasma Sour. Sci. Technol., vol. 23, 045001]. Hence, we have decided to keep the title as it is.

There is some confusion in description of the method. It is mentioned in the abstract and Eq. (6) says that the velocity of the merged particle is defined by conservation of momentum. On the other hand, according to the description of the method the initial velocities are not assigned to the molecules; neither positions nor the probability of sticking depend on the velocities. The particle positions are completely defined by diffusion equations and the velocity is just unnecessary detail in the simulations.

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 passanges.

It is not clearly explained how the evaporation is incorporated into modeling. The correct procedure is compare the value exp(- γt) to the generated random number r between 0 and 1. If exp(- γt) > r, the evaporation doesn’t happen, otherwise – yes. Perhaps, it is done so but just not said.

In order to check for evaporation we use the criterium $r < 1-\exp(-\gamma t)$, $r \in [0,1)$ which is

equivalent to the criterium mentioned by the referee. We have clarified this.

As far as I could deduce from the text all values are obtained from one single run (one realization of the random process). The spatial and size distributions and size from one single run are not comparable to experiments. It is necessary to have big number of realizations (I recommend 10 000 - 100 000 for smooth results) with different initial positions of molecules. The procedure for the calculating of the average nucleation rate is correct since the ensemble averaging can be substituted with the time averaging.

Of course, the statistics would be better if more simulation runs were performed and the average were taken. However, this is not crucial for the benchmarking and thus for our conclusions.

The major flaw in the manuscript is that movement of particles is considered as diffusional. It is well known that if ratio L/R (Knudsen number) much more than 1, the collision frequency between the particles is defined by the rate from the gas kinetic theory rather than by the diffusional rate constant; here L is the mean free path, R is the size of the particle. Despite that most of the way particles move in the diffusional regime at large Knudsen numbers the limiting stage for collision is the last step when the particles move in the free-molecular regime. Fuchs ("Mechanics of Aerosols", Pergamon Press, London, 1964) discusses this problem at length in the book. For particles as large as 0.85 nm, the pressure of 1 bar, and temperatures 200-300 the Knudsen number is roughly 40 – 60.

The mean free path of sulphuric acid clusters in air is approx. 10-60 nm [J.H. Seinfeld and S.N. Pandis, 2006. Atmospheric Chemistry and Physics. John Wiley & Sons, New Jersey. Table 9.5, p. 422] whereas the diffusion term is in the order of $(2D_0 \Delta t)^{1/2} \approx 10$ *μm for* $D_0 = 10^{-6}$ m^2/s *and* $\Delta t = 100$ *μs. Hence, since the mean free path is much smaller, we argue that the diffusion controlled approach is still valid.*

The method employed in this study is not novel. If it were applied properly, it should give results identical to the ones from the solution of Smoluchowski problem since no new physics is introduce into the model.

With the corrected model we now observe clusters with sizes above 0.85 nm. Figure 1 of this reply shows the size distribution after 50 s for a temperature of 200 K. We now calculate the nucleation rate based on counting the actual particle number.

I do not recommend the manuscript for publication in the journal Atmospheric Chemistry and Physics.

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