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 #4:

This paper attempts a Monte-Carlo study of the vapor-phase evolution of sulfuric acid molecules under clustering and evaporation of monomer. These species are treated in the paper as spheres with initial monomer size of 0.15nm and nucleation rate derived from the formation of clusters at 0.85nm. It is not clear what the critical nucleation cluster size is, but it is presumably smaller than 0.85nm. Initial gas-phase concentrations are at 10ˆ7 and 10ˆ8 sulfuric acid molecules per cc in an ambient atmosphere of pressure 1 bar.

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.

Under the simulated conditions the mean-free path is about 70nm, which is much larger than even the 0.85nm size considered for nucleation to occur. Therefore clusters are in the free-molecular size regime (mean free path much larger than the particle size). The diffusion controlled regime occurs when the mean free path is much smaller than the particle size. So it is not clear why the authors use the diffusion-controlled model of Fransaer and Penner, cited on page 12 line 14, which applies to Brownian-like diffusive motion of individual molecules or ions in dilute aqueous electrolytes. Unfortunately, this is a problem with the manuscript that affects the growth law throughout and makes it unacceptable for publication.

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 $(2D_0\,\Delta t)^{1/2} \approx 10\ \mu m$ *for* $D_0 = 10^{-6}\ m^2/s$ *and* $\Delta t = 100 \mu s$*. Hence, since the mean free path is much smaller, we argue that the diffusion controlled approach is still valid.*

Additional comments: The authors appear to be dealing with a much simpler problem than they treat: The clusters are treated as spheres and there is no explicit structure or inter-molecular potential assigned to them. The authors might as well be treating clusters in the capillarity approximation of nucleation theory, which treats clusters as spheres with sharp interface and no inherent structure other than that of the bulk liquid (for density) and a surface tension for evaporation rate from the Kelvin relation that is much like the author’s Eq. 7.

The referee is right in the sense that we do not include the structure or the intra-molecular potential of clusters. However, we do take into account the admixture of water as well as the cluster evaporation which depends on the strucutre of the clusters. In that case, we do include the strucutre implicity which is sufficient to determine the position of particles in 3D space as well as the size distribution.

Such simplicity suggests that collisions might be tracked through Fokker-Planck type diffusion-drift coagulation/evaporation equations without knowing their precise positions in 3D – as only a detailed dynamics would require. Then MC could be used for calculation of arrivals and departures based statistically on cluster number densities and evaporation rates. Presumably the authors would end up with a Boltzmann distribution of cluster size. The reviewer is not an expert in molecular simulations but it does seem that detailed knowledge of 3D molecule/cluster position is overkill for spherically symmetric molecule/cluster interaction. Moreover, such detailed knowledge might be washed out anyway given the assumption of randomness that is already part of the MC method.

It is true that there are other ways to obtain the size distribution of the clusters. However, the aim of the present manuscript is to introduce a new model to model nucleation and the evolution of the size distribution.

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