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 #2:

The authors present a Monte Carlo scheme for simulating the evolution of a set of particles in a spatial volume, designed to represent sulphuric acid monomers and their clusters. The particles combine together when a stochastic spatial move takes them within an overlap distance of one another, and they fragment with the emission of a monomer according to a stochastic thermal evaporation process. In my opinion, there are numerous problems with this manuscript and I cannot recommend publication.

The authors state in the introduction that the technique might possibly provide ’new insights into the process of nucleation’. However, I am not persuaded that this has been achieved, and the authors do not enlarge on this claim in the conclusions. The MC method presented is essentially a numerical implementation of the stochastic evolution of a cluster size distribution, and I suspect that the outcomes are consistent with much less elaborate treatments, such as a simple Becker-Doering rate equation approach.

So far what we get out of the model is indeed nucleation rates and size distributions which can be obtained faster using other methods, as the referee mentions. We do this in an attempt to validate the model. If we are convinced that the model produced reliable results regarding the parameters where we can compare to other peoples work then we can, with some confidence, start looking for any new information that can be gained from seeing the entire 3D-picture. We have added this now to the conclusion and outlook section.

Namely, the events are infrequent in the situations considered (and probably do not give rise to spatial correlations between potential collision partners) and are dominated by single monomer attachment and detachment processes rather than cluster-cluster collisions. If the reported cluster size distributions were compared with the results of such a rate equation scheme, involving the solution of a few ODEs for a set of spatially averaged cluster populations, I would expect to find the outcomes compatible. This would have been a very useful benchmarking procedure to assess the value of using a 3D approach.

We agree that this would have been a possible approach. However, we think that the comparison *with Dunne et al. is a valid approach, too.*

The updating of the configuration is not entirely clear. In a couple of places, the authors refer to the velocities of the particles. However, the dynamics, in equation (1), seems to involve stochastic moves in spatial position only. What is the purpose of considering the velocities? Is the update a combination of ballistic motion and diffusive jumps? The discussion seem to imply only diffusion.

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.

Furthermore, the selection of the direction of diffusive motion does not seem right. The spherical polar angles theta and phi are sampled uniformly from their respective ranges (page 3, line 10). This is fine for phi, but the angle theta should be sampled nonuniformly (in proportion to sin(theta)) in order to provide a uniform sampling of the 4 pi of solid angle. Uniform sampling of theta improperly favours the polar regions of a globe rather than the equator and if this is indeed the scheme implemented, then the particles will tend to diffuse up and down (with respect to the z axisof the simulation cell) and not sideways. Since the MC scheme is intended to be physically representative, this is a significant drawback. But perhaps this is a typo in the manuscript.

Yes, the referee is right. It should have been $\vartheta=\arccos(2r_3-1)$*. We have corrected for this in our manuscript as well as in our code.*

The authors are apparently unaware that other 3D ’brute force’ numerical simulations have previously been carried out to investigate the process of nucleation. These have involved molecular dynamics rather than (kinetic) Monte Carlo configurational evolution, but the aim is very similar, as is the computational expense. Recent papers (2014-16) by Diemand, Angelil and the Tanakas should be consulted, and older studies by Wedekind et al (2006-2007).

We do not disagree that there have been previous papers about molecular dynamics. However, so far there has not been any molecular dynamics approach towards the nucleation of sulphuric acid clusters. We mention now papers [J. Diemand et al., 2013. Large scale molecular dynamics simulations of homogeneous nucleation. J. Chem. Phys., vol. 139, 074309. R. Angelil et al., 2015. Homogeneous SPC/E water nucleation in large molecular dynamics simulations. J. Chem. Phys., vol. 143, 064507] in the introduction.

The authors seek to compare their results with experimental values of nucleation rates for sulphuric acid clusters of radius 0.85 nm, even though no clusters of this size are generated in their simulations. In order to make this assessment, they fit an exponential function (equation (8)) to the cluster size distribution at each timestep and extrapolate to the target size. This is not a convincing approach since it is likely to introduce large uncertainty. But even if there were reason to use such a function, the nucleation rate is not a mean population at a certain size divided by the elapsed time, as given in equation (9); instead it is a current or flow of clusters through that size. In an asymptotic stationary state, the definition used by the authors would produce a nucleation rate of zero. Only if there were a maximum size cluster in the scheme, receiving clusters from the size below but not losing them to sizes above or below (i.e. equivalent to a cluster sink), would such a definition be appropriate. The extracted nucleation rates are stated to be compatible with experimental values of sulphuric acid, within error bars, but the statistical errors quoted in Table 1 are very large, and the claim of consistency is weak.

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.

Finally, I have reservations about the assumed evaporation rate in equation (7). The authors have introduced a factor of R_1/R on the grounds that the saturated vapour pressure over a curved interface is lower than that over a flat interface, such that the evaporation rate should increase as the radius decreases. But it is the Kelvin term (the exponential in equation (7)) that represents this effect: I do not see why a new factor is required. The Kelvin term is a consequence of the capillarity approximation used in the construction of the excess free energy of cluster formation from monomers, and so the extra factor corresponds to a non-classical term (in the sense of an addition to Classical Nucleation Theory (CNT)) in the excess free energy. The introduction of such a new term has not been justified.

Thank you for making us aware that the size dependency is included in the exponential. We have revised the whole calculation of the evaporation frequency. We have added these changes in the paper.

In passing, setting the evaporation rate equal to the Kelvin form ought to lead to a nucleation rate consistent with CNT, at least in some circumstances, and this would also be a useful benchmark exercise. Another useful benchmark would be to compare the simulations at 200 K with known analytical results for a Brownian coagulation model.

An analytical benchmark would certainly also be useful, but has not been included at this stage.

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