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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations” *by* M. J. McGrath et al.

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General comments.

Referee 1 has provided some very insightful comments, and by addressing them fully we are convinced that the quality of our manuscript is improved.

“Works that are cited as "in preparation" (Vehkamäki et al., 2011) must be submitted or published before the present manuscript can be published.”

This manuscript has been submitted to the Journal of Chemical Physics, and we are awaiting reviewer comments.

“Why was the manuscript submitted to ACP rather than to Geoscientific Model Development (GMD)? It appears GMD would be a more appropriate venue.”

GMD is a well-respected journal, and certainly an appropriate venue for publication of this manuscript. However, we felt that the use of quantum mechanically-derived evaporation rates, as well the dimethylamine (DMA), sulphuric acid, and ammonia constituents warranted submission to the broader Atmospheric Chemistry and Physics audience, in particular the insights found for the effects of ammonia vs. DMA on sulphuric acid cluster growth.

“The version of ACDC presented in the manuscript describes clusters with two constituent species (an acid and a base). Without accounting for water in the clusters, the model does not represent atmospheric clusters. Please explain in the text that water needs to be added in ACDC, and add a brief outline of the required development work.”

Clarification of this has been added on Page 25275. The existing sentence, “Water is not included in the system, because sufficient quantum chemical data for clusters containing water, sulfuric acid, and a base are not yet available. ” has also been moved to the next paragraph.

“Water is not included in the system, because sufficient quantum chemical data for clusters containing water, sulfuric acid, and a base are not yet available . While this omission means that we are not examining a true atmospheric system in this manuscript, this is no shortcoming of the ACDC model itself. Rather, the effort required to compute the cluster free energies of water/acid/base clusters using quantum mechanical methods is quite significant for the clusters sizes we are exploring here. In fact, we have run test calculations on the quaternary H_2SO_4/NH_3/DMA/H_2O system, for both neutral and negatively charged molecules, using both quantum mechanical free energies and those derived from the liquid drop model. The qualitative behavior of the system was not altered by the inclusion of water, although further simulations need to be performed when the quantum mechanical results for water are available.”

“Please add a brief note in the manuscript that the particle formation rate (the flux out of the system, Eq. 5) is not necessarily the nucleation rate - readers may easily mix up these two. If possible, please add the definition of the nucleation rate within ACDC.”

This is an important distinction, and we attempted to emphasize this on page 25275, including the definition of J used in ACDC. We have added the following sentence on the next page to make this more clear.

“In addition, the particle formation rate given by Eq. 5 is not the nucleation rate, and therefore care must be taken when comparing the values of J reported here to true nucleation rates.”

“Please add a brief note in the manuscript that explains why ACDC is used as a steady state model - it would seem that it could just as well be used as a timeresolved model.”

This is true. The following has been added on page 25267.

“As ACDC is solving the birth-death equations explicitly, the concentrations of all constituents are known as a function of time. In the interest of keeping the amount of material presented in this article concise, here we report only the steady-state results. The time-dependent data are, however, readily available and will be used as required by future applications. ”

Specific comments:

Page 25270, line 20: "As soon as these clusters form, they are "lost" (the material cannot reenter the system). In the case where all the clusters on the boundary are unlikely to evaporate to smaller sizes, this loss does not affect the system significantly."

- *The clusters which leave the system represent a condensation sink for the species in the gas phase which the clusters form from, and a coagulation sink for the clusters in the system. How did you determine that this does not affect the system significantly?*

For our system, we explored the effect of the boundary conditions in Figure 6 (including and removing these sinks), concluding that they did not have a large effect for the “standard” conditions we are interested in, but showing that there can be a significant effect if both the concentrations of DMA and sulphuric acid are relatively high (10^{15} m^{-3}).

You could declare that what you are interested in is the steady state particle formation rate calculated under the following conditions:

- *the clusters in the system are in steady state against formation from the gas phase growth by condensation of gas phase molecules and cluster collisions*
- *decay due to evaporation of molecules and cluster breakup*
- *coagulation onto pre-existing aerosol*
- *the concentration of clusters outside of the system is zero*

This would solve the issue with clusters outside of the system for which you solve the differential equations.

We have added the following to the manuscript on page 25276, following the explanation of the particle formation rate used in ACDC.

“In practice for our system of interest, the “steady state” means that the clusters in the system are in a steady state against formation from the gas phase, growth by condensation of gas phase molecules and cluster conditions, decay due to evaporation of molecules and cluster breakup, and coagulation onto pre-existing aerosols. The concentration of the clusters outside of the system is assumed to be zero.”

Page 25272, line 6: "This equation keeps track of the concentration of a generic negative ion (it currently has the mass and molecular volume of an oxygen molecule, as the oxygen concentration in the atmosphere is many orders of magnitude above the sulfuric acid concentration)."

This is a viable assumption at the current development stage of ACDC, but please keep in mind that anions in the troposphere are on average much heavier than O2 , and in the course of the ion chemistry leading up to these clusters, ions will be lost due to recombination. All of this will reduce the rate of particle formation from ions.

This is a good point, and future work containing ions will attempt to account for this more carefully. The sentence has been modified in the following manner.

"This equation keeps track of the concentration of a generic negative ion (it currently has the mass and molecular volume of an oxygen molecule, although the precise mass may be heavier in the troposphere)."

Page 25272, line 14: "... every neutral cluster has a loss term and every ionic cluster has a source term corresponding to the third term on the right in Eq. (4)."

... every neutral cluster has a loss term and every ionic cluster has a source term corresponding to the third term on the right in Eq. (4), which represents attachment of ions to neutral molecules.

This change has been made.

Page 25272, line 20: "It is well-known that the collision rate coefficient between ionic and neutral clusters is higher than between two neutral clusters (Tammet and Kulmala, 2005)."

The formulation, juxtaposed with the reference to Tammet and Kulmala (2005) must raise eyebrows - if not the stiff upper lip - to my knowledge, this has been well-known for more than one hundred years (Langevin, 1905). Credit where credit is due.

This change has also been made.

Page 25273, line 10: "Preliminary results have shown that neither of these more realistic descriptions give results that are outside of the estimated uncertainty range of the results obtained from using a constant factor. Similarly, in the current model collisions of ionic clusters with the wall are enhanced by a factor of two." This passage is a real problem child:

- *The preliminary results are not discussed*

- *No explanation is given how the uncertainty range was estimated*
- *According to the text on page 25270, wall losses are not included, but here, collisions of ionic clusters with the wall are enhanced by a factor of two - how can this be reconciled?*

The issue of ionic clusters has raised the eyebrows of all three referees, and rightfully so as no results were given. This section is, in truth, a problem child. It is important to emphasize that the ACDC model and the data it uses are separate issues. As this manuscript was intended to be a complete description of the model, and as the model can incorporate ionic clusters, we felt it most beneficial to include this section here; consequently, one would only need to cite a single manuscript when discussing ACDC. The ionic free energies have not yet been completed, while the neutral clusters have. Therefore, we have decided to keep the model description while removing references to the preliminary tests.

Given that, the three points raised by this referee can be addressed as follows. First, the preliminary results are no longer discussed, but they will be when the full set of ionic data is available. This also removes references to the uncertainties. Third, this was an error, and should have referred to the coagulation sink. That sentence now reads “Similarly, in the current model the coagulation sink of ionic clusters is enhanced by a factor of two.”

The final paragraph of the ionic section now reads (including other corrections),

“It is well-known that the collision rate coefficient between ionic and neutral clusters is higher than between two neutral clusters (Langevin, 1905). In sulphuric acid containing systems, this is due to the fact that the ion interacts strongly with the permanent dipole moment of the acid molecule, resulting in more attractive forces and a larger collision cross-section. Consequently, Eq. (2) needs to be multiplied by an enhancement factor in the case that one of the clusters contains an ion (if both of the clusters contain ions of the same polarity, electrostatic repulsion will prevent then from colliding, so such collisions are not allowed in ACDC). The exact form of the enhancement factor is not well known, and several formulae exist. In ACDC, three factors are currently possible. The first one is to simply multiply every ion-neutral collision (and, because of detailed balance, every evaporation of an ionic cluster) by a constant factor (taken to be equal to ten). The second factor is given by Hoppel and Frick (1986), and depends on the size of the ionic cluster (using the rational that the more solvated the ion, the less impact it should have, so the value should tend towards unity as the cluster increases). The final option is given by Lovejoy et al. (2004), and depends also on the nature of the colliding cluster. Similarly, in the current model the coagulation sink of ionic clusters is enhanced by a factor of two. In future work containing ionic clusters, this effect will be examined in more detail."

Page 25274, line 7: "accurate approximation"

That's a touch too much - either it is accurate or it is an approximation.

We have changed this to "a valid assumption when solving the birth-death equations and considering only monomer collisions and evaporations."

Page 25275, line 14: "... the operative definition for the particle formation rate in smaller systems is somewhat unclear. If it is defined as the flux of all material out of the system, the rates produced in this system might be artificially inflated."

The formation rate of a particle can be defined unambiguously - the problem is that it may not be possible to calculate it according to the definition. However, at least with ACDC, the problem can be solved if following the suggestion in my comment to line 20 on page 25270 (see above).

The text on page 25275 has been modified, and now reads,

"As noted above, in smaller systems the flux out of the system does not give the actual particle formation rate. Since the evaporation of clusters outside the simulation system is artificially prevented, the simulated rate is larger than the actual formation rate if the clusters leaving the simulated system are not large enough to be stable against

evaporation."

Page 25276, line 16: "...the differential equations (Eq. 1) for the monomers were set to zero..."

Better "...the derivatives of the monomer concentrations were set to zero (Eq. 1)..."

This change has been made.

Page 25276, line 21: "When solving a series of differential equations ..."

When solving a system of differential equations...

Page 25276, line 21: "When solving a series of differential equations, it is important to make sure that the simulation has reached the steady state."

This statement is too general - it is in fact not always important.

Page 25276, line 22: "All the simulations were initially run for 50 000 s, and the concentrations of species at several conditions were examined to ensure they reached the steady state."

Please add an explanation in the text how it was determined that steady state was reached.

We have changed this sentence to be, "When examining the steady state properties of the system, one must always verify that the solutions to the system of differential equations have reached the steady state. The system was determined to be in the steady state when the concentrations of each component were within 0.1

Page 25278, line 4: "... it clearly will not be valid when there are stable pre-nucleation clusters (Vehkamäki et al., 2011). This should be explained in more detail in the text, so that the relevance of stable prenucleation clusters is easily understood.

We have added the following sentences on page 25278. "Stable pre-nucleation clusters correspond to a free energy minimum and have a negative formation free energy compared to (some) of the monomers, and thus their concentrations exceed the concentrations of (some of) the monomers. Therefore, the collision of any cluster with a stable pre-nucleation cluster is more likely than with a monomer."

Page 25278, line 6: "From Fig. 3, we can see a rather large difference in the rates by excluding non-monomer interactions ... this suggests that there are stable pre-critical clusters in this system ..." This is not obvious to me, and I suspect that this statement may be incorrect - stable pre-nucleation clusters may not be required for the observed model behavior: Excluding non-monomer collisions means coagulation of the clusters is switched off - but at high cluster concentrations, coagulation will be important for particle formation whether there are stable pre-nucleation clusters or not. Please explain.

We have changed the manuscript text to be,

“From Fig. 3, we can see a rather large difference in the rates by excluding non-monomer interactions (several orders of magnitude under certain conditions). This indicates that the concentrations of clusters in the system are comparable to those of the monomers, which suggests either local minima in the free energy surface at small clusters or at least relatively stable pre-critical clusters in this system; indeed, e.g. Ortega et al. (2011) have noticed the relatively stability of clusters consisting of two acids and two DMA molecules.”

Page 25278, line 19: "For each flux, the path back to the monomer using the highest flux option was traced." It is not clear what "highest flux option means". Please add an explanation in the text.

This following sentences have been modified to attempt to clarify this statement.

“2) For each flux, the path back to the monomer using the highest magnitude of flux for each step was traced. This means that not all flux pathways are shown, since there are numerous ways to get to most clusters from the monomers. For example, the concentration of one DMA/one acid clusters is high enough that self-collision to form the two amine/two acid cluster is significant; however, that collision is not included in Figure 5 because the addition of one acid to form the two acid/one DMA cluster, followed by addition of a single DMA has a greater overall flux. ”

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 25263, 2011.