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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.

Anonymous Referee #1

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Summary

The manuscript presents a newly developed model (ACDC) which describes processes of gas phase molecular clusters, which constitute the initial steps of aerosol formation from the gas phase. Several features of the model stand out in comparison to earlier works: a) The model describes the temporally resolved cluster processes for two constituents species, while most earlier models only describe the temporally resolved cluster processes for one constituent species, and assume equilibrium for processes of other constituents. b) Thermochemical data for the cluster processes can be specified by the user without manually changing the model code, which allows

flexible use of data from different sources. c) The computer code for the numerical integration of the differential equations for the system is generated automatically, with a flick of the switch, based on the user-provided specification of the system, which greatly facilitates the study of systems with different properties.

The ACDC code is a very promising development and has the potential to greatly improve our understanding of aerosol formation from the gas phase, but it's a long way to the top - the manuscript is well written, but certain parts need to be explained in more detail prior to publication. Works that are cited as "in preparation" (Vehkamäki et al., 2011) must be submitted or published before the present manuscript can be published.

General questions and comments

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

- 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 time-resolved model.

Specific comments

Page 25270, line 13: *"Using the parametrized formula from Kulmala et al. (2001) for a cluster size dependent coagulation sink coefficient did not have a significant effect on the steady-state cluster concentrations."*
It's not clear which formula in Kulmala et al. (2001) this refers to, and Kulmala et al. (2001) do not discuss any parameterization. Are you refering to the coagulation coefficient as given in (Fuchs, 1964; Seinfeld and Pandis, 1998), which would be equation 17 in Kulmala et al. (2001)? Why then not citing Fuchs (1964) and Seinfeld and Pandis (1998) directly?
Page 25270, line 20: *"As soon as these clusters form, they are "lost" (the material cannot re-enter 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?
- 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.

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 O_2^-, 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.
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.
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.
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?

Fewer or more details are needed.
Page 25274, line 7: *"accurate approximation"*
That's a touch too much - either it is accurate or it is an approximation.
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).
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)..."
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.
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 pre-nucleation clusters is easily understood.
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.
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.

References

Langevin, P. M. (1905). Une formule fondamentale de théorie cinétique. *Ann. Chim. Phys. 8*(5), 245–288.

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