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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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Referee 2 has made several important observations on this manuscript, and we will attempt to address them thoroughly.

Key assumptions of the work are that clusters containing more than 4 acid and/or base molecules leave the system never to return, and that such clusters are formed by colliding clusters containing at least one acid molecule. Neither of these assumptions appears to be well-substantiated and although the authors note that formation rates may be "artificially overestimated," they do not discuss to what extent the behaviour they observe in their results may be artefacts of these assumptions. In single component nucleation it is essential to include clusters of the critical size

in any simulation and I would expect something similar in the two component case considered in here (although the definition of "critical size" may be less clear). What steps have the authors taken to ensure that they are not just looking at subcritical clusters?

This is always an important considering when dealing with finite-sized simulation codes, and we have attempted to account for it as best as the data set allows. It should be emphasized here that both of assumptions are related to the choice of dataset used in this calculation, and are not restrictions of the ACDC model itself. For this manuscript, we want to rely on purely quantum chemical data, which puts significant restrictions on our system size. Therefore, we must account for the boundary conditions in an intelligent way, as opposed to simply adding more clusters to the system.

As mentioned on page 25270, the issue of boundary effects needs to be strictly examined in any code such as ACDC. The best way to determine if the system size is large enough is to add more clusters to the system; if the results do not change, the system is large enough. As that is not possible for this system (more quantum chemical data cannot be generated at the present time, and making the system smaller seems like a bad decision), we tried to examine the boundaries in more detail. By our reasoning, there are two extreme boundaries that one can impose: either all clusters can freely grow outside of the system and be lost, or no clusters can. At the "standard" conditions (i.e. the conditions chosen for all the tests, such that are similar to those observed in a boreal forest environment), the steady-state concentrations do not vary by that much by disallowing collisions that create clusters outside the system (as shown in the left hand side of Figure 6). If the monomer concentrations are increased significantly, this does become an issue (the right hand side of Figure 6); however, all of the other tests are performed under the standard conditions, i.e. if one carefully considers the conditions, one can avoid this problem, which we feel we have done here. As mentioned above, we are also limited by the size of the data set given by Ortega et al. 2011, and those authors are limited by the expense of quantum mechanical calculations on large clusters (not only the cost of each individual calculation, but also the cost of search-

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ing configurational space for the lowest-energy configurations). We have made some attempts to expand the size of the data set by using liquid-drop model calculations, but proper mixing of liquid-drop model and quantum mechanical multidimensional free energy surfaces is not a trivial problem.

The second assumption perhaps requires more explanation, and again is a result of the dataset chosen. As mentioned on Page 25275, "Ortega et al. (2011) observed that clusters with more bases than acids are generally not stable ". It was felt that this is a significant source of the artificially overestimated formation rates, as the 3,4 cluster (3 sulphuric acids, 4 DMAs) has a relatively high concentration. Requiring that a sulphuric acid be present in the colliding cluster is identical to disallowing x,4 collisions with a DMA monomer to form x,5 clusters. Since, in our system, x must be between 0 and 4, the x,5 clusters are almost certainly not stable (according to the results of Ortega et al., the most stable clusters seem to be along the diagonal, with equal numbers of acids and bases, or with one more acid than base), and consequently this assumption appears justified.

The authors find that cluster concentrations vary strongly with temperature and sticking probability. The strong dependence on temperature is well known and not particularly surprising, since (as noted by the authors) the evaporation coefficients are strongly temperature dependent. On the other hand, the variation with sticking probability needs more discussion. The authors attribute the large effect to the "highly non-linear behaviour" of the system and promise to examine this effect in more detail in future, but a more specific cause should be given in the present work. It should be noted that for single component nucleation, changing the sticking probability has only a limited effect on nucleation rates, since reducing collision coefficients also reduces the evaporation coefficients when the detailed balance condition, eq. (3), is used to determine the latter.

We are very grateful to the referee for pointing this out. Indeed, the referee is correct. There was a bug in our computer script in the inclusion of the sticking probabilities which caused them to only be added to collision coefficients. We have fixed this and

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uploaded a new figure with the results. There is significantly less difference seen by reducing the sticking probabilities now, without only a few orders of magnitude difference appearing for the largest clusters (which have the smallest concentrations), and those of the smallest clusters is essentially unchanged. Consequently, the paragraph in the discussion concerning this had to be rewritten as follows:

"Since collisions between clusters play a major part in the birth-death equations, the question of sticking probabilities naturally arises. While many kinetic codes (including ACDC) increase the sticking probabilities for ion–neutral cluster collisions (as described above), to our knowledge the reverse case has not been explored in detail, i.e. when two neutral clusters collide, they will always stick together. However, there is no guarantee that this is always the case, and therefore the effect of sticking probabilities less than unity was examined. It has to be noted here that the sticking probability can also be thought to be taken into account in the evaporation (Kulmala and Wagner, 2001). Figure 9 shows the difference in concentrations when the sticking probability is reduced to 0.1 for collisions involving clusters that have the highest concentrations at the standard conditions. These clusters include the monomers and clusters consisting of 1) one acid and one DMA, 2) two acids and one DMA and 3) two acids and two DMA molecules. They were found to be the most important clusters regarding the effect of changing the sticking probability by performing the following test. First, the sticking probability in all collisions was set to 0.1. Second, the sticking probabilities in collisions involving the aforementioned clusters were set to 0.1, while probabilities in all the other collisions were reset to 1.0. These two tests gave the same results for the cluster concentrations. This implies that the sticking probabilities in collisions involving the most numerous clusters have the largest effect on the cluster distribution. As can be seen in Figure 9, reducing the sticking probabilities has an effect on the largest clusters in the system, but it is not very strong. Reducing the sticking probabilities to 0.01 has a more significant effect (results not shown), but Kurten et al. (2010) have shown that is is unlikely that the sticking factor would differ by that much from unity, especially for larger clusters."

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In addition, both the conclusion and abstract have been altered to reflect that changing the sticking probabilities does not have a major effect for likely values of the sticking probabilities.

The colour contour plots look somewhat monochromatic to my eyes, mostly appearing varying shades of blue, with some violet and red regions. I am not sure if this is a feature of the plotting software used, but I would find them clearer if there were a wider range of colours (e.g. also green, orange and yellow) in the plots.

The colours of the plots are something that we deliberated for an extended period of time amongst our group. For the difference plots in particular, we wanted a colour scheme that would best show if a particular change caused a large effect or a small effect. By using the current colour scheme, the left side of figure 6, Figure 8, and (now) Figure 9 do not have a lot of variation, indicating that the effects of those changes are not large, while the right side of Figure 6 and Figure 7 show extensive changes. This illustrates nicely our conclusions that changing the temperature and boundary conditions (at high concentrations) have significant effects, while the boundary conditions (at standard concentrations), the coagulation coefficients, and the sticking probabilities are a much smaller effect. If we change the colour scheme to include all colours of the rainbow, all graphs will show a lot of variation, and it will be more difficult to see that the variation in some of them is not, in truth, that significant. Consequently, we would like to maintain the current colour schemes, unless there are strong objections from the referee or editor despite our explanation here. It should also be noted that the colour bars on all the difference plots are exactly the same, so more colour on one plot does signify a greater than less colour on a different plot, making Figures 6, 7, 8, and 9 directly comparable. We have inserted a brief explanation of this into the text on Page 25279, in hopes of making it more clear for the general reader. The has resulted in the removal of the existing mention of the colour scale on the same page.

"It is important to make a brief note on the colouring scheme used in the next four figures here. Most importantly, the colour bar for all four figures is exactly the same.

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This enables a quick comparison between them, as strong colours on one plot means that the effect of changing that particular parameter is more significant than dull colours on a second plot. It should also be noted that any changes that are larger than this colour scale are now the same colour as the limit values, which attempts to prevent a single large change from skewing the whole colour scheme."

In addition, all instances of "color" have been replaced by "colour".

I would suggest omitting section 2.2 on ionic clusters as only preliminary results for these are presented in the paper- I think it would be better to include this section in the promised future work examining ionic clusters in more detail.

As mentioned in our response to referee 1, we would like to keep it in this manuscript for completeness and to make future citations simpler. We have removed mention of preliminary test results in that section and rephrased the final paragraph.

Kurtén, T., Kuang, C., Gómez , P., McMurry, P. H., Vehkamäki, H., Ortega, I., Noppel, M., and Kulmala, M.; The role of cluster energy nonaccommodation in atmospheric sulfuric acid nucleation , J. Chem. Phys., 132, 024304, 2010.

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