Review of ACPD 12-11351-2012 by Riccobono et al.

This paper explores the contributions of organic vapors to growth of particles formed from sulfuric acid and water. The title suggests that the role of organics in the nucleation process is also explored, but the contribution there is much more limited. The experiments do show that, with α-pinene and TMB, and at high sulfuric acid concentrations, nucleation rates are at the low end of Hyytiälla data.

develops a new approach to estimating growth rates of small particles that form during nucleation events, based upon measurements made using either a battery of condensation particle counters (CPCs) or a scanning mobility particle sizer (SMPS). The new analysis is then applied to chamber experiments involving sulfuric acid and organic vapors in order to examine the enhancement in particle growth due to the organic reaction products.

The new method for estimating growth rates attempts to eliminate the ambiguity that accompanies measurements made with CPCs that have different size dependent response functions. While many studies have used the nominal detection limit of the CPC to define the time at which particles grow to that particular size, i.e., the particle size that his counted with 50% efficiency, the present study uses the leading edge of the instrument response function – as represented by the size that is detected with 1% efficiency. Though detection efficiencies this low are rarely included in the calibration data for CPCs (including in the data presented in the appendix of this paper), the CPC response functions enable extrapolation to this value with reasonable confidence. The growth rate is then estimated from the time delay between CPC detectors with increasing $D_{1\%}$ thresholds.

To establish the viability of this method, the authors simulate the analysis data obtained during the growth of particles at a constant growth rate. The nucleation rate is also assumed to be constant. For small, free-molecular regime particles, the growth rate increases with increasing size due to the reduction in the Kelvin-effect enhancement of the evaporation rate. As particles grow, this effect diminishes, and the constant growth rate model becomes quite reasonable. Figure 3 shows the opposite trend in the measurements, the growth rate of the leading edge is faster than that observed at the mode of the size distribution.

If I consider the presented model, the number of particles formed in a time interval between time t_f and $t_f + \Delta t$ is

$$\Delta N = J\Delta t.$$

Since all particles grow at the same rate, the diameter change in that same time interval is, for all particles,

$$\Delta D = G\Delta t,$$

where G is the growth rate. The size distribution is then

$$n(D,t) = \frac{\Delta N}{\Delta D} = \frac{J}{G} = constant$$

for all particle sizes between $D_{max} = Gt$ and $D_{min} = D^*$ where I have assumed that a critical cluster size was specified in the model, though it is not stated. The curvature in the plots shown in Fig. 2, boxes a1-a3 arises solely due to the shape of the CPC detection efficiency curves used to estimate the responses. This is a rather extreme and artificial size distribution, and is not likely the best test of the ability of this method to capture the growth rates, particularly if growth rates vary with size due to the Kelvin effect or other factors that are discussed in the paper. It would be useful to compare the performance of the method for CPCs and SMPS using similar size distributions, such as that which was used to illustrate the use on SMPS data. Growth of a Gaussian distribution would be a logical choice since, as noted below, that was used for the SMPS data.

The procedure used to extract the growth rate from the SMPS data involves fitting a Gaussian distribution to the measured size distribution. Clearly, the simple model used to examine the growth rate estimation for the CPC battery cannot be applied to the SMPS analysis. Instead, the authors examine data from a α-pinene experiment. The caption to Fig. 3 should clearly indicate the source of the data to avoid any confusion between the approaches being taken in examining the data analysis for the CPCs and the SMPS.

Growth rate enhancement factors are estimated as the ratio of the observed growth rate to that estimated assuming kinetically limited growth without organics. These clearly show substantial contribution of the organics to the particle growth, and that sulfuric acid enhances the growth rate due to organics. Though the uncertainties are large, the analysis presented here supports previous findings. The paper clearly demonstrates the value of direct measurements of sulfuric acid vapor, and the need for better measurements and property data for the organic vapors that contribute to particle growth.

Specific points

In the methods, the authors note that they used the diffusional deposition model for straight tubes to account for particle losses in the sampling lines. Since the measurements involve extremely small particles, any bends in the tubes will greatly enhance the losses. Please discuss whether there were any bends, and, if there were, either use published results on the effects of bends in the loss corrections, or, better yet, measure the transmission efficiency of the sampling lines.

Editorial Suggestions

1. p. 52, l. 19: is already dominated. Delete already in l. 20.
2. l. 21: insert comma after size
3. l. 24: Finally, the size resolved growth analysis indicates....
4. p. 53, l. 7: primary emissions
5. l. 11: underlying aerosol nucleation. Replace "when estimating" with "in estimation of"
6. l. 14: insert comma after "i.e." here and everywhere it appears in the text
7. l. 17: coagulation of the new particles onto the pre-existing ones
8. l. 18: replace maximum with greates
9. l. 22: main vapor responsible for...
10. p. 54, l. 3: find better wording for "contributors to the chemical composition"
11. l. 6: delete commas after "both" and "(i.e., monoterpenes)"
12. l. 15: our previous nucleation experiemnts
13. l. 17: environmental chamber (Metzger et al., 2010) which reproduced ... In that work, considerable uncertainty arose from using a model to determine the sulfuric acid...
14. l. 21: retrieve the concentration of OH
15. l. 23: "In the present study...
16. l. 28: We investigated the role of ...
17. p. 55, l. 1: nanoparticles through eight photo-oxidation experiments. we measured the size-dependent...
18. l. 17: The discussion of the experimental equipment is a new topic so insert a paragraph break before: The PSI environmental chamber includes the following instrumentation:
19. l. 22: insert comma after vapors. Delete "In addition to these instruments, we employed". Insert "was also used" at the end of the sentence.
20. p. 56, l. 19: delete respectively
21. l. 21: replace "are" with "were" and "is" with "was"
22. l. 23: replace "are" with "were" and "as well as of" with "and the"
23. l. 24: and that produces stable clusters that grow to detectable sizes by...
24. p. 57, l. 3: minimum detectable size
25. l. 6: replace "using the following equation" with "from the time it takes to grow past succesive size thresholds, i.e., "
26. p. 58, l. 26: delete comma after method.
27. l. 27: do you mean "the beginning of the detection"

28. p. 59, l. 3-5: insert commas after "that" and "setting)"

29. p. 61, l. 11: delete "the" before background

30. l. 16: insert comma after compounds

31. l. 20: move Eq. 2 to immediately following "growth model is" and delete "shown in Equation 2"

32. p. 62, l. 1: Dimensionless numbers, such as the Knudsen number are presented without italics or subscripts, i.e., "Kn" not "K_n"

33. l. 4: For sulfuric acid, we assume $\alpha = 1$

34. p. 63, l. 1: is due only to sulfuric...

35. p. 64, l. 14: binary sulfuric acid/water nucleation

36. l. 16: insert comma after nucleation

37. l. 17: insert comma after chamber

38. l. 25: NucOrg represents the organic...

39. l. 26: The sentence beginning "The correlation ... " awkwardly stated and confusing

40. p. 65, l. 2: may also contribute

41. l. 3: delete "together ... pinene"

42. l. 4: TMB also appears to ...

43. l. 6: work in which sulfuric acid concentrations were directly measured. Insert comma after (2010)

44. l. 7: all lie at the higher end of the sulfuric acid concentration range of the earlier study. Delete the remainder of the paragraph.

45. l. 12: This paragraph needs to begin with a statement that you are modeling using the parameters of Metzger. Then "Figure 5 compares the time series..."

46. l. 13: concentrations. Note that the measred peak concentrations agree within the model and measurement uncertainties, but the model underestimates ...

47. l. 19: injection, even before

48. l. 17: α-pinene. Further experiments ...

49. l. 25: Another possible reason for underestimating the sulfuric .... about half of the sulfuric acid lifetime ______ add something that says where the new estimate comes from

50. p. 66, l. 13: organic compounds dominates throughout the particle size distribution.

51. l. 16: vapors, supporting the findings of ...

52. l. 18: insert comma after that

53. l. 19: increase, indicating that the condensation driving force (...) for organics increases as the particles grow (Eq. 6), either by increasing the partial pressure, p, or by decreasing the equilibrium vapor pressure, p_{eq}, due tothe growth of particle size (Kelvin effect), or due to changes in particle chemistry (Raoult's [sp] law). – delete sentence beginning with "Usually"

54. p. 67, l. 22: ... , sulfuric acid seems to enhance ...

55. l. 26: remains unknown (or uncertain), we can make some observations from Figs. 7 and 7.

56. l. 9: Both of these effects

57. p. 68, l. 1: concentrations

58. l. 8: On the other hand, Fig. 6 suggests ..

59. l. 17: The importance of reactive uptake in growth ...
60. l. 25: same time, organic compunts that have low saturation vapor pressures accumulate, increasing ....
61. p. 69, l. 4-5: insert commas after "which" and "experiment"
62. l. 7: Figure 7 also shows
63. l. 17: of the species involved, do tho allow us to conclude whether organic
64. p. 70, l. 3: were estimated using a kinetic model
65. l. 7: experiments, and compared the new approach with ...
66. l. 12: insert comma after that
67. l. 13: compounds dominate nearly the entire size distribution
68. Fig. 1: add D_{50}'s to the legend so the reader can tell what is happening. You may also want to add D_1 since that is so important in your paper.
69. Fig. 3: In the caption, tell the reader the source of the data, i.e., that it came from a particular experiment.