

## ***Interactive comment on “Aerosol nucleation spikes in the planetary boundary layer” by J.-P. Chen et al.***

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Received and published: 13 March 2011

We are grateful to the reviewer’s detailed and constructive comments, especially the demonstration of the condensation growth calculation. In the following we answer the reviewer’s questions in detail.

### Major Comments

1. Page 26942, Lines 13-19: In this text, the authors discuss the evaporation of sulfuric acid from interstitial aerosols in the cloud. This is due to the equilibrium vapor pressure of sulfuric acid in the very dilute cloud droplets being lower than over the more concentrated solutions of the interstitial aerosol particles. This is analogous to Bergeron–Findeisen process in mixed-phase clouds where ice crystals grow and liq-

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uid drops shrink due to the lower equilibrium vapor pressure of water vapor over ice compared to liquid water. Therefore, if the condensation-sink timescale of sulfuric acid in the cloud is significantly shorter than the time in the cloud, the sulfuric acid concentrations in the vapor phase can become lower than the equilibrium vapor pressure of sulfuric acid over the interstitial aerosol particles, and these particles will start to shrink. However, these particles will shrink VERY slowly. I believe the amount of evaporation will be negligible:

Reply: The fast evaporation in our calculation could be due to our considering the Kelvin effect. For example, the Kelvin effect will cause the surface vapor pressure (of both water and sulfuric acid) of 10 nm particles by 10% and of 1 nm particles by nearly 300%. In addition, the loss of sulfuric acid will also cause a loss of water. Even though the evaporation itself is not very fast, the reduction in size also enhances the Brownian collection. In any case, we have state that the Brownian collection should be the main cause, and total evaporation pertains to those that were not collected by Brownian collection.

2. The interstitial aerosols will be small ( $D < 100$  nm) so they should very quickly reach equilibrium with the water vapor. I used E-AIM (<http://www.aim.env.uea.ac.uk/aim/model2/model2a.php>) to calculate the equilibrium vapor pressure of sulfuric acid droplets in equilibrium with 99% RH (maximum RH allowed in the calculation) and 283 K. The vapor pressure was found to be  $1E-22$  atm (the vapor pressure would be even lower at 100% RH due to additional water in the drops). This vapor pressure corresponds to an equilibrium vapor mass concentration of  $4E-22$  kg m<sup>-3</sup>. The growth/evaporation rate of particles in the kinetic regime is given by:  $dD/dt = 1/2 * v_{ms} / \rho_a * (C_{amb} - C_{eq})$  Where  $v_{ms}$  is the mean speed of sulfuric acid (250 m/s at 283 K),  $\rho_a$  is the density of the aerosol (1000-2000 kg/m<sup>3</sup>) and  $C_{amb}$  and  $C_{eq}$  are the ambient and equilibrium (over the aerosols) vapor mass concentrations of sulfuric acid. Note that the growth/shrink rate is not diameter dependent in the kinetic regime (ignoring surface tension effects. I’ve also assumed that the accommodation

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coefficient is unity. I then assumed that the eqm vapor pressure of sulfuric acid over the cloud drops was much smaller than that over the aerosols and that the condensation sink was very large such that:  $\text{Camb-Ceq} \approx \text{Ceq}$  (this gives a maximum shrink rate for a given RH) I then calculated the shrink rate to be  $1\text{E-}10$  nm/hr! Even if I assume the sulfuric acid interstitial particles to be in eqm with only 20% RH (which is a bad assumption to make here), the vapor pressure is then  $1\text{E-}15$  atm and the shrink rate is still only  $1\text{E-}3$  nm/hr. The text mentions that some particles evaporate entirely and suggests that the evaporation is a non-trivial source of sulfuric acid vapor. This seems highly unlikely. However, if you assume that the particles are essentially pure  $\text{H}_2\text{SO}_4$  ( $\text{H}_2\text{SO}_4$  in eqm with 1% RH in E-AIM), the vapor pressure is then  $1\text{E-}10$  atm and the particles will have a fast large shrink rate.

Reply: Thanks for providing detailed analysis. As mentioned in the reply of the previous comment, Brownian collection should be the main cause of disappearance of small aerosols. Evaporation may occur for small particles with large Kelvin effect. But the suggestion that evaporation is a non-trivial source of sulfuric acid in the downdraft might be erroneous. So we have removed the relevant sentence (same as in the reply to comment #4).

3. How do you calculate your vapor pressures of sulfuric acid in the model? I'm worried that there is an error somewhere (perhaps you are using the vapor pressure of  $\text{H}_2\text{SO}_4$  over a pure  $\text{H}_2\text{SO}_4$  particle?). I don't think it will affect your big-picture conclusions regarding the role of turbulence in nucleation spikes, but it will affect your discussion. It is a very common assumption in models of sulfuric acid in the troposphere to assume that the equilibrium vapor pressure of water is 0 because it doesn't take much water or base (e.g. ammonia) to make any evaporation prohibitively slow even under the most favorable conditions.

Reply: The sulfuric vapor pressure and water vapor pressure of the drop surface are calculated according to the activities of the solution and with modification of the Kelvin effect. The growth is then calculated with the two-stream mass transfer equations as

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stated in Section 2. If we apply vapor pressure of  $\text{H}_2\text{SO}_4$  over a pure  $\text{H}_2\text{SO}_4$  particle, the evaporation would certainly be too fast. But then the condensation would be too slow, and our results do not indicate that. Also, in such a situation, the evaporation of water will not affect the evaporation of sulfuric acid as discussed in the next reply. We do not assume that the equilibrium vapor pressure of water is 0.

4. Page 26942, Lines 28-29: Here you address evaporation of sulfuric acid again, but it seems to be outside of the cloud. Is this because of loss of water from the aerosols? It's not clear what is causing the sulfuric acid to evaporate here. Again, the RH can't be getting so low that you're getting appreciable evaporation.

Reply: The evaporation may occur to very small aerosols which have large Kelvin effect thus higher surface vapor pressure. But since such a situation can be applied to only a very small fraction of the aerosol population, and is not crucial to the overall discussion, we have deleted this sentence.

5. Page 26945, Lines 2-6 and other discussion of the turbulence amplitude/frequency variation: Could you do one more additional analysis where you simulate many different trajectories with different amplitudes/frequencies, and then have a "surface measurement simulation" where the various trajectories take turns passing by a surface measurement site in some realistic way? There are a wide array of reasonable assumptions that could be made to alternate between air parcels at the measurement site. This would help more clearly show how turbulence can lead to spikes in number concentrations.

Reply: Thanks for the excellent suggestion. We have performed additional simulations with varying vertical amplitudes (see Fig. 8 in the manuscript), and plot only those points that are close to the surface ( $<5$  m). The spikes at the surface are apparently associated with the varying vertical amplitudes. This new result has been added in the revision. But we do not combine results from different trajectories, partly because the figure will be cluttered, and partly because the figure below should be sufficient.

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Minor comments

1. Page 26933, Line 10: "...being collected by old particles." Probably better to say "larger particles". Recent primary emissions may scavenge the nuclei mode, but aren't necessarily old.

Reply: Modified as suggested.

2. Page 26934, Line 13: Ions also may enhance nucleation (e.g. Yu, F., From molecular clusters to nanoparticles: Second-generation ion-mediated nucleation model, *Atmos.Chem. Phys.*, 6, 5193-5211, 2006.)

Reply: Agree. The ion-mediate nucleation is mentioned in the next sentence as one of the "other mechanisms".

3. Page 26934, Line 26: "requires" should be "required".

Reply: Corrected.

4. Page 26934, Line 28: "i.e." (meaning "in other words") should be "e.g." (meaning "for example") here.

Reply: Corrected.

5. Page 26936, Line 15: Please give lower limit diameter too (important for nucleation modelling).

Reply: Values are added.

6. Page 26936, Line 24: Why was just one nucleation scheme tested? Since many schemes are available through parameterizations or look-up tables (e.g. Yu, F., Ion mediated nucleation in the atmosphere: Key controlling parameters, implications, and look-up table, *J. Geophys. Res.*, 115, D03206, doi:10.1029/2009JD012630, 2010. and Merikanto, J., I. Napari, H. Vehkamäki, T. Anttila, and M. Kulmala (2007), New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric

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conditions, *J. Geophys. Res.*, 112, D15207, doi:10.1029/2006JD007977.), it would be interesting to see if these schemes yield the same conclusions as was found in the paper. The two reasons you found for nucleation spikes due to turbulence were 1) condensation sink changes (including RH effects on aerosol swelling) and 2) the affect of changing temperature and RH on the nucleation rate. Different nucleation schemes have different dependencies on temperature and RH. A general pattern is when other species are involved (e.g. Ammonia and ions), the dependence on RH on nucleation rate is reduced.

Reply: We fully agree that there are other nucleation schemes or theories. We also tested the scheme of Kulmala et al. (1998) and Vehkamaki et al. (2002), but the end results are quite similar, mainly because the nucleation process is self limiting. The figure below (Fig. A) shows a test of model sensitivity to the nucleation rates which is varied by two orders of magnitude (i.e. multiply the original rates by a factor of 10 or 0.1). The change of total aerosol concentration is within a factor of 2, rather small comparing to the two orders change in nucleation rates.

Kulmala, M., Laaksonen, A., and Pirjola, L., 1998: Parameterization for sulfuric acid/water nucleation rates. *J. Geophys. Res.*, 103, D7, 8301-8307. VehkamaÄlki, H., M. Kulmala, I. Napari, K. E. J. Lehtinen, C. Timmreck, M. Noppel, and A. Laaksonen, 2002: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions. *J. Geophys. Res.*, 107, D22, 4622, doi:10.1029/2002JD002184.

7. Page 26938, Line 3: Since the surface tension appears to be very important (classical H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O homogeneous nucleation is rarely predicted in typical boundary-layer conditions), can you give an example the bulk surface tension under certain conditions as well as the value you used under these conditions?

Reply: Good suggestion. For a drop of 1 and 3 nm, the curvature effect causes the surface tension to reduce by 9% and 24%, respectively. We have added a sentence to

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describe this.

8. Page 26938: Lines 11-29: Can you add a tables with the various simulations that show which options (e.g. Up and down motion, stratocumulus, stratus) are used for each case. When reading the results section, I was often confused to which of the options were being used in each case, and this would make things more clear.

Reply: Certainly. A table has been added.

9. Page 26943, Lines 18-28: Throughout the preceding section I was frustrated you hadn't addressed the distinction between spikes of particle number along the trajectory (e.g. Figure 4) vs. spikes at a surface measurement station (e.g. Figure 1). You do address this here, however, it would be nice to have it earlier (to avoid others from being worried you may be missing this distinction).

Reply: Good point. A sentence is added in the beginning of this section to caution the reader.

10. Page 26945, Line 18-20: The effect of increased condensation sink (from increased particle concentrations) to reduce nucleation and growth is well established in the aerosol community. It might be good to rephrase this last sentence to say something like "...consistent with other studies of nucleation."

Reply: Agree. The sentence has been modified accordingly

11. Page 26946, Lines 9-11: Make sure to say that the fluctuations increase "when following the trajectory". This is an important distinction that you discuss elsewhere, but its not clear from this paragraph alone.

Reply: Agree. The sentence has been modified accordingly.

12. Figures 1 and 6: The captions refer to "solid", "dotted" and "dashed" lines in the figures, but there are only solid lines.

Reply: The color change was made during the manuscript typesetting and production

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because some of the curves do not come out correctly. But we forgot that the text also needs to be changed. Much thanks for pointing that out. The corrections have been made.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26931, 2010.

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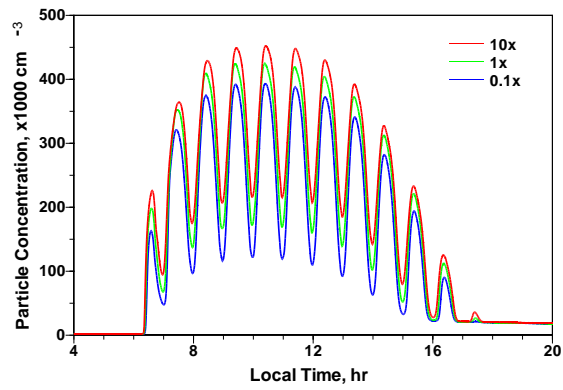


Figure A: Variation of total aerosol concentration when the binary nucleation rates are altered artificially by 10 and 0.1 times. The simulation setup is similar to that for Fig. 4, except that a longer cycling period of 1 hour and a shorter vertical amplitude of 250 m were used to make the figure more legible.

Fig. 1.