Atmos. Chem. Phys. Discuss., 10, C12947–C12952, 2011
www.atmos-chem-phys-discuss.net/10/C12947/2011/

Atmospheric
Chemistry
and Physics
Discussions

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

J. Pierce (Referee)

jeffrey.robert.pierce@gmail.com

Received and published: 30 January 2011

Review of "Aerosol nucleation spikes in the planetary boundary layer" by J.-P. Chen, T.-S. Tsai and S.-C. Liu

This paper explores two potential reasons for short-term spikes in particle number concentrations during nucleation events, broken clouds causing variation in [OH] and turbulence causing variations in temperature, RH and other properties. The paper shows that important variations can occur in nucleation/growth rates due to turbulence, particularly when the air parcel cycles in and out of clouds.

The results are interesting and certainly stress that we need to continue to understand how boundary-layer motions affect aerosol nucleation and growth processes. I feel

that the paper should be published in ACP. However, I believe that there is an error in their model and/or model interpretation regarding the evaporation of sulfuric acid in the aerosol. I do not believe that this error will greatly affect their main conclusions; however, it must be fixed (or perhaps I need to be shown why I am wrong) before the paper is published in ACP. There is one other analysis I would like to see added as well as some more minor corrections.

Major comments:

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 liquid 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:

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 eqiullibrium vapor mass concentration of 4E-22 kg m-3.

The growth/evaporation rate of particles in the kinetic regime is given by:

dD/dt = 1/2*ms/rho*(Camb-Ceq)

Where ms is the mean speed of sulfuric acid (∼250 m/s at 283 K), rho is the density of the aerosol (∼1000-2000 kg/m3) and Camb and Ceq 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 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:

Camb-Ceq ≈ -Ceq (this gives a maximum shrink rate for a given RH)

I then calculated the shrink rate to be 1E-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 1E-15 atm and the shrink rate is still only 1E-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 H2SO4 (H2SO4 in eqm with 1% RH in E-AIM), the vapor pressure is then 1E-10 atm and the particles will have a fast large shrink rate.

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 H2SO4 over a purse H2SO4 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.

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? Its 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.

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.

Minor comments

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.

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.)

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

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

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

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. Geophy. 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 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.

Page 26938, Line 3: Since the surface tension appears to be very important (classical H2SO4-H2O 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?

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.

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).

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."

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.

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

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