

Interactive
Comment

Interactive comment on “Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events” by J. R. Pierce et al.

A. Laaksonen (Referee)

ari.laaksonen@uku.fi

Received and published: 29 June 2011

In this manuscript, the authors apply two techniques in order to obtain information about the volatility of newly formed atmospheric particles. They perform extensive aerosol dynamics modeling in order to mimic observed particle growth, and perform a number of sensitivity tests in order to find out how different values of effective saturation vapour density and other particle properties affect the growth. They also model particle evaporation in volatility TDMA to obtain constraints for the effective volatilities based on VTDMA measurements. I think that this is a well written (although there seem to be some typos and missing words) and valuable manuscript that fits the scope of ACP

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Interactive
Comment

very well. However, I have some concerns that the authors should address before I can recommend publication.

I am very surprised, especially given the author list of the ms, that Kulmala et al. (Tellus 50B, 449,1998) has not been referenced. It should be referred to, and in fact it should be extensively discussed in the final paper. Kulmala et al performed very similar aerosol dynamics modeling as has been done here, albeit using a simpler model (three monodisperse modes instead of a spectrum of size classes). However, the simplicity of the model should not prevent the results they obtained to be in the same ballpark as the present results. But the fact is that the upper limit of effective saturation vapour density reported by Kulmala et al. (10^5 molecules per cc) is almost two and half orders of magnitude lower than what is given in the present work. It appears to me that one reason for the discrepancy is that Kulmala et al. paid more attention to the growth rate of the nucleation mode in the beginning of the growth, while in the present work the main criterion appears to be the final size of the particles. Note that the final size depends on the integral of the condensable vapor production, and the same integral can be achieved with very different concentration profiles as a function of time - e.g. a flat and a strongly peaked profile can yield the same integral. However, the growth rate of the particles depends on the concentration of the vapour, and in these two cases the growth would appear quite different.

Specifically, in such a case that the effective saturation vapour density is relatively high, the Kelvin effect may prevent the growth altogether unless the concentration of the condensable vapor peaks at a high value, which on the other hand can easily lead to an "overshoot" in the growth rate as the particle size increases to around 3 nm and the Kelvin effect is already smaller than at 1.5 nm. The limit given by Kulmala et al. is based on that: When the saturation vapor density was set to 10^7 (i.e. still 3 times lower than the highest number given in the present ms), the peak vapor concentration needed to initiate growth was so high that the nucleation mode "shot straight up" once the growth began. Thus, I think that in this ms, the authors should also compare the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

modeled growth rate (and specifically, the growth rate during the first 1-2 hours) to the measured, and based on the comparisons, re-asses the upper limit of their stated saturation vapour density.

Regarding the Kelvin effect, I see no basis for the simulations in which the surface tension has been set to zero (the authors themselves note that "The surface tension of the aerosols cannot be 0"). They should be removed, or at least it should be made sure that they do not affect the assessment of the upper limit of the effective saturation vapour density. If the simulations are retained, it should at least be explained why they are useful.

In my opinion, the authors downplay the importance of the results obtained from the TDMA results. It is true that the size change can take place because of other reasons than evaporation - for example, ammonium sulfate will decompose at 280 centigrades, but such an effect will only cause an overestimation of the saturation vapour pressure. Pyrolysis is somewhat more complicated as it leaves a non-volatile char residue. A sensitivity calculation could be done: pyrolysis should not take place below 200 centigrades, and if the particle undergoes pyrolysis, it should be stable until its temperature reaches at least 200 centigrades. Thus, a high estimate of the vapour pressure could be reached by assuming that a complete evaporation takes place at 200 degrees.

Note also that Raatikainen et al. (ACP 10, 2063-2077, 2010) found that measured volatilities of Hyytiälä aerosols can be correlated rather well with AMS organic and inorganic groups, which suggests that pyrolysis might only play a small role if any.

Regarding the aerosol-phase chemistry calculations, I wonder what would the reaction rate coefficients need to be for the reactions to proceed rapidly enough to be able to drive particle growth? See Vesterinen et al. (Atmos. Environ. 41, 1768, 2007) for some discussion on these matters.

In the introduction, three (numbered) complications are mentioned. As shown by Virtanen et al. (Nature 2010), the growing particles are solid at least when they are larger

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

than about 30-40 nm. I believe this may cause a severe complication to the growth calculations, as the mixture of different organics and sulfate may not be homogeneous throughout the particle, but the particle could have a layered structure. Furthermore, it may be the case that when the particles are in the few nm size range, they are still liquid, and a phase change takes place while they are growing. These possibilities should be mentioned.

In the second paragraph, the authors refer only to modeling papers when noting that new particle formation can produce CCN. Before the modeling papers, this was shown in a number of experimental papers (Lihavainen et al. JGR 108, 4782, 2003; Kerminen et al. GRL 32, L14803, doi:10.1029/2005GL023130; Laaksonen et al. GRL 32, L06812, doi:10.1029/2004GL022092) .

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14495, 2011.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)