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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Droplet activation of wet particles: development of the Wet CCN approach" *by* S. Nakao et al.

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This is an interesting paper introducing a method how particles' hygroscopicity can be determined if not the dry but a wet diameter (at a known relative humidity) of the particles is measured/selected during a CCNC measurement. In some cases this method can be really useful, especially if the dry mobility diameter measurement fails to sufficiently predict the volume of the solute. The "CCN state space" analysis is a good idea, but it is not completely new. An HTDMA (Hygroscopicity Tandem Differential Mobility Analyser) humidogram (widely known and applied) measurement contains the same information and is very similar. The wet CCN approach is accompanied with nice examples, but the interpretations are not always correct. I can recommend the

manuscript for publication in AMT, however it needs significant improvement. Please find my comments below.

Major comments:

1. Section 2: You state, that the theory for wet CCN approach will be described first for the "traditional" Köhler theory, then for the kappa Köhler theory. 2.1. includes the "traditional" Köhler theory and then some equations in case of an ideal solution. This is not a theoretical description of the wet CCN approach. A significant improvement and clarification is needed here.

Section 2.2 includes the description of the kappa Köhler theory, but not the derivation of the hygroscopicity parameter from the wet diameter and critical supersaturation measurement (which should be the main focus here). Eq. 7-9 contain this, please move the discussion of these equations to section 2.2, using one common kappa for both instruments. And modify eq. 9 such that it contains the RH and not the water activity because you measure the RH and not the aw, and the wet diameter is needed to derive the aw from the RH. You could also include the equation how the volume equivalent solute diameter (dry diameter) can be calculated.

2. Section 2.3: most of this section belongs to section 2.2 and it does not contain a real discussion and error estimation what happens if the kappa values below and above saturation do not agree. The hygroscopicity parameter is derived from a single wet diameter and critical supersaturation measurement using the kappa Köhler theory and this part should definitely go to Section 2.2. Please Investigate here, that in how much error will it result if a certain difference in the kappa at sub and supersaturation exists. Please investigate how much does this error depend on the RH where the wet diameter is selected and on the particle's dry size.

3. Section 3.3: emphasize more, that the "CCN state space" is a good tool, if kappa (for some reasons) changes significantly with the saturation ratio otherwise one wet measurement is enough to derive the kappa value.

4. You discuss nicely in details how the particles in the “CCN state space” behave if kappa is not constant, if efflorescence is present or if the particle is not spherical and collapses during water uptake. However these effects can also influence the shape of the activation curve and in some cases it might cause error in the D50 derivation, dependent on how D50 is determined. Please add a discussion about this to the text including how your D50 was exactly derived, and please estimate the error as well which is associated with D50. Include error bars on figures 8 and 9.

5. Some of the measurements are interpreted strangely. Some very strong conclusions are drawn that (even if they are expected) are in my opinion not viewable. These are:

Page 270, L 7-8: This sentence states that your observations for ammonium sulphate agreed well with the E-AIM theory. It is true, that the agreement is not bad, but if I look at the graph the points agree better with the kappa=0.5 isoline than with the E-AIM.

Page 270, L 23-24: The statement about the non-spherical into droplet transition is far too strong. The “diameter gap” between the 5-6 points at the lowest saturations and the rest of the points is not higher than the difference between the neighboring points (which is probably measurement noise). With this you only cannot exclude that a small effect of particle restructuring occurs, but for sure figure 8 does not suggest it strongly, even if it is expected. Anyway, if the dynamic shape factor is known for ammonium oxalate you could estimate how big "the jump" in the mobility diameter is expected to be.

Page 271, L 11: I don’t see here any efflorescence. Again, the measurement noise is too high to make such strong statements.

Page 272, L 17: it is not sure, that the particles are nearly non-hygroscopic. It can very well be, that the humid reaction IOP have highly non-spherical shape with a high deliquescence point. In this case your mobility diameter does not agree with the volume equivalent diameter of the solute (not even at the highest measured RH if the particle is still not deliquesced), and therefore your derived kappa does not represent the

real hygroscopicity of the particles. Please modify the discussion about the possible compositional differences between the wet and dry reaction as well, taking this into account.

Minor comments:

Page 261, L21: I think "May impact“ should be change to “Impact”

Page 262, L 17: “A” is not defined in eq. 6!

Page 263, L 23: Sentence starting with “Similarly” is awkward, because the water activity still includes the wet diameter, if it is converted to RH

Page 265, L 6: please add details about the precision of the hygroclips and how they were calibrated

Page 265, L 18-21: the kappa value of ammonium sulphate at the point of activation changes with the dry diameter, but you used a constant single value of 0.6. It is unnecessary to introduce such an error to the CCNC calibration even if it is small. Later on you show E-AIM data in the results section for ammonium sulphate, you should use the same for the calibration as well.

Page 266, L 12: carried out

Page 267, L 1: kappa isoline

Page 267, L 2: the curve fitting is not a good option if kappa is continuously changing with in-creasing saturation ratio. It can only be done if the kappa jumps from a kappa_gf value at sub-saturation to a kappa_ccn value at the point of activation. This is usually not the case. One needs several measurement points for a sufficient curve fit, and these have to be made at different RHs. If the kappa_gf is changing with the RH then the fit assuming a constant one will most probably not work. Please comment on this.

Page 267, L 15-17: the sentence is only true if the kappa is not changing with the saturation ratio. Add this to the sentence please!

Page 270, L 13: The efflorescence looks to be a bit higher than 35% on figure 8.

Page 270, L 14: Why don't you give a precise kappa value for glucose? Why only an approximately value, it can be clearly seen that the measurement points lie on a kappa line which is a bit lower than 0.2

Page 270, L 17-18: "unpublished data" is not a reference. Please cite at least a paper which is in preparation.

Page 270, L 20: is it possible to give some info on how much those particle are non-spherical?

Page 270, L 25-27: This sentence has to be reformulated, such that it makes clear that the dry CCN measurement gives most probably false kappa values because the true solute volume cannot be calculated from the dry mobility diameter. The sentence suggests now that the difference in the kappa between the dry and wet CCN measurement exists due to some kind of limited dissolution of the particle.

Page 271, L 13-15: please use another verb instead of "narrow down", your kappa value is out-side of the range of the previous measurements.

Page 271, L 23: please change the term "fully dissolved" to collapsed or restructured.

Page 271, L 24: please comment on the point at around 70% relative humidity having significantly lower kappa

Page 272, L 18: if I understood correctly during the generation of IOP, the particles did not experience higher RH than 65%, and with this you have to talk about deliquescence here and not efflorescence.

Page 274, L 12-13: The evaporation is strongly dependent on the temperature. The temperature in the DMT CCNC depends on the applied supersaturation (temperature gradient in the activation column) and on the ambient temperature. Comparing the "extent of the gap" to the Romakkaniemi et al., 2013 study makes only sense if the temperatures were similar in the two DMT CCNCs.

Figure 6. I find this figure unnecessary. If you still decide to keep it in the manuscript, please correct it, you cannot be sure, that IOP is spherical after wetting (it is even suggested by your humid IOP results, that they are not).

Figure 10. It would be nice to investigate whether the spread in the data points have something to do with the temperature in the CCNC or if it is just measurement noise. You could colour the points after the CCNC's temperature and if there is a trend then include it in the manuscript and discuss it.

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