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Interactive comment on "On the hygroscopic growth of ammoniated sulfate particles of non-stoichiometric composition" *by* H. Kokkola et al.

Anonymous Referee #1

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Kokkola et al. measured the hygroscopic growth factor of 50-nm particles having ammonium-to-sulfate ratios (ASR) of 1.90, 1.78, and 1.46. The experimental results are the three data sets presented in Figure 2. The authors state that the modeling of the data set requires the assumption that an impenetrable shell of crystalline ammonium sulfate coats a core of crystalline letovicite. As a result, water uptake does not occur until ammonium sulfate separately deliquesces. In the absence of such an effect of particle morphology, significant water uptake should occur at 10% lower relative humidity than observed because of the co-dissolution of crystals of letovicite and ammonium sulfate at the eutonic composition.

The report of an inferred morphology by the authors is important. I recommend, however, that this manuscript not be taken beyond a Discussion paper for the following two reasons:

1. The critical mass of a scientific study is lacking.

Three hygroscopic growth curves were measured, and an interesting phenomenon was seen. More axes of measurement are necessary for this manuscript to pass the threshold of expectations as a scientific study (e.g., effects of drying rate? of chemical composition? just three ASR's is incomplete).

2. The presentation and write-up are not acceptable and beyond what can be amended in simple revisions.

2a. Large issues

2a1. organization: 50-nm particles are not identified as the size studied until page 8, line 12 (i.e., nearly at the end of the manuscript)

2a2. Why confuse the reader with 6 to 50 nm on page 4, line 14? Why have an entire section (page 7, lines 15 through page 8, line 5) about size dependence of crystal solubility just to let the reader infer later that none of the section is relevant when the studied size of 50 nm is revealed later in the manuscript?

2a3. Inclusion of Figure 2 in the manuscript does not appear relevant to explaining the data.

2a4. The source of Figure 2 is not cited.

2a5. Lines in Figure 2 are not explained. I infer they are liquidus lines that assume only one solid is present, although the lines are erroneously labeled as deliquescence.

2a6. Antonoff's rule is a gross approximating tool. The citation to Amundson used by the authors is a publication that equally invokes Antonoff's rule without justification. Equation 2 therefore cannot be the basis of quantitatively accurate growth curves.

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2a7. Page 7, lines 23-26: The authors mention that Eq. 2 is employed to estimate the interfacial surface tension between the crystal and the liquid. They do not specify, however, how they obtain the surface tension of the liquid-air interface. How is the dependency of surface tension on solute concentration and droplet size treated?

2a8. Paragraph #1 is in conflict with paragraph #2 of the conclusions. Paragraph #1 sates the particles are solid until the DRH of ammonium sulfate. Paragraph #2 and the data show hygroscopic growth prior to DRH, suggesting the presence of a liquid layer (impurities?).

2a9. Page 6, lines 4-5: It seems that the RH of the aerosol is controlled by adjusting the temperature of the water surrounding the Gore-Tex tube. Changing the temperature of water, apart from controlling the RH of the aerosol, can also change its temperature. Changes in temperature can further affect the DRH values of the aerosols. The authors should mention what is the range of temperatures used (both of the water and the aerosol), and whether any potential changes in DRH would affect their results.

2b. A range of small errors.

2b1. title does not correspond to content

2b2. sentences such as "detailed... in detail" (pg 4, lines 11-12 and "formation... of formation" (pg 3, line 6)

2b3. abstract does not clearly state only 3 ASR's are studied

2b4. "theoretical deliquescence relative humidity"—starting in abstract and used throughout the manuscript is not tightly defined—does the expression mean eutonic RH, final DRH, what?

2b5. Abstract states particle were multiphase (i.e., liquid and solid) yet conclusions and last sentence of abstract state particles have a shell of ammonium sulfate and a core of letovicite.

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2b6. Page 3, lines 1-2: The HTDMA does not give information of the composition, but rather it provides indication of the composition of the particles based on their hygroscopicity.

2b7. page 5, line 17, NH4HSO4 given as ammonium sulfate

2b8. page 6, lines 3-6, the model does *not* assume what is stated. Rather, there are two versions of the model.

2b9. page 6, lines 10-11, DRH is equal to the activity of water only in the absence of a Kelvin effect. This effect is not fully negligible for 50-nm particles.

2b10, lines 20-22, this sentence has two points entirely wrong. (1) AIM does not predict ERH. Martin et al. 2003 have, however, provided a polynomial for ERH. (2) ERH of letovicite is less than that of ammonium sulfate.

2b11. Page 9, line 3: The particles are large compared to what?

2c. Citations to literature are not fully appropriate.

2c1. Page 10, line 12, sentence is outdated by several years (e.g., Colberg et al. 2003, Martin et al. 2004, and references therein).

2c2. Page 3, line 22ff, this account of literature omits many experimental publications (cf. Table 2 in review by Martin, 2000) and the selected publications omit much important recent work published on the crystallization, deliquescence, and aspects of morphology of the ASR chemical system. Schlenker et al. 2005 for example also provide some information concerning particle morphology. The authors do not provide a comparison-and-contrast of their results on morphology with that study and possible explanations for any differences.

2c3. Page 3, line 22ff, the cited publication to Colberg is to 10-micron particles. There is no relevance of the morphology of supermicron-sized particles to the morphology of 50-nm particles.

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2c4. Page 3, line 29. Amundson et al. 2005 is not an original model of hygroscopic growth. Theirs is an original approach about computational efficiency, essentially using the core equations of AIM as the hygroscopic model.

2c5. Page 4, lines 23ff. Reischl (1991) does provide a data inversion algorithm for stepping mode (DMPS) operation of the DMA. Knutson and Whitby (1975), however, only provide the transfer function of the predecessor of the TSI Long-DMA. They provide no algorithm to invert the data. More information should also be provided to the reader about the method used to estimate the size distributions from the mobility measurements.

2d. Application of the model to 1.46 ASR appears problematic since the lever rule prohibits a particle of letovicite and ammonium sulfate. Furthermore, numerous studies show that these acidic particles do not crystallize. The authors make no mention of this fact and appear to assume crystallization in their calculations.

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