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Atmospheric
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Discussions

Interactive comment on "Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment" *by* D. Rose et al.

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We thank David Topping for constructive comments and suggestions, which are highly appreciated and will be taken into account upon revision of the manuscript. Responses to individual comments are given below.

1) Presentation and discussion of Köhler theory and models

Our study was not intended to present a first-principles derivation and comprehensive overview of Köhler theory and models, but we had intended to provide a systematic ac-

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count of the modeling approaches most frequently used in the cloud condensation nuclei (CCN) measurement community and literature. In doing so, we had tried to outline the way from the fundamental Köhler equation via frequently applied approximations to widely used simplified versions of the Köhler equation. In section 3, we have tried to clearly define and distinguish different types of “Köhler models”, corresponding to different forms of equations, and different parameterizations of the variables occurring in these equations. In section 4.6, we have systematically explored and characterized the influence of different parameterizations of solution density, surface tension, and water activity, and we have quantified the deviations between different modeling approaches (Figure 10). Most of the referees and commentators seem to have appreciated our approach, but we will think about possibilities for further clarification and improvement upon manuscript revision. Beyond that, we agree that “establishing a definitive hierarchy in validity of modelling approaches” would be desirable, and that one should generally try to use the most accurate model available. However, in view of the findings and uncertainties outlined below, we did not feel able to decide about and establish such a ranking.

2) Use of Aerosol Inorganics Model (AIM)

As expected, the results obtained with the osmotic coefficient (OS) Köhler model of our discussion paper, which is based on the ion-interaction model of Pitzer and Mayorga (1973), are nearly identical to the results obtained with an activity parameterization (AP) Köhler model based on the Aerosol Inorganics Model (AIM, Pitzer-Simonson-Clegg mole fraction based model; http://www.aim.env.uea.ac.uk/aim/aim.html; Clegg et al., 1998a,b). In the revised manuscript we will include this additional Köhler model and refer to it as AP3 (surface tension and density parameterizations like in the OS model). Over the investigated range of conditions, the differences in supersaturation calculated with the OS and AP3 models is less than 1% (relative) for both ammonium sulfate and sodium chloride.

In practice, however, the OS model appears more straightforward and easy to use, because it builds on a simple semiempirical parameterization of the osmotic coefficient (Eq. 18 of our discussion paper). In contrast, models like AP3, which build directly on water activity calculations of the AIM, require internet access to the online model which is not readily available for offline calculations. To achieve high precision over a wide range of relative humidity/water activity, we had to download multiple files and either use a polynomial fit or interpolate the AIM output data for every step of iteratively determining the critical supersaturation corresponding to a given dry particle diameter. These procedures appear to be more difficult to communicate in a way that allows others to easily reproduce the exact same results.

3) Comparison and accuracy of models

As mentioned above, the AP3 model building on AIM water activity calculations is in very good agreement with the OS models for both ammonium sulfate and sodium chloride. For both substances, however, the AP3 and OS model results strongly deviate from the AP1.1 model results, which are based on the electrodynamic balance (EDB) data and parameterizations of Tang and Munkelwitz (1994) and Tang (1996) - see Figure 10 of our discussion paper.

As outlined by David Topping, one would expect that both the AIM model and the EDB parameterizations provide high accuracy water activities, and that Köhler models building on these water activities (and using the same Kelvin term) should give the same results. Instead, the critical supersaturations calculated for ammonium sulfate with the AP1.1 model (EDB-based) results were 10-15% (relative) higher than those calculated with the OS and AP3 models (AIM-based) - see Figure 10a of our discussion paper. For sodium chloride the AP1.1 model results were 3-5% (relative) higher than the OS and AP3 model results - see Figure 10b of our discussion paper. It appears to us that there are still some open questions concerning the accuracy and consistency of the AIM model and the EDB data/parameterizations, at least with regard to the concentration range relevant for CCN activation.

With regard to our CCN activation measurements of ammonium sulfate and sodium chloride particles (section 4.7 of our discussion paper), the supersaturations obtained with the OS and AP3 models (AIM-based) were 6-18% lower for ammonium sulfate than for sodium chloride, when a constant dynamic shape factor of 1.08 was used for NaCl (1.00 for ammonium sulfate). Under these conditions the supersaturations obtained with the AP1.1 model (EDB-based) were 3-7% higher for ammonium sulfate than for sodium chloride - see Figure 11 of our discussion paper (note that for ammonium sulfate the OS and AP3 results are near-identical to VH4.1, as illustrated in Figure 10).

Using a size dependent shape factor for NaCl and a shape factor of 1.02 for ammoniums sulfate as suggested by G. Biskos (ACPD, 7, S3482-S3487, 2007), we obtained the following new results, which will be included in the revised manuscript (future Figure 11b): The supersaturations obtained with the OS and AP3 models (AIM-based) were 14-23% lower for ammonium sulfate than for sodium chloride, whereas the supersaturations obtained with the AP1.1 model (EDB-based) agreed to within 1% for ammonium sulfate and sodium chloride. These latest results seem to support the EDB-based model AP1.1 rather than the AIM-based model AP3. They are illustrated in a preliminary revised version of Figure 11 from our discussion paper, which is available under the following web address: `http://www.mpch-mainz.mpg.de/~poeschl/Rose2007/Rose2007_Fig11_rev2007-08-17.pdf`

In view of these results, it is not clear to us that the AIM can indeed be regarded as an entirely accurate source for the water activity in the systems investigated in this study. As already pointed out in our discussion paper, we see a need for further evaluation and experimental confirmation of preferred data sets and parameterizations/models for the activity of water in dilute aqueous solutions of ammonium sulfate and sodium chloride.

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4) Miscellaneous

In the more recent EDB studies referenced by David Topping, we found no results for pure ammonium sulfate or sodium chloride particles that would validate or supersede the earlier studies and water activity parameterizations of Tang and Munkelwitz (1994) and Tang (1996).

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