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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into haze and clouds" *by* S. Metzger and J. Lelieveld

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We thank the referee for the time and effort in reviewing our manuscript, in which we address fundamental aspects of aerosol and cloud thermodynamics, not easy to digest. We have addressed all concerns and hope to have improved the readability and the perspicuity of the manuscript. Furthermore we have replied to the Short Comments in the interactive discussion in which some confusion could be cleared, so that it should now be more transparent that all approaches/algorithms presented in our work are new (traditional concepts are presented in the supplement). We have also clarified which limitations are associated with our new method.

1) Yes. p.850 (25-30) these are really main results/findings/conclusions. In particular

(c) is very important. We have added a sentence for clarification. However, to prevent further extension of the manuscript this will be addressed in a separate publication.

2) We would like to point out that there is better knowledge about the chemical composition of the emissions available than used in the lumped aerosol schemes, although it is generally not well applied in models. In addition, the observational basis of aerosol composition is growing rapidly, and this information can be included as it becomes available. Our new concept will help refine the lumped categories like mineral dust, biomass burning, organic aerosols, etc., and chemically define the mixture of species as observed in the atmosphere. Showing in our paper that information on aerosol chemical composition can directly be used in modeling studies will hopefully motivate further improvements of emission inventories and the chemical characterization of aerosol particles.

3) We appreciate that the referee requests improvements in the reader friendliness of the manuscript, and we have attempted to improve this aspect by deleting repetitions, as mentioned in the review. However, we had to add a several new sentences to better explain the many equations. To help the reader with the various equations and deductions, we have added an appendix in which all symbols and acronyms are listed and defined.

4) The solubility of the solute can either be taken from measurements (as readily compiled for various compounds of interest in e.g. the CRC-Handbook) or estimated. EQSAM3 (currently) uses, however, values listed in the CRC-Handbook. When needed, the values used can easily be updated.

5) Sect. 4.2 (p. 875) Yes. The day-to-day variability of the concentration comes in from the measurements; advection is not accounted for in these box-modeling studies. p. 875 (12-20). Reference model only in the sense that ISORROPIA is coded to achieve the highest possible numerical accuracy (though demanding considerably more CPU-time and being much more expensive than EQSAM3). This has been rewrit-



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ten accordingly.

6) Yes. of visibility ... Changed. Especially with the box-modeling results (Figure 3 but also Figure 2) it was shown that EQSAM3 accurately simulates the aerosol chemical composition and water uptake. Note that the comparison of deliquescence relative humidities (RHDs) presented in Table 2 and 3 provides an independent support of the applicability of EQSAM3, whereby all our equations can be solved analytically.

This allows an easy verification of all equations, simply by using the thermodynamic data presented in Table 1 and e.g. solving the equations with a pocket calculator. For instance, we have added examples of RHDs for mixed solutions, and efflorescence $RH$, as both can be directly calculated with Eq. (21). This is now described in Sect. 4.1 (point 5 and 9); for three pure salt compounds (1) $NH_4NO_3$, (2) $NH_4HSO_4$ and (3) $(NH_4)_2SO_4$, we obtain the following efflorescence humidities $RH_{cr,1} = 0.11(0.10)$, $RH_{cr,2} = 0.07(0.02)$ and $RH_{cr,3} = 0.34(0.39)$, respectively; values in brackets are reported in the literature by ten Brink et al. (1996) for $NH_4NO_3$, and Tang and Munkelwitz (1994) for the two other salts, while we obtain a mixed solution $RHD = 0.522$ for a solution composed of $(NH_4)_2SO_4$ + $Na_2SO_4$ + $NH_4Cl$, which is lower than the RHDs of the individual compounds (which are according to Table 3, $0.798, 0.939, 0.7659$, respectively). The corresponding values used in ISORROPIA (Nenes et al., 1998) are $0.54$ (mixed solution), and according to Table 2, $0.7997, 0.93, 0.771$, respectively, for the individual compounds.

In addition, we give an example to calculate the mean molal binary activity coefficient for ammonium nitrate $\gamma_{\pm s(molal)} = 0.1389[kg(H_2O)/mol(solute)]$; Hamer and Wu (1972) give a value of $0.131$ (which is also used and discussed in Mozurkewich, 1993).

We hope that these additional examples provide additional confidence in the accuracy of our method and the global-scale calculations. Note the uncertainties in emissions, which certainly are important and substantial, do not directly affect the accuracy of the EQSAM3 chemical composition and water uptake calculations.



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6) Distribution/transport of nitrates and ammonium are different, since nitrates largely partition into the coarse mode (e.g. condensation on sea salt), which causes a more effective deposition (shown is only the fine mode). Hazy conditions are promoted by a high aerosol load (dominated by hygroscopic salt solutes) and low temperatures, as stated in the manuscript. The EQSAM3 based results for ice clouds compare qualitatively, though remarkably well with the original E5M1 parameterized ice clouds, in particularly for the UTLS region. This mainly indicates that cirrus formation is strongly linked to the meteorology (at least in these model simulations). The conclusion might seem unexpected, but they are fully consistent with our new concept.

The reason is that atmospheric dynamics (including model resolved cloud dynamics) determine the temperature and the water vapor mass available for condensation. This subsequently determines the amount of aerosol water, and it also limits the equilibrium growth. Thus, this quasi-equilibrium approach - and in particular its temperature dependency - implicitly accounts for all aspects of atmospheric dynamics (to the extent resolved by the model), including moisture and temperature fluctuations in the UTLS.

6) We have scrutinized section 5, and enhanced its perspicuity.

7) The limitations of our new concept are now stressed more clearly (by an additional discussion point). We also note that EQSAM3 still needs further validation by direct comparisons with observations under a range of different conditions.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 849, 2007.