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Atmospheric
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Interactive comment on "A comparison of water uptake by aerosols using two thermodynamic models" *by* L. Xu et al.

L. Xu et al.

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L. Xu, J. E. Penner, S. Metzger, and J. Lelieveld:

We appreciate the evaluation of the reviewer, which has allowed us to improve the manuscript and clarify ambiguities. We address each comment below. The reviewer's comments are in bold followed by our response.

Referee 1: 1) "The two models in question are often chosen for their computational efficiency and open ended architecture, whilst known to compromise some accuracy in reference to more detailed models such as E-AIM. However the ability to include further compounds and reduce complexity within representations of detailed processes can be the overriding factor……Model versus model

comparisons, whilst informative, are slightly limited in scope, particularly without benchmark comparisons……Without comparisons against models such as E-AIM it is difficult to ascertain which is correct, if any. On page 9554, lines 18 onwards you present rationale for the comparison presented. I would like to see a brief discussion or statement as to why you have not conducted benchmark analysis for water uptake and activity coefficients. These comparisons would be of great use to the community if it becomes clear that regions of model discrepancy when compared with ambient data are caused by a basic inability to capture fundamental properties."

Reply: We agree that E-AIM models are currently regarded as the most accurate inorganic aerosol thermodynamic models available in the scientific community. We choose the same 10 cases conducted in the study of Zhang et al. (2000) so that we could make a direct comparison of the results simulated by EQSAM3 and EQUISOLV II with the results from four other thermodynamic modules (MARS-A, SEQUILIB, SCAPE2 and AIM2) for the same initial conditions since Zhang et al. (2000) have already conducted a comprehensive comparison of five inorganic aerosol thermodynamic equilibrium modules for their similarities, differences and likely causes of discrepancies. In section 3, we revised the text as follows: "Note that we also include some of the same cases in each of these three regimes that were included in the inter-comparison of Zhang et al. (2000), which allows us to make a direct comparison of the results simulated by EQSAM3 and EQUISOLV II with the results simulated by four other inorganic aerosol thermodynamic modules (MARS-A, SEQUILIB, SCAPE2 and AIM2) for the same initial conditions." We also added the particulate matter concentration from AIM2 for these 10 cases in Table 5 for reference.

Referee 1: 2) "I think the title is a little bit confusing. In a sense it seems to convey a subset of your work which includes particulate mass loading, chemical speciation and of course, water uptake. Whilst the ability to predict water uptake relies on all factors, the two models which you are comparing have subtle dif-

ferences which, of course, you have explored in various levels of detail. I would suggest maybe changing the title to reflect comparison between two thermodynamic equilibrium models as referenced to your chosen metrics."

Reply: We changed the title as "A comparison of inorganic aerosol thermodynamic properties predicted by EQSAM3 and EQUISOLV II".

Referee 1: 3) Whilst it is difficult to include organic components it would be nice to reference the extent to which predictions of solid precipitation for inorganic systems are of any use. Multiple experimental, theoretical and ambient studies on water uptake have indentified that aerosol particles remain aqueous and/or amorphous even at low RH. In any case, the ability to include predictions of solid precipitation is restricted to only a very small subset of organic functionality in mixed inorganic/organic systems.

Reply: Since we are conducting a comparison of the inorganic system, solid precipitation is still of interest though we agree that the importance of this process to real atmosphere which includes aerosols mixed with organics, is of less importance. We also agree that it would be important to add organics to the model, although we consider this to be beyond the scope of our present project.

Referee 1: 4) Sections 3.1- 3.7 all discuss comparisons between key aspects of the two chosen models whilst no reference to any broad results are ascertained by the reader within the abstract. In some respect this makes it hard to follow and slightly turgid. It would be nice to broader the scope of the abstract.

Reply: The abstract is updated in the revised version.

Referee 1: Section 2, page 9556, lines 15-18. To the best of my knowledge, Bromley's mixing rule cannot be relied upon to accurately reproduce activity coefficients in moderate to concentrated solutions. Can you provide reference to studies which suggest this is or isnt the case?

Reply: "Zaveri et al (2005) suggest that the Bromley mixing rule is reasonably accurate for subsaturated solutions and their applicability for saturated and supersaturated multicomponent solutions is limited by maximum ionic strengths up to which the mean binary activity coefficient parameterizations are valid. Because of its simplicity and reasonably good accuracy, Bromley mixing rules have been widely adopted in a number of aerosol models (Bassett and Seinfeld, 1983; Saxena et al., 1986, Kim et al., 1993a; Pilinis et al., 1987; Jacobson, 1996, 1999; Nenes et al., 1998; Fountoukis and Nenes, 2007)". This will be added to Section 2 in the revised version. "Zaveri, R.A., Easter, R.C. and Wexler, A.S.: A new method for multicomponent activity coefficients of electrolytes in aqueous atmospheric aerosols, J. Geophys. Res., 110, D02201, doi: 10.1029/2004JD004681, 2005" will be added in the reference in the revised version.

Referee 1: Section 2. The ability of ZSR to reproduce water content and growth factors in moderate to highly acidic solutions depends largely on how the partitioning of ions to relevant solutes is treated (H_2SO_4, $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$). For example, Zaveri et al (2005) present a parameterised scheme which accounts for any partial dissociation on the stability of appropriate solutes. Can you comment at this stage on how the ZSR method is used in EQUISOLV II?

Reply: Jacobson (1996, 1999) stated that the liquid water content in EQUISOLV II is determined by the ZSR method, which is function of the molality of the electrolyte pair in the solution at the ambient RH (Eqn. 4 in Jacobson 1999). Moreover, the molality of the electrolyte pair in the solution is fitted to polynomials as a function of the water activity. The polynomial coefficients are listed in detail in Appendix Table B.10 of Jacobon (2005) and Table 8 of Meng et al (1995). Basically, in EQUISOLV II, the equilibrium concentration of each species including liquid water content are calculated by numerically solving the equilibrium equation for each species separately, accounting for each chemical reaction. The solute activity coefficient and water contents are updated once the local convergence criterion is met (i.e., the level-2 and -3 iterations are completed). All equilibrium reactions and temperature dependent rate coefficients are listed in Jacobson (2005). The partitioning of ions to relevant solutes (H_2SO_4, $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$) can be inferred by solving these solid-liquid equilibrium reactions as a function of the temperature and relative humidity. These comments are added in Section 2 in the revised version.

Referee 1: Section 2, page 9558, lines 15-21. Has the ability of models to prescribe crystallization relative humidity (CRH) been tested against experimental data?

Reply: The CRH data that we used are based on laboratory data and are listed in Table 17.4 of Jacobson (2005). We also show the use of these data in Fig. 8 which shows a comparison between the upper branch and lower branch of the hysteresis loop for EQSAM3 and EQUISOLV II.

Referee 1: Section 2, page 9558, line 24. 'Since the RH fixes the water activity of atmospheric aerosols in equilibrium with the ambient air..' This is true only when there is a negligible Kelvin effect. Please add comment accordingly.

Reply: To the best of our knowledge, the Kelvin effect is considered in a few equilibrium models, such as KEQUIL (Bassett and Seinfeld, 1984) and MESA (Zaveri et al, 2005), but the effects can be neglected for particles larger than 0.1 μm. In the study of Bassett and Seinfeld (1984), it was found that there is no significant change in the amount of the condensed species with the exception of water when the effect of surface curvature is considered or not. However, the differences in the amount of water with and without the Kelvin effect did not exceed 8 percent. Thus, ignoring the Kelvin effect, as we do here, is a good approximation for the sake of computational efficiency. We have changed the text in Section 2 of the manuscript to:

"Since the RH fixes the water activity of atmospheric aerosols in equilibrium with the ambient air……Note that Kelvin effect, an effect which can be neglected for the particles larger than 0.1 μm (Bassett and Seinfeld (1984), is not considered in these two

models".

Referee 1: Section 3, page 9559, lines 10-20. In this section you refer to chosen compositions for which you perform model comparisons. Are these compositions representative of certain environments?

Reply: Yes. These compositions are adopted similar to the study of Zhang et al. (2000), which cover most of the expected range of thermodynamic equilibrium regimes under typical urban and coastal atmospheric conditions. The concentrations of metal species we added were inferred from the study by Fountoukis and Nenes (2007).

Referee 1: Section 3.1 Aerosol water. A difference in water content by a factor of two between EQSAM3 and EQUISOLV II is a tad worrying, specifically in reference to sulphate rich regimes in which the assumption employed within EQSAM3 may not hold. If EQUISOLV II is to be regarded as the benchmark code in this study, as indicated by comments such as 'EQSAM3 under/overestimated..' then I think a clear description of the ZSR scheme in EQUISOLV II, or at least an adequate reference, is required in line with my previous comments. Section 3.3, page 9564, line 25. The statement 'coupling with an aqueous phase chemistry module is foreseen instead' is very vague. What exactly does this mean?

Reply: A description of the ZSR scheme and references will be added in the revised version. We will remove the statement 'coupling with an aqueous phase chemistry module is foreseen instead' since it is not relevant to our study.

Referee 1: Section 3.6. Compared with all previous sections, this section is particularly small. The opening statement 'there is a larger discrepancy between predictions of potential of hydrogen (pH) in the solution system between these two models for the sulphate rich and neutral regimes.' seems a touch out of context and jumps into a particularly discussion too soon. Wouldn't we expect a large discrepancy between predicted pH in sulphate rich regimes? I would like to see some more statistics in this section.

Reply: Section 3.6 is revised to “There is a larger discrepancy between the predictions of potential hydrogen (pH) in the solution system between these two models for the sulfate rich regime. According to Table 4, we see that EQSAM3 predicts about a factor of 6 higher pH for the solution system than does EQUISOLV II in the sulfate rich regime. This may be ascribed to the partial dissociation of bi-sulfate (e.g., NH_4HSO_4(s) ⇔ NH_4^+ + HSO_4^- and HSO_4^- ⇔ H^+ + SO_4^{2-}) in EQUISOLV II when sulfate is in excess while the dissociation of the sulfate salt (e.g., $(NH_4)_2SO_4$(s) ⇔ 2NH_4^+ + SO_4^{2-}) is preferred in EQSAM3. For most cases in sulfate poor and neutral conditions, the difference between EQSAM3 and EQUISOLV II is well within a factor of 2”. The statistics for pH will be added to Table 4.

Referee 1: Section 3.8 Growth Factor. In this section you present a derivation for hygroscopic growth factor. However this equation seems to be incorrect. If you derive the ratio of wet to dry radius then the density ratio should be that of the solution over the dry particle, not solution density over that of water. Can you check this and reference where you found this equation if possible. The sensitivity of growth factor to assumed stable salt, thus dry density, has been probed by numerous researchers and would change the conclusions significantly.

Reply: Right, but this was only a typo in the manuscript. The paragraph in the Section 3.8 is revised to “where GF is the growth factor, is the density of the dry aerosol mass, is the density of liquid water, is the aerosol water predicted by the model, and PM is the dry mass”.

Referee 1: Section 4 page 9571. I think the inability of both models to capture nitrate mass loadings, particularly for EQSAM3 needs to be portrayed in the abstract. This would have impacts for future scenarios with reduced sulphate emissions.

Reply: This is true only for small nitrate loadings for which are limited under atmospheric conditions. So we feel it is not necessary to highlight this in the abstract. Also,

it is clearly mentioned in the conclusions.

Referee 1: Section 5, page 9574, line 14. Again, please elucidate on the comment ‘..coupling with an aqueous phase chemistry module is foreseen instead’.

Reply: We removed this statement in the revised version since it’s not relevant.

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