

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

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On the weight of the reviews, the short comments and the responses to the reviews, I am unable to recommend publication of the manuscript at this time. The particular circumstances surrounding the current manuscript are extraordinary. It may be that the manuscript, with only moderate modification, is publishable following extensive published and peer-reviewed clarification of the many aspects of the original manuscript presenting the EQSAM3 model (ML07) raised by the discussion comments and the last two solicited reviews. The last responses by authors Metzger and Lelieveld (M & L) go some way to clarifying some of the points in these two reviews and the unsolicited comments, but the current manuscript and its discussion forum is not the place for the presentation of such material. Were the rebuttals to be comprehensive,

unambiguous, convincing and overwhelming, then their distillation and inclusion in the current manuscript may be possible with a major rewrite. However, there are remaining outstanding criticisms surrounding the construction of EQSAM3 that are of concern. These need to be addressed prior to publication of a manuscript comparing it with an established equilibrium solver.

Very briefly, specific outstanding criticisms include the following:

i) the comment by M & L: "Nevertheless, we would agree that our  $v_w$ -approach could be called a parameterization or a semi-empirical approach, similar to the activity coefficients methods used in thermodynamic models. All other parameters, however, are directly derived from  $v_w$  and not parameterized in EQSAM3" acknowledges that the  $v_w$  expression is a parameterisation and it is stated that it is similar to the approach used in thermodynamic models (not that it is a thermodynamic model). It remains without any obvious derivation. This is the essence of Lescroart's first criticism. Furthermore, semi-empirical models using activity coefficients are based on models of the excess Gibbs free energy with conceptually well-defined empirical parameters, in this way differing from the  $v_w$  approach.

ii) It is also acknowledged by M & L that the approach in ML07 was "unconventional". It is evident that the combination of hydration and hydrolysis in this first paper is so unconventional as to have caused a great deal of confusion within the community of established experts in atmospheric aerosol thermodynamics. The attempts at terminology clarification by M & L in the discussion may go some way to satisfying the criticisms, but an extensive and entirely transparent explanation needs to be in the peer-reviewed literature.

iii) There remain a number of specific queries by the third anonymous reviewer, many relating to the language of the original paper, but some directly querying the thermodynamic basis (e.g. on page C1905) that need to be addressed in the peer-reviewed literature.

In summary, there are some interesting ideas in the EQSAM3 approach, for exam-

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ple parameterising activity coefficients as a function of water activity, but there is no comprehensible theoretical derivation of the non-iterative analytical solution to the gas-solid-liquid equilibria that has been claimed. From the comparisons in the Xu et al. paper, it appears that EQSAM3 is capable of prediction of some properties in some sub-spaces of the system with some accuracy, but that it does not behave well across the full space accessible to thermodynamic models. It is completely insufficient to state (as M & L do) that "What would be most relevant for reviewing the Xu et al. manuscript is that models are judged upon their predictive capability." ... and... "We propose that Lescroart et al. (and Referee 3 and R. Zaveri) consider the testing of eqs. 19-23, being at the core of EQSAM3, which is done in Xu et al." Such an approach to the critical evaluation of EQSAM3 would be entirely inadequate, neither following scientific method nor capable of insightful progress - the basis of the construction of EQSAM3 must first be transparently established.

I agree that, as stated by M & L, "Therefore it is important to disentangle the concept discussion from the application in the present manuscript by Xu et al.", but application cannot precede conceptual acceptance by the community. Since Xu et al. have made a significant effort in putting together the comparison for the current manuscript, I would suggest that it would may be publishable once the above clarifications have been fully peer-reviewed and published. Alternatively, it may be possible to resubmit the manuscript (including the AIM & ISORROPIA2 comparison, and working across the "difficult" regions of the composition space highlighted by Rahul Zaveri) as the second part of a 2-part paper that were reviewed as a pair. The first part would need to contain all the above clarifications.

As a final note, I too find it regrettable and unhelpful that open comments were posted about the Discussion paper outside the normal review process whilst the Discussion was open. I would urge that such detailed comments on papers in ACP open Discussion are posted through the Discussion forum.

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