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Interactive comment on "ANISORROPIA: the adjoint of the aerosol thermodynamic model ISORROPIA" *by* S. L. Capps et al.

Anonymous Referee #2

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I come to this review with expertise in aerosol and solution thermodynamics, but not in atmospheric modelling, nor in the mathematical techniques involved in inverse modelling.

I will begin by discussing a potential problem for which I think some additional calculations are required, and follow that with the (many) instances of poor, obscure, or inaccurate explanation that should be rectified.

(1) The division of chemical composition by ISORROPIA into different composition "spaces" for reasons of efficiency is clearly a disadvantage for the purpose of the work described in the ms, as identified by Jim Kelly. The effect of this division is illustrated in Figure 6 (particularly part (a)). In that case the value of the partial differential 'flips' from zero to about unity along a straight line. This may be correct within the model

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but the degree to which it is really true is not demonstrated by the authors. Two other points about this and the other plots in Fig. 6: first, the chemical system is simple enough that, it seems to me, the values of the partial differential ought to vary rather simply on the triangle diagram. Instead, the pattern is irregular with much perplexing fine detail (which I certainly can't explain). Second, are the axes correctly labelled? In Figure 6a the bottom right apex of the triangle is 100% HNO3 according to the label. But if this is correct then (according to the figure) the partial differential is greatest (2.0) for compositions with the highest HNO3 in which this acid is in excess (and has presumably neutralised all the NH3 so that essentially all of it is present in particle phase as NH4+). The figure makes better sense - although my comments about the pattern of values are unchanged - if the bottom left apex is HNO3, the top one is H2SO4, and the bottom right one is NH3.

It is important that the authors both correct the figure, and produce a comparison plot in which the same quantity is calculated using some general thermodynamic model of the system in which no division into composition regimes is made. This will be valuable (here and perhaps elsewhere) to evaluate the effects of this division.

(2) The development of ISORROPIA in terms of a series of different 'composition spaces' also seems to have led to the development of shorthand language that, taken as statements of simple chemistry, is either mystifying or just wrong. For example, in section 2.2 it is stated that the acidity of the aerosol is equivalent to the relative abundance of positive and negative ions. Is it really necessary for a reviewer to have to point out the errors in this? There are a number of instances in which the term 'neutralize' is misused. For example: '..sufficient ammonium and sodium are present to neutralize the aerosol sulphate.' The term only makes sense when referring to the addition of an alkali to an acid, of vice versa. To compound their error, the authors mention elsewhere that the ion NH4+ 'neutralizes' SO42-, and that '...Na+(aq) reaches its full potential to the neutralize SO42-(aq)...' (sic). These are chemically meaningless and incorrect statements, and can only mislead and confuse. I have to wonder whether

the first author really understands the behaviour of the modelled system in the way it ought to the understood and explained: equilibria between gas and aqueous phase NH3 and HNO3 (plus aqueous ammonia/ammonium, sulphate/bisulphate, and water dissociation). The systems that also contain Na+ do so in the form of an added salt, referring to these systems as having sulphate partially or wholly 'neutralized' by Na+ is quite wrong. I would not regard this ms as good enough for publication unless these descriptions are corrected throughout.

(3) I agree with Kelly's comment about Pitzer vs. K&M: Pitzer is more accurate over the range of ionic strength for which it is valid. At much higher ionic strengths 'unphysical' behaviour is often predicted, hence the use of K&M.

(4) The introduction places the present study in the context of other work in the same and related fields. I do not have the expertise to judge how well this has been done. However, much of the text is unclear or obscure - in some cases I could see what the authors mean, in others not at all. Some re-writing is required. I have listed the offending sentences below, in many cases without further comment. I assume that the senior authors of the paper will see the problems.

p23471: "as well as providing a means of refining emissions estimates with observations." Do you mean inferring emissions directly, or working out what emissions values need to be known most/more accurately? If the former, then the process seems rather circular.

p23471 "..challenges the robust assessment.." Language for a bad press release.

p23472 "..reveals the impact .. without perturbing the model state."

p2372 "..source oriented sensitivities.."

p2372 "..gas phase sensitivity relationships.." Be specific: sensitivity of what to what?

p23472 "Gas phase 4D-Var data assimilation..." Introduced without explanation.

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p23473 "recently increased impetus for their utility."

p23474 "..the entire deliquescence curve.." Do you just mean RH range? See also Kelly's comment.

p23475 "weights the difference of modeled concentrations translated into observation space" Difference from what? The first part of the sentence isn't any clearer.

p2376 "a priori pa" . ?

p23476: "model parameters". Parameters are usually fitted coefficients within a model. Here they seem to mean, much more loosely, the quantities of interest that are either output by the model or are input to it. Some specific examples, and more exact use of language, would be helpful.

p23479: "If the governing equations are differentiated and then transformed into a numerical algorithm, the adjoint is termed a continuous adjoint; hence, the discretization of the adjoint model may not be in accordance with the underlying model." I do not understand what is meant by the last part.

p23479: "checkpoint the solution regime".

p23479 "was used to augment the forward model with sensitivity calculations capable of treating adjoint forcing vectors provided in a box modeling context". Clarify.

p23482 "Partitioned concentrations". I think this just means "results".

p23481 "differentiable calculation".

p23482 "metastable assumption". I know what this means (even though it comes out of the blue); others may not.

p23485: "Model input ranges"

p23485 "...so that calculations, not variable writing processes, were evident in the comparisons." This is about execution time. Say so.

p23487. The differentials are all unitless, but are either on a molar or mass basis. Writing "mol mol-1" is not the best way to express this.

p23487: molar mass not molecular weight. Nitrate is not a molecule.

p23492: "..is used the reveal the sensitivity regimes..". "Reveal" suggests a stage performance, such as pulling a rabbit out of a hat, or (an old IBM term, I'm told) "opening the kimono". I'll leave that one to your imagination. "Determine" is a more appropriate word in a scientific manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 23469, 2011.