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Atmospheric Chemistry and Physics Discussions

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

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Capps et al. ... The potential impact of such limitations on the applications that motivate ANISORROPIA's development should also be discussed.

We thank Dr. Kelly for his overall enthusiastic support of ANISORROPIA, and the thoughtful and very extensive review. Our responses to all the issues raised are presented below.

General Comments:

On p. 23482 line 12, the . . . The authors also mentioned on p. 23482 that the adjoint

code returns a flag for appropriate handling by the host model when the model is unsuccessful. However, it is unclear what the host model can do with this flag except count the number of failures (a similar comment applies to the statement on p. 23491, line 18).

This is an excellent point. Errors arise from i) cases where the post convergence application of Newton-Raphson did not work, and, ii) very highly concentrated solutions (at low RH) for which the value of ionic strength met the maximum allowed value (MAXIONIC=100) during the calculation of activity coefficients. Subsequent sensitivity tests allowed us to reduce the error occurrences to slightly below 10% (without significant increases in disagreement of the adjoint and CVM sensitivities) by increasing MAXIONIC to 200. Figures 2, 4, 5, 6 and 7 are revised to include data produced with these adjusted threshold values and discussion revised to clarify the sources of errors.

The first implementation of ANISORROPIA in a chemical transport model adjoint simply refrains from repartitioning species in calls to the thermodynamic module that result in internal errors. Identical time steps and grid cells are ignored in the forward and adjoint code. This approach was inspired by similar treatment of physically unrealistic results that occurred before implementation errors were resolved in the CMAQ aerosol module. Mass is conserved, and non-physical results are appropriately ignored with this setup. The revised discussion includes a brief description of this method.

The complex variable method (CVM) is implemented to evaluate ANISORROPIA adjoint sensitivities because of challenges arising from the "highly nonlinear, discontinuous solution surface of ISORROPIA". . . . . Perhaps other representative scenarios could be considered and included for reference in a supplement.

Branching and discontinuity is not unique to ISORROPIA. In fact, there is hardly *any* science routine without some discontinuity in the form of "GO TO", "IF", "MAX/MIN", "ABS", etc . The probability that a perturbation-based evaluation of the derivative spans across the point of discontinuity is finite and happens in reality, though orders of mag-

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nitude less frequently with CVM than FD. ANISORROPIA does not suffer from this problem however, because it is a *discrete* adjoint with a continuous set of solutions and derivatives for each subdomain of the code.

The motivation for developing ANISORROPIA is to calculate sensitivities that can be used in practical applications (e.g., inverse modeling, emission control strategy development, etc.) where a finite perturbation in a model parameter would generally be made based on the linear adjoint sensitivities. . . . I recognize that a full evaluation of these issues is beyond the scope of a single study, but this article should at least raise the key issues that will need to be addressed in practical applications with ANISORROPIA.

Applicability of forward formal sensitivities (DDM) in 3D applications including ISORROPIA has been discussed before (e.g., S. L. Napelenok et al. 2006; Koo et al. 2007; S. Napelenok et al. 2008; Zhang et al. 2011). Adjoint sensitivities should behave similarly. In fact, adjoint sensitivities are less likely to be impacted by nonlinearities in 3D applications than (more commonly used) brute force forward sensitivities. Nonlinearity in atmospheric response generally occurs when changing an input parameter causes a sufficiently large shift in the chemical state of the atmosphere. Forward sensitivity applications often deal with domainwide changes in inputs such as emissions while adjoint applications often relate to cases that correspond to making changes in individual sources. As such, applications that more readily lend themselves to adjoint sensitivity analysis are less likely to be affected by nonlinearity as the result of a significant shift in the chemical state of the atmosphere.

With the above said, two applications of ANISORROPIA in 3D modeling frameworks will be seen shortly in the publication record: the adjoints of GEOS-CHEM and CMAQ. They will effectively demonstrate the practicality and stability of the code.

The results presented in the ternary diagrams in Figures 6 and 8 appear to disagree with results in Figure 7. ..The overall effect of these figures and statements is confus-

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ing. I apologize if I am misunderstanding something basic here, but please clarify or fix these sections as necessary.

Thank you for the attention to detail. The issue of switched axes labels, caused by a bug in the graphics program, has been corrected; the discussion, likewise, has been revised.

The purpose of discussing inverse modeling in the manuscript is vague since this application is not considered . . . directly on the mathematical background of the approaches used in applications in the current study or on better relating the 4D-var example to the approaches considered in the current study.

Excellent point. Section 2.1 is revised to describe a cost function in species-space only rather than introducing the inverse modeling framework. The Introduction and Conclusions sections are modified accordingly.

Specific Comments:

p. 23471, lines 1-2: It is unclear why . . . applies to p. 23477 lines 6-8.

Corrected in both instances. Particle phase is now indicated rather than aqueous (i.e., $Na^{+}_{(p)}$).

p. 23474, line 9-10: Is there a better . . . as metastable solutions, because particle solutions are stable at high RH.

Agreed on both accounts. "Deliquescence curve" now reads "water uptake curve". "these CTMs often ... aerosol." now reads "CTMs neglect the formation of solid phases in aerosol."

p. 23474, lines 23-24: By "produce a field . . . applications"?

Not exactly, rather "to produce a field of requisite perturbations in input parameters" now reads ", indicating the corresponding perturbations of input parameters required to effect the infinitesimal change in output."

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p. 23477, lines 10-11: I think . . . could just be stated.

Agreed. "The timescale of equilibration. . . surrounding gases" now reads "CTMs often treat fine mode particles as existing in thermodynamic equilibrium with the surrounding gases based on the short equilibration time scales for these particles." Thank you for the phrasing.

p. 23478, lines 1-2: This seems like a strong statement. Is it true that K-M is more accurate than the Pitzer model? The studies by Kim et al. (1993a,b) actually state that the Pitzer method is superior up to I = 20m, and the Kim et al. studies do not consider updates by Clegg et al. (1992a,b).

Thank you for clarifying. The text now states "K-M compares well with experimental results as does Pitzer but also continues to produce physically reasonable results at higher ionic strengths (i.e., greater than 30m) (Harvie et al. 1984; Cohen et al. 1987; Kim et al. 1993).".

p. 23479, lines 10 and 18: Please clarify "formed by hand" and "checkpoint"

The text is revised from "formed by hand" to read "developed by manually processing the code line by line" and "checkpoint" to read "checkpoint, or store to a file,".

p. 23480, lines 21-23: Has this intercomparison been performed? Can it be included here?

This method describes precisely the source of the discussion in Section 3.2 and all data in Figure 4, which is now made clear in the text.

p. 23481, line 17: Is "post-convergence Newton-Raphson method" supposed to indicate that bisection output is being used as the initial guess for N-R?

Yes, this is now clarified on line 22 of the same page.

*p. 23482, line 7: Why not consider lower temperatures since they will frequently be encountered in 3D simulations?*As noted on p. 23484, line 20, the range from 268 –

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308 K was evaluated. This wider range is now reflected in the revised Figures 4 and 5 as well as the corresponding discussion.

p. 23483, lines 20-21: Can you reword for clarity?

Certainly. The text now reads “CVM maintains the sensitivity information for variables in their imaginary part; thus, complex variables must be altered commensurately in the real and imaginary parts.”

p. 23484, equation (5): Since this approach could be used in the future, it might be worthwhile to state that (5) arises from

Good point. It arises from $df = \frac{\partial f}{\partial x}|_{x=x_o} dx + \sum_{i=1}^{3} \frac{\partial f}{\partial A_i}|_{x=x_o} dA_i$, where $dx = Im(x_o)$, and $dA_i = Im(A_i)$. This explanation is incorporated in the revised text and helps clarify the discussion on lines 20-22.

p. 23484, line 20: Is the performance for results at 268-288 K similar to that at 288-308 K? These results could be included in a supplement for future reference for users who might be interested in low-T applications.

Performance diminishes slightly at lower temperatures. Figures 2, 4 and 5 as well as the corresponding discussion now include assessment of results at 268-308 K.

p. 23485, line 11: Does use of the same convergence criteria imply that the same number of unsuccessful attempts occurred for both models, and so failures did not impact timing results?

True, for the adjoint versus forward comparison, the same number of failures occurred and the ratio of these times reflects solely the additional computational time required for the adjoint. The forward versus original comparison does not necessarily have the same number of failures, but the ratios of almost unity for the ANISORROPIA forward to original ISORROPIA indicate an insignificant effect.

p. 23488, line 3-4: Can you provide a better explanation for the negative sensitivities

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at low T?

The water uptake associated with sulfate versus nitrate at low temperatures causes a shift in the balance of these species, which causes negative sensitivities by virtue of the ratio of the molar masses of these entities.

Figure 7: The parts of the figure where the regions overlap may generate confusion. I would recommend clarifying these regions in the figure or text. Also, the figure legend refers to the "increasing gradient from left to right" but the vertical gradient is more clearly apparent.

The overlapping regions are now clarified in the text. True, the changing concentration of H_2SO_4 creates a vertical gradient; however, the authors intended to highlight the role of the positive ions and thus focused on the horizontal gradient.

p. 23488, line 21-22: As mentioned above, I think a supplement with figures for alternative scenarios could be a handy reference for future studies that apply ANISORROPIA to a wide range of conditions.

Certainly future applications of ANISORROPIA should be able to reference this introductory paper as a means of ensuring that the results are reliable across a wide range of conditions, which the evaluations in the revised manuscript demonstrate. The authors intend only to demonstrate the capabilities of the new tool rather than provide a comprehensive view of atmospherically relevant thermodynamic sensitivities with examples; these will be immediately apparent when the tool is applied at a variety of conditions and trustworthy due to the wide range of evaluated data in the revised manuscript.

p. 23489, lines 13-14: Nowak et al. (2006) concluded that "the assumption . . . conclusions of that study.

The reviewer misread our statement; perhaps a better wording would be "demonstrated the level of accuracy of ISORROPIA" and is now included in the text.

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By the way, it is not a stretch to say that ISORROPIA did a very good job in Atlanta. The slope of predicted-versus observed ammonium was indeed 1.25, but the R^2 was remarkably high for an ambient aerosol study. The bias could arise from unconstrained parameters not included in the calculations, which include amines, size-dependent chemistry and transients.

p. 23491, line 5: Here it is suggested that precipitation of solid phases have a minor impact on results, but the previous page (p. 23490, line 23) suggests precipitation of salts has a significant impact on results. Please clarify.

Assuming the aerosol is in a metastable state affects the results of ISORROPIA to a minor degree (p. 23491, line 5); however, the sensitivities of the system (metastable or not) are significantly affected by the change in relative humidity. The two lines of thought do not conflict.

p. 23491, lines 11-13. It is hard to understand the differences in results because significantly different versions of ISORROPIA are being compared. Are the results the same when the Fountoukis et al. (2009) finite difference calculations are repeated with ISORROPIA (rather than ISORROPIA-II)?

The forward calculations of ANISORROPIA produce results consistent with ISORROPIA II (Fig. 2), so the two differences arise solely from assumptions necessary due to the current capabilities of ANISORROPIA. The metastable assumption employed in the adjoint sensitivity calculations produces a slight underprediction in NO_3(p) concentrations (Fig. 4 of ...Fountoukis et al. 2009), which would be reflected in the sensitivities. The approximation of crustal species as equivalent sodium is demonstrated by Moya et al. (.....Moya et al. 2001, Fig. 2) to be reasonable for predicting aerosol nitrate.

p. 23491, lines 17: Do results with unrealistic sensitivities imply that the success percentage of 70% reported here is an upper estimate (i.e., in addition to cases that do not converge, results from other challenging cases may not be usable)?

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In short, yes; however, the relatively insignificant deviation from expected values in nitrate sensitivities demonstrated in Figure 9 may suggest that reasonable information still exists even in these challenging cases that could be included depending on the application. The sentence is removed.

p. 23491, lines 18-21: Do the differences in sensitivities for the adjoint, backward difference, and central difference approaches imply that making finite perturbations in model input parameters based on adjoint sensitivities will produce unintended behavior in practical applications?

To the contrary, these differences demonstrate that large finite perturbations (e.g., zero-out, 50% emissions changes) do not accurately capture the relationship of modeled concentrations to emissions. As no perturbation from the realistic or typical state of the model is required for assessing adjoint-based sensitivities, these reflect the dynamics of the system rather than the fractured surface imposed for the sake of computational efficiency.

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