

Response to reviewer #2 comments

We thank the anonymous reviewer #2 for their review.

We feel strongly the reviewer overstates the severity of the issues he identifies. It seems to us that many if not all of the reviewer's major comments are related to weaknesses in the clarity of the manuscript. We have revised the manuscript to address this, giving additional explanation where appropriate.

There are 3 elements the reviewer identifies as together meaning major revisions would be required before publication in GMD:

(1) “(...) (T)he box model tests and global modeling results presented do not clearly demonstrate the accuracy of the solver against a benchmark method and fail to properly evaluate its efficiency (for a chosen level of accuracy) or directly compare it with previously published solvers.”

We assert strongly that our use of the fully dynamic implementation of the Jacobson (1997) scheme as a benchmark to test the hybrid dissolution solver is entirely justified. The potential of the embedded fully dynamic scheme to serve as a benchmark is documented in the literature (Zaveri et al., 2008). Similarly, this manuscript builds on the previous testing of the thermodynamic scheme against AIM (Topping et al., 2009), and there should be no need to redo this here.

(2) “The new solver is also incomplete because it presently appears to ignore gas-particle mass transfer to solid particles, which may be present under low relative humidity conditions.”

Our paper describes a hybrid solver to calculate the dissolution of inorganic gases into the aerosol aqueous phase. We agree that we should perhaps have stated more clearly that aerosol solid phase processes are not included. However, the purpose of the paper is to describe and evaluate the new solver in the box model, and assess its numerical reliability and computational efficiency within the framework of a global model. We content strongly that the paper is consistent and adequate as being directed towards these aspects.

(3) “The manuscript is lengthy and a bit confusing in various places due to imprecise notations and terminologies.”

We acknowledge that the paper is long, but when writing it, we considered carefully to what extent it should be shortened. We concluded that the level of detail provided is important and will help to ensure reproducibility of results and to rigorously describe the solver. We note that reviewer 1 states that “*all parts seem essential and show the logical steps from development, over sensitivity studies in a box model to application in a global model.*”

We also are puzzled that the reviewer regards the use of ‘size bin’ and ‘size increment’, ‘dissolving’ and ‘non-dissolving’, the way Eq. 9 is introduced and an apparent typing error in Eq. 15 as major issues,

while the large amount of effort that was put into the explanation of the solver appears not to find any credit.

Finally, some of the reviewer's concerns, like the confusion around Figure 1, could have been easily addressed via a question to the authors.

Within the following we will address the points of the reviewer in the order given within his/her comment.

Major comments:

1) “The new hybrid solver described here treat dynamic (and equilibrium) gas-particle partitioning of HNO₃, HCl, and NH₃ for aqueous particles only. The implicit oversimplifying assumption is that all aerosol particles are always fully deliquesced at all relative humidities. This assumption may not hold at low relative humidities (below about 35-40%) where dissolved salts can effloresce to form a solid phase. The solver also ignores heterogeneous uptake of HNO₃ on dust particles containing calcite, which is an important sink for nitrate. The proposed solver is therefore incomplete and premature for implementation in a global atmospheric transport model. These are major weaknesses that must be rectified before the present work can be considered for publication.”

The reviewer observes that the heterogeneous and solid phase processes are not treated by the solver, and maintains that its implementation within a global model is premature. We agree that solid phase processes are not included and that these play an important role for the aerosol inorganic composition. The revised manuscript now makes it much clearer that these processes are not included and gives reference for papers which include them and assess their effects.

Also, we would like to stress that the paper is clearly set out to describe and evaluate a new solver for the reversible dissolution of inorganic species into the aerosol liquid phase. As stated within Section 5.1, the solver is implemented into a global model to verify that it is able to give realistic results for the full parameter space encountered in a global 3D chemistry-aerosol transport model, to demonstrate the importance of the non-equilibrium property of dissolution, and to evaluate its computational efficiency.

All of these do not require a complete mechanism of aerosol/gas exchange. Given the explanations of Section 5.1, we had assumed that the discussion of the global modelling results within Section 5.3 would be understood from this perspective.

We have made additions to the conclusion and Section 5 that emphasize the limitations of the global simulations in the context of their scope.

2) “Page 2, Lines 24-25: The literature review of dynamic partitioning solvers is inadequate as there is lot more work done than what's discussed here. In addition to Capaldo et al. (2000) and Zaveri et al. (2008), the following papers describe different approaches to dynamically solving partitioning of

HNO₃, HCl, and NH₃, which need to be properly discussed. Also, MOSAIC is incorrectly classified under the hybrid approach as it always performs fully dynamic mass transfer for all size bins.”

The reviewer has drawn our attention to the fact that the discussion of the literature requires improvement. We have expanded the discussion on the basis of the additional references that were provided, as Jacobson (1997), (2002) and (2005) are discussed within Section 4.1 in the context of the motivation for the choice of the benchmark scheme, and Zhang and Wexler (2006) and Wexler and Seinfeld (1992) in the Introduction. We preferred to discuss Wexler and Seinfeld (1992) rather than (1991), because the earlier appears to be the more relevant one.

- 3) “Figure 1. There are quite a few things that I don’t understand in this example/figure:
- This example is shown before the different solvers are introduced in section 3, so it is not clear which solver was used to illustrate this example. Please clarify. Also what relative humidity was used?
 - According to the text on page 3 and the figure caption, the initial particles are pure H₂SO₄ with radius 50 μm and the number concentration 100 cm⁻³? If this is correct, then nearly all of the NH₃ will be absorbed into the particles in less than 10 s. But since the gas-phase NH₃ does not change appreciably with time, I am assuming the initial radius is 0.05 μm (not 50 μm).
 - Assuming the radius is 0.05 μm, why does it take NH₃ about 200 s before it begins to dissolve appreciably into H₂SO₄ particles? My calculation shows that NH₄/SO₄ molar ratio reaches approx. 0.8 at 200 s.
 - Why does substantial amount of HNO₃ gas dissolve in H₂SO₄ particles during the first 200 s when NH₃ hasn’t yet neutralized the acidity to some extent?
 - Why are there no oscillations for the time step of 10 s?
 - Please clearly define in the caption the short forms for terms used in the legend: “part” and “atm”.
 - Are the units on the Y-axis [molecule m⁻³(air)] for both gas- and particle-phase species concentrations?
 - Why do the gas- and particle-phase concentrations of become equal (blue line and green line) after 400 s for both NH₃ and HNO₃?”

The reviewer points to Figure 1 and asks for clarification. First, the reviewer diagnosed correctly that the initial size of the particles is not 50 micrometres but rather 50 nanometres. Second, a great deal of the confusion might have arisen due to what seems to be a lack of sufficient clarity on what is exactly shown within Figure 1. The graph does not compare the gas phase molecule number concentration against the gas phase equivalent concentration of molecules in the liquid phase but rather against the partial pressure at particle surface, which is expressed as a molecule number concentration equivalent via the perfect gas law (as given by the terms ‘particle surface concentration’ and ‘pressure’ in the figure caption). For this reason, the accuracy of the dynamic formalism is actually demonstrated by the figure, as the particle surface pressures tend to the gas phase partial pressures in the process of system equilibration.

These explanations should clarify the reviewer’s points b), c), d), g) and h).

Concerning question a), the graphs were produced with the same fully dynamic approach that is used later on as a benchmark to demonstrate the accuracy of the hybrid solver, that is the Jacobson 1997 scheme used at fixed time step (see below).

This relates then to the reviewer's point e): The 10 second run does not oscillate because close to equilibrium the Jacobson scheme proves to be sufficiently stable when the time step is in accordance with the dynamical properties of the simulated system and its characteristic equilibration time interval. The oscillation is the result of an initial overshoot close to equilibrium, followed by consecutive of under- and overshoots. Both equilibrium regimes, the steady state and the artificial oscillation regime, are stable, meaning that if the system was sufficiently perturbed at equilibrium, it could quite well be that the system would oscillate at a time step of 10 seconds, just as it could remain at steady state at a time step of 30 seconds if brought sufficiently close to it.

As to point f), we have added an explanation of 'part' and 'atm' to the figure caption. Short additions were made to the figure caption (and within Section 3 for point e) that should correct and clarify the issues raised by the reviewer.

4) "What is the difference between "size bin" and "size increment"? If they mean the same thing, then please stick with "size bin." Otherwise, please clearly define a "size increment." "

The difference between size bin and increment is close to none, we have used them as synonyms. We scrapped both 'increment' and 'bin', and replaced them with the term 'class', for the reason that 'bin' is frequently used in the literature context in reference to a 'bin' in opposition to a 'modal' model, although this distinction might not be totally clear and appropriate either.

5) "Page 5, Line 16: What are the "dissolving" and "non-dissolving (=passive)" species considered in this work? It's not clear what a "non-dissolving" species even means. This terminology becomes especially confusing on page 8, lines 10-15, where a monoacid is treated as "dissolving" but the anions and cations are treated as "nondissolving" in Eq. 11. This equation is supposed to give H⁺ ion concentration from the difference between anions and cations, so I don't understand why the additional term "c_i" is even included here."

We changed the terminology, as 'non-dissolving' is scrapped for 'passive' to remain, which is now introduced by formal definition along with 'dissolving'. The monoacid within Eq. 11 is the only species whose semi-volatile and time-depending nature is considered at this point: it is the dissolving species while all others are passive. We feel this change in terminology and the adaptations to the text clarify the issue.

6) "The derivation of Eq. 9 is also very confusing. First, please clearly define the terms a, b, and c of the generic differential equation $dx/dt = ax^2 - bx + c$. Then show the solution using the same notations."

We partially followed the reviewer's request, and reformulated the expression of Equation 9, as we now state parameters a, b and c. However, it is not reasonably possible to formulate the solution as an explicit function of these parameters. This is the reason why parameters λ and B had been introduced in the first place. Note that there was a typing error within Eq. 9, which is corrected as the parameter b is squared now inside the square root function.

7) "Will the numerator in Eq. 15 always be positive? What happens if a species in a given bin has a tendency to evaporate during a time step (e.g., HNO₃ displacing HCl from sea salt)?"

It has to be ensured that the numerator of Equation 15 is always positive. Within the solver this is ensured via the use of the absolute value function. The fact that it was missing here is due to a typing error, which we corrected.

8) "How does the dynamic solver handle simultaneous mass transfer of H₂SO₄, HNO₃, HCl, and NH₃ to a size distributed aerosol? It seems mass transfer of H₂SO₄ is not included in the derivation of the dynamic solver equations. Also, none of the box model test cases include gas phase H₂SO₄ that condenses along with HNO₃, HCl, and NH₃."

H₂SO₄ is not currently treated by HyDiS as (1) it is assumed to be non-volatile and (2) the condensation of non-volatiles is formally considered to be a separate process. In principle it could be treated as a semi-volatile species by the solver if found appropriate and thermodynamic data is made available, and provided that some slight adaptations to the chemical equilibrium solver are made, considering that the maximum number of chemically fully interacting species that may be accounted for by the solver may not exceed 3. Non-volatile species are treated within the combined condensation and nucleation routine of the microphysics scheme. HyDiS is the last routine to be invoked by the aerosol model. Concurrent condensation of H₂SO₄ and dissolution of HNO₃ and NH₃ is not shown within the box modelling experiments as we put priority on showing the transition of the system towards forced dynamic equilibrium. We have made changes within Section 4 and Section 5.2 for improved clarity with respect to these circumstances.

Question 9 is split in two:

9a) "While the present box model tests are useful in showing the benefits of the hybrid solver over the equilibrium approach, they do not demonstrate the accuracy of the new dynamic solver introduced here. To evaluate accuracy, it is necessary to compare the dynamic solver for monodisperse aerosol (similar to the example shown in Figure 1) and 4 size bins (as already shown in series 1 and 2) against a benchmark dynamic solver (e.g., LSODE) with strict error tolerances for a range of initial gas concentrations (of H₂SO₄, HNO₃, HCl, and NH₃) and aerosol sizes, concentrations, and compositions."

The reviewer assumes that the credibility of the benchmark solver that we use is not given and that an established stiff solver of ordinary differential equations, like lsode, should be used instead. We acknowledge that the reviewer's suggestion is justified in the context of insufficient explanation of our

methodology and the lack of clarity that surrounded Figure 1. However, although Zaveri et al 2008 used lsode as a benchmark, this is no absolute proof that it is the better choice in any case. We actually believe that the Jacobson 1997 Analytical Predictor for Dissolution (APD) we use as a benchmark is more appropriate, for the reasons that we will now expand upon. A solver may serve as a benchmark, if it is (1) mathematically precise, (2) formally different from the one it is compared against, and (3) compatible with the numerical formalism it is embedded in. First, although it has a propensity for oscillations at larger timesteps, the Jacobson 1997 APD is mathematically sound, as by inspection for an internal timestep $\delta t \rightarrow 0$ its numerical integration method tends to the mathematically correct solution. Its capacity to deliver precise results is illustrated by Zaveri et al 2008 (though for the Jacobson 2005 semi-implicit version of the APD, which is formally similar to a large degree), as lsode and the APD tend to give similar results. Second, for Zaveri et al the use of the fully dynamic 1997 exponential APD as a benchmark was not appropriate as formally too close to its 2005 semi-implicit cousin. With HyDiS and its mixed dynamic and equilibrium approach, its selective setting to equilibrium of species within non-equilibrium bins and its use of the pseudo-transition approach, the fully dynamic APD is formally dissimilar. Third, the APD is the better match to HyDiS and its numerical formalism: (1) it is already in use in combination with an as large as possible timestep for species in bins that are simulated dynamically, a comparison between the hybrid and the fully dynamical runs may thus serve to demonstrate that HyDiS chooses the internal timestep without loss of *relative* accuracy, and (2) the APD actually tends to be more precise than lsode provided that the internal timestep is set to an appropriate value. lsode solves for all species within all size bins concurrently, while the APD solves for all size bins however separately for each species, which might appear to be a clear advantage for lsode. However, lsode keeps the parameters constant during the entire overall timestep Δt , while the APD updates them after each internal timestep δt . For a chemical process that involves relatively constant parameters lsode definitely is the better stiff solver, but for dissolution and its stiffness causing fast changing parameters, as given by the water content, the activity coefficients and surface pressure, it might not be. Quite on the contrary, it will introduce an amount of imprecision that will not be readily quantifiable. It is thus hard to tell whether the use of lsode is more accurate via the accurate simultaneous solution of a system of stiff ODE's, or actually less accurate via the variability of the parameters. The only ways we can think of to overcome this uncertainty would be to (1) compare runs with activity coefficients and water content held constant, which might not be the best choice for the purpose of solver verification, or (2) attempt to formally resolve the highly non-linear properties of the parameters via their explicit inclusion as variables, which would be using a sledgehammer to crack a nut at best or might turn out to be not feasible at worst, or (3) drastically reduce the overall timestep at which lsode is used, to an order of magnitude that is more or less similar to the one that is used internally by the APD, which would be largely tantamount to the use of the APD as a benchmark solver, as demonstrated by Zaveri et al 2008. For all of these reasons we chose to use the Jacobson 1997 scheme, which is mathematically precise if the internal timestep is chosen appropriately. This we did by simple inspection, as sketched within Figure 1 for a monodisperse aerosol and total species amounts of 1 ppt: 30 seconds induce oscillation, and 10 seconds are precise to the extent that the simulation is graphically indistinguishable from a run at a much shorter timestep (therefore not shown). We have added a paragraph to the text in order to describe and motivate our choice of the APD as the benchmark solver.

9b) “The predicted equilibrium (after sufficient time) gas and aerosol concentrations (including aerosol pH) for the monodisperse test cases must also be compared to a benchmark thermodynamics model such as AIM (available online) to evaluate the accuracy of the thermodynamics treatment in the present solver. For example, see the dynamic solver evaluation done in Zaveri et al. (2008). Such an evaluation against a benchmark solver is especially warranted in the light of the several discrepancies found in the results of the dynamic solver shown in Figure 1 (see #3).”

The reviewer suggests that we use AIM as a benchmark for the equilibrium solver. Interestingly this is a possibility that we had considered before submission but ultimately had decided against it. From our point of view, the scope of this publication is not so much whether the equilibrium that is determined is accurate thermodynamically (this was done by Topping et al 2009), but rather whether the solver is numerically correct, which is demonstrated as fully dynamic and hybrid runs converge towards full equilibrium, thus validating each other mutually. Also, as pointed out by the reviewer, the online version of AIM does not allow for a size discretized aerosol. We would thus have to add another experiment with a monodisperse aerosol to an already lengthy paper. We have added one sentence detailing that the thermodynamic scheme was tested against AIM by others.

10) “The main goal of the present work is to introduce a new hybrid solver that is computationally efficient. But since any solver can be made efficient by compromising its accuracy, it becomes necessary to evaluate computational efficiency as a function of accuracy. The CPU costs presented for the various dynamic solvers in Table 1 are of little use without stating their accuracies against a benchmark solver (see #9).”

The reviewer asserts that the CPU times are of little use in the absence of a reliable reference as given by a benchmark solver. For the reasons given within 9a) we believe that the Jacobson 1997 APD, if used appropriately, actually is a valuable benchmark solver. No changes to the text apart those made in the context of point 9a).

11) “As the authors have already acknowledged, the comparison of the computational cost of the present solver with that of MOSAIC is fraught with many issues: different model configurations and chemical/physical complexities, computer hardware and computing architectures, etc. Also, the 125 μ s CPU cost for MOSAIC quoted here includes microphysical calculations (in addition to gas-particle mass transfer and thermodynamics) whereas the 20 μ s given for the present hybrid solver appears to be for gas-particle mass transfer and thermodynamics calculations only. Furthermore, the CPU costs given in Table 5 for cases 4-7 (aqueous particles only) range from approx. 20-40 μ s (depending on the case, hardware, and compiler), which is more directly comparable to the CPU cost presented here for the hybrid solver. Having said that, the accuracy and efficiency of both solvers should be evaluated for the same set of problems on the same machine for the comparison to be meaningful.”

The reviewer states that a comparison with MOSAIC in terms of CPU time as done within the manuscript is of questionable relevance due to dissimilarity of both the computing facilities that are

used and the schemes themselves. We agree that the relevance of the comparison is limited. However, in this respect we do not believe that the comparison would not carry meaningful information. The fact that we overlooked that for MOSAIC the microphysics are included in their estimation of CPUtime does not affect our conclusion that the expense should be of the same order of magnitude, thus demonstrating our due caution. We believe that our conclusion carries a useful piece of information to the reader, considering that a more detailed assessment is reserved to a global modelling framework that is more comparable, which is not currently available to us. The reviewer might have suggested to carry out the comparison with box model simulations instead, as done by Zaveri et al 2008. The relevance of box model comparisons of computation time is also limited, as these may not be representative to the parameter space that is encountered within a global modelling environment. Likewise, cases 4-7 within Zaveri 2008 might not be representative to the computational expense that is encountered in relationship with fully liquid particles, as the small particle sizes, which should require a smaller timestep, are not assessed with the given monodisperse setups. At this point, we have to mention that reviewer #1 seems to appreciate and does not criticize the way we established the comparison of CPUtime, on the contrary he would favour a similar comparison between the simulated and the observed aerosol composition. Within this partially conflicting situation we would like to leave it to the editor as to whether more CPUtime comparisons are essential, and as to how these should be done. In the meantime, we have further relativised our assessment within Sections 5.4 and also 6, in accordance with the reviewer's observations.

The following questions will be answered together, as related:

- 12) “Table 2: In GLOMAP sea-salt chloride is treated as non-volatile. Then how do H₂SO₄ and HNO₃ condense on sea salt aerosol without evaporating HCl? Non-volatile treatment of HCl becomes problematic especially for condensation of HNO₃, because both HNO₃ and HCl are semivolatile and the extent of HNO₃ partitioning crucially depends on HCl.”
and 13) “How is HNO₃ uptake on calcite containing dust particles treated in GLOMAP?”

The reviewer asks a question with respect to the representation of the volatility of HCl in the context of sea salt within Glomap, and the representation within Glomap of gas/solid phase exchange with respect to calcite. We are aware that these are important questions for the simulation of the atmospheric aerosol, although of limited relevance in the context of the present publication (see (1)). HyDiS may account for the chemical interaction of a maximum of 3 dissolving species. As such it may account for the interaction of HNO₃, NH₃ and HCl, provided that they are comprised within the atmospheric chemistry scheme of the hosting aerosol model. As mentioned within Section 5.2, we cannot treat HCl as a semi-volatile in the present version of Tomcat-Glomap. Gas/solid phase exchange is not currently part of Glomap and it is a process that is not treated by HyDiS, this also applies to calcite. We have made additions to Sections 5.2 and 6 that detail these limitations.

Minor Comments

p. 2 l. 10: order of acid and base is changed.

Fig. 11: resolution of figure is improved.