

Response to reviewer #1 comments

We thank the anonymous reviewer #1 for their review and note that they have identified that “the new solver can capture the dynamical, time-dependent features of nitrate partitioning that are not properly by equilibrium assumption”.

We take their point about the paper being “somewhat lengthy”. However, when writing the paper we considered carefully whether or not we could shorten the paper, and concluded that the level of detail provided is important and will help to ensure clarity and rigour.

In our response here we address each of the points made by the reviewer in the order that is given in his/her review:

Major Comments

1) Throughout the manuscript, the particle phase is referred to as ‘liquid phase’. Many recent studies have suggested that there might be multiple liquid phases (aqueous/organic) in an aerosol particle. Therefore, I suggest changing ‘liquid’ to ‘aqueous’ in the text.

We agree entirely and have changed the terminology.

2) Eq. 4 and p. 8, l. 15: Usually the effective Henry’s law constant H^* for acids includes the acid dissociation constant K_a , i.e. $H^* = H (1 + K_a/[H^+])$ Eq1 Does the fact that you assume H_2SO_4 as being completely dissociated lead from Eq1 to Eq-4? Would your approach be applicable using Eq1 for acids that are not completely dissociated?

The total dissociation of acids assumption and the negligence of OH in the ion balance introduce a simplification into the formalism that allows us to focus on other important phenomena, such as the numerical stiffness property of the system and the related computational efficiency. The partial dissociation of acids and the presence of OH each add one additional degree of freedom to the system, that increases the degree/order of any relevant resolving/differential equation accordingly. For instance, within the dynamical solver, neglecting OH reduces Eq. 8 to a second order differential equation rather than third order, and also matches the similar approach taken in the thermodynamic scheme PD-FiTE. Most importantly, within the chemical equilibrium solver, and in relationship with its analytic approach, the simplification allowed us to take the chemical interaction of the dissolving species into account. If the partial dissociation of the dissolving species and H_2SO_4 , and OH were taken into account, the resolving equation for one dissolving base or acid would be of the 5th degree. If only the partial dissociation of H_2SO_4 is taken into account, which is done in the circumstance of one dissolving species, the resolving equation is still of the 3rd degree. As one of the underlying reason for the numerical stiffness is chemical interaction, it is necessary to restrict the degree of the resolving equation to a value that is manageable. We have added the following paragraph underneath equation 4 to explain these circumstances more appropriately.

“In the preceding expression, the partial dissociation property of the dissolving species is neglected, which is an underlying assumption for HyDiS-1.0. It will allow us to reduce the number of degrees of freedom of the considered chemical system by one unit for each dissolving species. In doing so other properties, such as the species’ chemical interaction, may be taken into account more thoroughly, as analytical solutions may be derived along with a critical reduction of the degree of the respective resolving equations. We have seen in the preceding section that the chemical interaction between acids and bases plays an essential role to the numerical stiffness property of the system.”

3) Currently, the number of interacting species is limited to three. Will it possible to rigorously extend the solver to more compounds, given the complex composition of ambient atmospheric aerosol?

In line with the preceding point, the number of dissolving species may not be consistently augmented beyond this number, unless the chemical interaction of the dissolving species will necessarily be accounted for less thoroughly within the chemical equilibrium solver. We have added the following sentence for clarity.

“Similarly, the number of dissolving species whose chemical interaction may be fully taken into account may not exceed three, as no analytical solution is readily available to an equation beyond the fourth degree.”

4) The discussion of the model results (both box and global) in Sections 4.2 and 5.3., respectively, are poorly connected to the figures. All figure panels should be labeled a, b, c, etc and the discussion should be tied more closely to the individual panel so that it is easier to reader to follow.

In accordance with the suggestion made by the reviewer we have numbered all panels of Figures 5-16 and linked them more thoroughly with the text.

5) It is not clear what the ‘entire microphysical box model’ (e.g., p. 28, l. 32; and Table 1) includes. How far is a comparison of the microphysical model meaningful to the chemical model that includes the new solver? Does using the new solver in the microphysical model lead to redundancy?

We have reshaped the explanation of how the percentage computational expense of HyDiS within the box model runs is obtained. Also, we have mentioned the processes that are comprised within the Glomap microphysical scheme and given more details on the implementation of HyDiS within this scheme.

6) The comparison to the efficiency of previous models is only touched on briefly (end of Section 5.4). Given the extensive length of the current manuscript already, I am not asking for a detailed discussion/ However, a brief statement of the ability of the model by Zaveri et al. (2008) to reproduce the dynamical features as opposed to equilibrium assumptions should be added. In general, how well did the model by Zaveri et al., to observations?

The reviewer asks for an extension of the comparison of HyDiS to other gas/particle exchange schemes with respect to the global aerosol composition. In principle, we agree with the reviewer about the relevance of such a comparison. However, a comparison to other schemes is not trivial and will require a lengthy analysis. At this point a comparison would be premature, as certain important processes, such

as particle crystallization and the dissolution of HCl, are not currently included in TOMCAT-GLOMAP, and certain other processes, such as heterogeneous chemistry and aerosol organic species, are not taken into account for the present preliminary simulations. For these reasons, we limited the analysis herein to solver computational efficiency and numerical reliability considerations, along with a preliminary assessment of the relevance of nonequilibrium dynamics as the one intended main plus of the solver relative to equilibrium approaches.

Minor Comments

p. 2 l. 11: [At most RH values, the amount of water exceeds the amount of solute mass, e.g. \(Liao and Seinfeld, 2005\). Do you mean here the increase of particle size due to solute mass and its associated water?](#) We mean both the increase of particle mass via efficient interaction of nitrate+ammonium and the amount of water that goes with it. The interaction of ammonium and nitrate may be efficient to the point that the loss of the particle water mass via the reduction of hygroscopicity along with the acidity of the aqueous phase does not exceed the gain of particle mass via the chemical interaction of ammonium, nitrate and water. Clarified.

p. 6 l. 3: [Do you mean ‘ the concentration of the dissolving species in the aerosol aqueous phase’?](#) Expression corrected for improved clarity.

p. 11 l. 17: [This is unclear, in particular for the conditions described here. 1\) Make clear that the aqueous s phase ‘is predicted to loose protons’. 2\) One would assume that under the acidic conditions described here, there is a huge excess of protons.](#) Sentence is clarified.

p. 14 l. 26: [Are these parameters \(activity coefficients, liquid water content, and dissociation\) held constant throughout the simulation or during one time step?](#) The mentioned variables are not considered as such by the analytical scheme. They are updated at the outer iteration level of the chemical equilibrium solver, this is clarified further down in the text, however cannot be mentioned here as the reader would not be able to follow at this point.

p. 16 l. 21: [What is the extent to which the pH varies within the iteration? Are these extreme values or are they realistic over the course of a time step, when aerosol might be exposed to ambient conditions?](#) Extreme variations of the particle pH occur frequently in the course of the execution of the equilibrium solver, and they are not necessarily related to exceptionally rapid modifications of ambient conditions. The extreme variability of particle pH is the most characteristic feature of the numerical stiffness property of dissolution, and occurs under all polluted conditions for $c > 1$ ppb approximately, with the diurnal cycle of temperature serving as one of the potential sources of sufficient perturbation (used in the box model experiments) in the context of an overall time step of 15 or 30 minutes. In this context, the convergence of the pH variability to less than 0.1 is an appropriate prerequisite for one outer iteration that updates the parameters, and a subsequent round of internal iterations with a renewed massive variability of the pH. We refer to Section 2 for further detail on the numerical stiffness properties of chemically interacting species via pH.

p. 17 l. 9: The wording is ambiguous, I think. The convergence criterion is stricter; however, the value is DEcreased from 0.1 to 0.01. If I misunderstood this, clarify. The convergence criterion is increased from 0.001 to 0.01. The criterion for this choice is set to 0.1. Clarified.

p. 18 Eq. 29: Does 'a' have a physical meaning? What is the range of meaningful values for this parameter? The proportionality constant has a qualitative physical meaning, as it stands for the amount of chemical interaction that one is willing to take into account in terms of the determination of the length of the internal time step of the dynamic solver. Although it has this qualitative physical meaning, it is hard to figure out how this would physically translate into a mathematical expression. Notwithstanding, this latter issue is of limited relevance, as the proportionality constant has another more relevant meaning, as it conditions the number of internal time steps of the dynamic solver. If a size class would require more internal time steps due to numerical constraints, it would be assumed to be in equilibrium whether this is accurate or not. It is clear that the computational expense will be roughly proportional to this number. We have chosen 'a' for the number of internal time steps to be limited to roughly 3. This number was shown by the box model experiments to produce reasonably accurate results, even under numerically stiff conditions of strong chemical interaction. It should be noticed at this point that a larger overall time step might require an accordingly smaller proportionality constant, unless the accuracy of the results might be critically diminished. The text was modified for more clarity.

p. 19 l. 18: What are the physical/chemical parameters that determine equilibration time of a dissolving species? Is it e.g. solubility (Henry's law constant) or something else? Could threshold values be given above/below which equilibration is achieved in short time, relatively to the model time steps? By virtue of Eq. 15 the equilibration time is given by the ratio of the difference between the equilibrium and the momentary atmospheric concentration of the dissolving species in the aqueous phase, and the potential of the dissolved species to evaporate from particle surface or the potential of the dissolving species to condense onto the particle surface, whichever potential is the largest. This quantity may be seen as a normalized degree of saturation of the aqueous phase, which correlates with the equilibration time. By virtue of the proportionality factor 'a' and the definition of the distinction criterion between equilibrium and dynamic simulation, the critical equilibration time is defined relative to the overall time step of the model: a particle is considered to be in equilibrium if its equilibration takes less than half the overall time step of the model. Due to its multivariable dependence no individual threshold value may be given that would determine a short equilibration time. We refer to the explanations around Eq. 15 for explanations within the manuscript on this question.

p. 20 l. 13: Does 'a' here have the same meaning as in Eq. 29? If not, choose a different symbol to avoid confusion. The notation of the second coefficient is changed to 'b'.

p. 23 l. 23: Not clear what 'its' refers to here. Corrected.

p. 23 l. 22 and 24: Spell our ADDEM, MANIC. Now spelled.

p. 24 l. 1: [What are the particle sizes for the various modes?](#) Mode sizes now indicated.

p. 24 l. 31: [Is the temperature dependence of HNO₃ dissolution very different than that of NH₃? Can you support this trend by numbers \(T-dependence of H₂O\)?](#) The temperature dependence of the solubility of HNO₃ and NH₃ is explained more thoroughly and references are added.

p. 26 l. 3ff.: [Are there any simultaneous measurements of NH₃ partitioning in gas and particle phase that show similar trends of subsaturation?](#) The observed undersaturation concerns a two-fold phenomenon, each related to a particular kind of numerical stiffness. On the one hand, the aqueous phase remains undersaturated as it tends to equilibrate very slowly in the context of the slow transit of the semi-volatiles through the gas phase. This dynamical phenomenon is now mentioned in the Introduction (Zaveri et al., 2008). On the other hand, the surface pressure of one dissolving species remains underneath the ambient pressure, depending on the choice that is made by the solver as a function of its configuration. This artificial phenomenon is related to the extreme numerical stiffness via particle pH and chemical interaction that is encountered at 100 ppb, which appears to cause a relative imprecision of the solver. This artifact has very little influence on the predicted concentrations of the dissolved species, because these are several orders of magnitude larger than the proton concentration. We point to the explanations that are given within Section 4.2 around Figure 10.

p. 27 l. 14/15: [What is different in terms of \(physico\)chemical properties of chloride and nitrate vs ammonium that could explain their different behavior?](#) The reason for the similarity of ammonium under dynamic and equilibrium conditions may be illustrated with the coarse mode. The particle pH is too low for the solubility of ammonia to be high, such that the equilibration time of ammonium remains relatively low. Furthermore, nitric acid and hydrochloric acid are competitors, as nitric acid drives out the latter and replaces it, and particle pH remains unaffected, which in turn tends to keep the solubility of ammonia low but constant. The only factor that affects the solubility of ammonia is its temperature dependence, which also results in a quick almost instantaneous adaptation, to the overall effect that the equilibrium and dynamic concentrations of ammonium are almost equal. We have added 2 sentences for explanation.

p. 27 l. 31: [‘Particle concentrations’ usually refers to mass or number concentration of particles. Do you mean ‘the concentration of ammonia and chloride in the aqueous phase’?](#) Corrected.

p. 29 l. 20: [What is included as sulphur chemistry? Both gas and aqueous phase processes? When sulphate is formed in the aqueous phase, does it contribute to the species that are equilibrated between the phases?](#) An explanation is added to the text.

p. 32 l. (1)5: [Reword: “: : the ambient concentration of ammonia over the Southern Ocean is predicted to be lower by 10-25% than predicted by the equilibrium approach” or similar in order to clarify that you compare two model results.](#) Inserted.

p. 32 l. 28: [Is this very low nitric acid concentration in the Arctic in agreement with observations?](#) The question of the validation of the model predictions against observations (and other models) certainly is an important one. Adams et al. (1999) give a few data points for their simulated mixing ratio of ammonia close to the western coast of Alaska during the Arctic summer. Their values of 2-5 ppt are similar to our estimations under the equilibrium assumption. With the hybrid configuration we obtain approx. 10 ppt. In their measurements off the east coast of Baffin Island during Summer 2014, Wentworth et al. (2016) find ammonia mixing ratios of around 30 ppt. With the hybrid configuration we obtain a simulated mixing ratio of approx. 10 ppt, with the equilibrium configuration we obtain approx. 1/3 of this value. It thus seems that non-equilibrium dynamics play an important role and that our simulations get the order of magnitude right in the Arctic. Having said this, the observed and the simulated variability of ammonia is large both in time and space, such that these matches are inconclusive. As detailed within our answer to the 6th major comment, the validation of the model results will be performed in much greater detail in follow-on publications, as the present largely focuses on solver presentation and numerical validation. We have modified the text to clarify the circumstance that we compare two model results.

Fig. 1, caption: [1\) Is the particle size the wet radius? At what RH?; 2\) Could you mark the steps 1-3 in the figure \(e.g. by shading or vertical lines\)?](#) 1) the dry radius is given, this circumstance is now indicated along with the relative humidity of 80%, 2) the regimes are now marked as requested.

Fig. 6, 7, 9 and 10 [should have a somewhat more detailed caption. What does the 10 ppb etc refer to?](#) The figure caption is reformulated and more details are added to Figs. 5 and 8, respectively.

Fig. 11: [Some of the text in the figure is very blurry, e.g., 'HCl', 'soluble nucl.' In the top panel and 'OH, NO2' \(?\) in the bottom panel.](#) The resolution of the figure is improved.

Fig. 12: [In the caption only two panel \(top and bottom\) are described, but there are three panels \(top, middle, bottom\) shown. Clarify and improve caption.](#) The figure caption has been partially reworded.

Technical comments: thank you for indicating these, all worked in.

Additional Reference:

Wentworth, G. R., Murphy, J. G., and Croft, B., et al.: Ammonia in the summertime Arctic marine boundary layer: sources, sinks, and implications, *Atmos. Chem. Phys.*, 16, 1937–1953, 2016.