

Interactive comment on “Size-resolved simulations of the aerosol inorganic composition with the new hybrid dissolution solver HyDiS-1.0 – Description, evaluation and first global modelling results” by F. Benduhn et al.

Anonymous Referee #2

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The authors have developed a new hybrid solver for partitioning NH₃, HNO₃, and HCl to aqueous aerosol particles. The solver is supposed to be computationally efficient while maintaining accuracy. However, the 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. 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. The manuscript is lengthy and a bit confusing in various places due to imprecise notations and terminolo-

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gies. Unfortunately, it would require a major revision before it can be considered for publication in GMD.

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.

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.

References:

Jacobson, M. Z. (1997), Numerical techniques to solve condensational and dissolutional growth equations when growth is coupled to reversible reactions, *Aerosol Sci. Technol.*, 27, 491–498.

Jacobson, M. Z. (2002), Analysis of aerosol interactions with numerical techniques for solving coagulation, condensation, dissolution, and reversible chemistry among multiple size distributions, *J. Geophys. Res.*, 107(D19), 4366, doi:10.1029/2001JD002044.

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Jacobson, M. Z. (2005), A solution to the problem of nonequilibrium acid/base gas-particle transfer at long time step, *Aerosol Sci. Technol.*, 39, 92– 103.

Wexler, A. S., and J. H. Seinfeld (1991), Second-generation inorganic aerosol model, *Atmos. Environ.*, 25A, 2731– 2748.

Zhang, K. M., and A. S. Wexler (2006), An Asynchronous Time-Stepping (ATS) integrator for atmospheric applications: Aerosol dynamics, *Atmos. Environ.*, 40, 4574– 4588.

3) Figure 1. There are quite a few things that I don't understand in this example/figure:

a) 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?

b) 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).

c) 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 ~0.8 at 200 s.

d) 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?

e) Why are there no oscillations for the time step of 10 s?

f) Please clearly define in the caption the short forms for terms used in the legend: "part" and "atm".

g) Are the units on the Y-axis [molecule m⁻³(air)] for both gas- and particle-phase

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species concentrations?

h) Why do the gas- and particle-phase concentrations of become equal (blue line and green line) after 400 s for both NH₃ and HNO₃?

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."

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 "non-dissolving" 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.

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.

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)?

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.

9) 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

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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 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).

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).

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 ~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.

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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.

13) How is HNO₃ uptake on calcite containing dust particles treated in GLOMAP?

Minor comments 1. Page 2, Line 10: Please change “dissolving acid and a dissolving base, such as NH₃ and HNO₃” to “dissolving acid and a dissolving base, such as HNO₃ and NH₃”.

2. Figure 11. The resolution of this figure needs to be improved.

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