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# Interactive comment on "A novel model to predict the physical state of atmospheric $H_2SO_4/NH_3/H_2O$ aerosol particles" by C. A. Colberg et al.

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### **General Comments**

The work presented by Colberg et al., addresses a very important topic, which is highly relevant to the atmospheric chemistry and physics community, i.e. the prediction of the physical state of atmospheric aerosol particles.

The authors propose a novel method to predict the physical state of atmospheric aerosol particles. The method consists of an application of an Aerosol Physical State Model (APSM) to Lagrangian trajectories that are computed from ECMWF (European Centre for Medium Range Weather Forecasts) analyses, by taking full account of the deliquescence/efflorescence hysteresis. As input APSM requires three data sets: (i) deliquescence and efflorescence relative humidities from laboratory measurements,

(ii) ammonia-to-sulfate ratios (ASR) calculated by a global circulation model, and (iii) relative humidities determined from the ECMWF analyses. The physical state of the H2SO4/NH3/H2O is then calculated with the APSM - which incorporates a thermody-namical model by Clegg et al. to calculate the liquid/solid partitioning - for two month-long trajectories on four levels (700, 600, 500 and 400 mbar) beginning at July 2000 and January 2001 with a 6-hr time step.

The authors conclude that globally averaged a significant fraction (17 - 57 %) of the ammoniated sulfate aerosol particles contain solids with the ratio of solid containing to purely liquid particles increasing with altitude (between 2 and 10 km). They further stress the global importance of letovicite, (NH4)3H(SO4)2, whose role as cloud condensation nucleus (CCN) and as scatterer of solar radiation remains to be scrutinized.

Unfortunately, the work as presented and the conclusions drawn are - to my understanding - not convincing. Furthermore, I doubt that the method does allow at all to make such strong statements as that letovicite is of global importance. The main problem and limitation of the method is that the APSM calculates the liquid/solid partitioning, although fairly detailed, offline, i.e. without feedback with the gas and cloud phase or aerosol chemistry. Considering the fact that aerosol concentrations are highly variable in space and time, the physical state of atmospheric aerosol particles needs, however, to be calculated online.

The novelty and the usefulness of the method are therefore to my opinion highly questionable. Nevertheless, the method certainly is useful as it allows to study systematically the affect of hysteresis on the aerosol state. The method should be therefore used in conjunction with online gas/liquid/solid partitioning calculations.

In order to be more convincing, the authors would need to critically view their results in the light of the uncertainties that are associated with the method. This would require a sensitivity study that tries to answer the (main) questions raised below in the specific comments; the brief paragraph presented is not sufficient (see point 2 of the specific

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comments).

I recommend publication at ACP after the authors have addressed the specific comments.

#### **Specific Comments**

In order to make the conclusions more convincing, a critical discussion of the uncertainty and validity range of the proposed method would be needed. Most convincing would be a sensitivity study, which address the following points:

(1) In order to show the advantage of the new method, the results should be compared with other efforts that try to predict the physical state of atmospheric aerosol particles based on hysteresis, including full gas/liquid/solid partitioning, in an Eulerian model (e.g. Metzger et al. JGR, 107, D16, 10.1029/2001JD001103, 2002). Although the treatment of the hysteresis effect in an Eulerian model is formally not correct, online calculations that include the hysteresis effect have the advantage of capturing the dynamics (that probably govern the overall uncertainties of the physical state modeling) and the high variability of the aerosol distributions as the aerosol concentrations are calculated in feedback with the cloud and gas phase chemistry. In contrast, APSM explicitly calculates the solid partitioning trajectories based on hyseteresis, however, without feedback to the actual aerosol formation, transport, deposition, or air chemistry.

(2) The following paragraph, which covers the section Sensitivity Studies, is too general. What do the authors explicitly mean with: "We have tested the importance of errors introduced by the various input parameters (DRH, ERH, ASR and RH) along trajectories. In general we find a variation of about 5 % in any one of these input parameter sets to be hardly visible in the resulting geographical plots of solid-containing fractions. The resulting global mean values of the total solid-containing fraction differed by less than 2 %. The overall result of significant amounts of mixed-phase ammoniated sulfate particles, and particularly of letovicite remains unaffected."

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What is 'in general'? What has been varied, e.g. different DRHs/ERHs for the single compounds (e.g. letovicite)? What are the values used? What's about mutual deliquescence relative humidities (MDRHs) of mixed salts that are known for the ammonium/sulfate/nitrate/water-system and which are generally lower than the DRHs of single salts? Or, ten Brink et al., 1996 (ATMOS ENV, 24, 4251-4261) showed that certain salt particles might remain supersaturated, depending on their composition (e.g. nitrate to sulfate ratio). What's about this effect? And what's about the uncertainty associated with the thermodynamic model used; different thermodynamic models might gives different results? How accurate is the aqueous phase determined by the thermodynamic model used; this very much depends on the DRH/MDRH, i.e. the deliquescence behavior of mixed aerosols (despite whether they are internally or externally mixed, and the exact shape of solid particles)? What's about the stability of the numerical scheme (usually many problems are associated with the prediction of solid compounds as many iterations are needed until convergence is reached)? How accurate is the prediction of the solid concentration? I don't want to stress the uncertainty of the aerosol activity and the activity coefficients at the high solute concentrations near the liquid/solid partitioning, rather I want to know the effect of its uncertainty on the hysteresis calculations with the Lagrangian approach, and in particular on the aerosol water content.

And is the homogeneous/heterogenous nucleation not too detailed for a global model (GCM) that provides ASP but even doesn't consider (because unknown) the seasonal cycle or the actual years of emissions for the simulation? What is the effect of e.g. different emissions (sources, years, seasonality) in particular of ammonia in this context?

How large are the uncertainties of the input ASR? The ASR is provided by Adams et al., 1999 used prescribed HNO3 fields; thus calculations of the ASR without feedback of the aerosol calculations with chemistry. However, this is likely to affect the ASP, not only because the HNO3 concentrations remains unchanged after part of it has been partitioned in the aerosol phase (e.g. through neutralization of HNO3 by ammonia).

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Also because the neutralization of acids by ammonia affects the pH of the aerosol, which in turn affects the formation of sulfate (via the oxidation of SO2 in the aqueous phase). And which uncertainty is meant by RH; different RH calculations, or input data, resolution ...?

What kind of geographical plots, which time averages, global means, which month? Because of the high variability of the aerosol distributions, it makes a big difference if one looks at a monthly mean, or for instance a monthly mean where only all 6hr morning or evening values are averaged (due to the temperature dependence of semivolatile compounds such as ammonium nitrate or water).

How do you determine a significant amount? Based on total mass vertically integrated (burden), for global mean, which month, ...? For burden, it is not new that sulfate, partly ammoniated, constitutes most of the aerosol mass for the ammonium/sulfate/nitrate-system.

And because of ammonia is emitted (in the GCM) only at the surface, neutralization of sulfate by ammonia also decreases with height, with sulfate fully neutralized (i.e. mostly aqueous ammonium sulfate, since often RH>RHD within the BL) near the surface at some locations, and partly neutralized at higher elevations (i.e. mostly solid ammonium bi-sulfate, since mostly RH<RHD in the FT). The mixture of both (wet or dry letovicite) might thus be a result of transport or due to thermodynamics. It is not surprising that global mean values of the total solid-containing fraction only differ by less than 2%, for a variation of about 5 % (?) in any one of the input parameter sets (?). If globally averaged, most of the (model) sulfate mass resides in 'dry' locations, i.e. where the RH<RHD (either in the free troposphere or in dry regions where most sulfate is formed due to photo-oxidation of SO2).

However, this also means that most of the solid-fraction would be independent of transport and the aforementioned uncertainties. Self-speaking, this is only true for global mean values. Hence, a much more detailed discussion of these numbers and uncerACPD

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tainties would be needed to be useful. And, btw., what is the value of a global monthly mean number for in time and space highly variable properties?

(3) Is the present study applicable for climate modeling? What is the extra computation time need for the Lagrangian model? Is it feasible for a multiyear GCM simulation with a fairly high spatial and temporal resolution? And if solids are, as claimed by the authors, relevant for the climate forcing (due to the water uptake), how can the APSM feedback the GCM?; the aerosol forcing needs to be calculated online.

(4) What is the relevance of letovicite in the real atmosphere? This point might be quite questionable, as the composition of the aerosol is likely to differ in the presence of the missing aerosol species (such as sea salt, mineral dust, black carbon, or organic compounds). All affect the solid/liquid partitioning (in addition to the gas/liquid/solid partitioning) which in turn affects the humidity growth and the radiative forcing.

Thus, to judge whether letovicite is of global importance, one would also need to discuss to which extent the neutralization of sulfate depends - besides the geographical location, vertical level, or season - on the presence on the missing aerosol species. Certainly, this needs to be scrutinized as mentioned by the authors. But does it make sense to stress that letovicite is of global importance at this preliminary stage?

(5) The feasibility of the global aerosol physical state modeling, as proposed, is highly questionable - because of the aforementioned problems. Once again, in order to reduce the large error bars associated with the last IPCC estimates, the aerosol forcing needs to be calculated online, simply because the forcing is very sensitive to the water uptake of the aerosol particles, which depends on the aerosol composition that in turn very much depends on emissions, meteorology, thermodynamics, chemistry, deposition and transport - all of that highly variable in time and space. Thus, the physical state of atmospheric aerosol particles, which might be of global importance, needs to be calculated online. However, the APSM can only provide these information offline, hence with limited use for the direct and indirect aerosol forcing calculations.

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(6) To my opinion, the results presented are very valuable for the community in the sense of a sensitivity study rather than in the sense of 'A novel model to predict the physical state of atmospheric H2SO4/NH3/H2O aerosol particles'. This study would be even more valuable, if the above problems would be addressed. Further, I suggest changing the title to: 'A sensitivity study of the physical state of atmospheric H2SO4/NH3/H2O aerosol particles'.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 2449, 2002.

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