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Atmospheric
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Discussions

Interactive comment on "Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing" *by* S. T. Martin et al.

Anonymous Referee #3

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General comments The authors evaluate the effect of physical state on global direct radiate forcing of tropospheric aerosol composed of ammonium-sulfate-nitrate-particles. They use a 3-dimensional chemical transport model to account for the mass of each species; they calculate Mie parameters of the aerosol (approximating it as homogeneous, spherical particles with average refractive index) and calculate the radiative transport. Because of the hysteresis loop the physical state of the particle depends on the relative humidity (RH) history. Since the model does not provide RH history, the authors use monthly average values for temperature and relative humidity and calculate the effect of physical state on the radiative properties by taking two limiting scenarios: at relative humidities below the deliquescence relative humidity (DRH), the particle is taken either as aqueous (metastable branch of the hysteresis loop) or as partially – or fully - crystalline according to a thermodynamic model. The conclusion for the global annual averages in aerosol radiative forcing is a circa 25% difference depending on the physical state of the aerosol.

The paper is well written and contributes new insight to a topic which is of central interest for the community.

The authors find a substantial difference in radiative forcing depending on the physical state of the aerosol but consider a limiting – and quite unrealistic – hysteresis loop for their aerosol particles. If the relative humidity is below the DRH they take the composition of the lower side of the hysteresis loop from a thermodynamic model. But for some of the solid phases the efflorescence relative humidity (ERH) is so low that this solid phase will almost never form in the atmosphere. An example is ammonium nitrate for which it is known that the ERH is below a few percent at room temperature. For example the authors do not consider – and I agree completely – sulfuric acid tetrahydrate (SAT) as a possible solid in their calculations even though it is thermodynamically stable below circa 245 K. But it is also well known not to effloresce even under high supersaturations. Colberg et al. [*ACP* **3**, 909-924 (2003)] have shown that ammonium bisulfate did not effloresce at typical tropospheric temperatures and the authors of the present paper have performed laboratory experiments for aerosol particles with the very composition discussed here [Martin et al., *GRL* **30**, 2102, doi:10.1029/2003GL017930 (2003)] showing also that ammonium nitrate and ammonium bisulfate does not effloresce but at relative humidities so low that they will rarely occur in the troposphere.

It is of course not easy to take this into account in the authors model, but since the ERH's of the system are known quite well [Martin et al., *GRL* **30**, 2102, doi:10.1029/2003GL017930 (2003)] one could for example do not allow ammonium nitrate and ammonium bisulfate formation and try to take a certain frequency of occurrences of relative humidities below 35% as a threshold where solid formation will happen. This will rule out entire regions/altitudes of the atmosphere for solid forma-

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tion. (It is instructive to see Figure 5 and Figure 6 of Colberg et al. [*ACP* **3**, 909-924 (2003] in this context). I am convinced such a scenario – and the authors probably find a better one – could provide some information about how realistic the 25% delta forcing effect described above really is. Such sensitivity studies would nicely supplement what has been done by the authors in chapter 6 and increase the value of the paper considerably.

The alternative approach – as e.g. done by Colberg et al. – namely taking into account directly the RH history of an air parcel, should be discussed more thoroughly by the authors, so that a reader not familiar with the specific field understands better that the present paper present an upper limit of the effect of physical state on radiative forcing. (The argument by the authors that it could also be a lower limit because not every solid thermodynamically conceivable is considered (see section 7) is rather weak, because these solid most likely never form in the atmosphere, see Martin et al. [*GRL* **30**, 2102, doi:10.1029/2003GL017930 (2003)]). This comment is closely connected to the one raised already by J. Heintzenberg. Although the authors write three sentences in connection with their use of monthly average RH (and T) in section 7 the reader would appreciate a more detailed discussion.

A further serious criticism – raised already by D. Cziczo - concerns the fact that organic material is excluded in the present study. I agree with Martin et al. that nevertheless the present study is important for improving our knowledge of how important physical state could be for aerosol radiative forcing. There is no alternative than proceeding in steps towards a more complex model, incorporating organics, elemental carbon inclusions, particles shapes and morphologies etc. (I want to stress again that a more realistic treatment for calculating the delta forcing would be very helpful). But I agree as well with D. Cziczo that the limitations of this study should be thoroughly discussed already in the introduction of the paper so that the reader not familiar with what is known about aerosol composition and the effect on aerosol phase get a better understanding. While the authors list the relevant studies in § 1.2 they should also explain and comment in more detail about the advantages and limitations.

Specific comments

Page 5403, line 6 and Figure 1: Since the authors use the ISORROPIA thermodynamic model with 4 possible solids, I recommend using the same model for Figure 1 for consistency and simply mentioning the additional solids incorporated in the AIM model.

Page 5403 and page 5404: Also it is known that $(NH_4NO_3)_3$ $(NH_4)_2SO_4$ is extremely difficult to nucleate even in bulk solutions [Jänecke et al., *Z. anorganische und allg. Chemie* **160**, 171-184 (1927)]. It is likely that it is of no atmospheric relevance.

Section 2.2: I recommend shortening it to what is absolutely essential for the present paper, see also comment by J. Heintzenberg.

Page 5411, line 11: Some comment is needed here, because NH_4HSO_4 will probably not effloresce, see Colberg et al. and comment above.

Section 3.1: Again the reader should be reminded at certain places (for example page 5415 line 3) that a solid whose formation is possible thermodynamically does not necessarily actually forms.

Page 5417, line 16: The sentence is misleading. Figure 12 of Colberg et al. considers not homogeneous nucleation, but heterogeneous nucleation of the bisulfate. This should be explained to the reader. If only homogeneous nucleation would be considered in Colberg et al. there would be no agreement with the results presented here.

Section 4 and 5: I find those very well written and instructive to the reader.

Page 5419, line 17: If besides the Bohren and Huffman citation another citation for optical properties and Mie theory is needed I would recommend citing the classic book of H. C. van de Hulst, Light Scattering by Small Particles, John Wiley & Sons, N. Y. 1957 instead of Han and Martin [2001] and Hung and Martin [2002].

Page 5420, line 3: A comment should be added to account for the vast literature of the

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effect an (soot) inclusion does have on scattering properties and radiative forcing, e.g. [Chýlek et al., *JGR* **100**, 16,325 (1995), Ioannidou et al., *Appl. Opt.* **39**, 4205 (2000)]

Page 5423, line 17: there is a circa 30% difference in β_{avg} between the present paper and Koch et al. and Charlson et al.. Is this really a ”small” difference?

general technical comment: I find some of the figures really hard to read because they are very small: If there is a chance to put less figures on each page and enlarge them I would recommend doing this.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 5399, 2003.