

Interactive comment on “Interaction of aerosol particles composed of protein and salts with water vapor: hygroscopic growth and microstructural rearrangement” by E. Mikhailov et al.

E. Mikhailov et al.

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We thank Ernest Weingartner for the thorough review, positive evaluation, constructive criticism and suggestions for improvement of our manuscript. Most suggestions will be implemented in a revised version. Answers to his specific comments (*italic font*; ACPD, 3, S1842-S1845, 2003) are given below.

Specific Comments

1) *P4759: What is the source of these proteins in the atmospheric aerosol? Is the same quantity also found in the ultrafine size range or do they arise from bioaerosols with diameters > 1 μm ? Please provide more information.*

The abundance, size-distribution, and sources of proteins in air particulate matter are

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subject to ongoing research and we hope to obtain and publish more information in the near future, but we are not yet able to answer the raised questions beyond the statements and references already included in the manuscript.

2) P4762 line 24: *It is assumed that in the DMA (where the particles "see" the different sheath air humidity, RH3) the particles attain their new equilibrium size nearly instantaneously (i.e. within a timescale much smaller than the particle residence time in the DMA drift zone). This assumption is not necessarily valid for particle that undergo a phase transition or when surface-active organic substances are present on the particles. In these cases the determined sizes may therefore differ from the final equilibrium size. This should be mentioned and discussed. P4775 (Fig3): The discussion is not satisfying. I attribute the fact that the growth factors measured during dehydration are larger than the one measured during hydration to the instrumental artefact described above (P4762, line 24). During dehydration the supersaturated droplets crystallize in the upper part of the DMA and therefore the measured sizes are larger than their final size. Maybe one could estimate a crystallization time from these differences... An analysis of the standard deviations of the SMPS size distributions could give more insights. See Gysel et al., Atmos. Chem. Phys. Discuss., 3, 4879-4925, 2003. P4776, discussion Fig.4 Again, using the second DMA simultaneously as a dryer as well as a sizer is problematic. I fully agree with the discussion of the observed microstructural rearrangement at $RH < 75\%$. But the stepwise increase at deliquescence RH might be a consequence of the instrumental artefact (see above). This should be mentioned.*

Kinetic limitations in the interaction of water vapor with aerosol particles - in particular salt particles and aqueous droplets with macromolecular organic coatings - and their potential influence on the results of H-TDMA measurements are among the main subjects and messages of our paper, as pointed out in the abstract, discussion and conclusions. We will further clarify this aspect in the revised manuscript.

The applicability of DMA 2 for both particle drying and sizing in the reported experi-

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ments (H-TDMA mode 3, hydration/dehydration) has been confirmed by analogous experiments in which the aerosol flow was dried to $RH_2 < 5\%$ before entering DMA 2. For both pure NaCl and mixed NaCl-BSA (50:50) particles the same stepwise increase at deliquescence RH was observed with and without pre-dryer. This confirms near-instantaneous efflorescence at the entrance into the DMA drift zone and will be mentioned in the revised manuscript. Further experiments extending the presented investigations and a detailed discussion of particle drying and sizing inside a DMA will be presented in a separate publication. This follow-up publication will also include an analysis and discussion of size distribution broadening (standard deviations), which is not required to support the conclusions of the present paper.

3) P4763, line 1 "modal diameter (local maxima) of number size distributions" How was the modal diameter exactly determined? Did you fit a log normal distribution to the data? If yes, what is the standard deviation (or spread) of the distribution? Did you observe a change of the standard deviation with changing RH? Please give also more information about the units of the number size distribution. Did you parameterise the raw CPC counts or did you use processed data (such as $dN/d\log D$)? What is the SMPS upscan time? Did you observe smearing effects?

The SMPS was operated with the TSI AIM 4.3 software, pre-impactor nozzle 0.0508 cm, size range 14.8–487 nm, upscan time 120 s, retrace time 15 s, delay time 10 s, CPC count time 0.1 s. Modal diameters were graphically determined from a B-Spline fit to the SMPS measurement data (Origin 7.0 software, CPC raw counts vs. mobility equivalent diameter, 64 channels per decade). This information will be included in the revised manuscript. The results of test experiments with processed data ($dN/d\log D$) were not significantly different from the ones obtained with CPC raw counts. Test calculations with normal and log-normal distribution fit functions yielded essentially the same results as the graphic analyses, except for a systematic 1 % shift of the determined modal diameters towards higher mobility diameters due to a tailing of the measurement data, which can be attributed to the limited SMPS scan time (Russel et

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al., Aerosol Sci. Technol. 23, 491-509, 1995; Weingartner et al., Environ. Sci. Technol., 2002). This systematic shift, however, is not relevant for the presented analyses and calculations and did not exceed the estimated overall accuracy of particle sizing (+/- 2 %). Longer scan times, on the other hand, would have prohibitively increased the overall duration of experiments. Smearing effects (broadening of mono- and bi-modal size distributions) have been observed and will be discussed in detail in the follow-up publication mentioned above.

4) P4763, line 8: "1% precision in diameter measurement". I am wondering how this high precision could be achieved over several hours with rotameters, needle valves and tube clips. This is a brilliant achievement.

Thanks. High precision can indeed be achieved without automation. The initial dry particle diameter ($D_{b,i}$) was regularly controlled to avoid drifts and measurement artifacts, and its relative standard deviation during H-TDMA experiments (up to 6 hours, up to 30 repeated measurements) was generally less than 1 %, often lower than 0.3 %.

5) P4764, line 10: Throughout the text I would change mass equivalent diameter to volume equivalent diameter. In this context it is less misleading and more common to use the volume equivalent diameter.

In our view the terms mass equivalent diameter and volume equivalent diameter are more or less synonymous, depending on the specific application. In the context of our paper which deals not only with particle (envelope) shape but also with porosity, we think that the term volume equivalent diameter might be more misleading. It could be more easily misunderstood as an equivalent diameter which is corrected only for the particle (envelope) shape but not for the porosity of the material. For this reason we used the term mass equivalent diameter already in our H-TDMA paper on the microstructural rearrangement of NaCl condensation aerosol particles (Krämer et al., 1999) and prefer to continue with this nomenclature.

6) P4788, line 17: Which location do you exactly mean with "inlet of DMA 2"? Is it the

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mechanical inlet or the zone inside the electrostatic field where the electrostatic sizing starts and the sheath air RH is mixed by diffusion with the aerosol RH? I assume that you mean the zone inside the DMA and I would therefore suggest to avoid the term inlet in this context. I have the impression that in this paragraph the authors assume that inside the DMA the particle already experience the higher sheath air RH BEFORE their electrostatic sizing starts. This assumption is NOT true.

We did not assume that the particles would experience the humidity of the sheath air flow before the electrostatic sizing starts. With inlet we meant the entrance of the aerosol flow into the drift zone (analyzer column) of the DMA, and we will use the latter wording in the revised manuscript to avoid confusion.

7) P4789, line 6 and 9: These conclusions cannot be drawn from these measurements!

We see no arguments and reasons why our conclusions and hypotheses (including the kinetic limitation of deliquescence and efflorescence transitions by a BSA surface coating) would not follow from our measurements. We think that they provide the most plausible and consistent explanation for our results, but we agree that further research is needed to prove them. We will try to clarify the argumentation and formulations in the revised manuscript. Additional measurement results and an extensive discussion on the observation and interpretation of kinetic effects in H-TDMA experiments will be presented in the follow-up publication mentioned above.

Technical Corrections

1) P4760, line 25: change to "18.2 M Ohm times cm"

Will be corrected.

2) P4761, line 24: change to "0.1 °C"

Will be corrected.

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3) P4768, line 17: did you mean eq. (7)?

Yes, will be corrected.

4) P4774, eq 30: use a more general expression and replace 133 nm with 2 times lamda, where lamda is the mean free path of air.

Will be generalized.

5) P4786, line 9: Figure 6C1 instead of figure 5.

Will be corrected.

6) P4788, line 3: Figure 13e should be 13d and e.

Will be corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 4755, 2003.

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