

Interactive comment on “Absorbing aerosols at high relative humidity: closure between hygroscopic growth and optical properties” by J. M. Flores et al.

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We are very grateful for the time and effort that the Reviewer has invested reviewing our work, and are pleased that you found our work interesting as well as an important contribution to the field. We appreciate all of the constructive comments you've given us. We apologize for the problems with the Figure captions. Specific comments:

P1025/L10: It is not clear what is being compared to establish whether the “dry measurement differed more than 5% from the initial.” Were the authors looking at absolute extinction levels or at extinction cross sections? The former is dependent on stability of the system with respect to particle generation while the latter is related to measurement

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precision and accuracy.

To make this clearer in the manuscript we changed the phrase: “If the final dry measurement differed more than 5% from the initial, the measurements of that substance were repeated” to “To ensure experimental stability, the measurements were repeated if the final dry extinction cross section differed by more than 5% from the initial one. “

P1025/L12: It is not clear whether the median diameter that was chosen refers to the median diameter of the singly charged particle mode or to the median diameter of the overall size distribution (including multiply charged particles). Depending on the contributions from multiply charged particles these could differ substantially. Additionally, it is my understanding that the discussion in Hoppel (1978) most relates to non-size selected particle size distributions (i.e. “full” distributions), which is not the case here. Finally, although the authors have chosen to use the median, as opposed to mean diameter of the size selected particles to minimize contributions of multiply charged particles, they should none the less explicitly consider the influence of multiply charged particles, as the influence is often found to be size dependent due to the influence of the original polydisperse distribution.

Following the comments from Reviewer #1 and #3 we have now corrected for multiply charged particles and added the following paragraph: “For each selected mobility diameter, singly and multiply charged particles of the same mobility are also transmitted through the DMA. The multiply charged particles affect the optical measurements, leading to overestimation of the optical extinction cross section. To reduce biases arising from multiply charged particles we used a solution concentration of 500 mg L⁻¹ for sizes between 200 nm to 300 nm, and a 1000 mg L⁻¹ solution for 350 nm to 550 nm diameter aerosol. We measured the resulting size distributions and using the Wiedensohler charge distribution parameterization (Wiedensohler, 1988 with subsequent erratum) found that at these solution concentrations, between 2.7–7% and up to 1% of doubly and triply charged particles, respectively exist in the flow. These percentages were used to correct for the contribution of multiply charged particles to the total ex-

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tion at each diameter using literature values of the complex refractive indices, when available (e.g. ammonium sulfate), and to correct the size distributions measured by the SMPS. When RI literature values were not available, only the size distributions were corrected. The median diameter from the corrected SMPS size distribution was taken as the measured diameter. “

P1029/L8: When I think of something having an “exponential behavior” I expect that to be some fundamental aspect of the relationship. Here, the relationship between fRH and size for ammonium sulfate might have some overall behavior that is generally describable as an exponential function of size, but the calculations show clearly that the relationship is not fundamentally exponential; it has bumps and wiggles that are natural aspects of Mie theory. This is perhaps a semantic distinction, but I think important. Ultimately, I would pose the question what is the point of fitting this to an exponential? Is the goal to develop a parameterization for use in models? Since no fit parameters are given, I assume this is not the case. Therefore, I would suggest removing discussion of the exponential behaviour and instead suggest the authors state that fRH generally decreases with size for AS particles, but non monotonically.

We agree with the reviewers comment and have changed the paragraph with the discussion about exponential behavior to: “The ammonium sulfate measurements show, generally, that fRHext(80%RH,Dry) and fRHext(90%RH,Dry) decreases with size non-monotonically. Garland et al. (2007) parameterized AS at 80% RH with an exponential function, however the theoretical calculations and measurements of fRHext at both RHs show that the relationship is not fundamentally exponential as it shows the existence of the Mie resonance structure.” Figure 3/Figure 4: I am having some difficulty reconciling the data and calculations shown in Figure 3 with those shown in Figure 4. The banded curve in Figure 3 is for volume mixing. For nigrosin, for example, the measured value at 300 nm (dry diameter) in Fig. 3 falls right in the calculated band. Yet in Figure 4 the same point (or at least I assume the third from left is the same point) does not agree with the calculated Qext. Perhaps I am missing something, but there

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appears to be an inconsistency here. Perhaps it would help if the authors again gave a band for the calculated volume mixing curves in Fig. 4? We believe the confusion lays on the x-axis. While for Figure 3 the x-axis shows the dry diameter, in Figure 4 is the ‘wet diameter’ after converting the dry diameter to size parameter using the measured growth factor (GF) and the wavelength of the incident light. However, in Figure 4 we have added a band (gray curve) to the calculated volume weighted mixing curve.

P1030/L25: The authors state in reference to the comparison between retrieved and volume weighted complex refractive indices: “There are greater differences in the imaginary parts, but the values are within measurement errors.” I disagree, at least for the Pahokee Peat. For this substance the derived and volume weighted values are outside the stated uncertainties. We can certainly ask the question of whether the uncertainties have been underestimated (since they are substantially smaller in absolute terms than for any other substance), but as reported the derived values are different outside of uncertainty. This is consistent with the very next statement where the authors indicate that for IHSS Pahokee peat and nigrosine particles the imaginary RI is overestimated. (The authors do not explicitly state what is overestimated referenced to what, i.e. retrieved vs. calculated or calculated vs. retrieved. This should be made clear.) We’ve change the phrase to read the following and make the statement clearer:

“There are greater differences in the imaginary parts. However, most values lie within the measurement errors. For the IHSS Pahokee peat and nigrosine aerosols, there is an overestimation of the retrieved imaginary part with respect to the calculated one with the volume weighted mixing rule at both wavelengths and RHs.”

The authors first compare results from calculations, considering how core-shell Mie theory will compare to homogeneous mixture. They demonstrate that the homogeneous mixture assumption tends to give larger Qext at a given size compared to core-shell, and the difference increases with particle size. They use this computational result to argue that their data suggest core-shell behavior because for nigrosine the difference between the observations and homogeneous mixing increases with particle size. How-

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ever, this neglects that fact that at intermediate sizes the core-shell method does just as poorly as the homogeneous method. In my opinion, their argument should hinge on the comparison of the core-shell method to the observations if they wish to argue that core-shell is appropriate, not on the disagreement between the homogeneous method and observations. In other words, they have presented reasonable evidence that homogeneous missing does not explain the observations, but I am not unconvinced by their assessment that core-shell does explain the observations (for nigrosine). Further, what they do not consider is the following: for somewhat soluble compounds (such as nigrosine), the actual behavior is likely some combination of homogeneous mixing and core shell. What I mean by this is that in the water layer that does exist, some of the nigrosin will dissolve to make the “coating” slightly absorbing. At the same time, the size of the “core” will have shrunk. Have the authors considered how such an accounting might influence their conclusions?

Following the Reviewer’s comment we have revisited the issue and have now changed the conclusions. We now conclude that neither the homogeneous assumption nor the core-shell assumption explain thoroughly the discrepancies. Please see the new paragraph: “For the IHSS Pahokee peat and nigrosine aerosols, there is an overestimation of the retrieved imaginary part with respect to the calculated one with the volume weighted mixing rule at both wavelengths and RHs. Both substances have a small GF ($GF(80\%)=1.09$ and $GF(90\%)=1.17$ for Pahokee peat, and $GF(80\%)=1.12$ and $GF(90\%)=1.24$ for nigrosine), which raises the question of their internal structures after humidification. It is not clear whether there is a complete dissolution or whether a small shell of water forms around the particles forming a core-shell structure. To explore whether there could be an optical distinction for Pahokee peat and nigrosine, the extinction efficiency as a function of size parameter was calculated separately for each case. For the homogeneously mixed case, $Q_{ext-homogeneous}$ was calculated with the RI obtained from the volume weighted mixing rule. For the core-shell structure, $Q_{ext-core-shell}$ was calculated using the diameter measured after humidification as the total diameter, and the dry diameter selected by the first DMA as the core diameter. The RI

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of the core was taken from the dry measurements, and the RI of water was used for the RI of the shell. The codes by Liu et al. (2007a) and Bohren and Hoffmann (1983) were used to calculate $Q_{ext-core-shell}$ and $Q_{ext-homogeneous}$, respectively. Lastly, the ratio of $Q_{ext-core-shell}$ to $Q_{ext-homogeneous}$ was calculated and plotted as a function of size parameter for both wavelengths in Figure 5. From Figure 5 at 80% RH, where the Pahokee peat and nigrosine particles only grew 9% and 12%, respectively, there is less than a 5% difference between the values obtained with a core-shell structure and those obtained by assuming homogenous mixture for size parameters less than 2.5. For 90% RH, the differences between the core-shell structure and a homogeneously mixed particle are more noticeable, with up to a 7% difference for the Pahokee peat. A clear distinction between the two mixing assumptions can be observed at size parameters greater than 3 with lower Q_{ext} values for a core-shell structure than for a homogeneously mixed case. Therefore, the nigrosine measurements shown in Figure 4b, show that the difference between the measurements (open circles) and the homogeneous mixing assumption (solid line) is greater at larger size parameters than the core-shell calculation (red solid symbols); which suggest a core-shell structure. However, the measured Q_{ext} still differs from the core-shell and homogeneous model at the intermediate sizes for nigrosine and it also does not seem to explain adequately the results for Pahokee peat at 80% RH and 532 nm (Figure 4a). Therefore we cannot conclusively say whether the core shell model explains fully the result. There is the possibility that partial dissolution of nigrosine or Pahokee peat dissolved into the surrounding water, causing the “coating” to be slightly absorbing. At the same time, the size of the “core” will have shrunk making our original assumptions of size and complex RI incorrect. Unfortunately, with the precision of the experiments performed in this study it is not possible to examine this hypothesis. However, we do observe from Figure 4 and 5 that if an aerosol with a $GF < 1.15$ is assumed to be homogeneously mixed, when in reality its internal structure resembles a core-shell, it will result in an underestimation of the imaginary part of the complex refractive index when the RI is calculated with the volume weighted mixing rule.”

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P1032/L8: The authors state: "With a GF of only 1.09 there is the possibility that only small water clusters formed instead of a complete layer of water around the aerosols." It is not clear where this statement comes from or how it is justified. For a 200 nm diameter particle, a GF of 1.09 translates to a coating thickness of $(200 \times 1.09 - 200)/2 = 9 \text{ nm} = 90 \text{ Angstroms}$ = many, many water molecules. If the authors want to make this argument, they must justify it more fully. It is also not clear how having "water clusters" as opposed to a complete layer of water would have caused the absorption of the humidified substances to be greater than of the dry substance. Can the authors elaborate on their hypothesis in terms of a plausible physical mechanism?

Please see the response to the previous comment.

Figure 6 and associated discussion: The figures and associated discussion has been removed from the manuscript Other comments:

P1022/L6: Stabling should be stabilizing. Fixed, thank you

P1022/L10: The reference to Kanakidou et al. appears a bit out of place. This reference has been omitted.

P1026/L15: "use d" is a typo. Fixed, thank you.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 1019, 2012.