

Flores et al. present results on the optical hygroscopicity of slightly absorbing particles. They compare theoretical predictions, constrained by direct observations of particle growth factors (GF), to observed optical growth factors (fRH). This study provides an important look at the influence of water uptake on the optical properties of absorbing aerosol, something which has not been investigated previously in nearly enough detail. In this regard, the manuscript is a strong contribution to the field. Concerning their results, in some cases they find good agreement between homogeneous mixing theory and observations whereas in others they find lesser agreement. They invoke a “core-shell” model to explain some of the model/measurement discrepancy, but I find this explanation to be only moderately convincing.

In what amounts to an entirely separate study, they consider the influence of absorbing aerosol on aerosol optical properties in the twilight region of clouds. Here, they conclude that absorption has no direct influence on the total extinction, but does on the single scatter albedo and asymmetry parameter. However, I believe that their analysis is based on a faulty assumption that absorption by particles is separable from their hygroscopicity. Both properties depend on particle composition and will likely vary in exactly opposite directions: as hygroscopicity increases, absorption will decrease for a given particle. This complication must be dealt with before I believe that the manuscript is publishable.

Specific comments follow below.

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 precision and accuracy.

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.

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 behavior and

instead suggest the authors state that fRH generally decreases with size for AS particles, but non-monotonically.

Figure 4: I recommend making sure that this figure is of higher resolution in the eventual final paper. It is a bit grainy and difficult to read currently.

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 Q_{ext} . Perhaps I am missing something, but there 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?

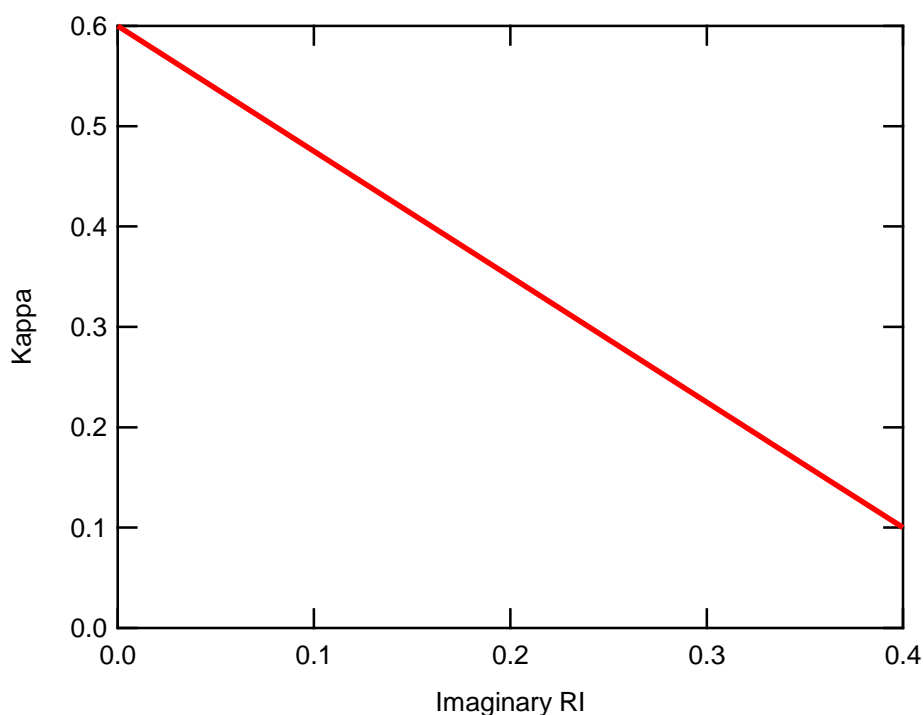
Table 1: I assume that in final publication Table 1 will not break over two pages? This should be avoided as it makes it difficult to follow on the 2nd page.

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.)

Discussion on P1031: The authors first compare results from calculations, considering how core-shell Mie theory will compare to homogeneous mixtures. They demonstrate that the homogeneous mixture assumption tends to give larger Q_{ext} at a given size compared to core-shell, and the difference increases with particle size. They then 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. However, 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 mixing does not explain the observations, but I am 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?

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 $(200 \times 1.09 - 200)/2 = 9$ nm = 90 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 substance to be greater than of the dry substance. Can the authors elaborate on their hypothesis in terms of a plausible physical mechanism?

Figure 6 and associated discussion: The authors use a kappa value (hygroscopicity parameter) of 0.6 that does not co-vary with their assumption of how absorbing the particles are. This, to me, does not seem justified. A kappa = 0.6 corresponds to a “3:7 organic:inorganic” mixture or approximately to ammonium nitrate (from Petters and Kreidenweis, ACP, 7, 1961, 2007). We can make the very reasonable assumption that the inorganic component is non absorbing and more hygroscopic than the organic (or black carbon) component. Thus, hygroscopicity should vary inversely with the imaginary refractive index. An example is shown in the following figure where it has been assumed that homogeneous mixing rules apply, that $\kappa(\text{inorganic}) = 0.6$, $\kappa(\text{other}) = 0.1$, the imaginary RI(inorganic) = 0 and imaginary RI(other) = 0.4. (Note that the exact values used are arbitrary, but the general behavior is independent of the exact values.) As (dry) particles become more hygroscopic they become less absorbing. Given this, I question the relationship shown in Figure 6 and the associated conclusion, that extinction is independent of absorption. This conclusion is only valid if they assume that absorption and hygroscopicity are decoupled, which I do not believe is likely the case. This general idea will propagate through to influence the results in Fig. 7 and 8 as well. As it currently stands, I believe that the authors’ conclusions in this section are based on a faulty assumption that must be revisited.



Other comments:

P1022/L6: Stabling should be stabilizing.

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

P1026/L15: “use d” is a typo.