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Interactive comment on "The absorption Angstrom exponent of black carbon with brown coatings: effects of aerosol microphysics and parameterization" *by* Xiaolin Zhang et al.

Anonymous Referee #1

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This paper uses the multi-sphere T-matrix method (MSTM) to analyze how BC size, aggregate fractal dimension, and mixing state affects the absorption Angstrom exponent (AAE). The article is well organized and well written, although it could benefit from some minor copy editing in some places. I find it suitable for publication after the corrections listed below.

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MAJOR ISSUES:

INTRODUCTION

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The introduction should be expanded somewhat, as there is significant work on this topic that the authors do not mention. For instance, see Liu, JQSRT 2019, Liu and Mishchenko, Rem. Sens. 2018 for aggregated BC computations. I would also search for more. As can be gathered from my comments below, much of the work cited in the intro is not consistent with what I have read in those articles.

Page 2, line 1, authors state: "... the absorbing organics, named brown carbon (BrC), is one type of organic carbon absorbing radiation in the ultraviolet and visible spectra [Clarke et al., 2007]."

This is a little misleading. BrC is not one type of organic carbon; rather, BrC is composed of many different absorbing organic species.

Page 2, line 5, authors state: "The lack of accurate understanding and parameterization of the AAE of aged BC has been a pivotal limitation on the assessment of BC radiative effects [e.g., Ramanathan and Carmichael, 2008; Bond et al., 2013]."

This is very misleading, as these articles do not attribute such large importance to AAE. In fact, I did a search for "Angstrom" in RC08 and did not get a single hit.

P2, L16, authors state: "Hence, the AAE can be utilized to quantify the separation of BrC absorption from BC absorption based on their distinctive functions of incident wavelength [e.g., Lu et al., 2015]."

This is an oversimplification of current AAE discussions, as there are plenty of articles in the literature stating that AAE can not unambigously separate BrC from BC (e.g., see Lack and Cappa (2010) and Lack and Langridge (2013), Schuster ACP 2016, part 2, etc.). If you want readers to take this article seriously, you should highlight the current AAE issues that are being discussed in the literature and then tell readers how your contribution fits into the overall discussion.

P2, L22, authors state: "The AAE values of BC-dominated aerosols produced with burning oil, are observed in the range of 0.8–1.1 [e.g., Chakrabarty et al., 2013]."

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But C13 concluded that only mustard oil was dominated by BC, and they measured an average AAE = 1.32 for mustard oil. How did the authors arrive at 0.8-1.1 from the C13 article?

P2, L24: I don't see AAE > 4 anywhere in Kirchstetter 2004.

P2, L26: I don't see BrC AAE ~8 anywhere in Clarke 2007.

METHOD:

The aggregates used to represent BC in this study seem to have been drawn out of thin air. The authors do not discuss why they chose N=200 or Df = 1.8, 2.8 in detail. Later, the authors draw some fairly broad conclusions based upon this numerical work, but the reader is left wondering how the results might differ if the authors had chosen different aggregates. This is especially important, since the spherical coatings in Figure 1 do not look terribly realistic. How might the results change if the authors used less particles per aggregate (e.g., N = 40, as in Adachi, JGR 2010) and non-spherical coatings? How big are the primary spherules in this work? How would the results change if one alters the spherule sizes? What if one alters N? What role does shielding play? Large N –> more shielding –> less efficient absorption. It would be nice to see one of these aggregate papers address the shielding issue. I realize that shielding is probably to much to add to this paper, but acknowledging that shielding is an important topic that is still unaddressed would be nice.

How do the authors' results compare to other work, such as Liu and Mishchenko (Remote Sensing, 2018)? LM18 computed AAE for particles with many different aggregate configurations and mixing scenarios. Placing the author's results in the context of this wider study could help the reader understand the range of applicability of the results presented here.

The authors frequently state that their calculations are "more realistic," but I have never seen TEM pictures that look like Figure 1b. There are also many articles with non-spherical aggregate coatings and therefore more realistic than Fig 1c (e.g., Adachi 2010). Many of these articles only address single particles, though.

Also, how do the fractal dimensions Df = 1.8, 2.8 shown in Fig 3 relate to the morphologies shown in Fig 1? That is, what are the Df for the morphologies of Fig 1? More importantly, what do the BC aggregates look like when Df = 1.8, 2.8 and N = 200?

P4, L22: Authors should make clear that these numbers pertain to aggregate sizes, not the monomers. Presumably these radii correspond to equivalent volume spheres, which should also be mentioned. Also, how is r_g related to the gyration radius of Eq 1, R_g?

P5, L28, authors state: "...and the bias induced by chosen absorptions at two wavelengths may be averted."

The authors seem to be stating that the AAE errors are not subject to absolute measurement errors of absorption. However, the AAE is an exponent; as such, it is highly sensitive to absorption measurement errors when AAE is derived from two wavelengths. A simple perturbation analysis using "typical" measurement errors will illustrate this.

RESULTS:

P7, L1, authors state: "On the whole, the impacts of ... BC position within brown coating on the AAE of coated BC are generally negligible."

That's because the shells are not that much larger than the cores (Dp/Dc > 1.6). There are many early papers that investigated the effect of "randomly placed inclusions" vs. a "concentric inclusion." See Fuller JGR 1999, for example. It is worth noting the similarities and differences between your results and the early core/shell work, here.

P7, L23, authors state: "The above simulations assume BC coated by BrC, whereas it may be contaminated by non-absorptive organic carbon in ambient air."

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Well, BrC is always "contaminated" with OC. That's because no-one has ever definitively separated BrC from OC. For instance, Kirchstetter separated OC from BC, so Kirchstetter's refractive indices represent a mixture of absorbing OC (now widely called BrC) AND non-absorbing OC. These are not two separate compounds, as both BrC and OC represent hundreds (thousands?) of compounds. I believe that this is why there is such a huge range of refractive indices for BrC in the literature. I believe that if anyone ever isolated the absorbing compounds of BrC from other OC, that the resulting BrC refractive index would be higher than the values that the community is using right now.

I really like the concept of this section, but the phrasing is misleading. What you are basically doing is assuming that the Kirchstetter BrC IRI is the upper extreme for BrC absorption, and then considering cases of BrC that are less absorbing than the Kirchstetter values. You could also look at the range of values provided by other groups as another (perhaps better) way of discussing variable BrC absorption. See Schuster ACP 2016 figures, for instance. Whatever you do, though, the wording should not convey the idea that Kirchstetter measured "pure" BrC. I don't believe that K04 meant to convey this.

P9, L8, authors state: "In addition, our results with more realistic geometries indicate that occurrence of BrC can only be made with confidence if the AAE of coated BC is larger than 1.4, as the AAE smaller than 1.4 can not necessarily exclude BrC as an important contributor to particle absorption."

This sentence does not make sense to me.

P10, L25, authors state: "Interestingly, BC coated by thin BrC with a large size distribution (i.e., large r_g) can have the AAE smaller than 1.0, and this implies that BC aerosols containing BrC can even show lower AAE than pure BC particles, which challenge conventional beliefs."

Pure and uncoated BC can also have AAE < 1 if the particles are large, according to

Fig 4 when F=0. This corresponds to the geometry of Fig 1a, right? It would be nice if the authors are also able tp present the AAE for a particles that are not touching another sphere, but I believe that they would still obtain AAE < 1 for large aggregates of BC. This should be mentioned here, because AAE is sensitive to particle size. See Fig 6, models 2 & 3 in Liu and Mishchenko (Rem. Sens., 2018); see also Gyawali (ACP, 2009) and Schuster (ACP, 2016).

I don't know what is considered to be "conventional belief," but the AAE = 1 assumption for BC is a by product of the Rayleigh small particle limit for absorption. Aggregates of BC do not necessarily satisfy the "small" criteria, so AAE = 1 does not necessarily hold (especially for collapsed aggregates with significant shielding). Open aggregates can be reasonably modeled as a loose collection of spheres, though, so the AAE = 1 approximations may hold for those cases. Thus, we expect a range of AAE for BC.

Page 10, L30, authors state: "Our results with more realistic geometries also indicate that occurrence of BrC may be made confidently unless AAE>1.4, which is a replenishment of related findings of Lack and Cappa [2010] produced by the core-shell Mie model."

This is exactly opposite of LC2010, per their abstract:

It has often been assumed that observation of an absorption Angstrom exponent (AAE)>1 indicates absorption by a non-BC aerosol. Here, it is shown that BC cores coated in C_Clear can reasonably have an AAE of up to 1.6, a result that complicates the attribution of observed light absorption to C_Brown within ambient particles. However, an AAE<1.6 does not exclude the possibility of C_Brown; rather C_Brown cannot be confidently assigned unless AAE>1.6. – LC2010

CONCLUSIONS:

P11, L16, authors state: "Meanwhile, BC coated by thin brown carbon with a large size distribution can show an AAE smaller than 1.0, implying that BC aerosols containing

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brown carbon can even show lower AAE than pure BC particles, and this challenges conventional beliefs."

Here again, a BrC coating is not necessary to achieve AAE < 1.

Also, AAE = 1 for all BC is not a "conventional belief," as many of us know that particle size is important. Lack and Cappa (2010) discuss this, for instance. See also Gyawali (ACP, 2009) and Schuster (ACP, 2016 part 2).

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MINOR ISSUES:

P4, L7, authors state: "...the volume of BC monomers within coating and overall BC volume..." It took me awhile to discern the meaning of this phrase. It would be helpful if the authors point the readers to Fig 1b, here.

P4, L8: k_f has not been defined thus far. Is this the same as the k_0 of Eq 1?

P5, Lines 1-7: This paragraph would be much stronger with an active voice. The authors are discussing things that are "normally" done and providing citations, which sounds like a literature review. The paragraph would be much clearer if the authors tell the reader what they are doing with an active voice; then the citations become the justification.

P5, L10 and throughout: I would avoid using the word "bulk" in this context, as bulk optical properties refer to bulk matter that is much much larger than the wavelength, which is not the topic of this paper.

P2, L9, authors state: "... can be calculated." Here again and throughout – get rid of passive voice. Tell the reader what you did, not what can be done.

P5, line 27: authors state that the slope of the line in Fig 2 is 2.1, but the figure indicates a negative slope. More precise wording is needed.

P6, L12: The authors state that "the AAEs of BC coated by BrC are sensitive to fractal dimension,..." but their Figure 3 indicates that this sensitivity is small when Dp/Dc > 1.5 or so for F =0, and that there is no sensitivity at all when F > 0. This should be mentioned in this paragraph.

P6, L22 and elsewhere: The authors frequently discuss the difference between compact and lacy BC aggregates, but they never tell the reader which Df is more compact (i.e., Df=1.8 or Df=2.8).

Figures 4-7: It is annoying that the colorbar in Figs 4-7 unconventionally decreases upward.

P9, L3 and throughout: "In general, among all sensitive microphysical parameters of coated BC, the absorbing volume fraction of coating plays a more substantial role in the AAE determination."

More substantial than what? Comparative words like 'more' have to be 'more than' something. This seems to happen fairly frequently in this paper (e.g., "more realistic geometries" – more realistic than what?).

P9, Eqs 9 & 10: I don't understand the utility of these empirical equations. The authors are using 3 parameters that are difficult or impossible to measure in order to approximate something that is relatively easy to measure (the AAE). I don't understand the point.

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