

# Black-carbon phase shift parameter and soot restructuring

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I found Beeler and Chakrabarty (egosphere-2022-163) very interesting, particularly from the perspective of having just finished a review of soot restructuring studies. That review concluded that only solid coatings or coagulation could allow soot to mix internally without restructuring, and is relevant to the interpretation of the results of this manuscript. I will expand this comment here in the conventional review format for clarity.

In this manuscript, B&C apply the phase-shift parameter  $\rho$  to the BC core of internal mixtures.  $\rho$  is defined relative to the radius of gyration  $R_g$ , wavelength  $\lambda$ , and BC monomer packing fraction  $\phi$  as

$$\rho = \frac{4\pi R_g}{\lambda} |m_{\text{eff}} - 1| \quad (1)$$

$$\rho = 2x |m_{\text{eff}} - 1| \quad (2)$$

Where  $x = 2\pi R_g/\lambda$  is the size parameter and  $m_{\text{eff}}$  is

$$\phi \left( \frac{m^2 - 1}{m^2 + 2} \right) = \frac{m_{\text{eff}}^2 - 1}{m_{\text{eff}}^2 + 2} \quad (3)$$

These equations illustrate that  $\rho$  is primarily a function of packing fraction  $\phi$  and size  $R_g$  (or  $x$ ). Packing fraction is a morphological parameter, and  $m$  is only expected to be a function of  $R_g$  for aggregates smaller than those considered here (Corbin et al., 2021). So, the main concept in this manuscript is come down to the BC-core packing fraction  $\phi$ .

Based on the above concept, the authors present an excellent discussion of the relationship between MAC,  $\rho$ , and the ratio of coating-to-BC-mass,  $R_{BC}$ , for model soot particles. Then, the authors place their work in the context of the literature by considering whether previous measurements of the relationship between MAC and  $R_{BC}$  can be attributed to  $\phi$ . I have two major questions for the authors:

1. Could the authors add a more quantitative discussion of  $\phi$ ? As stated, the entire discussion of the BC-core  $\rho$  comes down to  $\phi$ , which can be constrained as about 0.1 to 0.4 (Zangmeister et al., 2018, <http://www.pnas.org/cgi/doi/10.1073/pnas.1403768111>; also Schnitzler et al. 2017 is relevant <http://dx.doi.org/10.1016/j.jaerosci.2017.01.005>). If there was some reason the authors did not discuss  $\phi$  directly could they please comment? If not,
  - (a) can the authors calculate  $\phi$  for their model aggregates, and discuss whether the upper-limit packing density identified by Zangmeister et al. 2018 allows the literature trends to be fully explained by  $\phi$ ?
  - (b) Also, can the authors provide more information about the  $\phi$  of their modelled particles, for example by plotting  $\phi$  versus  $\rho$  or MAC?
2. The authors state that “Our results indicate that studies which find little to no increase in  $MAC_{BC}$  with increased  $R_{BC}$  are measuring BC aggregates which have undergone significant coating-induced restructuring, while studies that find significant increases in  $MAC_{BC}$  are measuring aggregates which have undergone little to no restructuring.” How confident are the authors that alternatives have been excluded, and that this statement is the most likely given all available evidence? For example:

- (a) Based on a recent review of soot-restructuring studies (Corbin, Modini, and Gysel-Beer, [arXiv.2206.03646](https://arxiv.org/abs/2206.03646)) I believe this statement should be reconsidered or discussed in terms of the fundamental physics it implies. To briefly summarize that review, we identified multiple studies that demonstrated unequivocally that liquid condensation typically induces restructuring. These studies used various materials including organics of varying polarity and sulfuric acid. Our review of these studies and complementary laboratory demonstration, showed that condensation-compaction coatings can only be avoided when solid coatings or liquids with very high contact angles (which may result in heterogeneous nanodroplet-activation and therefore avoid compacting surface tension forces) were used. Examples of such solids include SOA formed at low RH or anthracene (relevant only to the laboratory). Compaction can also be avoided by coagulation. So, if internally mixed BC has not undergone extensive restructuring, it must have mixed with solids (including highly viscous glasses) or by coagulation.

My impression from the recent studies by Fierce et al. (cited by the authors) is that while night-time coagulation can be significant, it is unlikely that most soot particles mix by coagulation. But, perhaps the authors' work implies that my impression was inaccurate. My impression is also that solid organic coatings form only rarely, since they require very low RH or low temperatures, while organic vapours are emitted most often at higher temperatures. It seems to me less likely that solid coatings explain the field data on absorption enhancement.

So, the authors' conclusions can be reconciled with the known mechanisms of soot restructuring by arguing that some studies primarily observe liquid-condensation coatings while other primarily observe solid-like coatings or coagulation coatings.

- (b) On Line 71, the authors state, "Recent studies have found that the non-sphericity of BC-containing particles (partial encapsulation of BC) can decrease absorption enhancement (Hu et al., 2022, 2021). While these findings are notable, previous studies have not observed a prevalence of partially-encapsulated BC, yet decreased light absorption is still observed". Is it possible that the authors have too readily rejected the hypothesis of H1) partially encapsulated, or off-centre mixing states, in favour of H2) condensation-without-compaction? Given the abovementioned review, I believe H1 is plausible while H2 is extremely unlikely. I would consider the entire manuscript to remain valid and valuable if H1 is rejected over H2. The only change is that  $\phi$  becomes  $\phi_{\text{eff}}$ . (Would the same trends in MAC be observed?)
- (c) This is more of an editorial comment. The highest  $\rho_{BC}$  in Figure 7b were measured at the shortest wavelengths and the two highest studies were both first-authored by Cappa. Some readers may wonder whether there was a systematic effect here (for wavelength, it is expected by definition; and for the Cappa group, the question is whether they use a unique experimental approach that caused a bias relative to other data sets). I do not personally believe that these are real issues but they deserve may a brief comment for the reader's benefit.

While reading, I also made various minor notes. I will list them below as suggestions for the authors.

- (a) I'd add a row showing partially encapsulated/collapsed examples in Figure 2.
- (b) Line 105-109 may need clarifying. Why would someone use the RDG MAC when estimating  $E_{\text{abs}}$ ? To me, a "literature value" would be a measured MAC of mature, open-structured BC (Liu et al., linked below). Text may not convey your intention here.
- (c) What is the role of  $\phi$  in Figure 3? No effect?
- (d) Line 161, there may be a better citation for the imaginary refractive index (Sun and Bond?).
- (e) Line 163, add SOA after pinene.
- (f) Line 164, consider citing Lu et al <http://dx.doi.org/10.1021/acs.est.5b00211>
- (g) Line 180, are the four digits of precision meaningful in 6.819 m<sup>2</sup>/g? What is the corresponding standard deviation? Also, it may be worth discussing this value in comparison to the measured mean value of  $8.0 \pm 0.7$  m<sup>2</sup>/g (Liu et al. <https://doi.org/10.1080/02786826.2019.1676878>)

- (h) Figure 4 uses both “ $\rho$ ” and “Core Phase Shift Parameter” for the same thing, which confused me initially. Consider harmonizing.
- (i) Figure 7a why are there 3 lines? Please label?
- (j) Figure 7b consider adding a column of the range of observed  $R_{BC}$ ?
- (k) Line 272 how could a ‘fresh BC’ particle have  $R_{BC} = 3.68$ ? It seems that ‘fresh’ is ambiguous. Maybe ‘uncompacted’.
- (l) Figure 8a consider omitting the instrument lists, which are incomplete and may become outdated in a shorter time than this work will. If you keep it, please revise (e.g. Single particle BC mass can be measured by SP-AMS and all of the “MAC” instruments measure absorption, not MAC.)
- (m) Figure 8b consider contours, I could not see the contrast on my B&W printout.
- (n) Caption of Figure 8 states that the low MAC of Cappa 2012 can be explained by compaction of the BC core, but Cappa 2012 shows lab data (their Fig 3) where compaction was absolutely expected yet absorption enhancement was still observed. (My expectation is based on the review of restructuring mentioned above, which includes a repeat of their same experiments and cites Ghazi and Olfert who also repeated those experiments.)
- (o) Figure 9a I found confusing but the caption I found clear. Consider linearizing the figure.
- (p) Discussion at end of 3.4.2 may have to change to reflect the restructuring comments above.
- (q) What are the uncertainties in  $k = 0.056$  in Section 3.4.3? Does the code include an uncertainty estimation feature? Monte Carlo? This would be helpful as a way to let users know when they have obtained meaningful results.
- (r) Why would coating filling the voids in the BC aggregate change  $\phi$ , the BC monomer packing fraction? That is only if the BC core collapses, as stated subsequently.