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A semi-empirical correction for the Rayleigh-Debye-Gans approximation for fractal aggregates based on phasor analysis: Application to soot particles

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Abstract

The Rayleigh Debye-Gans approximation for Fractal Aggregates (RDG-FA) is commonly used for the evaluation of the radiative properties of fractal aggregates of nanometer-scale nearly spherical particles as soot particles. The cost of its simplicity, however, is the precision of the aggregate cross sections when the refractive index deviates from unity and when the aggregate's spheres, or monomers, are not sufficiently small compared to the wavelength. While correction factors have been highlighted before, their physical origin is not clear and no universal correction factors are proposed. The present study develops an approach based on phasor analysis of the aggregate's internal electric field rigorously determined by the discrete dipole approximation. Aggregates representative of the Diffusion Limited Cluster Aggregation (DLCA) regime having a fractal dimension of $D_f = 1.78$ are considered as representative of a soot aggregate. The results reveal that correction factors to the RDG-FA for forward scattering (A) and the absorption cross section (h) are due to a competition between internal-field hot-spots caused by point contact between the spherical monomers and a decrease of the field amplitude as the field propagates through the aggregate. Both phenomena are neglected in the RDF-FA by definition. The absorption phenomenon explains the aggregate-size dependence of A and h . These effects are then studied as the aggregate size varies according to the number of monomers N_m ranging from 10 to 1000, as the monomer radius varies from $R_m = 5 \text{ nm} - 30 \text{ nm}$, and as the wavelength varies from $\lambda = 266 \text{ nm} -$

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1064 nm. Both constant and wavelength dependent refractive indices for organic, graphitic, and amorphous soot are considered. Finally, a semi-empirical model is proposed intended to correct the RDG-FA theory based on the analysis.

Keywords: Soot fractal aggregates, RDG-FA, Internal coupling, DDA, Phasor analysis, Scattering cross sections, Absorption cross sections

1 **Highlights**

- 2 • The internal electric field of fractal aggregates is studied with a phasor approach.
- 3 • Internal coupling and absorption explain the RDG-FA discrepancies for large aggre-
4 gates.
- 5 • Aggregate size, monomer radius, refractive index, and wavelength dependencies are
6 investigated.
- 7 • Semi-empirical corrections for the RDG-FA derived forward-scattering and absorption
8 are proposed.

9 1. Introduction

10 Soot, or black carbon (BC), particles are produced by the incomplete combustion of fossil
11 fuels and biomass. Once emitted in the atmosphere, these aerosols pose a concern for human
12 health [1, 2], contribute actively to atmospheric radiative forcing of the climate [3], and
13 affect atmospheric chemistry [4]. For these reasons, climate models need a simple, robust,
14 and precise description of soot aerosol optical cross sections. Such descriptions could also
15 serve to enhance the precision of optical diagnostics for *in-situ* characterization of similar
16 aerosols [5] and the control of their generation for industrial purposes [6].

17 The absorption and scattering cross sections of aggregates can be accurately calculated
18 by the Generalized Multiparticle Mie (GMM) [7] method and the superposition T-matrix
19 (STM) [8] method. For soot, however, these methods are limited to aggregates of spherical
20 particles, i.e., monomers, that are in point contact. More realistic models of soot, with
21 overlapping monomers, necking between monomers [9], and coating of the monomers [10],
22 are studied with the Discrete Dipole approximation (DDA) [11–13], which is not limited by
23 particle geometry. The DDA considers a particle as a set of interacting dipoles on a cubic
24 lattice with spacing d and yields accurate results provided that $|m|kd < 0.5$, where m the
25 complex-valued refractive index and $k = 2\pi/\lambda$. Because the DDA involves a numerical cost,
26 namely the computation time, it is not implemented in current climate models nor is it
27 frequently used to interpret data from light scattering measurements.

28 For these reasons, light interaction models with simple analytical expressions are pre-
29 ferred, but one should be aware of their intrinsic limitations [14]. The most used one is
30 the Rayleigh-Debye-Gans approximation [15]. The essence of this approximation is that
31 the particle is divided into a number of small volume elements. Each element is treated
32 as a Rayleigh scatterer (small compared to the wavelength) and the interactions between
33 these elements are neglected. The RDG approximation can be applied to different type of
34 aggregates like snowflake aggregates at millimeter wavelength radar [16] or aerosol Fractal
35 Aggregates (RDG-FA) [17] as long as the criteria $|m - 1| \ll 1$ and $x_m|m - 1| \ll 1$ are re-
36 spected. The performance of the RDG-FA is often studied in terms of the correction factors
37 A and h , which are needed to bring the RDG-FA forward scattering and absorption, respec-
38 tively, in agreement with exact calculations via the DDA. This has been studied for soot

39 particles [18–20] because their optical indices m do not enable the respect of the aforemen-
40 tioned criteria for visible light. The present authors have shown in a previous work [21] that
41 for a bi-sphere and for typical soot materials the corrections depend on the orientation of
42 the bi-sphere and the values of m and λ . This was explained by regions of enhanced internal
43 electric field, i.e., hot spots, occurring at the vicinity of point contact between the monomers.
44 Hot spots can increase or decrease the RDG-FA correction factor for forward scattering [21].
45 This finding is related to [20] where “positive deviations” are induced by the increase of
46 $\text{Re}\{m\}$ and “negative deviations” with increasing $\text{Im}\{m\}$. The bi-sphere study [21] also
47 reveals that the coupling distance for the monomers is relatively short. Specifically, when
48 the monomers (spheres) center-to-center distance is larger than $4R_m$, they can be treated as
49 independent-scattering. This complicates the understanding of the N_m dependence of the A
50 and h correction factors reported in [19, 20] which remain poorly understood [22]. Moreover,
51 a law providing the correction factors for the RDG-FA, i.e., A and h , for all practical values
52 of N_m , λ , and m , does not yet exist.

53 Introduced in [23, 24] and used in the aforementioned bi-sphere study [21], the method of
54 phasor analysis can link the field within a particle to the external light scattering behavior,
55 such as, the angular scattering pattern and cross sections. The method is unique in that
56 it provides this link via both quantitative and graphical means, and thus, can engender
57 understanding for the light scattering behavior of a given particle, e.g., see [24–26].

58 In the present study, the method is used to examine the dependence of these RDG-FA
59 correction factors on N_m , λ , and m while fractal dimension and prefactor are considered
60 constant and representative of soot particles (obtained by Diffusion Limited Cluster Aggre-
61 gation [27], ≈ 1.78 and 1.4 respectively). Indeed, more compact aggregates characterized
62 by larger fractal dimensions or prefactors will certainly have stronger interactions between
63 monomers than more open structures, which will lead to stronger corrections. Readers inter-
64 ested in understanding the role played by the prefactor and the fractal dimension can find
65 information in the work of Liu *et. al.* [28, 29]. Soot particles are very complex and their com-
66 position is generally unknown. Indeed, in the same flame, we can find nascent soot, which
67 are mostly made of organic compounds with an amorphous carbon matrix and what is called
68 mature soot, which are made of carbon and hydrogen atoms essentially with a certain level

69 of graphitization [30]. For this reason, extreme optical index behaviour will be considered
70 (respectively graphitic, amorphous and organic soot particles) as previously studied in [31].
71 It may be noted that some of these indices (organic particles at lowest wavelengths) cover
72 larger imaginary parts than those proposed by Chang and Charalampopoulos. [32]. This can
73 be explained by the specific composition. Also, it must be noticed that Bescond *et. al.* [31]
74 considered the fractal aggregates morphology in their inversion process whereas Chang and
75 Charalampopoulos treated the particles as spheres. In this study, one will see the important
76 role played by absorption within the monomers, which decreases the internal electric-field
77 amplitude as light propagates within the aggregate material. An observation of universal
78 trends in the phasor analysis then ultimately leads to the proposition of a semi-empirical
79 law A and h .

80 2. Methodology

81 2.1. Fractal aggregates

82 This study will focus on soot aggregates that form under the diffusion limited cluster
83 aggregation (DLCA) regime. In DLCA, a fractal scaling-law describes the average aggregate-
84 size as [33]:

$$N_m = k_f \left(\frac{R_g}{R_m} \right)^{D_f} \quad (1)$$

85 where k_f is a scaling prefactor, D_f is the fractal dimension, and R_g is the radius of gyration of
86 the aggregate [17]. A selection of simulated DLCA aggregates obeying Eq.(1) is considered
87 here. Three aggregates are taken from [20] with $N_m = 284$, $N_m = 444$, and $N_m = 833$ where
88 $D_f = 1.78 \pm 0.04$ and $k_f = 1.35 \pm 0.10$. To access a larger range of aggregate size, specifically
89 $N_m \in [10, 1000]$, a selection of 1000 different aggregates are taken from [34] where $D_f \approx 1.78$
90 and $k_f \approx 1.4$.

91 2.2. Internal electric field

92 The scattering properties of an aggregate include the total scattering C^{sca} , absorption
93 C^{abs} , and extinction cross sections C^{ext} , in addition to the angular scattered light intensity
94 I^{sca} . These properties can all be derived from the scattered electric field $\mathbf{E}^{\text{sca}}(\mathbf{r})$, which for
95 \mathbf{r} in the aggregate's far-field zone are linked to the internal field \mathbf{E}^{int} inside the aggregate

96 material via the volume integral equation (VIE). When expressed in discrete form, i.e., for
 97 N cubic volume elements ΔV in the aggregate, the VIE reads [35]:

$$\mathbf{E}^{\text{sca}}(\mathbf{r}) = \frac{k^2 \exp(ikr)}{4\pi r} (m^2 - 1) \left(\overset{\leftrightarrow}{\mathbf{I}} - \hat{\mathbf{r}} \otimes \hat{\mathbf{r}} \right) \cdot \sum_{i=0}^N \mathbf{E}^{\text{int}}(\mathbf{r}_i) \exp(-ik\hat{\mathbf{r}} \cdot \mathbf{r}_i) \Delta V, \quad (2)$$

98 In Eq (2), $\overset{\leftrightarrow}{\mathbf{I}}$ is the Cartesian identity dyadic, $\hat{\mathbf{r}} \otimes \hat{\mathbf{r}}$ is the dyadic formed by the direct product
 99 of $\hat{\mathbf{r}}$ with itself [35, 36]. Due to the assumed far-field limit for the observation point \mathbf{r} , it
 100 is useful to examine the behavior of the scattered field in terms of the scattering amplitude
 101 $\mathbf{E}_1^{\text{sca}}$ given from Eq. (2)

$$\mathbf{E}^{\text{sca}}(\mathbf{r}) = \frac{\exp(ikr)}{r} \mathbf{E}_1^{\text{sca}}(\hat{\mathbf{r}}). \quad (3)$$

102 Note that $\mathbf{E}_1^{\text{sca}}$ depends only on direction (θ, ϕ) , i.e., $\hat{\mathbf{r}}$, and not on the distance r .

103 The DDA method can be used to find \mathbf{E}^{int} accurately within the aggregate. Indeed, the
 104 DDA can be thought of as a numerical solution of Eq (2) [13]. Here, the code DDSCAT
 105 developed by [37] is used to numerically determine \mathbf{E}^{int} . An aggregate's physical 3D shape
 106 is discretized on a cubic lattice of volume elements ΔV that are $d \times d \times d$ in size. Each
 107 element is then assigned an electric dipole moment, which are excited by the incident field
 108 and couple to each other. Following the numerical solution for value of these dipoles, i.e., the
 109 solution of Eq (2), \mathbf{E}^{int} can be obtained from each dipole [13]. The accuracy of the solution
 110 is determined by the fineness of this lattice as quantified by the condition $|m|kd < 0.5$. To
 111 satisfy this condition, a number of dipoles per monomer N_d/N_m is specified, where N_d is the
 112 total number of dipoles representing an aggregate and N_m is the number of monomers. Below,
 113 $N_d/N_m \approx 110$, which is sufficient for point-contact monomers in [24] where $N_d/N_m \approx 34$.

114 The incident wave is planar, propagating along the x -axis, with linear polarization where
 115 \mathbf{E}^{inc} is along the y -axis in the aggregate's reference frame. Thus, $\mathbf{E}^{\text{inc}}(\mathbf{r}) = E_o \exp(ik\hat{\mathbf{x}} \cdot \mathbf{r})\hat{\mathbf{y}}$
 116 where E_o is the field magnitude. A wide range of wavelengths are considered, $\lambda \in [266 \text{ nm} -$
 117 $1064 \text{ nm}]$, and values for the refractive index appropriate for soot particles are considered.
 118 Specifically, $m = 1.75 + 1.03i$ is used from [38] as representative of mature soot (or Black
 119 Carbon) as shown by [39] for $\lambda = 550 \text{ nm}$. In order to also consider the wavelength depen-
 120 dence of m for material other than purely graphitic or mature soot, the spectral dependence
 121 of m found in [31] for organic, graphitic, and amorphous soot compositions are also taken
 122 into account [20].

123 *2.3. Phasor analysis*

124 The dyadic terms in Eq. (2) will simplify if the observation point resides along the prop-
 125 agation of the incident wave, i.e., the forward-scattering direction, see Appendix C in [21].
 126 In terms of polarization, if the vertical direction is the y -axis, the incident wave is vertically
 127 polarized, which will be denoted by the subscript v. Moreover, if the scattered light is de-
 128 tected through a linear polarizer oriented in the vertical direction – a common configuration
 129 – then a detector measures the vertical-vertical (incident-scattered) polarization configura-
 130 tion, denoted by the subscript vv. The following will consider only this polarization case.
 131 Equation (2) now simplifies by virtue of Eq. (3) to give the scattering amplitude as:

$$\mathbf{E}_{1,vv}^{\text{sca}}(\hat{\mathbf{x}}) = \frac{3k^2}{4\pi} \frac{m^2 - 1}{m^2 + 2} E_o \sum_{i=1}^{N_d} z_{y,i}(\hat{\mathbf{x}}) \Delta V \hat{\mathbf{y}}, \quad (4)$$

132 where $z_{y,i}$ is the phasor, or complex-valued number, for the i^{th} volume element. As a re-
 133 minder, $\hat{\mathbf{x}}$ is the forward-scattering direction and $\hat{\mathbf{y}}$ is the vertical polarization direction.
 134 There is no distance, r , dependence in the scattering amplitude. The phasor for a volume
 135 element, or equivalently, a dipole, is determined by the internal field at the location of the
 136 element, \mathbf{r}_i , and by a phase factor accounting for the position of the element as

$$z_{y,i}(\hat{\mathbf{x}}) = \frac{m^2 + 2}{3E_o} E_y^{\text{int}}(\mathbf{r}_i) \exp(-ikx_i). \quad (5)$$

137 In Eq. (5), x_i is the x -component of the volume element positioned at \mathbf{r}_i .

138 Phasor analysis offers a graphical means to illustrate the contribution of each volume
 139 element to the forward scattering amplitude. It is a descriptor of the spatial variability of
 140 the internal electric field accounting for the phase shifts due to the different positions of
 141 the elements. As demonstrated in [21], the phasors are directly related to the RDG-FA
 142 correction factors for the forward differential scattering cross section:

$$A_{vv}(\psi) = \frac{\frac{dC_{vv}^{\text{sca}}}{d\Omega}(0^\circ)}{\frac{dC_{\text{RDG},vv}^{\text{sca}}}{d\Omega}(0^\circ)} = |\overline{z_y}|^2. \quad (6)$$

143 In Eq. (6), ψ denotes the aggregate's orientation with respect to the incident wave, $\frac{dC_{vv}^{\text{sca}}}{d\Omega}(0^\circ)$
 144 is the true (from DDA) forward differential scattering cross section and $\frac{dC_{\text{RDG},vv}^{\text{sca}}}{d\Omega}(0^\circ)$ is the

145 forward differential scattering cross section predicted by the RDG-FA. The horizontal bar
 146 denotes averaging of all the phasors in the aggregate, i.e., $\overline{z_y} = (1/V) \sum_{i=1}^{N_d} z_{y,i} \Delta V$ where V
 147 represents the total volume of all the monomers. Further explanation for the derivation of
 148 Eq. (6) is given in Appendix F of [21]. Note that the forward scattering correction factor
 149 A refers to the average of Eq. (6) over many aggregate orientations, i.e., $A = \langle A_{vv}(\psi) \rangle_\psi$,
 150 where the brackets denote orientation averaging. Here, at least 500 isotropically distributed
 151 orientations of a single aggregate or 1000 different aggregates having the same morphological
 152 descriptors, R_m , D_f , and k_f , are considered according to the reciprocity theorem [40].

153 3. Results

154 3.1. Phasor plots for a fractal aggregate

155 The first row of Fig. 1, plots (a) and (b), show the phasor distributions in the complex
 156 plane (horizontal axis: $\text{Re}\{z_{y,i}\}$, vertical axis: $\text{Im}\{z_{y,i}\}$) for an aggregate with $N_m = 284$
 157 monomers with monomer radius $R_m = 15$ nm for $\lambda = 1064$ nm in (a) and for $\lambda = 266$ nm
 158 in (b). That is, each point in the plot represents the complex number $z_{y,i}$ corresponding to
 159 the i^{th} volume element in the aggregate according to Eq. (5). Organic monomer-material is
 160 chosen because it is known to manifest important corrections to the RDG-FA theory [20].
 161 This means that we take $m = 1.83 + 0.26i$ for $\lambda = 1064$ nm and $m = 0.94 + 0.96i$ for
 162 $\lambda = 266$ nm. In both cases, $|m|$ is significant, which highlights a strong non-uniformity of
 163 the internal electric field. To see this, the plots show a unit semicircle representing the
 164 location phasors would have if their magnitude were unity $|z_{y,i}| = 1$; this corresponds to the
 165 RDG-FA prediction in case of forward scattering (see Eq 6). The average phasor, $\overline{z_y}$, is shown
 166 as the red star and is clearly outside the semicircle for $\lambda = 1064$ nm in (a) and inside for
 167 $\lambda = 266$ nm in (b). This indicates, respectively, an underestimation of the RDG-FA, $A > 1$,
 168 and an overestimation, $A < 1$, in accord with the findings in [19, 20]. The magnitude of the
 169 phasor distribution's spread is greater for $\lambda = 1064$ nm with a line-like shape similar to the
 170 behaviour observed for intersecting bi-spheres in [21]. For $\lambda = 266$ nm, a more pronounced
 171 spread is seen in the distribution.

172 Referring again to Fig. 1(a)- 1(b), one can see that the phasor dots are colored. The
 173 meaning of these colors is to express the x_i coordinate in Eq. (5) as indicated by the color

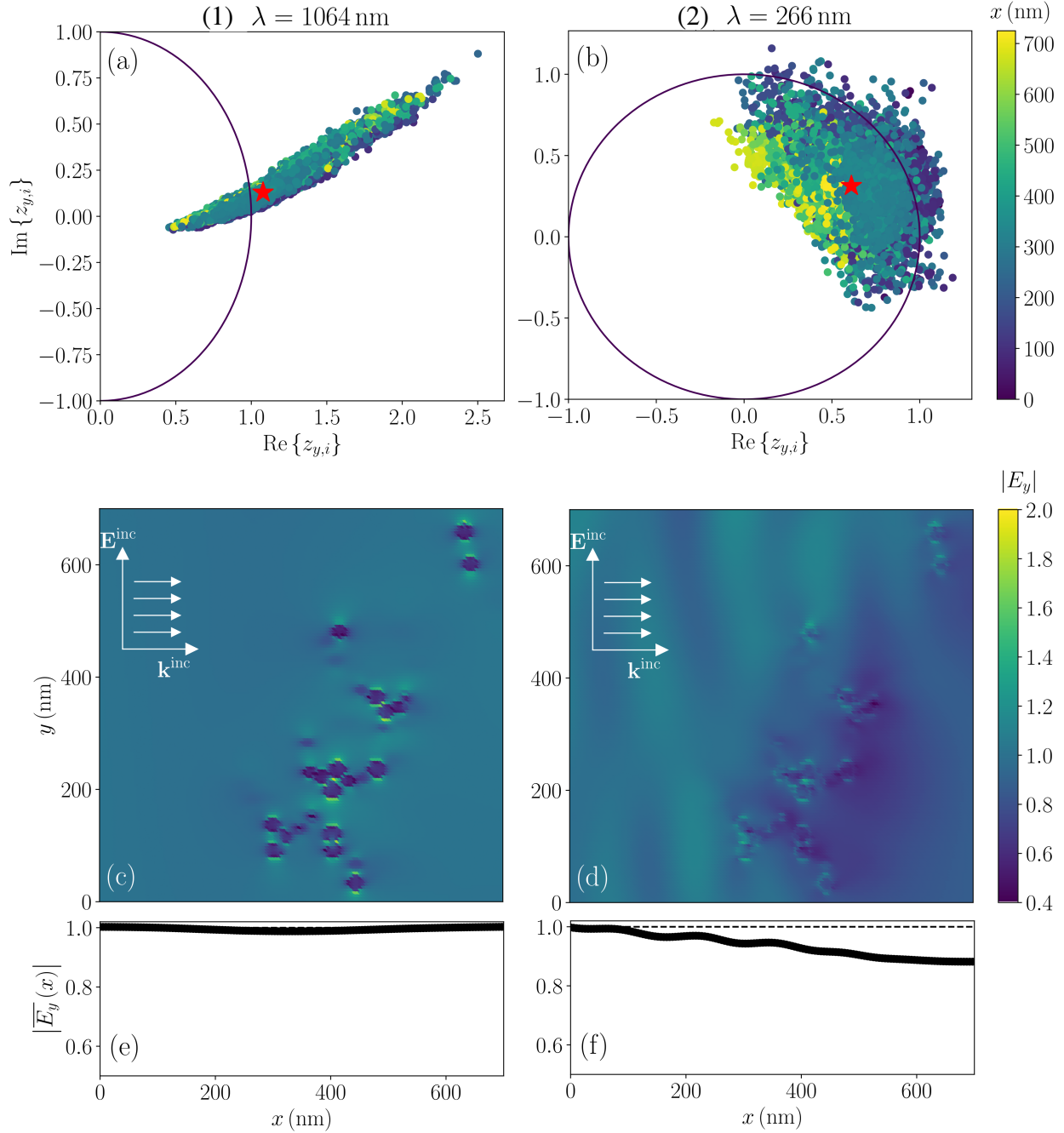


Figure 1: Phasor distributions and internal electric-field analysis of an aggregate composed of $N_m = 284$ monomers with monomer radius $R_m = 15$ nm for organic monomer material. The left column corresponds to $\lambda = 1064$ nm with $m = 1.83 + i0.26$ whereas the right column corresponds to $\lambda = 266$ nm with $m = 0.94 + i0.96$. Distributions of the phasors $z_{y,i}$ in the complex plane are shown in (a) and (b) where the semi-circle (or circle) represents unit phasor-magnitude. Each phasor is displayed as a point. The star symbol in each plot represents the average of all the phasors shown, i.e., $\overline{z_y}$. Plots (c) and (d) show the magnitude of the near field and internal field in the x - y plane through the origin. Finally, plots (e) and (f) show the average of the near field taken in the y - z plane for a given x .

174 scale appearing with the phasor plots. In other words, these colors tag the location of the
 175 phasor according to the location's influence (in phase) on the value of $z_{y,i}$. Recall that the
 176 x -axis is also the propagation axis for the incident wave (direction of the incident wave vector
 177 \mathbf{k}^{inc}). One observes that for $\lambda = 266$ nm, Fig. 1(b), there is an overall decrease of the phasor
 178 magnitude with increasing x_i . This demonstrates an overall decrease of the internal field
 179 magnitude $|E_y^{\text{int}}|$ along the x -axis, i.e., in the direction that the incident light propagates
 180 through the aggregate. For $\lambda = 1064$ nm, the same effect is not observed as the full range of
 181 phasor-dot colors can be seen throughout the distribution.

182 Following the resolution of the Maxwell equations inside and outside the scattering object
 183 the total electric field everywhere in space is mathematically

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}^{\text{inc}}(\mathbf{r}) + \mathbf{E}^{\text{sca}}(\mathbf{r}), \quad (7)$$

184 where the scattered electric near-field in discrete form is expressed in terms of the total field
 185 inside the scattering object as follows: (see Section 2.1 in [41])

$$\mathbf{E}^{\text{sca}}(\mathbf{r}) = \frac{k^2}{4\pi} (m^2 - 1) \left(\overset{\leftrightarrow}{\mathbf{I}} + \frac{1}{k^2} \nabla \otimes \nabla \right) \cdot \sum_{i=0}^N \mathbf{E}^{\text{int}}(\mathbf{r}_i) \frac{e^{ik|\mathbf{r}-\mathbf{r}_i|}}{|\mathbf{r}-\mathbf{r}_i|} \Delta V, \quad (8)$$

186 with \otimes representing the dyadic product. Note that, the expression of the VIE in Eq. (2)
 187 is different from this one due to the far-field zone assumption. Another way to study the
 188 overall variation of field magnitude is presented in Figs. 1(c)- 1(d). Here, the magnitude of
 189 the y -component of the total electric field, $|E_y| = |\mathbf{E}(\mathbf{r}) \cdot \hat{\mathbf{y}}|$, in the x - y plane through the
 190 aggregate is shown. For points not residing in a monomer, the field plotted corresponds to
 191 the total near-field, i.e., $|E_y| = |E_y^{\text{inc}} + E_y^{\text{sca}}|$ whereas $|E_y^{\text{int}}|$ is plotted for points residing in
 192 a monomer. In Fig. 1(c) where $\lambda = 1064$ nm, there is little departure from the magnitude
 193 of the incident field, $|E_y^{\text{inc}}| = 1$ except very close to the monomers, i.e., hot spots. However,
 194 in Fig. 1(d) where $\lambda = 266$ nm, there is structure to this near field extending beyond the
 195 monomer length scale.

196 To better test whether there is an overall trend in near field across the aggregate,
 197 Figs. 1(e)-1(f) plot the average of $|E_y|$ within the y - z plane located at x . The result re-
 198 veals trends of the field magnitude along the x -axis, i.e., along the propagation direction
 199 of the incident wave. In Fig. 1(e), the average field is almost invariant from one, which

200 reveals that the field is close to the magnitude of the incident field across the aggregate.
 201 Fig. 1(f), however, shows a clear decay of the field magnitude along x . The decay can be
 202 explained by absorption of the incident field; an effect that is neglected by the RDG-FA. In-
 203 deed, $\text{Im}\{m\} = 0.96$ for Fig. 1(f), where $\lambda = 266$ nm, which is larger than the corresponding
 204 value for $\lambda = 1064$ nm, i.e., $\text{Im}\{m\} = 0.26$, Fig. 1(e).

205 To summarize the findings thus far, at large wavelength, the hypothesis of a uniform
 206 near-field appears valid. Point contact between the monomers induce local “hot-spots” of
 207 the internal electric field (internal coupling), which causes $A > 1$ as revealed by the bi-
 208 sphere analysis [21] and the large spread of phasors in Fig. 1(a). At smaller wavelength, the
 209 absorption dominates causing $A < 1$ with an effect becoming more marked as the aggregate
 210 increases in size. Thus, we qualitatively explain the observations reported in [19, 20].

211 3.2. Sliced phasors

212 The qualitative difference between the spread of points in Fig. 1(a) and Fig. 1(b) suggests
 213 that the phasors may be helpful to understand the effect of absorption on the RDG-FA
 214 correction factors. The effects of absorption are expected to be most noticeable by analyzing
 215 the phasors as groups in a way that isolates the absorption-based decay in magnitude of the
 216 internal field. Returning to the VIE of Eq. (2), from which the phasors are eventually derived
 217 in Eq. (5), one sees that \mathbf{E}^{int} is accompanied by the term $\exp(-ik\hat{\mathbf{r}} \cdot \mathbf{r}_i)$. When evaluated
 218 in the forward-scattering direction, $\hat{\mathbf{r}} = \hat{\mathbf{x}}$, the phase of this term becomes $-ikx_i$, which is a
 219 constant across the y - z plane for the given value of x_i ; this is why the y - z plane is specifically
 220 considered in Fig. 1(e) and Fig. 1(f). The variation in the phasor *magnitudes* corresponding
 221 to volume elements in the plane are then only due to the internal field component, E_y^{int} .

222 With this understanding, let $\Pi(x)$ be the y - z plane at x and define a “sliced phasor” as

$$\overline{z_y(x)} = \frac{1}{N_d(x)} \sum_{\substack{i=1 \\ i \in \Pi(x)}}^{N_d(x)} z_{y,i}(\hat{\mathbf{x}}), \quad (9)$$

223 where $N_d(x)$ is the number of dipoles (volume elements) of the aggregate that reside in the
 224 plane $\Pi(x)$. Equation (9) represents the average of the phasors in the $\Pi(x)$ plane, which
 225 means that all of these phasors will have the same phase factor discussed above. Then, sum

226 all of the sliced phasors for the complete aggregate:

$$z_y(\psi) = \frac{1}{N_d} \sum_x \overline{z_y(x)} N_d(x), \quad (10)$$

227 where ψ expresses the (implicit) aggregate orientation. With this definition, $|z_y(\psi)|^2 =$
 228 $A_{\text{vv}}(\psi)$ because of the weighting factor $N_d(x)$ included in Eq. (10), i.e., $\sum_x N_d(x) = N_d$.

229 In order to obtain the RDG-FA correction factor for forward scattering, A , the sliced-
 230 phasors must be averaged over aggregate orientation. To do this, the orientation average of
 231 a sliced phasor, $\langle \overline{z_y(x)} \rangle_\psi$, is calculated in addition to the orientation average of the number
 232 of dipoles $\langle N_d(x) \rangle_\psi$ in the associated plane $\Pi(x)$. Then, the orientation averaged correction
 233 factor is taken as

$$A_{\text{vv}}^{\text{slice}} = \left| \frac{1}{N_d} \sum_x \langle \overline{z_y(x)} \rangle_\psi \langle N_d(x) \rangle_\psi \right|^2, \quad (11)$$

234 The fact that squaring is done before or after the orientation averaging makes $A_{\text{vv}}^{\text{slice}}$ not
 235 strictly identical to $\langle A_{\text{vv}}(\psi) \rangle$ and thus to A . Nevertheless, due to the weak effect of the
 236 orientation on the sliced phasors, this approximation is shown to be acceptable as confirmed
 237 by Fig. 2 that reports the correlation between the exact forward scattering correction factor
 238 A and the newly introduced one based on the orientation averaged sliced phasor $A_{\text{vv}}^{\text{slice}}$. The
 239 correlation is shown for 4 different DLCA aggregates with different numbers of primary
 240 particles ($N_m = 10$, $N_m = 100$, $N_m = 284$, $N_m = 444$ with a monomer radius $R_m = 15$ nm)
 241 by varying the wavelength and the refractive index considering organic, amorphous and
 242 graphitic material in respect of the Table 1 in [31]. As can be seen in the figure both
 243 quantities are linearly correlated (slope coefficient of 0.994 ± 0.002 with a Pearson's linear
 244 coefficient of determination 0.997). This result supports the idea that correction A is only
 245 driven by the x dependence of the phasor.

246 3.3. Effect of monomer number

247 In this section, the effect of the number of monomers, N_m , on the RDG-FA forward-
 248 scattering correction factor is studied in terms of the sliced phasors of Eq. (9). To do this,
 249 express a given orientation-averaged slice phasor as:

$$\langle \overline{z_y(x)} \rangle_\psi = \Lambda(x) \exp[i\Theta(x)], \quad (12)$$

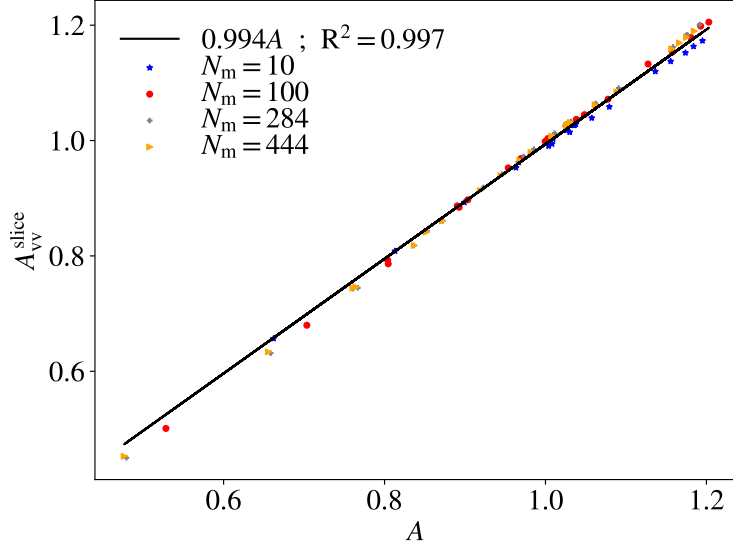


Figure 2: Correlation between the exact forward scattering correction factor A and the newly introduced one based on orientation averaged sliced phasor $A_{\text{VV}}^{\text{slice}}$. A linear regression is displayed in a continuous black line.

250 where Λ represents the magnitude of the phasor $|\langle \overline{z_y(x)} \rangle_\psi|$ and Θ represents its phase angle
251 $\tan^{-1} \left[\text{Im} \left\{ \langle \overline{z_y(x)} \rangle_\psi \right\} / \text{Re} \left\{ \langle \overline{z_y(x)} \rangle_\psi \right\} \right]$. Figure 3 shows the Λ in plot (a) and the phase Θ
252 in plot (b) as a function of the coordinate x for the $\Pi(x)$ plane. Here, the x coordinate is
253 normalized by the monomer radius R_m rather than the gyration radius R_g (see [Appendix](#)
254 [A](#)), i.e., x/R_m where $R_m = 15$ nm. Here, six different DLCA aggregates are considered
255 with different N_m as indicated. For the illustration, the wavelength and refractive index are,
256 respectively, $\lambda = 266$ nm and $m = 1.75 + 1.03i$. The chosen optical index has been reported
257 recently as a good approximation for mature soot at 550nm [39]. In the following, this optical
258 index will be considered constant at any wavelength when dealing with the parametric study
259 of the wavelength even if the optical index should vary with λ . This dependence to the
260 wavelength will be considered later for graphitic, organic and amorphous materials. In the
261 present case, the shorter wavelength is considered without loss of generality for illustration
262 since RDG-FA is less accurate. As N_m increases the larger the aggregate is, and the longer
263 the curve extends along the x/R_m axis. One will notice that the curves for Λ show a similar
264 trend overall that appears independent of the aggregate size. The magnitude, Λ in (a),
265 decays with x whereas the phase shift, Θ in (b), grows with x . Recall that the incident wave

266 propagates along the x -axis, and thus, this decay of Λ is unambiguously due to absorption
 267 in the aggregate because of the direct dependence of the sliced phasors on the internal field.
 268 The reason that the trends in Fig. 3(a) or Fig. 3(b) are similar is thought to be because the
 269 aggregates share similar morphological parameters, D_f , k_f and R_m . In Fig. 3(c) is plotted
 270 the average number of dipoles $\langle N_d(x) \rangle$ in the Π plane at x . The curves grow from zero to a
 271 maximum with x and decrease back to zero because Π encompasses more dipoles as it scans
 272 from outside the aggregate up to the aggregate's center. The comparison between aggregates
 273 and spheres of equivalent volume (equivalent volume radius: $R_v = N_m^{1/3} R_m$) is presented in
 274 graphs (a) and (b). The x coordinates of the spheres are normalized by the monomer radius
 275 of the aggregates ($R_m = 15$ nm) in order to keep the same scale on the x -axis. Spheres
 276 of equivalent volumes show more pronounced trends than aggregates. This is because the
 277 volume density of a sphere is higher than that of an aggregate due to the fractal dimension
 278 D_f . The denser the material, the more pronounced the absorption and phase shift along the
 279 volume.

280 A general conclusion from Fig. 3 is that whatever the size of the aggregate, the overall
 281 behavior of a sliced phasor depends mainly on its distance x into the aggregate. Recalling
 282 that the incident wave propagates along x , this behavior is similar to the Beer-Lambert law.
 283 Thus, adding more monomers to an aggregate while keeping its D_f , k_f and R_m constant will
 284 further decrease the phasor magnitude and increase the phase shift for the largest values of
 285 x . In other words, there is a shielding effect that is driven primarily by absorption and not
 286 by multiple scattering. This is consistent with findings in [21, 42] where coupling effects are
 287 limited several monomer radii for DLCA aggregates. The exception to this behavior is seen
 288 when x is small and where Λ exceeds one. Given that $\lambda = 266$ nm and $R_m = 15$ nm, the
 289 monomer size-parameter is $x_m = kR_m = 0.35$, which from [21] favors the appearance of "hot
 290 spots" in the vicinity of point-contact between neighboring monomers.

291 Nevertheless, at short x , where the quantity of material interacting with the light is
 292 reduced and phase shift quite null (b), the amplitude of the phasor can be larger than
 293 1 (notice the amplitude of the incident light E_0 in Eq. (4) is 1). This is explained by the
 294 internal coupling enhanced by the contact between spheres. This phenomenon is predominant
 295 compared to the self-absorption phenomena only for small x .

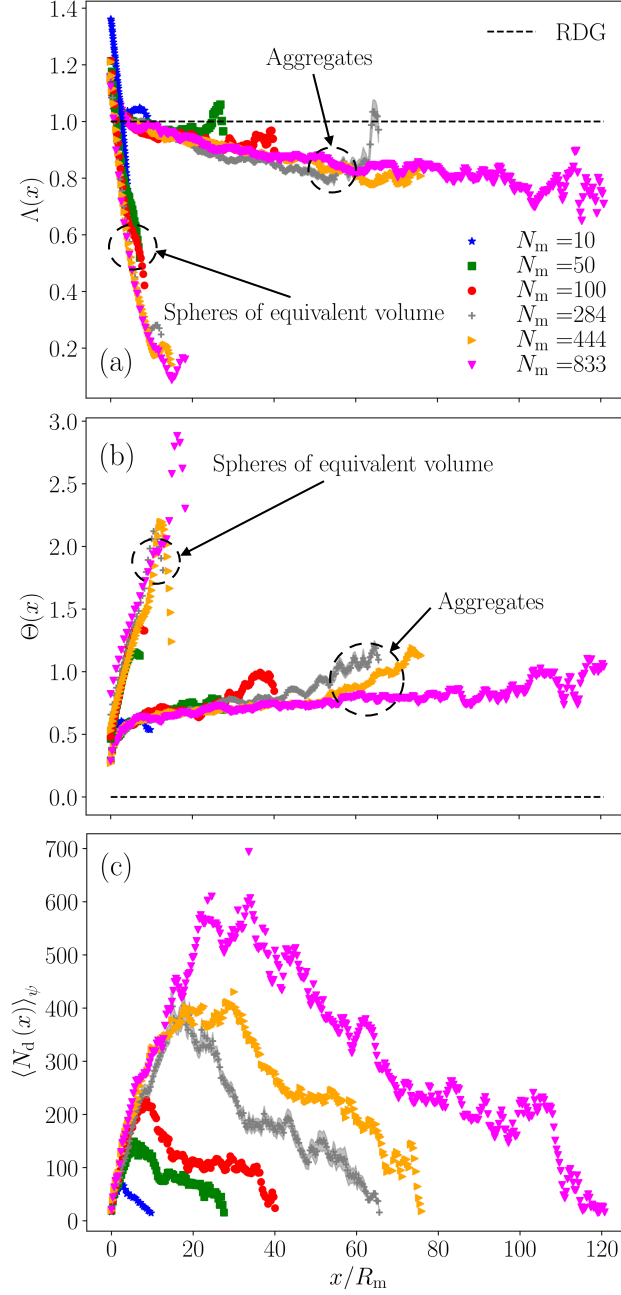


Figure 3: Impact of the number of monomers on the sliced phasor dependence on the position in the aggregates or the spheres of equivalent volume. Plot (a) reports the amplitude $\Lambda(x)$, plot (b) the phase $\Theta(x)$ and plot (c), the averaged number of dipoles per slice. The radius of the monomers of the DLCA aggregates is kept constant ($R_m = 15$ nm) as well as the wavelength ($\lambda = 266$ nm) and refractive index ($m = 1.75 + i1.03$, [38]). The continuous grey interval surrounding the $N_m = 284$ curve (symbols : plus sign in grey) corresponds to a confidence interval at 95%.

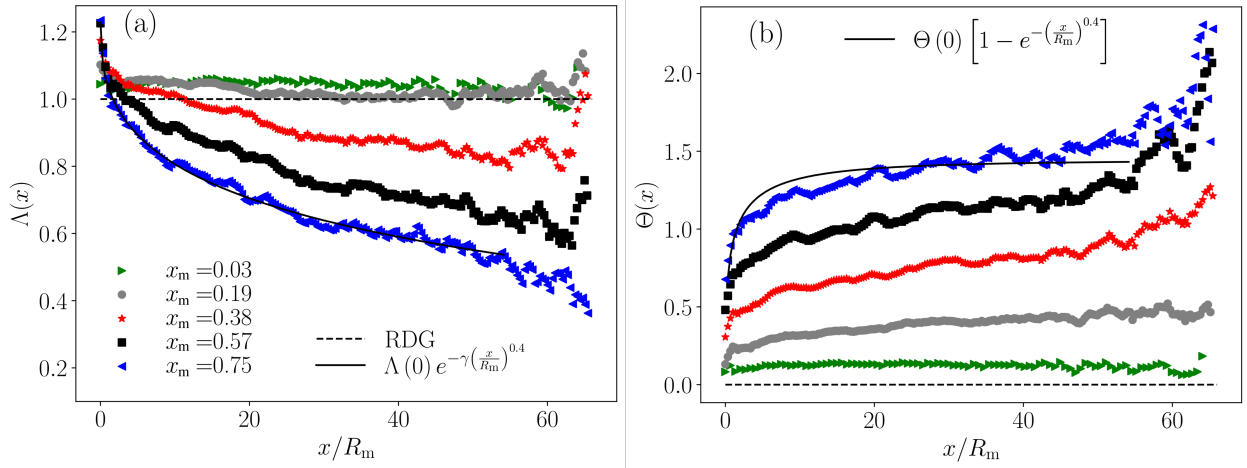


Figure 4: Plots of the amplitude $\Lambda(x)$ (plot (a)) and phase $\Theta(x)$ (plot (b)) versus the normalized axis of the light propagation x/R_m of an DLCA aggregate composed of 284 monomers with a monomer radius $R_m = 15$ nm and a refractive index $m = 1.75 + i1.03$ for different size parameters x_m . The continuous black lines correspond of an empirical fit of the phasor amplitude by $\Lambda(x) = \Lambda(0)e^{-\gamma(\frac{x}{R_m})^{0.4}}$ (a) and its phase by $\Theta(x) = \Theta(0) \left[1 - e^{-\gamma(\frac{x}{R_m})^{0.4}} \right]$ (b).

297 To study the effect of monomer size on the sliced phasor behavior, the monomer size
 298 parameter $x_m = kR_m$ is varied in Fig. 4 for the same aggregate with $N_m = 284$ for $\lambda = 266$ nm
 299 and $m = 1.75 + 1.03i$. This consists of a dilation of the objects which then retain their
 300 morphology (N_m , D_f and k_f). Increasing R_m will change the internal (dipole-dipole) coupling
 301 within the monomers, generally resulting in greater departure of the internal field from the
 302 RDG-FA prediction. Increasing R_m will also mean absorption will further decrease the
 303 phasor magnitudes Λ while increasing their phase Θ . For small $x_m < 0.20$, the impact of
 304 absorption is negligible and $\Lambda \sim 1$ (slightly greater than 1 due to the hot spots) and the
 305 phase is small, $\Theta \ll 1$. Thus, $\langle \overline{z_y(x)} \rangle_\psi \approx 1$ and $A \approx 1$, meaning that the RDG-FA is valid.
 306 As R_m increases, absorption occurs over a larger volume explaining the progressive deviation
 307 of $\langle \overline{z_y(x)} \rangle_\psi$ and of A from one, revealing the inaccuracy of the RDG-FA theory. Indeed, [43]
 308 shows that the RDG-FA is a reasonable approximation to within 10% error if $x_m < 0.3$.

309 **4. Unification**

310 From Figs. 1-4, one can see the competition between the effects of internal-field enhance-
 311 ments (hot spots), which increase the phasor magnitudes, and absorption, which decreases
 312 the phasors magnitudes and increases their phase angle. Absorption explains the aggregate-
 313 size dependence of the forward-scattering correction factor for the RDG-FA. Yet both effects
 314 are affected by x_m and m . As illustrated in Fig. 4, the x dependence of the sliced phasor
 315 magnitudes (a) and phasor phase (b) can be fit empirically by

$$\Lambda(x) = \Lambda(0)e^{-\gamma\left(\frac{x}{R_m}\right)^{0.4}} \quad \text{and} \quad \Theta(x) = \Theta(0) \left[1 - e^{-\left(\frac{x}{R_m}\right)^{0.4}}\right]. \quad (13)$$

316 The functions in Eq. (13) are shown in Fig. 4 by continuous black lines. Note that the fit
 317 to $\Lambda(x)$ is an exponential decay, which, again, is reminiscent of the Beer-Lambert for the
 318 attenuation of intensity through the aggregate due to absorption.

319 The phasor-magnitude behaviour is driven by two parameters, namely $\Lambda(0)$ and γ . The
 320 former is insensitive to absorption, and thus, only depends on the strength of coupling
 321 between monomers and internal coupling within the monomers themselves, i.e., hot spots.
 322 The other parameter, γ , is determined by the absorption decay; the greater γ is, the more
 323 absorption will be important for the correction factor. With regard to the phase fit in
 324 Eq. (13), a single parameter is involved, $\Theta(0)$. This parameter corresponds to the phase
 325 shift due to the first plane Π to intersect the aggregate along the x -axis in the direction of
 326 propagation of the incident wave. In other words, this part of the aggregate is the first to
 327 “see” the wave. Initially the power 0.4 was also considered as a variable parameter but we
 328 observed that fixing it at 0.4 had a reduced impact.

329 Figure 5 reveals a universal behavior of the three governing parameters $\Lambda(0)$, γ and
 330 $\Theta(0)$ by varying the wavelength from $\lambda = 266$ nm to $\lambda = 1064$ nm. Due to dispersion,
 331 m will change with λ and this wavelength dependence is known for graphitic, amorphous,
 332 and organic soot material [31]. However, the wavelength dependence also complicates an
 333 understanding for how the wavelength affects the fit parameters of Eq. (13). Thus, Fig. 5
 334 considers two cases: The data shown in black triangles shows the fit parameters as λ varies
 335 for a *constant* refractive index $m = 1.75 + 1.03i$ in order to isolate the effect of the refractive
 336 index. The other data points show the parameters when the wavelength dependence of the

337 optical index is taken into account.

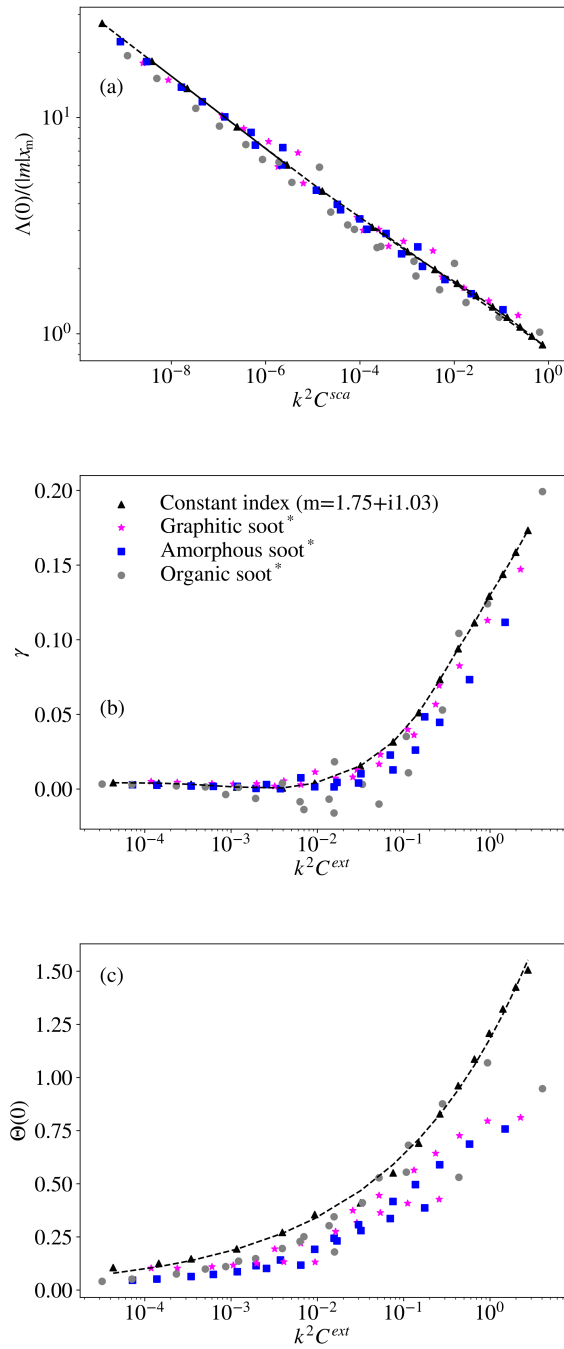


Figure 5: Parameters of the modelled amplitude of the phasor ($\Lambda_i(0)$ and γ) and phase ($\Theta_i(0)$) of the phasor as it evolves by crossing the aggregates. The symbol * in the legend refers to the optical indices provided by Bescond et al.[31] which vary with wavelength.

338

Recall that $\Lambda(0)$ is driven by the internal coupling between neighboring monomers. Thus,

339 it seems plausible that this coupling is related to the scattering efficiency of each monomer.
 340 This is confirmed by Fig 5(a), where $\Lambda(0)$ is shown normalized by the factor $|m|x_m$ (found
 341 empirically) as a function of the dimensionless product k^2C^{sca} where C^{sca} is the total scat-
 342 tering cross section of an isolated monomer in the RDG-FA:

$$C^{\text{sca}} = \frac{8\pi}{3}k^4R_m^6F(m), \quad C^{\text{abs}} = 4\pi kR_m^3E(m), \quad C^{\text{ext}} = C^{\text{sca}} + C^{\text{abs}}, \quad (14)$$

343 where $F(m)$ is the norm squared and $E(m)$ the imaginary part of the Lorentz-Lorenz factor
 344 $(m^2 - 1)/(m^2 + 2)$. The product of k^2 with the optical cross sections ensures that the scale
 345 invariance rule (SIR) [44] is obeyed for the case that m is invariant with λ , i.e., in our
 346 case $m = 1.75 + i1.03$. Note that the linear dependence observed in the log-log plot (a) is
 347 dominated by the λ dependence for fixed m and R_m .

348 Fig 5(b) shows the behaviour of γ , which represents absorption in the aggregate, and
 349 thus, should be function of the extinction cross section C^{ext} of the monomers via Eq. (14).
 350 Obviously, the more the monomers absorb, the greater the C^{ext} , and the more efficient light
 351 is removed by the entire aggregate. The effect is not linear and absorption appears significant
 352 for $k^2C^{\text{ext}} \geq 0.02$. Note that negative values are shown in (b), in particular for the organic
 353 material. This means that the amplitude of the phasor tends to increase leading to $A \geq 1$
 354 (as already observed in Fig. 13 of [20]). In that case, local ‘‘hot-spots’’ of the internal
 355 electric field dominate the absorption. Figure 5(c) shows that the phase shift induced by the
 356 aggregate depends on its capacity to extinguish the light.

357 Despite the quasi-universal behaviour in Fig 5, the detailed behavior of the data is not
 358 perfect due to dispersion, $m(\lambda)$. Dispersion violates the standardization predicted by use of
 359 the SIR. Indeed, the reader can observe that the curve corresponding to constant refractive
 360 index (black triangles) is perfectly continuous since only the wavelength varies, contrarily to
 361 other wavelength-dependent cases.

362 5. Improved correction of the RDG-FA for forward scattering

363 Based on the findings above, a semi-empirical model for the correction to the RDG-FA for
 364 forward scattering in the vertical-vertical polarization configuration is proposed in Eq. (15).
 365 This is a continuous expression of Eq. (11) expressed in terms of amplitude and phase of the

366 sliced phasor $\langle \overline{z_y(x)} \rangle_\psi$.

$$A_M = \left| \frac{\int_0^{2R_{\max}} \Lambda(x) \exp [i\Theta(x)] dV(x)}{\int_0^{2R_{\max}} dV(x)} \right|^2. \quad (15)$$

367 Here, R_{\max} is the radius of a sphere encompassing an aggregate, $dV(x)$ models the volume
 368 of material contained in a slice of thickness dx of the sphere in the y - z plane (see Fig. 6)
 369 and the subscript “m” stands for model. Note that, since the volume distribution of the
 370 encompassing sphere follows the fractal law its distribution differs from the one of a “full”
 371 sphere (see Fig. B.11). The volume element is taken as:

$$dV(x) = \alpha (R_m, D_f, \varphi) G(x, D_f, R_m) dx. \quad (16)$$

372 where α and G are functions whose development from the fractal scaling law, Eq. (1), are
 373 reported in Appendix B. Note that, A_M depends only on G since α in Eq. (16) is independent
 374 of x and thus divides out from the fraction in Eq. (15).

375 Figure 7 shows A_M as a function of the exact correction A for different numbers of
 376 monomers per aggregate. For each case, the model is tested by fitting the sliced phasor
 377 results as described above for wavelengths between $\lambda = 266$ nm and $\lambda = 1064$ nm. As with
 378 Fig. 5, dispersion is taken into account here. Even if the model is tested for a large range
 379 of wavelengths and covers very different soot material, the agreement is good as the slope is
 380 0.997 ± 0.005 .

381 The model is valid only for $N_m \geq 10$ corresponding to the minimum aggregate-size that
 382 expresses the fractal properties of an aggregate. In order to extend the validity of the model
 383 to smaller aggregates, an extended model A_{EM} is proposed, which empirically forces the
 384 correction to one for $N_m = 1$:

$$A_{EM} = A_M (1 - A_M) \exp \left(-\sqrt{\frac{N_m - 1}{N_c}} \right), \quad (17)$$

385 where $N_c = 9/4$ is related to the critical number of monomers below which the Eq. (15)
 386 requires modification.

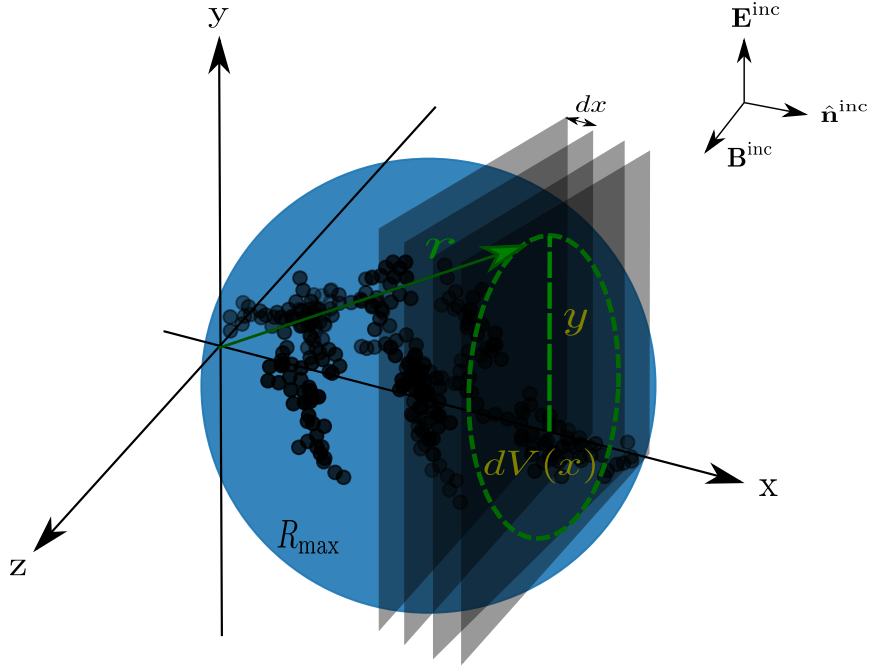


Figure 6: Depiction of the slicing method for the volume of the encompassing sphere of radius R_{\max} .

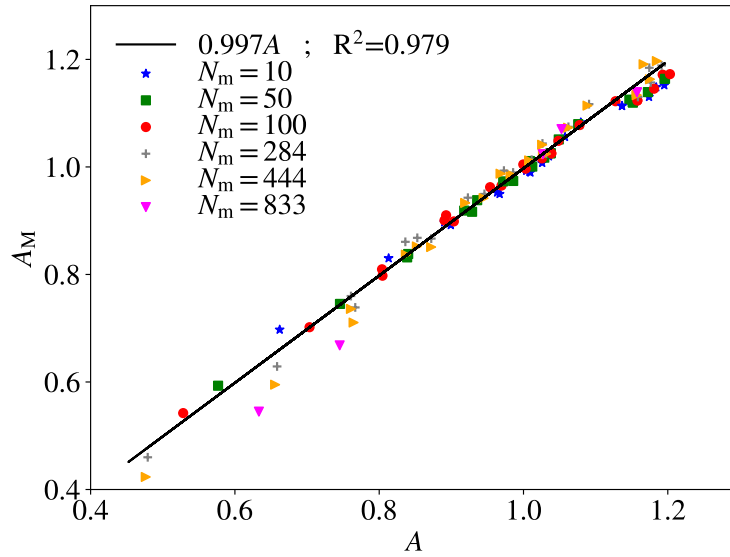


Figure 7: Comparison between the modelled RDG-FA correction for the vertically-vertically polarized forward scattering and the exact one A . The comparison covers the range of wavelengths 266–1064 nm and the corresponding refractive index for organic, graphitic and amorphous soot material. $R_m = 15$ nm. A linear regression is displayed as a continuous black line.

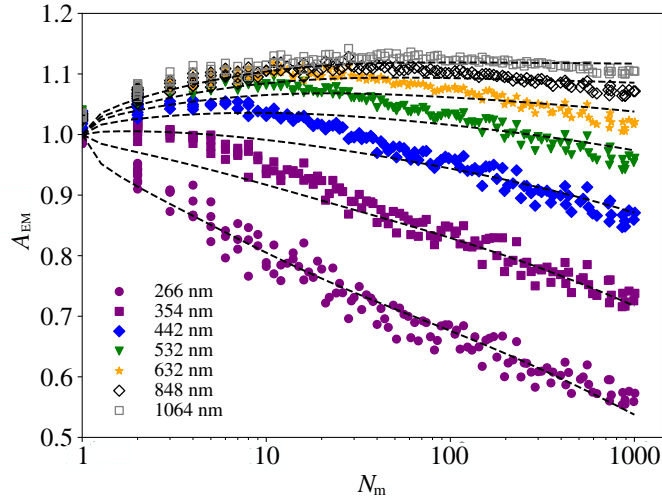


Figure 8: Comparison of the proposed model of correction A_{EM} (dash lines) and the exact correction A (symbols) reported by Yon et al. [19] for Diesel.

387 Figure 8 shows in symbols the correction factor found by [19] for the same wavelength
388 range as considered here, but with a different m appropriate for Diesel soot. These aggregates
389 are also generated by a DLCA code, i.e., $D_f = 1.78$ and $k_f = 1.44$, but the monomers feature a
390 Gaussian dispersion in size characterized by a mean radius of $\overline{R_m} = 17.1$ nm and a standard
391 deviation of 3.43 nm. To compare to this data, Eq. (15) and Eq. (17) are evaluated by
392 computing the sliced phasor behaviour. An ergodicity hypothesis is made to evaluate the
393 phasors no longer on 500 orientations of the same aggregate but rather on 1000 different
394 aggregates each in a random orientation. These aggregates vary in size, from $N_m = 10$ to
395 $N_m = 1000$, and have a monomer radius $R_m = 17$ nm, i.e., the polydispersity of [19] is
396 not taken into account. The results for these 1000 aggregates are reported in dashed lines
397 in Fig 8, where comparison to the [19] data (symbols) illustrates the performance of the
398 proposed model, Eq. (17). The deviations seen can be partially explained by the fact that
399 the polydispersity is neglected and that there is a loss of the fractal nature of the aggregate
400 for small N_m . Nevertheless, the new correction factor model, Eq. (17), performs well and
401 is thus useful to extend the range of validity of the RDG-FA to large aggregates for a large
402 range of soot optical properties.

403 6. Total scattering and absorption

404 It is reported in [19] that for fractal aggregates multiple scattering mainly affects forward
405 scattering and does not significantly impact the functionality of the phase function, i.e, the
406 structure of the angular scattered intensity. Thus, the total scattering cross section, C^{sca} ,
407 can be obtained by applying the same correction factor as above as for forward scattering.
408 Furthermore, a linear relationship between the RDG-FA correction factor for forward scat-
409 tering and the absorption cross section is empirically observed for soot without coating in
410 [9, 19, 20, 45]. We have recently explained this linearity by showing the absorption cross
411 section correction factor, h , can be formulated in terms of the averaged phasors as

$$h_v(\psi) = \overline{|z_x|^2} + \overline{|z_y|^2} + \overline{|z_z|^2}, \quad (18)$$

412 where x , y , and z denote the components of the internal electric field used in the phasors, see
413 Appendix F. in [21]. However, as seen in [21], the components $\overline{|z_x|^2}$ and $\overline{|z_z|^2}$ are practically
414 negligible compared to $\overline{|z_y|^2}$ for a bisphere. This seems to be also true for aggregates. Indeed,
415 the contribution of $\overline{|z_x|^2}$ and $\overline{|z_z|^2}$ to the total correction h is evaluated for the aggregate
416 reported in Fig. 1 to be respectively 4% and 3.5% for $\lambda = 266$ nm and 1.6% and 1.6% for
417 $\lambda = 1064$ nm. This explains the observed linear relationship between h and A which is
418 proportionnal to $\overline{|z_y|^2}$. Consequently, A_{EM} is linearly connected to h , which can be shown
419 rigorously from the ratio between the DDA absorption cross section and that given by the
420 RDG-FA. This relationship is demonstrated in Fig. 9 for different aggregate sizes for the
421 same range of λ and m as in Fig. 7. The linearity is evident and the slope is similar to that
422 in [19]. Thus, the h correction is simply a multiplication of A_{M} by 1.071 ± 0.007 , the slope
423 observed in Fig. 9. For aggregates with small N_{m} , a similar correction to Eq. (17) could be
424 applied.

425 7. Conclusion

426 The RDG-FA is a simple theory that is extensively used for the modeling of soot radiative
427 properties and for the interpretation of signals delivered by laser diagnostics. Nevertheless,
428 soot particles and other absorbing aggregates of nanoparticles generally do not fulfill the
429 requirements of the approximation, $x_{\text{m}} \ll 1$ and $|m(\lambda) - 1| \ll 1$, rendering it use in such

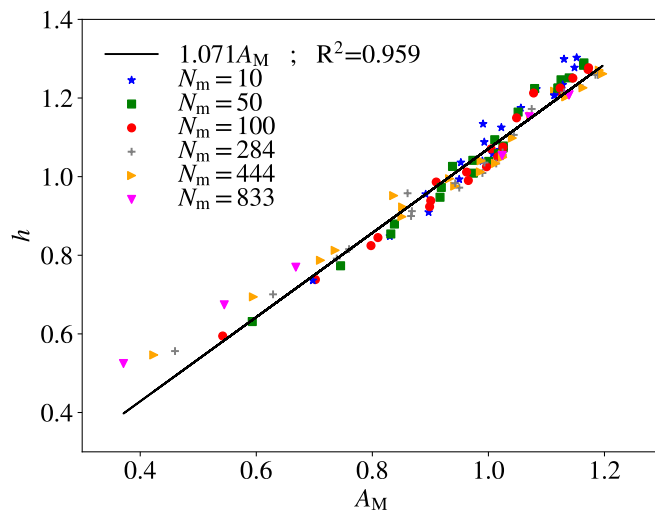


Figure 9: Correlation between the absorption correction factor h and our own model A_M . A linear regression is displayed in a continuous black line.

430 cases approximate. Indeed, errors up to 60% have been reported. Although deviations
 431 between the RDG-FA cross sections and the exact values have been observed in previous
 432 works, no model has been proposed to correct them. Our study provides such a correction
 433 model valid over a large range of wavelength and for refractive indices relevant to black
 434 carbon, organic carbon, graphitic, amorphous, and diesel-like soot materials. The model is
 435 made possible by the analysis of the internal electric field using phasors.

436 Here, to study the behaviour of the internal field as light passes through an aggregate,
 437 phasors are averaged in slices through the aggregate, orthogonal to light propagation direc-
 438 tion. We see that corrections to the RDG-FA have to take into account two phenomena.
 439 First, the internal coupling between monomers is generally a source of field hot-spots in the
 440 vicinity of the contact between monomers. Second, absorption decreases the amplitude of
 441 the internal field and increases the phase shift as the light propagates through the aggregate.
 442 The first phenomenon violates the RDG-FA hypothesis of a uniform internal field and is
 443 characterized by a short spatial range. It can explain the underestimation of the RDG-FA
 444 cross sections, $A \geq 1$. The second phenomenon violates the hypothesis that each monomer
 445 is exposed to the same incident field and explains why the RDG-FA overestimation is en-
 446 hanced when the number of monomers increases (a shielding effect). Both phenomena and

447 their dependence on location in the aggregate are analysed through the dependence of three
448 parameters for different wavelengths and refractive indices. Due to the direct relationship
449 between the phasors and the RDG-FA correction factors, this work allows the evaluation of
450 the correction factors for scattering and absorption. The corrections are compared to exact
451 calculations showing good agreement for a wide range of wavelength, aggregate size, and
452 soot material.

453 Beyond improving our understanding, this work advances the range of validity of the
454 RDG-FA in applications involving soot and BC particles, both in modeling and diagnostics
455 contexts, while also being easy to apply. The reader can download a python script for
456 calculating the corrected RDG-FA based on the current work by using the link <https://gitlab.coria-cfd.fr/c-rdgfa/C-RDGFA>.
457

458 As a pursuit of this work, the current methodology will be applied to more realistic ag-
459 gregates by considering, for example, monomer polydispersity, necking, overlap and different
460 fractal dimension and prefactor. It could be also adapted to larger range of refractive indices
461 in order to be applicable to other aggregate materials.

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470 **Appendix A. Size normalization**

471 Figure A.10 reports the amplitude of the sliced phasor at the position x by comparing
472 the normalization of this positioning parameter. The left plot normalizes the position x by
473 the gyration radius R_g whereas the right plot considers the monomer radius R_m . As it can
474 be seen the normalization by R_m produced a better unification of the results. The reason of

475 this better agreement is that R_m normalization is representative of the amount of material
 476 crossed by the incoming light source whatever the aggregate's size.

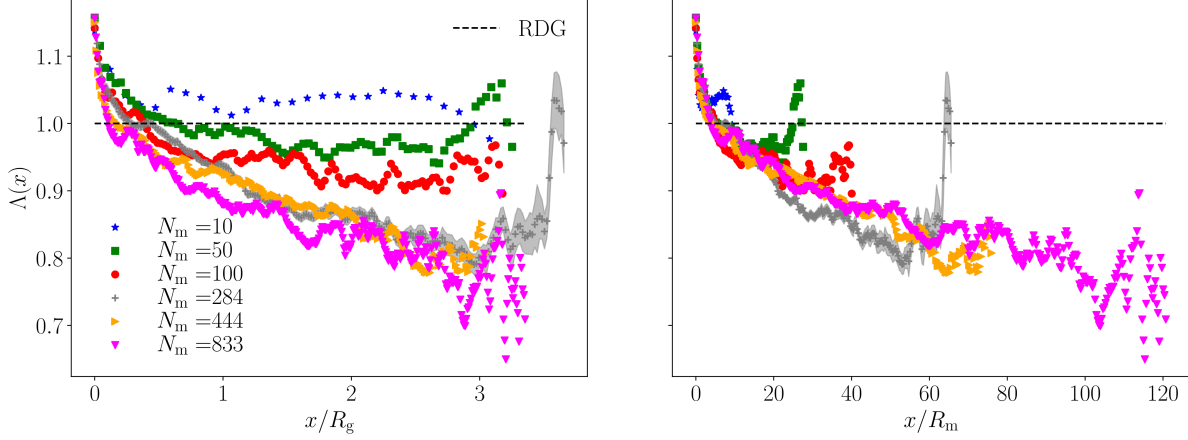


Figure A.10: Impact of the normalization of x by R_g or R_m on the sliced phasor amplitude $\Lambda(x)$.

477 Appendix B. Volume distribution

478 In order to compute A , the phasor approach in slices implies to use the number of dipoles,
 479 i.e., the volume in each disk of thickness dx in Fig. 6 as a weighting factor in Eq. (15). We
 480 can express the number of monomers of an aggregate of radius R_{\max} , contained in a sphere
 481 of radius r whose center corresponds to the aggregate center of mass, with $r \in [0, R_{\max}]$ [46]:

$$482 \quad N_m(r) = \varphi \left(\frac{r}{R_m} \right)^{D_f}. \quad (\text{B.1})$$

483 In this equation, φ is the packing fraction which represents a local compaction in the aggregate.
 484 It is different from the fractal prefactor k_f used in Eq. (1) since r is a variable which
 485 not corresponds to the gyration radius of the aggregate [34]. From this equation, one can
 486 express the probability to find material at a distance r from the aggregate's center of mass:

$$\rho(r) = \frac{1}{4\pi r^2} \frac{dN_m(r)}{dr} V_m = \frac{\varphi D_f}{3} \left(\frac{r}{R_m} \right)^{D_f-3}, \quad (\text{B.2})$$

487 with $(V_m = 4\pi R_m^3/3)$, the volume of a monomer. Therefore, the elementary volume of
 488 aggregate in the plane Π corresponding to the green dash circle in Fig. 6, having a radius y

489 becomes:

$$dV(x, y) = 2\pi\rho(r)ydydx. \quad (\text{B.3})$$

490 By integrating this expression in the plane II, the elementary volume of material contained
 491 in a slice of thickness dx positioned at a distance $x \geq R_m$ from the left part of the aggregate
 492 is:

$$dV(x) = \underbrace{\frac{2\pi\varphi D_f dx}{3R_m^{D_f-3}}}_{\alpha(R_m, D_f, \varphi)} \underbrace{\int_0^{\sqrt{r^2 - (x-2R_{\max})^2}} y [(x - R_{\max})^2 + y^2]^{\frac{D_f-3}{2}} dy}_{G(x, D_f, R_m)}. \quad (\text{B.4})$$

493 By symmetry from the aggregate center of mass, for $x \leq R_m$, the expression is identical
 494 excepted the upper bound of the integral that becomes $\sqrt{r^2 - x^2}$.

495 Fig. B.11 shows the normalized volume distribution $\int_0^{2R_{\max}} dV(x)/V$ along the normalized
 496 $x/2R_{\max}$ abscissa for the porous encompassing sphere which models a DLCA aggregate
 497 ($D_f = 1.78$) averaged over orientations and the one from a full sphere (dimension $D_f = 3$).

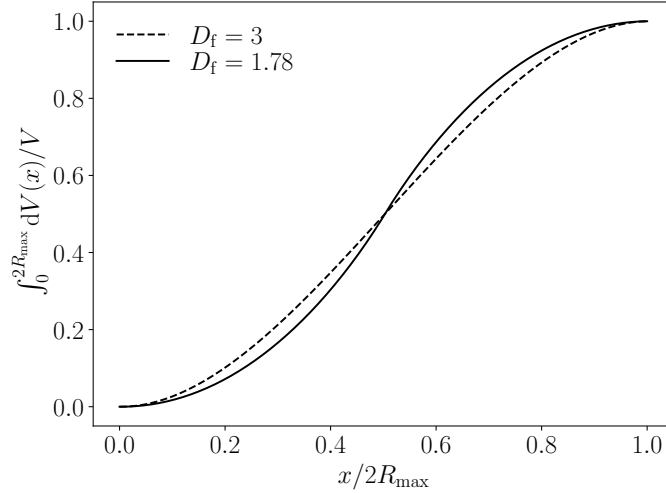


Figure B.11: Normalized volume distribution of the encompassing sphere.

498 References

- 499 [1] A. T. Juarez-Facio, C. Castilla, C. Corbière, H. Lavanant, C. Afonso, C. Morin,
 500 N. Merlet-Machour, L. Chevalier, J.-M. Vaugeois, J. Yon, et al., Development of a
 501 standardized in vitro approach to evaluate microphysical, chemical, and toxicological

- 502 properties of combustion-derived fine and ultrafine particles, *Journal of Environmental*
503 *Sciences* 113 (2022) 104–117.
- 504 [2] A. Wierzbicka, P. Nilsson, J. Rissler, G. Sallsten, Y. Xu, J. Pagels, M. Albin, K. Öster-
505 berg, B. Strandberg, A. Eriksson, M. Bohgard, K. Bergemalm-Rynell, A. Gudmundsson,
506 Detailed diesel exhaust characteristics including particle surface area and lung deposited
507 dose for better understanding of health effects in human chamber exposure studies., *At-*
508 *mospheric Environment* 86 (2014) 212–219. doi:[10.1016/j.atmosenv.2013.11.025](https://doi.org/10.1016/j.atmosenv.2013.11.025).
- 509 [3] G. Myhre, F. Stordal, K. Restad, I. S. A. Isaksen, [Estimation of the direct radiative](#)
510 [forcing due to sulfate and soot aerosols](#), *Tellus B: Chemical and Physical Meteorol-*
511 *ogy* 50 (5) (1998) 463–477. arXiv:<https://doi.org/10.3402/tellusb.v50i5.16230>,
512 doi:[10.3402/tellusb.v50i5.16230](https://doi.org/10.3402/tellusb.v50i5.16230).
513 URL <https://doi.org/10.3402/tellusb.v50i5.16230>
- 514 [4] P. J. C. Meinrat O. Andreae, [Atmospheric aerosols: Biogeochemical sources and role in](#)
515 [atmospheric chemistry](#) 276 (1997). arXiv:[https://doi.org/10.1126/science.276.](https://doi.org/10.1126/science.276.5315.1052)
516 [5315.1052](https://doi.org/10.1126/science.276.5315.1052), doi:[10.1126/science.276.5315.1052](https://doi.org/10.1126/science.276.5315.1052).
517 URL <https://doi.org/10.1126/science.276.5315.1052>
- 518 [5] J. Yon, J. Morán, F. Lespinasse, F. Escudero, G. Godard, M. Mazur, F. Liu, A. Fuentes,
519 Horizontal planar angular light scattering (hpals) characterization of soot produced in
520 a laminar axisymmetric coflow ethylene diffusion flame, *Combustion and Flame* 232
521 (2021) 111539.
- 522 [6] N. Rattanasom, T. Saowapark, C. Deeprasertkul, [Reinforcement of natural rubber with](#)
523 [silica/carbon black hybrid filler](#), *Polymer Testing* 26 (3) (2007) 369–377. doi:<https://doi.org/10.1016/j.polymertesting.2006.12.003>.
524 [//doi.org/10.1016/j.polymertesting.2006.12.003](https://doi.org/10.1016/j.polymertesting.2006.12.003).
525 URL <https://www.sciencedirect.com/science/article/pii/S0142941806002182>
- 526 [7] J. A. Lock, G. Gouesbet, [Generalized lorenz–mie theory and applications](#), *Journal*
527 *of Quantitative Spectroscopy and Radiative Transfer* 110 (11) (2009) 800–807, light
528 Scattering: Mie and More Commemorating 100 years of Mie’s 1908 publication.

- 529 [doi:https://doi.org/10.1016/j.jqsrt.2008.11.013](https://doi.org/10.1016/j.jqsrt.2008.11.013).
- 530 URL <https://www.sciencedirect.com/science/article/pii/S0022407308002653>
- 531 [8] L. Liu, M. I. Mishchenko, [Scattering and radiative properties of complex soot and](#)
532 [soot-containing aggregate particles](#), Journal of Quantitative Spectroscopy and Radiative
533 Transfer 106 (1) (2007) 262 – 273, iX Conference on Electromagnetic and Light Scatter-
534 ing by Non-Spherical Particles. [doi:https://doi.org/10.1016/j.jqsrt.2007.01.](https://doi.org/10.1016/j.jqsrt.2007.01.020)
535 [020](https://doi.org/10.1016/j.jqsrt.2007.01.020).
- 536 URL <http://www.sciencedirect.com/science/article/pii/S0022407307000350>
- 537 [9] J. Yon, A. Bescond, F. Liu, On the radiative properties of soot aggregates part 1:
538 Necking and overlapping, Journal of Quantitative Spectroscopy and Radiative Transfer
539 162 (2015) 197–206.
- 540 [10] F. Liu, J. Yon, A. Bescond, On the radiative properties of soot aggregates–part 2:
541 Effects of coating, Journal of Quantitative Spectroscopy and Radiative Transfer 172
542 (2016) 134–145.
- 543 [11] E. M. Purcell, C. R. Pennypacker, Scattering and Absorption of Light by Nonspherical
544 Dielectric Grains, The Astrophysical Journal 186 (1973) 705–714. [doi:10.1086/152538](https://doi.org/10.1086/152538).
- 545 [12] B. T. Draine, The Discrete-Dipole Approximation and Its Application to Interstellar
546 Graphite Grains, The Astrophysical Journal 333 (1988) 848. [doi:10.1086/166795](https://doi.org/10.1086/166795).
- 547 [13] M. A. Yurkin, A. G. Hoekstra, The discrete dipole approximation: An overview and re-
548 cent developments, Journal of Quantitative Spectroscopy and Radiative Transfer 106 (1-
549 3) (2007) 558–589. [arXiv:0704.0038](https://arxiv.org/abs/0704.0038), [doi:10.1016/j.jqsrt.2007.01.034](https://doi.org/10.1016/j.jqsrt.2007.01.034).
- 550 [14] M. Lapuerta, S. González-Correa, F. Cereceda-Balic, H. Moosmüller, [Comparison of](#)
551 [equations used to estimate soot agglomerate absorption efficiency with the rayleigh-](#)
552 [debye-gans approximation](#), Journal of Quantitative Spectroscopy and Radiative Transfer
553 262 (2021) 107522. [doi:https://doi.org/10.1016/j.jqsrt.2021.107522](https://doi.org/10.1016/j.jqsrt.2021.107522).
- 554 URL <https://www.sciencedirect.com/science/article/pii/S0022407321000157>

- 555 [15] C. F. Bohren, D. R. Huffman, Absorption and scattering of light by small particles,
556 John Wiley & Sons, 2008.
- 557 [16] R. J. Hogan, C. D. Westbrook, [Equation for the microwave backscatter cross section of](#)
558 [aggregate snowflakes using the self-similar rayleigh-gans approximation](#), Journal of the
559 Atmospheric Sciences 71 (9) (2014) 3292 – 3301. doi:10.1175/JAS-D-13-0347.1.
560 URL [https://journals.ametsoc.org/view/journals/atsc/71/9/jas-d-13-0347.](https://journals.ametsoc.org/view/journals/atsc/71/9/jas-d-13-0347.1.xml)
561 [1.xml](#)
- 562 [17] C. Sorensen, Light scattering by fractal aggregates: a review, Aerosol Science & Tech-
563 nology 35 (2) (2001) 648–687.
- 564 [18] F. Liu, G. J. Smallwood, [Effect of aggregation on the absorption cross-section of fractal](#)
565 [soot aggregates and its impact on lii modelling](#), Journal of Quantitative Spectroscopy
566 and Radiative Transfer 111 (2) (2010) 302 – 308, eurotherm Seminar No. 83: Computa-
567 tional Thermal Radiation in Participating Media III. doi:[https://doi.org/10.1016/](https://doi.org/10.1016/j.jqsrt.2009.06.017)
568 [j.jqsrt.2009.06.017](#).
569 URL <http://www.sciencedirect.com/science/article/pii/S0022407309002325>
- 570 [19] J. Yon, F. Liu, A. Bescond, C. Caumont-Prim, C. Rozé, F.-X. Ouf, A. Coppalle, Ef-
571 fects of multiple scattering on radiative properties of soot fractal aggregates, Journal of
572 Quantitative Spectroscopy and Radiative Transfer 133 (2014) 374–381.
- 573 [20] C. M. Sorensen, J. Yon, F. Liu, J. Maughan, W. R. Heinson, M. J. Berg, Light scat-
574 tering and absorption by fractal aggregates including soot, Journal of Quantitative
575 Spectroscopy and Radiative Transfer 217 (2018) 459–473.
- 576 [21] C. Argentin, M. J. Berg, M. Mazur, R. Ceolato, J. Yon, Assessing the limits of rayleigh-
577 debye-gans theory: Phasor analysis of a bisphere, Journal of Quantitative Spectroscopy
578 and Radiative Transfer 264 (2021) 107550.
- 579 [22] R. Ceolato, L. Paulien, J. B. Maughan, C. M. Sorensen, M. J. Berg, [Radiative properties](#)
580 [of soot fractal superaggregates including backscattering and depolarization](#), Journal
581 of Quantitative Spectroscopy and Radiative Transfer 247 (2020) 106940. doi:<https://doi.org/10.1016/j.jqsrt.2020.106940>

- 582 [//doi.org/10.1016/j.jqsrt.2020.106940](https://doi.org/10.1016/j.jqsrt.2020.106940).
- 583 URL <http://www.sciencedirect.com/science/article/pii/S0022407319307939>
- 584 [23] M. J. Berg, [Power-law patterns in electromagnetic scattering: A selected review and](#)
585 [recent progress](#), Journal of Quantitative Spectroscopy and Radiative Transfer 113 (18)
586 (2012) 2292 – 2309, electromagnetic and Light Scattering by non-spherical particles
587 XIII. doi:<https://doi.org/10.1016/j.jqsrt.2012.05.015>.
588 URL <http://www.sciencedirect.com/science/article/pii/S002240731200266X>
- 589 [24] M. J. Berg, C. M. Sorensen, [Internal fields of soot fractal aggregates](#), Journal of the
590 Optical Society of America. A 30 (10) (2013) 1947–1955. doi:[10.1364/JOSAA.30.](https://doi.org/10.1364/JOSAA.30.001947)
591 [001947](https://doi.org/10.1364/JOSAA.30.001947).
592 URL <http://josaa.osa.org/abstract.cfm?URI=josaa-30-10-1947>
- 593 [25] M. Berg, C. Sorensen, A. Chakrabarti, Reflection symmetry of a sphere’s internal field
594 and its consequences on scattering: A microphysical approach, Journal of the Optical
595 Society of America. A, Optics, image science, and vision 25 (2008) 98–107. doi:[10.](https://doi.org/10.1364/JOSAA.25.000098)
596 [1364/JOSAA.25.000098](https://doi.org/10.1364/JOSAA.25.000098).
- 597 [26] M. J. Berg, C. M. Sorensen, A. Chakrabarti, Explanation of the patterns in mie theory,
598 Journal of Quantitative Spectroscopy and Radiative Transfer 111 (2010) 782–794.
- 599 [27] P. Meakin, Formation of fractal clusters and networks by irreversible diffusion-limited
600 aggregation, Physical Review Letters 51 (13) (1983) 1119.
- 601 [28] F. Liu, D. R. Snelling, G. J. Smallwood, Effects of the fractal prefactor on the optical
602 properties of fractal soot aggregates, in: International Conference on Micro/Nanoscale
603 Heat Transfer, Vol. 43901, 2009, pp. 363–371.
- 604 [29] F. Liu, C. Wong, D. R. Snelling, G. J. Smallwood, [Investigation of absorption and](#)
605 [scattering properties of soot aggregates of different fractal dimension at 532 nm using](#)
606 [rdg and gmm](#), Aerosol Science and Technology 47 (12) (2013) 1393–1405. arXiv:[https:](https://doi.org/10.1080/02786826.2013.847525)
607 [//doi.org/10.1080/02786826.2013.847525](https://doi.org/10.1080/02786826.2013.847525), doi:[10.1080/02786826.2013.847525](https://doi.org/10.1080/02786826.2013.847525).
608 URL <https://doi.org/10.1080/02786826.2013.847525>

- 609 [30] J. Yon, J. J. Cruz, F. Escudero, J. Morán, F. Liu, A. Fuentes, [Revealing soot maturity](#)
610 [based on multi-wavelength absorption/emission measurements in laminar axisymmetric](#)
611 [coflow ethylene diffusion flames](#), *Combustion and Flame* 227 (2021) 147–161. doi:
612 <https://doi.org/10.1016/j.combustflame.2020.12.049>.
613 URL <https://www.sciencedirect.com/science/article/pii/S0010218021000018>
- 614 [31] A. Bescond, J. Yon, F.-X. Ouf, C. Rozé, A. Coppalle, P. Parent, D. Ferry, C. Laffon,
615 Soot optical properties determined by analyzing extinction spectra in the visible near-
616 uv: Toward an optical speciation according to constituents and structure, *Journal of*
617 *Aerosol Science* 101 (2016) 118–132.
- 618 [32] H. Chang, T. T. Charalampopoulos, Determination of the Wavelength Dependence of
619 Refractive Indices of Flame Soot, *Proceedings of the Royal Society of London Series A*
620 430 (1880) (1990) 577–591. doi:[10.1098/rspa.1990.0107](https://doi.org/10.1098/rspa.1990.0107).
- 621 [33] S. R. Forrest, T. A. Witten Jr, Long-range correlations in smoke-particle aggregates,
622 *Journal of Physics A: Mathematical and General* 12 (5) (1979) L109.
- 623 [34] J. Yon, J. Morán, F.-X. Ouf, M. Mazur, J. Mitchell, From monomers to agglomerates:
624 A generalized model for characterizing the morphology of fractal-like clusters, *Journal*
625 *of Aerosol Science* 151 (2021) 105628.
- 626 [35] M. I. Mishchenko, *Electromagnetic Scattering by Particles and Particle Groups: An*
627 *Introduction*, Cambridge University Press, Cambridge, 2014.
- 628 [36] J. D. Jackson, [Classical electrodynamics; 2nd ed.](#), Wiley, New York, NY, 1975.
629 URL <https://cds.cern.ch/record/100964>
- 630 [37] B. T. Draine, P. J. Flatau, [Discrete-dipole approximation for scattering calculations](#),
631 *Journal of the Optical Society of America. A* 11 (4) (1994) 1491–1499. doi:[10.1364/](https://doi.org/10.1364/JOSAA.11.001491)
632 [JOSAA.11.001491](https://doi.org/10.1364/JOSAA.11.001491).
633 URL <http://josaa.osa.org/abstract.cfm?URI=josaa-11-4-1491>
- 634 [38] T. C. Williams, C. R. Shaddix, K. A. Jensen, J. M. Suo-Anttila, Measurement of the

- 635 dimensionless extinction coefficient of soot within laminar diffusion flames, *International*
636 *Journal of Heat and Mass Transfer* 50 (7-8) (2007) 1616–1630.
- 637 [39] F. Liu, J. Yon, A. Fuentes, P. Lobo, G. J. Smallwood, J. C. Corbin, Review of recent
638 literature on the light absorption properties of black carbon: Refractive index, mass
639 absorption cross section, and absorption function, *Aerosol Science and Technology* 54 (1)
640 (2020) 33–51.
- 641 [40] G. Shu, T. T. Charalampopoulos, [Reciprocity theorem for the calculation of average](#)
642 [scattering properties of agglomerated particles](#), *Applied Optics* 39 (31) (2000) 5827–
643 5833. doi:10.1364/AO.39.005827.
644 URL <http://ao.osa.org/abstract.cfm?URI=ao-39-31-5827>
- 645 [41] M. I. Mishchenko, L. D. Travis, A. A. Lacis, *Scattering, Absorption, and Emission of*
646 *Light by Small Particles*, Cambridge University Press, Cambridge, 2002.
- 647 [42] I. Romero, J. Aizpurua, G. W. Bryant, F. J. G. de Abajo, [Plasmons in nearly touching](#)
648 [metallic nanoparticles: singular response in the limit of touching dimers](#), *Opt. Express*
649 14 (21) (2006) 9988–9999. doi:10.1364/OE.14.009988.
650 URL <http://www.opticsexpress.org/abstract.cfm?URI=oe-14-21-9988>
- 651 [43] T. L. Farias, Ü. Ö. Köylü, M. d. G. Carvalho, Range of validity of the rayleigh–debye–
652 gans theory for optics of fractal aggregates, *Applied optics* 35 (33) (1996) 6560–6567.
- 653 [44] M. I. Mishchenko, [Scale invariance rule in electromagnetic scattering](#), *Journal of Quan-*
654 *titative Spectroscopy and Radiative Transfer* 101 (3) (2006) 411 – 415, light in Planetary
655 Atmospheres and Other Particulate Media. doi:[https://doi.org/10.1016/j.jqsrt.](https://doi.org/10.1016/j.jqsrt.2006.02.047)
656 [2006.02.047](https://doi.org/10.1016/j.jqsrt.2006.02.047).
657 URL <http://www.sciencedirect.com/science/article/pii/S0022407306000598>
- 658 [45] J. Yon, C. Rozé, T. Girasole, A. Coppalle, L. Méès, Extension of rdg-fa for scattering
659 prediction of aggregates of soot taking into account interactions of large monomers,
660 *Particle & Particle Systems Characterization* 25 (1) (2008) 54–67.

661 [46] W. Heinson, C. Sorensen, A. Chakrabarti, [A three parameter description of the structure](#)
662 [of diffusion limited cluster fractal aggregates](#), Journal of Colloid and Interface Science
663 375 (1) (2012) 65–69. doi:<https://doi.org/10.1016/j.jcis.2012.01.062>.
664 URL <https://www.sciencedirect.com/science/article/pii/S0021979712001178>