Journal of Quantitative Spectroscopy & Radiative Transfer ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Notes

The single-scattering properties of black carbon aggregates determined from the geometric-optics surface-wave approach and the *T*-matrix method

Y. Takano [a,*], K.N. Liou [a], M. Kahnert [b,c], P. Yang [d]

[a] *Joint Institute for Earth System Science and Engineering, and Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA 90095, USA*
[b] *Swedish Meteorological and Hydrological Institute, 601 76 Norrköping, Sweden*
[c] *Department of Earth and Space Science, Chalmers University of Technology, 412 96 Gothenburg, Sweden*
[d] *Department of Atmospheric Sciences, Texas A&M University, College Station, TX 77845, USA*

ARTICLE INFO

Article history:
Received 18 March 2013
Received in revised form
7 April 2013
Accepted 8 April 2013

Keywords:
Black carbon
Soot
Aggregated aerosol
Geometric optics and surface wave
Rayleigh–Gans–Debye scattering
T-matrix method

ABSTRACT

The single-scattering properties of eight black carbon (BC, soot) fractal aggregates, composed of primary spheres from 7 to 600, computed by the geometric-optics surface-wave (GOS) approach coupled with the Rayleigh–Gans–Debye (RGD) adjustment for size parameters smaller than approximately 2, are compared with those determined from the superposition *T*-matrix method. We show that under the condition of random orientation, the results from GOS/RGD are in general agreement with those from *T*-matrix in terms of the extinction and absorption cross-sections, the single-scattering co-albedo, and the asymmetry factor. When compared with the specific absorption (m^2/g) measured in the laboratory, we illustrate that using the observed radii of primary spheres ranging from 3.3 to 25 nm, the theoretical values determined from GOS/RGD for primary sphere numbers of 100–600 are within the range of measured values. The GOS approach can be effectively applied to aggregates composed of a large number of primary spheres (e.g., >6000) and large size parameters ($\gg 2$) in terms of computational efforts.

1. Introduction

Aerosols are an important factor in regulating climate and weather processes. Black carbon (BC or soot) emitted from anthropogenic combustion sources has a potential effect on regional and global climate change by means of absorbing incoming sunlight [1–3]. However, determination of the absorption and scattering properties of soot is extremely difficult due to its agglomerated structure and inhomogeneous composition.

We developed a geometric optics approach coupled with surface-wave contributions for light scattering by homogeneous spheres and spheres with a shell–core structure [4]. The geometric-optics surface-wave theory, referred to as GOS, for light scattering by spheres considers the surface-wave contribution as a perturbation term to the geometric-optics core that includes the Fresnel reflection–refraction and Fraunhofer diffraction. The hit-and-miss Monte Carlo photon tracing program for homogeneous particles was extended to concentrically stratified spheres [5]. Results computed from GOS and the "exact" Lorenz–Mie type solution for spheres and rigorous numerical approaches for ice plates and columns revealed close comparisons in terms of the extinction cross-section, single-scattering albedo, and asymmetry factor. Liou et al. [6] further developed computer-generated aggregates by stochastic processes using homogeneous and shell–core spheres with and without rough surfaces as

* Corresponding author. Tel.: +1 310 794 9832; fax: +1 310 794 9796.
E-mail address: ytakano@atmos.ucla.edu (Y. Takano).

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http://dx.doi.org/10.1016/j.jqsrt.2013.04.006

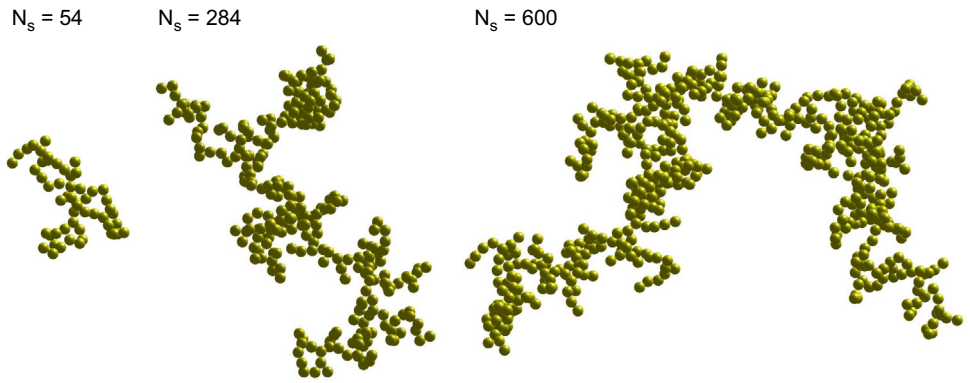

Fig. 1. Black carbon (BC, soot) fractal aggregates containing primary spheres N_s of 54, 284, and 600 used for light scattering and absorption calculations.

the building blocks and conducted the computation of the single-scattering properties of aggregated soot particles with closed- and open-cell structures using the GOS approach. Application has been made to the study of radiative forcings produced by contrail cirrus contaminated by soot particles internally and externally mixed with small ice crystals [7].

The *T*-matrix method, which was originally implemented for homogeneous star-shaped particles with axisymmetric [8,9] and non-axisymmetric [10,11] geometries, has been extended to aggregated particles by means of a superposition approach [12]. The superposition *T*-matrix method solves Maxwell's equations for fractal aggregates, i.e., a cluster of spheres. Optical properties can be computed for particles in either fixed or random orientations. For the latter case, an analytic orientation-averaging procedure has been followed. Numerical problems and high CPU-time demands can become an issue for particles much larger than the incident wavelength and for large numbers of primary particles in the aggregate. For the latest parallelized implementation of the code [13], stable results have been reported for particles consisting of up to 3000 primary spheres.

In this note, we present comparison of the single-scattering properties of soot aggregates computed from GOS and the results determined from the superposition *T*-matrix method [12] presented in various studies (e.g. [14–16]). The accuracy of the *T*-matrix method applied to BC aggregates has been extensively tested by comparisons to discrete dipole computations [17] and by use of the reciprocity condition [17–19]. In the course of this comparison, we developed a Rayleigh–Gans–Debye (RGD) approximation for aggregates with volume-equivalent size parameters less than approximately 2 to supplement limitations of the GOS approach. In Section 2, the computed single-scattering properties derived from GOS/RGD and *T*-matrix are shown and discussed, followed by the concluding remarks denoted in Section 3. The RGD approximation is presented in the Appendix.

2. Computational results and discussions

Black carbon (or soot) aggregates produced by combustion usually have fractal structures. In this work, we have adopted the diffusion limited cluster aggregates (DLCA, [20]) composed of N_s homogeneous primary spheres of equal radius a. Using random numbers, DLCA can be generated stochastically in a different way as compared to the diffusion limited aggregates (DLA) presented in Liou et al. [6]. It allows collisions among agglomerates in addition to collisions between primary spheres undergoing a random walk and agglomerates. For this reason, its fractal dimension of 1.82 is smaller than that of DLA, which has a value of 2.27. Following Kahnert [15,16], we have assumed eight different fractal aggregates composing of primary spheres N_s of 7, 23, 54, 105, 180, 284, 423, and 600. The corresponding volume-equivalent radii r_v are given by $a(N_s)^{1/3}$ with $a=25$ nm, unless stated otherwise. Fig. 1 depicts three examples of the fractal aggregates composing of N_s of 54, 284, and 600.

In the course of comparison between GOS and the superposition *T*-matrix method, we find that the results computed from GOS diverge from those obtained from *T*-matrix for size parameters smaller than $\sim$2. For this reason, we have developed a modification of the Rayleigh–Gans scattering approximation [21,22] for a sphere which incorporates Debye's form factor theory [23] for aggregates, referred to as the RGD adjustment presented in the Appendix. The RGD approximation is generally valid for size parameters smaller than $\sim$2 and it compensates for limitations of the GOS approach. The unification of the two is shown to be a very useful method for the calculation of the single-scattering properties of soot aggregates.

Fig. 2 illustrates comparison of the extinction and absorption cross-sections C_{ext} and C_{abs}, the asymmetry factor g, and the single-scattering co-albedo $(1-\varpi)$ computed from GOS/RGD and the *T*-matrix method. In the calculations, the complex index of refraction for soot at a visible wavelength λ of 533.2 nm is taken to be $1.76-i0.63$. The size parameter for the volume-equivalent sphere x_v $(=2\pi r_v/\lambda)$ corresponding to N_s is displayed at the top of each panel. The results cover a range of N_s from 7 to 600 [15,16]. The extinction cross-section increases with the number of spheres N_s almost linearly. Differences between the two are less than 10%. Results of the single-scattering co-albedo, the ratio of the absorption cross-section to the extinction cross-section, obtained from the two methods show differences of less than 3%. The asymmetry factor

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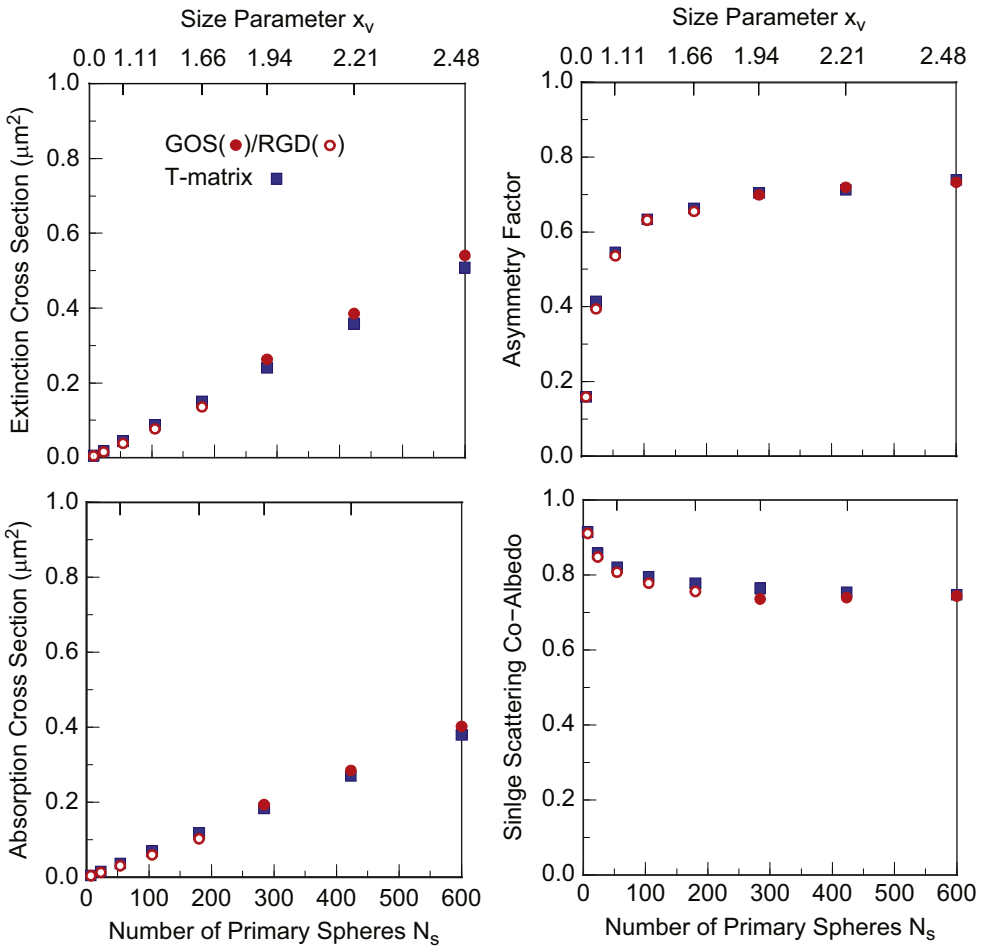

Fig. 2. Comparison of the extinction and absorption cross-sections, the asymmetry factor, and the single-scattering co-albedo for randomly oriented homogeneous soot aggregates between GOS/RGD and *T*-matrix. GOS and RGD are shown, respectively, by solid and open circles. The total numbers of primary spheres N_s depicted in the figure are 7, 23, 54, 105, 180, 284, 432, and 600 (see Fig. 1). The radius of a primary sphere a is 25 nm. The wavelength is 533.2 nm with a refractive index of 1.76–*i*0.63. The scale of volume-equivalent size parameter is displayed at the top of the diagrams.

results determined from the two methods exhibit close comparison.

In Fig. 3, we illustrates comparison of the scattering phase matrix for randomly oriented soot aggregates of $N_s=105$, corresponding to a size parameter of 1.39, between RGD and *T*-matrix. The phase function P_{11} depicts a peak around scattering angle of 0° resulting from diffraction and becomes flat at backscattering directions. The degree of linear polarization $-P_{12}/P_{11}$ has a maximum value 1.0 at the scattering angle of 90°, which is the same as the Rayleigh scattering results. The values of P_{22}/P_{11} are close to 1, while P_{43}/P_{11} is ~0. The element P_{33}/P_{11} is essentially equal to P_{44}/P_{11} at all scattering angles. Results computed for all matrix elements from the two approaches reveal close comparison.

Fig. 4 illustrates comparison of the specific absorption α_a (m^2/g) between theoretical calculations and laboratory measured values presented by Sheridan et al. [24] at $\lambda=530$ nm and compiled by Bond and Bergstrom [25] at $\lambda=550$ nm. The measured α_a has a value of 7.5 ± 1.2 m^2/g. It is defined by $C_{abs}/\rho V$, where ρ is the soot density taken to be 1.8 g/cm^3 [25] and V is aggregate volume. According to Wentzel et al. [26] and Bond and Bergstrom [25], the radii of primary spheres range from 3.3 to 25 nm. However, the total number of primary spheres was not estimated from the aggregate photo. Using the preceding two radii, we obtained α_a ($a=3.3$ nm) of ~9.9 m^2/g and α_a ($a=25$ nm) of ~5.8 m^2/g from GOS/RGD (two red lines), which are comparable with the range of the measured values. The specific absorption appears to be largely independent of the number of primary spheres between 100 and 600. The *T*-matrix results for C_{abs} [15,16] were divided by ρV and are depicted in blue line. For the case of α_a ($a=25$ nm), the results computed from GOS/RGD are larger than those from *T*-matrix by ~6%.

3. Concluding remarks

In this note, the extinction and absorption cross-sections, the single-scattering co-albedo, and the asymmetry factor of eight soot fractal aggregates (with primary spheres from 7 to 600) are computed by means of the geometric-optics surface-wave (GOS) approach, coupled with the Rayleigh–Gans–Debye (RGD) adjustment for

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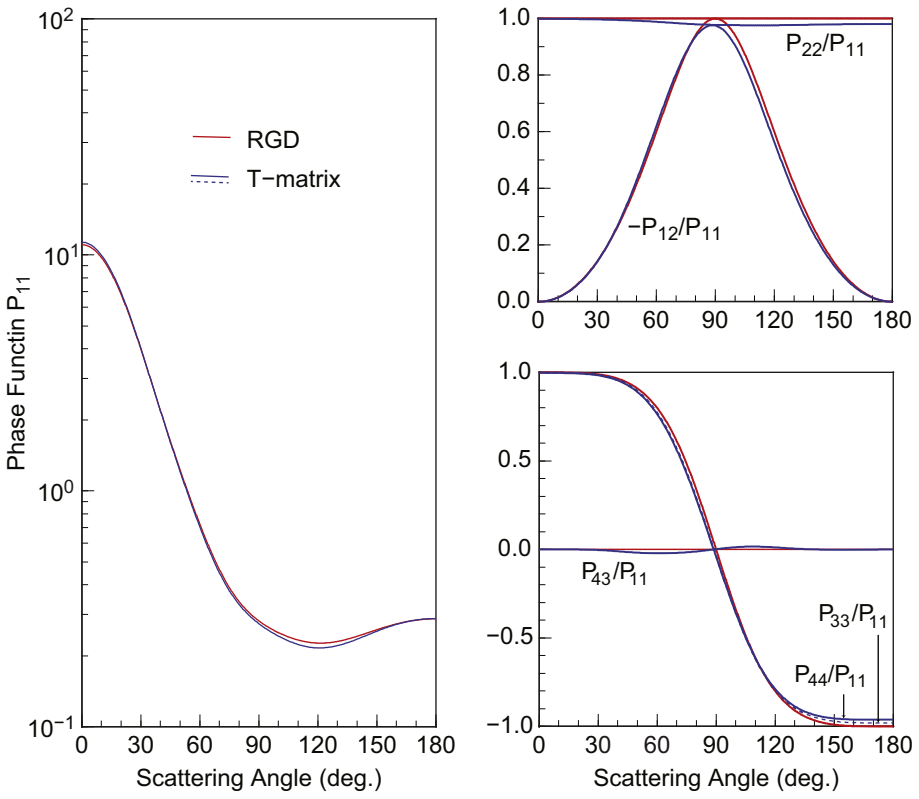

Fig. 3. Comparison of the scattering phase matrix elements for a soot aggregate with $N_s=105$ ($x_v=1.39$) between the Rayleigh–Gans–Debye (RGD) approximation and the superposition T-matrix.

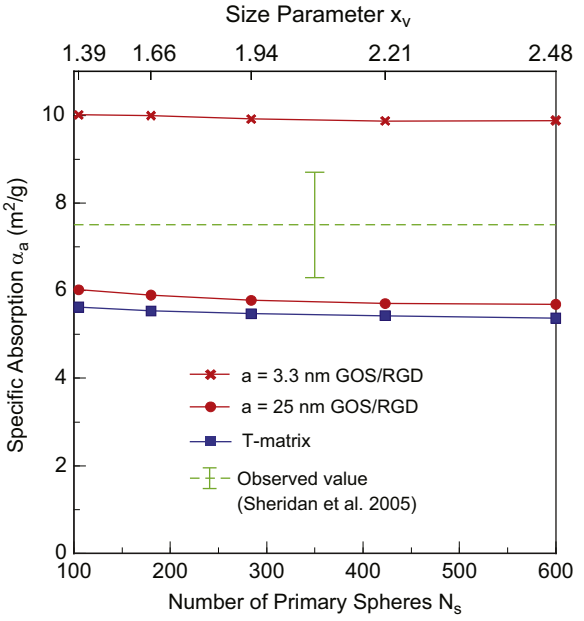

Fig. 4. Comparison of the specific absorption α_a (m^2/g), i.e., the mass absorption cross-section (MAC) computed from GOS/RGD for two cases involving the primary-sphere radius of $a=3.3$ and 25 nm (in red) and the measured values with mean and standard deviation presented by Sheridan et al. [24]. The T-matrix results for $a=25$ nm are also shown (in blue). (For interpretation of references to color in this figure, the reader is referred to the web version of this article.)

volume-equivalent size parameters smaller than approximately 2. The results are compared with those determined from the superposition T-matrix method. Under the condition of random orientation, the single-scattering results determined from GOS/RGD compare reasonably well with those obtained from T-matrix. We further illustrate that using the observed radii of primary spheres ranging from 3.3 to 25 nm, the theoretical values for specific absorption determined from GOS/RGD for primary sphere numbers of 100–600 are within the range of laboratory measured values. Finally, we wish to note that the GOS approach coupled with the RGD adjustment is an attractive and efficient method for the calculation of the single-scattering properties of soot aggregates covering a wide range of size parameters and internal inhomogeneity, particularly for high number of primary spheres (e.g., >6000) and size parameters much larger than 2.

Acknowledgments

This research was supported by the National Science Foundation under Grant AGS-0946315, by NASA under Grant NNX11AK39, and by Subcontracts S100097 and S100034 from the Texas A&M Research Foundation. M. Kahnert acknowledges funding support from the Swedish Research Council under Project 621–2011-3346. We are also grateful to D. Mackowski for making his superposition T-matrix code publicly available.

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Appendix

Rayleigh-Gans scattering for a spherical particle is an extension of Rayleigh scattering to particle sizes larger than molecules by taking into account the interference effect from all elements at different positions in a sphere. In order to apply to particles for the real index of refraction $m_r \gg 1$, we have replaced the factor $(m-1)^2$ in the Rayleigh–Gans scattering intensity [21] by the exact formula for polarizability given by $(9/4)|(m^2-1)/(m^2+2)|^2$such that

$$I^{RG} = \frac{k^4 a^6}{2r^2}\left|\frac{m^2-1}{m^2+2}\right|^2 I_0 G^2(u)(1+\cos^2\theta), \tag{A1}$$

where a is the radius of a sphere, $k=2\pi/\lambda$, λ is the wavelength, r is the distance from the scattering particle to an observation point, $m(=m_r-im_i)$ is the complex refractive index, where m_r and m_i are the real and imaginary parts, $i=(-1)^{1/2}$, I_0 is the incident intensity, and θ is the scattering angle. According to Gans [22], the factor $G(u)$ is given by

$$G(u) = \frac{3}{u^3}(\sin u - u\cos u), \tag{A2}$$

where u is given by $2x\sin(\theta/2)$ and x is the size parameter ka. Integrating Eq. (A1) over all directions, we obtain the scattering cross-section:

$$C_{sca}^{RG} = \frac{1}{I_0}\int I^{RG} r^2 d\Omega = \pi k^4 a^6 \left|\frac{m^2-1}{m^2+2}\right|^2 \int_0^\pi G^2(u)(1+\cos^2\theta)\sin\theta\, d\theta. \tag{A3}$$

The asymmetry factor is defined by

$$g = \frac{\int_0^\pi I^{RG}\cos\theta \sin\theta\, d\theta}{\int_0^\pi I^{RG}\sin\theta\, d\theta}. \tag{A4}$$

Because the interference effect does not affect absorption, the absorption cross-section for Rayleigh–Gans scattering is the same as that for Rayleigh scattering in the form

$$C_{abs}^{RG} = -3kV\,\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right), \tag{A5}$$

where V is the volume.

For an aggregated particle consisting of N_s spheres, we may define a form factor F as the ratio of the scattered intensity for N_s spheres to that for a single sphere. Debye [23] developed a form factor F in the form

$$F = \sum_{j=1}^{N_s}|e^{i\mathbf{q}\cdot\mathbf{r}_j}|^2 = \sum_{j=1}^{N_s}\sum_{k=1}^{N_s} e^{i\,\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)} = \sum_{j=1}^{N_s}\sum_{k=1}^{N_s}\cos(\mathbf{q}\cdot\mathbf{r}_{jk})$$
$$= \sum_{j=1}^{N_s}\sum_{k=1}^{N_s}\cos(|\mathbf{q}||\mathbf{r}_{jk}|\cos\eta), \tag{A6}$$

where $\mathbf{q}$ is the scattering wave vector and its magnitude is given by $|\mathbf{q}| = 2k\sin(\theta/2)$, $|\mathbf{r}_{jk}| = |\mathbf{r}_j - \mathbf{r}_k| = r_{jk}$, where $\mathbf{r}_j$ and $\mathbf{r}_k$ are the position vectors of the primary spheres, and η is an angle between $\mathbf{q}$ and $\mathbf{r}_{jk}$. Each primary sphere is governed by the Rayleigh–Gans scattering and to a good approximation, it can be considered to be independent of other primary spheres. When an ensemble of aggregates is oriented randomly, we obtain

$$I^{RGD} = \int_0^1 I^{RG} F d\cos\eta \cong I^{RG}\int_0^1 F d\cos\eta = I^{RG}\overline{F}, \tag{A7}$$

where

$$\overline{F} = \int_0^1 F\, d\cos\eta = \sum_{j=1}^{N_s}\sum_{k=1}^{N_s}\int_0^1 \cos(|\mathbf{q}||\mathbf{r}_{jk}|\cos\eta)\, d\cos\eta$$
$$= \sum_{j=1}^{N_s}\sum_{k=1}^{N_s}\frac{\sin[2kr_{jk}\sin(\theta/2)]}{2kr_{jk}\sin(\theta/2)}. \tag{A8}$$

Accordingly, the scattering cross-section is given by

$$C_{sca}^{RGD} = \pi k^4 a^6\left|\frac{m^2-1}{m^2+2}\right|^2 \int_0^\pi G^2(u)(1+\cos^2\theta)\overline{F}\sin\theta\, d\theta. \tag{A9}$$

The absorption cross-section is simply N_s times of the Rayleigh absorption cross-section given by

$$C_{abs}^{RGD} = N_s C_{abs}^{RG} = -3N_s kV\,\mathrm{Im}\left(\frac{m^2-1}{m^2+2}\right). \tag{A10}$$

The preceding Eqs. (A7)–(A10) constitute the Rayleigh–Gans–Debye (RGD) approximation for size parameters smaller than about 2.

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