Journal of Quantitative Spectroscopy & Radiative Transfer 133 (2014) 374–381

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Effects of multiple scattering on radiative properties of soot fractal aggregates

Jérôme Yon [a,*], Fengshan Liu [b], Alexandre Bescond [a], Chloé Caumont-Prim [a], Claude Rozé [a], François-Xavier Ouf [c], Alexis Coppalle [a]

[a] UMR 6614 CORIA, CNRS, Université et INSA de Rouen, BP12, 76801 Saint Etienne du Rouvray cedex, France
[b] Black Carbon Metrology, Measurement Science and Standards, National Research Council, Ottawa, Ontario, Canada
[c] Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, SCA, LPMA, Gif-Sur-Yvette 91192, France

ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form
10 July 2013
Accepted 30 August 2013
Available online 7 September 2013

Keywords:
Light scattering
Soot fractal aggregates
Multiple scattering
GMM
DDA
RDG-FA

ABSTRACT

The in situ optical characterization of smokes composed of soot particles relies on light extinction, angular static light scattering (SLS), or laser induced incandescence (LII). These measurements are usually interpreted by using the Rayleigh–Debye–Gans theory for Fractal Aggregates (RDG-FA). RDG-FA is simple to use but it completely neglects the impact of multiple scattering (MS) within soot aggregates. In this paper, based on a scaling approach that takes into account MS effects, an extended form of the RDG-FA theory is proposed in order to take into account these effects. The parameters of this extended theory and their dependency on the number of primary sphere inside the aggregate ($1 < N_p < 1006$) and on the wavelength ($266\text{ nm} < \lambda < 1064\text{ nm}$) are evaluated thanks to rigorous calculations based on discrete dipole approximation (DDA) and generalized multi-sphere Mie-solution (GMM) calculations. This study shows that size determination by SLS is not distorted by MS effect. On the contrary, it is shown that fractal dimension can be misinterpreted by light scattering experiments, especially at short wavelengths. MS effects should be taken into account for the interpretation of absorption measurements that are involved in LII or extinction measurements.

1. Introduction/theoretical background

Soot particles are well known for their toxicological impact due to their ultrafine size and content in carcinogenic molecules (PAH) [1] and for their strong influence on global warming [2]. These particles appear as aggregates composed of primary spheres with optical properties similar to the graphitic carbon. Their specific spatial layout permits to establish a fractal like behavior, i.e., a power law relationship between the aggregate mass m and its gyration radius R_g [3–6]

$$m \propto N_p = k_f \left(\frac{2R_g}{D_p}\right)^{D_f} \tag{1}$$

In this equation, N_p is the number of primary spheres in the aggregate and D_p is the diameter of the primary spheres, D_f and k_f are respectively the fractal dimension and prefactor which permit to define the aggregates morphological properties. There is a rise in the use of optical diagnostics for in situ characterization of soot particles. Indeed, measurement of light extinction by soot particles is often considered as a reliable and convenient way to determine soot volume fraction. Laser induced incandescence (LII) has also been widely used to measure soot volume fraction in many applications or to evaluate the wavelength dependence of soot radiative properties [7,8]. However, light extinction yields no soot particle size information and LII is potentially able to provide primary soot particle size information, but not aggregate size or soot morphology. Angular light scattering is usually used to determine the particle size or fractal dimension D_f (morphological parameter) with the help of the Rayleigh–Debye–Gans theory

* Corresponding author. Tel.: +33 232953630; fax: +33 232953794.
E-mail address: yon@coria.fr (J. Yon).

0022-4073/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jqsrt.2013.08.022

for fractal aggregates (RDG-FA) [9–11]. The RDG-FA theory predicts that light absorption is proportional to the number of primary spheres in the aggregates (proportional to the particle volume) and the light scattering to N_p^2 [12,13]:

$$C_{abs}^a = N_p \frac{4\pi x_p^3}{k^2} E(m) \quad \text{with } x_p = \frac{\pi D_p}{\lambda},\ k = \frac{2\pi}{\lambda} \quad \text{and}$$
$$E(m) = Im\left(\frac{m^2-1}{m^2+2}\right)$$
$$C_{sca}^a = N_p^2 \frac{8\pi x_p^6}{3k^2} F(m) g(kR_g, D_f) \quad \text{with } F(m) = \left|\frac{m^2-1}{m^2+2}\right|^2$$
$$\frac{dC_{vv}^a}{d\Omega} = N_p^2 \frac{x_p^6}{k^2} F(m) f(qR_g, D_f) \quad \text{with } q = \frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) \qquad (2)$$

In these equations C_{abs}^a, C_{sca}^a and $dC_{vv}^a/d\Omega$ are respectively the aggregate absorption, total scattering and angular scattering for vertical–vertical polarization cross sections. E and F are the absorption and scattering functions depending on the optical index m, λ is the wavelength of the incident light source and θ is the scattering angle. Different expressions of the g and f functions can be found in the literature [14] including the ones defined by Dobbins and Megaridis [12]:

$$g = \left(1 + \frac{4}{3D_f}(kR_g)^2\right)^{-D_f/2}$$
$$f = \exp\left(-\frac{1}{3}(qR_g)^2\right) \quad \text{if } (qR_g)^2 < 1.5D_f \text{ (Guinier regime)} \quad \text{and}$$
$$f = \left(\frac{3D_f}{2e}\frac{1}{(qR_g)^2}\right)^{D_f/2} \quad \text{if } (qR_g)^2 \geq 1.5D_f \text{ (Power law regime)} \qquad (3)$$

The f function permits the description of the angular dependency of the scattered intensity by fractal aggregates and is of key importance for the determination of the particle size or fractal dimension by the angle resolved light scattering method.

The simplicity of the RDG-FA theory comes from several important hypotheses that are made in the development of this theory. The first one requires that primary spheres are in the Rayleigh limit, implying that the optical index and the primary sphere size have to be such that the phase shift hypothesis $|m-1| \ll 1$ and $2x_p|m-1| < 1$ is satisfied and $x_p \ll 1$ [15]. Second, each primary sphere is supposed to be exposed to the incident light source and multiple scattering inside the aggregate is assumed negligible. Indeed, by neglecting internal multiple scattering, the structure factor f can be derived numerically from the knowledge of the autocorrelation function by applying Fourier transform [16].

Despite these important hypotheses, many studies dealing with the optical characterization of soot aggregates employed the RDG-FA theory to interpret the detected light scattering signals. This was supported by several numerical studies that evaluated the accuracy of RDG-FA [13,17–20] and experiments that showed that the RDG-FA theory appears to be reasonably reliable relative to the experimental uncertainties [21–23]. Nevertheless, several studies have demonstrated that the RDG-FA theory often give rise to 10–30% error in the prediction of soot absorption and scattering properties [14,18–20,24]. Because of the complex morphology of these particles, the accurate evaluation of their radiative properties is difficult and time consuming [25]. Interpretation or inversion of optical data by the use of look up tables generated using numerical results from exact numerical approaches is impractical since the number of parameters involved is too large (primary sphere diameter D_p, fractal dimension D_f and prefactor k_f, wavelength λ, soot size distribution, optical index m). For these reasons, it is highly desirable to employ a simple yet accurate theory, naturally an extended RDG-FA theory based on extensive accurate numerical results, in the interpretation of the detected angle resolved scattering signals or extinction measurements to infer morphological parameters and soot concentrations.

The role played by MS on the scattered intensity was considered negligible for $D_f < 2$ by Berry and Percival [26] and important (within 10%) "*when parameters appropriate to soot are used*" following the results of Nelson [27]. The same order of magnitude of MS effects was found by di Stasio and Massoli [28]. Chen et al. [17] also shown by a numerical study that MS can alter the magnitude of the scattered intensity but not the slope of the structure factor in the power law regime. This is in agreement with the experimental observations by Cai et al. [29] who compared D_f determined by angular light scattering and by TEM analysis. They found similar results; however, they also recognized that a possible difference between the two methods could exist, though the difference cannot be clearly distinguished due to the different uncertainties in the two methods and the small size of the considered aggregates. Nevertheless, a shift between the theoretical D_f (RDG-FA) and the one deduced from accurate numerical light scattering results has been observed by Brasil et al. [30], by Farias et al. [31] who considered a "*possible artifact of the computer-simulated aggregates*" and also by Yon et al. [20] who attributed that effect to MS. This effect is illustrated in Fig. 1 by comparing the structure factor f determined by the rigorous numerical calculations using DDA approach (described in the next section) shown in

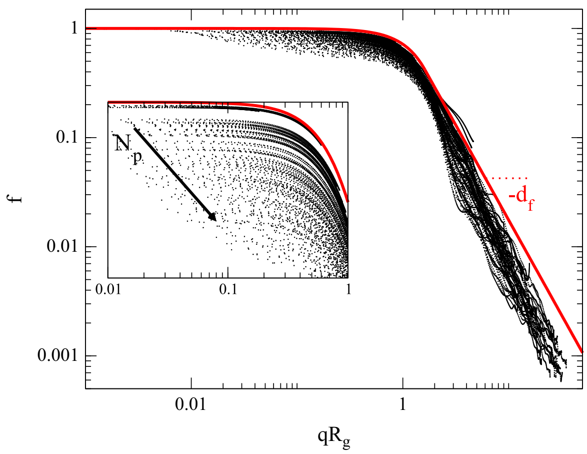

Fig. 1. Comparison between rigorous calculations (DDSCAT, black dots) of aggregate structure factor $f = I_{vv}(\theta)/N_p^2(x_p^6/k^2)F(m)$ and prediction by RDG-FA theory (solid red lines) at $\lambda = 266$ nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)