Journal of Quantitative Spectroscopy & Radiative Transfer 126 (2013) 130–139

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Numerical investigation of the possibility to determine the primary particle size of fractal aggregates by measuring light depolarization

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ARTICLE INFO

Article history:
Received 15 June 2012
Received in revised form
11 October 2012
Accepted 12 October 2012
Available online 26 October 2012

Keywords:
Depolarization
Static light scattering
Fractal aggregates
Primary sphere
Overlapping
Necking
DDA

ABSTRACT

In this paper, depolarization of light $\rho = I_{vh}/I_{vv}$ by fractal aggregates of nanoparticles is considered as a possible way to infer the primary particles radius R_p. A numerical study makes it possible to evaluate the impact of optical and morphological parameters of fractal aggregates (number and size of primary spheres, fractal dimension, overlapping and necking effects) on depolarization ratio and a model is proposed. It appears that for large aggregates, an asymptotic behavior of the depolarization ratio as a function of qR_p ($q = 4\pi/\lambda \times \sin(\theta/2)$) is established promoting the experimental measurement of R_p. Nevertheless, there is evidence that particle anisotropy, optical index, primary sphere overlapping and necking effects strongly impact the depolarization ratio. By taking into account all these parameters, a good correspondence is found between experimental and numerical results.

1. Introduction

The characterization of nanoparticles fractal aggregates has given rise to numerous investigations in the past. Indeed, it is crucial to be able to evaluate the emission of nanoparticles at their source in terms of mass or volume fraction. The size is also a key parameter in determining their optical properties for in-situ metrology development and in evaluating their capacity to be captured in the bronchi. Different quantities are used to characterize the particle size, depending on the measurement technique: (i) gyration radius can be determined by TEM images analysis [1,2], angular light scattering [3–5], (ii) mobility diameter can be determined by ex situ scanning mobility measurements, and (iii) aerodynamic diameter can also be determined using impaction measurements [6]. But whatever its definition, the global size is not enough to characterize the complex shape of the aggregate. The number N_p of primary particles, the diameter of the primary particles D_p and the fractal dimensions are essential quantities. Primary sphere diameter can be determined by observing TEM (Transmission Electron Microscopy) images but this method is ex situ, expensive and implies the sampling and storage of the particles [7] which induce inevitable structural changes. An in situ optical technique can also be used for measuring D_p leading to a better accuracy (for example, Small Angle X-Ray Scattering [8–10]). This technique has limitations and cannot be used in industry. Laser-Induced Incandescence (LII) is another technique, which is sensitive to primary particle size: it has been shown that the decay of the signal is correlated to D_p [11–13]. This experimental method, although appealing, needs a complex model taking into account many thermodynamical parameters to deduce D_p leading to a difficult interpretation of the signals [14].

It is therefore crucial to develop another transportable, simple optical method enabling the in situ determination

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http://dx.doi.org/10.1016/j.jqsrt.2012.10.011

of the primary sphere diameter. Measurement of the ratio of depolarization of the light by aggregates is potentially a good candidate. Indeed, whereas the theory of light interaction with fractal aggregates (Rayleigh Debye-Gans Theory for Fractal Aggregates, RDG-FA) predicts that polarized intensities $I_{hv}=I_{vh}=0$, experimental measurements show the existence of non-zero angular scattering of such intensities [15].

Different depolarization parameters can be defined by combining polarized intensities with vertical–vertical scattered signal (I_{vv}) or horizontal–horizontal one (I_{hh}). For example, di Stasio [16] measured the ratio I_{hv}/I_{vv} whereas Lu et al. [17] proposed the following ratio:

$$\rho = I_{vh}/I_{vv} \quad (1)$$

Since the reciprocity theorem [18] suggests $I_{hv}=I_{vh}$, these two definitions are supposed to be equivalent. Nevertheless, di Stasio [16] provided experimental evidence that the reciprocity theorem does not apply for certain degrees of agglomeration. Francis et al. [19] used a non-polarized incident laser beam and defined another parameter related to the depolarization effect called *degree of linear polarization*. Sun et al. calculated a depolarization definition close to Eq. (1) for aggregates of 2 and 4 spheres and Gaussian deformed spheres [20]. The results show that depolarization ratio is small at forward light scattering and larger at backscattering direction, especially for larger particles. Because of the diversity of parameters defining depolarization, the comparison between various authors remains difficult. Nevertheless, some of these studies indicate an impact of D_p on the amount of depolarized light scattering [19,21]. In the present work, prior to any numerical study, experimental measurements of depolarization have been performed in order to verify this impact. Fig. 1 presents the measured depolarization ratios defined by Eq. (1) for two aerosols characterized by very different sizes of primary spheres ($D_{p,Soot}=34.2$ nm for ethylene soot and $D_{p,Palas}=6.4$ nm for PALAS aggregates), as a function of the dimensionless parameter qR_p $(q=4\pi/\lambda\times\sin(\theta/2), R_p=D_p/2)$ (see Appendix A for the experimental details). In Fig. 1, we first observe that depolarization is an increasing function of qR_p

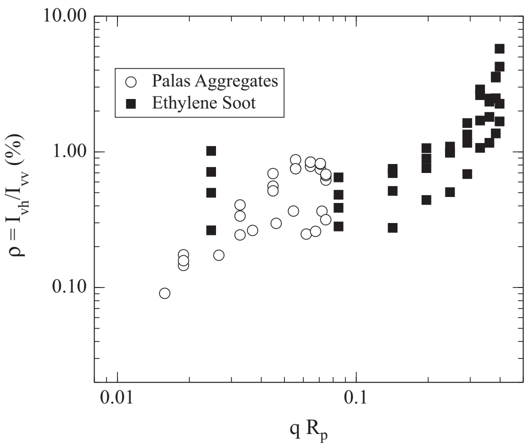

Fig. 1. Experimental depolarization measurements on ethylene soot and PALAS aggregates.

indicating that depolarization is an increasing function of the scattering angle. Secondly, we can see that the highest value determined for ethylene soot is larger than the highest value determined for PALAS GFG 1000 particles according to $D_{p,Soot} > D_{p,Palas}$. Finally, we observe that, when depolarization is represented as a function of qR_p, both experimental curves are globally superimposed.

This preliminary experiment suggests that for a fixed wavelength and scattering angle, the measured depolarization ratio could be used for determining the primary particle size. Nevertheless, the present experiment focuses on the role played by the primary particle size and does not permit to show, by an experimental approach, a possible dependence of the depolarization ratio on other physical parameters. However, using a numerical approach based on DLCA (Diffusion Limited Cluster Aggregation) aggregates and electric-dipole-induced-dipole calculations, Lu and Sorensen [17] showed, at constant scattering angle ($\theta=20^\circ$) by changing the number of primary spheres in the aggregates ($3\le N_p \le 98$), a power law dependency of the depolarization ratio to the number of primary particles

$$\rho \propto N_p^{-x} \quad \text{with } x = 0.6 \pm 0.1 \quad (2)$$

And, by comparison, the same authors observed a weak dependency (0.1%) of the depolarization ratio on a change of the primary diameter ($20\text{ nm} \le D_p \le 60\text{ nm}$). Additionally, Lu and Sorensen [17] observed that experimentally determined depolarization exceeded the numerical prediction by a factor of 8. They attributed this over-estimation to the non-point contacts or necking between monomers in real soot clusters. These results underline the fact that ρ does not only depend on D_p, which makes difficult the use of empirical relationships between ρ and D_p as the one proposed by di Stasio [21] and also the one shown in Fig. 1. The objective of this paper is to clarify the possibility of the quantitative determination of the aggregates' primary particle diameter from depolarization measurements.

The second section of this paper is devoted to listing the different parameters involved in the process of depolarization by fractal aggregates. A simple model of depolarization is also proposed. The numerical set up for generation of aggregates and depolarization calculations is described in the third section. The main results are presented in Section 4 by showing the impact on depolarization ratio defined in Eq. (1) of the aggregate compactness (fractal dimension D_f), number of primary spheres N_p, optical index m, primary particle diameter D_p (or corresponding radius R_p), wavelength λ and scattering angle θ, overlapping effect C_{ov} and necking effects α. The paper ends with a final conclusion.

2. Model of depolarization

Lu and Sorensen [17] explained that depolarization is a process driven by a multi-scattering phenomenon. By changing the scattering volume and the wavelength, they found that the intra-cluster multiple scattering is the source of the depolarization and that the interaction between various aggregates has no effect on depolarization. When a primary sphere "*i*" is exposed to light, part of this light is scattered in the whole space, and illuminates others primary spheres "*j*" contributing to the depolarization of the scattered light by