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Effect of structure factor on aggregate number concentration estimated using Rayleigh–Debye–Gans scattering theory

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We suggest that the structure factor could be a source of uncertainty when the number concentration of non-absorbing aggregate particles is experimentally determined from Rayleigh–Debye–Gans (RDG) scattering theory. Different characteristics of various structure factors have been examined as a function of qR_g. We present deviation of various structure factors from the exponential structure factor. Number concentrations estimated from various structure factors differ in the range of $1.0 < qR_g < 10$ where most of flame-synthesized non-absorbing particles are present as aggregates. We compare aggregate number concentrations of silica particles determined using various structure factors.

Keywords: Rayleigh–Debye–Gans (RDG) scattering, aggregate particles, non-absorbing particles.

1. Introduction

Aggregate volume fraction and number concentration are important parameters in the field of nanoparticle generation using flame synthesis as they should be controlled for mass production and quality control. Industrially, for example, silica particles are widely used in the optical fiber manufacturing process such as outside vapor deposition (OVD), chemical vapor deposition (CVD) and the vapor-phase axial deposition (VAD). The number concentration of silica particles should be determined since it is directly related to the production rate. The aggregate volume fraction is calculated from the aggregate number concentration and the aggregate particle size which are measured using Rayleigh–Debye–Gans (RDG) light scattering theory. The uncertainty of the value of aggregate number concentration and volume fraction has been an issue for two decades [1–7]. Specifically, ZHAO and MA [6] have suggested applicable range of RDG light scattering theory for calculating the Mueller scattering matrix of soot aggregates. The valid range for the RDG light scattering theory is applicable for soot characterization by light scattering [7]. To better understand the uncertainty associated with RDG light scattering theory, we investigate the influence of various structure factors on the aggregate number concentration of silica particles.

2. Theory

Structure factor S is defined as a light scattering intensity I normalized by the square of the number N_p of primary particles included in an aggregate. Thus, the structure factor is proportional to the scattering intensity as:

$$S(q) = \frac{I(q)}{N_p^2} = \frac{\left| \sum_{i=1}^{N} e^{i\mathbf{q}\mathbf{r}_i} \right|^2}{N_p^2} \tag{1}$$

The magnitude of the scattering wave vector **q** is denoted as q [5].

Structure factor can be obtained from experimental intuition as well as derived from explicit mathematical formula. For example, FISHER and BURFORD derived a structure factor shown below Eq. (2) by investigating the scattering wave at a critical point [8]

$$S(u) = \left(1 + \frac{2}{3D_f} u^2\right)^{-D_f/2} \tag{2}$$

where D_f is the fractal dimension and u is defined as qR_g, where R_g is the radius of gyration. Equation (2) is called as a modified Ornstein–Zernike form [9]. Structure factors show unique characteristics depending on qR_g (= u). For $u \ll 1$, the structure factor is approximated to the Guinier equation which allows us to determine the radius of gyration. For $u \gg 1$, the structure factor is approximated to power-law formula which enables us to find the fractal dimension. DOBBINS and MEGARIDIS [10] suggested a well-known structure factor as follows:

$$S(u) = \begin{cases} \exp\left(-\frac{u^2}{3}\right) & u^2 < 1.5D_f \\ \left(\frac{\sqrt{2e}\, u}{\sqrt{3D_f}}\right)^{-D_f} & u^2 > 1.5D_f \end{cases} \tag{3}$$

Equation (3) is widely used to determine the fractal dimension and the radius of gyration for aggregate particles. For small u, structure factor is simply expanded to $S(u) = 1 - u^2/3$. For large u, an explicit aggregate density autocorrelation function is used. An aggregate density autocorrelation function depends on the cut-off function, which mathematically describes the boundary of aggregate. Note that the cut-off function determines the extent of growth of aggregate. An aggregate density autocorrelation function also depends on fractal nature. The cut-off function is related to the relative distance of spherules on imaginary surface from the center of an aggregate.

As the cut-off function becomes sharper, the aggregate structure becomes more compact. The structure factor is expressed as follows

$$S(q) = \int g(\zeta) \frac{\sin(q\zeta)}{q\zeta} 4\pi\zeta^2 \mathrm{d}\zeta \tag{4}$$

where the aggregate density autocorrelation function is given as $g(r) \sim r^{D_f - d} C(r/\zeta)$ and the cut-off function is given as $C(r/\zeta) = e^{-(r/\zeta)^\beta}$.

Structure factor obtained from an exponential cut-off function ($\beta = 1$) is shown in the following equation [9, 11, 12]:

$$S(u) = \frac{\sin\left[(D_f - 1)\tan^{-1}\left(\sqrt{\frac{2}{D_f(D_f+1)}}\, u\right)\right]}{(D_f - 1)\sqrt{\frac{2}{D_f(D_f+1)}}\, u\left(1 + \frac{2}{D_f(D_f+1)} u^2\right)^{(D_f-1)/2}} \tag{5}$$

SORENSEN *et al*. [1] proposed a Gaussian cut-off function ($\beta = 2$). To obtain the structure factor using a Gaussian cut-off function, one should take a Fourier transform of the aggregate density autocorrelation function. The structure factor is analytically given as

$$S(u) = {}_1F_1\left[\frac{D_f}{2}, \frac{3}{2}; -\frac{u^2}{D_f}\right] \tag{6}$$

where ${}_1F_1$ is the Kummer confluent hypergeometric function [1]. The Gaussian cut-off function has a sharper decline than the exponential cut-off function, which implies that the effect of stretching growth of an aggregate is hardly reflected for the case of the Gaussian cut-off function. The structure factor simulated using the Gaussian cut-off function at $D_f = 3.0$ gives an asymptotic curve to the RDG light scattering intensity for a spherical particle [5].

3. Results and discussion

When it comes to the scattering intensity I derived from the RDG light scattering theory for spherical particle, periodic humps appear as u increases more than the value of 3. Since the u value from the flame-synthesized particles at the measurement angle of 90° ranges from 1 to 10, these humps can cause a significant error in the calculation of the aggregate number concentration for non-spherical particles. Usually, flame--generated particles are not spherical particles but aggregate particles, thus we need to introduce a light scattering theory for aggregate particles. Even small molecules can

be studied using RDG light scattering theory [13]. Aerosol physical properties even in the coastal area can also be studied using the RDG light scattering theory [14].

As described earlier, structure factors highly depend not only on the fractal dimension but also on the radius of gyration. The shape of the Fisher–Burford structure factor is smooth in all regime of u. Such a simple shape of the structure factor is one of the reasons why the Fisher–Burford formula is extensively used to determine the gyration radius and the fractal dimension. The structure factor with the exponential cut-off function showed similar trend to the Fisher–Burford structure factor. This is due to the fact that Fisher–Burford formula has the same form as the exponential structure factor when D_f is equal to 2. We calculated the deviations of each structure factor from the exponential structure factor. Figure 1 shows that the structure factors behave differently even though they are calculated with the same fractal dimension. The different behavior of each structure factor leads to the uncertainty of aggregate number concentration. Note that the slopes in the region of $qR_g \gg 1$ for each structure

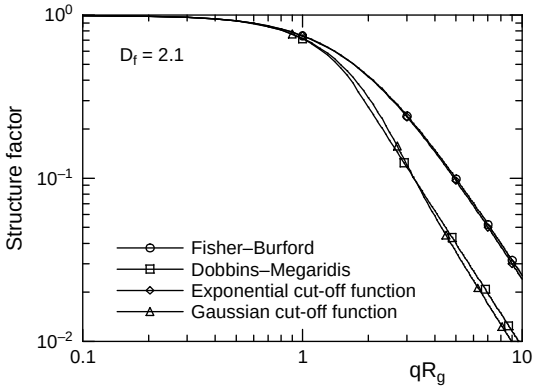

Fig. 1. Various structure factors for the case of D_f = 2.1. The circle, square, rhombus and triangle are indicators that distinguish each model.

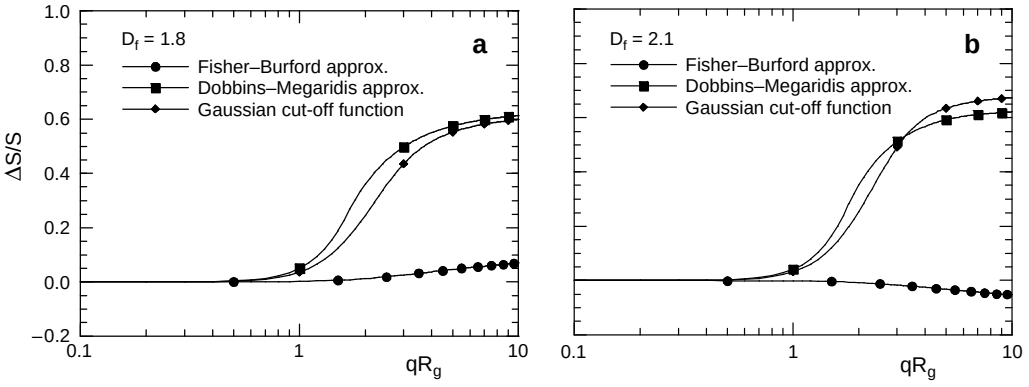

Fig. 2. Deviations of various structure factors from exponential structure factor: D_f = 1.8 (**a**), D_f = 2.1 (**b**). The circle, square and rhombus are indicators that distinguish each model.

factor are the same since the slope approximates to the fractal dimension as qR_g increases.

Figure 2 shows that the Fisher–Burford structure factor is slightly larger than the exponential structure factor for aggregate particles with D_f = 1.8 and the deviation does not exceed about 10%. For aggregate particles with D_f = 2.1, on the other hand, the exponential structure factor is larger than the Fisher–Burford structure factor. The Dobbins–Megaridis structure factor and the Gaussian structure factor are deviated from the exponential structure factor more than 50% as qR_g increases. The volume fraction calculated by multiplying the number concentration and the aggregate particle volume can be different depending on the structure factor.

The number concentration of non-absorbing aggregate particles is usually obtained from the scattering intensity which is proportional to structure factor. Thus, the deviation of volume fraction is easily estimated from the ratio of structure factors. Figure 3 definitely shows that the aggregate number concentration is apt to change depending on which structure factor is used. The value of qR_g for the flame-generated silica aggregate particles ranges from about 1.0 to 10 at the measurement scattering angle of 90°. Structure factors dramatically change in this range, thus a proper structure factor should be used when calculating aggregate number concentration and aggregate volume fraction by using RDG light scattering theory. The aggregate number concentrations were measured at various positions using RDG scattering theory with various structure factors.

Figure 4 demonstrates that the aggregate number concentration measured from the scattering intensity of silica particles generated in counterflow diffusion flame highly depends on the structure factors. Radius of gyration (R_g) of the silica particles was measured at every position by the analysis of images obtained from transmission electron microscope. As can be seen in Fig. 4, the aggregate number concentration estimated using the Gaussian structure factor is nominally twice larger than that estimated using the exponential structure factor. Since Dobbins and Megaridis (DM) structure factor has been extensively used due to its simplicity, it is suitable for

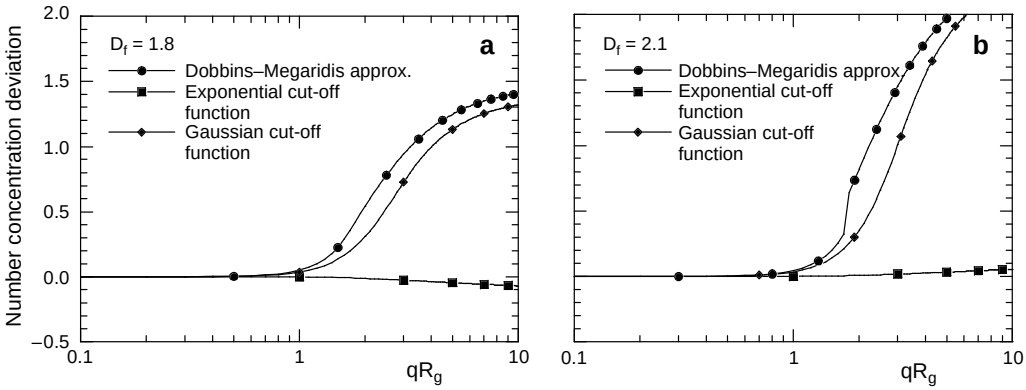

Fig. 3. Deviations of number concentration from exponential structure factor: D_f = 1.8 (**a**), D_f = 2.1 (**b**). The circle, square and rhombus are indicators that distinguish each model.

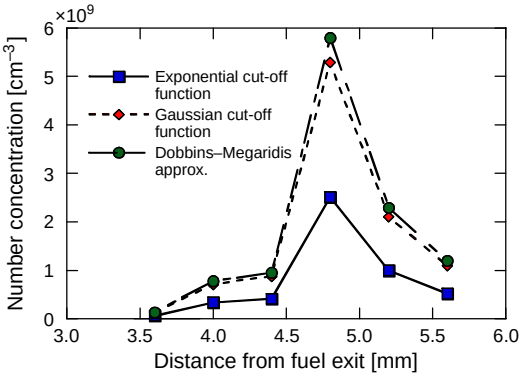

Fig. 4. Dependence of aggregate number concentration on various structure factors for silica particles at various positions.

choosing the DM structure factor for the analysis of silica particles. However, the DM structure factor has two different forms depending on qR_g. It would be recommended that the continuous structure factor providing similar results to the DM structure factor be chosen. Among structure factors investigated in this study, the Gaussian structure factor best fits the DM structure factor. In summary, structure factor should be properly selected and specified for better estimation of particle characteristics such as an aggregate number concentration and a volume fraction. The question about the selection of structure factor remains open and requires a further study.

4. Conclusions

We report that different structure factors could be a source of uncertainty when the number concentration of non-absorbing aggregate particles is experimentally determined from Rayleigh–Debye–Gans (RDG) light scattering theory. Various structure factors were compared in the range of qR_g from 1.0 to 10. Structure factors dramatically change in this range, so that a proper structure factor should be used when aggregate number concentration and the aggregate volume fraction of non-absorbing particles are calculated by using RDG light scattering theory.

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