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On the impact of the internal coupling on Fractal Aggregates structure factors

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Abstract

Angular light scattering by aerosol particles, including complex particles such as fractal aggregates, can give access to the size and morphology through an *in-situ* approach. For this purpose, the angular scattering signal must be processed by a theory that provides a structure factor, which takes into account particle shape. Such a function is accurately determined for X-rays or for transparent objects in the visible range since the assumption of no internal coupling is fairly well respected. However, for some materials such as fractal soot aggregates, the internal coupling is suspected to modify the morphological and size dependence of the structure factor. The objective of this work is to understand and quantify such a deviation from the internal electric field analysis using a phasor approach.

1 Context and motivations

Aerosols such as soot become a matter of concern in our daily life. Due to their impact on human health but also on global warming, their characterization is of extremely high relevance. Angular light scattering is a technique that enables the *in-situ* characterization of such particles in terms of size (radius of gyration R_g) as well as in terms of morphology (fractal dimension D_f) for fractal aggregates. For nano-aerosols, the Rayleigh-Debye-Gans (RDG) approximation for fractal aggregates (FA) is frequently used essentially due to its simplicity since it provides a simple analytical expression of the angular scattering pattern (called structure factor). However, this approximation implies two strong assumptions. First, the monomers composing the aggregate behave as Rayleigh spheres, i.e., they are small enough compared to the wavelength and transparent enough to make the phase shift negligible. Second, it is supposed that there is no electromagnetic coupling between the monomers, i.e., each one sees only the incident light and not the light scattered by its neighbors. As explained by Sorensen [1] when internal coupling is neglected, it is possible to link mathematically the structure factor to the particle pair-correlation by a simple Fourier transform.

Nevertheless, as shown by Yon *et al.* [2], in certain cases, as for Diesel soot particles, this approach can lead to errors up to 45% on the predicted forward scattering by RDG-FA and could alter the determination of the fractal dimension by a factor up to 10% since the slope in the power-law regime (large qR_g) can be affected (see Fig. 1). Conversely, the same authors concluded that the impact on the optical determination of radius of gyration is limited.

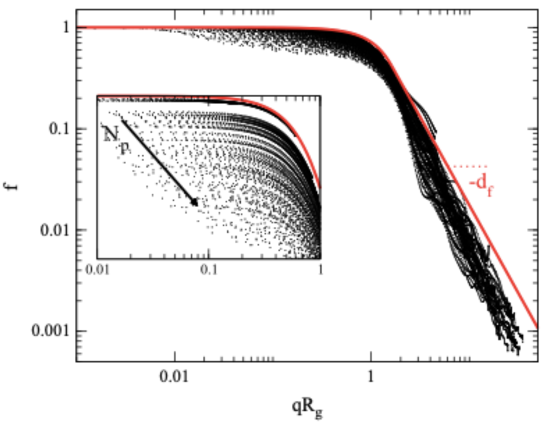

Figure 1: Comparison between rigorous calculations (DDSCAT, black dots) of aggregate structure factor f and prediction by RDG-FA theory (solid red lines) at λ=266 nm.

In a recent study [3], we have shown how the non-uniformity of the internal electric field affects the forward scattering using a phasor approach. The aim of the present study is to extend the phasor approach to understand how internal coupling affects the structure factor, in particular at large angles and especially at 180° as a better evaluation of the backscattering using the RDGFA is essential for lidar applications measuring smoke and soot plumes.

2 Phasor approach of the structure factor

According to [1], in respect of the RDG hypothesis, the scattered light at angle θ is proportional to the structure factor defined as

$$f = \frac{\sum_i^N \sum_j^N \exp\left[i\mathbf{q}.\left(\mathbf{r}_\mathrm{i} - \mathbf{r}_\mathrm{j}\right)\right]}{N^2} \tag{1}$$

where i denotes all the volume elements composing the aggregate and $\mathbf{q} = \mathbf{k}_\mathrm{i} - \mathbf{k}_\mathrm{s}$ is the scattered wave vector which depends on θ and on the wavelength λ. This expression is valid if the internal electric field is uniform. The non-uniformity generated by internal coupling can be quantified by a complex number called phasor which is proportional to the local internal electric field [4]:

$$z_{y,i}(\hat{\mathbf{x}}) = \frac{m^2+2}{3E_0} E_{y,i}^{\mathrm{int}}(\mathbf{r}_i) \exp(-ikx_i) \tag{2}$$

In this equation, $E_{y,i}^{\mathrm{int}}$ is the y-component of the local internal electric field and $\hat{\mathbf{x}}$ is the direction of propagation of the light, m is the complex refractive index, E_0 the amplitude of the incoming electric field and k the wavenumber. The phasor can be seen as the wavelet scattered by a volume element to the detector for a vertical polarization (along $\boldsymbol{y}$) of the incident and the scattered light "vv".

By developing the Volume Integral Equation based on the phasor formalism, one can express the structure factor according to the spatial distribution of the phasor (Ceolato and Berg [5] did it for backscattering). Here we retain the Eulerian expression of the phasor $z_y = \Lambda \exp(\Phi)$ to show that the classical expression of the structure factor Eq.(1) is finally decomposed into two terms when internal coupling is considered Eq.(2):

$$f_{\mathrm{IC}} = f_r - f_i \text{ with}$$

$$f_r = \frac{\sum_i^N \sum_j^N \Lambda_i \Lambda_j \cos(\Phi_i - \Phi_j) \cos[\mathbf{q}.(\mathbf{r}_\mathrm{i} - \mathbf{r}_\mathrm{j})]}{\sum_i^N \sum_j^N \Lambda_i \Lambda_j \cos(\Phi_i - \Phi_j)} \tag{3}$$

$$f_i = \frac{\sum_i^N \sum_j^N \Lambda_i \Lambda_j \sin(\Phi_i - \Phi_j) \sin[\mathbf{q}.(\mathbf{r}_\mathrm{i} - \mathbf{r}_\mathrm{j})]}{\sum_i^N \sum_i^N \Lambda_i \Lambda_i \cos(\Phi_i - \Phi_i)}$$

Without internal coupling ($\Lambda = 1$ and $\Phi = 0$), the first term corresponds to Eq.(1) and becomes purely morphology-dependent. This term is noted f_r because it remains when phasors are purely real. In turns, without internal coupling, the second term is null. It becomes non-null only if $\Phi \neq 0$ and varies in space, justifying the subscript "i" for "imaginary". It is therefore interesting to observe that the contribution tends to reduce the amplitude of the structure factor.

3 Numerical setup

All the presented results correspond to monodisperse DLCA aggregates composed of $N_\mathrm{m} = 284$ monomers with a radius $R_\mathrm{m} = 15$ nm, a fractal dimension $D_\mathrm{f} = 1.78$ and a fractal prefactor $k_\mathrm{f} = 1.44$. DDSCAT is used to compute the internal electric field over 500 orientations of the aggregates relatively to the incoming light source. While Figs. 5 and 6 correspond to a fixed random orientation of the aggregate, the remaining figures correspond to cases where the phasors are averaged over the considered orientations. The wavelength is set to $\lambda = 266$ nm because lower wavelengths favor multiple scattering effects. The impact of the refractive index is evaluated by considering $m = 1.1 + i0.01$, $m = 1.1 + i0.4$, $m = 1.1 + i0.8$ to study the effect of increasing $Im\{m\}$ and $m = 1.1 + i0.8$, $m = 1.5 + i0.8$, $m = 1.9 + i0.8$ to study the effect of increasing $Re\{m\}$.

4 Results

4.1 Structure factor contributions

Fig. 2 first validates the proposed methodology by comparing the structure factor directly provided by DDSCAT with the one reprocessed by the phasor approach f_{IC}. Indeed, both curves are perfectly superimposed.

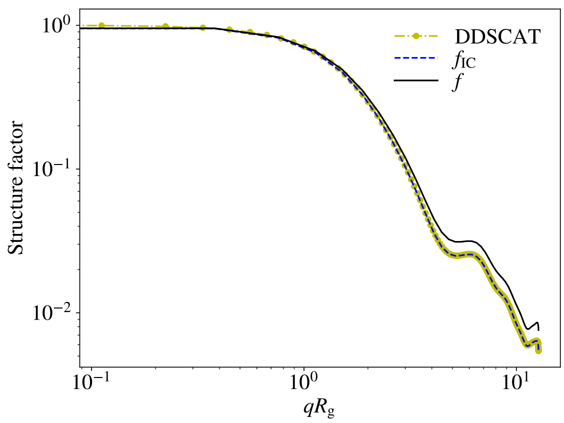

Figure 2: Comparison between DDSCAT calculation (circle marker) of aggregate structure factor and Eqs. (1) (solid line) and (3) (dashed line) for $m = 1.1 + i0.8$

This figure also reports the purely morphologically dependent structure factor f obtained by imposing the phasor to be 1 ($\Lambda = 1$ and $\Phi = 0$ in Eq.(2)). It appears that the inclusion of an internal coupling globally decreases the angular scattering amplitude, in particular at large scattering angles (large q). Moreover, since the fractal dimension is evaluated as the opposite of the slope in the power-law regime, it seems that internal coupling can provoke an over-estimation of the optically determined fractal dimension as previously suggested [2].

To better understand this phenomenon, let's study the relative departure of f_r and f_i to f. Fig. 3 shows the ratio f_r/f in the upper plot and f_i/f in the bottom plot for three different indices, $m = 1.1 + i0.01$ (in green dash dot line), $m = 1.1 + i0.4$ (in orange dot line) and $m = 1.1 + i0.8$ (in blue dashed line).

First, we observe that $f_\mathrm{i}/f\ (qR_\mathrm{g} = 0) = 0$. This explained by the term $\sin[\mathbf{q}.(\mathbf{r}_\mathrm{i} - \mathbf{r}_\mathrm{j})]$ which tends toward zero at small angles (see Eq.(3)). This term never exceeds 5% of deviation for the range of investigated qR_g and optical indices. At small scattering angles (Guinier Regime) f_r/f is close to 1. It is the reason why the gyration radius measurement is not so affected by internal coupling as already observed [2].

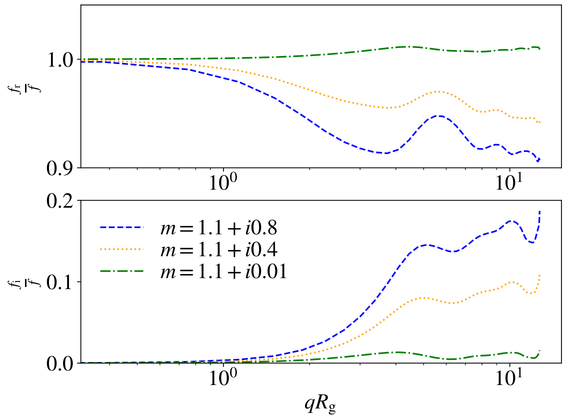

Figure 3: Deviation of f_r and f_i with respect to f for m=1.1+i0.01 (in green dash dot line), m=1.1+i0.4 (in orange dot line) and m=1.1+i0.8 (in blue dashed line).

Still, both terms play a role in the deviations at larger scattering angles. Indeed, f_r can reach 10% of deviation whereas f_i/f can be twice. Because $f_{IC} = f_r - f_i$, the maximum deviation for this aggregate can reach almost 30% at 180° showing the importance of internal multiple scattering for backward measurements as used for LIDAR. Note that, depending on the morphology of the aggregate the maximum deviation is not necessarily at 180°.

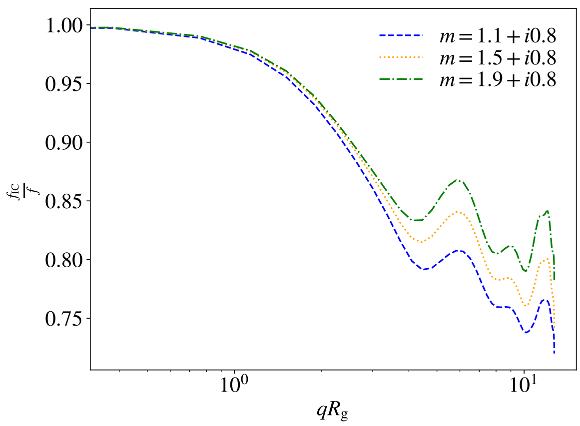

Figure 4: Deviation of f_IC with respect to f for m=1.9+i0.8 (in green dash dot line), m=1.5+i0.8 (in orange dot line) and m=1.1+i0.8 (in blue dashed line).

We also observe the role played by the imaginary part of the optical index. Indeed, the higher $Im\{m\}$ is, the more the deviation is important. In comparison, Fig. 4 shows the impact of the real part of the optical index ($m = 1.1 + i0.8$, $m = 1.5 + i0.8$ and $m = 1.9 + i0.8$).

It seems that the impact of the real part of the optical index is less important than the one induced by changing $Im\{m\}$ as the three curves are similar. From this observation, we conclude that $Im\{m\}$ have a predominant impact on the structure factor.

4.2 Physical interpretation

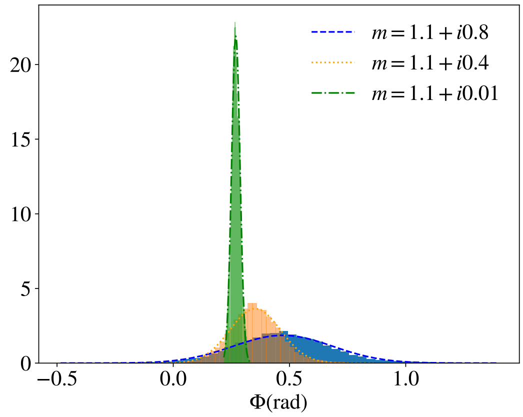

Figure 5: Probability density of the phase of the phasors for a fixed orientation of the aggregate for m=1.1+i0.01 (in green dash dot line), m=1.1+i0.4 (in orange dot line) and m=1.1+i0.8 (in blue dashed line).

According to Eq.(3) f_r and f_i are driven by the phasor amplitude Λ and its phase Φ. Fig. 5 reports the probability density of the phasors's phase Φ for a fixed orientation of the aggregate.

Indeed, this figure highlights an increase of the phase dispersion when $Im\{m\}$ is increased. Therefore, the more the phase dispersion is important the more $cos(\Phi_i - \Phi_j)$ will be weak, and inversely, the more $sin(\Phi_i - \Phi_j)$ will increase.

This explains the relative deviations of f_r and f_i. Absorbing materials favor internal trapping which increases the phase shift as the light propagates through the particle [3]. This provokes a dispersion of the phase at the origin of the deviation of the structure factor to the purely morphologically predicted one.

Similarly, Fig. 6 shows the probability density of the phasor amplitudes. It can be seen that the product $\Lambda_i\Lambda_j$ will decrease with $Im\{m\}$ as the average of Λ decreases due to absorption phenomena. As the amplitude decreases and the phase shift increases f_r will weaken with $Im\{m\}$, whereas f_i will increase. Nevertheless, as f_i varies in $sin(\Phi_i - \Phi_j)$ we can possibly encounter a case where the phase dispersion grows faster than the amplitude decreases, therefore, in such case f_i will not be necessary higher with $Im\{m\}$.

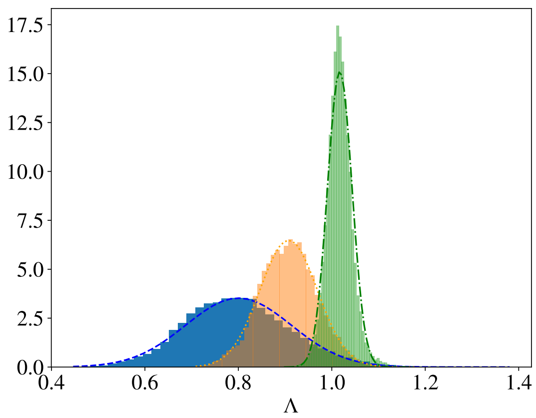

Figure 6: Probability density of the amplitude of the phasors for a fixed orientation of the aggregate for m=1.1+i0.01 (in green dash dot line), m=1.1+i0.4 (in orange dot line) and m=1.1+i0.8 (in blue dashed line).

Without phase dispersion, f_i would be equal to zero whatever the amplitude value is and f_r will almost overlap with f. Therefore, we can imagine cases where the indices created strong local amplitudes of the internal electric field, called "hot spots" without causing important trapping (decrease in amplitude and increase in phase along the direction of light propagation). In that case, forward scattering would be moderately affected but structure factor. Still, strongly absorbing material will promote internal trapping which alter significantly the structure factor, especially at large scattering angles.

5 Perspectives

The phasor analysis of the structure factor enables a decomposition of the structure factor into two distinct terms driven by the amplitude and phase dispersion of the internal electric field. This decomposition allows for the understanding of the impact of the internal multiple scattering on the angular light scattering pattern. This work has to be pursued in order to investigate the role played by fractal dimension and more complex morphologies (primary spheres polydispersion, overlapping, necking, coating…).

6 References

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