ADDRESSING THE CLASSIFICATION OF NON-SPHERICAL PARTICLES BY MEANS OF THE SPES TECHNOLOGY

INTRODUCTION

In characterizing particles for scientific and industrial applications, it is sometimes essential to consider their shape since it can impact the results obtainable with the most common instruments for particle analysis. Light scattering by particles is affected by several parameters, each of which gives its peculiar contribution. While size is the parameter that contributes most, others can be detected and identified if enough data is collected. Generally, the refractive index is the second most important characteristic affecting scattering, since together with the size it determines the optical thickness of the particle, i.e. its degree of interaction with the incoming light. However, this can be significantly altered by the shape and by the orientation of the particle under consideration. For example, a non-isometric shape can be responsible for a change in the effective particle refractive index which reaches values substantially lower than expected.

In this technical note, we focus on some significant examples of non-spherical particles that can be easily distinguished during data analysis. Some key points on how to recognize non-isometric particles are provided giving a comprehensive overview of the main effects and added values in particle classification and analysis through the data acquired by the EOS Classizer™ ONE.

PARTICLE ANALYSIS METHOD

Among the several methods currently adopted, optical ones have unique advantages and, therefore, have brought light scattering into the forefront of analytical methods in many scientific and industrial applications. Unfortunately, the number of parameters typically affecting the scattering properties of a given particle is such that the basic measure of the scattering power (or even the power removal from a light beam -extinction- from one particle) is far from being enough to recover something more than a rough estimate of its size. Things change appreciably when considering a collection of many scatterers, with the immediate drawback of introducing the need for mathematical inversion and ill-posed problems to interpret experimental real data.

EOS Classizer™ ONE – front view.

EOS Classizer™ ONE particle analyser is based on the patented Single Particle Extinction and Scattering (SPES) method. It introduces a step forward in the way light scattering is exploited for single particle characterization. EOS Classizer™ ONE provides data that go beyond the traditionally optical approaches by discriminating, counting, and analysing single particles through their optical properties. It retrieves to the user several pieces of information such as particle size distribution of the single observed populations, absolute and relative numerical concentrations, particle stability, information on optical particle structure, and oversize. Classizer™ ONE works offline and online/real-time, enabling the verification of the consistency of intermediate and final formulations with target QbD, SbD, and Quality Control target expectations.

For a general introduction to SPES data please refer to the Application Note AN001/2021, available online along with other application notes and examples of applications at EOS website: www.eosinstruments.com/publications/

NON-SPHERICAL PARTICLES

Particles may be cast into three main classes according to their overall shape: isometric (spherical), oblate, or prolate, depending on whether they are predominantly flat or elongated, respectively. The non-sphericity of prolate and oblate particles is quantified by the ratios of their main axes, known as the aspect ratio. The aspect ratio of a sphere is equal to "1" for our convention.

For spherical or primarily isometric particles, it is possible to compare data to the Lorentz-Mie theory to determine their (average) refractive index. As they deviate from the isometric form, however, some of their physical characteristics begin to dominate over the refractive index of the material of which they are composed, especially for larger particles. Although this means that it is much harder to strictly compare the data with theory, it is also an advantage from an experimental point of view. Indeed, this is an effective way of diagnosing non-spherical particles and improving the characterization of traditional sizing methods (Simonsen MF et al., Clim. Past 14, 2018).

Non-spherical particles, whether flat or oblate, do not strictly fall under the Lorentz-Mie theory, but the latter is nevertheless a useful model for two main reasons. It can provide an approximation of the population of particles with effective spherical-equivalent size and refractive index parameters, and more importantly, it serves as a benchmark to assess how much the sample under investigation deviates from the isometric case.

EOS Classizer™ ONE/SPES retrieves for each particle two scattering features: the Extinction Cross Section C^*_{ext}, and the Polarizability α^*. Values are reported on the log-log histogram EOS CLOUDS creating data clouds as the optical fingerprint of the particle populations in the sample. Please refer to application note AN001 for further details.

Useful estimations may be derived from the analysis of the clouds of non-spherical particles. From their precise location and vertical width, it is possible to investigate the shape of the particles, if their refractive index is known. Specifically, the higher the variability in shape the broader the distribution of optical thickness due to the many possible orientations of particles with respect to the laser beam, which results in a spread in α^* at any given value of C^*_{ext}. Moreover, the distribution is located higher in the plot than it would if the particles were spheres of the same material. The retrieved *effective* refractive index must thus be managed carefully when analyzing the data because its apparent value is altered by the shape of the particles.

APPLICATION EXAMPLES

Mineral particles are considered as an example of non-spherical particles in this document. An emulsion of olive oil is considered as the reference case for data generated by a polydisperse sample of spherical particles. We do not need a laboratory standard to suit our purpose of generating spherical particles.

1) Spherical particles: oil emulsion

In Figure 1 a typical emulsion of a small aliquot of olive oil in filtered water is presented. The data from such particles are distributed along an oblique line on the plane due to size polydispersity, however, the distribution is narrow because the variability of the optical thickness of a particle of any given size is low. The refractive index is well-defined, and the data compare well to Lorentz–Mie model (red line), which gives $n = 1.47$, as expected.

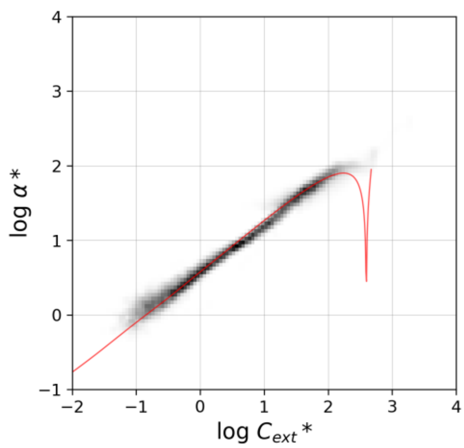

Figure 1 An example of the EOS CLOUDS from an emulsion of size-polydisperse oil droplets with n=1.47. The corresponding Lorentz–Mie model for spherical particles is shown with a red solid line. Notice that the distribution is very thin vertically since the variability of the optical thickness for any given size is low.

2) Non-Spherical particles: mineral particles

A significant example of non-isometric particles can be found in minerals. The particles considered here have a refractive index in the range of $n = 1.55 \pm 0.02$, like most species that can be found in airborne mineral dust. We can take this as a reference value for the practical examples and evaluations presented in this paragraph.

As a first example, we consider the case of kaolinite particles. This mineral crumbles into predominantly flat particles (Villa S et al., J Appl Phys, 119.22:224901, 2016). A polydisperse population of these particles can be obtained by sonicating a water suspension of standard monophasic mineral powder for some minutes. The results are shown in Figure 2. The first thing that meets the eye by comparison with Figure 1 is that the distribution is much more spread out, even in the lower part of the plot. This is thanks to the random orientations of the particles in the cell inside the EOS Classizer™ ONE. Such an effect is accentuated in the top-right part of the plot where larger particles fall.

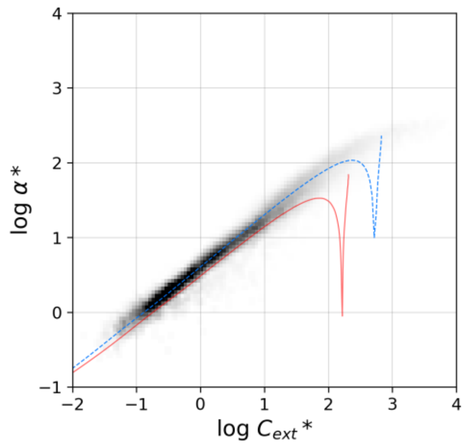

Figure 2 EOS CLOUD of oblate kaolinite dust particles. The solid red line corresponds to the predicted values for spherical particles with $n = 1.55$; the dashed blue line is the best fit for the upper part of the data, which gives the effective value $n = 1.45$. This difference is determined by the shape.

By comparing the data to the theoretical curves, we see that now the Lorentz–Mie model does not describe well the sample if taken literally. The red solid line is obtained from the bulk value of the refractive index: such a value should be avoided when analyzing the data since it would give a distorted size distribution. Instead, the dashed blue line fitted by the analysis program gives the effective value of $n = 1.45$ due to particle shape. This is a much lower and more appropriate approximation of such a parameter in this context, notwithstanding its nominal value. A similar example is given in Figure 3 for k-feldspar particles; notice the appreciable opening of the distribution especially at higher values of C^*_{ext}.

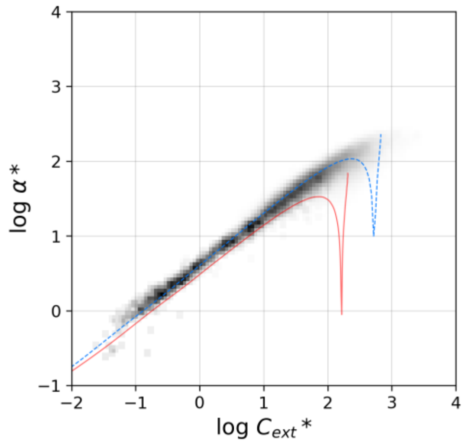

Figure 3 EOS CLOUD obtained from micrometric k-feldspar particles dust particles. As in Figure 2, the solid red line corresponds to spherical particles with $n = 1.55$ whereas the dashed blue line corresponds to $n = 1.45$.

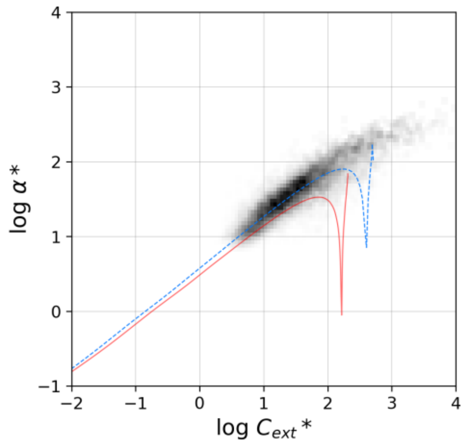

Figure 4 EOS CLOUD obtained from micrometric quartz dust particles. The solid red line corresponds to spherical particles with $n = 1.55$; the dashed blue line corresponds to $n = 1.47$.

Another significant example is found in quartz dust particles; we report the results in Figure . This specific sample contains a mixture of oblate and prolate irregular particles. However, due to the random orientation of the particles as described above, the analysis is still possible even if the shape of the particles is not very well-defined or known. As in the previous case, the distribution extends along the vertical axis α^*. While the nominal value of the refractive index of the particles is around $n = 1.55$, we see that the population is shifted higher in the plane; a fit gives a considerably lower 'effective' value of $n = 1.47$. In general, the vertical broadening of the distribution depends on the ratio between the principal axes of the particles, i.e., the aspect ratio. The quantitative analysis of this relationship is rather complicated and requires several simulations via e.g., Discrete Dipole Approximation computational approaches, nevertheless, EOS Classizer™ ONE distinguishes particles whose aspect ratio is 0.6 or lower from isometric particles. As a rule of thumb, if the EOS CLOUDS extend over half a decade vertically then the particles have an aspect ratio (the ratio between height and width) ranging between 0.3 and 0.5. As seen from the examples reported in Figure 2 and Figure , non-sphericity also lowers the effective refractive index of the particles. It should be noted that this effect is mitigated for small particles with roughly $C^*_{ext} < 10$ because, even if particles are asymmetric, light scattering has a weaker dependence on particle shape. Another important point to consider is the stability of the sample; we conclude our overview with an example of particles that interact with each other. If the interacting particles create aggregates, the morphology is more complicated and consequently so is the analysis. Tracing back these effects on the particle scattering is not so straightforward. One of the reasons for this is that, in aggregate particles, the surface roughness or the particle porosity can have a similar effect to those seen above for the particle shape. Interacting clay particles are a clear example of this. In Figure , we report the data of a water suspension of a standard illite powder sonicated for a few minutes and measured after 10 minutes. The particles are polydisperse and predominantly flat. In addition to the broadening of the distribution due to the shape of the particles, a deviation from the expected curve (red line) even among the smaller particles is observed due to the presence of non-compact aggregates. Moreover, the curve is distinctly detached from the EOS CLOUD, whereas in the previous cases the theoretical line was tangent to the lower end of the data.

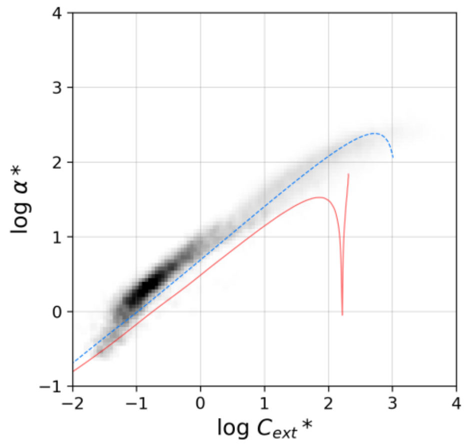

Figure 5 EOS CLOUD obtained from a suspension of illite particles. The solid red line corresponds to spherical particles with $n = 1.55$; the dashed blue line corresponds to $n = 1.41$. Besides the vertical broadening of the distribution, note that it lays considerably higher than the red solid line due to aggregates.

CONCLUSIONS

The capability of EOS Classizer™ ONE and SPES patented method of classifying particles based on their optical properties allows an unprecedented value-added characterization of non-spherical objects. A shape-sensitive instrument offers advantages even in the case of simple characterizations such as sizing. SPES data provide physical and statistical information such as particle size distribution, effective refractive index, an estimate of the behavior and stability, as well as the sizing. Each of these characteristics can be crucial to improve the knowledge and the quality of a population of non-spherical particles like mineralogical powders.

RELEVANT PUBLICATIONS AND REFERENCES

Presentation of Single Particle Extinction and Scattering (SPES) method for particle analysis
AN001-2021 Analysis of Polymeric Particle Mixes via SPES Technology – an introduction to SPES method

AN006-2021 Multiparametric Classification of Particles as a Pathway to Oversize Analysis in Complex Fluids via SPES Technology

Potenza MAC *et al.*, «Measuring the complex field scattered by single submicron particles », AIP Advances 5 (2015)

Example of CFA application of SPES technology
AN002-2021 Continuous SPES Flow Analysis CFA-SPES

Example of PCA application of SPES technology
AN005-2022 Multiparametric Principal Component Analysis of Heterogeneous Samples via SPES Technology

Classizer™ ONE with Sample Manager Autosampler
AN008-2022 Automatic Liquid Sample Management, Dilution, and System Cleaning with EOS Sample Manager

AN009-2022 Standardize SPES Operative Procedure of Liquid Samples Analysis via EOS Autosampler

Example of SPES application to aggregates
AN003-2021 Addressing the Issue of Particle Wetting and Clustering by means of SPES Technology

Potenza MAC *et al.*, «Single-Particle Extinction and Scattering Method …», ACS Earth Space Chem 15 (2017)

SPES application to non-spherical particles
AN004-2021 Addressing the Classification of Non-Spherical Particle by means of SPES Technology

Simonsen MF *et al.*, «Particle shape accounts for instrumental discrepancy in ice …», Clim. Past 14 (2018)

Example of SPES application to emulsions w/o payload in environmental waters
AN012-2021 Monitoring the Fate of a Lipid/ZnO Emulsion in Environmental Waters

AN015-2022 Classification of Oil and Oil Mixes Emulsions via SPES Technology

Examples of SPES application to particle analysis and behavior characterization in biotech applications
AN011-2021 Quantitative Classification of Particles in Biological Liquids via SPES Technology

AN017-2022 SPES Classification of Probiotics Formulations

Sanvito T *et al.*, «Single particle extinction and scattering optical method unveils in real…", Nanomedicine 13 (2017)

Potenza MAC *et al.*, «Single particle optical extinction and scattering allows real time quantitative…», Sci Rep (2015)

Example of SPES application to oxide particles, abrasives, and industrial slurries w/o impurities
Potenza MAC *et al.*, «Optical characterization of particles for industries», KONA Powder and Particle 33 (2016)

AN013-2022 Analysis of Abrasives via SPES Technology

Example of SPES application to ecotoxicity analysis
Maiorana S *et al.*, «Phytotoxicity of wear debris from traditional and innovative brake pads», Env Int., 123 (2019)

Example of SPES application to aerosol analysis
Mariani F *et al.*, «Single Particle Extinction and Scattering allows novel optical …», J Nanopart Res 19 (2017)

Cremonesi L *et al.*, «Multiparametric optical characterization of airborne dust …. », Env Int 123 (2019)

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