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Light scattering simulation for the characterization of sintered silver nanoparticles

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Abstract

Light scattering is a useful tool in optical particle characterization. It can help to understand the nature of single particles as well as systems or clusters of particles; information about particle sizes, materials or shapes can be gathered. In this paper we investigate the application of light scattering studies to the analysis of a sintering process of silver nanoparticles. For this we first simulate the scattering behavior of two silver spheres. Then we assume sintering between them, leading to a single particle with a concave, peanut-like shape. We approximate this shape by a Cassini-oval. For light scattering studies we use an advanced T-matrix algorithm, the Nullfield Method with Discrete Sources. This method proved to be capable of simulating light scattering by concave particles. To make sure that the calculated data are correct we do comparative simulations using the Discrete Sources Method.

Keywords: Nullfield Method with Discrete Sources; T-matrix; Discrete Sources Method; Nanoparticles; Silver; Sintering; Concave

1. Introduction

The special optical properties of small metal particles have been of scientific interest for a long time. The work of Gustav Mie about the optical behavior of the suspension of colloidal gold particles [1] started a development still proceeding today. Over the years a broad variety of scattering algorithms has been devised, which enabled to calculate scattering of more and more particle types and shapes in an efficient way.

In the last years nanotechnology and nanoengineering became research topics of high interest. Both terms refer to a wide field of many different investigations, approaches and applications. The knowledge of the optical properties of small particles can help to understand and predict attributes of nanoparticles. A special role in light scattering investigations was always held by small noble metal particles as they show special luminous optical properties, which are connected to shape and size. More detailed information can be found

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e.g. in the paper by Gunnarsson et al. [2], the paper by Hohenester and Krenn [3] or the chapter by Burda et al. [4].

An example of an actual research field is the sintering of silver nanoparticles, because such particles show good electrical conductivity. Therefore a polymer consisting of silver nanoparticles could be used as a conducting ink, paste or glue. It was found that the electrical conductivity increases, if the silver nanoparticles are sintered, especially if they build aggregates, see e.g. the paper by Jiang et al. [5]. The question now is: can light scattering provide the information whether such particles are sintered or not—or can it even give information about the stage of the sintering process? Simulation of the light scattering process can help to get an estimation.

For this it is necessary to know the particle shapes resulting of the sintering process. A detailed investigation of the sintering mechanism of two spheres can be found e.g. in the paper of Shimosaka et al. [6]. The particle shape presented in this paper can be described as two spheres with a distinct, curved neck as connection between them and therefore reminds of the shape of a peanut. For light scattering investigations this means that it is a single particle with an aspect ration about 2:1 and a concavity at the waist. This shape is definitely different to approaches using two spheres touching each other, two overlapping spheres or even spheroids. Therefore such particles might be not good enough as shape approximations.

In this paper we investigate light scattering by four different types of particles. We calculate scattering diagrams for two well separated silver spheres, the same spheres touching each other, an elongated single particle representing a sintered state of the two spheres and finally a more compact sintered state of the two spheres. The sintered particles with their peanut-like shapes are modeled by a Cassini-oval approach, resulting in a well fitting shape comparable to the results of Shimosaka et al. [6]. We intend to find out, whether there are any distinct differences in the scattering spectra and whether this allows to make assumptions about the state of the sintering process from light scattering. Additionally we can check, if two spheres touching each other are suitable to model a sintered particle. Corresponding, elaborated investigations of the optical behavior of such clustered nanoparticles can be found for example in the publications by Garcia de Abajo [7] or Felidj et al. [8], which give good insights into the effects caused by aggregation.

For light scattering simulation we use the Nullfield Method with Discrete Sources (NFM-DS) [9], an advanced T-matrix algorithm. To check the quality of our results calculations with the Discrete Sources Method (DSM) [10] are done.

2. Nullfield Method with Discrete Sources

The Nullfield Method (NFM), which is also known as the extended boundary condition method, is based on the work by Waterman [11]. This method allows to calculate the T-matrix, which contains all information about the scattering process. With the T-matrix further investigations like varying the direction of the incident light or orientation averaged scattering calculations can be done easily. The conventional NFM is restricted to nearly spherical particle shapes—for strongly deformed particles the NFM shows instability due to a necessary matrix inversion process and the need for finite series expansions [12]. Therefore several modifications and improvements were introduced to overcome this problem. A comprehensive overview of the available T-matrix publications can be found in the publications by Mishchenko et al. [13,14]. The NFM-DS is such a modification; it uses distributed vector spherical wave functions instead of localized vector spherical functions for field expansion. This increases the numerical stability of the algorithm compared to the conventional T-matrix approach. In this case discrete sources are distributed along the rotational axis, as the particles we are investigating can be considered prolate and axis-symmetric. Additionally, the numerical stability can be increased by varying the position of the discrete sources along the rotational axis [15].

For a more detailed description of the theory of the NFM-DS we would like to refer to the book by Doicu et al. [9], which also includes a collection of Fortran programs.

The NFM-DS enables to calculate light scattering by non-trivial particles like prolate or oblate particles with very high aspect ratios up to 100:1 [16,17] or non-symmetrical particles like superellipsoids [18] or rough particles [19] and also clusters [20]. For the investigation we are going to present in this paper it is especially of interest that the NFM-DS allows to calculate light scattering by concave particles [21].