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Statistics for Surface Modes of Nanoparticles with Shape Fluctuations

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Abstract. We develop a numerical method for approximating the surface modes of sphere-like nanoparticles in the quasi-static limit, based on an expansion of (the angular part of) the potentials into spherical harmonics. Comparisons of the results obtained in this manner with exact solutions and with a perturbation ansatz prove that the scheme is accurate if the shape deviations from a sphere are not too large. The method allows fast calculations for large numbers of particles, and thus to obtain statistics for nanoparticles with random shape fluctuations. As an application we present some statistics for the distribution of resonances, polariziabilities, and dipole axes for particles with random perturbations.

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Key words: Electrostatic (boundary-value problems), collective excitations (plasmons), shape fluctuations, numerical scheme, spherical harmonics, projection method.

1 Introduction

The excitation of surface plasmons can cause strong interaction between light and metallic nanoparticles. These plasmons are hybrid modes of the electromagnetic field and the electron gas and are confined to the surface of the particle. They give rise to an enhancement of the incident field by several orders of magnitude [1–3]. This enhancement enables a variety of applications ranging from the well-established surface-enhanced Raman spectroscopy (SERS), which allows the detection of even a single molecule [4,5], to the emerging field of plasmonics [6,7], which has led to prototypes of plasmonic waveguides which effectuate optical energy transfer below the diffraction limit [6,8,9].

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A simple realization of a plasmonic waveguide is a chain of metallic spheres. A surface plasmon mode, typically a dipole mode, of the first sphere of the chain is excited and the scattered field of this first particle excites a surface mode in a sphere nearby and so the excitation can travel through the chain. There are two crucial points for an efficient transport: the spatial structure of the scattered field in the region of the neighboring sphere must allow for an efficient excitation of the favored mode, and the overlap of the resonances of the bordering spheres has to be big enough. Since any realization of a sphere will deviate from an ideal one, thus introducing random fluctuations, it is important to estimate the typical magnitude of such deviations which still allow for an efficient transport. Therefore a simple and efficient numerical method for approximating the surface modes of the sphere-likes particles is needed.

There are many numerical methods for the determination of the electromagnetic field in the present of nanosized scatterers, like the finite difference time domain approach (FDTD), or so called *semi-analytical methods* based on expansions into special function systems like the multiple multipole method (MMP), or the discrete dipole approximation (DDA) (see, e.g., [10, 11]) for reviews. Essentially, all methods able to calculate the fields also allow to determine the surface modes. For example, in [12] the DDA is used for the determination of the surface modes of nanoparticles, and in [13, 14] a boundary integral approach is proposed, which focuses on the surface modes, and has been used in [15] to determine the surface modes of single and coupled spheres, cylinders and cube-like nanoparticles.

Here we use a semi-analytical approach based on an expansion of the potentials into spherical harmonics, i.e., into modes

$$r^l Y_l^m(\theta,\phi) \quad \text{and} \quad r^{-(l+1)} Y_l^m(\theta,\phi),$$

and on the determination of the expansion coefficients by the *physically motivated* projection of the boundary conditions onto the modes $r^l Y_l^m(\theta,\phi)$. See also [16, Section 6] for a review of various ways to determine expansions from the boundary conditions in a variety of related problems. For nonspherical particles, our approach corresponds to an expansion into non-orthogonal modes and therefore is similar to the usage of the Rayleigh hypothesis in the theory of scattering in optics, where the scattered field at a perturbed interface is likewise expanded in the solutions of the scattered field of the unperturbed one [17]. It is known that such expansion methods may fail if the deviations from the ideal geometry become too large (see, e.g., [18] and the references therein). Nonetheless, additional to its simplicity and easy implementation the distinct advantage of our approach is its computational efficiency for nearly spherical particles. Thus it allows to calculate the surface modes for many realizations of randomly distorted nanospheres and so to statistically characterize their optical responses.

The paper is organized as follows: the numerical method is explained in Section 2, and validated in Section 3, using the cases of an ellipsoid and of a sphere with certain shape distortions as benchmarks. In Section 4 we give a statistical study of the optical response of spheres and spheroids with random perturbations.