Doctoral Thesis

Numerical study of plasmon resonant nanowires

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Numerical Study
of
Plasmon Resonant Nanowires

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Publications


A finite element method is developed and applied to the investigation of plasmon resonant 2D silver particles (nanowires).

First, a finite element scattering technique based on the volume integral equation associated with Maxwell’s equations is developed and implemented. A new regularization scheme is introduced to handle accurately the strong singularity of the Green’s tensor. This regularization scheme is extended to neighboring elements, which improves the accuracy of our approach. In particular, our technique is capable of accurately compute plasmon resonances of silver particles, as explicitly assessed for the 2D implementation of our scheme.

Second, our model is applied to the study of non–regular plasmon resonant silver nanowires with cross sections in the 20 – 100 nm range. For individual nanowires we give a detailed picture of the relationship between the shape and size of the cross-section and its resonance spectrum. We observe complex spectra, with many different resonances, for non–regularly shaped particles. These spectra are much more complex and cover a broader wavelength range than those associated with regular shape nanowires, like cylinders or ellipses. Each resonance is associated with a specific field distribution that can be related to the corresponding polarization charge distribution induced in the particle. For specific particle shapes we observe a dramatic near–field enhancement, with the electric field amplitude reaching several hundred times that of the illumination. We show how the particle background affects the plasmon resonances and evidence that for non–symmetric shapes the illumination direction determines which resonances can be excited.

We then investigate interacting nanowires and show that additional, large resonances are excited when the separation distance is smaller than 5 nm. We also observe very large and homogeneous field enhancements in the gap between the wires. For intersecting wires the spectrum becomes quite complex, with several resonances that can be related to different polarization charge topologies.

Finally, we emphasize the importance of our results for different experimental configurations currently under investigation in surface enhanced Raman scattering (SERS) and near–field optics. We show quantitatively the SERS enhancements for non–regular individual and coupled nanowires on the entire optical range. Our results are in good agreement with recent experiment in SERS and shall provide further guidance for designing extremely efficient SERS substrates. We further discuss how non–regularly shaped plasmon–resonant silver nanoparticles may help increase the resolution and sensitivity of scanning near–field optical microscopes, and how they could be implemented in new integrated optical devices, thereby allowing a further miniaturization step.
Zusammenfassung

Es wird eine Finite-Elemente Methode entwickelt und angewandt, um Plasmon-Resonanzen von zwei-dimensionalen Silberpartikeln (Silber-Nanowires) zu untersuchen.


Schliesslich betonen wir die Bedeutung unserer Ergebnisse für verschiedene experimentelle Anordnungen, die gegenwärtig im Bereich surface enhanced Raman scattering (SERS) sowie in der Nahfeldoptik untersucht werden. Für unregelmäßige, sowohl einzelne als auch gekoppelte Nanowires zeigen wir quantitativ die SERS-Verstärkung über den ganzen optischen Bereich. Unsere Ergebnisse sind in guter Übereinstimmung mit jüngsten SERS-Experimenten und sollen eine weitere Anleitung liefern, um sehr effiziente SERS-Substrate zu entwickeln. Wir diskutieren ferner, wie unregelmäßig geformte Nanoteilchen die Auflösung und Empfindlichkeit in der Nahfeld-Mikroskopie steigern können, und wie sie in integrierte optische Devices eingebaut werden können, um eine weitere Miniaturisierung zu ermöglichen.
Chapter 1

Introduction

This chapter gives an introduction to the topic of the thesis. We first stress the importance of plasmon resonant structures in several fields of nanoscience, then define the objective of the thesis, and finally give the outline for the present document.

1.1 Motivation

Small silver and gold particles can interact strongly with light, manifesting in very large scattering cross-sections with several resonances. As these resonances occur for specific wavelengths, these particles exhibit a particular color, which depends on the size and shape of the particle. This was already used long ago to give stained glass windows their color, and Faraday noted “that a mere variation in the size of its particles gave rise to a variety of colors” [1].

These plasmon resonances are reserved to particles with dimensions in the sub-micron range, and are associated with very large electromagnetic near-fields, particularly for dimensions below 100 nm [2]. The interest in how the plasmon resonance spectrum is exactly related to the particle size and shape has been limited, as such small structures could not be fabricated in a controlled manner until recently. With the birth of nanofabrication, however, this has changed dramatically. Nowadays nanoparticles with specific shapes can be fabricated in a reproduceable manner, and the properties of plasmon resonant particles can now be systematically investigated. Fabrication techniques for metal nanostructures below 100 nm include electron beam lithography [3, 4], electron beam induced deposition [5], ion beam irradiation [6], thermal deposition [7], laser pulse irradiation [8], and photo–catalytic deposition [9]. Small silver islands may even be fabricated and moved on surfaces with scanning tunneling microscope tips [10], and sharp tetrahedral silver particles can be produced using latex sphere lithography [11]. Metallic nanowires and nanorods with cross–section dimensions down to a few nanometers can be made either by step decoration [12, 13], chemical etching [14, 15], template–directed electro–synthetic techniques [16], or by filling carbon nanotubes [17].

The optical properties of metallic nanostructures – particularly silver structures, but also gold and copper – make them very attractive for a wide range of applications. In surface enhanced Raman spectroscopy (SERS), the Raman signal of molecules adsorbed on small silver and gold particles is enhanced by several orders
of magnitude \([18-20]\), and even single molecule detection can be achieved with this technique \([21-23]\). Chemical and biological sensors have been proposed based on plasmon resonant particles \([24-27]\). For scanning near-field optical microscopy (SNOM), metallic particles provide large, yet well-localized near-field sources \([28-34]\), and can therefore increase the resolution. Small particles and wires of silver or gold are also highly interesting for optical devices, as they provide efficient, frequency-selective scatterers with sub-wavelength dimensions, allowing further device miniaturization \([35-37]\). Moreover, silver and gold nanowires can guide electromagnetic modes over several microns \([38]\), coupled plasmon resonant nanoparticles can be used for evanescent optical transport \([39-42]\) and nanoholes in metal films allow the filtering of optical signals \([43]\). Most recently, an active optical component, similar to a transistor, was proposed using the local field amplification associated with the excitation of plasmon resonances \([44]\).

Numerical computations are necessary to understand the optical properties of arbitrarily shaped plasmon resonant particles in detail. In particular, the knowledge of the complex relationship between shape and size of the particle, and its plasmon resonance spectrum, including the electrical near-field associated to it, should help to design particles for specific applications. This knowledge is required both for individual and interacting metal particles.

1.2 **Objective of this thesis**

The objective of this thesis is to study numerically the plasmon resonances of silver nanowires, with cross-sections in the \(20 - 100\) nm range. We develop a numerical finite element method that can accurately handle this demanding problem for an arbitrary particle shape. We then study how the plasmon resonances of single silver nanowires are related to the shape and size of their cross-sections and the illumination direction. We further investigate the influence of the separation distance for interacting nanowires, including the case when they intersect. We finally discuss the implications of our results for specific areas of nanoscience.

1.3 **Outline**

This thesis consists of a general part (Chaps. 1–5), and a series of publications (P1–P8) that were written during this research project.

In Chapter 2 we present the original model that we developed. We briefly describe the mathematical framework, which is based on the volume integral equation associated with Maxwell’s equation. We then propose a finite element technique which includes a new regularization scheme and assess its performance and accuracy.

In Chapter 3 we apply this technique to the study of the plasmon resonances of silver nanowires. As the phenomenon of plasmon resonances is not widely known, its basic properties are first summarized. We then present results for silver nanowires. We study in detail the influence of the size and shape of the cross-section on the resonance spectrum, and investigate the near-field for different illumination
directions. The various resonances, as observed for non-regular particle shape, are analyzed with the corresponding polarization charge distributions. Finally, we study the influence of coupling in interacting wires, on the plasmon resonance spectrum. Different separation and intersection distances are investigated, and we study the possibility of optical transport using a chain of cylinders.

In Chapter 4 we discuss the implications of the results obtained in Chapter 3, for three areas of nanoscience, namely surface enhanced Raman scattering, scanning near-field optical microscopy and nanooptical devices.

In Chapter 5 we draw our conclusions and give an outlook for future work.
Chapter 2

Computational approach

In this Chapter we propose a model to accurately compute plasmon resonant structures. After describing the physical problem, we briefly introduce the volume integral equation (VIE) associated with Maxwell’s equations. We then present a finite element model to solve the VIE numerically. In particular we develop a new regularization scheme, which dramatically improves the accuracy, as assessed for the two-dimensional implementation of our approach.

2.1 Introduction

Plasmon resonances can only be treated analytically for simple shapes, like spheres and ellipsoids in homogeneous space [2, 45], a sphere or cylinder near a surface, or two small spheres [46, 47]. For more complicated geometries, one has to rely on semi-analytical or numerical approaches. Semi-analytical methods can give very accurate results for scattering problems, particularly for smooth structures [48]. Our aim is to accurately compute the plasmon resonances of arbitrarily shaped particles and we must rely on a purely numerical method. This is quite a challenging task, as the computation of plasmon resonances of non-regular structures is very demanding. As we will see, the numerical approach has to accurately handle field amplitude variations of three orders of magnitude within a few nanometers [49]. Moreover, the system is not very stable at a resonance, or in other words, small changes in parameter space and little inaccuracies can lead to a completely different response of the system.

No accurate electric field solutions for non-regular plasmon resonant structures in the 10–100 nm range have been presented so far. Time domain methods such as finite difference time domain (FDTD) are not suitable for the study of highly dispersive materials [50]. Our approach will be based on the volume integral equation (VIE) formulation of Maxwell’s equation, which will be briefly described in the next section. An advantage of this approach lies in the fact that only the scatterer has to be discretized. Another advantage of the VIE formulation is that complex backgrounds may be included in the corresponding Green’s function. Very recently, the Green’s tensor for arbitrarily layered background has been successfully implemented [51–53]. In the present work, however, we focus on homogeneous backgrounds.

A broadly used method for solving the VIE is the coupled dipole approximation
Chapter 2: Computational Approach

Figure 2.1: Scattering problem: the scatterer (which might also be more than one) is described by its complex permittivity $\varepsilon(\mathbf{r})$ and is illuminated with an incident field $\mathbf{E}^0(\mathbf{r})$.

(CDA) [54, 55]. As the name suggests, this approach consists in modeling the scatterer with a uniform grid of dipoles. Although there have been several attempts to overcome its intrinsic limitations [56–58], this method does not seem suitable to account for high permittivity scatterers and for plasmon resonant structures [59].

Our approach is a new finite element technique to solve the VIE numerically. Before we present and assess our model, let us first define in the next section our physical problem.

2.2 Volume integral equation and Green's tensor

The mathematical background for the VIE associated with Maxwell's equation is fully described in Ref. [55] and we give here only the most elementary basics.

Our goal is to compute the vectorial electrical field $\mathbf{E}(\mathbf{r})$, scattered by one or many bodies illuminated with an incident field $\mathbf{E}^0(\mathbf{r})$ (Fig. 2.1). The scatterer is described by its complex dielectric function $\varepsilon(\mathbf{r})$ and is embedded in an infinite homogeneous background with permittivity $\varepsilon_B$. The scatterer needs not be homogeneous. Throughout this thesis we assume a $\exp(-i\omega t)$ time dependence for the fields, where $\omega$ is the frequency.

The total electrical field $\mathbf{E}(\mathbf{r})$ is then a solution of the volume integral equation (VIE)

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}^0(\mathbf{r}) + \int_V d\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}') \cdot V(\mathbf{r}') \mathbf{E}(\mathbf{r}') ,$$

where the integration runs over the entire scatterer volume $V$. In Eq. (2.1), $V(\mathbf{r})$ represents the scatterer polarizability, given by

$$V(\mathbf{r}) = k_0^2 \varepsilon(\mathbf{r}) - \varepsilon_B,$$

with $k_0$ the vacuum wavenumber. $\mathbf{G}(\mathbf{r}, \mathbf{r}')$ is the Green's tensor associated with the homogeneous background. This dyadic is a solution of the vectorial wave equation

\footnote{We will use the singular in the rest of this section, although there might be more than one scatterer.}
2.2. VOLUME INTEGRAL EQUATION AND GREEN’S TENSOR

With a point source term \([60]\):

\[
\nabla \times \nabla \times G(r, r') - k_0^2 \varepsilon B G(r, r') = \mathbf{1} \delta(r - r'),
\]

where \(\mathbf{1}\) is the unit dyad. The solution of Eq. (2.3) gives the Green’s tensor

\[
G(r, r') = \left(1 + \frac{\nabla \nabla}{k_B^2}\right) g(r, r'),
\]

where \(g(r, r')\) is the scalar Green’s function associated with the background \(\varepsilon_B\). For 3D systems, the scalar Green’s function is given by

\[
g_{3D}(r, r') = \frac{\exp(ik_B R)}{4\pi R},
\]

whereas for 2D systems, i.e. systems that have a translation symmetry along \(z\)-direction (Fig. 2.2), it is given by

\[
g_{2D}(r, r') = \frac{i}{4} H_0^{(1)}(k_{\rho} \rho) \exp(ik_z z).
\]

In Eq. (2.6) we introduced the transverse coordinate \(\rho = |(x, y)|\), and accordingly \(k_{\rho} = |(k_x, k_y)|\). Such a 2D problem is illustrated in Fig. 2.2.

The integral in Eq. (2.1) has to be performed only for the scatterer volume, as \(V(r)\), defined by Eq. (2.2), vanishes outside the scatterer. This is important for the practical implementation of our approach: Eq. (2.1) is implicit (the unknown field is on both sides of the equal sign) only for \(r \in V\). On the other hand, Eq. (2.1) shows that once the field \(E^{sc}(r)\) inside the scatterer is known, the field \(E^{out}(r)\) at any other location in the system can be easily determined.

The practical calculation of the scattered field is therefore performed in two steps. First, the field \(E^{sc}(r)\) inside the scatterer is computed self-consistently according to Eq. (2.1):

\[
E^{sc}(r) = E^0(r) + \int_V dr' G(r, r') \cdot V(r') E^{sc}(r'), \quad r \in V.
\]
VA; f(r),..., f(r)

BA(r) = \sum_{i=1}^{m} a_i f_i(r)

Figure 2.3: The scatterer is discretized into several tetrahedral (3D), or triangular (2D) elements. Each element A is assigned a constant polarizability VA and a set of basis functions f_A(r),..., f_A(r). The unknown field E_A(r) within each element is then expanded into this set of basis functions, with unknown vectorial coefficients a_i.

The unknown field E^sc(r) is here on both sides of the equation. Once this is done, the field E^out(r) outside the scatterer can be easily obtained from

E^out(r) = E^0(r) + \int_V dr' G(r, r') \cdot V(r') E^sc(r'), \quad r \notin V, \quad (2.8)

where all the quantities on the right hand side of Eq. (2.8) are known.

As we want to investigate scattering cross-sections (SCS), we further need the far-field scattered in (θ, φ)—direction (φ—direction in 2D):

E^∞_3D(θ, φ) = \int_V dr' G^∞_3D(θ, φ, r') \cdot V(r') E^sc_3D(r') \quad (for 3D) \quad (2.9)

E^∞_2D(φ) = \int_V dr' G^∞_2D(φ, r') \cdot V(r') E^sc_2D(φ) \quad (for 2D). \quad (2.10)

Here, G^∞_3D(θ, φ, r'), respectively G^∞_2D(φ, r'), is the far-field Green's dyadic for the 3D, respectively 2D scattering problem, and is explicitly given in Appendix A. The SCS for 3D and 2D can then be computed with

SCS_3D = \frac{1}{4\pi} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi \, |E^∞_3D(θ, φ)|^2 \quad (2.11)

SCS_2D = \frac{1}{2\pi} \int_0^{2\pi} d\phi \, |E^∞_2D(φ)|^2. \quad (2.12)

2.3 Finite elements

We use finite elements [61] to solve Eq. (2.1). The basic idea of this method is to discretize the geometry, and define a set of basis functions on each discretization element (see Fig. 2.3). Triangular (2D) and tetrahedral (3D) elements are most often used, as these can discretize any non-regular scatterer both accurately and efficiently.

Applying this concept to the VIE we are in the comfortable situation that only the scatterer has to be discretized. The unknown field E^sc(r) inside each discretization element of the scatterer is then developed in a series of basis functions defined
on each discretization elements (see Fig. 2.3). If the number of discretization element is \( N \), and if \( m \) basis functions are defined on each element, this Ansatz reads

\[
\mathbf{E}^{sc}(\mathbf{r}) = \sum_{A=1}^{N} \sum_{j=1}^{m} \mathbf{a}_A^j f_A^j(\mathbf{r}),
\]

with \( \mathbf{a}_A^j \) the unknown vectorial coefficients (see Fig. 2.3). Inserting this Ansatz in Eq. (2.7), and assuming the scatterer polarizability \( V(\mathbf{r}) \) to have a constant value \( V_A \) within each discretization element \( A \), gives

\[
\sum_{A=1}^{N} \sum_{j=1}^{m} \mathbf{a}_A^j f_A^j(\mathbf{r}) = \mathbf{E}^0(\mathbf{r}) + \sum_{A=1}^{N} \int_{V_A} d\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}') \cdot \mathbf{a}_A^j f_A^j(\mathbf{r}'),
\]

where for the integration part we have used that \( f_A^j(\mathbf{r}) \) vanishes for \( \mathbf{r} \notin A \).

A further step is necessary to obtain a system of equations for the unknown vectorial coefficients \( \mathbf{a}_A^i \). One has to build scalar products in function space by multiplication with a set of test functions and integration [61, 62]. One such set of test functions are Dirac delta–functions. This is known as the point–matching technique and leads to rather simple expressions [62, 63]. However, this seems not appropriate for our purpose, as point–matching does not provide accurate enough results. A more suitable choice for the test functions is to use the same set than for the basis functions. This is known as Galerkin’s scheme [62, 63]. Following this scheme, we end up with a system of \( mN \times mN \) vectorial equations:

\[
\sum_{j=1}^{m} b_{ij}^j \mathbf{a}_A^i - \sum_{B=1}^{N} \sum_{j=1}^{m} d_{AB}^i \mathbf{a}_B^j = \mathbf{e}_A^i, \quad i = 1, \ldots, m, \quad A = 1, \ldots, N
\]

with

\[
b_{ij}^j = V_A \int_{V_A} d\mathbf{r} f_A^i(\mathbf{r}) f_A^j(\mathbf{r}),
\]

\[
e_i^j = V_A \int_{V_A} d\mathbf{r} f_A^i(\mathbf{r}) \mathbf{E}^0(\mathbf{r}),
\]

\[
d_{AB}^i = V_A V_B \int_{V_A} d\mathbf{r} f_A^i(\mathbf{r}) \int_{V_B} d\mathbf{r}' \mathbf{G}(\mathbf{r}, \mathbf{r}') f_B^j(\mathbf{r}').
\]

In our approach we use polynomial basis functions, which are first defined on the canonical element and then mapped on each element with an affine transformation, as detailed in P1. An accurate numerical computation for Eqs. (2.16) and (2.17) is then straightforward, using Gaussian quadrature (see P1).\(^2\) The computation of the integrals Eq. (2.18), however, is rather complicated. When the integration elements \( A \) and \( B \) in Eq. (2.18) are identical, for instance, the integral contains the strong singularity of Green’s function. In P1 we detail how we overcome these difficulties by introducing a new regularization scheme. Moreover, we extend this regularization scheme to neighboring elements, which significantly improves the accuracy of the

\(^2\)The integrals of type (2.16) may even be computed analytically for polynomial and other simple basis functions.
results, as shown in P1. This renormalization procedure represents an essential part of our technique to compute plasmon resonant structures in an exact manner, and its basic ideas are outlined in the next section.

For the rest of this section let us assume that we have computed the integrals Eqs. (2.16)–(2.18). Equation (2.15) can then be formulated as a matrix equation for the unknown coefficients $a^j_A$:

$$\mathbf{M} \cdot \mathbf{a} = \mathbf{e},$$

where each matrix element of $\mathbf{M}$ is in fact a $3 \times 3$–tensor. The right hand side $\mathbf{e}$ contains the illumination field $\mathbf{E}^0(r)$. The matrix equation (2.19) can be solved with an iterative matrix equation solver, giving the numerical solution for the field inside the scatterer, according to Eq. (2.13). The field $\mathbf{E}^{\text{out}}(r)$ outside the scatterer can then be determined easily from the field inside the scatterer using the discretized form of Eq. (2.8). Furthermore, the far–field can then be obtained by the discretized form of Eq. (2.9), as detailed in Appendix A.

### 2.3.1 Regularization scheme

In this section we give the basic idea behind the new regularization scheme, as introduced in P1, to accurately compute the integrals Eq. (2.18) for identical and neighboring elements.

For this purpose, it is sufficient to consider the inner integral of Eq. (2.18):

$$\int_{V_A} dr' G(r, r') f^j_A(r').$$

Note that $r \in V_A$, since the integration volume for the integration variable $r$ of the outer integral in Eq. (2.18) is $V_A$.

Let us first consider the case when the elements $A$ and $B$ are identical [Fig. 2.4(a)]. In this case the integral contains the strong singularity of the Green’s dyadic, and a numerical integration scheme like Gaussian quadrature is not applicable. Although there exist quadrature techniques for functions with a singularity, these are not applicable here, as the Green’s function contains strong singular $1/R^D$ terms (with $D$ the space dimension), which are not generally integrable. These singularities are sometimes referred to as hyper–singularities [64], and the theory of generalized functions must be applied [65].

Thus, for identical elements $A = B$ we have the situation that the integral (2.20) can be neither performed analytically nor with a numerical technique. The idea out of this dilemma is to subtract from the integrand a function with the same singular behavior, but which can be integrated analytically. This is fulfilled by rewriting Eq. (2.20) as

$$\int_{V_A} dr' G(r, r') f^j_A(r') = \int_{V_A} dr' \left( G(r, r') f^j_A(r') - \frac{\nabla \nabla}{k_B^2} g^e(r, r') f^j_A(r) \right) + f^j_A(r) \int_{V_A} dr' \frac{\nabla \nabla}{k_B^2} g^e(r, r'),$$

(2.21)
2.3. FINITE ELEMENTS

Figure 2.4: (a) For identical elements ($B = A$) the integral Eq. (2.20) contains the singularity, and the radial component $R$ runs from 0 to $a$. (b) For the neighboring elements $A$ and $B1$ the distance $R$ is still small, and $R$ runs from $b$ to $c$. For larger distances between the discretization elements ($A$ and $B2$), $R$ runs from $d$ to $e$.

where we used $B = A$. Here, $g^s(r, r')$ is the scalar static Green's function, given by

\begin{align}
g^s_{3D}(r, r') &= \frac{1}{4\pi |r - r'|} \quad \text{for 3D} \quad (2.22) \\
g^s_{2D}(r, r') &= -\log |r - r'|/(2\pi) \quad \text{for 2D}. \quad (2.23)
\end{align}

It is important to note that in Eq. (2.21) we subtract a term that contains $f_A^s(r)$, and not $f_A^s(r')$ as in the original integrand. By this, we nevertheless remove the strong singularity from the integrand, while the integral of the singular term has not to be performed for the basis function [see last term in Eq. (2.21)]. Thus, the singular term does not depend on the explicit form of the basis function and can be performed analytically.

A simplified illustration of this regularization scheme is given in Fig. 2.5(a), where $G$ corresponds to the integrand on the left hand side of Eq. (2.21), whereas $G - G^s$ and $G^s$ correspond to the integrands of the first and second integral on the right hand side of Eq. (2.21).

This regularization scheme allows us to accurately compute the integral (2.20) for identical elements. Let us next consider the case when the elements are different [Fig. 2.4(b)]. We may now use Gaussian quadrature for the integral (2.20). In the case of neighboring elements, however, the integrand still varies strongly within the integration volume, and Gaussian quadrature would give poor results. This is illustrated in Figs. 2.4(b) and 2.5(b): the radial integration variable $R$ runs from $b$ to $c$ [Fig. 2.4(b)]. In this interval, the Green's function $G$ varies strongly [Fig. 2.5(b)]. However, it may again be divided into a singular part $G^s$ that can be integrated analytically, while Gaussian quadrature gives accurate results for the smooth function $G - G^s$ [Fig. 2.5(b)].

We finally consider the case where the distance between $r$ and the integration volume is large (right hand side of Fig. 2.4(b)), where the radial component runs here from $d$ to $e$. As Fig. 2.5(b) shows, $G$ behaves smoothly within this interval, and we may use Gaussian quadrature for $G$.

Obviously, this graphical illustration was a simplification. The integrals have to be performed in 3D, respectively 2D, for a complex, tensorial function. We further neglected the variations of the basis functions on the integration interval. Moreover,
Figure 2.5: Schematic illustration of the regularization scheme. (a) For identical elements \([A=B, \text{Fig. 2.4}]\) \(G\) has to be integrated in the interval \([0, a]\), and numerical quadrature is not possible. \(G\) is divided into the singular part \(G_s\) that can be integrated analytically and into the regular part \((G−G_s)\), which behaves smoothly and can be accurately integrated using Gaussian quadrature. (b) For neighboring elements \([A \text{ and } B1, \text{Fig. 2.4}]\), the integration interval is \([b, c]\) and numerical quadrature of \(G\) is possible. However, \(G\) varies strongly within the interval, and even high order Gaussian quadrature could give poor results. Application of the regularization scheme, as established for identical elements, improves the accuracy considerably. Finally, for a larger distance between the elements \([A \text{ and } B2, \text{Fig. 2.4}]\), where the integration interval is \([d, e]\), Gaussian quadrature of \(G\) gives good results.
the first integral on the right side of Eq. (2.21) is still singular. However, this singularity is now weak (\( \sim 1/R \) in 3D and \( \sim \log(R) \) in 2D) and can be handled with a modified Gaussian quadrature scheme (see P1). We again refer the reader to P1, where all the expressions and their derivations are detailed. Moreover, for the 2D case with incidence in the 2D plane, we give in P1 explicit expressions for the analytic integrals appearing in the regularization scheme. Explicit analytic expressions for the general 2D case (oblique incidence), as well as for the 3D case with tetrahedral elements, are given in Appendix B.

### 2.3.2 Accuracy

In this section we assess the accuracy of the 2D implementation of our approach and discuss the influence of our regularization scheme. We show in Fig. 2.6 the error of our results, as defined in P1, for high-permittivity cylinders as a function of the number of discretization elements. Fig. 2.6(a) demonstrates that our technique is capable of handling high permittivity scatterers. The error rapidly decreases with increasing number of elements. This indicates that there is no principle source of errors in our method, i.e. no errors that do not converge to zero for finer and finer discretization. This is not the case for example with CDA [58].

In Fig. 2.6(b) we stress the importance of the extension of our regularization scheme to neighboring meshes. We see that this extension is necessary for the convergence of the results. The widening with increasing discretization elements of the accuracy gap between the results with and without regularization for neighboring meshes can be understood with Figs. 2.4 and 2.5: a finer grid is associated with a decreasing distance to neighboring elements. This corresponds to shrinking the interval \([b, c]\) in Fig. 2.5, and shifting it towards zero. In this case the regularization scheme for neighboring elements becomes more important, as the integrand "sees"
more and more of the singularity of the Green’s tensor [Eq. (2.4)]. We think that this is the reason why the approach without the full regularization scheme fails to converge for high-permittivity scatterers, and moreover, fails to accurately compute plasmon resonant structures. We believe that this is also the main reason why CDA fails to give good results for plasmon resonant structures. Instead of integrating the Green’s function properly over the cubical (3D) or rectangular (2D) mesh the value at the center is taken in CDA, weighted with the mesh volume. Particularly for a fine discretization, where the Green’s function takes large values within neighboring elements, this leads to an ill-conditioned matrix equation, and the matrix equation solver then even fails to converge.

Let us finally show that the plasmon resonance of a 100 nm diameter cylinder, illuminated with a TE-polarized plane wave (wave vector and incident field in the plane of the cylinder), is correctly reproduced with our model. For this problem an analytic solution exists (Mie solution) that can be used as a reference solution [2]. As is shown in Fig. 2.7, the agreement between our numerical SCS and the Mie solution is excellent, even with only 132 triangles.

2.4 Implementation details

The most CPU time-consuming part of our technique is the Gaussian quadrature for the convolution integral, as given by Eqs. (P1-14) and (P1-15). The CPU time strongly depends on the order $O$ of the Gaussian quadrature. If, for example, we choose $O = 7$, where 13 Gaussian points are defined on each triangular element, the Green’s function has to be called $13^2 = 169$ times for each matrix element $d_{AB}^{ij}$ [Eq. (2.18)], whereas for order 2, with 3 Gaussian points defined on each element, it has to be called only $3^2 = 9$ times. As the accuracy increases with higher quadrature order $O$, we have to find a suitable trade-off between these two requirements: high
accuracy and reasonable CPU time. An efficient trade-off is obtained by adapting the order of Gaussian quadrature to the distance between the two discretization elements. We take a high quadrature order $\mathcal{O}$ for identical and neighboring elements, and then gradually decrease $\mathcal{O}$ for larger distances without any significant losses in accuracy. The reason for this is quite simple: for a small distance (relative to the sizes of the elements), the Green’s function varies strongly on the integration volume, which requires a high order of Gaussian quadrature [see also Fig. 2.5(b)]. For a large distance, on the other hand, the Green’s function behaves smoothly within the integration volume, and a low order of Gaussian quadrature is sufficient for a good numerical approximation.

In our practical implementation, we use $\mathcal{O} = 7$ to compute $d_{AB}$ when the spacing between the meshes $A$ and $B$ is smaller than twice the size of the larger mesh. We then gradually decrease the order, down to $\mathcal{O} = 1$ (where only one Gaussian point is used) when the mesh spacing is larger than twelve times the larger mesh. Using this adaptive Gaussian quadrature scheme, and $N = 3000$ discretization elements, the CPU time to compute the matrix elements on an UltraSPARC-II 360 MHz processor is about 1.5 hours. The value of $N$ is typical for the discretization of the non-regular cross-sections presented in Chap. 3. The CPU time roughly goes with the square of $N$.

The CPU time to solve finally the matrix equation (2.19) using the technique of conjugate gradients depends on the scattering problem. It takes longer at resonance than out of resonance, since at resonance the iterative solver converges slower to a stable solution. However, this time is in general shorter than the CPU time to compute the matrix elements. Note that for different illumination directions the matrix elements have to be computed only once, and the CPU time to find the solution for the electrical field $\mathbf{E}(\mathbf{r})$ for other illuminations is solely determined by the matrix equation solver.
Chapter 3

Plasmon resonances of silver nanowires

In this chapter we study plasmon resonant silver nanowires. We first show how plasmon resonances can be described using Maxwell’s theory, and explain why the permittivity of silver becomes negative at optical frequencies. After briefly discussing the limits of this classical description for particle sizes well below 20nm, we show numerical results for single and interacting nanowires, with regular and non-regular cross-sections in the 20—100 nm range.

We are interested in nanowires mainly for two reasons. First, these structures can now be fabricated in a controlled manner, using for instance electron beam lithography [4], chemical etching [14, 15], template-directed electro-synthetic techniques [16], step decoration [12, 13], or by filling carbon nanotubes [17]. Hence, the study of such structures is relevant for experimental situations, and our results can give optimization guidelines. Second, the most important effect, namely the relation between the particle shape and size and its spectrum of plasmon resonances, is likely to be similar in 2D and 3D geometries.

3.1 Electromagnetic description

The interaction of matter with light can be studied with Maxwell’s theory, where the matter is described by its complex permittivity $\varepsilon = \varepsilon' + i\varepsilon''$, the complex part $\varepsilon''$ accounting for damping. For dispersive media, this permittivity largely depends on the illumination wavelength $\lambda$. The function $\varepsilon(\lambda)$ that relates these two quantities is known as the dispersion relation of the medium.

For media with permittivities below 1 in a certain wavelength range, Maxwell’s equations allow a range of quite outstanding phenomena. Longitudinal bulk modes can be excited when $\varepsilon' = 0$ [66, 67], and surface plasmons are supported along a vacuum/metal plane interface when $\varepsilon' = -1$ [68]. The most spectacular phenomenon, however, is the excitation of so-called plasmon resonances in tiny particles, associated with very large scattering efficiencies and huge electromagnetic enhancements in the near-field. These plasmon resonances occur at wavelengths when $\varepsilon'$ becomes negative, for specific values that depend on the particle size and shape, the spacing to
neighboring particles, and on the particle background $\varepsilon_B$.\footnote{Note that these resonances are sometimes referred as the surface modes of the particle \cite{2}, although this is somehow misleading, as the electromagnetic field is not confined to the particle boundary.} Unfortunately, only simple scatterer geometries can be treated analytically using Mie theory \cite{2}. Like this, a sphere much smaller than the wavelength exhibits a resonance when $\varepsilon' = -2\varepsilon_B$, whereas a cylinder, illuminated by a transverse electric field, exhibits a resonance when $\varepsilon' = -\varepsilon_B$. Spheroids have two or three different resonances depending on the ratio which can be separately excited for specific illumination directions \cite{45}. When the size of all these objects increases, the resonance permittivities become more negative, and higher order resonances can also be excited \cite{2}.

Whereas it is mainly $\varepsilon'$ that governs the resonance wavelength of a particle of given size and shape, it is $\varepsilon''$ that determines how broad — for a given particle size — the resonance is, and related to it, how large the electromagnetic near-field becomes. Note that for high-dispersive media $\varepsilon''$ cannot become arbitrarily small due to the Kramers-Kronig relation, which relates $\varepsilon'(\lambda)$ and $\varepsilon''(\lambda)$ \cite{2}.

The resonances also broaden with increasing particle size. The additional modes that can then be excited start to overlap, and cannot be resolved anymore for dimensions of several hundred nanometers, while the field amplitude enhancements strongly decrease \cite{2}. Increasing the particle size further, and the metal particles finally loose their resonant behavior, obtaining the optical properties that we associate with metals, like a high reflectivity. This is why plasmon resonances are reserved for very small particles, and the largest field enhancements are obtained for dimensions below 100 nm.

### 3.1.1 Dispersion relation of silver

At optical wavelengths the dispersion relation for any medium is governed by its electrons. Whereas non-conductors have only bound electrons, which are well-described with the Lorentz model \cite{2}, conductors have also unbound electrons, which form the electron gas. (For semiconductors, whether or not such an electron gas exists depends on the wavelength.) An important parameter for the interaction between these electrons and light is the so-called plasma frequency $\omega_p$ of the electron gas, which is mainly determined by the electron gas density and the effective mass of the electrons in the positive charged background of the ions lattice \cite{69}. The dispersion relation due to the electron gas is classically described by the Drude model, which gives \cite{2}

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \tag{3.1}$$

where $\gamma$ accounts for losses, governed by electron scattering at the ions lattice. Eq. (3.1) shows that when the illumination frequency $\omega$ passes by the plasma frequency $\omega_p$, the real part of the permittivity changes its sign. It is therefore the strong resonant interaction between the illumination field and the collective oscillations of the electron gas that renders the dispersion relation negative. This is why the resonances of small metal particles that occur when the permittivity is negative are called plasmon resonances. The metals that have their plasma frequency in or
near the optical range, and therefore the metals which can act resonantly with visible light, are the so-called coinage metals: silver, gold and copper. Among these three metals, silver has the lowest damping $\varepsilon''$, and as a result, produces the largest electromagnetic near-field. Silver is therefore the most relevant coinage metal for optical applications, and we shall focus our study on silver structures.

More sophisticated models than the classical Lorentz model for the bound electrons, respective the Drude model for the unbound electrons, exist to describe the dispersion relation of silver, like for example the quantum hydrodynamic model [69]. However, it is not the purpose of this work to model the dispersion relation of silver, and we shall use experimental data for $\varepsilon(\lambda)$. These experimental values, as obtained by Johnson and Christie [71], are shown in Fig. 3.1. We observe that the plasma frequency $\omega_p$ is at about 328 nm, and $\varepsilon'$ then becomes negative for larger wavelengths.

### 3.1.2 Limits of the classical description

In this work we assume that plasmon resonances of small silver particles can be treated with classical electrodynamics, using the concept of a local dispersion relation. Indeed, it was shown by Kreibig that for very small gold and silver particles the predictions from the classical model are in excellent agreement with experimental results for spherical particles even down to a size of 2 nm [69]. For silver particles between 2 nm and 30 nm the dispersion relation must be modified with respect to the bulk values, as the electron mean free path – the average path between two scattering processes – is decreased due to electron scattering at the particle surface. Whereas for silver the real part $\varepsilon'$ of the permittivity remains almost unaffected, the complex part $\varepsilon''$ is inversely proportional to the electron mean free path. Kreibig found that near the plasma frequency, the size dependence of $\varepsilon''$ can be described

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2 For silver, $\varepsilon''$ is below 0.5 in the optical range where $\varepsilon'$ is negative, whereas for gold, $\varepsilon''$ is between 1 and 6. For copper, it is even larger [70].
2.64 nm \epsilon'' = 0.23 + \frac{2.64 \text{ nm}}{A}, \quad (3.2)

with A the particle dimension. For a particle size of 12 nm, the complex part of the permittivity is therefore approximately twice the bulk value. Note that doubling the imaginary part leads roughly to doubling the resonance width, and related to it, to halving the near-field intensity enhancement [69].

Finally, for particles smaller than 2 nm, the classical description only gives a rough estimate for \epsilon and more sophisticated models, like jellium and quantum hydrodynamic models, or models based on a non-local dispersion relation, have to be used [69,73–75]. This, however, is beyond the scope of this thesis, as we consider particles in the 20 – 100 nm range.

3.2 Numerical results

Our aim is to give a full and detailed picture of the plasmon resonances for nanowires. We illuminate with plane waves, with the wave vector in the plane of the cross-sections. We consider TE-polarization, where the electrical field is in the plane of the cross-section. (Plasmon resonances are not excited for TM-polarization, where the electrical field is parallel to the symmetry axis [2].) Note that the excitation of plasmon resonances with a plane wave is sufficient for our purpose: on the scale of the cross-sections – well below the wavelength – most realistic light sources can be well-approximated by a plane wave. Exceptions include the excitation by evanescent surface waves along an interface, and a very small source close to the scatterer, modeled with a dipole.

To be more realistic, and to avoid numerical difficulties, the corners of all the non-regular cross-sections studied in this Chapter are rounded off by 0.25 nm. In P3 we demonstrate that this does not affect our numerical results.

3.2.1 Individual nanowires

(a) Shape effects

In this section we investigate for individual nanowires the relationship between the shape of its cross-section and its resonance spectrum. Figure 3.2 shows the SCS of nanowires with simplex cross-sections corresponding to that of a circle, a hexagon, a square and a triangle. The diameter of the circle is \( d = 20 \text{ nm} \), and all the particles have the same area, so that the SCS should be comparable. The illumination direction is along one of the particle’s symmetry axis. For the circle we recover the well-known result of a single resonance, at \( \lambda = 338 \text{ nm} \) (corresponding to \( \epsilon = -1.07 + 0.29 i \)), with a full width half maximum (FWHM) of about 25 nm. The structure of the SCS becomes more complex for less regular particles, and the main resonance is red-shifted, up to \( \lambda = 385 \text{ nm} \) for the triangle (Fig. 3.2). An additional resonance appears for all the non-circular particles, and a third resonance can be observed for the triangle. The influence of the direction of illumination on the SCS is very small due to the symmetry of the simplexes (not shown).
The large SCSs that occur at the plasmon resonances are associated with large field amplitudes at the vicinity of the particle. In Fig. 3.3 we show this near-field amplitude distribution for the main resonance of each simplex. The amplitude is normalized to the incident amplitude, and the illumination direction is from the top.

The amplitude inside the circular particle is almost homogeneous, about 7 times the incident field. The boundary of the cylinder is not visible in the amplitude distribution because the resonance happens when $\varepsilon'$ is close to $-1$. Maxwell’s boundary conditions impose then that the field amplitude is continuous [76]. The field amplitude decays rapidly outside the particle. The field becomes strongly heterogeneous for the non-regular structures. At the main resonance, the field amplitude takes large values near the corners transverse to the incident wave vector (Fig. 2). The relative field amplitude exceeds 20 for the hexagon and the pentagon, 70 for the square and 150 for the triangle. Let us stress here that the large fields observed near the corners are not produced by the lightning rod effect. For the rounded-off corners used here, the lightning rod effect provides only a field amplification factor in the order of 5, even for very large negative permittivity values, as illustrated in Fig. 4(c) of P2. It is even less for wavelengths corresponding to positive permittivities [see Fig. 3.5(a)].

We now break the symmetry of the simplex triangle. In Fig. 3.4 we show the SCS of a right-angled, 2:1 aspect ratio triangular particle for two different illumination directions, along and normal to the hypotenuse. We observe a complex
Figure 3.4: SCS for a right-angled, 2:1 aspect ratio triangular particle, for two different illumination directions indicated by the arrows.

resonance spectrum, with many resonances. Fig. 3.4 stresses the importance of the illumination direction that determines which resonances can be excited in the particle. More aspects of the influence of the illumination direction are discussed in P4, where we study both regular (elliptical) and non-regular cross-sections for different illumination directions.

In Fig. 3.4, the SCS is extremely large for the main resonance for illumination normal to the hypotenuse. Moreover, it is red-shifted with respect to the main resonance of the simplex triangle. The influence of the aspect ratio of the triangle onto the main resonance wavelength is studied in more detail in P3.

In Fig. 3.5 we show the near-field distributions for this non-symmetrical triangular cross-section, corresponding to three different resonances observed in Fig. 3.4, as well as out of resonance at $\lambda = 300$ nm. Fig. 3.5 shows how both the field topology, as well as the maximum field amplitudes, strongly depend on the illumination wavelength. Out of resonance we have a very homogeneous and low field [Fig. 3.5(a)], whereas we obtain confined fields at the lower-left corner [Fig. 3.5(b)], and at the sharp corner [Fig. 3.5(c) and (d)], for specific resonance wavelengths. The maximum enhancement with about 10 is rather moderate for the resonance at $\lambda = 329$ nm [Fig. 3.5(b)]. However, this resonance is most remarkable, as it exists for all illumination directions, with the field always enhanced at the corner longitudinal.

Figure 3.5: Relative field amplitude distribution for the right-angled, 2:1 ratio triangular particle, at (a) $\lambda = 300$ nm, (b) $\lambda = 329$ nm, (c) $\lambda = 392$ nm, and (d) $\lambda = 458$ nm. Scale as indicated, illumination along the (11) direction.
to the illumination direction. As discussed in P2 and P3, this resonance can be related to the bulk mode.

For both the main resonance ($\lambda = 458\text{ nm}$), and the neighboring resonance at $\lambda = 392\text{ nm}$, we obtain field amplitude enhancements of more than 200 near the upper left corner [Fig. 3.5(c) and (d)]. This is a very important observation, as such large field enhancements have not been obtained so far for individual particles. The field topology is very different for these two resonances. This can be related to the polarization charge distribution, as analyzed in P5: charges of one sign accumulate near the corner for the main resonance, leading to the symmetrical, point-charge like field distribution near the corner. Contrarily, charges of both signs are near the corner for the higher order mode at $\lambda = 392\text{ nm}$, leading to the dipole-like field. In P5 we analyze in greater detail this exemplary non-regular cross-section, and as a reference an elliptical cross-section. We show the time evolution of the vectorial field distributions for the resonances, and relate the different modes to the different complexity of their polarization charge distributions. Moreover, we observe that the resonance-driven near-field of the particle is out of phase with respect to the illumination field. Such a phase shift is typical for a resonant system.

Other aspects of the relationship between particle shape and the corresponding resonance spectrum are studied in P3. In particular, we investigate different aspect ratios for triangular and rectangular cross-sections with respect to the resonance wavelengths and the field enhancements.

In P4 the near-field distribution of elliptical and triangular cross-sections are presented in movies for the entire optical range. These movies emphasize again the sensitivity of plasmon resonant nanowires to the illumination wavelength. Moreover, the results in P4 stress the importance of the illumination direction that determines which resonances are excited in non-symmetrical particle.

(b) Size effects

In this section we investigate how the size of the cross-section affects the resonance spectrum of silver nanowires. Whereas we have shown in Fig. 3.2 the SCS of simplexes in the 20 nm range, we show in Fig. 3.6 the SCS for simplexes in the 50 nm range.
range (i.e. the circle diameter $d$ is now 50 nm, and the other simplexes have again the same area than this circle). We observe mainly two differences with respect to the SCS of the smaller simplexes (Fig. 3.2). First, all resonances are red-shifted. For the triangular simplex, for instance, the main resonance is shifted from $\lambda = 385$ nm to $\lambda = 398$ nm. Second, the resonance FWHM is roughly doubled (i.e. for the circle it is now more than 50 nm, compared to 25 nm previously). We also see in Fig. 3 that an additional resonance can be resolved for the square at $\lambda = 351$ nm, whereas two additional resonances start to emerge for the triangle at approximately $\lambda = 350$ nm and $\lambda = 382$ nm.

In Fig. 3.7 we study the influence of the size for one exemplary non-regular cross-section over a larger size range. The cross-section is a right-angled, isosceles triangle. Again, we observe that with increasing size the resonances shift to larger wavelength, and the spectra become more complex. Although more resonances are excited for larger particles, the broadening leads to an overlapping of the resonances such that they cannot all be resolved.

This broadening of the resonances is associated with a decrease of the average near-field amplitude, as evidenced in P4 for the entire optical range. In P3 we show that the maximum enhancement at the corresponding main resonance is constant in the 20 nm to 50 nm range, and then decreases for larger particles. This will also be addressed in Sec. 4.1.

Let us next study the influence of the particle background on the resonance spectrum. In Fig. 3.8 we show the SCS for a triangular cross-section, embedded in air ($\varepsilon_B = 1$) and in water ($\varepsilon_B = 1.778$). We observe that for higher background permittivity the resonance spectrum is red-shifted and broadened, very similarly to the size effect (see Fig. 3.7). The reason why these two effects are closely related is obvious: when increasing the background permittivity, the particle simply becomes larger with respect to the effective wavelength of the background, and retardation – which is responsible for the size effect – comes into play already for smaller particle size.
3.2. NUMERICAL RESULTS

3.2.2 Interacting regular nanowires

Even at the plasmon resonance, the maximum field enhancement for individual silver cylinders does not exceed a factor of 10. In the last section we have observed that much larger electromagnetic field enhancements, locally up to several hundred, are obtained by changing the shape of this regular cross-section. The purpose of this section is to show that regular cylinders, although harmless individually, can also provide strong enhancement when they are coupled together.

(a) Influence of inter–particles spacing

In this section we study the coupling between two cylinders (diameter \( d \)) with different separation distances \( a \) (see Fig. 3.9).

In Fig. 3.10 we first investigate the resonance spectrum for two cylinders with a diameter \( d = 20 \text{ nm} \) and a spacing \( a = 2 \text{ nm} \), illuminated both along and normal to the major axis defined in Fig. 3.9. To ease comparison, we also show the SCS for a single cylinder, which has a single resonance at \( \lambda = 338 \text{ nm} \). No additional resonances are excited when the cylinders are illuminated along the major axis. Contrarily, an additional mode is excited at \( \lambda = 368 \text{ nm} \) for illumination from the top, with a SCS eight times larger than for the single cylinder resonance.

In Fig. 3.11 we show the field distribution corresponding to the single resonance

Figure 3.9: Investigated scattering geometry: the diameter of the cylinder is \( d \) and the separation distance \( a \). We simply refer the joint symmetry axis (dashed line) as the major axis.
observed for illumination along the major axis [Fig. 3.11(a)], and for the two resonances observed for illumination normal to the major axis [Fig. 3.11(b),(c)]. The two resonances at $\lambda = 338$ nm [Fig. 3.11(a),(b)] correspond to the resonances of the single cylinder, although the field distribution is slightly modified by the neighboring cylinder with respect to the single cylinder [see Fig. 3.3(a) on p. 21]. The field amplitudes are similar and do not exceed a factor of 10. Note that for illumination from left (i.e. along the major axis), the field amplitudes are smaller in the right cylinder, as the field has already been damped by the left one [Fig. 3.11(a)].

In Fig. 3.11(c) we show the field distribution corresponding to the additional, coupling-induced resonance at $\lambda = 372$ nm, as observed for illumination normal to the major axis (see Fig. 3.10). The field enhancement in the gap of the cylinders is very large, almost 100 times the illumination amplitude. Even for regular 2D particles, the coupling effect can therefore give rise to field enhancements similar to those obtained for individual, non-regular particles (Sec. 3.2.1).

The existence of this coupling induced resonance, as well as the non-existence of an additional resonance for illumination along the symmetry axis, can be understood with an illustration of the polarization charge (Fig. 3.12). For illumination from left (i.e. along the major axis), negative charges oppose in the upper halves of the

Figure 3.11: Relative field amplitude distribution for two interacting, $d = 20$ nm cylinders with spacing $a = 2$ nm. (a) $\lambda = 338$ nm, (b) $\lambda = 338$ nm, (c) $\lambda = 368$ nm. Illumination direction as indicated.
3.2. NUMERICAL RESULTS

Figure 3.12: Polarization charge distribution for two interacting, $d = 20$ nm cylinders with spacing $a = 2$ nm, illuminated (a) along, and (b) normal to the major axis, at the corresponding main resonance.

cylinders, whereas positive charges oppose on the lower half [Fig. 3.12(a)]. As charges of the same sign repel each other, coupling cannot act constructively, and we do not observe an additional mode. In fact, the charge density on the cylinder segments near the gap is even lower than on the rest of the circumference due to the repelling force. This is why we observe a minima in the field amplitude in the gap [Fig. 3.11(a)].

For illumination from the top, contrarily, charges of different sign oppose in the gap [Fig. 3.12(b)]. At the coupling resonance wavelength, additional polarization charges are then induced due to the attractive force. This leads to highly concentrated polarization charges at the cylinder segments near the gap [Fig. 3.12(b)], that give rise to the large field enhancement observed in [Fig. 3.11(c)].

We next study how the resonance spectrum for illumination normal to the major axis is modified when the particle spacing $a$ is varied. In Fig. 3.13 we show the SCS for $a = 5, 10,$ and $-5$ nm. We observe that the coupling resonance rapidly moves towards the single cylinder resonance at $\lambda = 341$ nm when the spacing is increased. For $a = 5$ nm, the resonance wavelength of the coupling resonance is at $\lambda = 354$ nm,

\[3\] This distribution oscillates in time and half a time period later it is vice versa.

Figure 3.13: SCS for two interacting, $d = 20$ nm cylinders, illuminated from the top, for three different spacings $a$. 

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**Figure 3.12:** Polarization charge distribution for two interacting, $d = 20$ nm cylinders with spacing $a = 2$ nm, illuminated (a) along, and (b) normal to the major axis, at the corresponding main resonance.

**Figure 3.13:** SCS for two interacting, $d = 20$ nm cylinders, illuminated from the top, for three different spacings $a$. 

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while for $a = 10 \text{ nm}$ the additional coupling resonance already begins to merge with the single cylinder resonance.

Contrarily, when the cylinders intersect (corresponding to a negative spacing $a$), the spectrum becomes much more complex, as visible in Fig. 3.13 for $a = -5 \text{ nm}$. Several resonances are excited, covering a broad wavelength range from $\lambda = 328 \text{ nm}$ to $\lambda = 460 \text{ nm}$. The resonance at $\lambda = 460 \text{ nm}$ corresponds to a mode where polarization charge flows from one cylinder to the other, and has therefore no equivalent when the cylinders are separated (P7).

In Fig. 3.14 we show the near-field distribution at main resonance for the three geometries studied in Fig. 3.13. We observe that for $a = 5 \text{ nm}$ the field amplitude maximum in the gap is with about 30 much lower than the field amplitude of almost 100 for $a = 2 \text{ nm}$ [Fig. 3.14(b)]. The field amplitude maximum in the gap for $a = 10 \text{ nm}$ is only slightly larger than for the main resonance of the individual cylinder, as already implied by the SCS curve which are very similar (Fig. 3.13).

In the intersecting case, on the other hand, very large field amplitude enhancements are obtained in the grooves (Fig. 3.14c). These very strong fields (locally more than 100) are however confined to a very small area.

In P7 we study $d = 50 \text{ nm}$ cylinders for several spacings $a$. We display in movies the near-field distribution for the entire optical range. We further show that the higher order modes, as observed for intersecting cylinders, correspond to complex polarization charge distributions near the grooves.

(b) Retardation–induced resonance

In the previous section we considered two coupled $d = 20 \text{ nm}$ cylinders and observed that an additional mode is only excited for illumination normal to the major axis. The size effect for this illumination, i.e. the modification of this coupling resonance when the diameter is increased, is detailed in P6. We do not detail it here, as it is very similar to the size effect observed for individual particles (Sec. 3.2.1).

For illumination along the major axis, where we have observed in the previous section that a coupling resonance does not exist for $d = 20 \text{ nm}$ cylinders, the size effect is more interesting. This is shown in Fig. 3.15, where we report the SCS for cylinders of varying diameter $d$, illuminated along the major axis. The spacing $a$ is scaled proportionally, so that the ratio $d/a$ remains constant: $d/a = 5$ (see Fig. 3.9). We observe that a coupling mode starts to appear when $d$ reaches about 50 nm.
This mode is then broadened and red-shifted to larger wavelengths with increasing values of \( d \) [Fig. 3.15(a)].

In Fig. 3.16(a) we show the near-field distribution corresponding to the coupling resonance wavelength \( (d = 50\,\text{nm}, \lambda = 372\,\text{nm}) \). We observe a field distribution in the gap that is very different from the homogeneous field observed for illumination from the top: now the field at the center vanishes. This can be understood with the polarization charge distribution associated with this mode [Fig. 3.16(b)]. We observe in this case a quadrupole–like polarization charge distribution, where charges of different sign oppose on the upper, respective lower half of the two cylinders. For this resonance, the electric field driving each scatterer is out of phase. This mode is therefore solely induced by the phase advance, or retardation, as the incident field propagates through the structure. It is the result of a subtle balance between particles size and separation. Small separation is required for the coupling between the particles, which in turn requires large enough scatterers so that their driving fields are out of phase. In particular, the phase difference between the particles is essential for this mode. This is why we do not observe this resonance for very small cylinders (Fig. 3.15).
Figure 3.17: SCS for two interacting, cylinders, illuminated from the left, for different diameters \( d \). The particle background is water (\( \varepsilon_B = 1.78 \)). The ratio between the cylinder diameter and the cylinder spacing \( a \) is \( d/a = 5 \) nm.

To illustrate the role played by retardation, we report in Fig. 3.17 the SCS for the same geometry as in Fig. 3.15, but with a water background (\( \varepsilon_B = 1.78 \)) \cite{77}. As expected, the overall SCS is more complex, with more resonances than in the vacuum case (compare Figs. 3.17 and 3.15). We see that the dimension onset \( d \) where the retardation induced resonance appears is now reduced. This is simply caused by the shorter effective wavelength in the surrounding medium, so that the required phase difference between both scatterers already occurs for particles in the order of \( d \approx 35 \) nm.

Let us finally show that this retardation–induced mode can propagate along a chain of coupled cylinders. In Fig. 3.18 we show for two different wavelengths the field distribution for eight \( d = 50 \) nm cylinders, with a spacing \( a = 10 \) nm. At the single particle resonance wavelength (\( \lambda = 340 \) nm), we observe that the field does not propagate along the structure, but is damped and mainly back–scattered.

Figure 3.18: (a) Relative field amplitude distribution for eight interacting, \( d = 50 \) nm cylinders with spacing \( a = 10 \) nm, illuminated from left. The wavelengths corresponding to the individual resonance (\( \lambda = 340 \) nm) and the coupling resonance (\( \lambda = 360 \) nm) are investigated.
Contrarily, the field propagates along the chain for the retardation-induced mode ($\lambda = 372\text{nm}$). This frequency selectivity, combined with the very small dimensions of the particles, could be extremely interesting for optical devices, as will be discussed in Sec. 4.2.

### 3.2.3 Interacting non–regular nanowires

In Sec. 3.2.1 we studied the relationship between particle shape and size and its plasmon resonance spectrum for individual non–regular nanowires, while in Sec. 3.2.2 we investigated interacting regular wires (i.e. cylinders). In this section, we want to briefly sketch how these two effects can act simultaneously.

In Fig. 3.19 we show the SCS for two nanowires with a 20 nm square cross-section, separated by a distance $a = 2\text{nm}$, and illuminated along the direction of the slot. For comparison, we also show the SCS for a single 20 nm square, and for a 40 nm × 20 nm rectangle that would be obtained if the two squares would merge. The SCS for the interacting nanowires is very similar – and slightly smaller – than the SCS of the 40 nm × 20 nm rectangle. The spectrum is governed by a broad resonance at $\lambda = 374\text{nm}$, and the bulk resonance at $\lambda = 329\text{nm}$ cannot be separately resolved, although it is adumbrated. An additional small resonance can be resolved for the coupled squares at $\lambda = 400\text{nm}$.

In Fig. 3.20 we show the field distributions corresponding to two resonances at $\lambda = 374\text{nm}$ and $\lambda = 400\text{nm}$. For the main resonance [$\lambda = 374\text{nm}$, Fig. 3.20(a)] we observe large field enhancements at the outer corners, similar to those obtained for the main resonance of the 40 nm × 20 nm rectangle (not shown). The slot, therefore, only slightly disturbs the field with respect to the main resonance of the rectangle. In other words, the polarization charges near the slot arrange in a manner to bridge the gap, leading to a field enhancement in the slot up to about 40 in the center [see Fig. 3.20(a)].

The field distribution for the small, coupling–induced resonance at $\lambda = 400\text{nm}$ is
very different. The field enhancement near the outer corners is here very moderate, while we have very large field enhancements at the inner corners, almost 100 times the illumination amplitude [Fig. 3.20(b)].

It is quite surprising that this additional resonance, which produces a similarly large near-field than the main resonance, is associated with a much smaller SCS (see Fig. 3.19). We believe that the reason lies in the difference of the charge oscillation paths. For the $\lambda = 374\,\text{nm}$ resonance, for each particle postive charges are distributed on one vertical side and a similar amount of negative charges on the opposite side. These distributions oscillate in time, so that the charges move on each entire particle. Contrarily, for the $\lambda = 400\,\text{nm}$ resonance both positive and negative charges are concentrated to the inner sides of the squares, as implied by the field distribution [Fig. 3.20(b)]. Very little charge is distributed on the rest of the particle. For that resonance, the oscillating charges motion is mainly limited to the inner side of each particle. This motion is confined to a shorter path, which we believe produces the smaller SCS.

Let us finally study two coupled nanowires with a rather large, truncated triangular cross-sections. A similar geometry has recently been realized by van Duyne et al. using latex sphere lithography [11]. The length of the simplex triangle is 100 nm and the radius of curvature for the truncated corners 10 nm. The spacing is 10 nm as well. In Fig. 3.21(a) we show the SCS of this coupled system, and for comparison, the SCS for a single truncated triangle. Like for the coupled cylinders that have just been studied, the coupling effect manifests here also as an additional resonance, excited at a larger wavelength than the main resonance of the single particle.

For a single nanowire with such a large, truncated cross-section the field enhancement is less than 20 over the entire optical range (not shown). In Fig. 3.21(b), where we show the field distribution for the coupled nanowires at main resonance, we observe that the coupling effect leads to a rather large field enhancement of about 40, confined to the gap between the opposing corners. Note that we did not observe such large field enhancement for cylindrical particles with a separation distance of $a = 10\,\text{nm}$.
Figure 3.21: (a) SCS for a single, and two interacting nanowires with a truncated, triangular cross-section (length 100 nm), illuminated from the top. (b) Relative field amplitude distribution for the coupled wires at main resonance ($\lambda = 480$ nm).
Chapter 4

Applications

In this chapter we discuss the implications of the numerical results described in Chapter 3 for three areas of nanoscience: surface enhanced Raman scattering (SERS), scanning near-field optical microscopy (SNOM), and optical nanodevices.

4.1 Surface enhanced Raman scattering

The Raman spectrum of a molecule gives characteristic information on the bonds between the molecules constituents. The knowledge of the Raman spectrum is important for many areas of chemistry or life sciences, as it allows to detect, identify and analyze molecules [78].

However, measuring the Raman signals of molecules is most often not very simple, as the Raman signal is very weak, typically much weaker than the noise of the system at the corresponding frequency. Hence, either the background noise has to be reduced to a minimum, or the Raman signal to be enhanced.

Plasmon resonant particles provide such enhancers. The Raman signal of molecules adsorbed on silver and gold nanoparticles is enhanced by several orders of magnitudes. This effect is known as surface enhanced Raman scattering (SERS) and was discovered in the mid-seventies [18, 19]. Meanwhile, SERS has become an important analysis tool, and even single molecule detection has been achieved, requiring Raman signal enhancements up to $10^{14}$ [21–23].

Although the adsorption mechanism of the molecule on the metal can participate in the Raman enhancement [79, 80], it is believed that the large electromagnetic near-field associated with the excitation of plasmons in the metallic nanoparticles contributes the major component of the SERS effect [78]. Instead of the illumination amplitude, the molecule sees the near-field amplitude of the nanoparticle at the molecule location. The Raman scattering – a two photons process – is then in a good approximation proportional to the fourth power of the local near-field amplitude [81].

For nanowires with cross-sections of different shape and size, we investigate now how large this local electromagnetic enhancements can be. Figure 4.1 shows the maximum enhancement, obtained at a 1 nm distance from the surface of the 20 nm simplexes, as a function of the wavelength. We observe that the field enhancement, which is a near-field quantity, is strongly correlated to the SCS (Fig. 3.2 on p. 21),
a far-field quantity. The maximum amplitude enhancement increases considerably for more complex shapes. Whereas it is 6 for the circle, it is about 35 for the triangle. The differences between the simplex shapes is much more pronounced for the Raman enhancement than for the SCS. For the triangle the maximum Raman enhancement exceeds $10^6$, for the square it is still about $10^5$, whereas it is below $10^4$ for the hexagon, the pentagon and the circle.

As previously discussed, the local variations of the near-field distribution determine the effective enhancement experienced by a molecule. This is investigated in Fig. 4.2, where we present the amplitude distribution as a function of the distance from the tip surface, for the triangle, square and circle. The data correspond to the main resonance, and two particle sizes (20 and 50 nm) are considered.

For the circle, the field amplitude on the surface reaches 6.9 (4.5), for the small (larger) circle. At 2 nm from the surface, the amplitude drops to 2.2 (1.7). For the triangle we observe a huge enhancement for both particle sizes: near the surface
more than 100 in terms of amplitude (10^8 Raman), and still more than 50 (6·10^6) at a half-nanometer distance (Fig. 4.2). For the square we obtain a similar behavior, although the amplitudes are about a factor of two smaller (the Raman enhancement being 16 times weaker). The strong field amplitude variations for such non-regular structures might explain the “hot spots” observed at specific locations both in SERS experiments and in direct measurement of the locally enhanced field [82, 83].

Figure 4.2 indicates similar results for the maximum amplitude distribution around the 20 nm and the 50 nm simplexes. This enhancement rapidly decreases for particle sizes above 50 nm, as described in P4. For example, the maximum amplitude enhancement at the corner of a 100 nm triangle is only half that of the 20 or 50 nm particles. Moreover, Fig. 4.2 also indicates that the efficiency, defined as the average Raman enhancement near the surface, decreases with larger particle size. This is of special importance for the optimal Raman enhancement of many, statistically distributed molecules, as discussed in P3.

As evidenced in Chapter 3, the resonance spectra of non-regular particles are more complex than those of regular particles. The possibility to address different resonances by tuning the illumination wavelength can prove useful for specific applications. In Fig. 4.3 we show the field amplitude as a function of the distance from the corner for the three resonances of the 50 nm triangle (see Fig. 3.6). We observe a similar enhancement of about 150 close to the surface for the main resonance (λ = 399 nm) and the resonance at λ = 364 nm. However, the field decays more rapidly for the latter resonance (Fig. 4.3). This behavior can be related to the polarization charge distribution associated with both resonances, as illustrated by the animations in P5. For the main resonance a point–like charge distribution builds at the corner. This distribution produces a field amplitude dependence in 1/d, where d is the distance from the surface. The resonance at λ = 364 nm is associated with a dipolar–like charge distribution, leading to a 1/d^2 distance dependence (Keep in mind that we have a 2D geometry, so the point–like and dipolar charge distributions correspond to 2D distributions).

For the small resonance at λ = 329 nm we show the field amplitude as a function of the distance from the longitudinal corner, where the field is maximum. The
amplitude maximum (about 10) is moderate, and at the corner the field decays rather slowly, compared to the other resonances.

Figure 4.4 shows that the near-field amplitude dramatically increases for higher aspect-ratios. For example at the very tip of the 4 to 1 triangle, the field enhancement exceeds 1000, corresponding to a Raman enhancement of $10^{12}$. At a distance of 1 nm from the tip, the field enhancement is still larger than 100 ($>10^8$ Raman).

Additional aspects of various individual plasmon resonant nanowires with respect to SERS have been investigated in P2 and P3. In particular, the dependence of the Raman enhancement on the illumination direction has been discussed in P2, whereas the size effect, and the effect of the aspect ratio for rectangular cross-sections, have been investigated in P3.

We have shown that large Raman enhancement occur for non-regular individual nanowires, and the large, localized fields can explain the hot spots observed in many SERS experiments [78]. The large field gradients that we evidenced might even explain the blinking effect observed in an experiment where single molecules are adsorbed on isolated nanoparticles [22]. Little thermal vibrations of the adsorbed molecules may indeed lead to fluctuations of the Raman signal if the molecule is placed in a strongly inhomogeneous field.

Many SERS experiments where large Raman signal enhancements are observed rely on silver structures where nanoparticles are strongly interacting [84]. In Sec. 3.2.2 we have shown that a large field enhancement also arises when two regular particles come close to each other. In Fig. 4.5 we study the field enhancement in the gap between two $d = 20$ nm cylinders, for three different separation distances $a$. We show this enhancement along the major axis, in the gap between the cylinders, as a function of the distance from one cylinder. Fig. 4.5 shows that large fields are obtained for a spacing $a = 2$ nm, leading to a Raman enhancement larger than $10^7$. Note that the field is very homogeneous, unlike the large field gradients observed for individual, non-regular cross-sections (Figs. 4.2–4.4).

Finally, for larger separations, the Raman enhancement becomes much smaller, about $10^5$ for $a = 5$ nm, and less than $10^4$ for $a = 10$ nm.
4.2 Optical devices

The dimensions of transmission lines and switches in integrated optical components is a limiting factor for further miniaturization towards nanometer scale devices.

For a conventional dielectric waveguide, the smallest beam diameter is given in principle by the effective wavelength in the core material [85]. Much interest has been recently addressed to dielectric microparticles and microcavities, which can act individually as very efficient light couplers due to internal resonances [86–88], or guide and switch frequency-selectively modes in photonic crystal arrays [89]. However, the dimension of these systems is still in the order of several wavelengths.

We have established in Chapter 3 that individual plasmon resonant nanowires, and for similar reasons plasmon resonant nanoparticles, provide extremely efficient scatterers that are highly sensitive to the optical wavelength. They might therefore be very useful for optical switching or signal processing on a nanometer scale. The results obtained in Chapter 3 might be important for this purpose. Whereas the resonance wavelength can be tuned by giving the particle a certain shape and size, the size of the particle determines the width of the resonance, and therefore the frequency range where the particle is active.

Interacting nanoparticles, on the other hand, can be used to guide electromagnetic modes via evanescent optical transport over several microns [35, 41, 42]. In Fig. 4.6 we show the near-field distribution of twenty $d = 25 \text{ nm}$ diameter cylinders, with a separation distance $a = 25 \text{ nm}$, illuminated along the major axis by a Gaus-
Figure 4.6: Field amplitude distribution for twenty 50 nm diameter cylinders with 25 nm spacing, illuminated from the left with a Gaussian beam (beam width: 725 nm).

Gaussian beam (beam width: 725 nm). We show two wavelengths, corresponding to the individual and the coupling resonances. For the individual resonance we observe that the interaction with the Gaussian beam is limited mainly to the first cylinder, and the field is highly damped. Note the considerable standing wave on the left side of the cylinders, although their diameter is twenty times smaller than the Gaussian beam width, stressing again that plasmon resonant particles are extremely efficient scatterers.

For the coupling resonance, on the other hand, most of the energy is transported along the chain. The amplitude of the standing wave in front of the cylinders is small. Moreover, the damping along the main axis is also very low, although the propagation distance is more than one micron. This is in good agreement with experiments, where it was recently shown that such a mode can propagate over several microns [36].

For the same geometry, we show in Fig. 4.7 the field distribution for illumination from the top. For both wavelengths we observe that most of the incoming light is back-scattered. However, some power is also transmitted. Its intensity strongly depends on the wavelength. Whereas it is less than 5% for $\lambda = 340$ nm, it is nearly 30% for $\lambda = 340$ nm. Hence, such cylinder gratings may be used to filter optical signals. Very similar to this observation is a recent experiment with nano-hole structures in thin silver films, where a large dependence of the transmittance on the wavelength was also observed [43].

Although not yet fully investigated, these examples shall give an impression how coupled plasmon resonant particles can be used to guide, filter or manipulate light.
4.3 Scanning near-field optical microscopy

In classical optical microscopy, the resolution of any object is limited to approximately half the effective wavelength of the illumination source [90]. This limit can be overcome by scanning a tip over the substrate at a distance of only a few nanometers. In that case, either the evanescent near-field of the object can be probed by the tip, or the evanescent near-field of the tip can interact with the object. Both set-ups are realized and lead to subwavelength-resolution. This technique is known as scanning near-field optical microscopy (SNOM) [91].

The bottleneck of SNOM is that information can only be obtained on the combined system object and tip. In particular, the lateral confinement of the tip near-field gives a lower boundary for the resolution [92]. Moreover, a high field intensity is required for a large enough light throughput, while large field gradients provide an important dynamic range [91, 30].

Non-regular plasmon resonant particles seem ideal for this purpose [30, 32, 33]. It was experimentally demonstrated how small metallic particles can be attached on the top of a cantilever [9, 93], or at the end of an apertureless fiber tip [34]. We will now investigate the near-field of specific metal nanoparticles and concentrate on the field distribution between 1 and 10 nm below the particle, representing the typical interaction range of SNOM tips.

Let us first investigate the field intensity below a triangular silver particle in the 20 nm range. In Fig. 4.8 we show the lateral field distribution at the main resonance, for different distances $\delta$. We observe that the field intensity is well confined both for $\delta = 1$ nm and $\delta = 2$ nm below the tip, with a FWHM of less than 5 nm. For larger distances we have a FWHM of more than 10 nm. The field intensity is very large below the tip: nearly 1500 for $\delta = 1$ nm, and still almost 500 for $\delta = 2$ nm. With larger distances the field intensity decays rapidly. Such a large decay – or a large gradient – is highly desirable for SNOM, since it provides a large dynamic range which might limit the artifact caused by the shear force feedback mechanism. Note that the decay curves in vertical direction have already been shown in Fig. 4.2 on
Figure 4.8: Lateral relative electric field intensity distribution, at different distances $\delta$ from the equilateral tip, at the main resonance ($\lambda = 385\text{ nm}$).

p. 36 (the figures give the field amplitude, i.e. the square root of the intensity shown here). Hence, we observe that at main resonance, such a triangular profile provides very large field intensities below the tip, and a strong confinement both in lateral and forward direction.

Figure 4.9 emphasizes the importance of the illumination wavelength on the near-field generated by such a plasmon resonant tip. Both the lateral field confinement, and the field intensity depend strongly on the wavelength. At the main resonance ($\lambda = 385\text{ nm}$), for instance, the field intensity is 30 times larger than for the resonance at $\lambda = 358\text{ nm}$. Moreover, the decay curves in vertical direction are very different for the several resonances, as shown in Fig. 4.3 on p. 37 (the figures give the field amplitude, i.e. the square root of the intensity shown here).

By changing the illumination wavelength it is therefore possible to change the tip throughput and its dynamic range. Hence, plasmon resonant silver tips provide a

Figure 4.9: Lateral relative electric field intensity distribution at a $\delta = 2\text{ nm}$ distance from the equilateral tip, for two plasmon resonances ($\lambda = 385\text{ nm}$ and $\lambda = 358\text{ nm}$) and out of resonance at $\lambda = 600\text{ nm}$.
means to obtain different optical systems without changing anything of the physical system.

Additional aspects of the intensity distributions generated by a plasmon resonant tip have been studied in P8. In particular, we investigate how the near-field of the dynamic range below the tip is modified when the shape of the tip is varied.
Chapter 5

Conclusion and outlook

A new finite element technique based on the Green’s tensor technique has been developed for the study of plasmon resonant particles. The technique was successfully applied to investigate the plasmon resonances of silver nanowires. We gave a detailed picture of the relationship between the shape and size of the cross-section, and the resonance spectrum, both for individual and interacting nanowires. It was shown that the electrical near-field of plasmon resonant nanowires is extremely sensitive to the illumination wavelength. For individual non-regularly shaped nanowires we observed several resonances, covering a broad wavelength range. The specific field distribution associated with each resonance was related to the corresponding polarization charge distribution induced in the particle. For specific resonances of individual non-regularly shaped nanowires, we observed dramatic near-field enhancements, in the order of several hundred times the illumination amplitude. A similar enhancement was observed for closely spaced and interacting cylindrical wires. We showed further that an additional, retardation induced resonance can be excited for larger interacting nanowires. This peculiar resonance allows optical transport along a chain of particles.

The implications of these results for surface enhanced Raman scattering (SERS) have been discussed in detail. Our results are in excellent agreement with recent SERS experiments, including the huge Raman signal enhancements reported for single molecules [21–23]. The electromagnetic near-fields, shown for silver nanowires of various shape and size over the entire optical range, may help design efficient SERS substrates, particularly when the illumination wavelength of the laser is given by the experimental set-up. As evidenced in this work, both high aspect-ratio triangular cross-sections, as well as small separation distances to neighboring particles, increase the available maximum near-field enhancement. To increase the SERS enhancement further, it may be very helpful to study in detail how these effects can act simultaneously. Moreover, the large field enhancements obtained near plasmon resonant particles, and those obtained at the internal resonances in microcavities [86, 87], might be combined to develop new generations of biosensors.

We further stressed in the present work that individual non-regular plasmon resonant particles provide a means to increase the resolution in near-field microscopy. The interaction of the silver particle with the bulk part of the SNOM tip, as well as the interaction with the sample under study, will certainly affect the plasmon
resonance. Also here, further investigations are necessary to get more insights in the complex image formation process in SNOM, using silver nanoparticles.

We showed that both individual and coupled nanowires are highly interesting for optical devices, as they provide a tool to guide, filter and manipulate light. We believe that it is worth investigating coupled nanowire systems in greater detail. Two demanding problems appearing in integrated optics devices are the optical transport on a very small scale, and the frequency selective optical signal processing. Both problems could be addressed using plasmon resonant nanoparticles. Our results show for example that the frequency range for optical transport along a particle chain can be tuned by changing the particle spacing. Several coupled nanoparticles, arranged and optimized in a more complex configuration could even provide additional signal processing capabilities.

In many experimental situations metal nanoparticles or nanowires are located on a surface, or embedded in a layered medium. When these substrates are metallic or have a high permittivity, they strongly influence the resonance spectrum of plasmon resonant particles embedded in them. These surface effects have not been considered in the present work. An advantage of our approach lies in the fact that such a stratified background can also be included by using the corresponding Green’s tensor [94]. Also in this case only the scatterer has to be discretized, as the information on the stratified background is already included in the corresponding Green’s tensor. The determination of this Green’s tensor is far from being easy and involves Sommerfeld integrals that cannot be solved analytically [94]. A numerical scheme for arbitrary stratified backgrounds has been recently developed in our group, both for 3D and 2D problems [51, 53]. The finite element technique presented in this work was recently combined with this stratified background approach, giving some promising first results. A regularization scheme for the reflected part of the stratified Green’s tensor should be the next step to undertake. Let us recall that in the regularization scheme we subtract the quasi-static Green’s tensor from the integrand, and perform the corresponding integral analytically. The reflected part of the stratified Green’s tensor can also become very large when two identical or neighboring meshes are close to a surface, which requires a specific regularization scheme. For a single surface, an appropriate static Green’s tensor that can be subtracted and then integrated analytically has also been derived recently [95].

Nanowires, i.e. structures infinitely long in the third (not shown) direction, have been studied in the present work. The different effects evidenced for these 2D structures are most likely similar for 3D particles. However, the investigation of arbitrarily shaped 3D particles is definitely a challenge that is worth taking. For 3D particles, we expect even larger near-field enhancements, as the polarization charges at the plasmon resonances can then be confined near corners, instead of edges in the 2D case. This should lead to a higher charge concentration and therefore produce higher local fields. We believe that a three-dimensional implementation of our formalism, as described in P1 and Appendix B, will in principle provide a highly accurate method to compute 3D electromagnetic scattering problems. From the numerical and mathematical point of view, nothing changes qualitatively with respect to the 2D case. However, the study of arbitrarily shaped 3D plasmon resonant particles based on our technique will require a very fine discretization. For our 2D
calculations we observed that about 2500 discretization elements are necessary to accurately compute non-regular cross sections, requiring 600 MByte of RAM. This number of elements in 2D \((2500 = 50^2)\) corresponds to \(50^3 = 125000\) elements in 3D. The RAM requirement for such a computation exceeds that of existing computers. Further, the condition number of the associated matrix equation might be so large, that it will be difficult to solve numerically.

We basically see two ways out of this. First, more appropriate basis functions might be found, rendering a coarser discretization sufficient. One possible choice might be higher order vectorial basis functions [96], as our formalism can easily be extended to vectorial basis functions. Alternatively, our regularization scheme, which is a key component for the accurate computation of plasmon resonant structures, might be used for a uniform mesh technique. Although one then gives up the advantage of a non-uniform tetrahedral grid to exactly model any scatterer, a uniform grid makes possible fast Fourier transform (FFT), thereby reducing both the amount of CPU time and the RAM requirement.

What might finally be further investigated is the dispersion relation used for very small silver particles. In Sec. 3.1.2 we described how the dispersion relation becomes a function of the particle size below 30 nm. To the best of our knowledge, all the theoretical considerations devoted to this topic were limited to spherical particles, where the dispersion relation of the bulk is modified according to Eq. (3.2) on p. 20. For very small non-regular particles, however, Eq. (3.2) might only be a rough estimate, as the dispersion relation should become a function of the location within the particle, and moreover, of the illumination direction. Near corners, for instance, the mean free path will both depend on the exact location and on the direction of the electric field, leading to a non-homogeneous, non-local, tensorial dispersion relation. Moreover, for very large field amplitudes the dispersion relation may also become a function of the electrical field in the particle. In that case, the dispersion relation becomes non-linear. Note, however, that a non-local tensorial permittivity could be implemented in the volume integral equation, which forms the basis of our approach.
Appendix A

Computation of the far-field

Scattering cross sections were often used in the present work to determine the plasmon resonances of silver particles. For both 3D and 2D we show here how the asymptotic field $E(\theta, \varphi)$ [E(\varphi) in 2D], as used for the definition of the SCS (Eq. 2.11), is obtained within our technique.

A.1 3D case

Let us assume that we have found the numerical solution Eq. (2.13) for the electrical field inside the scatterer. The field scattered in $(\theta, \varphi)$-direction is then given by

$$E(\theta, \varphi) = \sum_{\mu} \sum_{m} G_{3D}^{\infty}(\theta, \varphi; r_A^\mu) \cdot V_A a^\mu_A \psi_{A}^{\mu_i}(r_A^\mu). \quad (A.1)$$

where we used the notation of P1. In Eq. (A.1) we introduced the asymptotic Green’s tensor $G_{3D}^{\infty}(\theta, \varphi; r)$, given by

$$G_{3D}^{\infty}(\theta, \varphi; r) = \frac{1}{4\pi} [1 - n n] e^{-ik_0n r}, \quad (A.2)$$

with $n$ defined by

$$n = \begin{pmatrix} \sin \theta \cos \varphi \\ \sin \theta \sin \varphi \\ \cos \theta \end{pmatrix}. \quad (A.3)$$

A.2 2D case

For 2D geometries the field scattered in $\varphi$-direction is given by

$$E(\varphi) = \sum_{\mu} \sum_{m} G_{2D}^{\infty}(\varphi; r_A^\mu) \cdot V_A a^\mu_A \psi_{A}^{\mu_i}(r_A^\mu), \quad (A.4)$$

where the asymptotic Green’s tensor $G_{2D}^{\infty}(\varphi; r)$ reads

$$G_{2D}^{\infty}(\varphi, z, r) = \frac{1 + i}{4(\pi k_0)^{1/2}} [1 - n n] e^{-i\varphi n r}, \quad (A.5)$$
with \( \mathbf{n} \) defined by

\[
\mathbf{n} = \frac{1}{k_0} \begin{pmatrix}
  k_\rho \cos \varphi \\
  k_\rho \sin \varphi \\
  k_z
\end{pmatrix}.
\]  

(A.6)
Appendix B

Explicit regularization terms

In P1 we present a finite element method to solve the VIE. The new regularization scheme requires the analytic computation of two types of integrals. Explicit expressions were given in P1 for the 2D case, with the incidence in the plane of the cross section, since we implemented, assessed and applied that case. Let us give here the explicit expressions for these integrals for the 2D case with oblique incidence, and moreover, for the 3D case using tetrahedral discretization elements. We follow here the notation of P1.

B.1 2D case – oblique incidence

The dynamic Green’s tensor is given by Eqs. (P1-3) and (P1-4). The singular part that we have to extract according to Eqs. (P1-18) reads

\[
\frac{\nabla \nabla}{k_0^2} g^S(r_A^o, r') = -\frac{1}{2\pi k_0^2} \begin{pmatrix}
\frac{\partial_x \partial_x}{i k_z \partial x} & \frac{\partial_y \partial_y}{i k_z \partial y} & \frac{\partial_z \partial_z}{i k_z \partial z} \\
\frac{\partial_x \partial_y}{i k_z \partial x} & \frac{\partial_y \partial_y}{i k_z \partial y} & \frac{\partial_z \partial_z}{i k_z \partial z} \\
\frac{\partial_x \partial_z}{i k_z \partial x} & \frac{\partial_y \partial_z}{i k_z \partial y} & \frac{\partial_z \partial_z}{i k_z \partial z}
\end{pmatrix} \log |\rho_A^o - \rho'|,
\]

where we dropped the \(\exp(-k_z Z)\) dependence after applying the derivative with respect to \(z\). The (3,3) component of this tensor is not singular with respect to the integration, and we will not subtract it.

If we perform straightforwardly the integration over the sphere \(S_A^o\) according to Eq. (P1-22), the off–diagonal terms vanish due to integration over the polar angle, and \(I_{AA}^R\) becomes

\[
I_{AA}^R = \sum_{\beta \neq \alpha} J_A w^\beta \left[ G(r_A^o, r_A^\beta) \phi^\beta(\xi^\beta) - \phi^\beta(\xi^\alpha) \mathbf{D} \left( -\frac{1}{2\pi} \log |\rho_A^o - \rho_A^\beta| \right) \right] (B.2)
+ \phi^\beta(\xi^\alpha) \left( \frac{i \pi R_A^\alpha}{4 k_0} H_1^{(1)}(k_0 R_A^\alpha) - \frac{1}{2k_0^2} \right) \mathbf{A},
\]

where the operator matrix \(\mathbf{D}\) and the diagonal matrix \(\mathbf{A}\) are given by

\[
\mathbf{D} = \frac{1}{k_0^2} \begin{pmatrix}
\frac{\partial_x \partial_x}{i k_z \partial x} & \frac{\partial_y \partial_y}{i k_z \partial y} & \frac{\partial_z \partial_z}{i k_z \partial z} \\
\frac{\partial_x \partial_y}{i k_z \partial x} & \frac{\partial_y \partial_y}{i k_z \partial y} & \frac{\partial_z \partial_z}{i k_z \partial z} \\
\frac{\partial_x \partial_z}{i k_z \partial x} & \frac{\partial_y \partial_z}{i k_z \partial y} & \frac{\partial_z \partial_z}{i k_z \partial z}
\end{pmatrix}
\]

(B.3)
The four components of Eq. (B.2) corresponding to the \((xy)\)-plane are exactly the same than for the TE-case in Sec.IIIB of P1. For \(\mathbf{I}_{AA}^S\), defined in Eq. (P1-18), we therefore may write

\[
\mathbf{I}_{AA}^S = \begin{pmatrix}
(I_{AA}^{S,TE})_{13} & (I_{AA}^S)_{13} \\
(I_{AA}^{S,TE})_{23} & (I_{AA}^S)_{23}
\end{pmatrix},
\]

where the \(2 \times 2\)-matrix \(\mathbf{I}_{AA}^{S,TE}\) is given by Eq. (P1-37). Defining the two-dimensional vector \(\mathbf{J}_{AA}\) as

\[
\mathbf{J}_{AA} = \begin{pmatrix}
(I_{AA}^S)_{13} \\
(I_{AA}^S)_{23}
\end{pmatrix},
\]

and using the definitions Eqs. (P1-35) and (P1-36) for \(r^\alpha_A(t)\) and \(\hat{N}^i_A\), we obtain

\[
\mathbf{J}_{AA} = -\frac{ik_z}{2\pi k_0^2} \phi^j(\xi^\alpha) \sum_{i=1}^{3} \left[ \int_0^1 dt \left( \log |r^\alpha_A(t)|^{N} |\hat{N}^i_A| \right) \right]
\]

\[
= -\frac{ik_z}{2\pi k_0^2} \phi^j(\xi^\alpha) \sum_{i=1}^{3} \hat{N}^i_A \left( 1 - \frac{(R_A^{i+1} - r^\alpha_A) \times (R_A - r^\alpha_A)}{|R_A^{i+1} - R_A|^2} L^i_A \right.
\]

\[
+ \frac{(R_A - r^\alpha_A)}{|R_A^{i+1} - R_A|^2} \log |r^\alpha_A - R_A| + \frac{(R_A^{i+1} - r^\alpha_A)}{|R_A^{i+1} - R_A|^2} \log |r^\alpha_A - R_A^{i+1}| \right] \tag{B.7}
\]

where \(L^i_A\) is given by Eq. (P1-39). Thus, we have all components of \(\mathbf{I}_{AA}^S\).

For neighboring elements we obtain

\[
\mathbf{I}_{AB}^S = \mathbf{I}_{AB}^R + \mathbf{I}_{AB}^S,
\]

with

\[
\mathbf{I}_{AB}^R = \sum_{\beta=1}^{\eta} \left[ J_B w^\beta \left( \phi^j(\xi^\beta) \mathbf{G}(r^\alpha_A, r^\beta_B) - \phi^j(\xi^\gamma) \mathbf{D}(-\frac{1}{2\pi}) \log |\rho^\alpha_A - \rho^\beta_A| \right) \right].
\]

with \(\mathbf{D}\) given by Eq. (B.3). \(\mathbf{I}_{AB}^S\) can be obtained from \(\mathbf{I}_{AA}^S\), Eqs. (B.5) - (B.7), by the substitutions \(r^\alpha_A(t) -> r^\beta_B(t), \phi^j(\xi^\alpha) -> \phi^j(\xi^\gamma), R_A -> R_B, N_A -> N_B\), where we want to keep in mind that the Gaussian point \(\xi^\gamma\) corresponds to the global Gaussian point \(r^\beta_B\) with minimal distance to \(r^\alpha_A\) (Fig. 2b in P1).

### B.2 3D case

To determine \(\mathbf{I}_{AA}\), defined by Eq. (P1-16), we first evaluate the analytical integral over \(S^\alpha_A\). Following Eq. (P1-22) and expanding the last integrand in a Laurent series, it turns out that for polynomial basis functions – like for the 2D case – all integrals over the relevant terms (i.e. the singular and constant terms with respect
to $|r' - r_A^o|$ vanish because of the integration over the polar angle $\varphi$. The other integral in Eq. (P1-22) can easily be performed, and Eq. (P1-21) becomes

$$I_{AA}^R = \sum_{\beta \neq \alpha} \left[ J_{\alpha} w^\beta \left( G(r_A^o, r_A^\beta) \phi^\alpha(\xi^\beta) - \phi^\alpha(\xi^\beta) \frac{\nabla^2}{k_0^2} \right) \right]$$  \hspace{1cm} (B.11)

$$+ \phi^\alpha(\xi^\beta) \frac{2}{3k_0^2} [(1 - ik_0 R_A^o) \exp(ik_0 R_A^o) - 1] 1,$$

where $R_A^o$ is the radius corresponding to $S_A^o$, namely

$$R_A^o = \left( \frac{3w_{\alpha} J_A}{4\pi} \right)^{1/3}. \hspace{1cm} (B.12)$$

We further need an analytic expression for $I_{AA}^S$, given by Eq. (P1-24). The integration over the surface boundaries can be reduced to a line integral along the edges with help of a further partial integration. To do this, we need the rotation matrices $A^i_\mu$ that (i) map the outside normal vector of the $\mu$'th surface of the tetrahedron $A$, spanned by the three corners $R^0_\mu, R^\mu_0$ and $R^\mu_\mu$, on the $z$-axis and (ii) map the vector along the $i$'th edge, defined by the corners $R^i_\mu$ and $R^{i+1}_\mu$, on the $x$-axis (with $R^i_\mu \equiv R^i_\mu$).

The explicit form of the rotation matrices $A^i_\mu$ is given in the next section. We further need the quantities $\eta^i_\mu, \eta^{i+1}_\mu, \xi^i_\mu$ and $\xi^{i+1}_\mu$, given by

$$\left( \begin{array}{c} \xi^i_\mu \\ \eta^i_\mu \\ \theta^i_\mu \end{array} \right) \equiv A^i_\mu \cdot (R^i_\mu - r_A^o) \hspace{1cm} (B.13)$$

and

$$\left( \begin{array}{c} -\xi^{i+1}_\mu \\ \eta^{i+1}_\mu \\ \theta^{i+1}_\mu \end{array} \right) \equiv A^{i+1}_\mu \cdot (R^{i+1}_\mu - r_A^o). \hspace{1cm} (B.14)$$

Let us further introduce

$$l^i_\mu \equiv |R^{i+1}_\mu - R^i_\mu|, \hspace{1cm} (B.15)$$

$$d^i_\mu \equiv |r_A^o - R^i_\mu|, \hspace{1cm} (B.16)$$

$$d^{i+1}_\mu \equiv |r_A^o - R^{i+1}_\mu|, \hspace{1cm} (B.17)$$

$$q^{i}_\mu = [(\eta^{i}_\mu)^2 + (\theta^{i}_\mu)^2]^{1/2}. \hspace{1cm} (B.18)$$

$I_{AA}^S$ is then given by

$$I_{AA}^S_{mn} = \frac{1}{4\pi k_0^2} \phi^\alpha(\xi^\beta) \sum_{\mu=1}^{4} \sum_{i=1}^{3} (-1)^{\mu+i} (A^i_\mu)_{mn3} \hspace{1cm} (B.19)$$

$$\cdot \left[ (A^i_\mu)_{n2} \log \left( \frac{d^{i+1}_\mu + l^i_\mu}{d^i_\mu + l^{i+1}_\mu - l^i_\mu} \right) \right], \hspace{1cm} (B.20)$$

$$-2(A^i_\mu)_{n3} \operatorname{sgn}(\theta^{i}_\mu) \arctan \left( \frac{\xi^i_\mu \eta^i_\mu}{(d^i_\mu + |\theta^{i}_\mu|)(d^i_\mu + q)} \right), \hspace{1cm} (B.21)$$

$$+2(A^i_\mu)_{n3} \operatorname{sgn}(\theta^{i+1}_\mu) \arctan \left( \frac{\xi^{i+1}_\mu \eta^{i+1}_\mu}{(d^{i+1}_\mu + |\theta^{i+1}_\mu|)(d^{i+1}_\mu + q)} \right). \hspace{1cm} (B.22)$$
B.2.1 Derivation of the rotation matrices $A^i_{\mu}$

We now give an explicit expression for the rotation matrices $A^i_{\mu}$ that have been used in the previous section. Note that these are twelve different matrices for each element $A$: one for each edge $i$ of each surface $\mu$.

Let us first introduce the outward normal unit vectors of the surface $\mu$ of the tetrahedron $A$:

$$\mathbf{N}_\mu = \frac{(\mathbf{R}_1^\mu - \mathbf{R}_3^\mu) \times (\mathbf{R}_2^\mu - \mathbf{R}_3^\mu)}{|(\mathbf{R}_1^\mu - \mathbf{R}_3^\mu) \times (\mathbf{R}_2^\mu - \mathbf{R}_3^\mu)|},$$

(B.23)

Here, $\mathbf{R}_1^\mu, \mathbf{R}_2^\mu$ and $\mathbf{R}_3^\mu$ are the corners of the surface $\mu$, and the indices have to be chosen such that $\mathbf{N}_\mu$ is directed outwards the tetrahedron. To simplify notation, we will further need $\mathbf{R}_4^\mu$, defined by $\mathbf{R}_4^\mu \equiv \mathbf{R}_1^\mu$.

We next introduce a rotation matrix $\mathbf{B}_\mu$ which rotates $\mathbf{N}_\mu$ parallel to the $z$–axis:

$$\mathbf{B}_\mu = \begin{pmatrix}
\frac{\hat{X}_\mu}{(1-\hat{Z}_\mu^2)^{1/2}} & \frac{\hat{Y}_\mu}{(1-\hat{Z}_\mu^2)^{1/2}} & -(1-\hat{Z}_\mu^2)^{1/2} \\
-\frac{\hat{Y}_\mu}{(1-\hat{Z}_\mu^2)^{1/2}} & \frac{\hat{X}_\mu}{(1-\hat{Z}_\mu^2)^{1/2}} & 0 \\
\hat{X}_\mu & \hat{Y}_\mu & \hat{Z}_\mu
\end{pmatrix},$$

(B.24)

where $\hat{X}_\mu, \hat{Y}_\mu$ and $\hat{Z}_\mu$ are the components of $\mathbf{N}_\mu$. We next focus on the unit vector $\mathbf{V}_\mu^i$ of the edge $i$ of surface $\mu$, given by

$$\mathbf{V}_\mu^i \equiv \frac{\mathbf{R}_i^{\mu+1} - \mathbf{R}_i^\mu}{|\mathbf{R}_i^{\mu+1} - \mathbf{R}_i^\mu|},$$

(B.25)

and will need its coordinates $\mathbf{V}_\mu^i$ in the rotated frame, given by

$$\mathbf{V}_\mu^i = \mathbf{B}_\mu \cdot \mathbf{V}_\mu^i.$$  

(B.26)

The rotation matrix $\mathbf{C}_\mu$ maps the vector $\mathbf{V}_\mu^i = (X_\mu^i, Y_\mu^i, Z_\mu^i)$ parallel to the $x$–axis:

$$\mathbf{C}_\mu = \begin{pmatrix}
X_\mu^i & Y_\mu^i & 0 \\
-\hat{Y}_\mu & \hat{X}_\mu & 0 \\
0 & 0 & 1
\end{pmatrix}.$$  

(B.27)

The matrix $A^i_{\mu}$ is then given by

$$A^i_{\mu} = C^i_{\mu} \cdot B^i_{\mu},$$

(B.28)

where $C^i_{\mu}$ is given by Eq. (B.27), and $B^i_{\mu}$ is given by Eq. (B.24).
Bibliography


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“Accurate Solution of the Volume Integral Equation for High Permittivity Scatterers”

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Transactions on Antenna & Propagation 48
Abstract—We present a formalism based on the method of moment to solve the volume integral equation using tetrahedral (3-D) and triangular (2-D) elements. We introduce a regularization scheme to handle the strong singularity of the Green’s tensor. This regularization scheme is extended to neighboring elements, which dramatically improves the accuracy and the convergence to compute the total scattered field \( \mathbf{E}(r) \), when a system described by a dielectric function \( \varepsilon(r) \) embedded in an infinite homogeneous background medium \( \varepsilon_0 \) is illuminated with an incident field \( \mathbf{E}^{0}(r) \) (throughout the paper, we assume nonmagnetic materials and an \( \exp(-i\omega t) \) time dependence for the fields). In (1), \( V(r) \) represents the scatterer polarizability

\[
V(r) = k_0^2(\varepsilon(r) - \varepsilon_0)
\]

(2)

with \( k_0 \) the vacuum wavenumber and \( G(r, r') \) the Green’s tensor.

The major advantage of this approach lies in the fact that only the scatterer must be discretized. Moreover, nontrivial backgrounds like multilayer structures can be included in the Green’s tensor [2].

Different techniques can be used to solve (1) numerically. In the coupled-dipole approximation [3], [4] the scatterer is discretized with cubes and the field assumed constant over each element. Although there have been several efforts to overcome its intrinsic limitations [5]–[7], this method does not seem suitable for high permittivities [8].

Another approach to solve (1) is to use finite elements. Since the work of Richmond [9], the finite-element method has been broadly used in computational EMs [10]–[14]. Here, the geometry can be well discretized by elements like tetrahedra, and the variation of the field over an element can be modeled using nontrivial basis functions.

However, applying the method of finite elements to the VIE is difficult because of the strong singularity of the Green’s tensor [15], [16]. To handle this singularity, a modified point-matching method [17] and modified Galerkin methods were proposed [18], [19]. Moreover, the strong singularity of the Green’s tensor can be circumvented by moving the derivatives that lead to the singularity of the Green’s tensor onto the test and basis functions using partial integration. To avoid surface integrals, rooftop functions defined on cubical or tetrahedral elements can then be used [10], [20]–[24]. In the same context, Mendes and Arvas computed high-permittivity two-dimensional (2-D) scatterers, using a special set of basis functions that avoids both spurious volume and surface charges [25]. However, this type of basis functions cannot be extended to three-dimensional (3-D) problems.

A formalism independent on the type of basis functions requires a regularization scheme to remove the singularity of the Green’s tensor [26]–[29]. In this paper, we introduce such a scheme. In Section II, a general formalism is proposed for the solution of the VIE using tetrahedral elements. We show how to remove the singularity of the Green’s tensor by subtracting a term that can be integrated analytically. To improve accuracy, this regularization scheme is extended to neighboring elements. In Section III, we apply this general formalism to 2-D geometries. Numerical results to assess the accuracy of the formalism are presented in Section IV.

II. Formalism

A. Basic Equations

The Green’s tensor \( G(r, r') \) in (1) can be written as [4]

\[
G(r, r') = \left( 1 + \frac{\partial^2}{k_0^2} \right) g(r, r')
\]

(3)
with \( g(r, r') \) the scalar Green’s function:

\[
g(r, r') = \frac{\exp ik_0 R}{4\pi R}, \quad \text{for 3-D (4)}
\]

\[
g(r, r') = \frac{i}{4} B_0^{(1)}(k_0 \rho) \exp(ikz'), \quad \text{for 2-D}
\]

where we introduced \( R = |R| = |r - r'| \). For 2-D, the geometry has a translation symmetry in \( z \)-direction and we introduced the transverse coordinate \( \rho \) defined by \( R = (\rho, Z) \) and the transverse wave vector \( k_\rho \) : \( k = (k_\rho, k_z) \).

To solve (1) we use the method of moments and divide the scatterer into \( N \) tetrahedra (triangles in 2-D) with volumes \( V_A \) (surfaces \( S_A \) in 2-D), \( A = 1, \ldots, N \). On each element, \( A \) we assume a constant polarizability \( \alpha_A \) and define \( m \) scalar basis functions \( f_A^i, \ldots, f_A^m \) that vanish outside \( A \). For the field \( E(r) \) inside the scatterer, we write

\[
E(r) = \sum_{A=1}^N \sum_{j=1}^m \alpha_A^j f_A^j
\]

with \( \alpha_A^j \) the unknown vectorial coefficients. Inserting (5) in (1), symmetrizing by multiplication with \( V(r) \) and applying Galerkin’s scheme, we obtain the system of \( mN \times mN \) vectorial equations

\[
\sum_{B=1}^N \sum_{j=1}^m b_{AB}^i \alpha_B^j = \sum_{j=1}^m d_{AB}^i \alpha_B^j = \sum_{j=1}^m \varepsilon_{AB}^i, \quad i = 1, \ldots, m
\]

with

\[
b_{AB}^i = V_A \int_{V_A} \mathrm{d}r f_A^i(r) f_B^j(r)
\]

\[
\varepsilon_{AB}^i = V_A \int_{V_A} \mathrm{d}r f_A^i(r) \mathbf{E}(r)
\]

\[
d_{AB}^i = V_A V_B \int_{V_A} \mathrm{d}r f_A^i(r) \int_{V_B} \mathrm{d}r' G(r, r') f_B^j(r').
\]

The numerical solution of (6) gives the unknown coefficients for the field inside the scatterer. The field outside the scatterer can then be determined from the field inside the scatterer using (1).

**B. Evaluation of the Integrals**

Standard Gaussian integration technique is applied to evaluate the integrals in (7)–(9). To carry out this numerical quadrature, we map each element \( A \) on the canonical element with the transformation \( T_A \) [Fig. 1(a)]. Since the Gaussian points and the basis functions are originally defined on the canonical element, we will use the inverse transformation \( T_A^{-1} \) [Fig. 1(b)]:

\[
r_A(\xi) = R_A^1 \left( 1 - \sum_{i=1}^D \xi_i \right) + \sum_{i=1}^D R_A^{i+1} \xi_i,
\]

\( A = 1, \ldots, N \).

In (10), \( D \) is the space dimension (3 or 2), \( R_A^1, \ldots, R_A^{D+1} \) are the edges of element \( A \), and \( \xi = (\xi_1, \ldots, \xi_D) \) is our new, local coordinate [Fig. 1(a)].

On the canonical element, we define \( \eta \) Gaussian integration points \( \xi^1, \ldots, \xi^\eta \) and their weights \( w^1, \ldots, w^\eta \) [Fig. 1(b)]. The corresponding global Gaussian points \( r_A^{1}, \ldots, r_A^{\eta} \) on element \( A \) are given by inserting \( \xi^1, \ldots, \xi^\eta \) in the transformation (10) [Fig. 1(b)]. The \( m \) basis functions \( \phi_1(\xi), \ldots, \phi_m(\xi) \) are also first defined on the canonical element. They are related to the global basis functions \( f_A^i(r) \) on element \( A \) via the transformation (10), i.e.

\[
f_A^i(r_A(\xi)) = \phi_i(\xi).
\]

Using (10) and (11), we perform the integration on tetrahedron \( A \) by Gaussian quadrature. Equations (7)–(9) become

\[
b_{AB}^i = V_A J_A \left( \sum_{\alpha=1}^\eta w^\alpha \phi^\alpha(\xi^\alpha) \phi_i(\xi^\alpha) \right)
\]

\[
\varepsilon_{AB}^i = V_A J_A \left( \sum_{\alpha=1}^\eta w^\alpha \phi^\alpha(\xi^\alpha) \mathbf{E}(r_A^\alpha) \right)
\]

\[
d_{AB}^i = V_A V_B \int_{V_A} \mathrm{d}r f_A^i(r) \int_{V_B} \mathrm{d}r' G(r, r') f_B^j(r')
\]

with \( J_A \) the Jacobian of the transformation (10). It represents the volume of element \( A \) in units of the volume of the canonical element (1/6 in 3-D and 1/2 in 2-D).

With (12) and (13), we have numerical expressions for the coefficients \( b_{AB}^i \) and \( \varepsilon_{AB}^i \) of (6). Note that for polynomial basis functions \( \phi(\xi) \) the coefficients \( b_{AB}^i \) can also be evaluated analytically [30]. To evaluate the tensorial coefficients \( d_{AB}^i \) we must distinguish two cases depending whether the elements \( A \) and \( B \) are different or coincide.

1) Evaluation of \( \mathbf{I}_{AB} \) for Different Elements: When \( A \neq B \), we can apply standard Gaussian integration to \( \mathbf{I}_{AB} \) in (14) and obtain

\[
\mathbf{I}_{AB} = J_B \left( \sum_{\beta=1}^\eta G(r_A^\alpha, r_B^\beta) w^\beta \phi^\beta(\xi^\beta) \right).
\]

Note that, even located in different elements, the two Gaussian points \( r_A^\alpha \) and \( r_B^\beta \) can be very close to each other, which leads to an inaccurate value for \( \mathbf{I}_{AB} \) using (15) because of the singular behavior of the Green’s tensor for small arguments. A workaround for this will be proposed in Section II-B-3.

2) Regularization of \( \mathbf{I}_{AB} \) for Identical Elements: For \( A = B \) we have to introduce a regularization scheme for the evaluation of \( \mathbf{I}_{AA} \) because of the strong singularity of the Green’s tensor for \( r' = r_A^\alpha \) (\( \sim 1/R^3 \) in 3-D and \( \sim 1/R^2 \) in 2-D).

The main idea of the regularization is to subtract from the integrand a function with the same singular behavior, but which can be integrated analytically. This is fulfilled by

\[
\mathbf{I}_{AA} = \mathbf{I}_{AA}^{\text{reg}} + \mathbf{I}_{AA}^{\text{reg}}
\]

where we choose for the regular part

\[
\mathbf{I}_{AA}^{\text{reg}} = \int_{V_A} \mathrm{d}r' \left[ G(r_A^\alpha, r') f_A^i(r') - \left( \nabla \nabla \mathbf{g}(r_A^\alpha, r') \right) \phi^i(\xi) \right],
\]

with \( \mathbf{g}(r, r') = \nabla \mathbf{g}(r, r') = 0 \).
\[ R^3 \hspace{1cm} T_A \hspace{1cm} \xi \]

\[ T^{-1}_A \hspace{1cm} R^3 \]

Note in (17) the important relation \( f^I_{A}(r^I_A) = \phi^I(\xi^I) \). The operator \( \nabla \nabla \) in (17), (18), and in the following has to be applied for \( r = r^I_A \).

The integrand in (17) is still singular for \( r' = r^I_A \). However, this singularity is now weak and Gaussian quadrature can be applied to the integral with a special treatment if the integration variable \( r' \) is near \( r^I_A \) [Fig. 2(a)]. For the numerical value of \( I_{AA}^R \) we take

\[ I_{AA}^R = \sum_{\beta=1, \beta \neq \alpha}^n J_A \omega^\beta \left\{ G(r^I_A, r^I_A) \phi^I(\xi^I) \right. \]

\[ - \left( \frac{\nabla \nabla}{k_0^2} g^I(r^I_A, r^I_A) \right) \phi^I(\xi^I) \left\} \right. \]

\[ + \int_{S^I_A} dr' \left[ G(r^I_A, r') f^I_A(r') \right. \]

\[ - \left( \frac{\nabla \nabla}{k_0^2} g^I(r^I_A, r') \right) \phi^I(\xi^I) \left. \right] \]

where \( S^I_A \) is a sphere with volume \( \omega^I \) centered at \( r^I_A \) [Fig. 2(a)]. This approach is illustrated in Fig. 2(a).

In a further step, let us divide the integral in (21) into two terms:

\[ \int_{S^I_A} dr' \left[ G(r^I_A, r') f^I_A(r') - \left( \frac{\nabla \nabla}{k_0^2} g^I(r^I_A, r') \right) \phi^I(\xi^I) \right] \]

\[ = \phi^I(\xi^I) \int_{S^I_A} dr' \left( G(r^I_A, r') - \frac{\nabla \nabla}{k_0^2} g^I(r^I_A, r') \right) \]

\[ + \int_{S^I_A} dr' G(r^I_A, r') \left[ f^I_A(r') - f^I_A(r^I_A) \right] \]

where we used \( \phi^I(\xi^I) = f^I_A(r^I_A) \). The first integral does not depend on the explicit form of the basis functions and can easily be performed analytically. The second integral, however, depends on the explicit form of the basis functions. It vanishes for constant basis functions since \( f^I_A(r^I_A) = f^I_A(r^I_A) \). For higher-order basis functions, the integrand must be expanded in a Laurent series with respect to \( |r' - r^I_A| \) using the spherical coordinates of \( r' - r^I_A \), and retaining only the singular and constant terms with
Fig. 2. (a) Gaussian integration is performed for $I_{AA}$. Instead of the (undefined) value for $r_A^m = r_B^m$, we take the integral inside a sphere of volume $w_a J_a$. (b) The point $r_B^m$ for the regularization in (26)–(28) is the Gaussian point on $B$ with the minimal distance to $r_A^m$.

respects to $|r' - r_A^m|$. (Note that, for a regular function without singularity, Gaussian quadrature corresponds to retaining only the constant term and dropping the others.) For polynomial basis functions this leads to integrals that can be solved analytically.

To determine the integral $I_{AA}^S$, given by (18), one has two options: The first one is to take the Cauchy principal value by introducing an exclusion volume around the singularity, as done by Yaghian [15]. This approach is well suited for simple elements, like a sphere or a cube, where the integration on the element volume is easily performed [4]. For tetrahedral elements, however, the theory of generalized functions described by Gel’fand and Shirkov is more appropriate, since it reduces to integration on the element boundary [31].

Following this approach, we obtain after one partial integration for the $m$th component of the tensor $I_{AA}^S$:

$$
(I_{AA}^S)_{mn} = \phi^j(\xi^a)(-1)^{m-1} \int_{\partial V_A} \partial_n g^S(r_A^m, r') dr_j', \ldots, dr_{m'}, \quad p^j \neq m
$$

with $\partial V_A$ indicating the boundary of element $A$. As stressed by Lee et al. in a similar context [26], one can write this tensor as

$$
I_{AA}^S = \phi^j(\xi^a) \frac{-1}{2(D - 1)\pi} \int_{\partial V_A} \frac{NQ}{Q^D} d\sigma.
$$

Here $N$ is the unit outward normal vector on $\partial V_A$, and $Q$ is defined as $Q = r_A^m - r'$. This integral can be solved analytically.

Combining (21) and (24), we finally obtain the value of $I_{AA}$ for identical elements

$$
I_{AA} = J_A \sum_{\beta=1}^{\eta} \left\{ w^\beta \left[ G(r_A^m, r_A^\beta) \phi^j(\xi^a) - \left( \frac{\nabla \cdot}{k_0^2} g^S(r_A^m, r_A^\beta) \right) \phi^j(\xi^a) \right] \right\}
$$

+ $\int_{S_A^m} dr' \left[ G(r_A^m, r') f^j_\beta(r') - \left( \frac{\nabla \cdot}{k_0^2} g^S(r_A^m, r') \right) \phi^j(\xi^a) \right]$

+ $\phi^j(\xi^a) \frac{-1}{2(D - 1)\pi} \int_{\partial V_A} \frac{NQ}{Q^D} d\sigma$ (25)

where the integral over the sphere $S_A^m$ has to be solved as in (22).

3) Regularization of $I_{AB}$ for Neighboring Elements: As discussed previously, even for different elements $A \neq B$, the evaluation of $I_{AB}$ with Gaussian integration [15] can be inaccurate when $r_A^m$ is close to the element $B$ [Fig. 2(b)]. It is, however, possible to apply a similar regularization scheme in that case.

As for identical elements, let us divide $I_{AB}$ into two parts (the tilde in $AB$ indicates neighboring elements)

$$
I_{AB} = I_{AB}^S + I_{AB}^R
$$

with

$$
I_{AB}^S = \phi^j(\xi^a) \int_{V_B} dr' \nabla \cdot g^S(r_A^m, r')
$$

and

$$
I_{AB}^R = \phi^j(\xi^a) \int_{V_B} dr' \frac{NQ}{Q^D} g^S(r_A^m, r').
$$

The Gaussian point $\xi^b$ in (27) is such that the corresponding global Gaussian point $r_B^m$ of (27) is the Gaussian point on tetrahedron $B$ with the minimal distance to $r_A^m$ [Fig. 2(b)].

Applying Gaussian quadrature to $I_{AB}^S$ and using (24) (which is also valid if $r_A^m$ is outside the integration region) we obtain

$$
I_{AB}^S = \sum_{\beta=1}^{\eta} \left\{ J_B w^\beta \left[ G(r_A^m, r_B^\beta) \phi^j(\xi^a) - \left( \frac{\nabla \cdot}{k_0^2} g^S(r_A^m, r_B^\beta) \right) \phi^j(\xi^a) \right] \right\}
$$

with $J_B = J_B^S + J_B^R$.

The Gaussian point $\xi^b$ in (27) is such that the corresponding global Gaussian point $r_B^m$ of (27) is the Gaussian point on tetrahedron $B$ with the minimal distance to $r_A^m$ [Fig. 2(b)].

Applying Gaussian quadrature to $I_{AB}^R$ and using (24) (which is also valid if $r_A^m$ is outside the integration region) we obtain

$$
I_{AB}^R = \sum_{\beta=1}^{\eta} \left\{ J_B w^\beta \left[ G(r_A^m, r_B^\beta) \phi^j(\xi^a) - \left( \frac{\nabla \cdot}{k_0^2} g^S(r_A^m, r_B^\beta) \right) \phi^j(\xi^a) \right] \right\}$$. 

...
which completes our general formalism.

III. APPLICATION OF THE SCHEME FOR THE 2-D-CASE

The general scheme derived in the previous section will now be applied to the 2-D case, i.e., we assume a scatterer with an infinite symmetry axis in the z-direction. Furthermore, we assume that the wave vector \( k \) of the incident field is in the \( xy \)-plane (i.e., \( k_z = 0, k_0 = k_\rho \)). In that case the Green’s tensor reads [4]

\[
G(r, r') = \left[ 1 + \frac{1}{k^2} \begin{pmatrix}
\partial_x \partial_x & \partial_x \partial_y & 0 \\
\partial_y \partial_x & \partial_y \partial_y & 0 \\
0 & 0 & 0
\end{pmatrix} \right] g(r, r')
\]

with \( g(r, r') \) now given by

\[
g(r, r') = \frac{i}{4} H_0^{(1)}(k_0 r_0) \]

As implied by the form of the Green’s tensor [(30)], we can distinguish two cases when the electrical field is polarized in \( z \)-direction [transverse magnetic (TM)] or when it is in the \( xy \)-plane [transverse electric (TE)].

We use triangular elements. The corresponding basis functions up to cubic order can be found in [11], [30], and [32], whereas appropriate Gaussian points up to order 10 can be found in [33]—[35]. Note that all the Gaussian points must be defined inside the element. The computation of the matrix elements \( I_{AA} \) and \( e_A \) is straightforward. We will only detail the procedure for \( d_{AB} \), i.e., we give expressions for \( I_{AB} \) defined by (14) for identical and neighboring elements \( A \) and \( B \).

A. TM Case

In the TM-case, the Green’s tensor is given by the scalar Green’s function itself, (31). Hence, no regularization is necessary and we only have to handle the weak singularity of the scalar Green’s function as described in Section II-B.2. (Note that the formulas of the general description are still valid, but all the derivatives vanish since \( k_0 = k_\rho \).

To determine \( I_{AA} \) (which now is a scalar), we first evaluate the analytical integral over \( S_A^0 \). Following (22) and expanding the last integrand in a Laurent series, it turns out that for polynomial basis functions all integrals over the relevant terms (i.e., the singular and constant terms with respect to \( |r' - r_A| \)) vanish because of the integration over the polar angle \( \varphi \). The other integral in (22) can easily be performed and (21) becomes

\[
I_{AA}^R = \sum_{\beta \neq \alpha}^n \left[ J_A w^\beta \left( G(r^\alpha_A, r^\beta_A) \phi^\beta(\xi^\beta) \right. \right.
\left. \left. - \phi^\beta(\xi^\alpha) \frac{k_0^2}{k^2} g^0(r^\beta_A, r^\alpha_A) \right] \right.
\]

with \( r = (x, y) \), and \( n = \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \).

Since a regularization scheme is not necessary for this polarization, neighboring elements can simply be treated with (15).

B. TE Case

In the TE-case, the Green’s tensor is a \( 2 \times 2 \) tensor, given by the \( xy \)-components of (30). To determine \( I_{AA} \) for identical elements, we first evaluate the analytical integral over \( S_A^0 \). Following (22) and expanding the last integrand in a Laurent series, it turns out that for polynomial basis functions all integrals over the relevant terms (i.e., the singular and constant terms with respect to \( |r' - r_A^i| \)) vanish because of the integration over the polar angle \( \varphi \). The other integral in (22) can easily be performed and (21) becomes

\[
I_{AA}^R = \sum_{\beta \neq \alpha}^n \left[ J_A w^\beta \left( G(r^\alpha_A, r^\beta_A) \phi^\beta(\xi^\beta) \right. \right. \left. \left. \frac{k_0^2}{k^2} g^0(r^\beta_A, r^\alpha_A) \right] \right.
\]

with \( r = (x, y) \), and \( n = \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \).

To determine the value of \( I_{AA}^T \), the parameterization of the boundary \( \partial S_A^0 \) of element \( A \) and determine its unit outward normal vectors. Defining \( R_A^i = R_A \), the parameterization of the \( i \)th side of triangle \( A \) is given by

\[
N_A^i = \frac{1}{|R_A^{i+1} - R_A^i|} \left( R_A^{i+1} - R_A^i \right), \quad i = 1, 2, 3
\]

Like this, (24) becomes

\[
I_{AA}^T = \sum_{i=1}^3 \left[ \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \left. \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \left. \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \left. \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \left. \frac{1}{2\pi} \phi^\beta(\xi^\alpha) \right] \right] \right.
\]

where we introduced \( K_A^i \) and \( L_A^i \) given by

\[
K_A^i = \log \left[ \left( |r_A^i - R_A^i|^2 \right) - \log \left[ \left( |r_A^i - R_A^{i+1}|^2 \right) \right] \right.
\]

\[
L_A^i = \arctan \left( \frac{N_A^i \times (r_A^i - R_A^i)}{|N_A^i \times (r_A^i - R_A^i)|} \right)
\]

where the 2-D vector product \( a \times b \equiv a_1 b_2 - a_2 b_1 \) is a scalar. The symmetry of the tensor \( I_{AA}^T \) is easily verified using the relation \( \sum_{i=1}^3 K_A^i = 0 \).

With these results, \( I_{AA} \) reads

\[
I_{AA} = I_{AA}^R + I_{AA}^T
\]
Fig. 3. Differential scattering cross section as a function of scattering angle for $\varepsilon = 4$ and size parameter $x = 10.43$, for both TM and TE polarization. The numerical results are compared to the reference solution obtained with Mie theory [30].

with $\mathbf{I}_{AA}^{R}$, respectively, $\mathbf{I}_{AA}^{T}$, given by (34), respectively, (37).

For neighboring elements, we obtain

$$\mathbf{I}_{AB}^{\tilde{R}} = \mathbf{I}_{AB}^{R} + \mathbf{I}_{AB}^{T}$$

(41)

with

$$\mathbf{I}_{AB}^{R} = \sum_{\beta = 1}^{n} J_{\omega} w^{\beta} \left( \phi^j(\xi^\beta) G(r^A_{\beta}, r^B_{\beta}) \right)$$

$$- \phi^j(\xi^\beta) \frac{\nabla^2}{k^2} g^S(r^A_{\beta}, r^B_{\beta}) \right)$$

(42)

and $\mathbf{I}_{AB}^{T}$ can be obtained from $\mathbf{I}_{AA}^{T}$, (37)–(39), by the substitutions $r^j_{\beta}(t) \rightarrow r^B_{\beta}(t)$, $\phi^j(\xi^\beta) \rightarrow \phi^j(\xi^\beta)$, $R^A_{\beta} \rightarrow R^B_{\beta}$, $N^A_{\beta} \rightarrow N^B_{\beta}$, where we want to keep in mind that the Gaussian point $\xi^\beta$ corresponds to the global Gaussian point $r^\beta_B$ with minimal distance to $r^A_{\beta}$ [Fig. 2(b)].

IV. 2-D CALCULATIONS

In this section, we present 2-D calculations. To assess the accuracy of the numerical results we choose examples where an analytical solution exists. Throughout the examples we use constant basis functions and Gaussian points corresponding to order 7.

In the first example we compare the differential cross section for a cylinder ($\varepsilon = 4$, diameter $d$) for both TM and TE with the analytic Mie solution. The size parameter $x \equiv \pi \sqrt{\varepsilon d}/\lambda_0$ is 10.43.

As Fig. 3 implies, for a certain scattering angle we can define an error for the numerical result by taking the square of the difference between the numeric and analytic far-field amplitude, normalized to the square of the analytic far-field amplitude. Integration over the scattering angles gives us the absolute error of our result.

To show the convergence of our formalism, Fig. 4 gives this absolute error as a function of the number of elements used to discretize the geometry for both TM and TE polarization. The cylinder diameter is 100 [nm] and the wavelength 546 [nm]. We show the result for $\varepsilon = 4$ and $\varepsilon = 16.65 + 0.23i$, the latter corresponding to silicon at that wavelength [1]. We see that even with few elements, the formalism gives very accurate results including for bodies with a high permittivity.

To demonstrate the importance of the regularization for neighboring elements presented in Section II-B.3, we compare in Fig. 5 the error of the numerical result with and without this regularization for TE polarization. We use the same parameters as in Fig. 4. These results emphasize the importance of the regularization for neighboring elements.

Dispersive materials like silver are known to exhibit a resonant behavior at particular optical wavelengths (plasmon–polariton) [36]. Many numerical methods are known to be inac-
accurate at the resonance. The scattering cross section of a silver cylinder with diameter $d = 100$ [nm] is represented in Fig. 6 as a function of the wavelength of the incident TE field (TM does not exhibit resonant behavior). 132 triangles were used. The resonance is very well reproduced by the present method.

In our numerical calculations, it turns out that higher-order basis functions like linear or quadratic basis functions provide even better results in the TM-case for the same number of elements. This is also the case for TE polarization. However, for a very small ratio of the element length to the wavelength, constant basis functions give better results for TE polarization. This surprising issue may be understood in the following manner: For very small elements (compared to the wavelength) a constant basis function can approximate the field over the element very well and therefore the natural advantage of high-order basis functions decreases. Furthermore, for higher-order basis functions, the size and the condition of the system of equations increase rapidly. Finally, for small elements, the Gaussian points lie very close to each other and the regularization procedure becomes extremely important. This regularization procedure is most accurate for constant basis functions since then $f_A(r') = \phi(\xi^*)$ [(17)].

V. CONCLUSION

We applied the method of moment to the VIE using 3-D and 2-D elements. We presented a regularization scheme to handle the strong singularity of the Green’s tensor. This regularization scheme was further developed to take into account neighboring elements, which strongly enhanced the accuracy and the convergence of the method. The formalism was given in a general way that can be easily implemented for 3-D systems. We demonstrated that our approach is well suited for scattering calculations in high-permittivity materials. Furthermore, we were able to accurately reproduce the plasmon resonances in small metallic particles.

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“Dramatic localized electromagnetic enhancement in plasmon resonant nanowires”

J.P. Kottmann, O.J.F. Martin, D.R. Smith and S. Schultz

Dramatic localized electromagnetic enhancement in plasmon resonant nanowires

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Abstract

We investigate numerically the plasmon resonances of 10–50 nm nanowires with a non-elliptical section. Such wires have a much more complex behavior than elliptical wires and their resonances span a larger frequency range. The field distribution at the surface of these wires exhibits a dramatic enhancement, up to several hundred times the incident field amplitude. These strongly localized fields can provide an important mechanism for surface enhanced Raman scattering (SERS). © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The interaction of light with small metal particles has been of great interest, ever since Faraday recognized that gold colloids are responsible for the wide color range of stained glass. Faraday noted 'that a mere variation in the size of its particles gave rise to a variety of colors' [1]. The interest in colloidal metals increased dramatically with the discovery of the phenomenon of surface enhanced Raman scattering (SERS), wherein the Raman signal of molecules ensembles adsorbed on rough metal surfaces can be enhanced by a factor of $10^7$ [2–5]. In recent experiments, Raman enhancement up to $10^{12}$ were even reported for single molecules located on so-called ‘hot spots’ [6–8].

The adsorption of the molecule on the metal can participate in the Raman enhancement [9,10]. However, it is believed that the excitation of plasmons in the metallic nanoparticles creates greatly enhanced local electromagnetic fields that contribute the major component of the SERS effect. Motivated by experiments on relatively large systems, recent theoretical efforts have been devoted to the understanding of plasmon resonances in aggregated or periodic metallic systems [11–14].

Recent experiments indicate that SERS can also be observed on individual or small clusters of nanoparticles [6–8]. However, not all similarly sized particles produce equivalent enhancements, and there appears to be a very significant shape or morphology dependence. It is thus essential to further our understanding of the behavior of plasmon resonances for isolated nanoparticles with arbitrary shape. Unfortunately, a complete description of the plasmon resonances of such
particles is not easy to obtain. Analytic methods are only known for very simple shapes, like spherical or ellipsoidal particles [15], and we must resort to numerical methods for more complex geometries. The resonances of cubic particles, for example, have been investigated in the electrostatic limit by Fuchs [16], while Jensen et al. [17] studied large truncated tetrahedra in the 100 nm range.

2. Model

In this Letter, we investigate metal nanoparticles in the 50 nm range, as these have been shown both to be individually observable by optical microscopy [18,19] and to individually exhibit the SERS effect [6,7]. Here, we concentrate on two-dimensional particles (wires) with triangular cross-sections, which exhibit strong field enhancements and – in spite of their simple shape – display a wide variety of complex behavior. A more systematic investigation of different particle shapes will be presented in another publication.

Nanowires can be fabricated in a controlled manner in the sub-100 nm range. Used as substrate, they produce a strong enhancement for SERS [20,21] and fluorescence [22]. Further, metallic nanowires sustaining plasmon resonances have become a very active research field over the last few years, with implications in optics and solid state physics [18,23,24].

Throughout the Letter we consider silver wires, illuminated by plane waves with the incident electric field in the plane of the figures (transverse electric polarization). For the permittivity \( \varepsilon \lambda \), as a function of the wavelength \( \lambda \), we use the bulk data of Johnson and Christy [25]. Note that particles down to 10 nm can well be modeled using bulk permittivity, while smaller particles require a modified value of \( \varepsilon \lambda \), with – in the case of silver – a larger imaginary part than the bulk [26].

Plasmons prove difficult to accurately characterize by numerical methods, because they generally have spatial variations of field and charge density on a scale much smaller than the wavelength of the light which excites them. We address these problems using a newly developed technique based on the integral equation

\[
\mathbf{E}_r = \mathbf{E}_0 + \int dr \mathbf{G}^B_{r,r} k_0^2 (\varepsilon_r - \varepsilon^B) \mathbf{E}_r
\]

for the electric field \( \mathbf{E}_r \) scattered by a particle, described by \( \varepsilon_r \), illuminated with the incident field \( \mathbf{E}_0 \). The dyadic \( \mathbf{G}^B_{r,r} \) is the Green’s tensor associated with the homogeneous background \( \varepsilon^B \). Contrary to the standard Green’s tensor technique or the coupled dipole approximation [14,17], we use finite elements to solve Eq. (1); i.e., we develop the unknown field \( \mathbf{E}_r \) on a series of linear basis functions defined on triangular elements and apply a Galerkin scheme to obtain a system of algebraic equations from Eq. (1). We refer the reader to [27], where this technique is described in detail.

To assess the accuracy of this approach, in Fig. 1 we compare the scattering cross-section for an elliptical wire with that obtained using Mie theory [15]. The agreement between the two is excellent: both the position and the amplitude of the resonances are accurately reproduced with our technique. Such an ellipse has two different resonances that can be excited independently for the two illumination directions considered here. For incidence in a direction off either of the principal axes, both resonances are excited.

![Fig. 1. Accuracy of the method: scattering cross-section for an elliptical particle (overall size 40 nm × 20 nm) computed with finite elements (solid line) and with Mie theory (cross). Two orthogonal propagation directions for the incident field, corresponding to two different resonances, are considered.](image-url)
3. Results

In Fig. 2 we present the scattering cross-section for a triangular particle. Dealing with sharp corners introduces additional numerical difficulties since the field becomes singular at short distances from an infinitely sharp, perfectly conducting corner [28]. However, the sharpness of a real particle is limited by surface and boundary energies; therefore, we have rounded off each corner by 0.25 nm, providing a more realistic model and removing the numerical instabilities. The results shown in Fig. 2 were obtained with 3000 triangular elements. We verified that both 2000 and 4000 discretization elements produced the same numerical results (within better than 1%).

The behavior observed in Fig. 2, with up to four different resonances, depending on the illumination direction, is much more complex than that in Fig. 1. The triangle resonances now cover a larger wavelength range, from 330 to 412 nm. (For the ellipse the two resonances are at 331 and 358 nm, respectively.)

For larger particles, the scattering cross-section increases and the different resonances are red-shifted (Fig. 3). This shift is actually larger for triangular particles compared to elliptical particles: the main resonance in Fig. 3 shifts from 401 to 427 nm when the particle size increases from 10 to 50 nm. For cylindrical particles with similar sizes this wavelength shift amounts to only 7 nm.

Increasing the particle size from 10 to 20 nm produces additional modes, including one on the short wavelength side of the main resonance (Fig. 3). These two modes merge into one broad resonance for the 50 nm particle, while several additional modes appear at shorter wavelengths, leading to a much more complex spectrum than one would obtain for a cylindrical particle of similar size.

In Fig. 4 we investigate the field distribution inside and just outside the surface of nanoparticles for selected wavelengths. A logarithmic color scale is used for the amplitude of the electric field; the amplitude of the incident electric field being one.

The data of Fig. 4a corresponds to the main resonance of a 20 nm particle at $\lambda = 412$ nm (see Fig. 2). Note the dramatic variations of the field in that figure: the field reaches 200 times the amplitude of the incident field at two of the corners, while vanishing at the third corner. During one half period of oscillation, large currents flow from one corner to the other as the large positive and negative polarization charges accumulate [29].

Although the incident field is oriented along the corner diagonals, the strong enhancement observed in Fig. 4a is hardly related to the lightning rod effect [28]. This is illustrated in Fig. 4b, where
the field distribution remains very symmetrical (i.e., dictated by the mode pattern), although the illumination direction is now different. An example which helps to set the scale of the non-resonant lightning rod contribution is illustrated in Fig. 4c, where the field distribution off-resonance at $\lambda = 600$ nm is shown. An amplitude enhancement of only 10 is obtained although the permittivity for this wavelength is strongly negative ($\varepsilon = -16.1 + i0.4$).

The field distribution in the vicinity just outside of the particle tip depends on the mode excited. While two corners radiate in all directions at $\lambda = 412$ nm (Fig. 4a), a minimum in the field is observed close to these corners at $\lambda = 365$ nm (Fig. 4d). For this resonance, both plus and minus polarization charges accumulate in the corner [29], leading to a dipolar-like field distribution.

An even more peculiar behavior is obtained for $\lambda = 329$ nm (Fig. 4e). The enhancement associated with this mode is only about 10, but surprisingly the field is amplified at the lower left corner, along the illumination direction. We believe this ‘longitudinal’ mode corresponds to the bulk plasmon since it occurs at the reflectance minimum [30]. Furthermore our results indicate that, contrary to the other modes, this resonance does not shift when the particle size increases, again indicative of a bulk rather than a surface mode.

Reducing the particle symmetry increases the field enhancement, as illustrated in Fig. 4f where the amplitude of the field is 400 the incident field.

To a first approximation, the enhancement of the SERS signal depends on the fourth power of the field amplitude enhancement at the molecule location [5]. We therefore computed the maximum field amplitude along the perimeter of a nanoparticle at a 1 nm distance from its surface. This field amplitude enhancement is presented as a function of the excitation wavelength, for three different particles of similar volume but different shape in

![Fig. 5. Maximum field amplitude enhancement at a 1 nm distance from the surface of different particles: 20 nm x 10 nm ellipse, 20 nm base isosceles triangle and 10 nm base, 20 nm perpendicular right-angled triangle. The particles are illuminated along the (11) direction.](image)

Fig. 4. Electric field amplitude distribution for triangular particles at different excitation wavelengths: (a), (b) $\lambda = 412$ nm; (c) $\lambda = 600$ nm; (d) $\lambda = 365$ nm; (e) $\lambda = 329$ nm; (f) $\lambda = 458$ nm. The propagation direction of the incident field is indicated by an arrow. (a)-(e) isosceles particles with a 20 nm base; (f) right-angled triangular particle with a 10 nm base and a 20 nm perpendicular. Logarithmic color scale.

![Fig. 5. These data illustrate the dramatic influence of the particle shape on the enhancement. It is quite remarkable that for the 10 nm base right-angled triangle, the field reaches 60 times the amplitude of the incident field, corresponding to a Raman enhancement of $10^7$. We note also that the different resonances visible in Fig. 5 span a very large wavelength range.](image)

4. Conclusions

In summary, we have investigated the plasmon resonances of isolated nanowires with non-regular shapes. We have obtained a much more complex
spectral response than for regularly shaped particles, with resonances covering a broader wavelength range. Triangular particles with dimensions smaller than 50 nm produce strong field enhancement near their vertices, reaching several hundred times the amplitude of the illumination wave. These strong fields are extremely localized, which can explain the hot spots and blinking phenomenon observed experimentally in Raman scattering.

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“Plasmon resonances of nanowires with a non-regular cross-section”

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Plasmon resonances of silver nanowires with a non–regular cross–section

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We investigate numerically the spectrum of plasmon resonances for metallic nanowires with a non–regular cross-section, in the 20–50nm range. We first consider the resonance spectra corresponding to nanowires whose cross-sections form different simplexes. The number of resonances strongly increases when the section symmetry decreases: A cylindrical wire exhibits one resonance, whereas we observe more than 5 distinct resonances for a triangular particle. The spectral range covered by these different resonances becomes very large, giving to the particle specific distinct colors. At the resonance, dramatic field enhancement is observed at the vicinity of non-regular particles, where the field amplitude can reach several hundred times that of the illumination field. This near-field enhancement corresponds to surface enhanced Raman scattering (SERS) enhancement locally in excess of $10^{12}$. The distance dependence of this enhancement is investigated and we show that it depends on the plasmon resonance excited in the particle, i.e. on the illumination wavelength. The average Raman enhancement for molecules distributed on the entire particle surface is also computed and discussed in the context of experiments in which large numbers of molecules are used.

I. INTRODUCTION

Nanosized metal particles with subwavelength dimensions exhibit a wealth of optical phenomena directly related to geometry–dependent surface plasmon resonances that can be excited in response to applied electromagnetic fields. Plasmon resonances lead to large scattering cross sections (SCS) at specific wavelengths in many metal nanoparticles, including those made of silver and gold, and are responsible for the characteristic color associated with suspensions of colloidal metal particles. The connection between the scattered spectrum of a nanoparticle and its physical properties was established long ago; medieval artisans, for example, made use of metal colloidal particles in the production of certain types of stained glass.

In addition to their large SCS, plasmon resonant particles have very large and very localized local electromagnetic fields. These local fields play a key role in surface enhanced Raman scattering (SERS), wherein the Raman spectrum of a molecule near a nanoparticle surface is enhanced by several orders of magnitude. This enhancement can be large enough that the Raman spectrum of a single molecule can be acquired. The enhanced local fields of plasmon resonant particles are useful for a variety of applications, including biosensors, and as sources for nanolithography, and as probes in scanning near-field optical microscopy (SNOM). Finally, their spectral selectivity may make plasmon resonant particles a key component in future passive optical devices based on evanescent optical transport, or even in newly proposed active optical components.

In recent years, considerable progress has been made in the fabrication of metallic nanostructures in a controlled manner, including features in the 10–50nm range. Metallic particles with a variety of shapes and dimensions are now readily available for experiments. A thorough understanding of the detailed local fields associated with plasmon resonant particles is therefore warranted, to enhance the design and optimization of applications based on these particles. However, the accurate solution of the local fields of plasmon resonant particles of arbitrary shape remains a theoretical challenge. Analytical solutions for the fields are known only for particles with a very simple shape, like that of a sphere or an ellipsoid, or spherical shells and periodic cylinder gratings. While electrostatic methods can provide some level of insight, complete electromagnetic solvers are needed to obtain accurate results. Many groups have developed methods of solving Maxwell’s equations to investigate non–regular plasmon resonant particles in the 100–200 nm size range, however, although particles of this size provide large SCS at the plasmon resonance, the resonances are very broad, and the field enhancement in the vicinity of the particles is relatively small.

Recently we have presented a numerical approach for the solution of the fields associated with plasmon resonant nanoparticles of arbitrary two-dimensional geometry, which leads to highly accurate, converged solutions, even for particles having extremely large local enhancement and field variation. Recently we demonstrated that nanowires with a triangular section had a very
complex spectrum of plasmon resonances. For sections smaller than 50 nm, we observed many distinct, narrow resonances, associated with strong near-field distributions. In Ref. 51 we illustrated with movies the spectral response of triangular particles and demonstrated that a strong near-field enhancement was obtained for particles smaller than about 50 nm. The topology of these different resonances was correlated to the polarization charges distributions induced in these particles in Ref. 52.

The objective of the present publication is to study in detail the relation between the cross-sectional shape of a nanowire and its resonance spectrum. In Sec. II we recall our formalism and address some of the specific issues related to the accurate simulation of plasmon resonances. In Sec. III we investigate the resonance spectrum corresponding to nanowires whose cross-sections form different simplexes and consider the implication of these results for SERS. We present our conclusions in Sec. IV.

II. FORMALISM

A. Theory

The electromagnetic scattering properties of metal nanoparticles can be described by solving Maxwell’s equations. In this model, the complete description of the material properties of the metal is encompassed in the dispersion relation, which gives the complex permittivity \( \varepsilon(\omega) \) as a function of the frequency (or wavelength). Near the metal plasma frequency \( \omega_p \) of the metal, the dispersion relation is governed by the interaction between light and the conduction electron gas, or expressed with their quantum counterparts, by the photon-plasmon interaction. The combined exciton is often referred to as plasmon-polariton. For certain metals such as silver, copper and gold, \( \omega_p \) is in the visible frequency range. At their quantum counterparts, by the photon-plasmon interaction, the combined exciton is often referred to as plasmon-polariton. For certain metals such as silver, copper and gold, \( \omega_p \) is in the visible frequency range. At specific negative permittivity values, plasmon resonances will be excited in these small particles. These specific permittivity values strongly depend on the particle size and shape, since the boundary conditions imposed by Maxwell’s equations determine whether such a particle resonance can build up. These resonances are often referred to as the surface modes of the particle.

The plasmon resonances are analytically known only for simple geometries, such as a sphere or a cylinder. In a very small sphere for instance, one single resonance can be excited, when \( \varepsilon = -2 \) (Ag: \( \lambda \approx 355 \text{ nm}, \text{Au: } \lambda \approx 490 \text{ nm} \)), whereas a cylinder is in resonance when \( \varepsilon = -1 \) (Ag: \( \lambda \approx 337 \text{ nm}, \text{Au: } \lambda \approx 253 \text{ nm} \)). With increasing particle size, these resonances are red-shifted and broadened, and additional higher order resonances can be excited.

More than one single resonance can be excited in a non-regular structure, irrespective of its size. A small ellipse, for instance, exhibits two resonances, corresponding to the illumination directions along and normal to its major axis. Recently we demonstrated that triangular nanoparticles have several resonances for each illumination direction.

Whether these different modes of a nanoparticle of arbitrary shape can be resolved, strongly depends on the material absorption (the imaginary part of \( \varepsilon \)): large absorption broadens the resonances, and can result in a nearly featureless band. Silver, compared with other metals that have their plasma frequency in the optical range (e.g., gold and copper), has a comparatively low absorption, and thus narrower resonances.

Another phenomenon that can arise at wavelengths where the permittivity changes its sign is the excitation of longitudinal plasmons. However, this is a very weak effect, and for flat boundaries this mode is hardly excited.

One may wonder whether the classical description of the material that we use, based solely on Maxwell’s theory and a local dispersion relation, is appropriate for the small structures investigated here. Actually, it has been experimentally shown that this microscopic approach is adequate for particle dimensions as small as 2 nm. Quantum effects must only be taken into account for smaller particles, using for example a jellium or quantum-chemical model. For particles in the 2–20 nm range, the dispersion relation depends noticeably on the particle geometry, since the electron mean free path decreases as electron scattering at the surface becomes more important. However, for the silver particles investigated here, only the imaginary part of the permittivity increases slightly, and the bulk values of permittivity still represent a good approximation. This point will be addressed in greater detail in Sec. III C.

B. Model

As established in the previous section, Maxwell’s equations are well suited to study the plasmon resonances of silver particles in the 20–50 nm range, and we shall use the experimentally obtained permittivity values from Johnson and Christie. For non-magnetic media, Maxwell’s equations reduce in the frequency domain to the vectorial wave equation, which is formally solved by the volume integral equation

\[
\mathbf{E}(\mathbf{r}; \omega) = \mathbf{E}_0(\mathbf{r}; \omega) + \int_V d\mathbf{r}' G^B(\mathbf{r}, \mathbf{r}'; \omega) \cdot k_0^2(\varepsilon(\mathbf{r}'; \omega) - \varepsilon_B) \mathbf{E}(\mathbf{r}'; \omega).
\]

Here \( \mathbf{E}_0(\mathbf{r}; \omega) \) is the incident electric field with vacuum wave number \( k_0 \), \( \mathbf{E}(\mathbf{r}; \omega) \) is the unknown total scattered field, \( \varepsilon(\mathbf{r}; \omega) \) the particle permittivity and \( \varepsilon_B \) that of the background. The dyadic \( G^B(\mathbf{r}, \mathbf{r}'; \omega) \) is the Green’s tensor associated with the infinite homogeneous background. Note that this formalism can also be used when the background is a surface or a stratified medium.
We study 2D silver particles, i.e. particles having a translation symmetry along the third (not shown) direction, such as nanowires or infinitely long nanorods. The particles are illuminated in the plane of the figures with the electric field in the same plane (transverse-electric polarization). For transverse-magnetic polarization, where the incident magnetic field is in the plane, plasmons cannot be excited.

We solve Eq. 1 with a newly developed technique based on finite elements. The arbitrary particle section is discretized using triangles, and the unknown field \( E(r; \omega) \) is expanded into a sum of basis functions defined on each triangle. A Galerkin test procedure is then used to obtain a system of algebraic equations for the unknown field. We refer the reader to Ref. 49 where this technique is described in detail.

Since the spectrum of resonances for non-regularly shaped particles is not known, it was very important to first assess the accuracy of this technique. In Refs. 49 and 50, we compared the results from our numerical approach with analytical reference solutions for simple geometries. The agreement between the solutions was exact. A key component in achieving these high accuracy results was a new regularization scheme that we developed to extract the singularity of the Green’s tensor. This regularization scheme was further extended to neighboring elements, which considerably improves the accuracy.

The particle cross-sections are discretized with two to three thousand triangular elements. We verified that this discretization number was large enough that the numerical results did not depend on it. To provide a more realistic model of a realizable nanoparticle, and to avoid numerical difficulties, all the particle corners are rounded off by 0.25 nm. This point will be discussed in detail in Sec. III D.

III. NUMERICAL RESULTS

A. Simplexes

Knowing that a cylindrical silver particle exhibits only one resonance, while a complex triangular particle exhibits at least five resonances, we anticipate that the resonance spectrum should increase in complexity as the cross-section of the particle is reduced from one of high symmetry to one of lower symmetry. In this section, we investigate the plasmon resonances of small silver wires with varying simplex cross-section.

Figure 1 shows the scattering cross section (SCS) from nanowires having cross-sections corresponding to that of a circle, a hexagon, a pentagon, a square and a triangle. The diameter of the circle is 20 nm, and all the particles have the same area, so that the SCS should be comparable. The illumination direction is along one of the particle’s symmetry axis.

For the circle we recover the well-known result of a single resonance, at \( \lambda = 338 \text{ nm} \) (corresponding to \( \varepsilon = -1.07 + 0.29i \)). The full width half maximum (FWHM) of the resonance is about 25 nm. As can be seen in Fig. 1, the structure of the SCS becomes more complex for less regular particles. The main resonance is red-shifted from \( \lambda = 338 \text{ nm} \) (circle) to \( \lambda = 350 \text{ nm} \) (hexagon), \( \lambda = 357 \text{ nm} \) (pentagon), \( \lambda = 361 \text{ nm} \) (square) and \( \lambda = 385 \text{ nm} \) (triangle). An additional resonance appears for all the non-circular particles. Moreover, a third resonance can be observed for the triangle at \( \lambda = 357 \text{ nm} \). The influence of the direction of illumination on the SCS is very small due to the symmetry of the simplexes (not shown).

The large SCSs that occur at the plasmon resonances are associated with large field amplitudes at the vicinity of the particle. In Fig. 2, we show this near-field amplitude distribution for the main resonance of each simplex. The amplitude is normalized to the incident amplitude, and the illumination direction indicated by the arrow.

The amplitude inside the circular particle is almost homogeneous, about 7 times the incident field. The boundary of the cylinder is not visible in the amplitude distribution because the resonance happens when \( \varepsilon \) is close to -1. Maxwell’s boundary conditions impose then that the field amplitude is continuous. The field amplitude decays rapidly outside the particle.

FIG. 1. SCS for the 20 nm simplexes

FIG. 2. Relative field amplitude distribution for the 20 nm simplexes, at their respective main resonance (see Fig. 1). The arrow indicates the propagation direction of the illumination field.
FIG. 3. Relative field amplitude distribution associated with the three resonances of the triangle (Fig. 1). (a) Main resonance, $\lambda = 385\text{ nm}$; (b) $\lambda = 358\text{ nm}$ and (c) $\lambda = 329\text{ nm}$.

The field becomes strongly heterogeneous for the non-regular structures. At the main resonance, the field amplitude takes large values at the corners transverse to the incident wave vector (Fig. 2). There the relative field amplitude exceeds 20 for the hexagon and the pentagon, 70 for the square and 150 for the triangle. Let us stress here that the large fields we observe near the corners are not produced by the lightning rod effect. The latter provides only a field amplification factor in the order of 5 to 10, even for very large permittivity values, as illustrated in Fig. 4(c) of Ref. 51.

In Fig. 3 we show the near-field distributions for the triangle corresponding to the three resonances observed in Fig. 1. For the main resonance ($\lambda = 385\text{ nm}$) and the resonance at $\lambda = 358\text{ nm}$ we observe very large fields near the corners transverse to the illumination direction. However, the field distributions have a very different topology for each resonance, which can easily be understood in terms of polarization charges.50 These two resonances correspond to what is also known as the particle surface modes of order 0 and 1.45>53 The polarization charge topology of the main resonance (order 0) is the most simple one, with charges of a given sign near each corner, leading to a point–like field distribution at the corners, as observed in Fig. 3(a). On the other hand, charges of both signs accumulate near the corner for the resonance at $\lambda = 385\text{ nm}$ (order 1), leading to a dipole–like field distribution around the corners, as observed in Fig. 3(b).

A different amplitude scale is used in Fig. 3(c) for the resonance at $\lambda = 329\text{ nm}$. Although the maximum field amplitude is comparatively small (10 times the incident field), this resonance is most remarkable: The field is maximum at the corner longitudinal to the illumination direction. As discussed in Ref. 51, this resonance does not appear to be red–shifted for larger particle sizes, contrary to the surface modes Figs. 3(a) and (b). This resonance is likely related to the bulk longitudinal mode, that appears in the bulk when the illumination frequency and the electron plasma frequency $\omega_p$ coincide (i.e. when $\varepsilon \sim 0$).55

In Fig. 4, we show the SCS diagram for larger simplices. All the particles have again the same area, the diameter of the circle being now 50 nm. We observe mainly two differences with respect to the SCS of the smaller simplices (Fig. 1): First, for all shapes the main resonance is red–shifted (e.g. for the triangle it is now at $\lambda = 399\text{ nm}$, compared to $\lambda = 385\text{ nm}$ for the 20 nm triangle).

Second, the resonance FWHM is roughly doubled (i.e. for the circle, it is now more than 50 nm, compared to 25 nm previously). We also see in Fig. 3 that an additional resonance can be resolved for the square at $\lambda = 351\text{ nm}$, whereas two additional resonances start to emerge for the triangle at approximately $\lambda = 350\text{ nm}$ and $\lambda = 382\text{ nm}$.

B. Implications for SERS

In this section we will focus on the near-field distribution and discuss practical implications for SERS. The utilization of this electromagnetic enhancement for scanning near-field optical microscopy has been discussed in Ref. 69 and shall not be discussed here.

1. Enhancement

For molecules excited far from an electronic absorption band, the intensity of Raman scattered light is proportional to the fourth power of the local electric field amplitude where the molecule is immersed.3 Plasmon resonant particles provide a convenient method of enhancing the electromagnetic fields, and therefore are ideal SERS substrates. A second enhancement mechanism, the so–called chemical enhancement, related to the adsorption of the molecule on the metal, can also contribute to SERS.70–72 However, electromagnetic enhancement is believed to play the major contribution to SERS.

The electromagnetic enhancement effectively experienced by a molecule depends on the location where the molecule is adsorbed on the metal, as well as the relative position of the Raman active site within the molecule. This becomes very important when the molecule is large and placed in a strongly inhomogeneous field. This was recently verified experimentally by van Duyne et al., who inserted different numbers of non–active linker molecules between the adsorption site of a molecule and the Raman active site.73 In this experiment, the Raman signal was
highly dependent on the number of linker molecules, and therefore on the distance between the surface and the Raman active site, particularly for non-regular (tetrahedral) nanoparticles. Further, when a large number of molecules are adsorbed on the same nanoparticle, a spectral shift in the particle resonances can be observed.74

In this section we will discuss the near-field distributions associated with the plasmon resonances of the simplexes, with emphasis on the local variation of the field amplitude around the particles.

Figure 5 shows the maximum enhancement obtained at a 1 nm distance from the surface as a function of the wavelength. The amplitude enhancement is shown on the left axis and the corresponding Raman enhancement on the right one. We observe that the field enhancement, which is a near-field quantity, is strongly correlated to the SCS, a far-field quantity (compare Figs. 1 and 5). The position of the main resonance is the same, but the resonance width is broader in the enhancement diagram (Fig. 5) than in the SCS (Fig. 1). This is simply because in Fig. 5 we report the maximum amplitude enhancement around the particle, whereas in Fig. 1 we report the SCS, which is related to the field amplitude squared. The maximum amplitude enhancement increases considerably for more complex shapes: Whereas it is 6 for the circle, it is about 35 for the triangle.

The differences between the simplex shapes is much more pronounced for the enhancement than for the SCS. For the triangle the maximum Raman enhancement exceeds $10^6$, for the square it is still about $10^5$, whereas it is below $10^4$ for the hexagon, the pentagon and the circle.

The field enhancement for the larger simplexes is shown in Fig. 6, again at a distance of 1 nm from the surface. We observe that the correlation with the SCS diagram is now weaker. The maximum enhancement is comparable to that obtained previously for the smaller particles.

As previously discussed, the local variations of the near-field distribution determine the effective enhancement experienced by a molecule. This is investigated in Fig. 7, where we present the amplitude distribution as a function of the distance from the tip surface, for the triangle, square and circle. The data correspond to the main resonance, and two particle sizes are considered.

For the circle, the field amplitude on the surface reaches $6.9 \times 10^4$, for the small (large) circle. At 2 nm from the surface, the amplitude drops to $2.2 \times 10^3$. For the triangle we observe a huge enhancement for both particle sizes: Near the surface more than 100 in terms of amplitude ($10^8$ Raman), and still more than $50 \times 10^6$ at a half-nanometer distance (Fig. 7). For the square we obtain a similar behavior, although the amplitudes are about a factor of two smaller (the Raman enhancement being 16 times weaker). The strong field amplitude variations for such non-regular structures might explain the “hot spots” observed both in SERS experiments and in direct measurement of the locally enhanced field.5,75

Fig. 7 indicates similar results for the maximum amplitude distribution around the 20 nm and the 50 nm simplexes. Although not shown here, this enhancement rapidly decreases for particle sizes above 50 nm.50
example, the maximum amplitude enhancement at the corner of a 100 nm triangle is only half that of the 20 or 50 nm particles.

Within our model we therefore observe that for a given particle shape the maximum field enhancement increases with decreasing particle sizes down to 50 nm and then remains fairly constant. Note that this maximum enhancement occurs at different wavelengths for different sizes.

Although the local maximum enhancement is similar for particles in the 20–50 nm range, the average over the entire particle may differ with the particle size. This is important for SERS experiments in which large numbers of molecules are used, since the measured Raman signal is proportional to the average Raman enhancement on the surface. This is illustrated in Fig. 5 of Ref. 51, where the overall near-field distribution for particles between 10 and 100 nm is shown. We shall now discuss this average enhancement in further details.

In Fig. 8 we show the averaged enhancement for the 20 nm simplexes. This average value is obtained by taking between 500 and 800 points (depending on the particle shape) distributed regularly around the particle, at a 1 nm distance from the surface. Note that the average amplitude [Fig. 8(a)] and the average Raman enhancement [Fig. 8(b)] must now be represented on separate graphs.

In Fig. 8(a) we observe that the average field amplitude is strongly correlated with the SCS (Fig. 1), both with respect to the wavelength and the width of the different resonances. The average field amplitude enhancement is quite similar for the circle, the hexagon and the pentagon: about 5.5 times the initial amplitude. For the square it is about 7.5 at the corresponding main resonance wavelength, whereas it reaches almost 12 for the triangle.

The average Raman enhancement, as shown in Fig. 8(b), is less than \(10^3\) for the circle, becomes then larger for the hexagon and the pentagon, and reaches about \(10^4\) for the square and almost \(10^5\) for the triangle (always at the corresponding main resonance wavelength). It is important to realize that, due to the rapid variations of the field, the maximum field amplitude on the particle circumference dominates the average Raman enhancement, as the fourth power of the field is taken. This is the reason why the average Raman enhancement is larger than the fourth power of the corresponding average field enhancement [compare Figs. 8(a) and (b)].

Similar results for the 50 nm simplexes are shown in Fig. 9. Comparing Figs. 8(a) and 9(a), we observe that these larger simplexes produce a smaller average field enhancement than their 20 nm counterparts. This is particularly the case for the triangular wires, where the maximum average enhancement drops from almost 12 to less than 7 times the illumination amplitude. (For the other shapes, the decrease of the maximum average enhancement is less than 15%.)
For the average Raman enhancement we also observe a smaller enhancement for the 50 nm circular particle than for its 20 nm counterpart. For the hexagon, pentagon and square particles, the average Raman enhancement is somewhat larger for the 50 nm than for the 50 nm simplexes [Figs. 8(b) and 9(b)]. For the triangular particle, the average Raman enhancement at the main resonance is slightly weaker for the 50 nm particle than for the 20 nm one, whereas for the next resonance it is more than ten times stronger. Again, this can be understood with the larger maximum Raman enhancement, as observed in Figs. 5 and 6: This larger maximum value outweighs the fact that, for the 50 nm particles, the field amplitude is in average smaller than for the 20 nm particles.

This illustrates the complexity of the interpretation of Raman experiments in which large numbers of molecules are used. The fact that the local Raman enhancement (Figs. 5 and 6) can be much stronger than the average enhancement [Figs. 8(b) and 9(b)], indicates that in such an experiment a very limited number of molecules can contribute the major part of the SERS effect. Let us finally note that the distance between the active Raman site and the surface can also influence the respective magnitude of the local and average enhancements. As a matter of fact, Fig. 7 indicates that at very short distances from the surface, the field is stronger for the 20 nm simplexes. In that case, both the average amplitude and the average Raman enhancements are larger for the 20 nm simplexes.

2. Spectral response

The resonance spectra of non-regular particles are more complex than those of regular particles. The possibility to address different resonances by tuning the illumination wavelength can prove useful for specific applications. In Fig. 10 we show the field amplitude as a function of the distance from the corner for the three resonances of the 50 nm triangle (see Fig. 4). We observe a similar enhancement of about 150 close to the surface for the main resonance ($\lambda = 399\text{nm}$) and the resonance at $\lambda = 364\text{nm}$. However, the field decays more rapidly for the latter resonance (Fig. 10). This behavior can be related to the polarization charge distribution associated with both resonances, as discussed in Sec. III A and illustrated by the animations in Ref. 52. For the main resonance ($\lambda = 399\text{nm}$) a point-like charge distribution builds at the corner. This distribution produces a field amplitude dependence in $1/d$, where $d$ is the distance from the surface. The resonance at $\lambda = 364\text{nm}$ is associated with a dipolar-like charge distribution, leading to a $1/d^2$ distance dependence. Keep in mind that we have a 2D geometry, so the point-like and dipolar charge distributions correspond to 2D distributions.

C. Influence of the dielectric function

As mentioned in the introduction, a more sophisticated model of the material would include the modification of the bulk permittivity for very small particle sizes, as the electrons mean free path is reduced by scattering at the surface. Let us briefly discuss how this would affect our results.

Kreibig found that for silver particles near the plasma frequency the imaginary part $\varepsilon'$ of the permittivity is given by

$$\varepsilon' = 0.23 + 2.64/A,$$

with $A$ the particle size in nanometers. The real part of the permittivity, which determines at which wavelengths the resonances occur, is nearly unaffected. This means that for a 12 nm particle, the complex part of the permittivity is almost doubled with respect to the bulk value. Using this modified value, the resonance would be broader, and the intensity of the scattered near- and far-field would be approximately half that obtained with the bulk value. For the 20 nm particles discussed here, the result would be accordingly less affected, whereas for 50 nm the results would barely be affected.

Taking this size-dependent permittivity, one might ask which particle size gives the largest enhancement. We would then have a tradeoff between the decrease of the enhancement due to retardation effects for larger particles (which sets in for particles larger than 50 nm), and the increase of the microscopic absorption for very small particles. Taking these two effects into account, we estimate the maximum enhancement to happen for particles in the 30–40 nm range.
D. Singular behavior at corners

Dealing with sharp corners introduces additional numerical difficulties since the field becomes singular at short distances from an infinitely sharp, perfectly conducting corner. However, the sharpness of a real particle is limited by surface and boundary energies. Therefore, we have rounded off each corner by 0.25 nm, providing a more realistic model. Nonetheless, our results indicate that plasmon resonances also produce extremely strong fields at the particle corners. It was therefore important to verify that the discretization of the corners does not introduce any numerical artifacts.

In Fig. 11 we present the field amplitude near the corner of the 20 nm triangle at main resonance, for the three different corner discretization schemes shown in the inset. We observe that the field near the corner is only slightly affected by the discretization. The somewhat larger field obtained for the smoothest discretization (solid line, Fig. 11) can be related to the fact that the field is effectively computed at a shorter distance from the surface (see the inset in Fig. 11). Besides the stability of the method this also demonstrates that the major role is played by the overall-particle shape and not by such a small detail as the discretization of one corner. Note that the SCS diagram is not at all affected by the discretization scheme (not shown).

![FIG. 11. Field distribution at the vicinity of the corner of the 20 nm triangle, at the main resonance. Three different discretization schemes for the rounded-off corner are investigated. The field is computed along the line, starting 0.2 nm from the rounded-off corner.](image)

E. Other geometries

We will now break the symmetry of the triangular simplex. In Fig. 12 we present the SCS diagram for three right-angled triangles, with different perpendicular to base aspect ratios. Again, the area of the triangles is the same as that of the 20 nm circle. The illumination direction is normal to the hypotenuse.

![FIG. 12. SCS for three right-angled triangles with the same area and a different perpendicular to base ratio.](image)

In Fig. 12 we now observe a much more complex structure than for the equilateral triangle. The main resonance is strongly shifted to higher wavelengths, namely from $\lambda = 385$ nm (equilateral) to $\lambda = 414$ nm (1 to 1), $\lambda = 470$ nm (2 to 1), and $\lambda = 596$ nm (4 to 1). The main resonance is therefore shifted into the red optical range for the 4 to 1 particle (note the different wavelength range in Fig. 12). The SCS at the main resonance also increases slightly for higher aspect ratios. Moreover, the higher order resonances becomes more numerous and more pronounced for higher aspect ratios. Note that a similar red-shifted main resonance and larger SCS with increasing aspect-ratio was recently observed experimentally for gold nanorods.

Figure 13 shows that the near-field amplitude dramatically increases for higher aspect-ratios. For example at the very tip of the 4 to 1 triangle, the field enhancement exceeds 1000, corresponding to a Raman enhancement of $10^{12}$; at a distance of 1 nm from the tip, the field enhancement is still larger than 100 ($>10^8$ Raman).

![FIG. 13. Amplitude enhancement at the main resonance, near the sharp corner of right-angled triangles with the same area and a different perpendicular to base ratio.](image)
Finally, we present in Fig. 14 the dependence of the field amplitude as a function of the distance from the sharp corner of the 4 to 1 triangle, for four different resonances. The three resonances at $\lambda = 596\,\text{nm}$ (order 0), $\lambda = 476\,\text{nm}$ (order 1) and $\lambda = 421\,\text{nm}$ (order 2) produce a similar enhancement on the particle surface, and then decay differently. This is similar to the behavior observed for the order 0 and 1 resonances of the triangular simplex (Fig. 10). As expected, the highest order mode ($\lambda = 421\,\text{nm}$) has the fastest decay, as it is associated with a triple polarization charge distribution (e.g. $+$ $-$ +) near the corner. The amplitude of the resonance at $392\,\text{nm}$ is rather moderate. For this resonance, polarization charges of different sign constitute also near the lower–right corner.

Although the aspect ratio influences the spectral response of the particle, its cross–sectional shape remains the dominant factor, as illustrated in Fig. 15, where we show the SCS for rectangular particles with increasing aspect ratio. These particles have the same area as the triangles investigated in Fig. 12, corresponding to the 20 nm simplexes (Fig. 1).

Again, the main resonance is red–shifted for increasing aspect ratio, although this shift amounts less than 100 nm between a square and a 4 to 1 elongated particle (Fig. 15). This is much less than for the right–angled particles in Fig. 12. On the other hand, the SCS at the main resonance strongly increases with increasing aspect ratio, reaching similar values as the right–angled particles (compare Figs. 15 and 12).

In Fig. 16 we show the field enhancement associated with different aspect ratio rectangular particles. This enhancement is a factor of 10 weaker than that of triangular particles (compare Fig. 16 with Fig. 13). Quite interestingly, at very short distances from the particle, the field is strongest for the square particle (1 to 1, Fig. 16). This is probably related to the strongest charges confinement that can occur on both sides of the corner for a square particle. At larger distances from the particle the field enhancement is larger for the higher aspect ratio particles (Fig. 16). This indicates that, although not as much confined, the amount of induced polarization charges is larger, in agreement with the larger SCS.

IV. CONCLUSION

Our results reveal the complexity of the plasmon resonances in 2D nanoparticles (nanowires) with a non–regular cross–section. We have shown that the resonance spectrum strongly depends on the particle shape. The higher the particle symmetry, the simplest its spectrum (e.g. a small cylindrical particle exhibits only one resonance, whereas a square has two and an equilateral triangle at least three distinct resonances). Several additional resonances are observed for right–angled triangular particles with a high perpendicular to base ratio.

These complex scattering cross sections are also associated with a dramatic near–field enhancement at close vicinity of the particle. We found the strongest enhancement for particles with dimensions smaller than 50 nm.
Right-angled triangular particles produce a field amplitude exceeding 1000 times that of the incident field at short distances from the surface. This dramatic near-field enhancement corresponds to a Raman enhancement in the order of $10^{12}$. Such enhancement can help understand recent SERS experiments, where single molecule detection was possible, thereby requiring an enhancement factor similar to that we computed. This is also confirmed by our results on average Raman enhancement, which indicate that a limited number of molecules can contribute the major part of the SERS signal, even in experiments in which large numbers of molecules are used.

The spectral response of these non-regular particles could also be used for near-field optical microscopy, non-radiative optical transfer, and for building new active optical components.

Although we focused the present article on individual, non-interacting particles with a non-regular shape, it should be emphasized that similar Raman enhancements can be observed in interacting, regularly shaped particles, as recently investigated in Refs. 79, 80.

This work should help design nanoparticles with tailored plasmon resonances for specific applications.

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“Spectral response of plasmon resonant nanoparticles with a non-regular shape”

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Spectral response of plasmon resonant nanoparticles with a non-regular shape

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Abstract: We study the plasmon resonances of 10—100 (nm) two-dimensional metal particles with a non-regular shape. Movies illustrate the spectral response of such particles in the optical range. Contrary to particles with a simple shape (cylinder, ellipse) non-regular particles exhibit many distinct resonances over a large spectral range. At resonance frequencies, extremely large enhancements of the electromagnetic fields occur near the surface of the particle, with amplitudes several hundred-fold that of the incident field. Implications of these strong and localized fields for nano-optics and surface enhanced Raman scattering (SERS) are also discussed.

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1. Introduction

Small metal particles are known to exhibit resonant behavior at optical wavelengths. The extremely large electromagnetic field enhancements associated with these plasmon resonances are of great importance for nanoscience: In surface enhanced Raman scattering (SERS) [2,3] they play a key role in the amplification of the Raman signal of molecules adsorbed on rough metal particles [4–7]. In near field optical microscopy, they can provide a strong, well-defined and localized light source to investigate subwavelength structures [8]. While metallic nanoparticles produced by standard techniques (e.g., colloidal or evaporation) can have a broad variety of shapes, an accurate and complete description of the electromagnetic modes associated with such particles has not been available [9,10]. Such a description is particularly relevant to forward our understanding of SERS, which appears to be critically dependent on the detailed shape, material composition and configuration of the underlying metal nanoparticles. As the electromagnetic field enhancements of scatterers with spherical shape cannot explain the experimentally observed enhancement factors in SERS, the study of particles with arbitrary shape, as well as clusters of interacting particles, is of great importance [11].

In this paper we study the plasmon resonances of metal particles in the 10–100 (nm) range. Special attention is focussed on this range for three reasons: First, it is known from the analytic solution that the field enhancement at resonance is maximized for spherical particles with diameters in this range; we assume (and will show) that this is also valid for non-spherical particles. Second, the experimentally observed enhancement in SERS is the largest for nanoparticle dimensions of this scale. Third, technology is now reaching the state where particles of this size can be produced in a controlled manner [12–14].

2. Model

The plasmon resonances of nanoparticles can be investigated using Maxwell’s equations [11]. As metals exhibit frequency dispersion, the permittivity varies with wavelength. For metals such as silver and gold, the permittivity can assume negative values at optical frequency. The underlying microscopic mechanism that leads to this negative permittivity is the interaction of the electromagnetic field with the conduction electrons.

For specific negative values of the permittivity, which depend on the size and shape of the particle, an external electromagnetic field can produce a resonantly enhanced polarization, leading to large scattering cross sections (SCS) and large electromagnetic fields near the particle. These distinct resonances are known as the surface polariton modes, or plasmon resonances of the particle. As we will see, different bounding surfaces have a strong impact on these plasmon resonances.

Since our focus here is the influence of the surface on the plasmon resonances, we do not consider further the fundamental processes that give rise to the dispersion, but rather use experimental values as obtained by Johnson and Christie [15]. Silver particles in the
10--100 (nm) size range, as investigated in this study, are well described with the bulk permittivity [16]. It is only for particles smaller than 10 (nm) that electron scattering at the particle boundary impinges on the conduction electrons mean free path. This however hardly influences the real part of the permittivity for silver nanoparticles, even below 10 (nm), and only increases the imaginary part of epsilon [11,16].

We investigate two-dimensional (2D) silver scatterers, illuminated with a transverse electric (TE) wave, where the electric field component lies in the plane of the figures. (In the transverse magnetic (TM) case, where the magnetic field is in the plane, plasmon resonances are not excited.) A 2D structure corresponds to an infinitely long structure in the third (not shown) dimension.

For our numerical simulations we use a recently developed finite elements solution of the volume integral equation [17]. The key point is a new regularization scheme that ensures a very high accuracy. Such an accuracy is mandatory for studying resonances numerically, because at the resonance a small change of the system parameters leads to a large change in the system response. We refer the reader to Ref. [17], where this numerical technique is described in detail and its accuracy assessed. The scatterers presented here are discretized with several thousand triangular elements.

Nanoparticles with triangular cross-sections are an exemplary case of non-regular particles. Triangular particles are interesting as they exhibit several complex phenomena, including multiple plasmon resonances, a longitudinal (bulk) plasmon mode, and a very large and localized field enhancement at the sharp tips [18]. To more closely match realistic particles, as well as to avoid numerical difficulties, we rounded off each corner of a particle by 0.25 (nm). For different geometries, we show the SCS as a function of the wavelength between 300 (nm) and 600 (nm). Since the extreme near field is of specific importance for SERS, we present detailed color maps of the field amplitude versus excitation wavelength in movies, with the wavelength as “time axis”. To ease comparison, the same color map for the field amplitude is used throughout the paper.

3. Results

Only the plasmon resonances for simple shapes like a cylindrical or elliptical particle have been studied in detail. To provide a common ground, we first consider a 20 (nm) x 10 (nm) elliptical profile. Such an ellipse has two resonances corresponding to the illumination directions along the major and minor axes. These resonances are shown in Fig. 1, where the SCS is given as a function of the wavelength for three different illumination directions. We see that the resonance at $\lambda = 331$ (nm) corresponds to the illumination direction perpendicular to the minor axis, whereas the larger resonance at $\lambda = 357$ (nm) corresponds to the illumination direction perpendicular to the major axis. For incidence
Fig. 2. Movies of the field amplitude distribution for a 20 (nm) × 10 (nm) ellipse illuminated along the (a) (01)-direction (609 KB), (b) (10)-direction (589 KB), (c) (11)-direction (606 KB) in the λ = 300 (nm) ... 600 (nm) wavelength range. Front pictures: (a) λ = 357 (nm), (b) λ = 331 (nm), (c) λ = 357 (nm).

in a direction off either of the symmetry axes, both resonances are excited.

The movies Figs. 2(a)–(c) display the electromagnetic field amplitude distribution as a function of the wavelength, for three different illumination directions. The amplitude of the incident plane wave is one. At the resonances λ = 331 (nm) and λ = 357 (nm) the field distribution inside the ellipse is nearly constant, consistent with the well-known quasi-static result [11]. In the main resonance at λ = 357 (nm) the field amplitude at close vicinity of the particle reaches 20 times that of the incident field. Note also that for oblique incidence the field distributions at the resonances [λ = 331 (nm) and λ = 357 (nm)] are nearly symmetric with respect to the particle axes. This emphasizes the dominant role played by the resonances.

Figure 3 shows the SCS for a triangular particle, again for three different illumination directions. We observe a much more complex structure, with five distinct plasmon resonances that now cover a broader wavelength range, from 329 (nm) to 412 (nm).

As illustrated by the movies in Figs. 4(a)–(c), the field distributions associated with the triangle resonances have a much more complex structure. We observe local field enhancements of up to 200 in the main resonance at 412 (nm) [Fig. 4(a)]. An analysis of the field divergence shows that each mode is associated with a different surface polarization charge distribution. In the main resonance at 412 (nm) both corners have accumulated charge of different sign, oscillating within a period, whereas for the resonance at 365 (nm) both negative and positive charges are accumulated near each corner, which leads to a completely different field pattern with a more rapid decrease of the near field amplitude just outside of these corners.

Note also that, as for the ellipse, there is a particular illumination direction that max-
Fig. 4. Movies of the field amplitude distribution of the 20 (nm) triangular particle illuminated along the (a) (11)-direction (775 KB), (b) (10)-direction (772 KB), (c) (11)-direction (768 KB) in the 300–600 (nm) wavelength range. Front pictures: (a) \( \lambda = 412 \) (nm), (b) \( \lambda = 365 \) (nm), (c) \( \lambda = 363 \) (nm).

Imizes the excitation of each resonance. For example, the main resonance at 412 (nm) corresponds to the (11)-direction. Illuminating the particle at this wavelength from another direction leads to a reduction of intensity. Illumination perpendicular to this direction, as in the movie Fig. 4(c) at 412 (nm), does not lead to the excitation of this resonance.

Let us emphasize that this strong enhancement is not a lightning rod or tip effect, but truly a resonance related to the overall particle shape. Lightning rod effect, occurring when the particle is off-resonance, provides only a very small amplitude enhancement as illustrated by the movies in Figs. 4(a)–(c) for \( \lambda = 300 \) (nm).

Although not shown in this paper, there is a phase shift, up to approximately \( \pi/4 \) at the main resonance between the incident field and the scattered field near the particle. This phenomenon is well known from classical mechanics, where such a phase shift is observed when the driving frequency and the eigenfrequency of the system are close.

In Figure 5 we study the SCS of a right-angled isosceles triangle, illuminated along the (11)-direction, for different particle sizes. Two features, common also to spherical scatterers, are evident in these SCS plots: First, the red-shift of the resonances increases with increasing particle size, as can be clearly seen for the main resonance, located at 401 (nm) for the 10 (nm) base triangle, and 458 (nm) for the 100 (nm) particle. Second, the resonances broaden with increasing size with an accompanying decrease of the near field amplitude at the resonances. Although more resonances are excited for larger particles, the broadening leads to an overlapping of the resonances such that they cannot be resolved.

For the resonance at 329 (nm) however, we observe no red-shift. This is characteristic...
of a longitudinal bulk mode (as opposed to a surface mode), the permittivity being close to zero at this wavelength. Moreover, this resonance exists for all incident directions [see Figs. 4(a)–4(c)], the field maxima being always located in a corner along the illumination direction. For the surface modes, on the other hand, the field maximum is located in a corner transverse to the illumination direction.

In the movies Figs. 6(a)–6(c) we see that with increasing size the near field amplitude decreases (as the resonance width increases), and that the field is more localized towards the surface of the triangle, as material losses become more important.

In Fig. 7 the SCS is shown for a 10 (nm) base, 20 (nm) perpendicular right angled triangle. Note the much more complex resonances for such a particle with low symmetry. These resonances extend over a broader wavelength range, the main resonance being obtained at \( \lambda = 458 \) (nm).

For (11) incidence, the field in the main resonance at 458 (nm) has extremely large values at the “sharp” corner where it reaches up to 400 times the incident amplitude [Fig. 8(a)]. In this mode, charge accumulates in the sharp corner, whereas the same charge amount of different sign is distributed over the remaining particle surface. Note also that in this main resonance the sharp corner acts like a point source, producing a radial field distribution in its vicinity, with a slow decrease of the field amplitude (\( \approx 1/r \)). Even at a distance of 10 (nm) from the sharp corner, the near field amplitude is still more than 10 times the incident amplitude.

For the resonance at 392 (nm) we obtain a similar large field enhancement at the sharp corner, however decreasing rapidly outside the particle, like for the resonance of the 20 (nm) triangle at \( \lambda = 365 \) (nm) [Fig. 4(a)]. Both negative and positive charges
are accumulated near the corner, leading to a dipole-like field behavior in its vicinity, similar to the resonance of the 20 (nm) triangle at $\lambda = 365$ (nm) [Fig. 4(a)].

Again, we observe the weak resonance at 329 (nm) for all three directions of incidence, corresponding to the bulk mode.

3. Conclusions

Using a triangular particle as our model system, we have shown that non-spherical metal nanoparticles have a very complex behavior at optical wavelengths, with multiple resonances. These resonances crucially depend on the size and shape of the subwavelength nanoparticle. We observed that the field amplitudes associated with these resonances can be extremely large, up to several hundred times the incoming field amplitude. Furthermore, these large electromagnetic fields are strongly localized at particular positions on the particle surface. Such strong fields can explain the large enhancement factors observed experimentally in SERS, where the Raman signal is proportional — to a first approximation — to the fourth power of the electromagnetic amplitude enhancement. Simulations of the plasmon resonances for non-spherical particles can provide useful guidelines for different areas of nanoscience where extremely large electromagnetic fields — eventually at different wavelengths — are required.

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“Field polarization and polarization charge distribution in plasmon resonant particles”

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Field polarization and polarization charge distributions in plasmon resonant nanoparticles

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Abstract. We study the plasmon resonances for small two-dimensional silver particles (nanowires) with elliptical or triangular shapes in the 20 nm size range. While the elliptical particle has only two resonances, a well known fact, we demonstrate that the triangular particle displays a much more complex behaviour with several resonances over a broad wavelength range. Using animations of the field amplitude and field polarization, we investigate the properties of these different resonances. The field distribution associated with each plasmon resonance can be related to the polarization charges on the surface of the particles. Implications for the design of plasmon resonant structures with specific properties, for example, for nano-optics or surface enhanced Raman scattering are discussed.

1. Introduction

For metals like silver and gold, the plasma frequency $\omega_p$ of the electron gas lies in the optical range. This renders very strong the interaction of these metals with light and leads to a highly dispersive dielectric function at optical frequencies [1, 2]. In particular, the real part of the permittivity $\varepsilon(\omega)$ changes sign when the illumination frequency $\omega$ passes close to $\omega_p$. For particles smaller than the skin depth, this microscopic interaction can result in a resonance of the entire particle, known as a plasmon resonance or a surface mode of the particle [1, 3].

The boundary conditions imposed by Maxwell’s equations on the surface of the particle determine whether such a resonance can build up. Therefore, the shape- and the frequency-dependent permittivity of the particle command the spectrum of resonances that can be excited in the particle. For example, it is well known that a spherical nanoparticle has its single resonance frequency when $\varepsilon(\omega) = -2$, whereas a cylindrical particle is resonant when $\varepsilon(\omega) = -1$ [1].
Contrary to these simple shapes with a single resonance, scatterers with a more complex boundary can have several resonances. The simplest case is that of an ellipse, where two different modes can be excited [1]. For more complex geometries this problem cannot be solved analytically and one must resort to numerical methods. The resonances of cubic particles, for example, have been investigated in the electrostatic limit by Fuchs [4], while Jensen et al studied truncated tetrahedra in the 100 nm range [5].

We recently developed a new computational technique for the study of the resonances of structures with an arbitrary shape [6]. In [7], we investigated, from a phenomenological point of view, the plasmon resonances of non-regular silver particles in the 10–100 nm range and discussed their dependency on the particle shape and size as well as on the direction of illumination.

In the present publication, we shall concentrate on two exemplary particle shapes, a regular one (ellipse) and a non-regular one (triangle), and investigate the phenomena that give rise to the much more complex resonance spectrum for the latter particle type. For this purpose, after determining the resonance spectra from scattering cross sections (SCSs) for these two classes of particles, we will present movies with the temporal evolution of the field distribution and the polarization charge distributions associated with each resonance.

2. Model

We investigate two-dimensional (2D) silver scatterers, i.e. particles with a translation symmetry along the third (not shown) space dimension (nanowires). The particles are illuminated using a plane wave propagating in the plane of the figure with the electric field also in the plane of the figure (so-called transverse electric wave).

We choose particles in the 20 nm size range, leading to narrow and well separated resonances (larger particles have much broader resonances [7]). Moreover, this size range is of particular interest because it is associated with the strongest local field enhancements [8], and structures of that scale can now be fabricated in a controlled manner [9]–[12].

For our numerical simulations we use a recently developed technique for the solution of the volume integral equation [6]

\[
E(r; \omega) = E^0(r; \omega) + \int_V \, dr' \, G^B(r, r'; \omega) \cdot k_0^2(\varepsilon(r'; \omega) - \varepsilon_B)E(r'; \omega) 
\]

that gives the total electric field \(E(r)\) scattered by a system with permittivity \(\varepsilon(r; \omega)\) embedded in an infinite homogeneous background \(\varepsilon_B\) when it is illuminated with an incident field \(E^0\). For a detailed derivation of (1), see [13] where expressions for the Green tensor \(G^B\) associated with 2D and 3D backgrounds are given.

To accurately accommodate the very strong field variations that occur in plasmon resonant particles we use finite elements to approximate the electric field \(E(r)\), as well as a new regularization scheme to handle the singularity of the Green tensor when \(r \to r'\). The scatterer is discretized using a few thousand triangular elements. We refer the reader to [6], where this numerical technique is described in detail and its accuracy assessed.

For the frequency-dependent permittivity \(\varepsilon(r; \omega)\) of the silver scatterers, we use the experimental data of Johnson and Christy [14].

Let us note that particles down to 2 nm can be well modelled using a local dielectric function [15]. However, this dielectric function might differ from its bulk value and depend on the particle geometry since the mean free path of the electrons decreases due to scattering at the surface. It
Figure 1. SCS for an ellipse (overall size 20 nm × 10 nm, as a function of the illumination wavelength.

Figure 2. Field distribution for three different wavelengths. The illumination direction is the (11) direction (i.e. the incident electric field is polarized in the (11) direction). The movies linked to figure 2 illustrate the variation of the field polarization over one period, each arrow indicating the instantaneous direction and the relative magnitude of the electric field.

When out of resonance, at λ = 300 nm where the real part of the permittivity of silver ε = 0.84 + i2.7 is still positive, the scattered field remains parallel to the illumination field (figure 2(a)). A small amplitude field enhancement, in the order of twice the illumination amplitude, is observed in the regions where the electric field is normal to the particle interface. This effect can be related to the continuity of the displacement field [18]. On the other hand, no enhancement appears where the electric field is parallel to the interface since the boundary conditions now require this field to be continuous (figure 2(a)).

3. Numerical results

To ease comparison we use the same colour scale throughout the paper for the maps of the electrical field amplitude. Since we observe very important variations in the scattered field from one case to another, we take a logarithmic colour scale to highlight the details of each field distribution. The amplitude of the incident field is always one. In the movies, each arrow that represents the orientation of the electric field is normalized to the local field amplitude. This allows one to visualize the orientation of the electric field despite the strong variation of its amplitude. For the polarization charge distribution we use a colour representation that emphasizes the charge motion during one period, and this is different for each figure.

We first consider a 20 nm × 10 nm elliptical particle, illuminated along the (11) direction. We recover the well known result that such an ellipse has two resonances, as illustrated in figure 1, where the SCS is given as a function of the wavelength [1]. We also give in this figure the SCSs for illumination directions parallel to either of the ellipse axes. In such a case the two resonances are decoupled: the resonance at λ = 331 nm being related to the electric field parallel to the minor axis and that at λ = 358 nm to the electric field parallel to the major axis (figure 1).

In figure 2, we show the field distribution for three different wavelengths. The illumination direction is the (11) direction (i.e. the incident electric field is polarized in the (11) direction). The movies linked to figure 2 illustrate the variation of the field polarization over one period, each arrow indicating the instantaneous direction and the relative magnitude of the electric field.
For the resonance at \( \lambda = 331 \) nm we observe that the field amplitude is enhanced homogeneously by a factor of about 10 inside the particle (figure 2(b)). Furthermore, the electric field inside the particle is parallel to the minor axis, although the incident field is polarized in the (11) direction. This can be easily understood. As seen in figure 1, the (01) electric field component is in resonance, and its influence on the near-field overweights that of the ‘non-resonant’ (10) component (figure 2(b)). For the other resonance, at \( \lambda = 358 \) nm, we have the converse effect: the (10) component is resonant and the electric field becomes parallel to the major axis (figure 2(c)). The field amplitude enhancement at the vicinity of the particle reaches now about 15.

Note, also, that there is a phase shift of approximately \( \pi/4 \) at the main resonance between the incident field and the scattered field near the particle (figure 2(c)). This phenomenon is well known from classical mechanics, where such a phase shift is observed when the driving frequency and the eigenfrequency of the system are close.

In figure 3 we show the polarization charge distribution, which is simply given by the divergence of the electric field [19]. (The numerical evaluation of this divergence is quite sensitive to the discretization used, which explains the roughness observed in some of the polarization charge images.) When out of resonance the particle is polarized parallel to the incident (11) electric field and oscillates in phase (figure 3(a)). For the resonance at \( \lambda = 331 \) nm, the positive and negative charge distribution is nearly symmetrical with respect to the major axis, again indicating the dominating role played by this resonance (figure 3(b)). As expected, this is conversely the case for the resonance at \( \lambda = 358 \) nm (figure 3(c)).

The SCS for a 10 nm base, 20 nm perpendicular right-angled triangle, illuminated along the (11) direction is reproduced in figure 4. Dealing with sharp corners introduces additional numerical difficulties since the field becomes singular at short distances from an infinitely sharp and perfectly conducting corner [20]. However, the sharpness of a real particle is limited by the surface and boundary energies. We therefore rounded off each corner by 0.25 nm, thereby providing a more realistic model and removing numerical instabilities. The results reported in figure 4 were obtained with 3000 triangular discretization elements. We verified that 2000 or
Figure 3. Polarization charge distribution for a 20 nm x 10 nm ellipse over a period: (a) out of resonance, $\lambda = 300$ nm (QuickTime movie, 0.6 MB), (b) resonance at $\lambda = 331$ nm (QuickTime movie, 0.6 MB), and (c) resonance at $\lambda = 358$ nm (QuickTime movie, 0.6 MB). Incident field propagating along the (11) direction.

Figure 4. SCS for a 10 nm base, 20 nm perpendicular right-angled triangle, as a function of the illumination wavelength.

4000 discretization elements produced exactly the same numerical results.

We now observe a much more complex structure with several resonances covering a broad wavelength range, from 329 nm to 458 nm. The response of the particle varies extremely rapidly and, for example, a 40 nm variation in the illumination wavelength (from 418 nm to 458 nm) leads to a change of more than two orders of magnitude in the SCS (figure 4).

It is difficult from the data in figures 1 and 4 to draw conclusions on the influence of the particle shape on the linewidth of the plasmon resonances. For example, the full-width at half-maximum (FWHM) of the main resonance in figure 4 ($\lambda = 458$ nm, FWHM $\approx$ 10 nm) is close to the value obtained for the ellipse ($\lambda = 358$ nm, FWHM $\approx$ 13 nm, figure 1). However, it is important to note that both particles do not have exactly the same area, a parameter that strongly influences the resonance linewidth (for a constant shape, the plasmon resonances broaden when the particle size increases [7]).

The field distribution corresponding to the four resonances labelled in figure 4 is reported.
Figure 5. Electrical field distribution for a 10 nm base, 20 nm perpendicular right-angled triangle: (a) $\lambda = 300$ nm (QuickTime movie, 3.3 MB), (b) main resonance at $\lambda = 458$ nm (QuickTime movie, 2.8 MB), (c) resonance at $\lambda = 392$ nm (QuickTime movie, 3.0 MB), (d) resonance at $\lambda = 369$ nm (QuickTime movie, 3.2 MB) and (e) resonance at $\lambda = 329$ nm (QuickTime movie, 3.2 MB). Incident field propagating along the (11) direction (i.e. incident electric field polarized along the $\vec{1}1$ direction).

In figure 5, together with the field distribution out of resonance ($\lambda = 300$ nm, figure 5(a)). In this last case, the field distribution inside the particle is homogeneous, as for the ellipse. This is not the case at the main resonance, where we observe a 400-fold amplitude enhancement at the sharp corner, while the field vanishes along the triangle’s base. Although the field is strongly localized at a vicinity close to particle, its amplitude remains 10 times that of the incident field at a 10 nm distance from the sharp corner (figure 5(b)). In the corresponding movie, we observe that the phase shift between the incident field and the scattered near field is nearly $\pi/4$.

The resonance at $\lambda = 392$ nm is also associated with a large enhancement near the sharp corner. The field distribution, however, is completely different and the field amplitude decreases much faster outside the particle (figure 5(c)). The third resonance, $\lambda = 369$ nm, is associated with a moderate enhancement (in the order of 60) at the lower right-hand corner (figure 5(d)).

Perhaps, the most surprising resonance is that obtained for $\lambda = 329$ nm (figure 5(e)). Although the corresponding near-field enhancement is comparatively modest (about 10), the field maximum is obtained at the corner longitudinal to the incidence (remark that for the previously discussed resonances, the maximum enhancement was obtained at a corner located transversely...
Figure 6. Polarization charge distribution for a 10 nm base, 20 nm perpendicular right-angled triangle: (a) out of resonance, $\lambda = 300$ nm (QuickTime movie, 0.6 MB), (b) main resonance at $\lambda = 458$ nm (QuickTime movie, 0.6 MB), (c) resonance at $\lambda = 392$ nm (QuickTime movie, 0.6 MB), (d) resonance at $\lambda = 369$ nm (QuickTime movie, 0.6 MB) and (e) resonance at $\lambda = 329$ nm (QuickTime movie, 0.6 MB).

to the propagation direction of the incident field, see figures 5(b)–(d)). As discussed in [7], this resonance has other surprising properties: in a triangular particle it exists for every direction of incidence and has its field maximum always in the corner longitudinal to the incidence. Moreover, in contrast to the other resonances, this mode is not red shifted when the particle size increases. These properties, plus the fact that the (negative) particle permittivity is close to zero at this wavelength, indicate that this resonance is related to the bulk mode [21].

To better understand the intrinsic properties of the different resonances illustrated in figure 5, we report in figure 6 the corresponding polarization charge distributions. We also give the charge distribution out of resonance, at $\lambda = 300$ nm (figure 6(a)). In this case we observe that the charges just oscillate, parallel to the direction of the incident field, between the two opposite corners.

For the three plasmon resonances, figure 6(b)–(e), we notice that each resonance is associated with a different charge distribution. In the main resonance, $\lambda = 458$ nm, we observe that charges of a given sign build up at the sharp corner, while opposite charges are distributed on the entire circumference of the particle (figure 6(b)). This distribution oscillates over time, the sign of the accumulated charges on the sharp corner changing every half-period.

For the next resonance, $\lambda = 392$ nm, both charge species accumulate simultaneously at
the sharp corner: one species accumulates at the very tip, while the species of opposite sign is distributed along the adjacent sides (figure 6(c)). This dipolar-like charge distribution determines the field at the sharp corner. As mentioned previously, at this wavelength the field intensity in the vicinity of the corner decreases much faster than in the main resonance, which is associated with a point-like charge distribution (compare with figure 6(b)). This difference of distance dependence as a function of excited resonance, i.e. as a function of illumination wavelength, could be evidenced by the approach curves in scanning near-field optical microscopy experiments [22].

For the third resonance, $\lambda = 369$ nm, a similar behaviour is observed, with both positive and negative charges accumulating simultaneously at the sharp corner and also now at the lower right-hand side corner (figure 6(d)).

Finally, for the bulk mode, at $\lambda = 329$ nm, we obtain a rather complex charge distribution (figure 6(e)): little charge now accumulates at both sharp corners, whereas a fair amount of charges is located near the lower left-hand side corner. Note, also, that in contrast to the previously discussed resonances, opposite charges accumulate on each side adjacent to this corner.

Let us finally mention that, since the spectrum of resonances is fairly dense and the resonances have a given width, each charge distribution in figure 6 does not correspond to a single isolated resonance, but can be influenced by neighbouring resonances (except maybe for the main resonance at $\lambda = 458$ nm).

4. Conclusions

We have studied the plasmon resonances associated with regularly shaped (elliptical) and non-regularly shaped (triangular) particles and have shown that the latter have a much more complex spectrum, with more resonances and which also covers a broader wavelength range.

The strong fields associated with these resonances can be related to the polarization charges accumulating on the particle surface. These charges determine the strength and polarization of the field distribution inside the particle and at its vicinity. This field distribution strongly depends on the resonance excited in the particle, i.e. on the illumination wavelength.

The calculations presented here, together with on-going work, should provide some insight into the plasmon resonances of metallic nanoparticles with non-regular shapes. They should help in the design and engineering of nanostructures with particular properties, which are used to generate strongly confined electromagnetic fields. Such fields play, for instance, a key role in surface enhanced Raman scattering, where the Raman signal of molecules located on plasmon resonant metal particles is enhanced by several order of magnitudes [23]–[26]. Furthermore, the study of metallic nanowires sustaining plasmon resonances is also becoming a very active research field, with exciting applications in nano-optics [27]–[29].

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“Retardation-induced plasmon resonances in coupled nanoparticles”

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Retardation-induced plasmon resonances in coupled nanoparticles

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We study the coupling induced by retardation effects when two plasmon-resonant nanoparticles are interacting. This coupling leads to an additional resonance, the strength of which depends on a subtle balance between particle separation and size. The scattering cross section and the near field associated with this coupled resonance are studied for cylindrical particles in air and in water. Implications for surface-enhanced Raman scattering and nano-optics are discussed. © 2001 Optical Society of America

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It is a well-known phenomenon that small individual metallic particles of specific metals, such as gold and silver, can support plasmon resonances in the optical wavelength range. These plasmon resonances play an important role in, for example, surface-enhanced Raman scattering (SERS), where the Raman signal of molecules adsorbed on these particles is enhanced by the strong near field associated with the plasmon resonances.

When two plasmon-resonant nanoparticles are brought together, the plasmon modes in the individual particles can interact, leading to additional resonances for the coupled system. These resonances have been investigated in detail when the external field $E^0$ is such that both particles are driven in phase. In this Letter we study another coupling mechanism that can occur when the particles are driven out of phase. The resulting resonance is therefore induced solely by the phase advance, or retardation, as light propagates with a finite speed through the particles.

All the results presented in this Letter were obtained with a newly developed technique for scattering calculations, based on the solution of the electric field integral equation by use of finite elements. We refer the reader to Ref. 8, in which this technique is described in detail and its convergence and suitability for computing the plasmon resonances in arbitrarily shaped scatterers are also assessed.

The geometry is depicted in Fig. 1. Two cylinders with the same diameter $d$ and a separation distance $a$ are illuminated with a plane wave propagating in the $k$ direction, with the electric field $E^0$ polarized in the same plane (so-called TE polarization; no plasmon resonances can be excited for the other polarization when the electric field is normal to the figure). Two different incident polarizations $E^0$ are investigated. Throughout this Letter we consider silver cylinders and use the experimental data from Johnson and Christy for the permittivity, $\varepsilon(\lambda)$, as a function of the wavelength, $\lambda$.

In Fig. 2 we show the scattering cross section (SCS) for cylinders of various diameters $d$. The spacing $a$ is scaled proportionally so that the ratio $d/a$ remains constant: $d/a = 5$. Figure 2(a) shows the SCS when the incident electric field $E^0$ is parallel to the line joining the cylinders’ centers ($E^0\parallel e_x$, Fig. 1). One can recognize two resonances in the figure. The first one, near $\lambda = 340$ nm, corresponds to the resonance of an isolated silver cylinder.

The second resonance visible in Fig. 2(a) results from the interaction of the two cylinders. It is associated with polarization charges, corresponding to the divergence of the electric field, that oscillate in phase on both cylinders, as illustrated in Fig. 1(a). Note that the distribution illustrated in Fig. 1(a) corresponds to an arbitrary snapshot: during one period, the polarization charges oscillate so that, after half a period, the same distribution but with opposite sign is observed, as illustrated in the movies in Ref. 10 for the case of irregularly shaped individual particles.

The coupling between the cylinders influences the corresponding charge distribution: The charge density is more concentrated on the sides of the gap between the particles than on the external sides [Fig. 1(a)]. Therefore the only requirement for this...
coupling to occur is that the separation distance $a$ be small enough. This is the reason why this resonance exists for any particles size, including extremely small ones [Fig. 2(a)].

A very different behavior is observed for the other illumination direction, as illustrated in Fig. 2(b). For small particles, only the resonance around $\lambda = 340$ nm associated with the individual cylinder is visible. It is only when the particles reach a diameter of $\approx 50$ nm that a second mode starts to appear [Fig. 2(b)].

The polarization-charge distribution associated with this second mode is illustrated in Fig. 1(b). In this resonance the electric field driving each scatterer is out of phase. This mode is therefore induced solely by the phase advance, or retardation, as the incident field propagates through the structure. The mode is the result of a subtle balance between particle size and separation: Small separation is required for the coupling between the particles, which in turn requires large enough scatterers that their driving fields are out of phase. Note that in Fig. 2, as expected, all the resonances broaden as the size of the cylinders increases.\(^{11}\)

To illustrate the role played by retardation, we show in Fig. 3 the SCS for the same geometry as in Fig. 2 but with a water background ($\epsilon_w = 1.78$).\(^{12}\) As anticipated, the overall SCS is more complex, with more resonances than in the vacuum case [compare Figs. 2(b) and 3]. One can see that the dimension onset $d$ where the retardation-induced resonance appears is now reduced. This is simply caused by the shorter wavelength in the surrounding medium, so that the required phase difference between both scatterers already occurs for particles of the order of $d = 35$ nm.

The SCS indicates the amount of light scattered in the far field. The field distribution at the vicinity of the particles is also very important. It plays, for example, a crucial role in SERS\(^{3,4}\) near-field optics,\(^{13}\) and nonradiative optical transfer.\(^{14,15}\) In Fig. 4 we show the near-field distribution between the particles along the dashed line indicated in Fig. 1(a). The same geometries as in Fig. 2 are considered. The cylinders are illuminated with a unit-amplitude plane wave. The amplitudes shown in Fig. 4 give the enhancement caused by the cylinders. The field distributions are computed for the wavelength corresponding to the maximum SCS, so a different wavelength is used for each cylinder’s dimensions.

We observe very different behavior depending on the illumination direction. For the incident field along the particle axis, the field in the gap is strongly enhanced for very small particles. For $d = 20$ nm, the field amplitude reaches 24 times that of the illumination field [Fig. 4(a)]. This corresponds to an intensity enhancement of more than 500 or a SERS enhancement of more than $3 \times 10^5$ (SERS enhancement is proportional to the fourth power of the amplitude enhancement).\(^4\)

For larger particles, the field in the gap decreases [Fig. 4(a)]. This result could actually be expected from the SCS in Fig. 2(a): Although the maximum SCS increases for larger particles, the corresponding resonance broadens immensely, indicative of a weaker near field.\(^{11}\)

For the other illumination direction, since the field is now computed along a line normal to the propagation direction, a symmetrical field distribution is observed [Fig. 4(b)]. The amplitude distribution is perfectly symmetrical, with a minimum in the gap and two maxima on each side of the horizontal axis, which can be related to the polarization charges depicted in Fig. 1(b). Note that the field amplitude on just the horizontal axis is not a good signature for this resonance.\(^{16}\)

For this polarization the field enhancement between the particles reaches a maximum for $d = 50$ nm.
Fig. 4. Amplitude enhancement as a function of the observation position in the gap between the two particles (dashed line in Fig. 1). Same geometry as in Fig. 2. Two incident polarizations are considered: (a) $E^\parallel_{ex}$ [corresponding to Fig. 2(a)] and (b) $E^\parallel_{ey}$ [Fig. 2(b)].

[Fig. 4(b)], which corresponds to the mode onset visible in Fig. 2(b). For a water background, the near-field has already reached a maximum for particles of the order of $d = 35$ nm, which corresponds to the dimensions where this retarded resonance appears in water (see Fig. 3).

These results for interacting particles, together with recent calculations for nonregularly shaped particles,\textsuperscript{10,11} should develop our insight into the plasmon resonances in complex systems. They could help us to design specific nanoparticle configurations in which extremely intense and localized electromagnetic fields are established in a controlled manner.

This plasmon-resonance engineering should pave the way toward useful applications in near-field optical imaging,\textsuperscript{13} single-molecule detection with SERS,\textsuperscript{16–18} and nonradiative optical transport.\textsuperscript{14,15} Further, the strong frequency sensitivity of these coupled resonances could be used to produce frequency-selective devices.

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“Plasmon resonant coupling in metallic nanowires”

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Plasmon resonant coupling in metallic nanowires

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Abstract: We investigate the plasmon resonances of interacting silver nanowires with a 50 nm diameter. Both non-touching and intersecting configurations are investigated. While individual cylinders exhibit a single plasmon resonance, we observe much more complex spectra of resonances for interacting structures. The number and magnitude of the different resonances depend on the illumination direction and on the distance between the particles. For very small separations, we observe a dramatic field enhancement between the particles, where the electric field amplitude reaches a hundredfold of the illumination. A similar enhancement is observed in the grooves created in slightly intersecting particles. The topology of these different resonances is related to the induced polarization charges. The implication of these results to surface enhanced Raman scattering (SERS) are discussed.

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1. Introduction

Over the last twenty years, much interest has been devoted to metallic nano-structures, and in particular to the strong electromagnetic enhancement they can provide via the excitations of plasmon resonances. With the rapid advances in the fabrication of very small particles [1, 2, 3] and nanowires [4, 5, 6], their optical properties are now used in a wide range of applications, including biosensors [7, 8, 9, 10], near-field microscopy [11, 12, 13] and new optical devices [14, 15, 16, 17]. Since the plasmons are associated with large electromagnetic fields near the particle surface, they play a key role in surface enhanced Raman scattering (SERS) [18]. For specific configurations, this enhancement can be so large that it allows single molecule detection [19, 20, 21].

Recently we demonstrated that nanowires with a non-regular cross-section have a very complex spectrum of plasmon resonances: while a cylindrical particle exhibits one resonance and an elliptical particle two, we observed that five or more distinct resonances can be excited in a triangular nanoparticle [22]. A dramatic near-field enhancement, with amplitude several hundred times that of the illumination field was also observed at the vicinity of these non-regular particles [23]. This enhancement was orders of magnitudes larger than that observed on regular particles. For example, the field amplitude at the vicinity of a 20 nm triangular particle can exceed 400 times the illumination amplitude, while this enhancement is only 10 for a cylindrical particle with the same size [24]. Raman enhancement being proportional to the fourth power of the amplitude enhancement [18], our results indicate Raman enhancement in excess of $10^{12}$ for non-regular particles, while a cylindrical particle provides a mere $10^4$ enhancement.

The objective of this paper is to demonstrate that cylindrical particles, although harmless individually, can also provide strong enhancement when they are coupled together. Infinite arrays of particles have been studied theoretically [25], while long chains of nanoparticles in the 200 nm range have been investigated experimentally [15, 16]. We shall concentrate here on a pair of interacting particles and illustrate the different coupling mechanisms that can occur. Some aspects of this coupling in spherical metal particles have been investigated by others [26, 27, 28, 29].

In Sec. 2 we briefly outline our model. Results are presented in Sec. 3 and we summarize in Sec. 4.

2. Model

The plasmon resonances of particles with dimensions down to 2 (nm) can be investigated using Maxwell's theory [30, 31]. Herein, the particles are described by their dispersion relation, i.e. by their complex permittivity $\varepsilon(\lambda) = \varepsilon'(\lambda) + i\varepsilon''(\lambda)$ as a function of the wavelength $\lambda$. For silver and gold this dispersion relation is quite complex in the optical range, as the plasma frequency $\omega_p$ of the conduction electron gas lies in this range.

When the illumination frequency passes nearby $\omega_p$, the real part $\varepsilon'(\lambda)$ of the dielectric function changes its sign, and for specific negative $\varepsilon'(\lambda)$ values, plasmon resonances can be excited in the structure. These specific values strongly dependent on the particle size and shape [24]. The width of the plasmon resonances, which is related to the scattering amplitude, depends on the imaginary part $\varepsilon''(\lambda)$ of the permittivity. This imaginary part, which accounts for damping, becomes a function of the particle size when its dimensions are similar to the bulk electron mean free path [31]. In that case, electron scattering at the particle boundary becomes a dominant effect, and the decrease of the electron mean free path leads to an increase of $\varepsilon''(\lambda)$ [32, 33, 31, 34, 35]. However, for particles in the 50 nm range, which are the focus the present study, the permittivity is nearly unaffected and we shall simply use the bulk experimental data obtained by Johnson and Christie [36].
Our numerical results are based on the finite elements method described in Ref. [37]. With this technique, we are able to accurately study the plasmon resonances of scatterers with an arbitrary shape [24]. Since we use a discretization in direct space, we can also investigate any arrangement of multiple scatterers, as is the case in the present work. Each cylinder section is discretized with about 1'500 triangular elements. A detailed convergence study of our numerical scheme is given in Ref. [37].

3. Results

Throughout the entire paper, we consider cylinders illuminated with a plane wave propagating in the plane of the figure, with the electric field in this plane as well (transverse electric polarization). All cylinders have a 50 nm diameter.

We first study two cylinders with a separation distance $d = 5$ nm. In Fig. 1 we show the scattering cross section (SCS) as a function of the wavelength $\lambda$ for illumination along and normal to the major axis, the axis joining the cylinder centers (the illumination direction refers to the propagation direction of the illumination field; the incident electric field is therefore normal to this direction). The SCS of an individual 50 nm cylinder is also shown; in that case a single resonance is excited at $\lambda = 344$ nm. This resonance, although slightly blue shifted to $\lambda = 340$ nm, still exists in the coupled system for both illumination directions (Fig. 1). Note however that for the coupled system this resonance has the same magnitude as for the individual cylinder, although two cylinders are now scattering [especially for illumination from the top, where the incident field sees a broader structure, one would expect a larger SCS (Fig. 1)].

For illumination along the major axis we observe an additional resonance at $\lambda = 372$ nm. However, Fig. 1 clearly demonstrates that the coupling effect is much stronger.
for incidence normal to the major axis (i.e. when the incident electric field is along the major axis). In that case we observe a rather broad resonance at $\lambda = 380\,\text{nm}$ with a SCS amplitude much larger than that of the individual cylinder ($\lambda = 344\,\text{nm}$).

The movies Figs. 2(a)–(c) show the electromagnetic near-field amplitude distribution corresponding to Fig. 1, as a function of the wavelength. For the single cylinder, the field distribution is very homogeneous, the field amplitude reaching about 8 (in units of the illumination amplitude) at the resonance ($\lambda = 344\,\text{nm}$), and decreasing for larger wavelengths [Fig. 2(a)].

For the illumination normal to the major axis, the field amplitude in the interacting cylinders is homogeneous and rather weak, up to the single cylinder resonance wavelength [$\lambda = 344\,\text{nm}$, Fig. 2(b)]. For larger wavelengths the coupling becomes quite strong, leading to a large field in the gap between the particles. There the field amplitude reaches almost 40 at the resonance ($\lambda = 380\,\text{nm}$).

A similar enhancement is observed for the other illumination direction, with a field amplitude of 35 between the particles. The field distribution in the gap is however very different from the other illumination direction: The field now vanishes in the middle of the gap [Fig. 2(c)]. Retardation is essential for this resonance, as will be discussed later.

In Fig. 3 we show the polarization charge distribution associated with the main resonances reported in Fig. 2. This polarization charge distribution, which is given by the divergence of the electric field, oscillates in time: half a period later, the opposite charge distribution is observed [38]. The distributions in Fig. 3 correspond to a specific moment in time, when the magnitude of the instantaneous electric field vector is maximum in the gap. The moment when the near-field amplitude is maximum does not coincide with the moment when the illumination field is maximum, since – at resonance – there is a phase shift between the illumination and the particle response [38].

The polarization charge distribution in the single cylinder is symmetrical with respect to the illumination direction, with plus charges on one side of the particle and minus charges on the other side [Fig. 3(a)]. At the main resonance for the interacting cylinders illuminated from the top, polarization charge of opposite signs are confined on the sides of the gap [Fig. 3(b)]. Each particle remains of course neutral and a same amount of opposite charges is distributed on the remaining of the particle. Both cylinders are in phase, i.e. their charges distributions have negative charges on the left of the particle and positive charges on the right [Fig. 3(b)].

The polarization charge distribution at the main resonance for the other illumination direction is completely different [Fig. 3(c)]. In that case, both cylinders are out of phase, with respect to the illumination direction: the first (left) cylinder has ± charges, whereas the second (right) has =p charges [Fig. 3(c)]. This leads to a quadrupole–like charge distribution around the gap between the particles, which explains that the field vanishes in the middle of the gap, as observed in Fig. 2(c). This peculiar resonance can only be
observed in particles large enough so that both cylinders are driven out of phase by the incident field. This coupling mechanism is therefore governed by retardation. It was investigated in Ref. [13], where we show that for silver cylinders, this coupled mode occurs only for particle diameters larger than 30 nm.

We now study the influence of the separation distance $d$ on the plasmon resonant coupling. We shall focus on the illumination direction normal to the major axis as it provides the strongest coupling, particularly for small separation distances.

Figure 4 shows the field distribution for different separation distances $d$, at the corresponding main resonance wavelength (i.e. not at a constant wavelength). For a separation distance equal to the diameter, there is almost no coupling, whereas the field enhancement becomes very large for $d \leq 5$ nm. Around $d = 2$ nm the field amplitude in the gap exceeds 200 times that of the illumination field.

Negative separation distances in Fig. 4 correspond to intersecting cylinders. In that case we observe a large amplitude enhancement in the grooves, exceeding 100 times the illumination amplitude. Similar enhancement has also been obtained by García-Vidal et al. for an infinite array of cylinders embedded in a surface [25]. When the cylinders intersect further this enhancement decreases and the field distribution finally merges into that of the single cylinder (Fig. 4).

Let us emphasize that the over hundredfold enhancement of the illumination amplitude observed for small separations or intersections, corresponds to an intensity enhancement larger than $10^4$. In SERS, where the Raman signal is in a good approximation proportional to the fourth power of the amplitude enhancement [18], this would lead to a local Raman enhancement in excess of $10^8$.

We now study the spectral response for particular separation distances $d$. In Fig. 5 we report the SCS for $d = 2, 5, 10$ and 20 nm. The SCS clearly demonstrate that the main resonance is red-shifted with decreasing separation distance $d$, from 350 nm ($d=50$ nm) to 358 nm ($d=20$ nm), 368 nm ($d=10$ nm), 380 nm ($d=5$ nm) and 404 nm ($d=2$ nm).
Fig. 6. Spectral variation of the field amplitude distribution for two interacting cylinders illuminated from the top, for different separation distances $d$: (a) $d = 2\text{ nm}$ (361 KB), (b) $d = 10\text{ nm}$ (359 KB), and (c) $d = 20\text{ nm}$ (313 KB). Front pictures: Corresponding main resonances (a) $\lambda = 404\text{ (nm)}$, (b) $\lambda = 368\text{ (nm)}$, and (c) $\lambda = 358\text{ (nm)}$.

Moreover, the complexity of the SCS increases for small separations, as higher order modes are excited (Fig. 5).

In Fig. 6 we report the spectral behavior of the field distributions for $d = 2, 10$ and $20\text{ nm}$ (the case $d = 5\text{ nm}$ is already shown in Fig. 2(b)). The two higher order resonances at $\lambda = 350\text{ nm}$ and $\lambda = 362\text{ nm}$, visible in the SCS for $d = 2\text{ nm}$ (Fig. 5), are also visible in Fig. 6(a). Between $350\text{ nm}$ and $370\text{ nm}$, we observe a rather complicated field distribution in the gap between the cylinders, related to the complex polarization charge distribution associated with these higher order modes [Fig. 6(a)]. These two resonances are closer than their width, and therefore strongly interfering, leading to the rapidly evolving field pattern visible at the vicinity of the gap. This pattern can be related to the charges distribution associated with the involved resonances. We verified that it was not correlated to the discretization mesh used for the calculation.

At the main resonance we then obtain a rather homogeneous field distribution in the gap, the amplitude reaching almost 100 times that of the illumination amplitude [$\lambda = 404\text{ nm}$, Fig. 6(a)]. For larger separation distances $d$, the field enhancement at the main resonance is much smaller than for $d = 2\text{ nm}$, as already observed in Fig. 4. The amplitude in the gap reaches now about 18 for $d = 10\text{ nm}$ [Fig. 6(b)], and about 12 for $d = 20\text{ nm}$ [Fig. 6(c)]. Contrary to the $d = 2\text{ nm}$ case, no higher modes can now be resolved for these separation distances.

The SCS for intersecting cylinders ($d = -2, -5, \text{ and } -20\text{ nm}$) is shown in Fig. 7. For $d = -2\text{ nm}$ we observe a very complex spectrum: Several resonances are excited, spanning a large wavelength range between $340\text{ nm}$ and $583\text{ nm}$. When the cylinders intersect further ($d = -5\text{ nm}$ and $d = -20\text{ nm}$), the spectra become less complex, and the resonances are blue-shifted. The reason for this is rather obvious: For larger intersection the spectrum will finally converge to that of a single cylinder.

The “main resonance” reported in Fig. 3 for $d < 0$ was not the first but the second resonance, from the right in Fig. 7. Indeed, this resonance can be seen as the continuation...
of the main resonance for two interacting (but non-touching) cylinders, as illustrated in Fig. 8. In that figure we report the polarization charge distribution associated with three resonances of the \(d = -2\text{ nm}\) intersecting cylinders. As charges can now flow over both cylinders, the fundamental mode has minus charges on one cylinder and plus charges on the other one \(\lambda = 540\text{ nm}, \text{Fig. 8(c)}\). The next resonance, \(\lambda = 430\text{ nm}, \text{Fig. 8(b)}\), has charges of both species on each cylinder, as was the case for non-touching cylinders [compare with Fig. 3(b)]. It is associated with strongly confined charges of opposite signs around each groove. These first two resonances provide the strongest near-field enhancement. The next order modes for intersecting particles have a fairly complex charges distributions, with rapid changes of signs over small distances. The last charges distribution reported in Fig. 8 corresponds to a resonance very similar to that of individual cylinders \(\lambda = 338\text{ nm}, \text{Fig. 8(a)}\). Contrary to the two previous resonances, where the charges were mainly concentrated around the grooves, a fairly homogeneous charges distribution on the entire surface of each cylinder is observed at \(\lambda = 338\text{ nm}\) [Fig. 8(a)].

The movies in Fig. 9 show the field distributions corresponding to the SCS reported in Fig. 7. For the small intersection \(d = -2\text{ nm}, \text{Fig. 9(a)}\), we recognize higher order modes between 348 nm and 384 nm. Since the spectral spacing between these modes is smaller than their width, a complex changing “interference” pattern is observed in the grooves (we verified that these patterns were not related to our discretization grid). The field enhancement in the groove exceeds 100 for the two resonances corresponding to the largest wavelengths \(\lambda = 430\text{ and } 538\text{ nm}\). This enhancement is concentrated on a very small area.

For \(d = -5\text{ nm}\) the field distribution is similar, but with a smaller field amplitude. For \(d = -20\text{ nm}\) the field amplitude is much smaller, as the grooves angle opens and charges are less easily confined.
3. Conclusions

We have investigated the influence of the coupling between two metallic nanowires, on their spectrum of plasmon resonances. Our results show that this coupling becomes extremely important for small separation distances, leading to additional resonances in the overall structure. These resonances produce extremely strong electromagnetic fields in the gap between the particles. The topology of these different modes was related to the distribution of polarization charge. A similar enhancement was also observed in the grooves between intersecting particles.

Although not shown here, we observed similar enhancement factors for nanowires with dimensions in the 20–80 nm.

The near-field enhancement observed, with an electric field amplitude exceeding hundred times the illumination amplitude, provides an important mechanism for SERS. The magnitude of this enhancement is sufficient for explaining recent SERS experiments where single molecule sensitivity was achieved [19, 20, 21]. Remarkably, this enhancement is obtained in interacting particles with a very simple shape and does not require complex geometries such as fractal system [39].

The rapid variations of the resonances spectrum as a function of the particles configuration that we observed, provides an explanation for the spectral insensitivity of the Raman signal measured on large ensembles of molecules deposited on a colloidal substrate. As a matter of fact, such a substrate contains many different particles with different sizes and spacing, so that coupled plasmon resonances are likely to be excited irrespective of the illumination wavelength.

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“Non-regularly shaped plasmon resonant nanoparticles as localized light source for near-field microscopy”

J.P. Kottmann, O.J.F. Martin, D.R. Smith and S. Schultz

Non-regularly shaped plasmon resonant nanoparticle as localized light source for near-field microscopy

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Summary

We study numerically two-dimensional nanoparticles with a non-regular shape and demonstrate that these particles can support many more plasmon resonances than a particle with a regular shape (e.g. an ellipse). The electric field distributions associated with these different resonances are investigated in detail in the context of near-field microscopy. Depending on the particle shape, extremely strong and localized near-fields, with intensity larger than 10 times that of the illumination wave, can be generated. We also discuss the spectral dependence of these near-fields and show that different spatial distributions are observed, depending which plasmon resonance is excited in the particle.

Introduction

A powerful, yet well localized source of light is probably the most important prerequisite for scanning near-field optical microscopy (SNOM). Such a source is in most instances realized by scattering some incident field on a small volume of polarizable matter with permittivity \( \varepsilon(\lambda) \) (apertureless probes work exactly with this principle; for an aperture probe, one can consider that the very tip plays the role of polarizable volume).

The scattering efficiency for a polarizable volume with a spherical shape, in vacuum, is given by (Bohren & Huffman, 1983)

\[
Q(\lambda) = \frac{8}{3} \frac{x^4}{\lambda^3} \left| \frac{\varepsilon(\lambda) - 1}{\varepsilon(\lambda) + 2} \right|^2,
\]

where \( x = 2\pi R/\lambda \) is the size parameter for the sphere, \( R \) its radius and \( \lambda \) the wavelength. Equation (1) holds when \( R \ll \lambda \).

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From Eq. (1) it is clear that the scattered field, and therefore the corresponding source intensity, for SNOM can be increased by raising the size parameter \( x \) (i.e. the sphere radius \( R \)). This, however, is not favourable for SNOM because a larger source impinges on the resolution.

Another possibility to increase the source intensity is to augment the dielectric contrast \( \varepsilon(\lambda) - 1 \). Unfortunately, quite important variations of the permittivity are required to increase \( Q(\lambda) \) in a noticeable manner. Furthermore, large permittivity materials at optical frequencies (like semiconductors) have a strong absorption, so that most of the field would be absorbed in the sphere.

The most effective way to realize a strong localized source with such a sphere is therefore to play with the denominator in Eq. (1). As a matter of fact, when \( \varepsilon = -2 \), the scattered field explodes. This corresponds to the excitation of a so-called plasmon resonance in the particle (Ruppin, 1982). At optical frequencies, this condition can be fulfilled for different metals. In the present work we shall concentrate on silver, using the experimental data of Johnson & Christy (1972) for \( \varepsilon(\lambda) \).

Plasmon resonances and the extremely large electromagnetic fields associated with them are playing a key role in surface-enhanced Raman scattering (Metiu, 1984; Moskovits, 1985). In near-field optics they have been used in subtle tip configurations for imaging (Koglin et al., 1995) or Raman spectroscopy (Stocke et al., 2000) and their optical response has been investigated experimentally using photon scanning tunnelling microscope (Hecht et al., 1996; Krenn et al., 1999a, b; Weeber et al., 1999)

However, very little is known about the relationship between the spectrum of plasmon resonances and the particle shape. Equation (1) shows that a small sphere has one single resonance, occurring at the wavelength \( \lambda_{\text{res}} \) where \( \varepsilon(\lambda_{\text{res}}) = -2 \). A spheroid has two plasmon resonances,
associated with its two principal axes (Bohren & Huffman, 1983), but no theory exists for nanoparticles with an arbitrary shape (except maybe Fuchs, 1975, who studied the response of a small cube in the electrostatic approximation). This is quite surprising because one can expect that the particle shape is determinant for the number and strength of resonances that can be excited in the particle. Actually this fact was already noticed in the middle of the 19th century by Faraday, who realized that gold colloids were giving their strong colours to stained glass and wrote: ‘that a mere variation in the size of its particles gave rise to a variety of colours’ (Kerker, 1991).

Very recently, we demonstrated that nanowires (i.e. two-dimensional (2D) nanoparticles) had indeed a very complex resonances spectrum that strongly depended on the particle shape (Kottmann et al., 2000b, c).

The objective of the present publication is to study the implications of this complex spectrum of plasmon resonances for near-field optical microscopy. In particular, we will investigate the localization of the electromagnetic field associated with these different resonances.

The numerical results presented in this paper were obtained using a newly developed finite elements techniques for scattering calculations. This technique is described in detail in Kottmann & Martin (2000), where its convergence and accuracy for the computation of plasmon resonant nanoparticles is also assessed. The particles are typically discretized with 3000 triangular elements. In the following we will consider particles with sharp corners, which introduces additional numerical difficulties, as the field becomes singular at short distance from an infinitely sharp, perfectly conducting corner. However, the sharpness of a real particle is limited by surface and boundary energies; therefore, we have rounded off each corner by 0.25 nm, providing a more realistic model and removing the numerical instabilities.

Results

Spectral response

Before investigating complex shape particles, it is educative to start with a regular geometry. Figure 1 gives the scattering cross-section (SCS) for an elliptical particle (SCS have nm units because we are dealing with 2D particles). Depending on the illumination direction, two different resonances can be excited in this geometry: each resonance being associated with one principle axis. For incidence in a direction off either of the principal axes, both resonances are excited (Fig. 1).

If now we consider a particle with a lower symmetry, we obtain a much more complex response, as illustrated in Fig. 2 for two triangular particles with the same area. For the equilateral particle three plasmon resonances are visible. This number increases further for the right-angled triangle. These resonances now cover a much broader wavelength range, up to $\lambda = 500$ nm for the first resonance of the right angled particle (the first resonance is that corresponding to the lowest energy, i.e. the longest wavelength). In Fig. 2 the very large SCS associated with this resonance is striking, five times larger than for the first resonance of the equilateral triangle, although both particles have the same area.

As for the elliptical particle, it is important to keep in mind that the SCS depends on the illumination direction. This dependence is actually stronger when the symmetry of the particle is reduced. The SCS reported in Fig. 2, as well as the different results presented in the next section, were obtained with particle illumination from the left (i.e. corresponding to the illumination direction a in Fig. 1).

Fig. 1. Scattering cross-section (SCS) for a 10 x 20 nm$^2$ elliptical particle, for three different illumination directions a, b and c.

Fig. 2. Scattering cross-section (SCS) for an equilateral triangle (side 27 nm) and a right-angled triangle with the same area and a 1 : 2 base : perpendicular ratio (base 17.8 nm). The particle is illuminated from the left side, corresponding to direction a in Fig. 1.
Fig. 3. Relative electric field intensity distribution for the elliptical particle described in Fig. 1, at the main resonance (λ = 359 nm). The arrow indicates the illumination direction.

Near-field enhancement

For SNOM applications, it is not the field scattered far away which is relevant, but the near-field in close vicinity of the particle. We shall therefore now concentrate on the near-field distribution generated by the particles discussed in the previous section.

Again we start with the simple elliptical particle. The electric field intensity distribution at the main resonance is reported in Fig. 3. For all the calculations presented in this section the intensity of the incident plane wave is one, the logarithmic colour scale in Fig. 3 gives directly, therefore, the intensity enhancement generated by the small metallic particle. To ease comparison, we will use the same colour scale throughout the paper.

The field intensity at the particle apex reaches about 200 times the incident intensity. This plasmon resonance is associated with polarization charges of a given sign accumulating at one end of the particle while opposite charges accumulate at the other end. During one period these polarization charges oscillate between the two extremities, as illustrated in the movies presented in (Kottmann et al., 2000a). The field inside the particle remains quite homogeneous.

This is not at all the case for the equilateral triangle, as illustrated in Fig. 4. At the main resonance the field intensity reaches $3 \times 10^4$ that of the incident field. This dramatic enhancement is caused by polarization charges accumulating at the particle tip, while opposite charges are distributed on the adjacent sides (Kottmann et al., 2000a). The fact that all corners light up is related to the particular illumination direction. If the particle was illuminated along one of its symmetry axes, only the two corners transverse to the illumination direction would light up.

The second resonance [λ = 358 nm, Fig. 4(b)], produces a somewhat reduced intensity enhancement, in the order of $3.5 \times 10^3$. The field distribution at the vicinity of the tip is also different, with two side lobes and a lower field intensity in the forward direction (Fig. 4(b)). In this mode plus and minus polarization charges accumulate in the corner, which produces this field distribution pattern (Kottmann et al., 2000a).

It is extremely important to realize that these plasmon resonances are no lightning rod or tip effects, but truly resonances related to the overall particle shape. The lightning rod effect, occurring when the particle is off-resonance, provides a much weaker intensity enhancement, reaching, for example, 70 at λ = 600 nm, although the permittivity of silver is quite high at this wavelength: $\varepsilon = (-16 + i0.4)$ (Fig. 4(d)).

The small resonance at λ = 329 nm (Fig. 4(a)) is quite interesting: it exists for any non-regularly shaped particle, independent of the illumination direction (see Fig. 2). It corresponds to the bulk plasmons and occurs at the wavelength $\lambda_{bulk}$ where $\varepsilon(\lambda_{bulk}) = 0$ (Ruppin, 1982). Contrary to the surface plasmon previously investigated, the bulk plasmon is a longitudinal mode. This explains why only the two edges in the propagation direction and not the particle apex light up in Fig. 4(a).

This bulk mode is also visible for the right-angled particle (Fig. 5(a); see also the SCS in Fig. 2). The intensity enhancement associated with the main plasmon resonance of this particle reaches $7 \times 10^5$, with a field distribution similar to a point source (Fig. 5(d)). Higher order
resonances also generate quite a strong field enhancement, with a more complex field distribution (Fig. 5(b) and (c)). Again, this behaviour can be related to the polarization charges that accumulate on the particle surface (Kottmann et al., 2000a).

The previous figures illustrated the extremely intense electromagnetic field that can be produced by non-regularly shaped plasmon resonant particles. As mentioned in the Introduction, it is mandatory for high resolution SNOM applications that these fields are also strongly localized. To quantify this localization let us now investigate the variation of the field distribution at the immediate vicinity of the particle.

In Fig. 6 we report the relative field intensity when one moves away from the particle tip, for three different particle shapes at their main resonance. First, note that the field intensity at the surface of the particle is about 10,000 times stronger for the right-angled triangle than for the elliptical particle. Furthermore, the field is much more localized for the non-regularly shaped particles: over the first nanometre the intensity decreases by a factor of about 120, respectively 24, for the right-angled, respectively equilateral triangle; whereas it decreases only by a factor of three for the elliptical particle.

For a non-regular particle with several resonances, the near-field intensity distribution depends on the mode excited in the particle, as illustrated in Fig. 7. In this figure we observe that the field decays more rapidly for the second resonance ($\lambda = 358$ nm) than for the first one ($\lambda = 385$ nm). This behaviour can be related to the charge distribution associated with each resonance. Indeed, as illustrated in Kottmann et al. (2000a) and mentioned in the discussion of Figs 3 and 4, the main resonance is associated with polarization charges of similar sign accumulating at...
the particle corner, whereas higher order resonances have a
more complex polarization charge distribution with plus
and minus charges accumulating at the corner. The former
charge distribution produces therefore a near-field intensity
distribution similar to that of a point source (i.e. \( \sim 1/d^2 \),
where \( d \) is the distance), whereas the latter produces a near-
field intensity distribution similar to that of a dipole (i.e.
\( \sim 1/d^3 \)). This explains the distance dependences observed
in Fig. 7. This difference of behaviour as a function of the
resonance, i.e. of the illumination wavelength, could be
evidenced in experimental SNOM approach curves.

At distances larger than say 5 nm, the decay of the field
intensity as a function of the distance is similar for the
different resonances (Fig. 7). The field generated by the
main resonance remains about 50 times stronger than that
of the other resonance. Choosing the correct illumination
wavelength can therefore have a dramatic influence on the
light throughput in a SNOM experiment, even for constant
height scans at some distances from the sample under
study.

The extremely important dynamic range also observed for
the right-angled particle in Fig. 7 could be useful in an
apertureless SNOM experiment, where the tip is vibrated
vertically above the sample.

The other deciding factor that determines the resolution
in a SNOM experiment is the lateral field confinement. In
Fig. 8 we report the lateral field distribution in the main
resonance, at different distances \( \delta \) from the tip of the
equilateral particle. Striking is the strong lateral confinement,
with a 2.5 nm full width half-maximum (FWHM) for
\( \delta = 1 \) nm. This lateral confinement decreases for larger
distances: for \( \delta = 2 \) nm we obtain FWHM = 4.5 nm and
for \( \delta = 5 \) nm, FWHM = 10 nm. However, it is important to
note that the field at close vicinity of the particle is confined
on dimensions much smaller than the particle size (27 nm
in that case).

As expected, the lateral field confinement also depends on
the plasmon resonance that is excited, as illustrated in
Fig. 9. Although the corresponding peak intensity is much
weaker, it is interesting to note in this figure that the field
obtained out of resonance is also well confined (FWHM for
the first plasmon resonance: 4.5 nm, for the second
resonance: 5.8 nm and out of resonance: 6.8 nm).

Finally we compare in Fig. 10 the lateral confinement for
the three different particle shapes. As already discussed, the
right-angled triangle produces by far the strongest field. Its
lateral confinement (FWHM = 4.4 nm) is similar to that of the equilateral triangle. By contrast, the elliptical particle has a lateral confinement only in the order of the particle size (FWHM = 8 nm).

Conclusion

We have demonstrated that two-dimensional particles in the 20–50 nm range with a non-regular section, for example a triangular section, have a much more complex spectrum of plasmon resonances than a regularly shaped particle, like an ellipse. Furthermore, the plasmon resonances for non-regular particles extend over a broader part of the wavelength spectrum.

These resonances are associated with extremely strong near-fields, with intensities larger than $10^5$ that of the illumination wave. The implications of these strong near-fields for optical microscopy, as well as their spatial and spectral behaviour, have been discussed in detail.

These new theoretical insights increase our understanding of plasmon resonances in non-regularly shaped particles and should pave the way towards the utilization of specific particle shapes to boost the resolution, light throughput and spectral sensitivity of near-field microscopy.

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References


