T-matrix Simulation of Plasmon Resonances of Particles on or Near a Surface

N. Riefler and T. Wriedt
University of Bremen, Germany

Abstract—We present the light scattering response of gold and silver particles on or near surfaces consisting of different materials. A comparison is made between a particle near a perfectly conducting surface and near a gold surface. The resulting scattering diagrams are found to be different. Beyond this, an approximation with a mirror particle shows little agreement with a particle near a metal surface. Furthermore, we compare the spectral response of a combination of gold and silver materials for particles at different heights.

1. Introduction

Surface plasmons of small noble metal spheres can be detected as resonance peaks in the measured light scattering spectra. Transmission dark field microscopy is a technique where only the particles scatter light into the direction of the microscope objective. Such a measuring device can visualize very small particles as colored discs. The surface plasmon resonance frequency from a nonspherical particle or from a particle aggregate is different compared with a single spherical particle. With this effect, measuring techniques which use white light as illumination are capable to differ between aggregated particles and a single particle because of their different color. Even when a bio receptor molecule attached to a gold or silver sphere detects a biomolecular counterpart, the resonance frequency changes.

In the following we first describe the underlying scattering theory. Then we give some simulation examples of particles on or near a surface. We compare these results to some approximations found in the literature. This leads us to statements about the applicability of these approximations.

2. Theory

The scattering geometry is shown in figure 1. The incident field $\mathbf{k}_0$ and the particle are in the same medium.

Figure 1: Scattering geometry; the z-axis is perpendicular onto $\Sigma$, the boundary surface.

In the T-matrix formalism using the null-filed method, the scattered intensities $I_{\text{scat}}$ are calculated from the scattered field coefficients $f_{mn}$ and $g_{mn}$. These coefficients are related to the T-matrix [1]:

$$
\begin{bmatrix}
  f_{mn} \\
  g_{mn}
\end{bmatrix} = T \left( \begin{bmatrix}
  a_{mn_1} \\
  b_{mn_1}
\end{bmatrix} + \begin{bmatrix}
  f_{Rmn_1} \\
  g_{Rmn_1}
\end{bmatrix} \right)$$

(1)

with the T-matrix $T = T_{mn,mn_1}$ of the particle, the total incident field coefficients $a_{mn_1} = a^0_{mn_1} + a^R_{mn_1}$ and $b_{mn_1} = b^0_{mn_1} + b^R_{mn_1}$ consisting of the direct ($a^0_{mn_1}$ and $b^0_{mn_1}$) and the reflected ($a^R_{mn_1}$ and $b^R_{mn_1}$) incident fields,
and the coefficients \( f_{Rmn} \) and \( g_{Rmn} \) representing the fields scattered on the particle and reflected back from the surface to the particle. The \( a_{Rmn} \) and \( b_{Rmn} \) involves the Fresnel reflection coefficients. The scattered reflection coefficients for the interacting fields \( f_{Rmn} \) and \( g_{Rmn} \) are related to the scattered fields \( f_{mn} \) and \( g_{mn} \):

\[
\begin{bmatrix}
  f_{Rmn} \\
  g_{Rmn}
\end{bmatrix} = \mathbf{A} \begin{bmatrix}
  f_{mn} \\
  g_{mn}
\end{bmatrix}. \tag{2}
\]

\( \mathbf{T} \) is calculated from well known algorithms \[2\] and \( \mathbf{A} \) can be found using radiating vector spherical wave functions \[1\]. By combining the matrix equations (2) and (3), the far field intensity can be computed. In the case of illumination from above (\( \mathbf{k}_0 \) shows in the reversed direction) the incident field is calculated in the way described so far. If the incident angle \( \beta_0 \) get bigger than the critical angle \( \theta_c = \arcsin(n_1/n_2) \) with \( n_1 < n_2 \) and \( n_1 \) and \( n_2 \) are the refractive indices of the medium above and below \( \Sigma \), respectively, then the incident field from above will be totally reflected on \( \Sigma \). However, an evanescent wave with typical exponential decrease is traveling into medium \( n_2 \). In this case the Fresnel transmission coefficients used in the T-matrix method are changing \[3\].

### 3. Results

We calculate intensities at different scattering angles over the visible spectrum of wavelengths of small particles with diameter \( d = 80 \) nm. The intensities will be detector integrated over a range of \( \theta_{NA} = 25^\circ \) which corresponds to a numerical aperture of \( NA = n \sin(\theta_{NA}) \) of the objective lens. The particles consist of silver or gold. The wavelength dependent refractive indices are interpolated values from Johnson et al., \[4\]. The numerical aperture depends on the medium surrounding the particle. We use air, water and immersion oil with an assumed constant refractive index.

In figures 2 and 3 the scattering diagrams of three systems are shown. In all systems the particle is a gold sphere and the scattering medium is air. The incident beam angle with respect to the normal is \( \beta_0 = 30^\circ \) with an incident wavelength of \( \lambda = 570 \) nm. For that wavelength, the refractive index of the particle is \( n = 0.296 + i2.899 \).

We first compare a system consisting of two spheres without an interface (‘double-sphere’ in the legend) with diameter \( d = 80 \) nm and distance \( z = 4 \) nm. The idea behind this system can be found in electrostatic theory where a system consisting of two point charges shows an identical electrical field compared to a point charge near a conducting plane. We approximate this second system with a surface having a nearly perfect conducting material (‘sphere-perfect-conductor’ in the legend of the figures) with a wavelength independent refractive index \( n = 0.00001 + i80 \), and the distance between the surface of the sphere to the plane surface is half of the first system (\( z = 2 \) nm). This idea is confirmed with figure 2.

![Figure 2: Scattering diagrams of a sphere before a perfectly conduction plane and two spheres.](image)

![Figure 3: Scattering diagrams of a sphere before a perfectly conduction plane and before a gold surface.](image)

Considering the different coordinate systems one can see that the horizontal-horizontal polarized scattering diagrams are very similar. The vertical-vertical polarized scattering diagram of the second system cannot be a straight line because of the Fresnel reflectance coefficients.
In contrast to the different geometries of the systems used in figure 2, the two systems of figure 3 are geometrically identical. A gold sphere with diameter of $d = 80$ nm is located near an infinite surface (distance between surface of the sphere to the plane surface $z = 2$ nm). The only difference is that in the first system the surface is an approximation of a perfectly conducting material used above, while in the second system the plane surface consists of gold (‘gold surface’ in the legend). The first system with the perfectly conducting surface shows a distinct minimum. This is due to a very small transmission coefficient and a corresponding reflection coefficient of nearly $r = 1$ [3]. Therefore the particle near to the surface is excited ‘ideally’ from a plane wave. In the second system this minimum vanishes because the Fresnel transmission coefficient do not vanish and therefore the particle is excited differently.

We state that the scattering response of a particle located near a noble metal surface cannot be well approximated with a system consisting of two identical spheres because of the different Fresnel reflection coefficients.

Now we want to consider measurement problems where an optical device pick up the light spectrum scattered from an object on or near a surface. For example a gold particle within a liquid medium is illuminated from a wave at oblique incidence. For the following examples the bottom (substrate) is an optically thick layer. In practice this means a thickness of a few hundred nanometers of a noble metal [5]. The particle medium is water ($n = 1.333$). We first show the scattering diagram for a particle with diameter $d = 80$ nm, $\beta_0 = 30^\circ$ and $\lambda = 570$ nm, but for three different heights (figure 4). At a distance of $z = 200$ nm, distinct minima appear because of multiple reflections between the particle (in the Rayleigh regime) and the surface. For a low distance these multiple reflections vanish and with it the minima.

![Figure 4](image1.png)

**Figure 4:** Comparison of the scattering diagram of three different systems.

![Figure 5](image2.png)

**Figure 5:** Detector integrated scattering diagrams of a particle at $z = 2$ nm in water.

In the following figures, the intensities are detector integrated values with an aperture angle of $\alpha = 25^\circ$. The spectral resolution of the wavelengths is $\Delta \lambda = 5$ nm. We use a spectrum of unpolarized incident waves ($\lambda = 450\ldots700$ nm) which irradiates four different scattering systems:
- silver particle in water above a silver surface;
- silver particle in water above a gold surface;
- gold particle in water above a silver surface;
- gold particle in water above a gold surface.

For a distance between substrate surface and particle surface of $z = 2 \text{ nm}$ (this means a $z_0 = 42 \text{ nm}$ in figure 1, the spectrum of detector integrated scattering intensities are shown in figure 5. When the particle is situated higher at a distance of $z = 20 \text{ nm}$ above the noble metal surface ($z_0 = 60 \text{ nm}$), the resulting scattering response of the same four systems can be seen in figure 6. A further increase of the height to $z = 200 \text{ nm}$ above the surface ($z_0 = 240 \text{ nm}$) results in figure 7.

Last of all we want to compare the spectral scattering response for a gold particle near to a gold surface for three different media:
- gold particle in air ($n = 1.0$) above a gold surface;
- gold particle in water ($n = 1.333$) above a gold surface.
- gold particle in immersion oil ($n = 1.518$) above a gold surface.

We assume constant refractive index over all wavelengths of the media (air, water and oil). The spectral detector integrated intensities are shown in figure 8.

The spectral response differs considerably. Especially the both liquid media show different characteristic spectras.

![Figure 6](image6.png)

Figure 6: Detector integrated scattering diagrams of a particle at $z = 20 \text{ nm}$ in water.

![Figure 7](image7.png)

Figure 7: Detector integrated scattering diagrams of a particle at $z = 200 \text{ nm}$ in water.
4. Conclusion

We show that approximations like the double sphere system are far away from a qualitative similarity with the system under investigation. This means that simulations of the real circumstances are necessary, particularly if one needs quantitative statements of an observed system.

The results of the spectral simulations suggest that for increasing heights of a particle above the surface there is a shift of the intensity maximum towards lower wavelengths (see figure 5–figure 7). This fact may be used for measuring techniques. So altogether, we want to emphasize the usage of exact techniques like the T-matrix method used for the simulations shown in this paper as a design tool for experimental investigations (e.g., [6]).

REFERENCES