CHAPTER 2

Physics of Surface Plasmon Resonance

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2.1 Introduction

In the last two decades, surface plasmon resonance (SPR) has evolved from a fairly esoteric physical phenomenon to an optical tool that is widely used in physical, chemical and biological investigations where the characterization of an interface is of interest. Recently, the field of SPR nano-optics has been added where metallic structures on a nanoscale can be designed such that they can perform certain optical functions. This chapter will be mainly concerned with the more conventional, well-understood SPR theory used in sensor applications and it will touch upon some of the newer developments relevant for this area.

Essential for the generation of surface plasmons (SPs) is the presence of free electrons at the interface of two materials – in practice this almost always implies that one of these materials is a metal where free conduction electrons are abundant. This condition follows naturally from the analysis of a metal-dielectric interface by Maxwell’s equations. From this analysis, the picture emerges that surface plasmons can be considered as propagating electron density waves occurring at the interface between metal and dielectric. Alternatively, surface plasmons can be viewed as electromagnetic waves strongly bound to this interface; it is found that the surface plasmon field intensity at the interface can be made very high, which is the main reason why SPR is such a powerful tool for many types of interface studies.

Experimental research on SPs started with electron beam excitation; in 1968, optical excitation was demonstrated by Otto [1] and Kretschmann and Raether [2]. This last approach turned out to be much more versatile, so in this chapter the focus will be on the optics of SPR. The following is by no means intended as an
in-depth treatment of surface plasmons, rather it is an attempt to provide a low-threshold introduction to the physics of SPR for those who are actually involved in SPR work and want to understand a bit more than “measuring the shift of the SPR dip”.

2.2 The Evanescent Wave

Before we discuss SPs in more detail, it may be appropriate to provide a mathematical description of the evanescent wave, which is so central in the concept of SPR sensing. This is conveniently done by considering the phenomenon of total internal reflection.

An electromagnetic plane wave that propagates in a medium with refractive index \( n \) can mathematically be described by an electric field \( E \):

\[
E = E_0 \exp(j \omega t - j \mathbf{k} \cdot \mathbf{r}) = E_0 \exp(j \omega t - j k_x x - j k_y y - j k_z z) \tag{2.1}
\]

where \( E_0 \) is the amplitude of the electric field, \( \omega \) is the angular frequency, \( \mathbf{k} \) is the wavevector, \( \mathbf{r} = (x, y, z) \) is the position vector and \( j = \sqrt{-1} \). Note that eq. (2.1) only represents a traveling wave if the exponent is complex.

In the present context, we will mainly be concerned with the wavevector \( \mathbf{k} \): its direction is parallel to that of the wave propagation; its magnitude is given by

\[
k = \sqrt{k_x^2 + k_y^2 + k_z^2} = n \frac{2\pi}{\lambda} = n \frac{\omega}{c} \tag{2.2}
\]

where \( \lambda \) and \( c \) are the wavelength and propagation velocity in vacuum, respectively.

Next we consider the refraction of such a wave at an interface between two media 1 and 2 with refractive indices \( n_1 \) and \( n_2 \), respectively (see Figure 2.1). Without loss of generality, we can choose the direction of the light beam such that \( k_z = 0 \) and our problem becomes essentially two-dimensional. From elementary physics we know that for this situation Snell’s law holds:

\[
n_1 \sin \alpha = n_2 \sin \beta \tag{2.3a}
\]

or, equivalently,

\[
k_{x1} = k_{x2} \equiv k_x \tag{2.3b}
\]

By using eqs. (2.2) and (2.3b), we can find an expression for the component of the wavevector \( k_y \) perpendicular to the interface:

\[
k_{y2}^2 = n_1^2 \left( \frac{2\pi}{\lambda} \right)^2 \left( \frac{n_2^2}{n_1^2} - \sin^2 \alpha \right) \tag{2.4}
\]

Now, let us assume that \( n_1 > n_2 \). From eq. (2.4), it is seen that for \( \sin \alpha > n_2/n_1 \) the right part is negative, and, consequently, \( k_y \) is purely imaginary. Returning to

\footnote{Note that the direction \( y \) is in this chapter always perpendicular to the surface.}
eq. (2.1), we conclude that for this case in medium 2 there is only a traveling wave parallel to the interface:

\[ E_2 = E_0 e^{-k_{y2} y} \exp(j\omega t - jk_z x) \]  

with the amplitude of the electric field exponentially decaying along the \( y \)-direction with a characteristic distance \( 1/k_{y2} = 1/jk_z \). For obvious reasons, this field in medium 2 is denoted as the evanescent field. Eq. (2.4) can be used to calculate its penetration depth, which is of the order of half a wavelength. This explains the interface sensitivity of the evanescent field: only close to the interface is an electromagnetic field present; therefore, only a changing dielectric property (e.g. a changing refractive index) in the vicinity of the interface will influence this field.

We will see that also in SPR an evanescent field is generated.

### 2.3 Surface Plasmons

#### 2.3.1 Surface Plasmon Dispersion Equations, Resonance

There are several approaches that all result in the dispersion relation for an SP, that is, a relation between the angular frequency \( \omega \) and the wavevector \( k \). In his last standard treatise on SPs, Raether [3] calculated the SP dispersion relation from first principles, viz. Maxwell’s equations. A particularly elegant approach was suggested by Cardona [4] and we will adopt it here. For reasons that will become clear in the course of Section 2.3.2, we will only discuss p-polarized\(^2\)

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\(^2\)p-Polarized light has its electric field vector in the plane of incidence.
light interacting with an interface. For any interface between two media, the complex reflection coefficient \( r_p \) for p-polarized incident light electric field is described by Fresnel’s equations (see, e.g., ref. [5] for a derivation on the basis of Maxwell’s equations):

\[
r_p = \frac{E_i}{E_r} = |r_p| e^{i\phi} = \left| \frac{\tan(\alpha - \beta)}{\tan(\alpha + \beta)} \right| e^{i\phi} \quad (2.6a)
\]

where \( E_i \) and \( E_r \) are the incident and reflected electric fields, respectively, and the angles \( \alpha \) and \( \beta \) are defined as shown in Figure 2.1.\(^3\)

Of course, the angles \( \alpha \) and \( \beta \) are again related by Snell’s law [eq. (2.3)]; in addition, a phase change \( \phi \) of the reflected field relative to the incident field occurs, depending on the refractive indices of the materials involved.

For the reflectance, defined as the ratio of the reflected intensities, the following relation holds:

\[
R_p = |r_p|^2 \quad (2.6b)
\]

Now, following Cardona [4], two special cases exist: if \( \alpha + \beta = \pi/2 \), then the denominator of eq. (2.6a) becomes very large and thus \( R_p \) becomes zero. This situation describes the Brewster angle, where there is no reflection for p-polarized light. The other special case occurs when \( \alpha - \beta = \pi/2 \): we see from eqs. (2.6a) and (2.6b) that \( R_p \) becomes infinite: there is a finite \( E_r \) for a very small \( E_i \). This circumstance corresponds to resonance. From this relation between \( \alpha \) and \( \beta \) we can deduce the dispersion relation if \( \alpha - \beta = \pi/2 \), then \( \cos\alpha = -\sin\beta \) and \( \tan\alpha = k_1x/k_1y = -n_2/n_1 \). For the components of the wavevector \( k = (k_x, k_y) \), we can write

\[
k_x^2 = k_1^2 - k_y^2 = k_1^2 - k_x^2 \frac{\varepsilon_1}{\varepsilon_2} \quad (2.7)
\]

\[
k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad \text{and} \quad k_y = \frac{\omega}{c} \sqrt{\frac{\varepsilon_2^2}{\varepsilon_1 + \varepsilon_2}} \quad (2.8)
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric constants\(^4\) of materials 1 and 2, respectively, and \( i = 1 \) or 2. Equation (2.8) is the sought SPR dispersion equation for an interface between two half-infinite media.

Next, we investigate the case where medium 2 is a metal. This medium then contains a large number of free electrons and the consequence is that at an angular frequency \( \omega < \omega_p \) its dielectric constant \( \varepsilon_2 \) will be negative (see, e.g., ref. [5]):

\[
\varepsilon_2(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad (2.9a)
\]

\[
\omega_p = \sqrt{4\pi n_e e^2/m_e} \quad (2.9b)
\]

\(^3\)Note that in Figure 2.1 the direction \( y \) (instead of \( z \)) is perpendicular to the surface.

\(^4\)Dielectric constant and refractive index are related by \( \varepsilon \equiv n^2 \).
where $\omega_p$ is the so-called plasma frequency, $n_e$ is the free electron density and $e$ and $m_e$ are the electron charge and mass, respectively.

Generally, this implies that for $\omega < \omega_p$ no electromagnetic field can propagate in a metal [cf. eqs. (2.1) and (2.2)]. More specifically, provided that $\varepsilon_2 > -e_1$, we find for the interface that $k_{yi}$ is imaginary, whereas $k_x$ remains real. Thus an electromagnetic wave exists, propagating strictly along the interface, with evanescent tails extending into both sides of the interface [cf. eq. (2.5)]. To get a feeling for the quantities involved, it is instructive to calculate penetration depths for a real case, on the basis of eq. (2.8). We take $\lambda = 700 \text{ nm}$, thus $\omega = 2.69 \times 10^{15} \text{ s}^{-1}$ and a gold/water interface. At this wavelength $\varepsilon_{\text{gold}} \approx -16$ and $\varepsilon_{\text{water}} \approx 1.77$. We calculate for the penetration depths $1/k_{yi,\text{water}} = 238 \text{ nm}$ and $1/k_{yi,\text{gold}} = 26 \text{ nm}$.

Now all ingredients are available to appreciate the use of SPR in sensor applications. Let us assume that we have a situation where molecules X are allowed to adsorb to the water/metal interface. We can view this as a process where water molecules are replaced by molecules X. Because, generally, $\varepsilon_X \neq \varepsilon_{\text{water}}$, the average dielectric constant close to the interface will change. Equation (2.8) then describes the concomitant change of the wavevector $k_x$.

Because the SP field is evanescent in the direction perpendicular to the interface, a change of the dielectric constant $\varepsilon_2$ is only detectable in SP characteristics if this change occurs within the penetration depth of the SP field: an SPR sensor will only be sensitive to molecular processes (binding, adsorption, etc.) that occur at a distance to the metal surface that is roughly half the wavelength of the used light.

### 2.3.2 Excitation of Surface Plasmons

By substitution of eqs. (2.9a) and (2.9b) into eq. (2.8), we obtain a graphical representation of the SPR dispersion relation as shown in Figure 2.2 (line f). In the same figure, the dispersion relation for “normal” light is depicted (line a). We immediately see that, apart from the origin, there is no point where the SPR curve and the light curve intersect, implying that in this geometry “normal” light cannot simultaneously provide the correct wavevector and angular frequency to excite a surface plasmon.

One way to circumvent this problem is to introduce a second interface, as depicted in the inset of Figure 2.2. Here a thin metal layer (dielectric constant $\varepsilon_m$) is sandwiched between two dielectric materials 1 and 3 with different dielectric constants $\varepsilon_1$ and $\varepsilon_3$, with $\varepsilon_1 > \varepsilon_3$. By applying Fresnel’s equations to the two interfaces, more complicated dispersion equations are found than eq. (2.8); however the essential physics remains unchanged. We now find two dispersion equations for $k_{yi}$, one for each interface, and we see that the line representing the dispersion relation for “normal” light in medium 1 (line b) intersects the SP dispersion line for the metal/medium 3 interface. This indicates that light incident from medium 1 can excite SPs: by proper adjustment of the incoming angle $\alpha$ (Figure 2.2, inset), we can tune the incoming wavevector $k_x = k n_1 \sin \alpha$ to
match the wavevector necessary for SP excitation. In this way, any \( k_x \) between the two lines, labeled a and b in Figure 2.2, can be set. As an example, one such line, labeled c, is indicated. This so-called attenuated total reflection (ATR) technique was first demonstrated\(^5\) by Kretschmann and Raether [2] and has since then almost become the standard technique for SP excitation.

Another way of providing a wavevector appropriate for SP excitation is the use of a metal layer on which a periodic structure is prepared [6] as illustrated in Figure 2.3.

When light with wavevector \( k_x = \frac{2\pi}{\lambda} n \sin \theta \) falls on such a structure, this acts as a diffraction grating and diffraction orders \( m = 0, \pm 1, \pm 2, \ldots \) are generated in the reflected light (see, e.g., ref. [7]). The generated wavevector \( k_{x,\text{net}} \) parallel to the interface can be written as

\[
k_{x,\text{net}} = k_x + m \frac{2\pi}{\Lambda} \tag{2.10}
\]

\(^5\)In fact, Otto was the very first to demonstrate this in a somewhat less versatile form.
where $\Lambda$ is the periodicity of the grating. Again, the wavevector $k_{x,\text{net}}$ can be tuned to the SPR wavevector, given by eq. (2.8),\(^6\) by changing the incident angle.

Up to now the required polarization direction of the incoming light remained unmentioned. As already pointed out, SPs are conductivity fluctuations brought about by collective surface charge density oscillations. These charge density waves have to be excited by an external electric field. Only an electric field with a component perpendicular to the interface can induce a surface charge density; only p-polarized light has a perpendicular electric field component.

### 2.3.3 Surface Plasmon Properties

With SPs, a number of specific properties are associated that are particularly relevant to sensor applications: (1) the field enhancement, (2) the phase jump of the reflected field upon SP excitation and (3) the SP coherence length.

*Field enhancement.* A calculation of the electric field transmission coefficient on the basis of Fresnel’s equations for the interface reveals that the electric field at the low index side of the metal can be much larger than that at the other side of the metal layer.

In Figure 2.4, the intensity enhancement is depicted as a function of the angle of incidence of incoming light for a number of different thicknesses of a gold layer. It is found that very close to the SPR angle the intensity can be enhanced by a factor of more than 30. This circumstance accounts for much of the

\(^6\)The dispersion equation eq. (2.8) is hardly affected if the metal surface has a shallow corrugation.
remarkable sensitivity that the SPR condition has for a changing dielectric environment.

*Phase jump.* As already mentioned in Section 2.3.1 and expressed in eq. (2.6), a reflection event at an interface is generally accompanied by a phase jump of the reflected field. This is illustrated in Figure 2.5a for a prism–gold–water system.

For comparison, the “conventional” SPR dip is shown in Figure 2.5b for the same layer system. We see that around the SPR dip the phase of the reflected electric field undergoes a relatively large change. The significance of this phenomenon for sensing purposes is more clear when we plot the reflectance and phase changes as a function of incident angle for a certain change in dielectric constant of the water. This is depicted in Figure 2.5c and d. In the following rough calculation, we assume that both the change in reflection coefficient $\Delta R$ and the phase change $\Delta \phi$ are proportional to $\Delta \varepsilon$. From Figure 2.5c we estimate that $\Delta R/\Delta \varepsilon \approx 30$, whereas from Figure 2.5d we find that $\Delta \phi/\Delta \varepsilon \approx 250$. Experimentally, a minimum $\Delta R \approx 10^{-3}$ can be measured, whereas a minimum $\Delta \phi \approx 10^{-3}$ is feasible, using interferometric techniques. The conclusion is that on the basis of reflectance measurements a minimum $\Delta \varepsilon \approx 4 \times 10^{-5}$ can be detected, whereas a phase measurement provides a sensitivity of $\Delta \varepsilon \approx 4 \times 10^{-6}$. In view of the very approximate character of this calculation,
the absolute values found are of limited validity; however, the finding that a phase measurement provides an order of magnitude better sensitivity is a hard conclusion and, indeed, this was demonstrated by Nikitin and co-workers [8,9]. The only drawback of this approach seems to be the much more complicated experimental setup.

**SP coherence length.** Generally, the metal’s dielectric constant $\varepsilon_2$ is complex and this circumstance results in a complex propagation constant $k_x = \kappa_x'' + j\kappa_x'''$ [cf. eq. (2.8)], where $\kappa_x''$ and $\kappa_x'''$ are real and imaginary parts, respectively. For a surface plasmon, traveling along the interface with wavevector $k_x$, this implies that the field intensity decays with a characteristic distance $1/2\kappa_x'''$. For gold and silver, the standard metals in sensor applications,
the imaginary part of the dielectric constant increases with decreasing wavelength and the SP propagation length decreases accordingly.

This is illustrated in Figure 2.6: here a layer system was prepared where a 30 nm SiO$_2$ strip was deposited on a 50 nm silver layer. For a series of wavelengths the angle of incidence was chosen such that SPs were excited in the area...
outside the strip and for each wavelength the whole area was illuminated with a collimated light beam under a constant angle of incidence. Because of the contrast in dielectric constant between the strip and its surroundings (air), the SP resonance condition is not fulfilled in the area below the strip and we see the decaying SP (increasing reflectance) at the left edge of the strip. Beyond the right edge of the strip the SPR condition is again fulfilled and the SP resonance builds up. The figure nicely demonstrates that with decreasing wavelength the SP propagation length becomes shorter: the blurring on the left side of the strip becomes less prominent for shorter wavelengths. It turns out that in the wavelength range 500–00 nm the propagation length varies between <10 and 40 μm.

For a quantitative description of the findings depicted in Figure 2.6, we have to analyze the interference between the several fields that are present in the layer.

In Figure 2.7, the layer system and the fields involved are indicated: the resonant SP field, the non-resonant SP field and the external exciting field with amplitudes $E_1$, $E_2$, $E_3$, respectively. For a resonant SP that enters the SiO$_2$ strip-covered layer, the total field reaching the detector can be written as [10,11]

$$E_{\text{tot}}(x) = (E_1 - E_2)e^{i(k'_1 + jk''_1)x} + E_2e^{ik''_0x} - E_3e^{ik'_0x} \quad (2.11)$$

where $k'_1$ is the wavevector corresponding to resonance in the covered area and $k''_0$ is the wavevector that excites SPs in the uncovered area.

Defining $A = E_1 - E_2$ and $B = E_2 - E_3$, the resulting intensity at the detector becomes

$$I_{\text{tot}}(x) = B^2 + A^2e^{-2k''_0x} + 2ABe^{-k''_0x}\cos(k'_1 - k'_0)x \quad (2.12)$$

When a non-resonant SP leaves the covered area, the resonant SP builds up and the intensity at the detector decreases accordingly [11]:

$$I_{\text{tot}}(x) = \left[ B + A\left(1 - e^{-k''_0x}\right)\right]^2 \quad (2.13)$$

From Figure 2.6, we see that this model gives a very accurate description of the experiments.

![Figure 2.7](image-url) **Figure 2.7** Definition of wave vectors and fields for the system consisting of a dielectric strip on top of a metal layer.
Both this model and the experiments indicate that a plasmon needs roughly four times the propagation length $L_x$ for a full decay or for a full build-up; this propagation length can be loosely defined as

$$L_x = \frac{1}{2\kappa_x}$$

(2.14)

This implies that SPs with mutual distances significantly larger than $L_x$ are independent. This is a very important conclusion because it is the fundament of surface plasmon microscopy [12,13], with its many applications in SPR imaging and SPR multisensing: on a substrate we can define areas that in an SPR experiment will behave mutually independently, provided that these areas are significantly larger than $L_x^2$. For SPs on gold, excited at $\lambda = 632$ nm, $L_x \approx 7$ $\mu$m and on a total sensor area of 1 cm$^2$ more than $10^4$ independent sensor “patches” that each have an area of somewhat smaller than $100 \times 100$ $\mu$m$^2$ can in principle be defined, of which the optical responses can be simultaneously read out by using an imaging system. As practical aspects are outside the scope of this chapter, the interested reader should consult Chapter 7 for more details.

### 2.3.4 Choice of Experimental Parameters

It is impossible to define a general set of optimum SPR parameters, for instance, optimal spatial resolution in an SPR microscopy/imaging setup requires values of the experimental parameters other than those to obtain maximum sensitivity for dielectric changes. Therefore, this section provides only some general guidelines, based on consideration of the properties of the metal layer.

To obtain maximum sensitivity, it is advantageous to maximize the steepness of the reflectance as a function of the angle of incidence, because this allows for a more accurate determination of the angle of minimum reflectance (cf. Figure 2.8).

This implies optimization of the reflectance minimum $R_{\text{min}}$ and minimizing the width of the resonance curve. $R_{\text{min}}$ can be made very close to zero by selecting the appropriate thickness of the metal layer; as can be seen in Figure 2.8, optimum thicknesses are somewhat dependent on the applied wavelength and are between 40 and 50 nm. The width of the resonance curve is mainly determined by the complex value of the metal’s dielectric constant. Generally, a large (negative) real part, together with a small imaginary part, results in narrow resonance curves. In practice only two options are available for the choice of the metal layer: gold or silver. As seen in Figure 2.8, silver has the better SPR characteristics in view of the larger real part of its dielectric constant; however, it is chemically less inert. In Figure 2.8, it is also seen that the use of higher excitation wavelengths has an appreciable effect on the width of the resonance curve. This is one of the reasons why (near-) infrared SPR experiments are attracting attention [14,15]. However, it should be realized that narrowing the reflectance curve necessarily implies increasing the SPR propagation length [eq. (2.13)], which can be a disadvantage in certain SPR imaging applications. For a
gold layer, it can be calculated that an increase in wavelength from 450 to 1500 nm results in a change in the propagation length from 100 to almost 1 mm. Finally, it should be mentioned that an increase in wavelength results in an increase in the penetration depth $1/k_y$ \[\text{cf. eqs. (2.4) and (2.5)}\], with the consequence that the reflectance minimum will become more sensitive to dielectric changes relatively far from the metal/dielectric interface; hence the surface-sensitive character of SPR becomes less prominent. This implies that for detection of the growth of thin layers the optimum choice of wavelength will be different from that in a situation where a more bulk-like change in refractive index has to be detected [33].

### 2.4 Analysis of Multi-layered Systems

In most SPR-based sensor applications, the system of interest consists of a gold or silver layer on which one or more thin layers are deposited in an aqueous environment. Often the desired parameters are the thicknesses of the several layers, which can be converted into surface concentrations of the layer-composing molecules (\textit{cf}. Chapters 4 and 5).

One way to obtain these parameters is a repeated application of the Fresnel equation [eq. (2.6a)]. The following relation holds for a system consisting of $N$
layers with dielectric constants and thicknesses $\varepsilon_i$ and $d_i$, respectively, placed between a prism with dielectric constant $\varepsilon_p$ and a medium (e.g. water) with dielectric constant $\varepsilon_w$ (see. e.g., ref. [5]):

$$
\begin{align*}
\beta_p(\alpha) &= \left( \frac{M_{11} + M_{12} \frac{k_{y,w}}{\varepsilon_p} k_{y,p}}{M_{11} + M_{12} \frac{k_{y,w}}{\varepsilon_w} k_{y,p} + (M_{21} + M_{22} \frac{k_{y,w}}{\varepsilon_w})} \right) \\
&= \left( \frac{M_{11} + M_{12} \frac{k_{y,w}}{\varepsilon_p} k_{y,p} - (M_{21} + M_{22} \frac{k_{y,w}}{\varepsilon_w})}{M_{11} + M_{12} \frac{k_{y,w}}{\varepsilon_w} k_{y,p} + (M_{21} + M_{22} \frac{k_{y,w}}{\varepsilon_w})} \right)
\end{align*}
$$

(2.15a)

where $M$ is the so-called transfer matrix:

$$
M = M_1 \cdot M_2 \cdot \ldots \cdot M_N
$$

(2.15b)

with

$$
M_i = \begin{bmatrix}
\cos(k_{y,i}d_i) & \frac{\sin(k_{y,i}d_i)}{k_{y,i}} \\
-\frac{\sin(k_{y,i}d_i)}{k_{y,i}} & \cos(k_{y,i}d_i)
\end{bmatrix}
$$

(2.15c)

The angular dependence of $\beta_p$ is contained in the wavevectors $k_{y,i}$, perpendicular to the layer system; these can be calculated using eq. (2.4). The reflectance can be obtained by application of eq. (2.6b).

Provided all thicknesses $d_i$ and dielectric constants $\varepsilon_i$ are known, eq. (2.15) gives an accurate description of the SPR experiment. Of course, in practice one is concerned with the inverse problem and $a$ priori knowledge, such as the dielectric constant and dimensions of the molecules composing a certain layer, is required for a satisfactory analysis of experimental SPR results. This precludes an unambiguous analysis of more than two or three layers.

Another, more intuitive, approach is the introduction of an effective dielectric constant, $\varepsilon_{\text{eff}}$. Here, the actual multi-layered system is replaced by a two-layer system, where $\varepsilon_1$ in eq. (2.8) is replaced by the effective dielectric constant $\varepsilon_{\text{eff}}$, given by the average of all dielectric constants in the layer system, weighted by the penetration depth $y_0$ of the SPR evanescent field [16,17]:

$$
\varepsilon_{\text{eff}} = \frac{2}{y_0} \int_0^\infty \varepsilon(y) e^{-2y/y_0} dy
$$

(2.16)

Of course, with the use of this equation, we face the same problems as those when we use eq. (2.15).

### 2.5 SPR Spectroscopy

#### 2.5.1 Enhancement of Fluorescence and Absorbance

Up to now we have only considered, apart from the metal layer, transparent layers, i.e. layers that are characterized by a positive, real dielectric constant. When one or more layers contain a light-absorbing compound, SPs can boost the fluorescence intensity from a thin layer more than 40-fold [18]. This effect is due solely to the large field enhancement that occurs on the low index side of
the metal layer when an SP resonance condition is established (cf. Figure 2.4). More information on this phenomenon can be found in Chapter 9. Another, more subtle, feature of the interaction between SPs and light-absorbing molecules is the increased sensitivity for the detection of absorbances in thin layers. The addition of a light-absorbing layer results in two effects on the SPR angular-dependent curve, which are quantitatively described by eq. (2.15): (1) the SPR dip shifts to a larger angle of incidence and (2) the value of the reflectance minimum increases. This last effect can readily be understood as light absorption necessarily results in a decreased reflectance. In addition, the SPR field enhancement on the low-index side of the metal layer will result in increased sensitivity for dielectric changes [19] and therefore also for changes in the absorbance. The first effect is a consequence of the Kramers–Kronig relation (see, e.g., ref. [20]), which in the present context can be expressed as the statement that any change in the imaginary part of the dielectric constant will be accompanied by a change in the real part; in SPR it is mainly the real part of the dielectric profile on top of the metal layer that determines the angular position of the SPR dip. It has been demonstrated [21] that an SPR-assisted monolayer absorbance measurement can result in a 40-fold reflectance increase as compared with a metal-lacking ATR system. In addition, it is possible to extract unambiguously the thickness and the dielectric constant of an absorbing layer from a single SPR experiment [22].

2.5.2 SPR and Metal Nanoparticles

SPR phenomena are not restricted to planar multilayers as discussed so far; it turns out that for metal particles with dimensions much smaller than the wavelength of the interacting light, SP effects can be much more prominent. Generally, the net electric field \( E_{\text{tot}} \) around a dielectric particle is composed of the superposition of an external applied field \( E_0 \) and the induced (dipole) field in the particle. For a polarizable spherical particle with radius \( r_m \) and dielectric constant \( \varepsilon \), placed in a medium with dielectric constant \( \varepsilon_1 \), the following expression is found (see, e.g., ref. [5]) for the field gain \( G \):

\[
G(\omega) = \frac{E_{\text{tot}}(\omega)}{E_0(\omega)} \approx 1 + \frac{\varepsilon(\omega) - \varepsilon_1}{\varepsilon(\omega) + 2\varepsilon_1} \left( \frac{r_m}{r + r_m} \right)^3
\]

(2.17)

It is seen that \( G \) can reach enormous values for \( \varepsilon \) close to \(-2\varepsilon_1\); in a “normal” dielectric medium where \( \varepsilon_1 > 0 \), this condition points to the use of a metal, where \( \varepsilon \) can be negative; additionally, the imaginary part of \( \varepsilon \) should be as small as possible. It turns out that this condition corresponds to the excitation of a surface plasmon in the metallic nanoparticle [23]. Particularly in the field of Raman spectroscopy this can result in enormous sensitivity enhancements\(^7\) (for a review, see ref. [24]).

\(^7\)Conventional Raman spectroscopy suffers from a very low scattering efficiency which can be 12 orders of magnitude lower than that of fluorescence.
Now consider a Raman-active molecule near a metal nanoparticle. The detected Raman intensity $I(\omega, \omega_{sc})$ can be expressed as

$$I_{\text{Raman}}(\omega, \omega_{sc}) = \gamma E_{\text{exc}}^2 \cdot E_{\text{sc}}^2 = \gamma G^2(\omega)G^2(\omega_{sc})I_0(\omega)I_{0,sc}(\omega_{sc})$$

(2.18)

where $E_{\text{exc}}$ is the total excitation electric field to which the molecule is exposed and $E_{\text{sc}}$ is the total Raman-scattered field. The constant $\gamma$ is an experimental constant that is unimportant in the present discussion.

By choosing an angular frequency $\omega$ that excites surface plasmons in the metal (usually gold or silver) and detecting scattering frequencies $\omega_{sc}$ not too far from the excitation frequency, both the excitation and the scattered field are enhanced by the presence of the metal particle. By substituting eq. (2.17) into eq. (2.18), we see that the distance dependence of the net Raman scattering intensity changes with the power $-12$ of the molecule–nanoparticle distance! Indeed, it has been found experimentally that a surface-enhanced Raman spectroscopy (SERS) experiment can result in experimental Raman signals that are enhanced $10^{12}$–$10^{14}$ times compared with those obtained from non-surface-enhanced experiments.

It should be added that apart from this SPR enhancement mechanism, another chemical enhancement effect is operational, which accounts for a 10–100-fold amplification of the bare Raman signal [24].

It has been demonstrated [25,26] that SERS is able to detect single molecules. Together with its very high molecular specificity, this offers great promise as a detection tool for very low concentrations of biomolecules, such as DNA strands or proteins.

In principle, these field enhancements should also be important in the detection of fluorescent molecules near a metal nanoparticle. However, the nearby presence of a metal layer leads to additional non-radiative decay paths of the electronic excited states of a nearby molecule, with the net result that in many cases the fluorescence will be largely quenched.

So far, metal nanoparticles were considered as surface plasmon-assisted field amplifiers. However, these particles can also be exploited as intrinsic refractive index sensors, analogous to the more familiar planar SPR experiments (for reviews, see refs. [27] and [28]). The physical basis of this application is the light extinction (absorption and scattering), which is heavily dependent on the nanoparticle’s dielectric constant, size and geometry and also on the dielectric constant $\varepsilon_1$ of the surrounding medium. Mie theory gives a reasonably adequate description of the extinction coefficient $A_{\text{ext}}$ and for spherical particles with diameter less than about 20 nm the following expression is found [23]:

$$A_{\text{ext}} = \frac{18\pi N_p V \varepsilon_1^{3/2}}{\lambda} \frac{\text{Im}(\varepsilon)}{[\text{Re}(\varepsilon) + 2\varepsilon_1]^2 + [\text{Im}(\varepsilon)]^2}$$

(2.19)

where $N_p$ is the number of nanoparticles, each of which has a volume $V$, and $\lambda$ is the wavelength of the applied light.
Again we see the pronounced influence of the occurrence of SPs: at \( \text{Re}(\varepsilon) = -2\varepsilon_i \)
we find a maximum in the extinction coefficient, which can reach large values for low values of \( \text{Im}(\varepsilon) \). Hence also in this situation we are led to the use of gold or silver as a metal nanoparticle.

More sophisticated models (see, e.g., ref. [29]) also account for the size and shape of the nanoparticles and computer programs are available in the public domain that can predict the extinction spectrum of nanoparticles of any shape [30], by modeling the particle as a series of dipoles placed in an oscillating electric field. However, the main features of nanoparticle extinction remain contained in eq. (2.19).

For one nanoparticle with a diameter around 25 nm, excited close to its SP resonance, eq. (2.19) results in
\[
A_{\text{ext}} \approx 10^{-16} \text{m}^2,
\]
which corresponds to the more familiar molar extinction coefficient in the order of \( 10^9 \text{m} \text{mol}^{-1} \text{cm}^{-1} \). This value, which indeed was observed experimentally [29], is more than three orders of magnitude larger than that of strong light-absorbing organic dye molecules, allowing for relatively simple optical detection and characterization of individual nanoparticles [31,32]. In another series of experiments, the shift of the extinction maximum as a function of the refractive index of the surrounding medium was investigated [28]. It was found experimentally that for silver nanoparticles the spectrum could shift as much as 20 nm for a change of 0.1 in the refractive index. Because molecules that adsorb to a nanoparticle change the refractive index around the particle, it is obvious that this, analogous to conventional SP resonance, can be used as a sensor principle. Indeed, it has been demonstrated experimentally that the full coverage of a silver nanoparticle with low molecular mass molecules resulted in a spectrum shift of approximately 40 nm. The full coverage corresponded to only \( 4 \times 10^4 \) molecules. Together with the single particle detection capability, this promises enormous sensitivity, allowing for near single molecule detection [32].

### 2.6 Concluding Remarks

The phenomenon of SPR is one of the many examples where an interesting physical phenomenon leads to applications that are highly important to both applied science and society. In a planar SPR system, it is particularly the combination of field enhancement and relatively short coherence length that allows for a unique sensor concept that provides both multiplexing capabilities and very high sensitivity. The general physical picture is well understood; however, some areas are still in vivid scientific debate (SERS, optics of nanoparticles).

From a technological point of view, the emerging field of nanotechnology will enable us to exploit to its full potential the SP phenomena of tailored nanoparticles. It is the author’s firm conviction that merging of (bio-)nanotechnology and SP phenomena of nanoparticles will ultimately lead to sensor concepts and sensor realizations that will really be important in numerous
aspects of society, varying from food safety monitoring and high-throughput screening to early *in vivo* detection of tumor growth.

### 2.7 Questions

1. Derive eq. (2.4) from eqs. (2.2) and (2.3).

2. Calculate for a gold/water interface at $\lambda = 700 \text{nm}$ ($\varepsilon_{\text{gold}} = -16$, $\varepsilon_{\text{water}} = 1.770$) the angular shift of the SPR dip when $\varepsilon_{\text{water}}$ increases to 1.775. For the light-incoupling we use a semi-circular glass piece with refractive index $n_{\text{glass}} = 1.5$.

3. Estimate the effective dielectric constant for the following system, when this interface is probed with a wavelength $\lambda = 700 \text{nm}$ (for dielectric constants of gold and water, see previous question)

![Diagram](image)

The squares in the figure represent cubes of protein molecules in an aqueous environment, adsorbed to the gold surface. Each protein molecule has a volume of $5*5*5 \text{nm}^3$ and a dielectric constant $\varepsilon_{\text{protein}} = 2.30$. The average distance between the edges of the cubes is 7 nm.

4. A particular SPR application could be the detection of micro-organisms in, e.g., waste water, by detecting changes in bulk refractive index. Which SPR excitation wavelength region would be more favourable, the blue/UV or the infrared region?

5. Express the extinction coefficient $A_{\text{ext}}$ (eq. 2.16) in units $\text{M}^{-1}\text{cm}^{-1}$.

### 2.8 Symbols

- $A$  \quad A = E_1 - E_2
- $A_{\text{ext}}$  \quad extinction coefficient
- $B$  \quad B = E_2 - E_3
- $\text{const}$  \quad experimental constant in surface-enhanced Raman spectroscopy
- $c$  \quad propagation velocity in vacuum
- $d_i$  \quad film or layer thickness
- $E$  \quad electric field strength
- $e$  \quad charge of electron
- $E_0$  \quad amplitude of electric field
- $E_0$  \quad external applied field $E_0$ (Section 2.5.2)
- $E_{\text{exc}}$  \quad total excited electric field (Raman)
- $E_i$  \quad incident electric field
- $E_r$  \quad reflected electric field
$E_{sc}$ total scattered field (Raman)
$E_{tot}$ net electric field around nanoparticles
$G$ field gain of nanoparticle SPR
$I$ intensity
$I_{Raman}$ Raman intensity near an SPR nanoparticle
$k$ wavevector
$k_y$ $y$ component of wavevector
$k_{x, \text{net}}$ $x$ component of wave vector
$L_x$ propagation length of a full decay or build-up
$m_c$ mass of electron
$m$ diffraction order
$N$ number of layers in system
$n_e$ free electron density
$n$ refractive index
$N_p$ number of nanoparticles
$n_i$ refractive index of material $i$
$r$ position vector
$r_m$ radius of polarizable spherical (nano)particle
$r_p$ reflection coefficient (complex)
$R_p$ reflectance
$V$ volume of nanoparticles
$y_0$ penetration depth of SPR evanescent field
$\alpha$ incident angle of light
$\beta$ refraction angle of light
$\varepsilon$ dielectric constant
$\varepsilon_0$ dielectric constant of medium
$\varepsilon_{\text{eff}}$ effective dielectric constant
$\varepsilon_p$ dielectric constant of prism
$\varepsilon_w$ dielectric constant of water
$\kappa_0$ wavevector excited in uncovered area
$\kappa_1$ wavevector corresponding to resonance of strip-covered area
$\lambda$ wavelength in vacuum
$\Lambda$ periodicity of grating
$\varphi$ phase change of the reflected field relative to the incident field
$\omega$ angular frequency
$\omega_p$ plasma frequency
$\omega_{sc}$ scattering frequency

References


