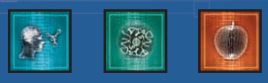
Surface plasmon resonance



Abstract

Biacore's SPR technology is a label-free technology for monitoring biomolecular interactions as they occur. The detection principle relies on surface plasmon resonance (SPR), an electron charge density wave phenomenon that arises at the surface of a metallic film when light is reflected at the film under specific conditions. The resonance is a result of energy and momentum being transformed from incident photons into surface plasmons, and is sensitive to the refractive index of the medium on the opposite side of the film from the reflected light. The phenomenon SPR was initially observed by Turbadar [1] although it was the works by Otto [2], Kretschmann and Raether [3], Agerwal [4], and Swalen [5] that brought understanding and showed the versatility of the technique.

In Biacore systems, SPR is used to monitor interactions occurring in a biospecific surface on a metal layer by measuring changes in the solute concentration at this surface as a result of the interactions. For reviews about SPR the reader is referred to Welford [6] and Raether [7].

In order to describe SPR, it is helpful to start with the phenomenon of total internal reflection (TIR) which occurs at an interface between non-absorbing media. When a light beam propagating in a medium of higher refractive index meets an interface at a medium of lower refractive index at an angle of incidence above a critical angle (see Mirabella [8], de Mello [9]), the light is totally reflected at the interface and propagates back into the high refractive index medium (see Figure 1).

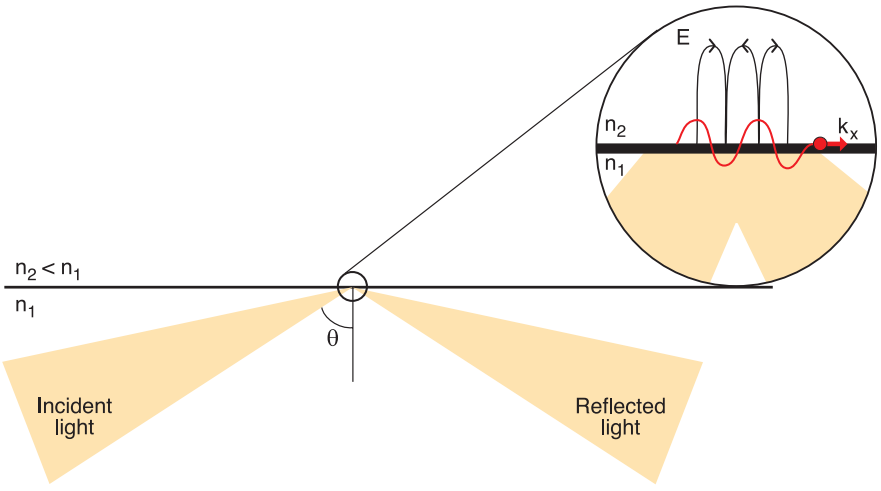


Figure 1. TIR for non-absorbing media. Light propagating in a medium of refractive index n_1 undergoing total internal reflection at the interface with the medium of a lower refractive index n_2. The evanescent field, E, is a non-transverse wave having components in all spatial orientations, decreasing in field intensity with penetration into medium of n_2 (Mirabella 7). θ is the angle of incidence.

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Although the fully reflected beam does not lose any net energy across the TIR interface, the light beam leaks an electrical field intensity called an evanescent field wave into the low refractive index medium. The amplitude of this evanescent field wave decreases exponentially with distance from the interface, decaying over a distance of about one light wavelength from the surface (Figure 4). If the lower refractive index media has a non-zero absorption coefficient, the evanescent field wave may transfer the matching photon energy to the medium. This is exploited in internal reflection spectroscopy (IRS) as reviewed by Mirabella [8]. The penetration depth of the evanescent field wave is usually defined as the distance over which the wave decays to 1/*e*, or about 37%, of its maximum intensity.

If the TIR-interface is coated with a layer of a suitable conducting material, such as a metal, of a suitable thickness the p-polarized component of the evanescent field wave, may penetrate the metal layer and excite electromagnetic surface plasmon waves propagating within the conductor surface that is in contact with the low refractive index medium (Figure 2). For a non-magnetic metal like gold, this surface plasmon wave will also be p-polarized and, due to its electromagnetic and surface propagating nature, will create an enhanced evanescent wave (Figure 4).

This evanescent wave has electric field components directed in all spatial orientations during penetration into the low refractive index medium. Because the electric field penetrates a short distance into the lower refractive index medium, the conditions for SPR are sensitive to the refractive index at the gold surface.

For plasmon excitation by a photon to take place the energy and momentum of these "quantum-particles" must both be conserved during the photon "transformation" into a plasmon. This requirement is met when the wavevector for the photon and plasmon are equal in magnitude and direction for the same frequency of the waves (the wavevector is a parameter in the mathematical formula for the electromagnetic wave related to the momentum). The direction of the wavevector is the direction of the wave propagation (i.e. the light ray direction), while its magnitude depends on the refractive indices of the media that the electromagnetic field wave interacts with along its propagation path.

Since the wave vector of the plasmon wave is bound to the conductor surface, it is the wavevector of the component of the incident light which is parallel to the conductor surface that can be equal to the wave-vector of the surface plasmons (k_{sp}, k_x in Figure 2). The magnitude of the surface-parallel wavevector, k_x, is the wavevector of the incident light times sin(θ), $k_x = (2*\pi/\text{wavelength})*n_1*\sin(\theta)$ (Figure 1).

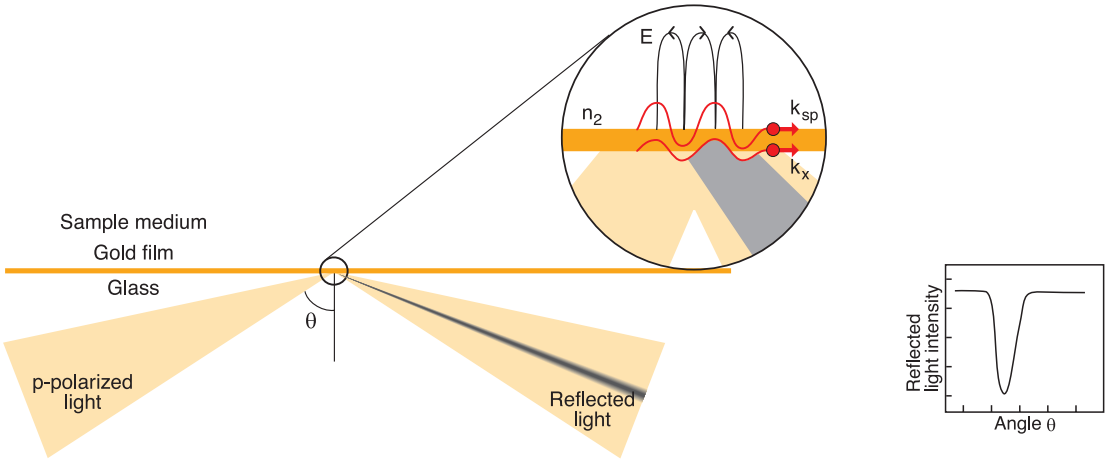

Figure 2. SPR is excited by p-polarized totally internally reflected light at a glass/metal film interface, the surface plasmon enhancing the evanescent field amplitude, E. In Biacore systems which use a sensor chip, this interface takes the form of an exchangeable gold-coated glass slide. SPR is observed as a dip in the reflected light intensity at a specific angle of reflection.

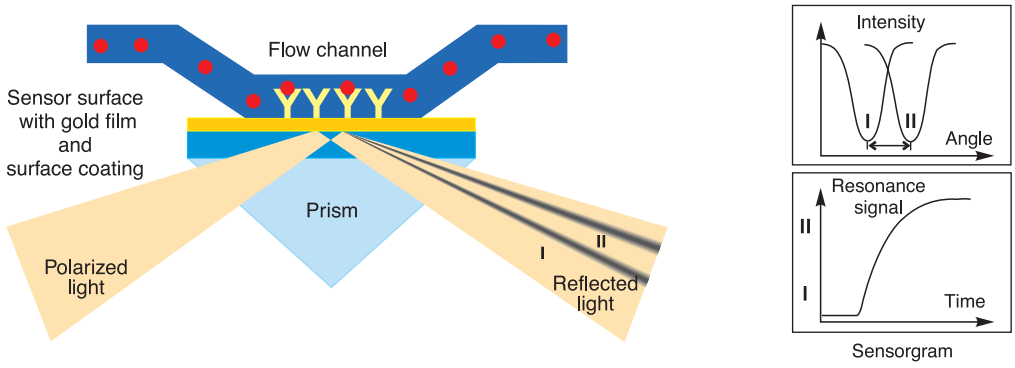

Figure 3. In Biacore systems, the incident p-polarized light is focused into a wedge-shaped beam providing simultaneously a continuous interval of light wavevectors k_x. This range covers the working range for the plasmon wavevector k_{sp} during biomolecular interaction analysis. An increased sample concentration in the surface coating of the sensor chip causes a corresponding increase in refractive index which alters the angle of incidence required to create the SPR phenomenon (the SPR angle). This SPR angle is monitored as a change in the detector position for the reflected intensity dip (from I to II). By monitoring the SPR-angle as a function of time the kinetic events in the surface are displayed in a sensorgram.

The wavevector of the plasmon wave, k_{sp}, depends on the refractive indices of the conductor, n_{gold}, (being a constant complex number) and the sample medium, n_2, as $k_{sp} = (2*\pi/\text{wavelength})*(n_{gold}^2*n_2^2/(n_{gold}^2 + n_2))^{0.5}$. In both expressions the wavelength is the value for the light wave in vacuum. Thus, an increased refractive index of the sample, n_2, penetrated by the plasmon enhanced evanescent field increases the wavevector of the plasmon wave.

The wavevector of the light k_x can be tuned to equate the plasmon wavevector by varying either the angle of incidence, θ, or the wavelength of the light, Figure 2. The dielectric equations describing this dependence and the application of this technology are discussed in detail by Swalen [5], Kovacs [10], Kretschmann [11], Liedberg [12], Jönsson [13] and Davies [14].

The wavevector and energy match enables a resonant absorption of energy via the light-evanescent wave field, a plasmon excitation (SPR) causing a characteristic drop in the reflected light intensity. For a given wavelength of incident light, SPR is seen as a dip in the intensity of reflected p-polarized light at a specific angle of incidence (Figure 2).

In Biacore systems which use sensor chips, monochromatic light is focused in a wedge-shaped beam on the TIR interface and the angle of minimum reflectance intensity is determined using a two-dimensional detector array (see Figure 3). The low refractive index medium is the surface coating of the sensor chip and the "surrounding" sample solution.

Biomolecular interactions occurring at the sensor surface change the solute concentration and thus the refractive index within the evanescent wave penetration range. The angle of incidence required to create the SPR phenomenon (the SPR angle) is therefore altered and it is this change which is measured as a response signal.

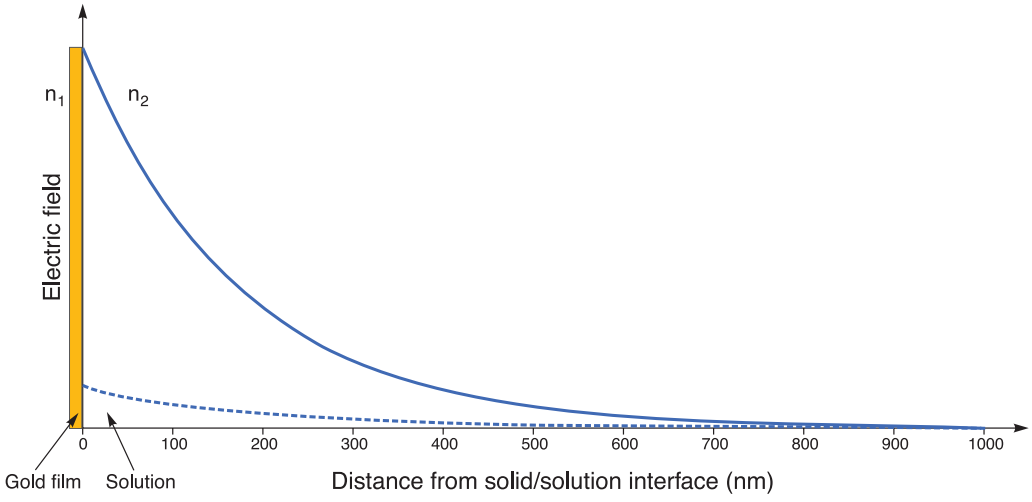

Figure 4. Relative evanescent electric field amplitude (E) versus distance to solid/solution interface (nm). Continuous line for SPR-evanescent wave (gold film), dashed line for non-absorbing TIR (no gold film).

In general, different proteins have very similar specific refractive index contributions, i.e. the refractive index change is the same for a given change in concentration (see Polymer Handbook[15]). Values for glycoproteins, lipoproteins and nucleic acids are of the same order of magnitude. SPR thus provides a mass detector which is essentially independent of the nature of the interactants. Most importantly, the technique requires no labelling of the interacting components, and the possibility of a mass detector is realized. Moreover, since it is the evanescent field wave and not the incident light that penetrates the sample, measurements can be made on turbid or even opaque samples. Sensitivity considerations for SPR have been discussed by Kooyman[16], and linear correlation between resonance angle shift and protein surface concentration has been shown by Stenberg[17].

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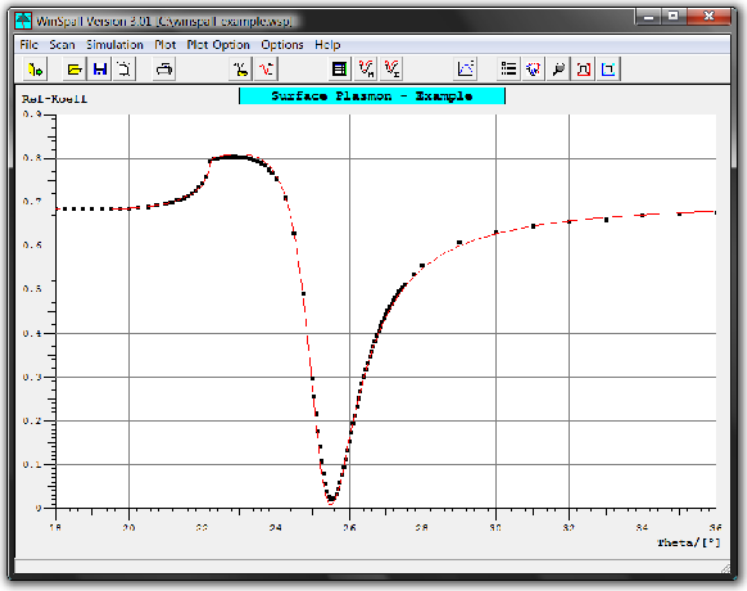
EXPLORE THE POWER OF EVANESCENT FIELDS

Surface Plasmon Resonance

Features of a SPR reflectivity curve

What influences the features of a surface plasmon resonance curve?



This little tutorial helps you understand the most important features of a SPR curve. We determine the features of such a curve and discuss all parameters that influence the “looks” of this curve. This will help you understand the data you measure.

By the way: The above plots were generated using WinSpall. Learn more about this SPR simulation software in our WinSpall tutorial (see www.res-tec.de).

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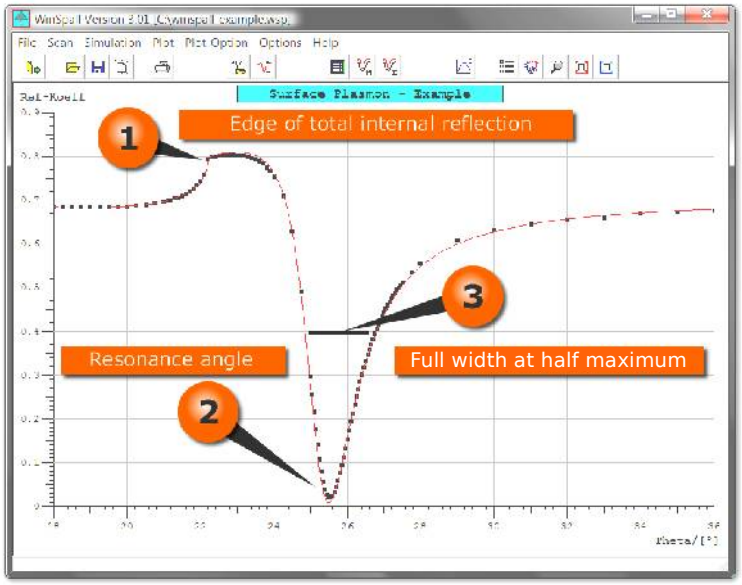
Surface Plasmon Resonance

Features of a SPR reflectivity curve

An overview



As we look at the plasmon resonance we can determine three different areas of interest:

1. The edge of total internal reflection. We will learn that this feature is not just there for some strange physical reasons: it is also an important feature to validate our measurement.
2. The resonance angle (or “the plasmon” itself). The actual angular position but also the depth will be important to learn something from “the plasmon”.
3. The full width at half maximum. Optical constants do matter. We will see how.

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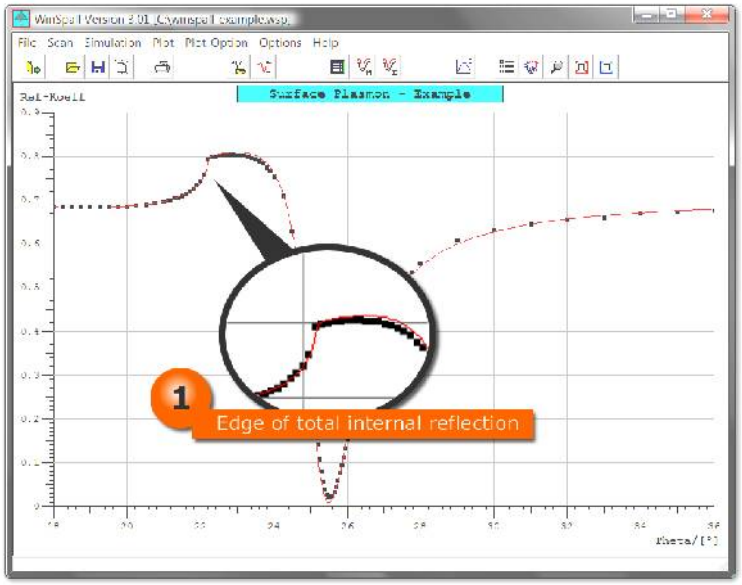
Surface Plasmon Resonance

Features of a SPR reflectivity curve

The edge of total internal reflection



The **edge of total internal reflection, Θ_c**. The position, i.e. the angle at which total reflection is found depends solely on the difference of the dielectric constants of the two infinite media – the prism and the cover medium, typically air or water. These values are known and, hence, Θ_c is fixed for a given system.

For this reason, this angle is an important value to validate correct sample alignment. Note, we sometimes try to measure very minute changes of the minimum position of the plasmon. It is important to crosscheck these small differences with neutral feature like Θ_c. We recommend to always include this region in any SPR experiment.

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Surface Plasmon Resonance

Features of a SPR reflectivity curve

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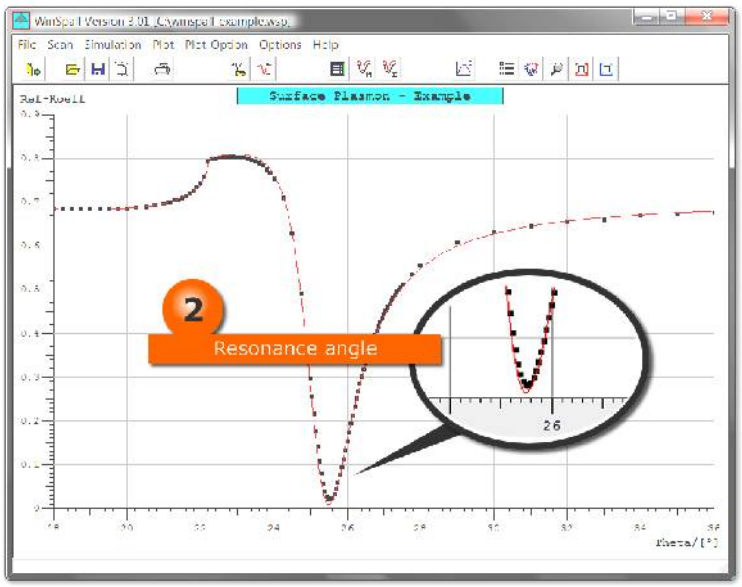
The resonance angle

The **resonance angle**. This is “our plasmon” – the quantity, we want to determine. In the absence of any film, its angular position is given by the optical constants of the prism, the surrounding medium, and the type of metal. Measuring the plasmon of such a “blank substrate” is important to determine exactly these parameters and use them later on for the analysis of the plasmon measured after layer deposition. The modeling of these reflectivity curves is then done using the parameters of the blank fit and adjusting only film related layer parameters.



Note, the plasmon must not always touch the zero line. This depends quite critically on the thickness of the metal layer. The closer this thickness is to 50 nm the “deeper” will the dip be.

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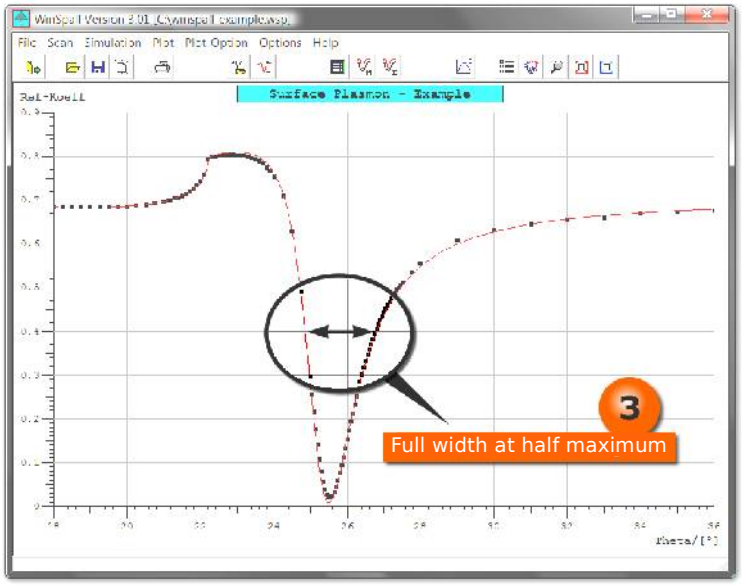
Surface Plasmon Resonance

Features of a SPR reflectivity curve

Full width at half maximum



The **full width at half maximum**. The “width of the plasmon” of a blank substrate depends on the imaginary part of the dielectric constant of the metal. This is why “silver plasmons” are much sharper, narrower than “gold plasmons”. For the blank measurement it is appropriate to adjust e'' such that the width of the model curve describes the measured data.

Most layers – if generated from organic molecules – do not absorb light at the typical SPR wavelength (red laser) and ε ''=0. Any broadening of the resonance curve is then typically caused by heterogeneities. In such cases the model calculation should capture the correct angular position of the plasmon and neglect the broadening.

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Note that these metals do show a metallic behavior (including in their optical properties) but are not expected to exhibit any plasmonic properties[4].

Among the other metals studied in Fig. 3.2, silver is the most promising one (and is in fact widely used for SERS and plasmonics). Gold and copper are also suitable, but only at longer wavelengths (typically more than ∼600 nm). At such wavelengths, the optical absorption of gold in fact becomes comparable to that of silver. Finally, lithium also exhibits suitable properties across the whole visible range, as silver, but has not been used much. Lithium reacts easily in water and does not occur freely in nature due to its chemical activity; it is therefore not very easy to be used as a plasmon-supporting material.

To these theoretical considerations, one should add the (very important) practical issues: availability, ease of manipulation, especially for the fabrication of nano-structures, toxicity, durability, cost, etc. Gold is certainly the most promising in these categories, and should therefore be the material of choice for applications beyond ∼600 nm (in the red and near IR). Silver, whose absorption is the smallest especially below ∼600 nm, can be used for large field enhancement applications (such as single-molecule detection). These two metals are by far the most widely used metals in plasmonics applications, including SERS.

Finally, it is interesting to remark that the conditions listed above also appear in other materials, but at different wavelengths. Similar effects are therefore expected, but are usually not considered as being part of the field of plasmonics. This is the case for example of doped semiconductors, whose conduction electrons result in a similar optical response as metals but with a plasma frequency in the far infrared (due to the smaller density of carriers). Another example is the optical response of phonons in ionic crystals, which also leads to negative $\mathrm{Re}(\epsilon)$, but again at much longer wavelengths. In this final case, plasmons do not even play a role, since the optical response is not dictated by free electrons but by phonons; the related effects may be referred to as 'phononics'.

3.3. WHAT ARE PLASMONS?

In the rest of this chapter, we will focus on plasmons and their relation to SERS and plasmonics.

3.3.1. The plasmon confusion

In the modern SERS literature (and in many other areas), many effects are attributed to plasmons or plasmon resonances, without further details about

[4] For example, SERS has been observed on these, but the enhancements are either 'chemical' (see Chapter 4) or small electromagnetic enhancements not arising from plasmon resonances.

what plasmons actually are. One can sometimes find a sentence or two about the origin of plasmons; the most common assertion being: 'plasmon resonances are due to collective charge oscillations of the free electrons of the metal'. However, there is hardly ever a real concern about these 'electron oscillations' in typical SERS studies. SERS enhancements are usually explained as an electromagnetic effect, not an electron oscillation effect. There seems to be a missing link between the electron oscillations and the large electromagnetic field enhancements. To add to this, the term plasmon is also used in contexts other than SERS; for example as a way to guide light (in a plasmonic waveguide) or in electron energy loss (EELS) experiments. Finally, adjectives are used in many cases to qualify the plasmons, in an attempt to clarify the situation. Examples of these are: surface plasmon, plasmon–polariton, radiative, non-radiative, propagating, and localized plasmons. Unfortunately, these terms are not always used consistently by authors or across disciplines (chemistry and physics in the first instance), and have even evolved over time to designate something different from what they were 40 years ago.

This general vagueness leads to numerous confusions about what plasmons are, which types of plasmons can be encountered, and what their respective importance is for applications such as SERS. This can be the source of frustration for people new to the field. The aim of the following discussion is therefore three-fold:

- Firstly, we will attempt to define clearly what plasmons are, and describe the different types of plasmons. Because of the confusion discussed above, some of the definitions and descriptions may however be slightly biased and not correspond exactly to the choices of other researchers.
- Secondly, we will highlight some of the most important applications of plasmons, including the main topic of this book which is SERS. We will emphasize in particular the different nature of plasmons used for different applications.
- Finally, one important message we wish to convey is that in most cases of interest to SERS and plasmonics, all plasmon-related effects can be understood as *electromagnetic effects*. The relation to the free electrons of a metal is only secondary (although important from a fundamental point of view). All information on plasmons, and plasmon resonances, is fully contained in the dielectric function and the geometry of a specific problem. **More precisely, the quantum physics of the electrons in the metal is contained in the dielectric function.**

3.3.2. Definition and history

Plasmons

The use of the term plasmon has evolved somewhat over the years, mainly because the types of experiments carried out on metals have changed. It is

however useful to look at the original definition of the term, which is still valid although it may now be used in a wider sense and in other frameworks.

The term plasmon was introduced by Pines in 1956 in the introduction of a review article [141] about collective energy losses. In Pines' work we find the following definition:

> The valence electron collective oscillations resemble closely the electronic plasma oscillations observed in gaseous discharges. We introduce the term 'plasmon' to describe the quantum of elementary excitation associated with this high-frequency collective motion.

A plasmon is therefore a quantum quasi-particle representing the elementary excitations, or modes, of the charge density oscillations in a plasma. Note that the study of these oscillations started earlier, even if they were not known or identified as plasmons [141]. We will come back to the notion of elementary excitations or modes of a system in the next section.

Although the term 'plasmon' is sometimes used in a broader context, the formal definition given above is the definition of reference. It draws its origin from quantum mechanics, even though we will see that quantum mechanics is, in fact, not necessary to study plasmons. A useful analogy to understand the meaning of this definition is to recall the formal definition of a photon: it is the quantum particle representing the elementary excitations, or modes, of the free electromagnetic field oscillations. *A plasmon is therefore simply to the plasma charge density what photons are to the electromagnetic field.* Many properties of photons can be studied within a classical framework, using Maxwell's equations. Similarly, many properties of plasmons can be studied within a classical description of the plasma and its interactions. There is, may be, a small difference in the vocabulary between plasmons and photons, but it is only artificial: people typically only use the term 'photon' when dealing with quantum aspects of the electromagnetic fields (such as absorption or emission by an atom). In classical situations, the term electromagnetic wave, or electromagnetic mode, is usually preferred. For reasons that are more historical than scientific, the term 'plasmon' tends to be used in all situations, quantum or classical, instead of equivalent (classical) denominations such as *charge density oscillations* . A more important and fundamental difference is that a photon is a real quantum particle while a plasmon is a *quasi-particle* because it is always *'lossy'* and highly interacting. A charge density oscillation, if not maintained by an external source of energy, will always decay because of various loss mechanisms (collisions, etc.).

Plasmon–polaritons

Another important type of elementary excitations, related to plasmons, is that of an electromagnetic wave propagating in a medium. By medium, we mean here an optically responsive medium (with a relative dielectric

No, a plasmon is a quasiparticle because it is an excitation of the many body electron gas and not a REAL single particle.

function $\epsilon \neq 1$ or relative magnetic permeability $\mu \neq 1$). From classical electromagnetism, it is known that such a situation can be described by Maxwell's equations for media, which introduce the notion of internal polarization, $\mathbf{P}$, or magnetization $\mathbf{M}$ (see Appendix C). These account for the fact that the electromagnetic wave excites the internal degrees of freedom of the medium (typically bound electrons in a dielectric). The energy of such a wave is therefore shared between the electromagnetic field oscillations (of $\mathbf{E}$ and $\mathbf{B}$), and the internal excitations of the medium (typically represented by oscillations of $\mathbf{P}$ and $\mathbf{M}$). The corresponding quantum particle is no longer a photon, but a photon coupled to the internal degrees of freedom of the medium. Such modes are usually called *polaritons*[5]. If the internal excitations of the medium are identified, then the polariton can sometimes be further qualified. For example, the optical response of an ionic crystal in the mid-infrared is dominated by the interaction of light with crystal vibrations (phonons). The electromagnetic waves in such a medium are then called phonon–polaritons (mixed photon–phonon modes). Similarly, the optical response of a metal in the visible and infrared is dominated by the interaction of light with the free-electron plasma. The electromagnetic waves in a metal are then called *plasmon–polaritons* (mixed photon–plasmon modes). As we shall see, SERS and plasmonics are mostly concerned with plasmon–polaritons, rather than 'pure' plasmon modes.

Surface Plasmon–polaritons

Finally, in 1957, shortly after the introduction of the term plasmon, Ritchie [143] predicted the existence of another family of plasma modes in thin films, corresponding to longitudinal charge density waves propagating at a metal/dielectric interface. This prediction was confirmed experimentally in 1959 [144] and these modes (once quantized) were called *surface plasmons* a year later in 1960 [145]. In fact, these surface plasmon modes were originally introduced [143] within the electrostatic approximation (to be treated in Section 5.1.4). If however retardation effects are not negligible, then these charge density waves cannot exist without being associated with a transverse electromagnetic wave (a photon). This then corresponds to a mixed mode where the energy is shared between the charge density wave (plasmon) and the electromagnetic wave (photon), and they should therefore be called *surface plasmon–polaritons*.

[5] The exact definition of a polariton remains a matter of choice. Some people reserve this name for media with a strongly resonant optical response (with phonons or plasmons for example), and keep the term photon for 'standard' dielectrics (with a constant relative dielectric function $\epsilon \neq 1$). However, strictly speaking, a photon corresponds only to an electromagnetic wave in vacuum, and it becomes a polariton in any media. See for example Ref. [142] for a detailed discussion on the nature of polaritons.

There is therefore a fundamental difference between plasmon modes and the surface plasmon modes as introduced by Ritchie [143]. Plasmons can exist either by themselves without mixing with a photon, or as a mixed plasmon–photon mode (plasmon–polariton). Surface plasmons however are always strictly speaking surface plasmon–polaritons (mixed modes). The 'pure' surface plasmon modes are only an approximation of a surface plasmon–polariton for which the photon contribution is small or negligible (for example in the electrostatic approximation). We will come back to this distinction later.

Bulk plasmons, oscillations of the electron gas, do not require photons.

3.3.3. The relation between plasmons and the dielectric function

The previous discussion in terms of elementary excitations and their quantization is useful to understand the origin of the term plasmon and the definition of the various types of plasmons. We will indeed come back to it shortly in more detail. However, one should bear in mind that plasmons and plasmon–polaritons are rarely viewed as quasi-particles, and are in fact mostly described as charge density oscillations (for plasmons), or electromagnetic waves in a medium (for plasmon–polaritons). *

The body of early work on plasmons in the late 1950s, both theoretical and experimental, was concerned primarily with electron energy loss (EELS) in metals, and not directly with the optical properties of metals themselves. The former relates more to the dynamics of the free-electron plasma by itself rather than to its interaction with an external electromagnetic field. However, this dynamics is partially governed by electromagnetic interactions within the electron gas and with its environment. Charges, static or moving, are sources of electromagnetic field and a charge density wave cannot exist without an associated electromagnetic (or at least electric) wave. Reciprocally, the optical response of the free electrons is determined by their dynamical properties. *The dynamics of the plasma is therefore intricately linked to its optical properties and both can be entirely described using the dielectric function of the metal.*

Depending on the context, it may therefore be useful to emphasize one aspect (charge density and free-electron-gas dynamics) or the other (optical response). In the case of plasmonics, and even more so for SERS, the 'optical response approach' is usually the most relevant. In this sense, *the only thing needed to study SERS and plasmonics effects with a given metal is a knowledge of its optical response described by a relative dielectric function* $\epsilon(\omega)$ (and possibly $\epsilon(\mathbf{k},\omega)$ if non-local effects are considered). One could then 'forget' about the fact that this optical response is the result of the free-electron dynamics, about the presence or not of charge and/or surface charge oscillations, or collective charge oscillations. Within this 'optical response approach', the plasmons and plasmon–polaritons can then simply be viewed as *electromagnetic modes* of the system under consideration. A detailed general discussion of electromagnetic modes will therefore be given in the rest of

*** This is because using Maxwell's equation and effective dielectric functions is infinitely easier than using quantum electrodynamics!**

Section 3.3. Its purpose is two-fold: firstly to show that plasmon-related effects are simply a specific class of a wider family of electromagnetic effects. Secondly, to introduce the terminology that is commonly used to qualify plasmon and plasmon–polariton modes. Note that this is somewhat a long theoretical digression in the fundamentals of plasmonics and it is possible to jump directly to the more practical aspects of plasmonics discussed in the rest of this chapter (Section 3.4 and beyond). In fact, this digression may be more digestible (and more useful) as a second read once the rest of the chapter has been understood.

3.3.4. Electromagnetic modes in infinite systems

The concept of elementary excitations or modes in infinite systems

The study of the elementary excitations or modes of a system is common in many areas of physics as part of linear response theory or Fourier analysis. In a nutshell, it consists in finding specific solutions (eigenvectors) of the physical system under study. In infinite systems with translational invariance, these solutions are propagating plane waves, i.e. solutions where all quantities (usually scalars like charge density, or vectors like electric field) have an oscillatory dependence (in space and time) of the form: $\cos(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)$, or in complex notation $\exp(\mathrm{i}\mathbf{k}\cdot\mathbf{r}-\mathrm{i}\omega t)$ (see Appendix C). Such solutions in general exist only for specific values (eigenvalues) of ω and $\mathbf{k}$. These solutions can usually be described by one or more *dispersion relations* $\omega(\mathbf{k})$. Each of the allowed solution with a given ω and $\mathbf{k}$ is then called an *elementary excitation or mode* of the system, and corresponds to a propagating plane wave. The reason why the modes are indexed here by their $\mathbf{k}$ vector is that the system is assumed to be invariant by translation in all directions.

When such a system is described in quantum mechanics, the elementary excitations are quantized, and they can be viewed either as plane waves, with frequency ω and wave-vector $\mathbf{k}$, or as particles with energy $\hbar\omega$ and momentum $\hbar\mathbf{k}$, linked by the dispersion relation $\omega(\mathbf{k})$. This step is, however, usually not necessary to discuss the classical properties of a system. Despite this, it is common to use the name of the quantum particle to designate the modes or elementary excitations, even when studied within a classical approach. This is in particular the case for plasmons.

Of course, the real excitations are quantized---the world is quantum mechanical!

Particles and quasi-particles

Many physical systems are affected by damping or losses in one form or another. In this case, a wave cannot propagate unchanged forever. Its amplitude must therefore decay in time and/or space. Such an excitation is called a *quasi-particle* (since it cannot exist 'forever' by itself). Note that plasmons are always quasi-particles (except in ideal non-absorbing metals).

WARNING: Again: this is not the physics definition of a quasiparticle!

Physics Definition: Virtual particles do not obey the dispersion relation; both the momentum (hbar k) and the energy (hbar omega) can be complex

This damping translates mathematically by the fact that ω and $\mathbf{k}$, which are related by the dispersion relation, cannot be both real for a quasi-particle. There are two possible points of view in this case:

- The first and most common approach is to consider ω real, which leads to $\mathbf{k}$ being complex. This implies an exponential decrease of the field amplitudes as $\exp(-(\mathrm{Im}(\mathbf{k}) \cdot \mathbf{r}))$. Such waves are called *evanescent waves or modes*, since they only propagate over a limited distance characterized by $1/|\mathrm{Im}(\mathbf{k})|$. The wave-vector for propagation is then $\mathrm{Re}(\mathbf{k})$.
- The second approach is to take $\mathbf{k}$ real, which leads to a complex frequency $\omega = \omega' - \mathrm{i}\omega''$ (with $\omega'' > 0$). This implies that the field amplitudes decay in time as $\exp(-\omega'' t)$ and such modes are then called *virtual modes* (this is the classical denomination, equivalent to a quasi-particle in the quantum point of view). The theory of virtual modes is common in nuclear and particle physics. These modes cannot exist as such (which is why they are called virtual), but they appear as resonances in the response of the system when the (real frequency) is equal to ω'. ω'' then characterizes the width of the resonance, or the lifetime of the virtual excitation ($\tau = 1/(2\omega'')$).

Both approaches are simply an attempt to represent *damped electromagnetic modes* or, from a quantum perspective, *quasi-particles*.

These two points of view are equivalent and which one is used depends on the exact physical situation and, in particular, on how the mode is excited:

- If an elementary excitation is maintained over time by an external source (acting in a given region of space, and driven at a given frequency ω), then it is logical to take ω real and $\mathbf{k}$ complex, and view the excitation as a wave decaying in space, i.e. an evanescent wave.
- If an elementary excitation is created at a given time by an external source (which is then switched off), then it is more logical to take ω complex and $\mathbf{k}$ real, and view the excitation as propagating in space but decaying over time, i.e. as a virtual mode. This point of view is also the only possible one for problems where $\mathbf{k}$ is not well defined (no translational invariance).

Finally, in infinite systems without losses and damping, elementary excitation can propagate 'forever' without decay in space and time. They are then called *propagating waves*, or from the quantum perspective, simply *particles*.

Longitudinal and transverse modes

One important concept for plasmon modes is that of longitudinal and transverse modes. A mode is described primarily by its frequency ω and

Physics Definition: They are particles if they are honest-to-god particles. They are quasiparticles if they are many body excitations that act like particles. For example, they will have quantized energy and momentum.

wave-vector $\mathbf{k}$, linked by the dispersion relation $\omega(\mathbf{k})$. If the oscillating quantity is a vector, as is the case for the electric field $\mathbf{E}$, then one can distinguish two situations in isotropic and homogeneous media:

- $\mathbf{E}//\mathbf{k}$ everywhere ($\mathbf{k} \times \mathbf{E} = 0$). This is then called a *longitudinal mode or wave.*
- $\mathbf{E} \perp \mathbf{k}$ everywhere ($\mathbf{k} \cdot \mathbf{E} = 0$), which then corresponds to a *transverse mode or wave.*

The origin of the name longitudinal and transverse is then clear; it refers to the orientation of $\mathbf{E}$ with respect to the direction of propagation $\mathbf{k}$. These definitions can also be extended mathematically to a general vector field $\mathbf{E}$, without the need for a wave-vector $\mathbf{k}$ (and therefore also valid in the absence of translational invariance):

- $\nabla \times \mathbf{E} = 0$ for a longitudinal field, and
- $\nabla \cdot \mathbf{E} = 0$ for a transverse field.

For a propagating mode, with a dependence on complex notation of the type $\exp(i\mathbf{k} \cdot \mathbf{r})$, this simply reduces to the previous simple definition in terms of $\mathbf{k}$. Finally, there is a theorem from vector analysis stating that any vector field can be decomposed (uniquely) into the sum of a transverse and a longitudinal field.

Electromagnetic modes in infinite (3D) vacuum – photons

One simple example of an infinite physical system is the electromagnetic field in vacuum. The electromagnetic modes are then derived easily from Maxwell's equations (see Section F.1). In particular, the equations $\nabla \cdot \mathbf{E} = 0$ and $\nabla \cdot \mathbf{B} = 0$ imply that $\mathbf{E}$ and $\mathbf{B}$ are transverse fields. The modes are then *transverse propagating plane waves* characterized by a wave-vector $\mathbf{k}$ and frequency ω, related by the dispersion relation: $\omega = c|\mathbf{k}|$. Each pair of real ω and $\mathbf{k}$ satisfying the dispersion relation corresponds to a *propagating electromagnetic mode.* After quantization, these modes can also be viewed as particles and are then called photons, but most of their properties can also be described classically using Maxwell's equations.

Electromagnetic modes in an infinite (3D) medium – polaritons

A similar situation occurs for transverse electromagnetic waves in a medium[6] with (local) relative dielectric function $\epsilon(\omega)$. The dispersion relation

[6] The media are always assumed to be non-magnetic (with relative magnetic permeability $\mu = 1$), unless otherwise stated.

is then modified to give (Eq. (F.2) in Section F.1):

$$\epsilon(\omega)\omega^2 = c^2\mathbf{k}\cdot\mathbf{k}. \tag{3.9}$$

Such an electromagnetic wave creates in the medium an internal polarization wave: $\mathbf{P} = \epsilon_0(\epsilon(\omega) - 1)\mathbf{E}$. These modes are then called polaritons because they couple transverse electromagnetic excitations (photons) with an internal polarization $\mathbf{P}$, which originates physically from internal excitations of the medium, such as excited bound electrons, phonons or plasmons. In non-absorbing dielectrics, such as glass, the polaritons are quantum particles similar in many ways to photons. For metals, in the region where the optical response is dominated by the free-electron plasma, these modes are usually called *bulk plasmon–polaritons* and are quasi-particles. Note that for these modes, $\mathbf{E}$ and $\mathbf{P}$ are transverse, and the internal charge density is therefore $\rho_{\text{int}} = 0$ everywhere. *There are no macroscopic charge density oscillations.* The denomination plasmon–polariton can be misleading in this respect since there is no net charge density wave, but only a polarization wave.

Longitudinal electric wave in an infinite (3D) medium

Finally, in an infinite medium, there is another family of electromagnetic modes that do not exist in vacuum. Maxwell's equations (C.27) – (C.27) state that the electric displacement $\mathbf{D} = \epsilon_0\epsilon\mathbf{E}$ is transverse: $\nabla\cdot\mathbf{D} = 0$. This condition was previously fulfilled by assuming that the electric field $\mathbf{E}$ was also transverse, but an alternative possibility is that $\epsilon(\omega) = 0$. Such a condition can be fulfilled in some media (and in particular in metals) at one or more specific frequencies ω. If this is the case, then $\mathbf{D} = 0$, and Eq. (C.27) implies that $\mathbf{H}$ is a longitudinal field. Because $\mathbf{H}$ is also a transverse field from Eq. (C.27), it must therefore be zero: $\mathbf{H} = 0$. The remaining equation (C.27) then implies that $\mathbf{E}$ is a longitudinal field. Such a solution therefore corresponds to a *longitudinal electric wave* (with zero magnetic field). This wave is associated with an internal polarization wave $\mathbf{P} = -\epsilon_0\mathbf{E}$ (since $\mathbf{D} = 0$). Moreover, because $\mathbf{P}$ is longitudinal, it also corresponds to an internal charge density wave $\rho_{\text{int}} = -\nabla\cdot\mathbf{P} \neq 0$. These modes therefore correspond to a *real charge density wave*, with an associated longitudinal electric wave. Because of the longitudinal nature of these modes (and of the structure of Maxwell's equations), these modes *cannot couple to light* or photons, which are transverse electromagnetic excitations. For metals, these modes are the 'pure' plasmon modes, as defined previously, and are usually called *bulk plasmons.*

In the local approximation, they exist only at specific frequencies for which $\epsilon(\omega) = 0$, and $\mathbf{k}$ can take any values (small enough for the local approximation to remain valid). For a more detailed non-local treatment, the dispersion relation of these modes is given by $\epsilon(\omega, \mathbf{k}) = 0$. Bulk plasmons are longitudinal modes and therefore do not couple to light.

- An incident photon can also couple to a bound mode provided ω (and if relevant $\mathbf{k}$) conservation is fulfilled. For virtual modes ($\omega = \omega' - \mathrm{i}\omega''$ complex), the ω conservation applies to real parts ($\omega = \omega'$) and is broadened with a width ω''. Similarly, for evanescent modes ($\mathrm{Im}(k) > 0$), the $\mathbf{k}$ conservation is broadened.

There are specific configurations where one electromagnetic mode may be excited, for example at a given incident angle, incident polarization, or wavelength. One then expects a resonant optical response (for example in reflectivity or absorption) when the parameters match the excitation condition of such a mode. When the electromagnetic modes are plasmons, or plasmon–polaritons, this is called a *plasmon resonance*. The nature and characteristics of such a resonance depends on the nature of the electromagnetic mode giving rise to it. The term *plasmon resonance* can, therefore, have different meanings depending on the context. It can, for example, correspond to enhanced energy loss at a specific electron beam energy, or to a decreased reflectivity at a specific incident angle on a surface, or to an increased field intensity at the surface (which can give rise to a SERS signal) at a specific wavelength, etc. In the context of SERS and plasmonics, plasmon resonances *refer in most cases to bound modes called surface plasmon–polaritons*, discussed in detail in Sections 3.4 and 3.5.

3.3.8. Summary and discussion

The somewhat formal discussion given in the last few subsections should hopefully become clearer when discussing specific examples in the following sections.

The various types of plasmon excitations are tentatively summarized in Fig. 3.5 along with their main properties. The *'pure' plasmon and surface plasmon modes*, as originally defined and studied by Pines [141], Ritchie [143], and others are not directly relevant to SERS and plasmonics because they do not interact with light[8]. This is because they correspond to *longitudinal* excitation of the electric field (electric wave) and cannot therefore couple to photons. These plasmons are also in fact those associated with true collective charge density oscillations.

The electromagnetic modes that interact with light are the *plasmon–polaritons*, which mix photons with internal excitations of the metal. *Bulk plasmon–polaritons* are those modes that exist in an infinite metal and can be viewed simply as photons propagating in a metal. These modes are again not directly relevant to SERS and plasmonics.

[8] They however play an important role in many other properties of metals and metal surfaces [129], in particular for other types of spectroscopies like Electron Energy Loss Spectroscopy (EELS).

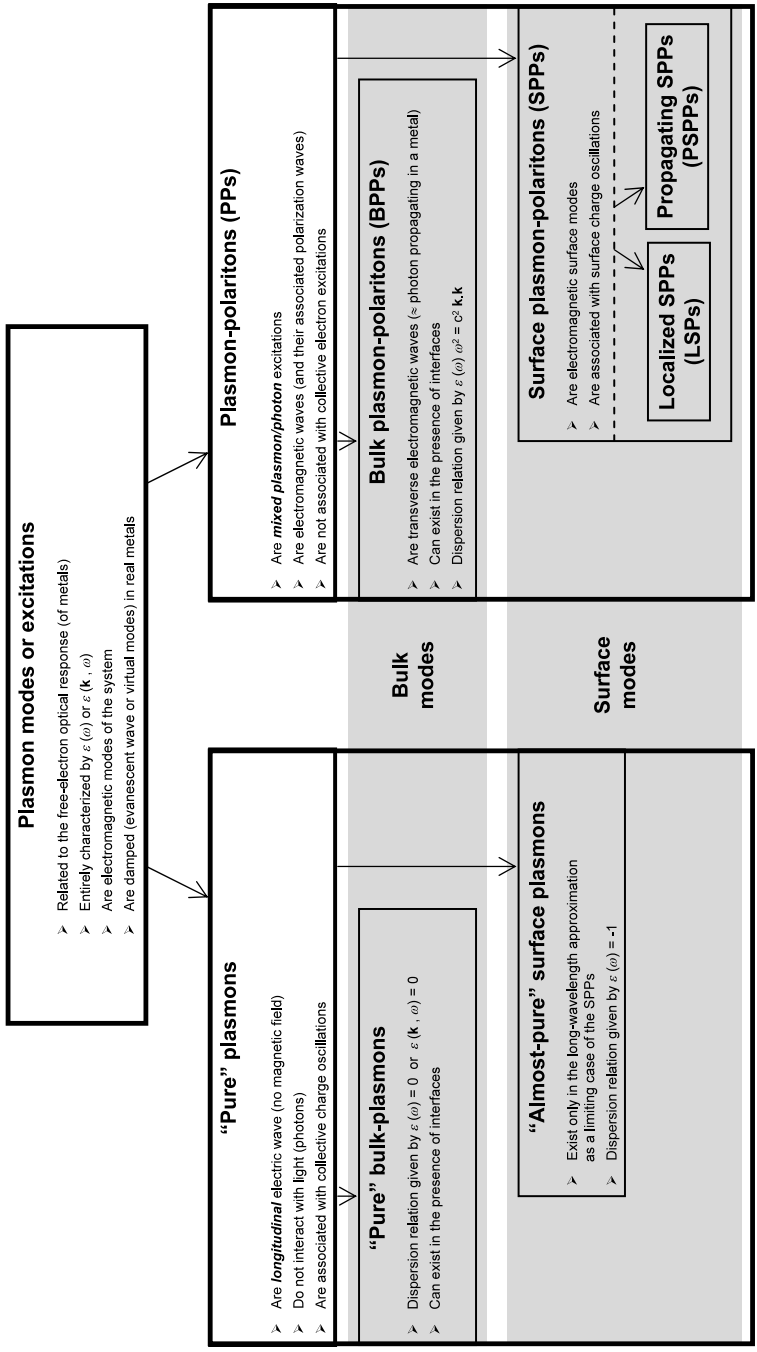

Figure 3.5. Schematic representation of the various plasmon types and their main properties.

The presence of an interface (typically metal/dielectric) gives rise to a new family of electromagnetic modes, which happens to be much more interesting for SERS and plasmonics. These additional modes are bound modes or *surface modes*, as described in the previous section in a more general context. In the case of metals, they are called *surface plasmon–polaritons* (SPPs) .

These electromagnetic surface modes are transverse inside and outside the metal (because $\epsilon \neq 0$). Note however that they do also have a longitudinal component because of the discontinuities at the interface, and are in this sense also partly longitudinal surface plasmon waves. A non-local description of ϵ, where the interface is no longer treated as a singularity, is necessary to identify clearly this mixed longitudinal–transverse nature, see for example Ref. [146]. The 'pure' longitudinal surface plasmons introduced by Ritchie [143] are simply a limiting case where the transverse contribution is negligible (in the electrostatic approximation). The strict decoupling between longitudinal ('pure' plasmons) and transverse (plasmon–polaritons) modes, which was natural for bulk modes in infinite media, is no longer possible for surface modes. Instead of introducing another terminology, these modes are simply called *surface plasmon–polaritons*.

Finally, let us note that there are typically three reasons (two good ones, and the last one partly flawed) that are put forward to justify the denomination of *surface* plasmon–polariton or *surface* mode:

- Firstly, they would not exist without the interface.
- Secondly, the characteristics of these modes depend not only on the optical properties of the metal, but also on that of the dielectric forming the interface.
- Finally, in many cases, these surface modes are localized at the interface (for example the electric field decays exponentially from it). This is however not really a good criterion, since as we will see later, for small metallic objects the electric field of such a surface mode can be almost uniform inside the object and extend infinitely outside (i.e. it is a radiative mode).

After this long digression, these SPP modes are finally the ones that are relevant to SERS and plasmonics. Whenever plasmons or surface plasmons as such are mentioned in a SERS context, it is arguably an abuse of language (although a very common one), and it is strictly speaking referring to surface plasmon–polaritons. As for general electromagnetic modes, these can come in several flavors: propagating, localized, radiating, non-radiating, bound, virtual, or evanescent. They can give rise to various resonance effects, which may be used for various applications. All these different cases will be the subject of the following sections, which focus on a more practical description of SPP modes in metals.

Although they can classified as SPPs, everyone just calls them surface plasmons. The important thing is what they are (what the physics is) not what they are called! They are coupled excitations of the electron gas and the electromagnetic field.