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Guillaume Baffou
Excerpt
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1 Nanoplasmonics

This introductory chapter deals with basic, general and important notions in nanoplasmonics that will be useful before entering the field of thermoplasmonics. The aim is to provide the reader with simple ideas and mathematical expressions that can be used to explain and understand the plasmonic response of metal nanoparticles.

The first section introduces the physics of the localized plasmon resonance for a dipolar spherical metal nanoparticle, for which closed-form expressions of the optical response exist. The section also describes what happens when enlarging the size of the nanoparticle or breaking its spherical symmetry. The second section explains why *gold* nanoparticles have been preferred in plasmonics compared with nanoparticles made of other materials. This second section also takes the opportunity to discuss a very recent branch of nanoplasmonics aiming to try and find alternative plasmonic materials. Finally, a third section introduces the field of thermoplasmonics by answering common experimental questions.

1.1 Localized Plasmon Resonance

1.1.1 Definitions

A *localized plasmon* (LP) is a normal mode of collective oscillation of the free electrons contained in a metal nanoparticle. A LP *resonance* can be excited using light when the electric field of the incoming light oscillates at a frequency close to the plasmon eigen frequency [49].

What I call a *localized plasmon* (LP) in this book is often coined *localized surface plasmon* (LSP) in the literature. I prefer to remove the word "surface" for the following reason. Apart from LP, there exist *bulk plasmons* (BP) and *surface plasmons* (SP). With a bulk plasmon, the excitation occurs in a metal extending over the three dimensions of space (3D). With a SP, the electronic oscillation occurs at the interface between a metal and a dielectric extending over two dimensions of space (2D). With a LP, the oscillation occurs in a space that is confined in all dimensions of space (0D). While "bulk" means 3D, "surface" means 2D, I find it appropriate to use the adjective "localized" to signify 0D, and not "localized surface."

In this book, I distinguish between the fields of *plasmonics* and *nanoplasmonics*. While plasmonics encompasses the physics of LPs and SPs, nanoplasmonics rather focuses on LPs; hence the title of this chapter.

In a striking coincidence, noble metal nanoparticles feature LP resonances in the UV–visible–NIR range, just like many aromatic compounds, although a metal nanoparticle has nothing to do with an organic molecule. This coincidence of Nature is responsible for the burgeoning activity of nanoplasmonics. Basically, due to this coincidence, metal nanoparticles can be advantageously put in standard optical microscopes with common light sources and detectors.

In the following sections, I will introduce basic notions of LP resonance starting from scratch and complicating the concepts step by step. I will successively discuss:

- the response of a metal sphere to a static electric field;
- the LP response of a dipolar sphere to a time-harmonic electric field;
- the LP response of large spheres and retardation effects;
- the LP response of particles of arbitrary morphology;
- the influence of the surrounding medium.

1.1.2 Dipolar Metal Nanoparticle

As usual in physics, the case of a sphere is simple and very instructive (see Figure 1.1). To introduce the physics of LP resonance, let us consider a metal sphere of radius a standing in a surrounding medium of refractive index $n_\mathrm{s} = \sqrt{\varepsilon_\mathrm{s}}$, along with a monochromatic incident illumination characterized by the electric field[1]

$$\mathbf{E}_0(\mathbf{r}, t) = \mathrm{Re}\left(\underline{\mathbf{E}}_0(\mathbf{r})\, e^{-i\omega t}\right), \tag{1.1}$$

an angular frequency ω and a wavelength in vacuum $\lambda = 2\pi c/\omega$. For a linearly polarized plane wave illumination, one has

$$\underline{\mathbf{E}}_0(\mathbf{r}) = \hat{\mathbf{u}}\, E_0\, e^{i\,\mathbf{k}\cdot\mathbf{r}} \tag{1.2}$$

where $\hat{\mathbf{u}}$ is the unit vector along the direction of the light polarization, and $k = 2\pi n_\mathbf{s}/\lambda$ is the norm of the wave vector $\mathbf{k}$. In the presence of the nanoparticle, the electric field at any location $\mathbf{r}$ reads

$$\mathbf{E}(\mathbf{r}, t) = \mathrm{Re}\left(\underline{\mathbf{E}}(\mathbf{r})\, e^{-i\omega t}\right). \tag{1.3}$$

Static Electric Field

Let us first consider a *static* applied electric field ($\omega \to 0$). The effect of the electric field is to displace the electrons from equilibrium, creating charge accumulation on the boundaries of the nanoparticle, as represented in Figure 1.2a. The magnitude of this charge displacement can be described by the dipolar moment $\mathbf{p}$ of the nanoparticle. $\mathbf{p}$ is collinear with the applied electric field and reads

$$\mathbf{p} = \varepsilon_0 \alpha \mathbf{E}_0. \tag{1.4}$$

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[1] In this chapter, underlined letters mean complex number quantities defined in the harmonic regime at the angular frequency ω; boldface letters correspond to vectors.

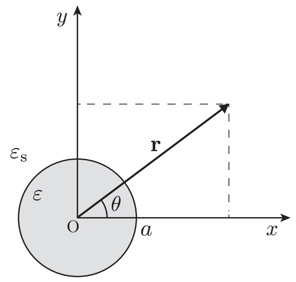

Fig. 1.1 Spatial description of the system under study: a spherical metal nanoparticle of relative permittivity ε in a dielectric medium of relative permittivity $\varepsilon_s = n_s^2$.

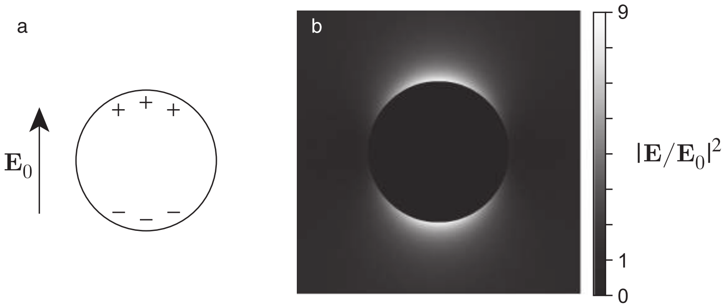

Fig. 1.2 (a) Representation of a spherical metal nanoparticle immersed in a static and uniform electric field. (b) Map of the normalized electric field intensity in the case of a metal sphere in vacuum.

α represents the polarizability of the nanoparticle and scales as a volume. For a metal sphere in a static electric field, one has

$$\alpha = 4\pi\varepsilon_s a^3 \tag{1.5}$$

$$\alpha = 3V\varepsilon_s \tag{1.6}$$

where $V = 4\pi a^3/3$ is the volume of the particle.

In such a simple problem, the electric potential surrounding the sphere reads in spherical coordinates [31]

$$\phi(r,\theta) = E_0\left(r - \frac{a^3}{r^2}\right)\cos\theta. \tag{1.7}$$

Using this expression of ϕ, the electric field can be calculated anywhere in the surroundings. In particular, one can show that it features a maximum value on the outer boundary of the sphere that is three times as big as the applied electric field intensity

$$E_{\max} = 3\,E_0 \tag{1.8}$$

This figure is independent of n_s and independent of the sphere radius. The total electric near-field *intensity* is thus nine times as big as the applied electric field intensity. Figure 1.2b plots the normalized electric field intensity $|\mathbf{E}/\mathbf{E}_0|^2$ calculated around a metal nanoparticle immersed in a static electric field, where a maximum value of 9 is evidenced at the vicinity of the nanoparticle, in the direction of the polarization of $\mathbf{E}_0$. The interest of discussing the static case is the following: strong enhancement of the electric near-field is a distinctive feature of metal particles. It occurs even out of the plasmonic resonance, like here in the static case. The effect of a plasmonic resonance will be to drive the near-field enhancement above this threshold value of 9.

In the static case, within the nanoparticle the electric field is rigorously zero, since it is cancelled out by the surface charges accumulated on its boundaries. But this feature no longer holds with non-static electric fields (see next subsection).

The charge separation depicted in Figure 1.2a is responsible for a restoring force within the nanoparticle that tends to move the charges back to their original stable configuration. As in many cases in physics, such a restoring force can be at the origin of a resonance effect (a LP resonance in our case), if the system is excited at the proper frequency. The excitation of a metal sphere with a time-harmonic electric field (*i.e.*, light) and the occurrence of a LP resonance is the purpose of the next subsection.

Time-Harmonic Electric Field (i.e., Light)

The occurrence of a LP resonance of the electronic gas at a given angular frequency ω stems from the restoring force acting between the positive and negative charges facing at each sides of the nanoparticle. For noble metal nanoparticles, such a resonance lies around optical frequencies ($\omega \sim 2\pi \times 10^{14}$ Hz). In this section we will only consider the quasistatic approximation, which assumes that the phase of the electric field oscillation is uniform in the nanoparticle, which amounts to neglecting retardation effects. This assumption is valid for nanoparticles much smaller than the wavelength ($ka < 1$). Within this approximation, one can consider the nanoparticle as a pure dipole (no multipolar term of the charge distribution) and simple closed-form expressions can be derived. In particular, the polarizability of a sphere with an electric permittivity $\varepsilon(\omega)$ reads [31, 55]

$$\boxed{\underline{\alpha} = 3\,V\,\varepsilon_s \frac{\underline{\varepsilon}(\omega) - \varepsilon_s}{\underline{\varepsilon}(\omega) + 2\varepsilon_s}.} \tag{1.9}$$

One can also define the enhancement factor $\underline{\xi}$

$$\boxed{\underline{\xi} = \frac{\underline{\varepsilon}(\omega) - \varepsilon_s}{\underline{\varepsilon}(\omega) + 2\varepsilon_s}} \tag{1.10}$$

which plays an important role in the physics of LP resonance. It represents the charge oscillation in the nanosphere in amplitude and phase. This is represented in Figure 1.3. The amplitude $|\underline{\xi}|$ equals 1 at low frequency (large wavelength) and features a resonance when the denominator of $\underline{\xi}$ reaches a minimum for a given angular frequency ω, *i.e.*, when $\mathrm{Re}(\underline{\varepsilon}) \approx -2\varepsilon_s$ (see Figure 1.3a). This situation is possible with metals, since they feature a negative value of the real part of their permittivity. Note that $|\underline{\xi}|$ does not diverge at the resonance due to the remaining imaginary part of $\underline{\varepsilon}$ in the denominator when $\mathrm{Re}(\underline{\varepsilon}) = -2\varepsilon_s$.

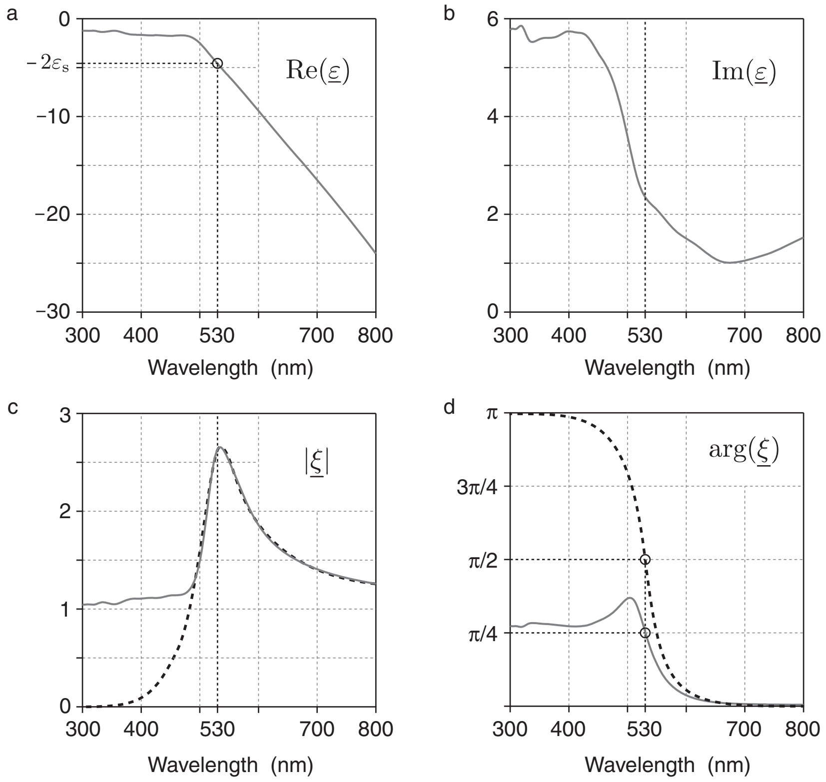

Fig. 1.3 (a) Real part of the permittivity of gold. The resonance wavelength (530 nm) of a dipolar gold sphere in water is indicated by a vertical dashed line. (b) Imaginary part of the permittivity of gold. (c) Norm of the enhancement factor $\underline{\xi}$. (d) Argument of the enhancement factor $\underline{\xi}$.

The static problem described in the previous section corresponded to $|\varepsilon| \to \infty$, *i.e.*, $\underline{\xi} = 1$. This is why $\underline{\xi} \to 1$ at large wavelength.

In general, the response of a resonator (like a spring-mass system) is universal. In particular, the phase delay at resonance is $\pi/2$ and the amplitude of the response vanishes at high excitation frequencies. This is not the case for a plasmon resonance. Figure 1.3c shows the response of a gold nanosphere (solid lines) compared to the response of a regular resonator (dashed lines). The plasmon resonance amplitude goes back to unity at high frequencies (small wavelengths), not to zero. This is due to the presence of another type of electron in the nanoparticles, which can be optically excited at higher photon energy (below $\lambda = 500$ nm) and which are mobile enough to screen the incoming field. These are the *d*-electrons of the metals as explained in the next section. The response of the nanoparticle when these *d*-electrons are not present is schematized by a dashed line in Figure 1.3c, which represents the response of a conventional resonator.

A similar unusual resonance behavior is observed in Figure 1.3d. The phase of the oscillation saturates at high frequencies (small wavelengths), whereas it normally approaches π for a normal resonance. The phase of the electronic oscillation *at resonance* is also not conventional. Instead of the usual $\pi/2$ delay in a resonance process, one has a reduced phase shift (see Figure 1.3d). For a gold nanosphere it is close to $\pi/4$, but this is a coincidence. Once again, this is due to the presence of mobile d-electrons that can be excited only with high photon energies. The phase response of the nanoparticle when these d-electrons are not present is schematized by a dashed line in Figure 1.3d.

The maximum amplitude of the electric field on the outer boundary of the sphere, which used to equal $3E_0$ in the static case, now reads

$$\underline{E}_{\max} = (1 + 2\,\underline{\xi})\,E_0. \tag{1.11}$$

Developing this expression highlights two terms: E_0, which is the incoming electric field, and $2\,\underline{\xi}\,E_0$, which is the near-field created by the charges of the nanoparticle, which superimposes constructively with the incoming field to yield a field enhancement. This term further evidences that $\underline{\xi}$ represents the electronic oscillation.

Another interesting quantity is the electric field observed *inside* the nanoparticle. While it was cancelled out by the charge accumulation in the static case, there is a nonzero electric field inside the nanoparticle, especially under plasmonic resonance. For a dipolar sphere, the inner electric field is uniform and equals

$$\underline{E}_{\mathrm{in}} = (1 - \underline{\xi})\,E_0. \tag{1.12}$$

Again, developing this expression highlights two terms: E_0, which is the incoming electric field, and $-\underline{\xi}\,E_0$, which is the screening field created by the charges of the nanoparticle, which superimposes destructively with the incoming field. From Equations (1.11) and (1.12), one can derive two useful parameters that quantify the enhancement of the electric field intensity outside and inside the nanoparticle [39]:

$$\eta_{\mathrm{out}} = |1\, +\, 2\underline{\xi}|^2 = 9\left|\frac{\underline{\varepsilon}}{\underline{\varepsilon}+2}\right|^2 \tag{1.13}$$

$$\eta_{\mathrm{in}}\ = |1\, -\, \underline{\xi}|^2\ = 9\left|\frac{1}{\underline{\varepsilon}+2}\right|^2. \tag{1.14}$$

The η values are important, first because they report on how a metal nanoparticle acts on the electric field, and then because they stand for universal dimensionless constants for a given metal, if considered at the plasmon resonance frequency ($\eta^{\mathrm{res}} = \eta(\lambda_{\mathrm{res}})$). For gold, one gets $\eta_{\mathrm{out}} = 19$ and $\eta_{\mathrm{in}} = 0.86$ when excited in vacuum at $\lambda = 526$ nm. Figure 1.4 plots the corresponding map of the electric field intensity. A maximum value of 19 is indeed observed on the outer boundary of the gold sphere. This map has to be compared with Figure 1.2b representing the map of the electric near-field in the static case, where a near-field enhancement of only 9 was obtained.

1.1.3 Band Energy Diagram of Metals

The excitation of d electrons is not beneficial in plasmonics as it increases loss (see the increase of $\mathrm{Im}(\varepsilon)$ in Figure 1.3b). This is why metals with fully occupied d-bands are preferred. Fully occupied bands necessarily lie below the Fermi level and can be optically excited only above a given photon energy. Figure 1.5a explains this effect by sketching the

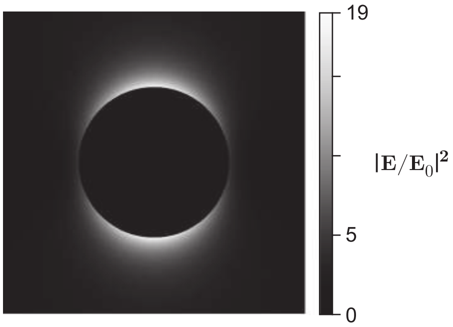

Fig. 1.4 Calculation of the normalized electric field intensity around a gold nanosphere in vacuum illuminated at its plasmon resonance frequency $\lambda = 526$ nm.

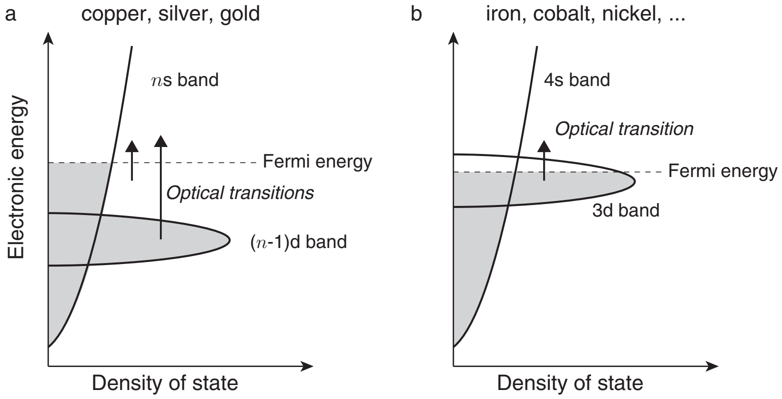

Fig. 1.5 (a) Schematic band energy diagram of metals of the 11th column of the Mendeleev's table, characterized by a fully occupied *d*-band. *d* electrons can be optically excited via an interband transition only above a certain photon energy threshold. (b) Schematic band energy diagram of metals featuring a partially occupied *d*-band, such as iron, copper, and nickel. *d* electrons can be excited by any photon energy.

band energy diagram of the family of elements corresponding to the 11th column of the Mendeleev's table, that is copper, silver and gold. *d*-bands of these materials are fully occupied, their electronic configurations being $4s^13d^{10}$, $5s^14d^{10}$ and $6s^15d^{10}$ respectively.

For metals with a partially occupied *d*-band, *d*-electrons can be excited for any photon energy, which creates additional non-radiative interaction and energy loss, detrimental in plasmonics (see Figure 1.5b).

1.1.4 Optical Cross Sections

The polarizability $\underline{\alpha}$ and the enhancement factor $\underline{\xi}$ of a nanoparticle are valuable parameters, since they render the nanoparticle response. However, they are usually not the parameters of interest in plasmonics. One usually prefers to deal with *optical cross sections*. The optical cross sections of a nanoparticle are directly related to the polarizability, but they are more useful since they can be used to estimate scattered or absorbed energies just from the knowledge of the light irradiance I (power per unit area). The absorption and scattering cross sections are defined such that the powers absorbed and scattered by the nanoparticle under plane wave illumination read:

$$P_{\mathrm{abs}} = \sigma_{\mathrm{abs}}\, I \tag{1.15}$$

$$P_{\mathrm{sca}} = \sigma_{\mathrm{sca}}\, I. \tag{1.16}$$

We also define the extinction cross section as the sum of the two above-mentioned cross sections:

$$\sigma_{\mathrm{ext}} = \sigma_{\mathrm{abs}} + \sigma_{\mathrm{sca}}. \tag{1.17}$$

Absorption cross sections can be defined for any particle interacting with light. For a dipolar sphere, they can be simply expressed as functions of the polarizability $\underline{\alpha}$ [53]:

$$\sigma_{\mathrm{sca}} = \frac{k^4}{6\pi}\, |\underline{\alpha}|^2 \tag{1.18}$$

$$\sigma_{\mathrm{ext}} = k\, \mathrm{Im}(\underline{\alpha}) \tag{1.19}$$

$$\sigma_{\mathrm{abs}} = \sigma_{\mathrm{ext}} - \sigma_{\mathrm{sca}}. \tag{1.20}$$

Figure 1.6 plots the extinction, absorption and scattering cross sections of a gold nanoparticle, 50 nm in diameter, in water. The line shapes are very similar to those of $\underline{\xi}$ (see Figure 1.3c), featuring a resonance around the same wavelength. However, the cross sections vanish at large wavelengths due to the factor k in their expressions.

For small spheres (typically smaller than 40 nm in diameter), $\sigma_{\mathrm{abs}} \gg \sigma_{\mathrm{sca}}$ and one can assume that $\sigma_{\mathrm{abs}} \approx \sigma_{\mathrm{ext}} = k\,\mathrm{Im}(\underline{\alpha})$. Still in this approximation, and using Equation (1.10), one can write the absorption cross sections as functions of the enhancement factor $\underline{\xi}$.

$$\sigma_{\mathrm{sca}} \approx \frac{8\pi}{3} k^4 \varepsilon_s^2 |\underline{\xi}|^2 a^6 \tag{1.21}$$

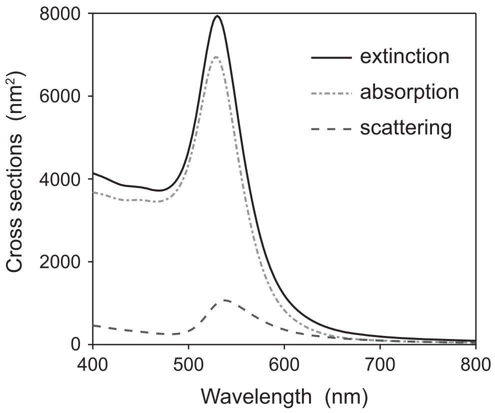

Fig. 1.6 Extinction, scattering and absorption cross sections of a 50 nm gold nanosphere in water.

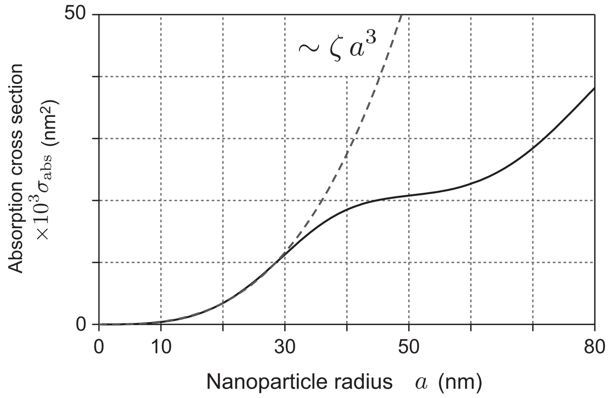

Fig. 1.7 Absorption cross section of a spherical gold nanoparticle in water as a function of its diameter (solid line) for an illumination wavelength of 532 nm. Fitting function for small diameter (dashed line). Reproduced with permission from Reference [52]. Copyright 2015, American Chemical Society.

$$\sigma_{\rm abs} \approx 4\pi\, \varepsilon_{\rm s} {\rm Im}(\underline{\xi}) a^3. \tag{1.22}$$

As a consequence, the absorption cross section of small spherical nanoparticles scales with the nanoparticle volume (a^3). This rule is valid for nanoparticles smaller than typically 60 nm, as observed in Figure 1.7. In this range of size, one can thus define a constant factor ζ such that the absorption cross section of a gold nanosphere reads

$$\sigma_{\rm abs} = \zeta\, a^3, \tag{1.23}$$

The use of this number avoids the need to conduct numerical simulations. For instance, for a gold nanosphere in water illuminated at 532 nm [52]:

$$\zeta = 0.430 \text{ nm}^{-1}. \tag{1.24}$$

1.1.5 Influence of the Particle Size: Retardation Effects

When increasing the size of a particle, the first trend will naturally be an increase of both the absorption and scattering cross sections. Interestingly, while absorption is dominant for small particles, scattering becomes more significant upon increasing the size of a particle since it scales as a^6, while absorption scales as a^3. For spherical gold particles in water, this transition occurs for a diameter $2a = 88$ nm, as represented in Figure 1.8a. For $2a = 88$ nm, the scattering and absorption cross section maxima are equal, as represented in Figure 1.8b. Note the small shift between the resonances in absorption and scattering. As a rule of thumb in plasmonics, the resonance wavelength in scattering does not necessarily match the one in absorption.

Another effect observed in larger particles is the red shift of the plasmonic resonance (see Figure 1.8c). This effect comes from the fact that the particle can no longer be considered as a point-like oscillating dipole. In the previous section, we considered that all the charges in the nanoparticle along with the inner electric field were uniformly oscillating in phase. This

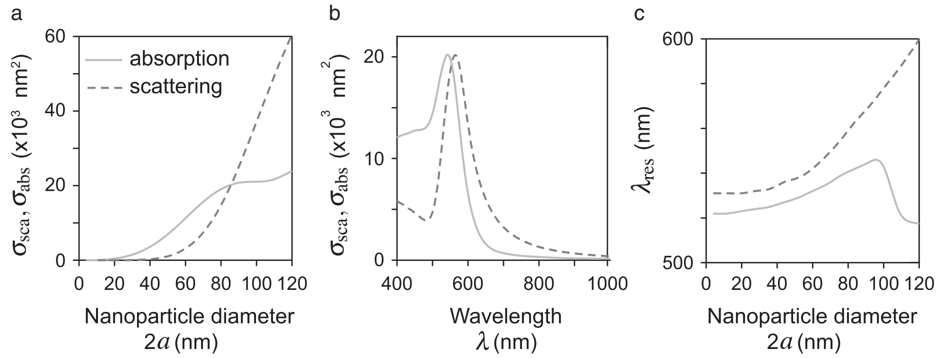

Fig. 1.8 Scattering and absorption cross sections of a gold sphere in vacuum calculated using Mie theory. (a) Plots of the cross sections as functions of the nanoparticle diameter, calculated at the resonance wavelength $\lambda_{\rm res}(a)$. (b) Plots as a function of the wavelength for a nanoparticle diameter $2a = 88$ nm. (c) Resonance wavelength $\lambda_{\rm res}(2a)$.

is the so-called quasistatic approximation. If the metal sphere is enlarged, such an ideal case no longer holds. First, if the particle size becomes of the order of the incoming wavelength, the exciting electric field $\mathbf{E}_0$ may be different in phase from one location to another, which will create some nonuniformities of the charge oscillation within the particle. But a finite wavelength λ is not what primarily invalidates the quasistatic approximation. Indeed, there is another typical length in this problem, the so-called plasmon wavelength, which is shorter than the incoming light wavelength. For gold, it is around 50 nm. If the particle is larger than this dimension, some retardation effects occur due to the electromagnetic interaction between distant charges within the particle. For this reason, for gold, the quasistatic approximation no longer applies for particles larger than typically 40–60 nm. Figure 1.8c plots the resonance wavelengths in absorption and scattering of spherical gold nanoparticles as functions of their radius, evidencing a rule of thumb in plasmonics: enlarging a nanoparticle red-shifts the plasmon resonance.

There is no simple analytical expression of the response of a metal sphere of arbitrary size. However, simple numerical simulations can be carried out using Mie theory, as described in Section 3.1, on page 81.

1.1.6 Influence of the Particle Morphology

We have seen that *enlarging* a particle could shift the plasmon resonance to the red, but it is not the most efficient strategy for playing with the resonance wavelength. With gold one can hardly shift the resonance above 600 nm, and the size of the nanoparticle cannot be arbitrarily increased for some applications, in particular for biomedical applications. The other strategy consists in deviating from a spherical shape. At least three categories of shape modification can be used to substantially red-shift the resonance:

- The most common approach to shift the resonance is to modify the *aspect ratio* of the nanoparticles [32], using rods or discs for instance, illuminated with a polarization along their longer dimension. Figure 1.9 plots absorption cross sections of a dipolar gold sphere