

Chapter 2

Theory

It is well known that light has the character of waves. Each electromagnetic (EM) wave propagates in space and time following the laws of electromagnetism, and consists of electric $\mathbf{E}(\mathbf{r}, t)$ and magnetic $\mathbf{B}(\mathbf{r}, t)$ fields oscillating in phase, perpendicular to each other and to the direction of propagation. The simplest form of EM wave is the *monochromatic plane wave*, as shown in Fig. 2.1, in which the $\mathbf{E}$ and $\mathbf{B}$ fields have the functional form of sinusoids, and that propagates along a fixed direction represented by its wave vector $\mathbf{k}$, with temporal period T and wavelength λ ; using the complex notation, we can write

$$E(\mathbf{r}, t) = E \exp [i (\omega t - \mathbf{k} \cdot \mathbf{r})] \quad (2.1a)$$

$$B(\mathbf{r}, t) = B \exp [i (\omega t - \mathbf{k} \cdot \mathbf{r})] \quad (2.1b)$$

As plane waves, the EM fields have the same amplitude and the same phase on each plane perpendicular to the direction $\hat{\mathbf{k}}$. The angular frequency ω and the wave number $\mathbf{k}$ are defined as

$$\omega = \frac{2\pi}{T} \quad (2.2a)$$

$$\mathbf{k} = \frac{2\pi}{\lambda} \hat{\mathbf{k}} \quad (2.2b)$$

The travelling velocity is $s = \omega/k = \lambda/T$, and in vacuum or air has the constant value $c \approx 3 \cdot 10^8$ m/s independent on λ or T .

Real light beams are not monochromatic, but are instead the superimposition (*wavepacket*) of several EM waves, having different periods and wavelengths. In these cases, the dispersion curve $\omega(k)$ describes how the frequency of the EM component of the beam is related to its wave number k ; in vacuum $\omega = ck$, while for propagation in dense media the relation is more complex. Since a wavepacket is composed of several waves propagating at different speeds, the term “wave velocity” is often ambiguous and can be defined in several ways. The *phase velocity* $v_p = \omega/k$ is the ordinary speed of any single component of the beam. The *group velocity*,

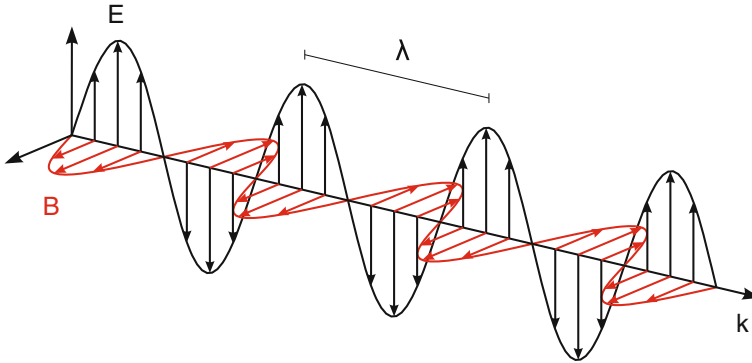


Fig. 2.1 Schematic representation of a plane monochromatic EM wave, linearly polarized, propagating along the direction defined by its wave vector $\mathbf{k}$. The electric $\mathbf{E}$ and magnetic $\mathbf{B}$ fields are in the vertical and horizontal planes, respectively

defined as $v_g = \partial\omega/\partial k$, is instead the velocity with which the overall envelope of the wavepacket propagates.

Equations (2.1) define the amplitudes of the EM fields in a plane wave, but do not specify their direction of oscillation. In general, the EM fields of the waves composing a light beam can be randomly oriented (perpendicularly to the direction of propagation), in which case the beam is said *unpolarized*. In contrast, when the state of oscillation of the EM fields, called *polarization*, is the same for all the components of the beam, light is said *polarized*. For a EM plane wave, three possible states of polarization can be defined, *linear*, *circular* and *elliptical*. For linear polarized light (Fig. 2.2a) the orientation of the electric fields is constant along a specific direction, so that, as the wave propagates, they oscillate in a fixed plane called polarization plane. Instead, when light is elliptically (Fig. 2.2b) or circularly (Fig. 2.2c) polarized the electric field vector viewed along the propagation direction describes an ellipse (or a circle) around its wave vector $\mathbf{k}$. The rotation is defined right-handed or left-handed when the observer sees the fields rotate counter-clockwise or clockwise, respectively.

2.1 Light and Matter

When light propagates inside a medium, its characteristics of propagation are modified by the interactions with the electrical charges of the material. From a microscopic point of view, each atom acts like a polarizable entity, which irradiates like a point dipole when excited by the oscillating electric field; the transmitted light is then determined by the superimposition of the incident radiation with the radiation emitted from all the atomic dipoles. Depending on the frequency of the exciting field, several mechanisms of polarization are possible (such as electric, atomic or orientational), and each of them is associated to a dielectric *polarizability* tensor α (frequency dependent), defined through the relation

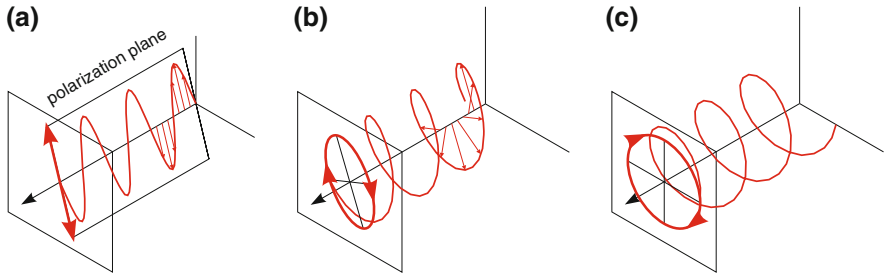


Fig. 2.2 Diagram of different states of polarization of light, and corresponding paths traced by the tip of the electric field vector (*red lines*). Panel **a** linear polarization, $\mathbf{E}$ oscillates along a constant direction. Panel **b** elliptical polarization, $\mathbf{E}$ traces an ellipse in each plane perpendicular the direction of propagation. Panel **c** circular polarization, special case of elliptical polarization where $\mathbf{E}$ traces a circle

$$\mathbf{p} = \varepsilon_0 \boldsymbol{\alpha} \otimes \mathbf{E} \quad (2.3)$$

where $\mathbf{p}$ is the induced electric dipole and $\mathbf{E}$ the exciting field; for isotropic polarization mechanisms, $\boldsymbol{\alpha}$ reduces to a constant and $\mathbf{p}$ and $\mathbf{E}$ are parallel. The *electric displacement field* $\mathbf{D}$ is defined as the sum of the exciting electric field and of the dipole density $\mathbf{P}$, and is proportional to the *complex dielectric constant* (or *complex dielectric function*) $\varepsilon \equiv \varepsilon_1 - i\varepsilon_2$:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \varepsilon \mathbf{E} \quad (2.4)$$

The complex dielectric function ε for a dense medium in general is a strong function of the radiation frequency, and contains all the information on the microscopic interactions between light and matter.

From the macroscopic point of view, the propagation of light in matter is characterized, in general, by a gradual decrease of the EM fields amplitude with the increasing distance travelled inside the dense medium (a phenomenon known as light *absorption*), and by the appearance of a frequency-dependent speed $s(\omega)$ of the propagating EM fields (a phenomenon known as light *dispersion*). These effects can be accounted for by the *complex refractive index* $\tilde{n}$, written as

$$\tilde{n} = N - iK \quad (2.5)$$

where

$$N = \frac{c}{s} \quad (2.6)$$

is the classic *refractive index* and K is the *extinction coefficient*.

The wave number inside a dense medium is redefined as

$$\mathbf{k} = \frac{\omega}{s} \hat{\mathbf{k}} = \frac{N\omega}{c} \hat{\mathbf{k}} \quad (2.7a)$$

or in the complex form

$$\tilde{\mathbf{k}} = \frac{\tilde{n}\omega}{c} \hat{\mathbf{k}} = \frac{\omega}{c} (N - iK) \hat{\mathbf{k}} \quad (2.7b)$$

The expressions (2.1) for the EM fields amplitudes then rewrite

$$E(\mathbf{r}, t) = E \exp \left[i \left(\omega t - \tilde{\mathbf{k}} \cdot \mathbf{r} \right) \right] \quad (2.8a)$$

$$B(\mathbf{r}, t) = B \exp \left[i \left(\omega t - \tilde{\mathbf{k}} \cdot \mathbf{r} \right) \right] \quad (2.8b)$$

from which, separating the real and imaginary part of the complex wave number, we obtain

$$\begin{aligned} E(\mathbf{r}, t) &= E \exp \left(-\frac{\omega K}{c} \hat{\mathbf{k}} \cdot \mathbf{r} \right) \exp [i (\omega t - \mathbf{k} \cdot \mathbf{r})] \\ &= E \exp \left(-\frac{\alpha}{2} \hat{\mathbf{k}} \cdot \mathbf{r} \right) \exp [i (\omega t - \mathbf{k} \cdot \mathbf{r})] \end{aligned} \quad (2.9)$$

The *absorption coefficient*

$$\alpha = \frac{2K\omega}{c} = \frac{4\pi K}{\lambda} \quad (2.10)$$

is defined as the fraction of power absorbed per unit length, as expressed by the *Beer law* $I(z+d) = I(z) e^{-\alpha d}$, where $I(z)$ and $I(z+d)$ are the intensities (optical power per unit area) at positions z and $z+d$. Then, we can see that the refractive index N and the extinction coefficient K are responsible, respectively, for the propagation of light and for the exponential decrease of the EM fields amplitudes.

For isotropic non-magnetic media, the complex refractive index and the dielectric constant are related by the simple expression

$$\varepsilon = \tilde{n}^2 \quad (2.11)$$

or equivalently for the real and imaginary parts

$$\varepsilon_1 = N^2 - K^2 \quad (2.12a)$$

$$\varepsilon_2 = 2NK \quad (2.12b)$$

and

$$N = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}} \quad (2.12c)$$

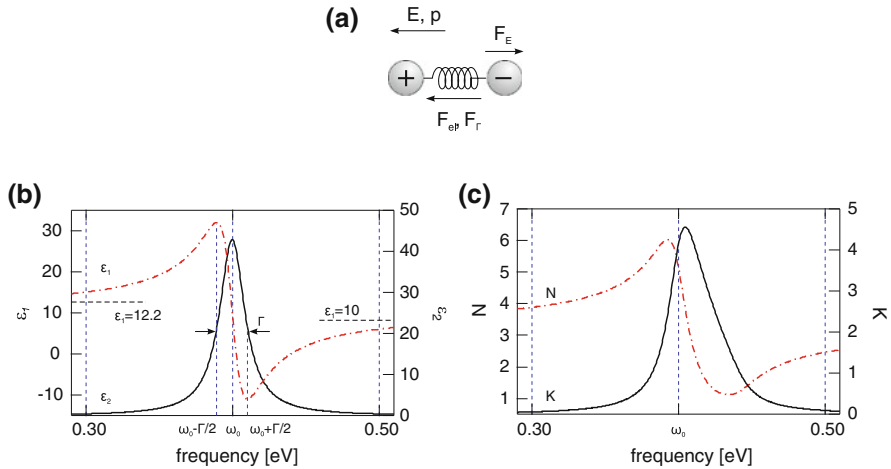


Fig. 2.3 *Top panel* physical representation of the Lorentz oscillator; when displaced by the application of an external electric field $\mathbf{E}$, the positive and negative atomic charges attract each other by an elastic restoring force $\mathbf{F}_{el}$, and their motion is damped by a viscous force $\mathbf{F}_\Gamma$. *Bottom panels* frequency dependence of the real and imaginary parts of the complex dielectric function (*left panel*) and refractive index (*right panel*), calculated according to the Lorentz model (2.13) ($\chi = 9$, $A = 0.36$, $\omega_0 = 0.4 \text{ eV}$, $\Gamma = 20 \text{ meV}$) at frequencies close to resonance

$$K = \sqrt{\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \varepsilon_1}{2}} \quad (2.12d)$$

2.1.1 Dipole Oscillator Model

As seen before, the dielectric constant can be put in relation with the microscopic characteristics of the dense medium. In this section, we will therefore shortly discuss the main features of the microscopic mechanisms that govern the light-matter interactions. In general, the functional form of ε is quite complex, as several kinds of polarizations can be induced. When an analytical representation is required, the usual approach is therefore to decompose and analyse the individual contributions, and then merge the results. In this respect, several models have been proposed, suitable to describe the specific properties of the samples. The *dipole oscillator* or *Lorentz model* follows from the classical theory of absorption and despite its simplicity it offers a good picture of the polarization mechanisms.

According to this model, when an atom is irradiated by an external electric field it behaves like a damped harmonic oscillator (Fig. 2.3a): the exciting field displaces the positive nucleus from the negative electronic cloud, inducing an electric dipole; the charges, being separated, attract each other with a restoring force proportional to

the displacement, realizing an oscillator; during the motion of the electrical charges under the influence of the fields, several energy losses can occur, like collisions with other atoms or spontaneous emission, effectively providing a damping mechanism for the oscillator.

The complex dielectric constant of a single Lorentz oscillator can be written as

$$\varepsilon^L(\omega) = 1 + \chi + \frac{A}{\omega_0^2 - \omega^2 + i\Gamma\omega} \quad (2.13)$$

where ω is the frequency of the exciting field, ω_0 the resonance frequency, Γ the damping rate, A a constant related to the electrons mass and density and χ is the susceptibility accounting for all the other contributions to the polarizability. The frequency dependence of the real and the imaginary parts of ε^L is plotted in Fig. 2.3b. ε_2^L is zero everywhere except near the resonance where a characteristic (*lorentzian*) peak is present, with full width at half maximum (FWHM) equal to Γ . ε_1^L , instead, has a more complex trend; at low frequencies it has a constant value of $1 + \chi + A/\omega_0^2$, then, approaching the resonance, it gradually rises up to a maximum at $\omega_0 - \Gamma/2$, it falls sharply to a minimum at $\omega_0 + \Gamma/2$, and it rises again, towards the high frequencies limit of $1 + \chi$.

Using the real and imaginary parts of (2.13), we can apply (2.12) to calculate the corresponding refractive index and extinction coefficient, as shown in Fig. 2.3c. Comparing Fig. 2.3b, c, we see that N is very similar to ε_1^L while K is peaked around $\approx \omega_0$ like ε_2^L . Indeed, if ε_2^L were much smaller than ε_1^L , it would follow $N \approx \sqrt{\varepsilon_1^L}$ and $K \approx \varepsilon_2^L/2\sqrt{\varepsilon_1^L}$. This correspondence, however, is only valid for gaseous phases, where the density of atoms is very low, while for solids it is only approximate because the absorptions are very strong; nevertheless, the absorption peak is generally observed at a frequency very close to ω_0 .

Equation (2.13) can be generalized to include the contributions of several concomitant resonances occurring in the same medium at different frequencies, writing:

$$\varepsilon(\omega) = 1 + \sum_j \frac{A_j}{\omega_{0j}^2 - \omega^2 + i\Gamma_j\omega} \quad (2.14)$$

where j is the index numbering the (supposed discrete) oscillators of the medium. The overall frequency dependence of the dielectric constants according to Eq. (2.14) is schematically shown in Fig. 2.4.

This classical picture of the interaction between light and matter offers a simple physical interpretation of the dielectric constant. Looking at Fig. 2.4, we can identify parts where ε_1 is slowly varying and ε_2 is almost null, and regions where ε_1 rapidly changes and ε_2 has a maximum. Moreover, every time a resonance is crossed, moving from low to high frequencies, the average value of ε_1 decreases, approaching the value of 1 beyond the last oscillator. This can be understood in terms of polarizability of the material: considering a single mechanism of polarization, the atoms can follow the external field, i.e. the medium can be polarized, only up to the resonance fre-

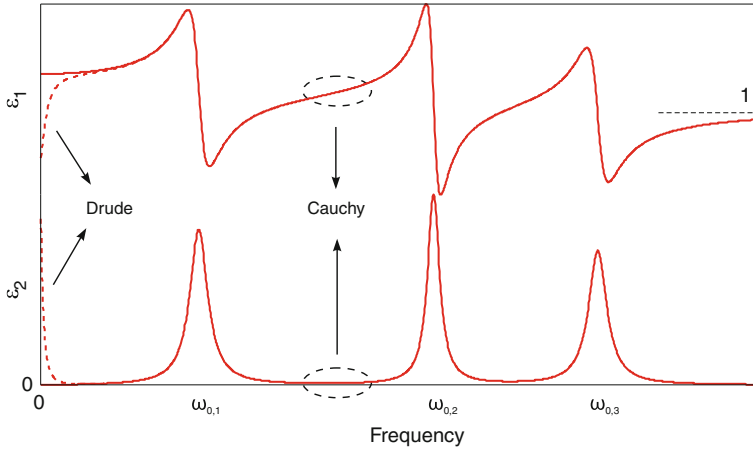


Fig. 2.4 Schematic diagram of the frequency dependence of the dielectric function of a hypothetical solid with three resonant frequencies ($\omega_{0,i}$). The Drude contribution is sketched in *dashed lines* at the lowest frequencies; an example of region of validity of the Cauchy parametrization is highlighted at the center of the figure

quency, where the polarization is maximum; at higher frequencies the field varies too fast and the average polarization reduces to zero. At very high frequencies, no polarization is more possible, and the material becomes completely transparent.

Drude Model for Free Electrons

The dipole oscillator model remains valid also to describe the free electrons in metals or the free carriers in semiconductors. These charges are not bound to the atoms nuclei, and therefore do not experience any restoring forces. Then, they can be treated as Lorentz oscillators with $\omega_0 = 0$, having dielectric constant (from (2.13))

$$\varepsilon(\omega) = 1 + \frac{A}{i\Gamma\omega - \omega^2}$$

This is usually rewritten in the form

$$\varepsilon_{Drude}(\omega) = 1 - \frac{\omega_P^2}{\omega^2 - i\Gamma\omega}, \quad (2.15)$$

known as the *Drude* dielectric function (Fig. 2.4).

According to the Drude-Sommerfeld model, the valence electrons in metals are considered as free particles, which do not interact with each other but can only undergo instantaneous collisions, with a characteristic scattering time $\tau = \Gamma^{-1}$. The sources of scattering can be various, for example impurities, defects or other electrons; if the mechanisms are independent from each other, the collision times

sum up according to the Matthiessen's rule:

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i} \quad (2.16)$$

The scattering time τ defines also a *mean free path* between subsequent collisions, given by $\lambda_{mfp} = v_F \tau$, where v_F is the Fermi velocity.

The quantity ω_P in (2.15) is known as the *plasma frequency*, and within the Drude model is given by

$$\omega_P = \sqrt{\frac{4\pi n e^2}{m}} \quad (2.17)$$

where n and m are the electron density and effective mass. It corresponds to the natural frequency of the free electrons charge density oscillations, i.e. periodic displacements of the free electrons gas as a whole. These excitations are called *plasmons*, and can be extended on the whole volume of the crystal or can be confined to the surface (*surface plasmons*). In addition, metallic structures with typical size of $1\text{--}10^2$ nm can also sustain *localized surface plasmons*; they will be discussed in Sect. 2.3.

Sellmeier and Cauchy Models

Since in this thesis we will deal with transparent materials, we report here two useful approximations of the Lorentz model commonly used to describe the optical properties of materials in the transparent regions of the EM spectrum.

The *Sellmeier model* is derived from the Lorentz model (2.13) for $\omega \ll \omega_0$, assuming $\varepsilon_2 \approx 0$ and $\Gamma \rightarrow 0$. Rewriting (2.13) in terms of the wavelength ($\omega/c = 2\pi/\lambda$) we obtain

$$\varepsilon(\lambda) = \varepsilon_1(\lambda) = 1 + \frac{A}{(2\pi c)^2} \frac{\lambda_0^2 \lambda^2}{\lambda^2 - \lambda_0^2} \quad (2.18)$$

with $\lambda_0 = 2\pi c/\omega_0$. Then, the Sellmeier dielectric constant is written as

$$\varepsilon_1(\lambda) = N^2(\lambda) = A + \sum_j \frac{B_j \lambda^2}{\lambda^2 - \lambda_0^2}, \quad \varepsilon_2(\lambda) = 0 \quad (2.19)$$

where A and B_j are numerical parameters.

The *Cauchy model* is a further approximation of the Sellmeier model, obtained from the series expansion of (2.18):

$$N(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \dots, \quad K(\lambda) = 0 \quad (2.20)$$

Kramers-Kronig Relationships

We conclude this section with an important consideration on the relation between the real and the imaginary parts of the complex dielectric function ε . Discussing the Lorentz model, we have seen qualitatively that ε_1 and ε_2 are not independent parameters but are related to each other. This is indeed a true property of ε , which follows from the principle of causality. In fact, from the definition (2.4) we can write the polarization of the medium as $P = \varepsilon_0(\varepsilon - 1)E$, which explicitly shows that $\varepsilon(\omega) - 1$ is the response function for the application of electric fields. Therefore, we can apply the laws of causality and derive the general *Kramers-Kronig* (KK) relationships between the real and the imaginary parts of $\varepsilon(\omega)$ (but also of the complex refractive index $\tilde{n}(\omega)$):

$$\varepsilon_1(\omega) = 1 + \frac{1}{\pi} \mathbf{P} \int_{-\infty}^{\infty} \frac{\varepsilon_2(\omega')}{\omega' - \omega} d\omega' \quad (2.21a)$$

$$\varepsilon_2(\omega) = -\frac{1}{\pi} \mathbf{P} \int_{-\infty}^{\infty} \frac{\varepsilon_1(\omega') - 1}{\omega' - \omega} d\omega' \quad (2.21b)$$

where $\mathbf{P}$ indicates the principal value of the integral.

The KK relations can be very useful because they allow, for example, to calculate the dispersion of the dielectric constant and of the refractive index by measuring the frequency dependence of only the optical absorption. They also provide a tool for checking the physical consistency of the dielectric constant approximations. For example, the Lorentz and Drude expressions for $\varepsilon(\omega)$ satisfy the KK relations, contrarily to the Sellmeier and Cauchy parametrizations, where $\varepsilon_2(\omega) = 0$ and $K(\lambda) = 0$ are not physically reasonable.

2.1.2 Light Refraction

When EM waves travel in homogeneous media they propagate according to (2.8), maintaining constant direction, frequency and wavelength. Instead, when light crosses different materials, it experiences a discontinuity of the refractive index, which strongly affects its propagation. As a consequence of this two main effects are observed (*refraction* of light): the transmitted beam propagates along a different direction and with a different wavelength, and a reflected beam is generated. This is illustrated in the following example.

Let us consider a flat interface between two media a and b with complex refractive indices $\tilde{n}_a$ and $\tilde{n}_b$; an EM wave is approaching from a at an angle θ_i with respect to the surface normal, while the reflected and the transmitted waves leave at angles θ_r and θ_t (Fig. 2.5). (In the following the subscripts i , r and t will be used for the

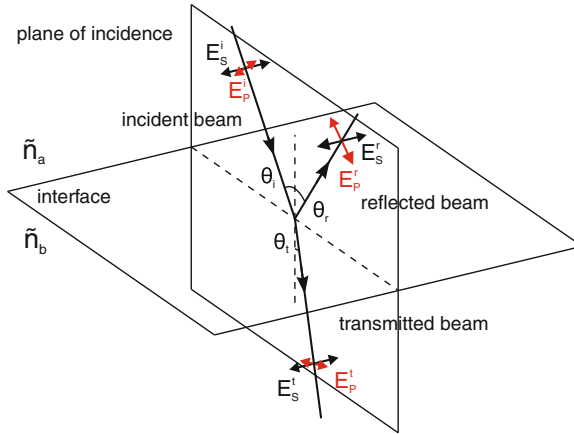


Fig. 2.5 Schematic representation of reflection and refraction of a monochromatic plane wave at the interface between two isotropic materials a and b

incident, the reflected and the transmitted beams, respectively). All the three beams are contained in the same plane, called the *plane of incidence*.

The refraction of light is usually computed imposing the continuity of the components of the EM fields at the interface, as follows from the Maxwell's equations. Requiring the equality of the phases ($\omega t - \mathbf{k} \cdot \mathbf{r}$) we obtain that the three beams have the same frequency ($\omega_i = \omega_r = \omega_t$), and that the reflected beam leaves at a direction specular to the incident one ($\theta_r = \theta_i$); the transmitted beam instead follows the *Snell law*:

$$N_a \sin \theta_i = N_b \sin \theta_t \quad (2.22)$$

The continuity of the amplitudes depends on the orientation of the EM fields, so usually two different directions are chosen as reference, the so-called p and s ; they are defined, respectively, as the components of the EM fields parallel and perpendicular (*senkrecht* in German) to the plane of incidence, as sketched in Fig. 2.5. Employing this notation, we obtain the following *Fresnel coefficients*, defined as the ratios between the amplitude of the electric field associated to the reflected or transmitted beam to that associated to the incident beam:

$$r_s = \frac{E_p^r}{E_p^i} = \frac{\tilde{n}_a \cos \theta_i - \tilde{n}_b \cos \theta_r}{\tilde{n}_a \cos \theta_i + \tilde{n}_b \cos \theta_r} \quad (2.23a)$$

$$r_p = \frac{E_s^r}{E_s^i} = \frac{\tilde{n}_b \cos \theta_i - \tilde{n}_a \cos \theta_r}{\tilde{n}_b \cos \theta_i + \tilde{n}_a \cos \theta_r} \quad (2.23b)$$

$$t_s = \frac{E_s^t}{E_s^i} = \frac{2 \tilde{n}_a \cos \theta_i}{\tilde{n}_a \cos \theta_i + \tilde{n}_b \cos \theta_r} \quad (2.23c)$$

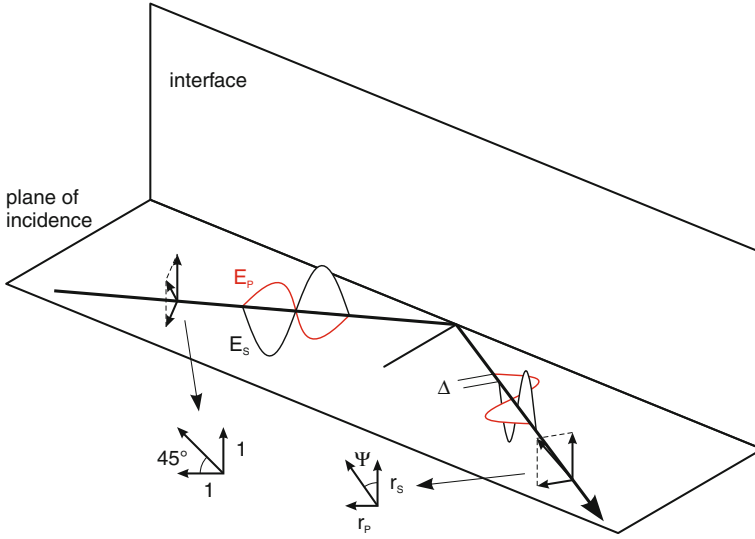


Fig. 2.6 An interpretation of Ψ and Δ upon reflection of a linearly polarized monochromatic beam at an interface between two media. The incident beam has two equally large s and p components. The p component experiences a reflection coefficient r_p , the s component a reflection coefficient r_s (adapted from Ref. [1])

$$t_p = \frac{E_p^t}{E_p^i} = \frac{2 \tilde{n}_a \cos \theta_i}{\tilde{n}_b \cos \theta_i + \tilde{n}_a \cos \theta_r} \quad (2.23d)$$

These coefficients are complex numbers, because the refraction modifies both the amplitudes and the phases of the fields.

The corresponding relations for the intensities, called *reflectance* and *transmittance*, are given by

$$R_{p,s} = |r_{p,s}|^2 \quad (2.24a)$$

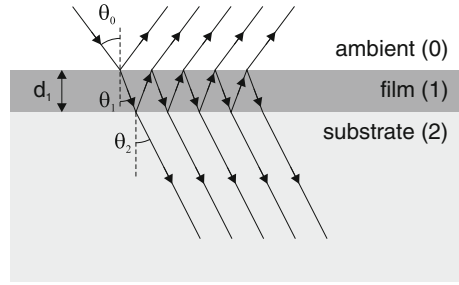
$$T_{p,s} = \frac{N_b \cos \theta_t}{N_a \cos \theta_i} |t_{p,s}|^2 \quad (2.24b)$$

As we will see later, other useful coefficients to describe the reflection of light from a surface are the so-called ellipsometric angles Ψ and Δ , defined through the polar form [2]

$$\rho = \tan \Psi e^{i\Delta} = \frac{r_p}{r_s} = \frac{|r_p| e^{i\delta_p}}{|r_s| e^{i\delta_s}} = \frac{|r_p|}{|r_s|} e^{i(\delta_p - \delta_s)} \quad (2.25)$$

From the previous definition it follows that $\tan \Psi$ is the ratio between the amplitudes of the p - and s -components of the reflected electric field; Δ instead is a more

Fig. 2.7 Reflection and refraction of a light beam incident on a transparent thin film supported on a substrate



subtle parameter. In (2.25), δ_p and δ_s are the differences of the phases of the s and p components between the reflected and incident electric fields; Δ is the ulterior difference between these values. A simple graphical interpretation of these parameters is reported in Fig. 2.6, adapted from Ref. [1].

2.1.3 Reflection from Thin Films

A configuration of considerable importance for the optical measurements related to this work is the ambient/film/substrate system, composed of a thin film on top of a semi-infinite substrate. The thickness of the film is comparable with the wavelengths of interest, so that multiple reflections between the interfaces must be taken into account.

Here we consider the case of homogeneous and isotropic materials, sharply separated by flat boundaries parallel to each other (Fig. 2.7). The refractive indices of ambient, film and substrate are, respectively, $\tilde{n}_0$, $\tilde{n}_1$ and $\tilde{n}_2$, while d_1 is the thickness of the film and θ_0 the angle of incidence (and also of the beam transmitted beyond the substrate). In the context of this work, the ambient will always be air ($\tilde{n}_0 \approx 1$) and the substrate a transparent medium, i.e. $\tilde{n}_2$ will be real.

The Fresnel coefficients for the reflection and transmission are given by [2]

$$r^\xi = \frac{r_{01}^\xi + r_{12}^\xi e^{-2i\beta}}{1 + r_{01}^\xi r_{12}^\xi e^{-2i\beta}} \quad (2.26a)$$

$$t^\xi = t_{20}^\xi \frac{t_{01}^\xi t_{12}^\xi e^{-i\beta}}{1 + r_{01}^\xi r_{12}^\xi e^{-2i\beta}} \quad \xi = p, s \quad (2.26b)$$

where r_{hl} are the Fresnel coefficients (2.23) for the single hl interface, and

$$2\beta = 2 \frac{2\pi d_1}{\lambda} \tilde{n}_1 \cos \theta_1 \quad (2.27)$$

is the phase shift acquired during a complete forward and backward reflection inside the film.

2.2 Heterogeneous Media

In the previous sections, we discussed the propagation of light inside homogeneous materials, and we saw that the optical response is completely resolved by the dielectric constant or the refractive index. It is not unusual, however, to deal with optical media that are formed by composites of several phases. In these cases it is well known that grain boundaries, voids, disordered regions or other inhomogeneities, on the length scale of several tens of nanometers, significantly affect the optical properties in the visible and near-UV range. In particular, screening charge developing at the grains boundaries and electrostatic interactions between adjacent grains considerably alter the local electric field and so the induced polarization; moreover, these effects depend on the shape and relative size of the microscopic structures.

Despite the extremely complicated microstructure of such composite media, in most cases it is still possible to describe the macroscopic response of such a heterogeneous material with an *effective* dielectric constant, that is an appropriate functional that “effectively” accounts for most of the optical characteristics of the specimens. In many cases, the effective dielectric constants of a mixture can be expressed in terms of a functional of the dielectric constants of each of the materials that enter the composite medium. Such approaches go under the name of “effective medium theories”. There are several methods to derive effective medium theory; here, we start from the Clausius-Mossotti (CM) problem and generalize the solution to obtain the Lorentz–Lorenz, Maxwell-Garnett and Bruggeman expressions [3, 4].

The CM problem applies to a simple cubic lattice of polarizable points, with polarizability α and lattice constant a . When a uniform electric field $\mathbf{E}$ is applied, an electric dipole $\mathbf{p} = \varepsilon_0 \alpha \mathbf{E}_{\text{loc}}$ is induced at each lattice point $\mathbf{R}_n$, which in turn generates an electric field; the local field $\mathbf{E}_{\text{loc}}$ is therefore determined by the superimposition of the external field and the fields $\mathbf{E}_{\text{dip}}$ from the other dipoles:

$$\mathbf{E}_{\text{loc}}(\mathbf{r}) = \mathbf{E} + \sum_{\mathbf{R}_n} \mathbf{E}_{\text{dip}}(\mathbf{r} - \mathbf{R}_n) \quad (2.28)$$

where

$$\mathbf{E}_{\text{dip}}(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \frac{3(\mathbf{p} \cdot \mathbf{r})\mathbf{r} - r^2\mathbf{p}}{r^5} \quad (2.29)$$

The macroscopic polarization $\mathbf{P}$ is defined as the average dipole moment per unit volume, and in this case reads

$$\mathbf{P} = \frac{N}{V} \varepsilon_0 \alpha \mathbf{E}_{\text{loc}} = n \varepsilon_0 \alpha \mathbf{E}_{\text{loc}} \quad (2.30)$$

where $n = a^{-3}$ is the volume density of points. In order to write $\mathbf{E}_{\text{loc}}$ as a function of $\mathbf{P}$ and $\mathbf{E}$ we need to evaluate the sum in (2.28). This can be done using the Lorentz cavity method. In the simplest approximation we consider a sphere of radius ρ centered in $\mathbf{r}$: we explicitly add the dipole fields from the points inside the sphere

and average the dipoles outside. Given the cubic symmetry of the lattice, the former contribution vanishes, while the latter equals to the volume integral of a dipole $\mathbf{P}$, which is $\mathbf{P}/3\epsilon_0$ [5]. Then, Eq. (2.30) becomes

$$\mathbf{P} = n\epsilon_0\alpha \left(\mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0} \right) \quad (2.31)$$

and we obtain for $\mathbf{P}$

$$\mathbf{P} = \epsilon_0 \frac{n\alpha}{1 - n\alpha/3} \mathbf{E} \quad (2.32)$$

Finally, applying the definition of the dielectric constant

$$\mathbf{D} = \epsilon_0\epsilon\mathbf{E} = \epsilon_0\mathbf{E} + \mathbf{P} \quad (2.33)$$

we found the CM relation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n\alpha}{3} \quad (2.34)$$

Now, the simplest heterogeneous medium can be realized by randomly assigning to the points of the preceding system two different polarizabilities α_a and α_b . In this case we find

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n_a\alpha_a}{3} + \frac{n_b\alpha_b}{3} \quad (2.35)$$

In this expression ϵ represents the effective dielectric constant of the composite. For practical uses, this form is not very useful, because it contains the microstructural parameters n_i and α_i , which are difficult to measure. Instead, if the dielectric constants ϵ_a and ϵ_b of the pure phases are available, we can use Eq. (2.34) to rewrite Eq. (2.35) as

$$\frac{\epsilon - 1}{\epsilon + 2} = f_a \frac{\epsilon_a - 1}{\epsilon_a + 2} + f_b \frac{\epsilon_b - 1}{\epsilon_b + 2} \quad (2.36)$$

where $f_{a,b} = n_{a,b}/(n_a + n_b)$ are the volume fractions of the two phases. This is the *Lorentz–Lorenz* effective medium expression.

In more realistic situations, however, the phases a and b are not uniformly mixed at atomic scale, but rather form grains large enough to possess their own dielectric identity.¹ Repeating the same derivation as before, we now identify these grains as polarizable entities, so we cannot assume anymore they are immersed in vacuum. If we suppose each entity immersed in a host with dielectric constant ϵ_h , Eq. (2.36) becomes

$$\frac{\epsilon - \epsilon_h}{\epsilon + 2\epsilon_h} = f_a \frac{\epsilon_a - \epsilon_h}{\epsilon_a + 2\epsilon_h} + f_b \frac{\epsilon_b - \epsilon_h}{\epsilon_b + 2\epsilon_h} \quad (2.37)$$

¹ The grains must contains an enough number of atoms to develop their characteristic band structure.

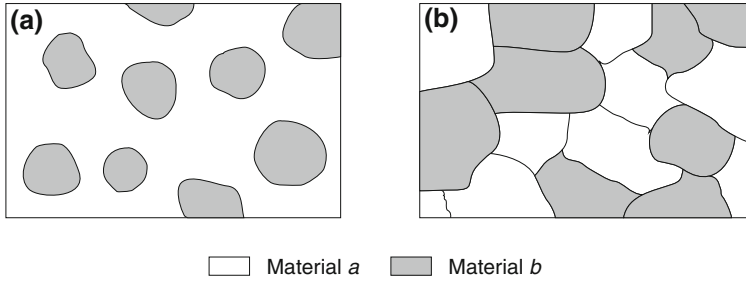


Fig. 2.8 Schematic representation of the microstructure of two different heterogeneous two-phases media. Panel **a** separate grains of material A dispersed in a continuous host of material B (suitable for Maxwell-Garnett EMA (2.38)). Panel **b** random mixture of grains of the two constituents (suitable for Bruggemann EMA (2.39))

This form is still somewhat incomplete, because the dependence of ε_h on ε_a and ε_b is unspecified.

Then, let's suppose that b is a dilute phase inside a , i.e. $f_b \ll f_a$: we can choose $\varepsilon_h \approx \varepsilon_a$, from which we obtain

$$\frac{\varepsilon^{MG} - \varepsilon_a}{\varepsilon^{MG} + 2\varepsilon_a} = f_b \frac{\varepsilon_b - \varepsilon_a}{\varepsilon_b + 2\varepsilon_a} \quad (2.38)$$

This and the equivalent equation for $f_a \ll f_b$ are the *Maxwell-Garnett* effective medium equations [6, 7]. They are usually applied when dealing with systems composed of well isolated particles or grains dispersed in continuous media (Fig. 2.8a).

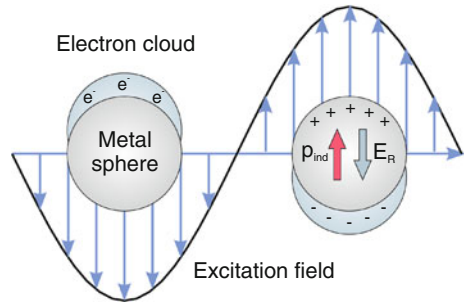
In cases where f_a and f_b are comparable, it may not be clear the distinction between host and inclusions. Then, we can make the self-consistent choice $\varepsilon = \varepsilon_h$, and (2.37) reduces to

$$0 = f_a \frac{\varepsilon_a - \varepsilon^{Br}}{\varepsilon_a + 2\varepsilon^{Br}} + f_b \frac{\varepsilon_b - \varepsilon^{Br}}{\varepsilon_b + 2\varepsilon^{Br}} \quad (2.39)$$

This is the *Bruggeman* expression [8], commonly known as *effective medium approximation* (EMA) and suited to describe uniform mixtures of two different materials (Fig. 2.8b).

The above effective medium expressions are few of the simplest approximations for describing the optical constants of heterogeneous media. One of the main assumptions is that all the phases feel the same equivalent mean field, implying that the domains are uniformly distributed in the volume of the medium. This is not the case, for example, when the grains are coherently arranged on a lattice [9, 10], so that the local field distribution has the same symmetry of the lattice, or are strongly coupled by EM radiation [11, 12], so that the local field is highly localized (see Sect. 2.3). Another situation where such EMAs fail is the proximity of percolation, when long-range conductive paths are established between the grains of the single

Fig. 2.9 Sketch of homogeneous metallic spheres placed in an oscillating EM field. The conduction electrons are displaced as a whole, polarizing the sphere ($\mathbf{p}_{\text{ind}}$), while the surface of the particles exerts a restoring force $\mathbf{E}_R$, so that resonance conditions can be established, leading to EM field amplification inside and in proximity of the particle



phases [13–15]. The application of effective medium theories must be therefore carefully evaluated depending on the specific case under scrutiny, taking into account that they are always a simplification of heterogeneous systems into equivalent single-phase media.

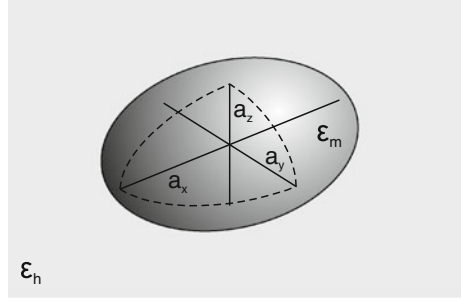
2.3 Optical Properties of Metallic Nanostructures

The optical properties of metals, from low energies up to the near-UV, are mostly dominated by the contribution of the free electrons, which are weakly bound to the metallic atoms and can freely move inside the crystal. These electrons, for example, are responsible for the high electric conductivity and the high optical reflectivity and absorption from DC up to visible and near UV frequencies.

On the other hand, metallic nanostructures with sub-micrometer dimensions exhibit very different optical responses with respect to their bulk counterparts. An external EM field can penetrate inside the volume of the particles, shifting the free electrons gas with respect to the ions lattice; consequently, charges of opposite sign accumulate on the opposite surfaces of the particles, polarizing the metal and establishing restoring local fields ($\mathbf{E}_R$ in Fig. 2.9). Therefore, in formal analogy with the Lorentz model, the particles can be viewed as oscillators, whose behaviour is determined by the free electrons effective mass, charge and density, but most importantly by the geometry of the particles [16–20]. Under resonance conditions, the free electrons gas is coherently dragged by the external excitation, so the electric dipoles induced inside each particles become extremely large. Correspondingly, the local fields in proximity of the particles are order of magnitudes enhanced with respect to the incident fields, the scattering cross section is enormously amplified, and very strong absorption peaks are observed. Such collective excitations are commonly known as *localized surface plasmons* (LSPs) [16–18, 21–23]; for “common” metals they are usually observed in the visible range (Ag [24, 25], Au [23] or Cu [26, 27]) and deep UV (Al [28, 29]).

In general, the optical response of metal nanoparticles can be quite complex, as the particles have more than a single resonant mode. These modes differ in their

Fig. 2.10 Sketch of a isolated metallic ellipsoidal particle, with principal semiaxis (a_x , a_y , a_z) and dielectric function ϵ_m , immersed in a dielectric host of dielectric constant ϵ_h



charge and field distribution, and are strongly dependent on the particle's size (with respect to the EM wavelength), shape and environment. The analytical treatment of LSPs for particles with arbitrary shape is therefore almost always not feasible, and computational methods are required. Indeed, only few simple configurations allow the exact solution of the optical response, which include spherical particles [30, 31], spheroids [32] and infinite long cylinders [33].

The *Mie* theory [30] is an exact solution of the Maxwell equations for the scattering and absorption problem of spherical particles, and it is usually employed to derive approximate solutions for similar geometries. According to this theory, the EM fields are expanded in spherical harmonics, and all the possible LSP modes correspond to the dipolar and multipolar EM eigenmodes of the particle. A full treatment of the EM interaction within the Mie theory is however a very challenging task, because the analytical description of the highest polar modes is very complex. Therefore, the Mie theory is often approximated to include only the most significant contributions. The excitation strength of each mode is determined by the corresponding expansion of the EM field; in particular, when the particles are much smaller than the involved wavelengths (typically up to tens of nanometers for EM fields in the visible range) the resonances are mainly dipolar in character, so only the first order terms can be retained. In such cases the Mie solution reduces to the *Rayleigh* approximation for the elastic scattering of light [31], and the quasi-static approximation can be invoked to apply the equations of electrostatics in electromagnetism.

2.3.1 Quasi-Static Approximation

For particles whose size is small compared to local variations of the incident light, the phase of the EM fields varies very little over the particles volume and we can assume uniform and non-retarded fields: this is called the *quasi-static approximation* (QSA). For common metals, like Ag, Au, Cu, Al, which have the LSP resonances in the visible and UV range, this approximation can adequately describe the optical response of spherical and ellipsoidal particles with sizes below ≈ 100 nm.

Let's consider a metallic ellipsoidal particle immersed in a transparent dielectric host and far from any other polarizable entity (Fig. 2.10). The ellipsoid has semiaxes

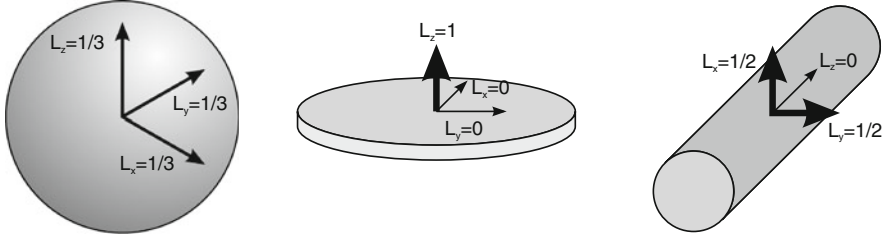


Fig. 2.11 Schematics of the depolarization factors for different shapes of homogeneous nanoparticles. *Black arrows* indicate the relative strengths of the induced electric dipoles along the principal axes. Panel **a** spherical particle, $a_x = a_y = a_z$. Panel **b** disc, $a_x, a_y \gg a_z$. Panel **c** cylinder, $a_x, a_y \ll a_z$

a_γ ($\gamma = x, y, z$) oriented along the cartesian axes, and the dielectric constants of the metal and the host are, respectively, ε_m and ε_h (the latter purely real). We start by considering the effects of a static applied electric field $\mathbf{E}_0$. As the particle is not spherical, the polarizability is a tensor $\boldsymbol{\alpha}$. Then, in general the induced electric dipole $\mathbf{p}$ is not parallel to $\mathbf{E}_0$ [5, 31]:

$$\mathbf{p} = \varepsilon_0 \boldsymbol{\alpha} \otimes \mathbf{E}_{loc} \quad (2.40)$$

where $\mathbf{E}_{loc}$ is the local field acting on the particle, and differs from $\mathbf{E}_0$ due to the polarization of the host. If the host is homogeneous and isotropic, then $\mathbf{E}_{loc} = \varepsilon_h \mathbf{E}_0$, and the previous equation becomes

$$\mathbf{p} = \varepsilon_0 \varepsilon_h \boldsymbol{\alpha} \otimes \mathbf{E}_0 \quad (2.41)$$

For ellipsoidal particles $\boldsymbol{\alpha}$ is diagonal, and has principal values α_γ given by [31]

$$\alpha_\gamma = v \frac{\varepsilon_m - \varepsilon_h}{\varepsilon_h + L_\gamma(\varepsilon_m - \varepsilon_h)} \quad \gamma = x, y, z \quad (2.42)$$

where $v = 4\pi/3 a_x a_y a_z$ is the particle's volume and L_γ are the *depolarization factors*, that can be written as

$$L_\gamma = \frac{a_x a_y a_z}{2} \int_0^\infty \frac{dq}{(q + a_\gamma^2) \sqrt{\prod_{\eta=x,y,z} (q + a_\eta^2)}} \quad (2.43)$$

and satisfy the sum rule $\sum_\gamma L_\gamma = 1$.

For spherical particles (Fig. 2.11a) we have $a_x = a_y = a_z \equiv a$ and the geometrical factors reduce to $L_\gamma = 1/3$ in all directions: the polarizability is isotropic and from (2.42) we find

$$\alpha_{\text{sph}} = 3 v \frac{\varepsilon_m - \varepsilon_h}{\varepsilon_m + 2 \varepsilon_h} \quad (2.44)$$

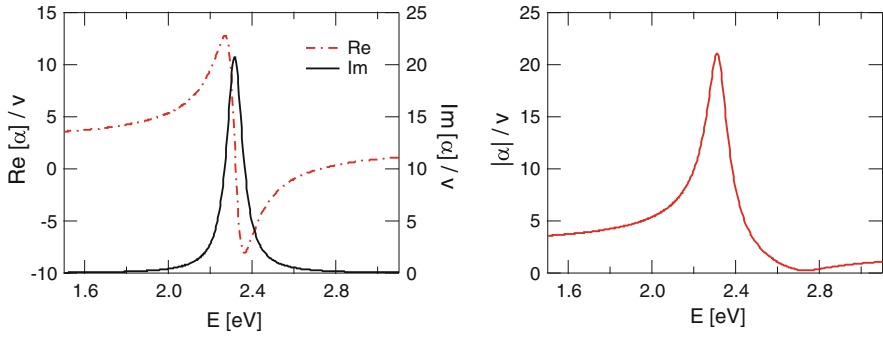


Fig. 2.12 Real (red line) and imaginary (black line) parts (left panel) and magnitude (right panel) of the complex polarizability α for a gold sphere of radius $a = 30$ nm, immersed in a homogeneous host with dielectric constant $\varepsilon_h = 1.4$. The complex dielectric function of gold is shown in Fig. 2.13

Two other interesting cases are the limits to disks and to cylinders. A disk is obtained when the ellipsoid is considerably stretched along two of the principal axes, or equivalently shrunk along one of them, so that, for example, $a_x, a_y \gg a_z$ (Fig. 2.11b). In such case the depolarization factors in the plane of the disk reduce to 0, while the one along the minor axis grows up to 1; correspondingly, no polarization becomes possible within the plane, and the disk can be polarized only along the normal axis. In the opposite case, i.e. $a_z \gg a_x, a_y$, the ellipsoid evolves instead to a cylinder (Fig. 2.11c). Now, the depolarization factor along the main axis (L_z) becomes 0, implying that the cylinder can be polarized only by electric fields lying in the xy plane.

In Fig. 2.12 the real and imaginary parts and the absolute value of α_{sph} are reported for a metallic sphere in air. We can clearly see a strong enhancement of the polarizability, corresponding to a minimum of $|\varepsilon_m + 2\varepsilon_h|$. The magnitude of α_{sph} at resonance does not diverge, but it is limited due to the imaginary part of the dielectric constant. If $\text{Im}[\varepsilon_m(\omega)]$ is small or slowly-varying, the resonance condition simplifies to

$$\text{Re}[\varepsilon_m(\omega)] = -2\varepsilon_h \quad (2.45)$$

which is called the *Fröhlich condition* for the LSPs resonances.

The total electric field outside the particle is the sum of the incident field and the dipolar field generated by the particle,

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0 + \frac{1}{4\pi\varepsilon_0\varepsilon_h} \frac{1}{r^3} \frac{3(\mathbf{r} \cdot \mathbf{p})\mathbf{r} - r^2\mathbf{p}}{r^2} \quad (2.46)$$

from which we can see that the resonances of α (and $\mathbf{p}$) also determine resonant enhancements of $\mathbf{E}$.

Given the solution for electrostatics, we can now turn our attention to EM fields. In the quasi-static regime we are dealing with particles much smaller than the wavelengths, i.e. $a_\gamma \ll \lambda$, so we can consider time varying fields and neglect spatial retardation effects. If we assume an incident plane wave radiation, the exciting electric field is given by $\mathbf{E}_{\text{ex}}(\mathbf{r}, t) = \mathbf{E}_0 e^{i\omega t}$ and induces a time-varying dipole moment

$$\mathbf{p}(t) = \varepsilon_0 \varepsilon_h \boldsymbol{\alpha} \otimes \mathbf{E}_0 e^{i\omega t}, \quad (2.47)$$

This oscillating dipole irradiates in the surrounding space, leading to the scattering of the incident plane wave. The dipole fields are now given by [5]

$$\mathbf{H}(\mathbf{r}, t) = \frac{c}{4\pi} \frac{1}{r^3} [(kr)^2 + ikr] \frac{\mathbf{r} \times \mathbf{p}}{r} e^{i(\omega t - kr)} \quad (2.48a)$$

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{4\pi \varepsilon_0 \varepsilon_h} \frac{1}{r^3} \left[(kr)^2 \frac{(\mathbf{r} \times \mathbf{p}) \times \mathbf{r}}{r^2} + (1 - ikr) \frac{3(\mathbf{r} \cdot \mathbf{p})\mathbf{r} - r^2 \mathbf{p}}{r^2} \right] e^{i(\omega t - kr)} \quad (2.48b)$$

In particular, we can identify two limiting spatial domains. A *near field* component dominates in the vicinity of the particle ($kr \ll 1$) and decays from the particle center proportionally to r^{-3} ; in this regime the electrostatic result (2.46) is recovered for the electric field (with the additional exponential time dependence), while the magnetic field reduces to

$$\mathbf{H}(\mathbf{r}, t) = \frac{ic}{4\pi} \frac{kr}{r^3} \frac{\mathbf{r} \times \mathbf{p}}{r} e^{i\omega t} \quad (2.49)$$

Then, in the near field regime the retardation effects can be neglected, and the fields are predominantly electric, as the magnitude of the magnetic field is about a factor $\varepsilon_0 c kr$ smaller than that of the electric field.

The other limit is the *far field* regime, acting at distances much larger than the wavelengths ($kr \gg 1$). In this regime the fields are proportional to r^{-1} and have the form of spherical waves:

$$\mathbf{H}(\mathbf{r}, t) = \frac{ck^2}{4\pi} \frac{\mathbf{r} \times \mathbf{p}}{r} \frac{e^{i(\omega t - kr)}}{r} \quad (2.50a)$$

$$\mathbf{E}(\mathbf{r}, t) = \frac{c}{\varepsilon_0 \varepsilon_m} \frac{\mathbf{H} \times \mathbf{r}}{r} \quad (2.50b)$$

Another consequence of the resonantly enhanced polarizability is the concomitant enhancement of the efficiency of the particle scattering and absorption. Within the quasi-static approximation, the corresponding cross-sections σ are given by the Rayleigh expressions [31]

$$\sigma_{\text{sca}, \gamma} = \frac{k^4}{6\pi} |\alpha_\gamma|^2 \quad (2.51a)$$

$$\sigma_{\text{abs},\gamma} = k \text{Im} [\alpha_\gamma] \quad (2.51b)$$

As the polarizability is proportional to the volume, we can see that σ_{sca} depends on the square of the volume while σ_{abs} scales only linearly with v . Therefore, small particles prevalently absorb light, while the scattering process is dominant in large particles. We note that in the derivation of (2.51) no explicit assumptions on the dielectric constants are made, so they are valid also for dielectric scatterers. In such a case, they demonstrate a very crucial problem for optical measurements of ensembles of nanoparticles: due to the rapid scaling of the scattering cross-section, $\sigma_{\text{sca}} \propto a^6$, it is very difficult to pick out small objects from a background of larger scatterers.

2.3.2 Beyond the Quasi-Static Approximation

Despite its simplicity, we can see from the polarizabilities (2.42) that the quasi-static theory already accounts for the main effects associated with the major parameters affecting the LSPs resonances, i.e. the influence of particle shape and size, the metal and the environment optical characteristics. However, comparing the experimental results with the QSA predictions some inconsistencies remain, mainly related to the linewidth of the resonances and the influence of the particle size. Remaining in the dipolar modes regime, we can introduce two corrections to the QSA, which account for surface damping in particles with dimensions smaller than the mean free path of the oscillating electrons, and retardation effects in larger particles.

Surface Damping

For very small metallic nanoparticles, with sizes comparable to the electrons mean free path λ_{mfp} , the bulk dielectric constant is modified by the additional scattering of the electrons at the particle surfaces. This *surface damping* destroys the coherent oscillations of the electrons, resulting in a broadening of the LSP resonances. For common metals λ_{mfp} is usually of the order of 30–50 nm, so the scattering is dominant for dimensions below ≈ 20 nm.

To account for these finite size effects, we start from the dielectric constant $\varepsilon_{\text{exp}}(\omega)$ measured experimentally for the bulk metal. This can be decomposed in contributions from interband transitions, between states separated by an energy gap, and intraband transitions, between states at the Fermi level in incompletely filled bands:

$$\varepsilon_{\text{exp}}(\omega) = \varepsilon_{\text{inter}}(\omega) + \varepsilon_{\text{intra}}(\omega) \quad (2.52)$$

Due to the presence of the gap, the former have features at high energies, usually starting from the near-UV range. On the contrary, intraband transitions are promoted by low-energy photons and involve quasi-free electrons at the Fermi level. Then, for $\varepsilon_{\text{intra}}$ we can employ the Drude theory (2.15):

$$\varepsilon_{\text{intra}}(\omega) = 1 - \frac{\omega_P^2}{\omega^2 - i\Gamma_0\omega} \quad (2.53)$$

where $\Gamma_0 = v_F/\lambda_{\text{mfp}}$ is determined by the electrons mean free path in the metal bulk (v_F is the Fermi velocity). Surface damping can be empirically modeled [34] as an additional size-dependent contribution $\Gamma_{\text{surf}}(a)$ to Γ_0 , which writes

$$\Gamma_0(a) = \Gamma_0 + \Gamma_{\text{surf}}(a) = \frac{v_F}{\lambda_{\text{mfp}}} + A \frac{v_F}{a}. \quad (2.54)$$

A is an empirical factor, of the order of 1, which incorporates the details of the scattering processes [21]; for a sphere it is usually chosen between 3/4 and 1 [16, 18, 35, 36]. Introducing Γ_0 in $\varepsilon_{\text{intra}}$, we obtain

$$\varepsilon_{\text{intra}}(\omega, a) = 1 - \frac{\omega_P^2}{\omega^2 - i\Gamma_0(a)\omega} \quad (2.55)$$

Now, we can modify the dielectric constant by subtracting from (2.52) the bulk intraband contribution (2.53) and adding the corrected term (2.55): we find the size-dependent $\varepsilon_m(\omega, a)$ given by

$$\begin{aligned} \varepsilon_m(\omega, a) &= \varepsilon_{\text{exp}}(\omega) - \varepsilon_{\text{intra}}(\omega) + \varepsilon_{\text{intra}}(\omega, a) \\ &= \varepsilon_{\text{exp}}(\omega) + \Delta\varepsilon(\omega, a) \end{aligned} \quad (2.56)$$

with [37]

$$\Delta\varepsilon(\omega, a) = \frac{\omega_P^2}{\omega} \left(\frac{1}{\omega - i\Gamma_0} - \frac{1}{\omega - i\Gamma_0(a)} \right) \quad (2.57)$$

In Fig. 2.13, the dielectric constants of gold nanoparticles with radius $a = 5$ nm and 50 nm are compared. We can see that reducing the particle size the imaginary part of ε_m increases at the larger wavelengths (lower energies), while the real part is only slightly raised. Then, according to the Fröhlich condition (2.45), the resonances do not experience significant shifts, and the main effects of surface damping is a broadening of the plasmons linewidth, in accordance with the experimental results [21].

Retardation Effects

In the previous sections we have seen that in the quasi-static approximation the incident EM radiation is considered uniform within the particles volume. This assumption can be adequate for particles with sizes up to 100 nm and EM frequencies in the visible range, however it fails to predict the dependence of the optical response on the NP dimensions. Moreover, as the variations of the incident EM fields cannot be neglected anymore, multipolar eigenmodes are also excited. Nevertheless, if the NPs sizes are lower than $\approx 10\%$ of the typical wavelength of the incident radiation [38] (≈ 40 nm in the visible range), multipolar contributions can still be neglected

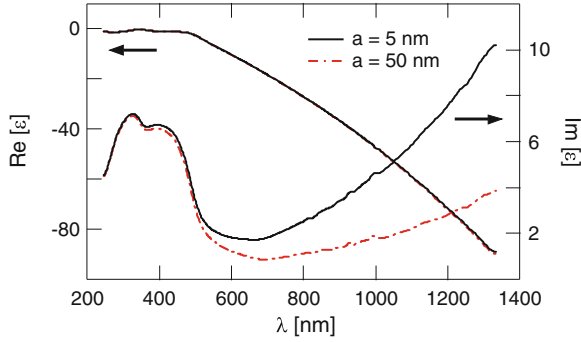


Fig. 2.13 Real and imaginary parts of the dielectric constant of gold spheres with different radii, computed applying the finite size corrections of Eq. (2.57). The optical constants of the bulk gold were extracted from ellipsometric measurements performed on a Au(111) crystal (Au/mica manufactured by Phases)

and retardation effects can be explicitly calculated for the dipolar modes [39]; this is sometimes called *modified long-wavelength approximation* (MLWA). For gold ellipsoidal nanoparticles, it has been shown that it consistently reproduces exact numerical solutions for particles with equivalent volumes up to a ≈ 40 nm radius sphere and aspect ratios below 10 [19, 40, 41], and it is still in qualitative agreement with results at ≈ 200 nm dimensions [42]. As the particles under scrutiny in this thesis have typical sizes of several tens of nanometers, we will also employ MLWA for calculating their polarizabilities.

Let's consider a spherical particle with radius a excited by an EM field. In QSA we found that the induced dipole $\mathbf{p}$ is proportional to the incident electric field (2.47). The electrodynamic corrections associated with MLWA are introduced by rewriting (2.47) as [39]

$$\mathbf{p} = \varepsilon_0 \varepsilon_h \alpha (\mathbf{E} + \mathbf{E}_{\text{rad}}) \quad (2.58)$$

where the radiative correction field $\mathbf{E}_{\text{rad}}$ is given by

$$\mathbf{E}_{\text{rad}} = \frac{1}{4\pi \varepsilon_0 \varepsilon_h} \left(\frac{k^2}{a} + i \frac{2}{3} k^3 \right) \mathbf{p} \quad (2.59)$$

The first term in (2.59) comes from the depolarization of the radiation across the particle surface, due to the finite ratio of particle size to wavelength; the main effect of this *dynamic depolarization* is red shifting the plasmon resonance as the particle size is increased. The second term is the *radiation damping* due to the radiative losses of the induced dipole; it grows rapidly with particle size, reducing the intensity of the resonances and making the spectrum broader and asymmetric.

The net effect of these terms is to modify the total induced polarization, so that the polarizability of the sphere now rewrites as

$$\alpha_{\text{sph}}^{\text{MLWA}} = \frac{\alpha_{\text{sph}}}{1 - \frac{\alpha_{\text{sph}}}{4\pi} \left(\frac{k^2}{a} + \frac{2}{3}ik^3 \right)} \quad (2.60)$$

where α_{sph} is the QSA expression (2.44). For ellipsoidal particles, excited along one of the principal axes, (2.60) remains valid substituting α_{sph} and a with the corresponding polarizability and semi-axis [19, 43].

2.3.3 Far Field Extinction Spectra of Nanoparticles Ensembles

In the previous sections the LSPs were reviewed within the quasi-static approximation, and we saw that many different factors affects the resonances, related both to the geometry of the system and to the dielectric environment. On the other hand, one of the key points of the current thesis is the fabrication and the detailed analysis of the plasmonic response of several arrays of gold NPs, characterized by different morphological and geometrical parameters. It is therefore very instructive, in order to better understand the experimental results and analysis, to present here some optical calculations for ideal ensembles of metallic nanoparticles, illustrating the behaviour of the LSP resonances under different system configurations.

We consider an ensemble of *non-interacting* metallic nanoparticles immersed in a homogeneous dielectric host. The latter has a purely real dielectric constant ε_h , while for the particles we employ a simple Drude model with finite-size corrections (2.55), thereby neglecting the contributions of the interband transitions; the physical constants have been chosen to fit the optical constants of gold [44]: $v_F = 1.4 \times 10^6$ m/s, $\omega_P = 9$ eV, $\Gamma_0 = 70$ meV. For these parameters, we present the calculated spectra for the extinction efficiencies Q_{ext} , defined as the sum of the absorption and scattering cross-sections (2.51) renormalized by the geometrical cross-sections πa_γ^2 , as a function of the wavelength:

$$Q_{\text{ext},\gamma} = (\sigma_{\text{abs},\gamma} + \sigma_{\text{sca},\gamma}) / \pi a_\gamma^2 \quad (2.61)$$

Influence of the Environment

We start by considering spherical particles of radius $a = 30$ nm, and analyse the effects of a variation of the host dielectric constant ε_h . Since the particles are immersed in a dense medium, the local electric field differs from the external excitation due to the polarization $\mathbf{P}_h$ of the medium. Furthermore the particles itself are sources of electric fields, which modify $\mathbf{P}_h$, and therefore, again, the local field.

In Fig. 2.14 we report the calculated curves for Q_{ext} with ε_h varying from 1 (vacuum) up to 3, computed without applying the MLWA correction. We can see that the position of the resonance moves to larger wavelengths (lower energies) at higher ε_h and correspondingly its magnitude increases. Employing the Fröhlich condition

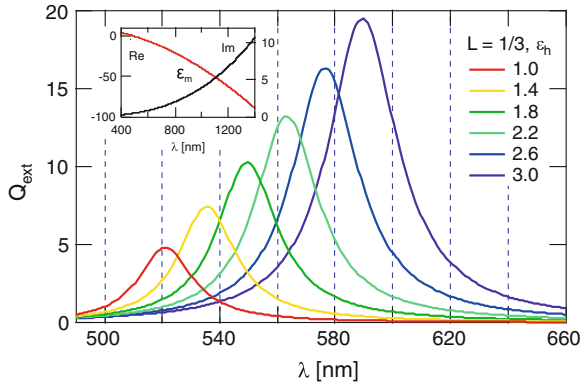


Fig. 2.14 Computed extinction efficiencies Q_{ext} for non-interacting gold spherical particles, of radius $a = 30\text{ nm}$, as a function of the dielectric constant ε_h of the host. The particles' dielectric function, employed for the calculations, is plotted in the inset of the figure

(2.45) and looking at ε_m in the inset of Fig. 2.14, we can deduce that the resonance red-shift is due to the negative slope of the real part of ε_m ; the enhancement of the resonances is instead related to the proportionality between the induced dipole and ε_h (see (2.41)), which at the resonance is about $p \propto \varepsilon_h^2$.

Influence of the Particle Shape

Now we set the dielectric constant of the host assuming, for example, $\varepsilon_h = 1.4$, and inspect the effects of the geometrical parameters on the extinction efficiency. In the case of a sphere, that we choose as a starting point, the isotropic particle shape leads to LSP resonances that are independent on the direction of the incident electric field. If we suppose to deform the sphere stretching it along one of its diameters, we obtain a so-called prolate spheroid, that is an ellipsoid with semi-axes $a_x = a_y < a_z$. The dielectric response becomes anisotropic depending on the orientation of the field with respect to the symmetry axis a_z , so that a so-called longitudinal (L) and a so-called transverse (T) mode can be identified, corresponding to excitation along the directions parallel or perpendicular to a_z . Stretching further the particle, these modes shift in frequency as a function of the ellipsoid aspect ratio, the longitudinal one red-shifting and the transverse one slightly blue-shifting. In general, for more anisotropic shapes, a greater number of different modes appear [18].

In Fig. 2.15 computed spectra for aspect ratios $a_z : a_{x,y}$ between 1 : 1 and 5 : 1 are shown. To understand the LSP shifts we look again at the resonance condition, which now becomes (cfr. Eq. (2.42))

$$\text{Re}[\varepsilon_m(\omega)] \approx -\frac{1 - L_\gamma}{L_\gamma} \varepsilon_h. \quad (2.62)$$

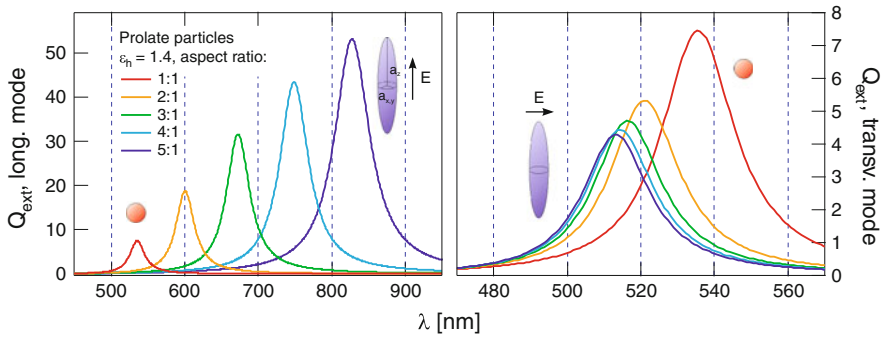


Fig. 2.15 Computed extinction efficiencies Q_{ext} for non-interacting gold prolate particles, having different aspect ratios, dispersed in a continuous homogeneous host ($\epsilon_h = 1.4$). Electric field applied along (*left panel*) and transverse to (*right panel*) the long axis. The particles dielectric function is plotted in the inset of Fig. 2.14

For prolate geometries, the transversal depolarization factors L_T are larger than the longitudinal L_L , therefore, increasing the asymmetry of the particle, the ratio in (2.62) becomes smaller for the T modes and larger for the L modes; moreover, under resonance conditions, the polarizability is roughly proportional to $(1 - 2L_T)/L_T \epsilon_h^2$. From these considerations, we can deduce that, in analogy with the previous case, the T (L) spectra are shifted towards high (low) energies, and the magnitudes are weakened (enhanced).

Influence of the Particle Size

The last parameter that we will consider in this analysis, which affects the LSP resonances, is the particle size. In Fig. 2.16a the extinction spectra, calculated employing the MLWA, are reported for spherical particles with radius between 5 and 75 nm; the corresponding peak positions and linewidths are highlighted in Fig. 2.16b. We can see that increasing the radius a the resonances are systematically red shifted, while their linewidth initially decreases, reaches a minimum at about 20 nm, and then monotonically increases. These trends are mainly due to surface damping and retardation effects. For small particles, the former is dominant, so the LSP position is slightly affected by the size, while the linewidth has a contribution $\Gamma(a) \propto a^{-1}$ (see Eq. (2.54)). At higher size, dynamic depolarization and radiation damping, respectively proportional to a^2 and a^3 , rapidly grow, inducing a strong red shift and broadening of the peaks, and reducing their intensity.

Lastly, in Fig. 2.17 the absorption and scattering contributions to the total extinction efficiency are shown separately for two different particles with radius $a = 5$ and 50 nm, respectively. As already predicted before, in the former case Q_{ext} is entirely determined by absorption ($Q_{\text{abs}} \propto a$), the scattering efficiency being more than three orders of magnitude smaller. Increasing the volume, Q_{sca} grows much more rapidly

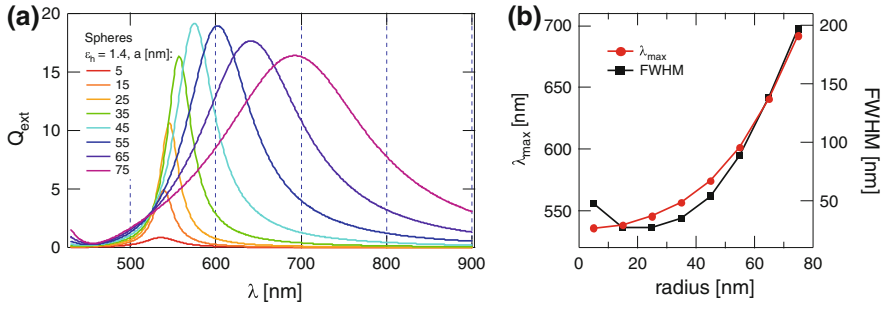


Fig. 2.16 *Left panel* computed extinction efficiencies Q_{ext} for non-interacting gold spherical particles, having different radii, dispersed in a homogeneous dielectric host ($\epsilon_h = 1.4$); the dielectric function of gold is plotted in the inset of Fig. 2.14. *Right panel* position (λ_{max} , red line) and full width at half maximum (FWHM, black curve) of the LSP peaks in panel (a) as a function of the particle radius

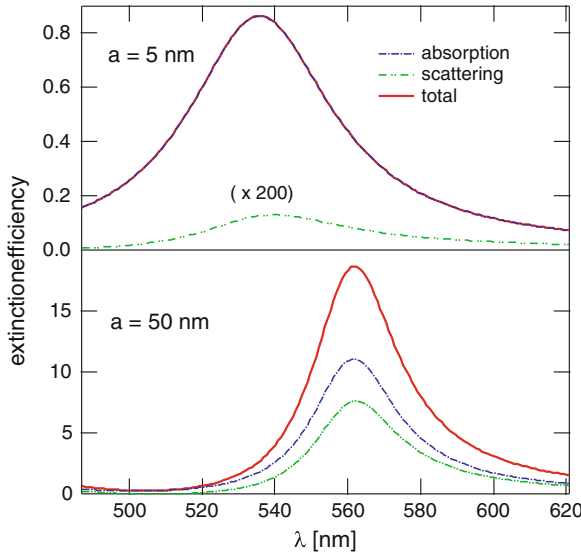


Fig. 2.17 Computed absorption (blue curves), scattering (green curves) and total (red curves) extinction efficiencies for gold spheres of radius $a = 5$ nm (*top panel*) and $a = 50$ nm (*bottom panel*) dispersed in a dielectric host ($\epsilon_h = 1.4$). The particles dielectric function is plotted in the inset of Fig. 2.14

than Q_{abs} ($Q_{\text{sca}} \propto a^4$), for $a = 50$ nm is comparable with Q_{abs} and eventually it becomes dominant at higher radii.

2.3.4 Effects of EM Interactions

Up to this point we always considered ensembles of isolated nanoparticles, where the particles spacing was so high that the direct interactions could be neglected. When several particles are brought close to one another, electromagnetic coupling effects set in, and the LSP resonances are determined by the collective behaviour of the system, so that the overall optical response can be significantly modified with respect to the isolated case. Usually, two different interactions regimes are distinguished, depending on the interparticle distance d : for closely spaced particles, $d \ll \lambda$, near-field interactions proportional to d^{-3} dominate and the particles can be described as an array of interacting point dipoles; due to the rapid scaling of the interaction strength with distance, this regime holds for particle separations below ≈ 150 nm. For larger separations, the near field can be neglected and the dipolar coupling is mainly through far field of the scattered light, which scales as d^{-1} . In this work we will not consider the latter case, but only concentrate on the so-called near-field. In particular, in order to gain qualitative insight on the effects of interactions, we will analyse two different configurations, namely an isolated particle supported on a dielectric substrate and a pair of close particles.

Substrate Effects

In this section we consider a spherical metallic nanoparticle in the near vicinity of a flat substrate. When the particle is polarized by an incident EM wave, the irradiated field induces a distribution of charges in the substrate, which in turn modifies the local field acting on the particle. In general, this substrate-induced field is not homogeneous in space, so multipolar modes of higher order can be excited in addition to the dipolar one (Fig. 2.18a). However, if the particle is not in direct contact with the substrate but at least few nanometers away (Fig. 2.18b), the spatial variations of the local field are less pronounced and the QSA is still suited to describe the particle optical response [18].

Within the QSA, the induced distribution of charges can be seen as the particle image charge; then we can treat the polarization of the substrate like a point dipole $\mathbf{p}_{\text{ind}}$ specular to the particle with respect to the substrate surface (Fig. 2.18). According to the electrostatic theory, $\mathbf{p}_{\text{ind}}$ is given by [5]

$$\mathbf{p}_{\text{ind}} = \frac{\varepsilon_s - \varepsilon_h}{\varepsilon_s + \varepsilon_h} (-p_x, -p_y, p_z) \quad (2.63)$$

where $\mathbf{p}$ is the particle dipole, ε_s and ε_h the dielectric constant of the substrate and the host.

Due to the presence of the substrate, the symmetry of the system is now broken and different plasmon modes can be found in the directions parallel or normal to the interface. To illustrate this, first let's suppose the external electric field $\mathbf{E}_{\text{ext}}$ perpen-

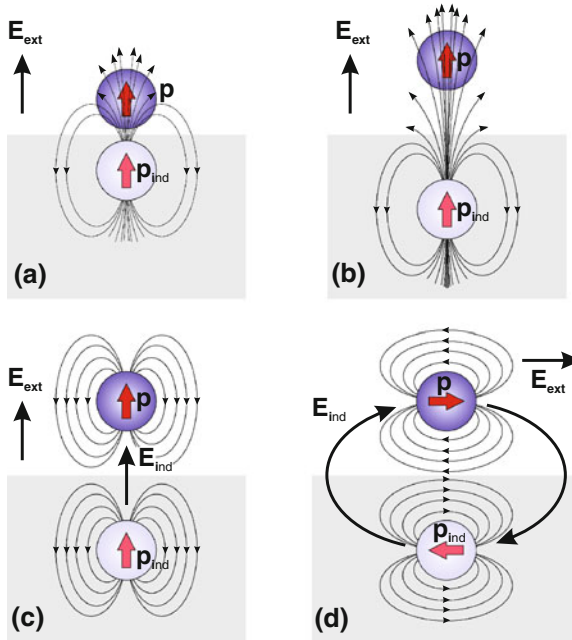


Fig. 2.18 *Top panels* metallic sphere in proximity of an interface between two different media, and electric field applied normal to the interface. When the sphere is nearly touching the interface, the electric field generated by the image charge is highly inhomogeneous within the particle's volume (panel **a**), and becomes more uniform as the particle moves away from the interface (panel **b**). *Bottom panels* image charge dipole, and corresponding dipolar field $\mathbf{E}_{\text{ind}}$ generated at the particle center, for excitation $\mathbf{E}_{\text{ext}}$ normal (panel **c**) and parallel (panel **d**) the interface. In both cases $\mathbf{E}_{\text{ind}}$ has the same direction of $\mathbf{E}_{\text{ext}}$

pendicular the plane of the substrate (Fig. 2.18c): both the particle and the image charge get polarized in the same direction of $\mathbf{E}_{\text{ext}}$; then, the electric field $\mathbf{E}_{\text{ind}}$, generated by $\mathbf{p}_{\text{ind}}$ at the particle position, has the same orientation like $\mathbf{E}_{\text{ext}}$ and acts against the restoring forces of $\mathbf{p}$. Recalling that the particle can be modelled as an oscillator, the lowering of the restoring force is reflected by a reduction of the resonance frequency, i.e. a red-shift of the LSP. The same effect occurs when the $\mathbf{E}_{\text{ext}}$ is oriented in-plane (Fig. 2.18d): in this case $\mathbf{p}$ and $\mathbf{p}_{\text{ind}}$ are in the same direction of the field but antiparallel with respect to each other, so that $\mathbf{E}_{\text{ind}}$ is again directed like $\mathbf{E}_{\text{ext}}$.

Particle Interactions

We now discuss the effects on the LSP induced by near field coupling in a system of close particles. Common ensemble of nanoparticles include linear chains [46–50] and bidimensional arrays [51–56], however for a basic understanding of the

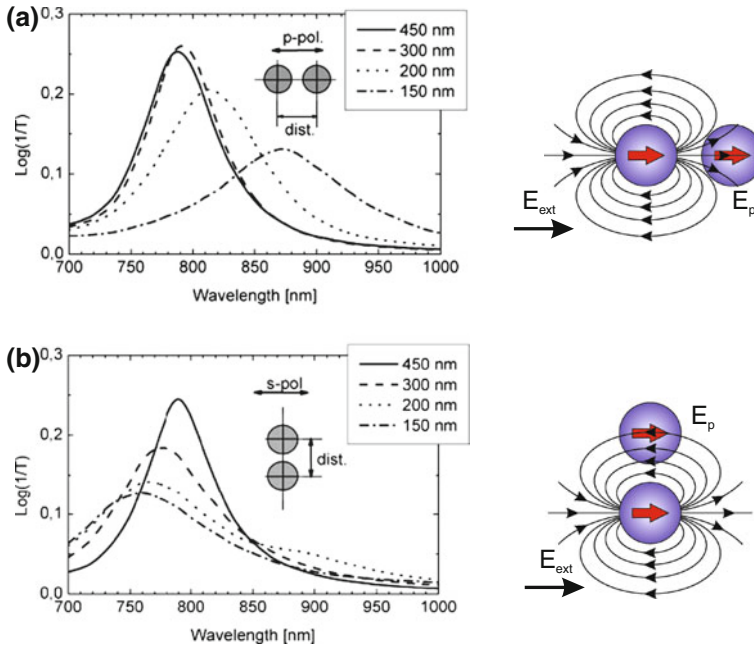


Fig. 2.19 Extinction ($=\log(1/\text{Transmission})$) spectra of 2D arrays of Au nanoparticles pairs (reprinted from Ref. [45], Copyright 2003, with permission from Elsevier), for different interparticle center-to-center distances. The polarization direction of the exciting light is **a** parallel to the long particle pair axis and **b** orthogonal to it

effects of interactions, we consider the simplest case of only two coupled particles [45, 57, 58].

In analogy to the previous configuration, if the particles are not too close to each other, we can employ the QSA and treat them as two interacting point dipoles. Again, the single particle symmetry is broken, and depending on the polarization with respect to the pair axis, we can distinguish a longitudinal (L) and a transverse (T) polarizations, respectively parallel and perpendicular the pair axis.

In Fig. 2.19a, c we report the experimental extinction spectra from Ref. [45], measured on arrays of pairs of nanodiscs for different interparticles spacings. When the external electric field is oriented along the pairs axis, the near field E_p generated by each particle on its companion is parallel to the polarization and acts against the restoring forces (Fig. 2.19b); then, similarly to the previous case, the longitudinal LSP is shifted at lower energies (Fig. 2.19a). On the contrary, if the electric field is perpendicular to the axis, E_p points in the opposite direction of the polarization, reducing the strength of the applied field or equivalently reinforcing the restoring forces (Fig. 2.19d); therefore, in this case the resonance frequency is increased, and the LPS mode blue-shifts (Fig. 2.19c). Moreover, due to the retardation effects of

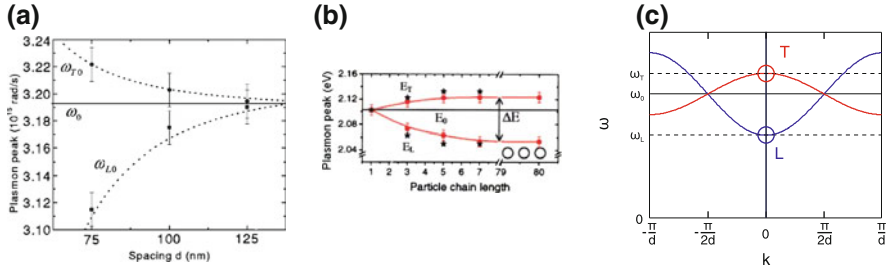


Fig. 2.20 Panel **a** dependence of the plasmon peak position on the interparticle spacing d for both the longitudinal (L) and transverse (T) excitation of the collective mode in 2D arrays of gold nanoparticles chains (reprinted with permission from Ref. [47]. Copyright 2002 by the American Physical Society); the *dotted* line shows the $1/d^3$ dependence predicted by a point dipole interaction model [61]. Panel **b** collective plasmon resonance energies for both L and T excitations for Au nanoparticle chains of different lengths (Reprinted with permission from Ref. [60]. Copyright 2002, American Institute of Physics). Panel **c** computed dispersion relation $\omega(k)$ for L and T LSP modes in a infinite chain of metallic nanoparticles, according to a point dipole interaction model [61, 62]

the interactions, the radiation damping of coupled particles is larger than of isolated ones, so the LSP modes become broader.

The splitting and broadening of the single-particle resonances are determined by the strength of the interactions between adjacent particles, and they can be tuned by varying the separation (Fig. 2.20a) or the number (Fig. 2.20b) of the particles forming the chain [36, 46, 47, 59, 60].

In particular, the splitting of the single-particle LSP modes has been demonstrated [61, 62] to play a key role for the coherent transport of EM energy. Exploiting the ability of metallic nanostructures to localize and strongly enhance the EM radiation, uniaxial chains of nanoparticles can be employed as waveguides at nanoscale, allowing the propagation of EM signals with lateral confinement beyond the diffraction limit [62]. All the main characteristics of the waveguide (group velocity, bandwidth, attenuation of the propagating waves) are dependent on the energy separation between the longitudinal and the transverse LSP modes, excited by electric fields along and normal the waveguide. For example, in Fig. 2.20c we report the dispersion relation $\omega(k)$ for the longitudinal L (blue line) and transverse T (red line) modes, computed for an infinite chain of spherical nanoparticles assuming dipolar interactions between nearest-neighbours [61, 62]; the group velocity v_g for energy transport corresponds to the slope of the curves. For both L and T modes, v_g is null and the frequency splitting $\Delta\omega$ is maximum for uniform excitations, i.e. $k = 0$ along the chain. Increasing the wave number k of the exciting field, v_g increases while $\Delta\omega$ decreases. For $k = \pi/d$ the splitting of the L and T modes collapses to zero and their energy reduces to the single-particle LSP; correspondingly, the group velocity reaches the maximum values and $v_g^L = 2v_g^T$, due to the stronger EM coupling for L waves than for T waves. Maximum values of v_g up to $0.1c$ and transmission efficiencies up to 64% were predicted [61].

In summary, the basic theory of the interaction between light and heterogeneous media has been reviewed, with particular emphasis on the optical response of metallic inclusions embedded in dielectric hosts. The main feature of interest in view of the current work is the resonant behaviour of metallic nanoparticles under the excitation of an external EM radiation, which leads to a very strong amplification of the EM fields inside and in the near field range outside the particles. Correspondingly, such systems exhibit strong resonance peaks in the reflection and absorption of light, whose characteristics (position and linewidth) depend on both intrinsic geometrical factors (single-particle size and shape) and extrinsic parameters (dielectric constant of the host, proximity of a surface or other polarizable entities). Such features, not observed in the bulk counterparts, are a characteristic effect of the collective oscillations of the electrons gas confined inside the metallic structures, and are given the name of localized surface plasmon resonances.

The observation and analysis of the LSP resonances in 2D arrays of gold nanoparticles will be the main topic of the current thesis. The arguments presented in this chapter will be recalled in Sect. 6.2.1 to formulate an effective medium theory describing the optical response of the Au NPs arrays, and to provide a theoretical support to the experimental data.

References

1. J.H. den Boer. *Spectroscopic Infrared Ellipsometry: Components, Calibration and Applications*. PhD thesis, Eindhoven University of Technology, 1995.
2. H. Fujiwara. *Spectroscopic Ellipsometry. Principles and Applications*. Wiley, 2007.
3. G. A. Niklasson, C. G. Granqvist, and O. Hunderi. Effective medium models for the optical properties of inhomogeneous materials. *Appl. Opt.*, 20:26, 1981.
4. D.E. Aspnes. Optical properties of thin films. *Thin Solid Films*, 89:249, 1982.
5. J.D. Jackson. *Classical Electrodynamics*. John Wiley & Sons, 1999.
6. J.C.M. Garnett. Colours in metal glasses and in metallic films. *Philos. Trans. R. Soc. London.*, 203:385, 1904.
7. J.C.M. Garnett. Colours in metal glasses, in metallic films, and in metallic solutions. ii. *Philos. Trans. R. Soc. London.*, 205:237, 1906.
8. D.A.G. Bruggeman. Berechnung verschiedener physikalischer konstanten von heterogenen substanzen. *Ann. Phys. Leipzig*, 24:636, 1935.
9. F. J. García-Vidal, J. M. Pitarke, and J. B. Pendry. Effective medium theory of the optical properties of aligned carbon nanotubes. *Phys. Rev. Lett.*, 78:4289, 1997.
10. B. Sareni, L. Krähenbühl, A. Beroual, and C. Brosseau. Effective dielectric constant of periodic composite materials. *J. App. Phys.*, 80:1688, 1996.
11. Cheng-ping Huang, Xiao-gang Yin, Qian-jin Wang, Huang Huang, and Yong-yuan Zhu. Long-wavelength optical properties of a plasmonic crystal. *Phys. Rev. Lett.*, 104:016402, 2010.
12. V. G. Kravets, S. Neubeck, A. N. Grigorenko, and A. F. Kravets. Plasmonic blackbody: Strong absorption of light by metal nanoparticles embedded in a dielectric matrix. *Phys. Rev. B*, 81(16):165401, 2010.
13. F. Brouers, J. P. Clerc, G. Giraud, J. M. Laugier, and Z. A. Randriamantany. Dielectric and optical properties close to the percolation threshold. II. *Phys. Rev. B*, 47:666, 1993.
14. G. Polatsek and O. Entin-Wohlman. Effective-medium approximation for a percolation network: The structure factor and the Ioffe-Regel criterion. *Phys. Rev. B*, 37:7726, 1988.

15. Z.-M. Dang, Y. Shen, and C.-W. Nan. Dielectric behavior of three-phase percolative Ni-BaTiO₃/polyvinylidene fluoride composites. *App. Phys. Lett.*, 81:4814, 2002.
16. Poelsema B. Stefan Kooij E. Shape and size effects in the optical properties of metallic nanorods. *Phys. Chem. Chem. Phys.*, 8:3349, 2006.
17. S. Link, M. B. Mohamed, and M. A. El-Sayed. Simulation of the optical absorption spectra of gold nanorods as a function of their aspect ratio and the effect of the medium dielectric constant. *J. Phys. Chem. B*, 103:3073, 1999.
18. Cecilia Noguez. Surface plasmons on metal nanoparticles: The influence of shape and physical environment. *J. Phys. Chem. C*, 111:3806, 2007.
19. K. Lance Kelly, Eduardo Coronado, Lin Lin Zhao, and George C. Schatz. The optical properties of metal nanoparticles: The influence of size, shape, and dielectric environment. *J. Phys. Chem. B*, 107:668, 2003.
20. J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz. Shape effects in plasmon resonance of individual colloidal silver nanoparticles. *J. Chem. Phys.*, 116:6755, 2002.
21. U. Kreibig. Optical absorption of small metallic particles. *Surf. Sci.*, 156:678, 1985.
22. E. Hutter and J. H. Fendler. Exploitation of localized surface plasmon resonance. *Adv. Mater.*, 16:1685, 2004.
23. Stephan Link and Mostafa A. El-Sayed. Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles. *J. Phys. Chem. B*, 103:4212, 1999.
24. Paul Mulvaney. Surface plasmon spectroscopy of nanosized metal particles. *Langmuir*, 12:788, 1996.
25. Arnim Henglein and Michael Giersig. Formation of colloidal silver nanoparticles: Capping action of citrate. *J. Phys. Chem. B*, 103:9533, 1999.
26. George H. Chan, Jing Zhao, Erin M. Hicks, George C. Schatz, and Richard P. Van Duyne. Plasmonic properties of copper nanoparticles fabricated by nanosphere lithography. *Nano Letters*, 7:1947, 2007.
27. Manjeet Singh, I. Sinha, M. Premkumar, A.K. Singh, and R.K. Mandal. Structural and surface plasmon behavior of Cu nanoparticles using different stabilizers. *Coll. Surf. A*, 359:88, 2010.
28. P.R. West, S. Ishii, G.V. Naik, N.K. Emani, V.M. Shalaev, and A. Boltasseva. Searching for better plasmonic materials. *Laser Photon. Rev.*, 4:795, 2010.
29. Y. Ekinici, H. H. Solak, and J. F. Löffler. Plasmon resonances of aluminum nanoparticles and nanorods. *J. App. Phys.*, 104:083107, 2008.
30. G. Mie. Optical absorption spectra for silver spherical particles. *Ann. Phys.*, 25:377, 1908.
31. Bohren C.F.; Huffman D.R. *Absorption and scattering of light by small particles*. Wiley, 1998.
32. S. Asano; G. Yamamoto. Light scattering by a spheroidal particle. *Appl. Opt.*, 14:29, 1980.
33. A.C. Lind; J. M. Greenberg. Electromagnetic scattering by obliquely oriented cylinders. *J. Appl. Phys.*, 37:3195, 1966.
34. H. Hövel, S. Fritz, A. Hilger, U. Kreibig, and M. Vollmer. Width of cluster plasmon resonances: bulk dielectric functions and chemical interface damping. *Phys. Rev. B*, 48:18178, 1993.
35. U Kreibig. Electronic properties of small silver particles: the optical constants and their temperature dependence. *J. Phys. F: Met. Phys.*, 4:999, 1974.
36. Chan C.T. Fung K.H. A computational study of the optical response of strongly coupled metal nanoparticle chains. *Opt. Comm.*, 281:855, 2008.
37. F. Bisio, M. Palombo, M. Prato, O. Cavalleri, E. Barborini, S. Vinati, M. Franchi, L. Mattera, and M. Canepa. Optical properties of cluster-assembled nanoporous gold films. *Phys. Rev. B*, 80:205428, 2009.
38. Foss Jr. CA. Feldheim DL. *Metal nanoparticles: synthesis, characterization, and applications*. New York: Marcel Dekker, 2002.
39. M. Meier and A. Wokaun. Enhanced fields on large metal particles: dynamic depolarization. *Opt. Lett.*, 8:581, 1983.
40. Cecilia Noguez. Optical properties of isolated and supported metal nanoparticles. *Opt. Mat.*, 27:1204, 2005.
41. Kaspar D. Ko and Kimani C. Toussaint Jr. A simple gui for modeling the optical properties of single metal nanoparticles. *J. Quant. Spectr. Rad. Trans.*, 110:1037, 2009.

42. E.J. Zeman and G.C. Schatz. An accurate electromagnetic theory study of surface enhancement factors for Ag, Au, Cu, Li, Na, Al, Ga, In, Zn, and Cd. *J. Phys. Chem.*, 91:634, 1987.
43. Linda Gunnarsson, Tomas Rindzevicius, Juris Prikulis, Bengt Kasemo, Mikael Kll, Shengli Zou, and George C. Schatz. Confined plasmons in nanofabricated single silver particle pairs: Experimental observations of strong interparticle interactions. *J. Phys. Chem. B*, 109:1079, 2005.
44. P. Tamarat S. Berciaud, L. Cognet and B. Lounis. Observation of intrinsic size effects in the optical response of individual gold nanoparticles. *Nano Letters*, 5:515, 2005.
45. W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht, and F. R. Aussenegg. Optical properties of two interacting gold nanoparticles. *Opt. Comm.*, 220:137, 2003.
46. Q.H. Wei, K.H. Su, S. Durant, and X. Zhang. Plasmon resonance of finite one-dimensional Au nanoparticle chains. *Nano Letters*, 4:1067, 2004.
47. Stefan A. Maier, Mark L. Brongersma, Pieter G. Kik, and Harry A. Atwater. Observation of near-field coupling in metal nanoparticle chains using far-field polarization spectroscopy. *Phys. Rev. B*, 65:193408, 2002.
48. Tian Yang and Kenneth B. Crozier. Dispersion and extinction of surface plasmons in an array of gold nanoparticle chains: influence of the air/glass interface. *Opt. Express*, 16:8570, 2008.
49. Yu Chen and A. M. Goldman. Formation of one-dimensional nanoparticle chains. *App. Phys. Lett.*, 91:063119, 2007.
50. Jiwen Zheng, Zihua Zhu, Haifeng Chen, and Zhongfan Liu. Nanopatterned assembling of colloidal gold nanoparticles on silicon. *Langmuir*, 16:4409, 2000.
51. Andrew N. Shipway, Eugenii Katz, and Itamar Willner. Nanoparticle arrays on surfaces for electronic, optical, and sensor applications. *ChemPhysChem*, 1:18, 2000.
52. Beomseok Kim, Steven L. Tripp, and Alexander Wei. Self-organization of large gold nanoparticle arrays. *J. Am. Chem. Soc.*, 123:7955, 2001.
53. N. Féridj, J. Aubard, G. Lévi, J. R. Krenn, A. Hohenau, G. Schider, A. Leitner, and F. R. Aussenegg. Optimized surface-enhanced Raman scattering on gold nanoparticle arrays. *Appl. Phys. Lett.*, 82:3095, 2003.
54. Christy L. Haynes and Richard P. Van Duyne. Nanosphere lithography: A versatile nanofabrication tool for studies of size-dependent nanoparticle optics. *J. Phys. Chem. B*, 105:5599, 2001.
55. Christy L. Haynes, Adam D. McFarland, LinLin Zhao, Richard P. Van Duyne, George C. Schatz, Linda Gunnarsson, Juris Prikulis, Bengt Kasemo, and Mikael Käll. Nanoparticle optics: The importance of radiative dipole coupling in two-dimensional nanoparticle arrays. *J. Phys. Chem. B*, 107:7337, 2003.
56. Marisa Mäder, Thomas Höche, Jürgen W. Gerlach, Susanne Perl, Jens Dorfmueller, Michael Saliba, Ralf Vogelgesang, Klaus Kern, and Bernd Rauschenbach. Plasmonic activity of large-area gold nanodot arrays on arbitrary substrates. *Nano Letters*, 10:47, 2010.
57. K.-H. Su, Q.-H. Wei, X. Zhang, J. J. Mock, D. R. Smith, and S. Schultz. Interparticle coupling effects on plasmon resonances of nanogold particles. *Nano Letters*, 3:1087, 2003.
58. Prashant K. Jain, Wenyu Huang, and Mostafa A. El-Sayed. On the universal scaling behavior of the distance decay of plasmon coupling in metal nanoparticle pairs: A plasmon ruler equation. *Nano Letters*, 7:2080, 2007.
59. Shengli Zou and George C. Schatz. Narrow plasmonic/photonic extinction and scattering line shapes for one and two dimensional silver nanoparticle arrays. *J. Chem. Phys.*, 121:12606, 2004.
60. Stefan A. Maier, Pieter G. Kik, and Harry A. Atwater. Observation of coupled plasmon-polariton modes in Au nanoparticle chain waveguides of different lengths: Estimation of waveguide loss. *App. Phys. Lett.*, 81:1714, 2002.
61. Mark L. Brongersma, John W. Hartman, and Harry A. Atwater. Electromagnetic energy transfer and switching in nanoparticle chain arrays below the diffraction limit. *Phys. Rev. B*, 62:R16356, 2000.
62. Stefan A. Maier, Pieter G. Kik, and Harry A. Atwater. Optical pulse propagation in metal nanoparticle chain waveguides. *Phys. Rev. B*, 67:205402, 2003.

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