Surface plasmon resonance in gold nanoparticles: a review

To cite this article: Vincenzo Amendola et al 2017 J. Phys.: Condens. Matter 29 203002

View the article online for updates and enhancements.

Related content

- When plasmonics meets membrane technology
  A Politano, A Cupolillo, G Di Profio et al.

- Direct photocatalysis of supported metal nanostructures for organic synthesis
  Xiayan Wu, Esa Jaatinen, Sarina Sarina et al.

- Sensing using plasmonic nanostructures and nanoparticles
  Judith Langer, Sergey M Novikov and Luis M Liz-Marzán

Recent citations

- Femtosecond Laser Fabricated Ag@Au and Cu@Au Alloy Nanoparticles for Surface Enhanced Raman Spectroscopy Based Trace Explosives Detection
  Moram Sree Satya Bharati et al.

- Cellular uptake of gold nanoparticles triggered by host-guest interactions
  Jesús Mosquera Mosquera et al.

- Marcelo Grijalva et al.
Topical Review

Surface plasmon resonance in gold nanoparticles: a review

Vincenzo Amendola1,2, Roberto Pilot1,2, Marco Frasconi1, Onofrio M Maragò3, Maria Antonia Iatì3

1 Department of Chemical Sciences, University of Padova, via Marzolo 1, I-35131 Padova, Italy
2 Consorzio INSTM, UdR Padova, Italy
3 CNR-IPCF, Istituto per i Processi Chimico-Fisici, v.le F. Stagno D’Alcontres 37, I-98158 Messina, Italy

E-mail: vincenzo.amendola@unipd.it

Received 2 March 2016, revised 1 January 2017
Accepted for publication 16 February 2017
Published 20 April 2017

Abstract
In the last two decades, plasmon resonance in gold nanoparticles (Au NPs) has been the subject of intense research efforts. Plasmon physics is intriguing and its precise modelling proved to be challenging. In fact, plasmons are highly responsive to a multitude of factors, either intrinsic to the Au NPs or from the environment, and recently the need emerged for the correction of standard electromagnetic approaches with quantum effects. Applications related to plasmon absorption and scattering in Au NPs are impressively numerous, ranging from sensing to photothermal effects to cell imaging. Also, plasmon-enhanced phenomena are highly interesting for multiple purposes, including, for instance, Raman spectroscopy of nearby analytes, catalysis, or sunlight energy conversion. In addition, plasmon excitation is involved in a series of advanced physical processes such as non-linear optics, optical trapping, magneto-plasmonics, and optical activity. Here, we provide the general overview of the field and the background for appropriate modelling of the physical phenomena. Then, we report on the current state of the art and most recent applications of plasmon resonance in Au NPs.

Keywords: plasmon resonance, gold nanoparticles, Mie theory, plasmon sensing, SERS, near-field enhancement

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

Contents

| Abbreviations | 2 |
| Introduction | 3 |
| 1. Fundamentals of SPR in Au NPs | 3 |
| 1.1. Plasmons, localized plasmons and plasmonic quality factor | 3 |
| 1.2. Dynamics of LSP | 6 |
| 1.2.1. SPR bandwidth | 6 |
| 1.2.2. Radiative decay | 7 |
| 1.2.3. Non-radiative decay | 7 |
| 1.2.4. Fate of the SPR | 7 |
| 1.2.5. Photoluminescence (PL) associated to SPR | 7 |
| 2. Factors influencing plasmon resonance | 7 |
| 2.1. Dielectric and physical-chemical environment | 7 |
| 2.1.1. Non-absorbing dielectric environment | 7 |
| 2.1.2. Absorbing dielectric environment | 8 |
| 2.1.3. Plexcitons | 9 |
| 2.1.4. Surface chemical interactions | 10 |
| 2.1.5. Temperature | 10 |
| 2.1.6. Pressure | 10 |
2.2. Size ............................................. 10
  2.2.1. Absorption and scattering cross-section .... 10
  2.2.2. Extrinsic size effects .......................... 10
  2.2.3. Intrinsic size effects .......................... 11
  2.2.4. Quantum size effects on the SPR .......... 12
2.3. Assembly ........................................ 12
  2.3.1. Fano resonances .............................. 13
  2.3.2. Magnetic plasmonic resonances (MPR) .... 13
2.4. Shape ............................................. 14
2.5. Composition ...................................... 14
  2.5.1. Electric charge ................................. 16
3. Modelling the SPR of Au NPs ........................ 16
  3.1. Optical constant ................................. 16
    3.1.1. Non-locality and quantum size effects ....... 17
  3.2. Analytical and numerical methods .............. 17
    3.2.1. Mie theory ...................................... 17
    3.2.2. Non-spherical shapes .......................... 17
    3.2.3. Effective medium theories (EMTs) .......... 20
4. Applications related to SPR optical extinction .... 20
  4.1. Sensing and imaging with plasmon resonance ... 20
    4.1.1. Sensing .......................................... 20
    4.1.2. Dark-field imaging ............................. 22
    4.1.3. Role of surface functionalization .......... 22
  4.2. Staining, information storage, and photoluminescence ........ 22
  4.3. Photothermal effects ............................ 22
    4.3.1. PT and cell killing ............................ 24
    4.3.2. Photothermal drug release and diffusion .... 24
    4.3.3. Photothermal contrast imaging ............... 25
    4.3.4. Nanobubbling ................................... 25
    4.3.5. Photocoustic imaging (PA) ................. 26
    4.3.6. Photothermal activation of phase transformation ...... 26
    4.3.7. Au NP welding, alloying, and shape transformation .... 26
    4.3.8. Photothermal activation of chemical reactions ........ 26
  4.4. Plasmon-induced hot-carrier effects ............... 27
5. Applications related to local-field enhancement .... 27
  5.1. Local-field enhancement ........................ 27
    5.1.1. Near-field redshift ............................ 28
  5.2. SERS ............................................. 28
    5.2.1. Chemical enhancement (CE) .................. 29
    5.2.2. Electromagnetic enhancement ................. 30
    5.2.3. Analyte contribution to SERS ................. 31
    5.2.4. Applications .................................. 31
    5.2.5. Coherent anti-Stokes Raman scattering ....... 31
    5.2.6. Hyper Raman scattering ........................ 31
  5.3. Fluorescence modulation .......................... 32
    5.3.1. Active plasmonic devices ....................... 33
  5.4. Surface-enhanced infrared absorption (SEIRA) ................. 34
  5.5. Enhanced optical absorption and photovoltaic applications ...... 34
6. Other applications and advanced phenomena ........ 34
  6.1. Optical trapping and manipulation ............... 34
    6.1.1. Optical trapping of Au NPs ................. 35
    6.1.2. Plasmonic tweezers with Au NPs ............. 35
  6.2. Plasmonic chiroptical effects .................... 35
    6.2.1. Intrinsic chiroptical effects in Au NPs ....... 36
    6.2.2. Enhancement of chiroptical effects in nearby molecules ...... 36
  6.3. Magneto-plasmonic effects ........................ 37
  6.4. Non-linear optical applications ........................ 39
    6.4.1. Optical Kerr effect (OKE) ........................ 39
    6.4.2. Multiple harmonic generation (MHG) .......... 39
    6.4.3. Multiphoton absorption-induced photoluminescence (MPPL) .......... 41
    6.4.4. Optical limiting (OL) .......................... 41
7. Conclusions ........................................ 41

Abbreviations

BEM Boundary element method
CARS Coherent anti-Stokes Raman scattering
CD Circular dichroism
CE Chemical enhancement
CID Chemical interface damping
DDA Discrete dipole approximation
DFT Density functional theory
EELS Electron energy loss spectroscopy
EF Enhancement factor
EMTs Effective medium theories
FDTD Finite difference time domain
FOM Figure of merit
FRET Fluorescence resonance energy transfer
GMT Generalized Mie theory
HM Hybridization model
HRS Hyper Raman scattering
LSP Localized surface plasmon
FEM Finite element method
LUMO Lowest unoccupied molecular orbital
MCD Magnetic circular dichroism
MHG Multiple harmonic generation
MOKE Magneto-optic Kerr effect
MOSPR Magneto-optical surface plasmon resonance
MPPL Multiphoton-absorption-induced photoluminescence
MPR Magnetic plasmonic resonances
NCs Nanocrystals
NIR Near infrared
NLO Nonlinear optics
NPs Nanoparticles
NRs Nanorods
NSs Nanoshells
NSET Nanosurface energy transfer
In recent decades, gold nanoparticles (Au NPs) have been the subject of a vast and exponentially growing amount of literature. As their name implies, the small size of Au NPs is attractive for biomedical use in sensing [1, 2], cellular imaging [3, 4], drug delivery [5], and cancer therapy [6], but intensive research effort is also directed to chemical analysis and catalysis [7–10], electronics [11, 12], and nonlinear optical processes [13, 14]. This broad range of applications fostered parallel research on a multitude of basic physical effects occurring in Au NPs [15, 16].

There are three main reasons behind the success of Au NPs in the panorama of nanoscience and nanotechnology [17–19]: (i) the high chemical and physical stability, also implying the intrinsic biocompatibility of gold nanostructures (colloidal gold has been exploited for curative purposes since the Middle Ages), (ii) the ease of surface functionalization with organic and biological molecules, and (iii) the multitude of optical properties related to surface plasmons. In particular, Au NPs have a large number of easily polarizable conduction electrons, which is a general prerequisite for preferential interaction with electromagnetic fields and the generation of nonlinear optical phenomena [4]. In fact, compared to other organic and inorganic chromophores, Au NPs with size above 2 nm have a larger extinction cross-section, possibility reaching 100% of light-to-heat conversion efficiency, high photosensitivity, and the ability to amplify the electromagnetic field at nanometric distance from the metal surface, as will be discussed in the following sections.

The characteristic bright red colour of spherical Au NPs has attracted the interest of manufacturers since ancient times [20], and Au NPs or their nanoalloys can be found in ornamental cups such as the Lycurgus cup (ca. 4th century) [21, 22], red ruby glasses coloured with the purple of Cassius’ (Middle Ages) [23, 24] and lustre plates (15th–16th century) [20]. One of the oldest samples is represented by a gold-plated Egyptian ivory dating back to the 8th century BC, where Au NPs accidentally formed a purple staining by the diffusion of gold from a thin foil into the porous ivory substrate (figure 1(A)) [25]. Indeed, this type of application has lasted till the present day [26].

The first scientist who related the optical properties of Au NPs to their small size was Michael Faraday, who in 1852 gave a lecture at the Royal Institute in London entitled ‘Experimental Relations of Gold (and Other Metals) to Light’ [27]. In his reports, Faraday described the Au colloid solutions as ‘a beautiful ruby fluid’, and attributed the effect to ‘a mere variation in the size of particles’. Later, Faraday’s study inspired the theoretical work of Gustav Mie in the early 1900s, which is still valid today, and is described in section 3 [28]

In this review, we summarize the main concepts behind surface plasmon resonance (SPR) in Au NPs, and the most relevant applications, with special attention to cutting-edge topics. The review is divided into six main sections: 1. Fundamentals of SPR in Au NPs; 2. Factors influencing plasmon resonance; 3. Modelling the SPR of Au NPs; 4. Applications related to SPR optical extinction; 5. Applications related to local field enhancement; 6. Other applications and advanced phenomena. Therefore, the contents include the linear optical properties deriving from the coherent oscillation of conduction electrons in Au nanostructures, as well as the influence of the local electromagnetic field enhancement associated to the SPR on other linear and nonlinear optical processes intrinsic to Au NPs, or observed in their proximity by placing a suitable molecular probe. In any case, it should be noted that this manuscript is not intended as a comprehensive review of the subject, but rather as a selection of helpful insights chosen from the literature. Besides, we focus the discussion on Au NPs or their assemblies with size below ~1 μm, i.e. to ‘nano’ Au, meaning that collective effects in ordered or disordered assemblies of Au nanostructures with the size of microns or larger, such as metamaterials, are outside the scope of this review. Due to the optical permittivity of gold, the NPs size range below ~1 μm sets the frequency of the majority of the optical phenomena discussed in the text in the visible and near infrared (NIR) region.

### 1. Fundamentals of SPR in Au NPs

#### 1.1. Plasmons, localized plasmons and plasmonic quality factor

‘Plasmons’ are collective oscillations of free electrons in metals [15, 29]. Since these oscillations occur at a well-defined frequency, a ‘plasmon’ is classified as a bosonic quasiparticle
excitation and corresponds to a quantum of plasma oscillation (thus the -on suffix) [15, 29, 30]. According to the Fermi liquid model, plasmons can be described as a negatively charged electron cloud coherently displaced from its equilibrium position around a lattice made of positively charged ions, in analogy to a real plasma (figure 2(A)) [15, 29].

Excitation of plasmons by the electric field of electromagnetic radiation is not allowed in bulk matter, i.e. below metal skin depth, where plasmon and photon energy dispersion curves never cross each other [15, 30]. On the other hand, the presence of a surface in real materials allows the existence of specific plasmon modes, which can be excited by the external electric field of the electromagnetic radiation [15, 30], causing displacements of the electron gas with respect to their equilibrium position around positively charged ions. The light with a high angle of incidence (i.e. with the wave vector nearly parallel to the surface, see figure 2(A)) couples most efficiently with the free electron gas, such as in the attenuated total reflection (Kretschmann or Otto) configuration [15]. In fact, these types of oscillations are called propagating surface plasmon polaritons (PSPP), in analogy with propagating phonon–polaritons [15, 29].

In the case of metallic NPs, i.e. with size comparable to the metal skin depth, the electric field of incident light can penetrate the metal and polarize the conduction electrons (figure 2(B)) [15, 30]. In contrast to PSPP, plasmons in NPs with size much smaller than photon wavelength are non-propagating excitations, called localized surface plasmons (LSPs), because the resulting plasmon oscillation is distributed over the whole particle volume [15, 30]. Such a coherent displacement of electrons from the positively charged lattice generates a restoring force that pulls the polarized electrons back to the lattice, i.e. the NPs act much like a ‘nanoantenna’ [31]. Hence, the plasmon in an NP can be considered as a mass-spring harmonic oscillator driven by the energy resonant light wave, where the electron cloud oscillates like a simple dipole in parallel direction to the electric field of the electromagnetic radiation (figure 2(C)) [31–33]. Only light with frequency in resonance with the oscillation is able to excite the LSP [15]. The simple mass-on-a-spring damped oscillator model, where the mass is represented by the electron density and the spring constant is set by the Coulomb restoring force between electrons and lattice atoms, has been utilized several times to gain conceptual and physical (semi-quantitative) understanding of plasmonic systems [31–33]. For instance, in the case of a spherical Au NP with size much smaller than the wavelength of light (quasistatic approximation), the distortion of the electron cloud in response to the electric field can be expressed by the metal polarizability [30, 34]:

$$\alpha(\lambda) = 3\varepsilon_m(\lambda)V_{NP}\frac{\varepsilon(\lambda) - \varepsilon_m(\lambda)}{\varepsilon(\lambda) + \chi\varepsilon_m(\lambda)}$$

(1)

where $\lambda$ is the light wavelength, $\varepsilon_m$ the dielectric constant of the non-absorbing ($\text{Im}[\varepsilon_m(\lambda)] = 0$) surrounding medium, $V_{NP}$ the NP volume, $\chi$ a geometrical factor ($\chi = 2$ in a sphere), and $\varepsilon(\omega)$ is the frequency ($\omega$) dependent complex dielectric function (figures 3(A) and (B)) [35, 36]:

$$\varepsilon(\omega) = \text{Re}[\varepsilon(\omega)] + i\text{Im}[\varepsilon(\omega)].$$

(2)

From equation (1), one can arrive to the quasistatic expression of the extinction cross-section ($\sigma_{\text{Ext}}$) in a spherical Au NP [15, 37]:

$$\sigma_{\text{Ext}} = \frac{18\pi[\varepsilon_m(\lambda)]^{3/2}}{\lambda} \frac{\text{Im}[\varepsilon(\lambda)]}{\text{Re}[\varepsilon(\lambda)] + 2\varepsilon_m(\lambda)} \frac{1}{\text{Im}[\varepsilon(\lambda)]^2 + \text{Im}[\varepsilon(\lambda)]^2}.$$

(3)

From equation (3), it is evident that:
The plasmonic properties of any material are defined by its $\varepsilon(\omega)$; (ii) $\sigma_{\text{Ext}}$ scales with particle volume; (iii) $\sigma_{\text{Ext}}$ is maximum when the denominator is minimized, namely the LSP is excited at the frequency where $\varepsilon(\omega) \chi \varepsilon_m(\omega) \approx -\text{Re} \, \varepsilon_m(\omega)$. Equation (4), also called the Fröhlich condition, defines the localized SPR condition. Clearly, the frequency of the SPR is tunable by changing the $\varepsilon_m(\omega)$ of the surrounding medium, but it is also strongly affected by NP size, shape, and composition [38, 39], as discussed in section 2. 

Obviously, the persistence of plasmonic oscillation is limited in time by loss [36, 40]. While $\text{Re}[\varepsilon_i]$ describes the resonance frequency of a plasmonic system, $\text{Im}[\varepsilon_i]$ describes its losses. Losses are due to many processes, including radiative damping, electron gas confinement, structural imperfections, and metal heating losses (see section 1.2) [36, 40]. However, in most plasmonic systems, such as Au NPs, the main source of loss is intraband transitions, i.e. single particle excitations from the occupied 5d valence band to the unoccupied levels of the 6s–6p conduction band of gold (see section 1.2) [36, 40]. This is because the formation of electron–hole couples, that is simultaneous to LSP excitation, dramatically increases the electron–electron scattering rate (see section 1.2).

From the plot of $\text{Im}[\varepsilon_i]$ in figure 3(B), one can see that Au suffers higher losses than Ag in the visible range [36, 40]. The reason is that the band edge frequency in Ag, i.e. the frequency at which interband (IB) transitions become allowed, is above the SPR frequency, so that LSP cannot decay into electron–hole pairs, whereas in Au nanospheres there is an overlap resulting in a reduced plasmon intensity [36, 40]. However, Au is often preferred to Ag for its higher biocompatibility and chemical stability, in particular against surface oxidation and dissolution in liquid environments over time [18, 19].

The considerations about SPR intensity can be quantified by the plasmonic quality factor $Q_{\text{SPR}}$. Every specific NP geometry has a different expression for the quality factor, but in the limit of low loss and in the quasistatic regime (i.e. when the NPs are much smaller than the wavelength of light, which means almost homogeneous electric field distribution along the whole NP volume), $Q_{\text{SPR}}$ can be written as:

$$Q_{\text{SPR}}(\omega) = \frac{-\text{Re}[\varepsilon_m(\omega)]}{\text{Im}[\varepsilon_m(\omega)]}.$$  

Figure 2. Graphical illustration of plasmons in bulk gold (A) and NPs (B). (A) Bulk plasmons can be excited by an electron beam (bottom), while PSPPs are excited by the evanescent field of light (top). (B) LSPs are excited by light propagating in free space or dielectric media. (C) The LSP in Au NPs can be modelled, as a first approximation, like a spring-mass harmonic oscillator, where the free-electron density is the equivalent of the mass.

(i) the plasmonic properties of any material are defined by its $\varepsilon(\omega)$; (ii) $\sigma_{\text{Ext}}$ scales with particle volume; (iii) $\sigma_{\text{Ext}}$ is maximum when the denominator is minimized, namely the LSP is excited at the frequency where $\varepsilon(\omega) \chi \varepsilon_m(\omega) \approx -\text{Re} \, \varepsilon_m(\omega)$.

Equation (4), also called the Fröhlich condition, defines the localized SPR condition. Clearly, the frequency of the SPR is tunable by changing the $\varepsilon_m(\omega)$ of the surrounding medium, but it is also strongly affected by NP size, shape, and composition [38, 39], as discussed in section 2.

According to equation (5), for a given plasmon resonance frequency $\omega_{\text{SPR}}$, the LSP quality factor is determined only by the complex dielectric function of the material, independent of the NP shape or the dielectric environment (figure 3(C)) [36, 40]. However, we will see in section 2 that it is possible to shift the LSP frequency in the region of highest $Q_{\text{SPR}}$ by acting on several factors.

The LSP is associated to two important physical effects [15, 41]:

(i) the Au NP optical extinction has a maximum at the SPR frequency, which occurs at visible–NIR wavelengths and with an extinction cross-section ($\sigma_{\text{Ext}}$) that can be much larger than their geometrical size;

(ii) Au NPs behave as nanolenses, i.e. the electromagnetic field near the particle surface (either inside or outside the NP) is greatly enhanced, and rapidly falls off with distance. This overcomes the resolution limit of ordinary far-field optics, allowing light localization on nanometric or subnanometric scale.
These two effects are at the core of the SPR applications described in sections 4–6. A higher $Q_{\text{SPR}}$ factor representing a sharper resonance is often desirable as it leads to higher optical extinction and stronger local-field enhancement.

The simplest way to probe the LSP is by measuring the optical extinction of ensembles of Au NPs by optical absorption spectroscopy [34, 42, 43]. For instance, the optical extinction spectrum of a colloidal solution of spherical Au NPs is characterized by an SPR band in the proximity of 520 nm, partially superposed to the tail of IB transitions at shorter wavelengths (figure 3(D)) [30, 43]. However, the LSP in single Au NPs can also be directly probed by far-field extinction microscopy (figure 4(A)) [44, 45], electron energy loss spectroscopy (EELS, figure 4(B)) [46–48], or cathodoluminescence (figure 4(B)) [49, 50]. In the last two cases, 3D mapping of the LSP over NP volume has also been demonstrated (figure 4(C)) [48, 49].

Figure 3. Plot of Re[$\varepsilon$] (A) and Im[$\varepsilon$] (B) for Au (black) and Ag (green), as reported in [160]. (C) Semi-log plot of $Q_{\text{SPR}}$ (in absolute value) for Au and Ag (adapted from [67]). (D) Extinction spectrum of spherical Au NPs (20 nm diameter, in water, calculated with the Mie model). Onset of IB and SPR regions are highlighted in blue and red, respectively.

Figure 4. (A) Photograph of Au NRs (red colour, bottom left inset) and 60 nm nanospheres (green colour, bottom right inset) in dark-field illumination (inset upper left). Reprinted with permission from [45]. Copyright 2002 by the American Physical Society. (B) EELS (top) and CL (bottom) maps of the dipolar LSP in an Au nanoprisim. Reprinted with permission from [50]. Copyright (2015) American Chemical Society. (C) 3D LSP mapping of a plasmonic nanocube. The colour bar indicates the SPR intensity for the five LSP modes considered. Reprinted by permission from Macmillan Publishers Ltd: Nature [48], copyright (2013).

1.2. Dynamics of LSP

1.2.1. SPR bandwidth. The plasmon bandwidth of a single Au NP is associated to the dephasing time of the coherent electron oscillation, with larger bandwidth corresponding to a faster loss of coherence [30, 51, 52]. Typical electron dephasing times in Au NPs are of 2–50 fs, depending on particle structure and environment, and this value sets the SPR bandwidth [30, 51, 52].

The total line width of the SPR band is contributed by a radiative term, producing elastically scattered radiation, proportional to the radiative decay rate $\Gamma_r$, and a non-radiative term depending on electronic relaxation processes $\Gamma_{\text{nr}}$, essentially producing heat [15, 30, 51].

Considering the LSP as an example of a harmonic oscillator composed by a charge-on-a spring, the SPR bandwidth
is proportional to the total relaxation rate $\Gamma$, that can be expressed as [33]:

$$\Gamma = \Gamma_{\text{nr}} + \omega^2 \Gamma_i$$  \hspace{1cm} (6)

where one can see that the $\Gamma_i$ term is multiplied for a $\omega^2$ factor, meaning that its importance rapidly decreases while lowering the SPR frequency.

1.2.2. Radiative decay. The $\Gamma_i$ term is associated with the far-field radiation emitted by accelerating and decelerating charged particles, and thus it is fully accounted by the classic electrodynamics theory (such as the Mie model, see section 3.2.1). Since classical laws of electrodynamics necessitate that an accelerating charge releases energy in the form of radiation, conservation of energy implies that this charge must consequently lose kinetic energy, and is referred to as the Abraham–Lorentz force or the radiation reaction force [33, 53]. The relative weight between the two contributions in equation (6) sets the proportion between light scattering versus light absorption (intended as transfer of photon energy to the NP lattice, see section 2.2.1). The relative weight of the two processes changes with NP size, and to a lesser extent also with NP shape and environment. The radiative decay contribution becomes more important for increasing NP size, but for 20 nm Au NPs it accounts for only a few percent of the total damping rate [45, 54, 55].

1.2.3. Non-radiative decay. Several groups extensively studied the non-radiative SPR relaxation rate with ultrafast spectroscopy [51, 52, 56, 57]. There are several dephasing mechanisms contributing to $\Gamma_{\text{nr}}$, and the principal ones are the electron–electron scattering ($1/\tau_{e-e}$), electron–phonon scattering ($1/\tau_{e-ph}$), electron–defects scattering ($1/\tau_{e-d}$), and additional damping effects due to surface effects ($1/\tau_s$, discussed in sections 2.1 and 2.2) [51, 52]. According to Matthiessen law, all these contributions can be expressed as [51, 52]:

$$\Gamma_{\text{nr}} = \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{e-d}} + \frac{1}{\tau_s}$$  \hspace{1cm} (7)

When a single Au NP is polycrystalline or highly defective, the damping frequency also increases, producing a larger SPR band [58].

1.2.4. Fate of the SPR. All the above scattering processes can be viewed as a unique Landau damping mechanism, with the damping rate depending on the phenomena listed in equation (7). In Landau damping, plasmon energy is transferred into lower-energy single or multiple electron–hole pair excitations on a time scale of 1–100 fs [59, 60]. The electron–hole pair’s excitation can be either intraband or IB (see figure 5(Λ)) [60–62].

Due to the energy overlap of plasmon absorption and the edge of IB transitions in spherical Au NPs, IB excitation corresponding to the excitation of one electron in the conduction band and creation of a hole in the lower-lying $d$ band has a remarkable contribution to the electron–electron relaxation rate [62], ultimately explaining why $Q_{1,SP}$ in Au is lower than in Ag [36, 40, 63].

After electron–hole formation by Landau damping, electron–electron scattering (such as Auger transitions) takes place on a time scale of ~500 fs, leading to electron thermalization (figure 5) [51, 52, 60, 62]. This can be seen as the relaxation of the IB electron–hole pairs and/or higher-energy IB pairs, by the formation of several lower-energy intraband electron–hole pairs in the conduction band [51, 60]. In this way, electron energies rearrange from a non-equilibrium to the quasi-equilibrium Fermi–Dirac distribution, corresponding to the system thermal energy plus the absorbed photon energy [51]. This means that for times $\leq$500 fs after plasmon excitation, the electronic temperature is still higher than the lattice temperature [51, 52].

In 1–5 ps, electron–phonon scattering leads to the thermalization of the electronic bath with the lattice [51, 52]. The last process involves phonon–phonon interaction between the lattice and the surrounding medium, with a time scale of hundreds of picoseconds up to nanoseconds [51, 52].

In general, one should consider that all these relaxation mechanisms are partially overlapping in time [64]. Besides, the precise time scale depends on the intensity of the light beam and on the external temperature, for instance, because all decay rates are temperature dependent [55].

The relaxation processes following plasmon loss of coherence can be modeled according to the two-temperature model (TTM), in which the electrons and the lattice are treated as two coupled subsystems with different initial temperature after LSP excitation, and with different heat capacities [51]. A different model was recently reported, which is based on a master equation incorporating transition rates for optical excitations and electron–electron collisions, while the interaction with phonons was introduced as a phenomenological inelastic attenuation [64].

1.2.5. Photoluminescence (PL) associated to SPR. PL efficiency of LSP (i.e. inelastic radiative relaxation, measured as the number of emitted photons over the number of extinct photons) is typically below $10^{-3}$–$10^{-5}$. This is expected for metals, where the non-radiative decay processes are very fast. Indeed, the entity of intrinsic PL due to SPR decay in Au NPs is debated, as it implies the radiative recombination of electron–hole couples [15, 51]. On the other hand, the PL efficiency in Au NPs is 105–107 times higher than in bulk Au, and in Au nanorods (NRs) it is ~105 times higher than in Au nanospheres [51, 63]. This is often reported as the ‘lightning rod’ effect, which consists in the enhanced radiative recombination efficiency of sp band electrons with d band holes, thanks to the local electric field associated to the LSP (see section 5) [51]. However, the strongest contribution to the PL measured so far in Au NPs is very often associated to the electronic states of surface impurities [65]. Besides, there is experimental and theoretical evidence that the PL yield decreases while increasing the local field at the junction between two NPs, indicating that the hypothesis of a plasmonically enhanced luminescence needs further investigation [66].

2. Factors influencing plasmon resonance

2.1. Dielectric and physical-chemical environment

2.1.1. Non-absorbing dielectric environment. Following equation (4), a change in $\varepsilon_m$ corresponds to a change in
the SPR frequency of Au NPs in a non-absorbing matrix \((\varepsilon_m = \text{Re}\{\varepsilon_m\})\) [15]. Since \(\text{Re}\{\varepsilon_{\text{Au}}\}\) decreases versus wavelength (see figure 3(A)), equation (4) implies that the SPR is redshifted for increasing \(\varepsilon_m\) (i.e. going from water to glass) and blueshifted for decreasing \(\varepsilon_m\) (i.e. going from water to air) [34]. The SPR redshift is associated to the increase of the Au NP extinction cross-section, because \(Q_{\text{SPR}}\) increases with wavelength in the 500–700 nm range (see figure 6(A)) [36, 40].

Due to the nanometric size of NPs, i.e. to the large fraction of surface atoms over the total, the SPR position is very sensitive to the environmental dielectric properties, such as changes in liquid or gas density, formation of organic shells such as those of stabilizing ligands, and in general to any surface adsorption of chemical compounds [34, 43]. This finds important applications in sensing, as described in section 4.1.

2.12. Absorbing dielectric environment. The integration of Au NPs with absorbing materials, such as graphene, semiconductor quantum dots, or metal oxides, is frequently sought for the realization of hybrid multifunctional materials. In this case, the SPR will experience both the spectral shift due to the change in the real part of \(\varepsilon_m\), as described above, and the shielding effect due to light absorption associated to the imaginary part of \(\varepsilon_m\). Depending on the geometry of the absorbing materials (size, thickness, shape, etc) and the coupling distance, the effect on the SPR can go from plasmon enhancement to complete quenching [67, 68]. For instance, the SPR of Au NPs embedded in several graphene layers is quenched up to reaching a lower extinction than the sum of the two isolated components (i.e. an ‘enhanced transparency’ effect) [67]. This effect is distance dependent: it is stronger below 1 nm, and lost when graphene is at a distance of about 5 nm from the Au NP [67]. This result is non-trivial considering that graphene layers are not transparent and contribute to the overall absorption cross-section of the nanostructure (see figure 6(B)). Therefore, coupling plasmonic NPs with graphene multilayers is a way to dramatically change the optical density in the SPR region without acting directly or irreversibly on the metal nanostructure.

2.1.3. Plexcitons. Coupling between the LSP and the electronic transition in molecules near Au NPs is possible [69, 70]. It was recently shown that the molecules’ electronic structure is modified after adsorption on the metal surface, with spectral changes in their absorption bands far from the SPR frequency [71]. A notable case is that of hybrid nanostructures made of plasmonic NPs and quantum emitters supporting excitons (such as J-aggregates, organic dyes, and quantum dots). The coupling between plasmonic and excitonic modes is possible in these hybrid systems, resulting in mixed plasmon/exciton resonances called ‘plexcitons’ [72, 73]. In plexcitons, Rabi splitting of the plasmon and exciton resonances occurs, i.e. a spectral shift in opposite directions of the two resonances [72]. The entity of this shift depends on the coupling strength and the spectral gap (detuning) between the two resonances, with highest effects observed for lowest detuning [72, 73]. For instance, Rabi splitting has been observed in extinction and emission spectra of plexcitonic nanostructures that combine Au NPs and J-aggregates [72, 73]. These complexes form through electrostatic self-assembly, due to the positively charged J-aggregates and negatively charged Au NPs (figure 6(C)), meaning that the contribution of Au NP aggregation to the experimental results is assumed as negligible [72, 73].

The coupling of plasmons and excitons can be described with the classical electromagnetic theory [72]. If both the excitons and plasmon modes are modelled as coupled harmonic oscillators, the energies of the new hybrid plexcitonic modes are given by [73]:

Figure 5. (A) Formation of electron–hole pairs in Au can be either intraband or IB. After LSP excitation (B), the athermal distribution of electron–hole (e–h) pairs decays in 1–100 fs by photon emission (radiatively) or through Landau damping and the formation of hot carriers (non-radiatively) (C). Hot carriers redistribute their energy by electron–electron scattering on a timescale ranging from 100 fs to 1 ps (D). Then, heat is transferred inside the NP by electron–phonon (e–ph) scattering on a time scale of a few picoseconds, and from the NP to the surroundings on a time scale of several picoseconds to nanoseconds (E). The Fermi electron population is reported in grey, hot electrons are represented by the red areas above the Fermi energy \((E_F)\), and hot-hole distributions are represented by the blue area below \(E_F\). Adapted by permission from Macmillan Publishers Ltd:Nature Nanotechnology [60], copyright (2015). (F) The complete timeline of SPR relaxation.

---

**Figure 5.** (A) Formation of electron–hole pairs in Au can be either intraband or IB. After LSP excitation (B), the athermal distribution of electron–hole (e–h) pairs decays in 1–100 fs by photon emission (radiatively) or through Landau damping and the formation of hot carriers (non-radiatively) (C). Hot carriers redistribute their energy by electron–electron scattering on a timescale ranging from 100 fs to 1 ps (D). Then, heat is transferred inside the NP by electron–phonon (e–ph) scattering on a time scale of a few picoseconds, and from the NP to the surroundings on a time scale of several picoseconds to nanoseconds (E). The Fermi electron population is reported in grey, hot electrons are represented by the red areas above the Fermi energy \((E_F)\), and hot-hole distributions are represented by the blue area below \(E_F\). Adapted by permission from Macmillan Publishers Ltd:Nature Nanotechnology [60], copyright (2015). (F) The complete timeline of SPR relaxation.
citonic coupling depends on the ratio of pure dephasing rates of the exciton. The strength of the plexciton coupling strength between the two oscillators, \( \gamma \), is a parameter measuring the interaction coupling strength between the two oscillators. \( \omega_{\text{SPR}} \) and \( \omega_{\text{exc}} \) are, respectively, the plasmonic and excitonic frequencies, \( \delta = \omega_{\text{SPR}} - \omega_{\text{exc}} \) is the detuning, \( \Gamma \) is the plasmonic damping, \( \gamma_0 \) and \( \gamma_d \) are, respectively, the spontaneous decay and the plasmonic dampings, and \( \Delta \) is the excitonic damping. The strength of the plexciton coupling depends on the ratio \( \delta = \omega_{\text{SPR}} - \omega_{\text{exc}} \) and the strong coupling regime (positive Rabi splitting) occurring when this value exceeds \( \sim -0.25 \) [73]. In this case, the new plexcitons with energies \( E_\pm \) are spectrally detectable as the anticross as \( \delta \to 0 \) (figure 6(D)). The LR peaks represent the states with the plasmonic and excitonic excitations in phase with each other, while the UR peaks are those states with the plasmonic and excitonic excitations out of phase [72]. The coupling strength between plasmons and excitons is given by the energy splitting at \( \delta = 0 \) [72, 73].

\[
E_\pm = \frac{h}{2} \left[ \omega_{\text{SPR}} + \omega_{\text{exc}} - \left( \frac{\Gamma}{2} + \gamma_0 + \gamma_d \right) \right] \\
\pm \frac{\hbar}{2} \sqrt{4 |\delta|^2 + \left( \gamma_0 + \gamma_d - \frac{\Gamma}{2} \right)^2} \\
\tag{8}
\]

where \( g \) is a parameter measuring the interaction coupling strength between the two oscillators.

2.1.4. Surface chemical interactions. Chemical modifications on the Au NP surface, such as reaction with thiolated ligands, physiosorption of chemicals such as alkylamines or citrate, or adsorption of reactive gas species such as H₂S, change the LSP properties in three ways (figures 6(E)–(H)):

(i) Increase the pure dephasing rate \( \Gamma_{\text{nr}} \) (see equation (7)) by introducing new electron relaxation pathways [51].

In particular, several models have been developed in which the lowest unoccupied molecular orbital (LUMO) of adsorbates couples with the free electron population via reversible charge transfer processes, contributing to a faster coherence loss [30, 74, 75]. Later, density functional theory (DFT) calculations demonstrated that electronic density of states near the Fermi level of Au NPs changes in the presence of adsorbates [57, 76], and with stronger effects going from amines to thiolated ligands (figure 6(E)) [57]. This effect is known as chemical interface damping (CID) [30, 57, 77].

(ii) Formation of a shell of non-metallic Au atoms (figure 6(G)) [78, 79], i.e. a change in the bond order [76], with overall reduction of the effective size of the plasmonic metal core in the NPs (for size effects see section 2.2) [80]. For instance, in the case of a thiolated monolayer protected Au cluster such as Au₃₁₄(SH)₉₆, each SH ligand withdraws one electron from the Au(6sp) subsystem and the effective ‘valence’ electrons are only 218 [80].

(iii) Variation of the dielectric environment of the Au NPs, with a consequent variation of the real part of the ‘effective’ matrix optical constant (figure 6(H)), with the effects described in section 2.1.1 [34].

The relevance of the chemical effects strongly depends on NP size, shape, and on the type of reagent. In the case of CID, different adsorbates have different LUMO energy and localization, and then couple in a different way with the metal conduction band and originate different SPR widths [57]. In monolayer-protected Au NPs, density and molecular weight of the ligands are also important [77]. For instance, the coating of small (i.e. <10 nm) Au NPs with a dense monolayer of short-chain thiolated ligands is typically associated to SPR
damping. It is worth noting that a 4 nm Au NP is composed of ~2000 atoms, of which 24% is located on the surface. In the case of large Au NPs (i.e., >10 nm) and long-chain ligands (i.e., MW > 1000 Da), only SPR redshift is observed as a consequence of the increase in the real part of the ‘effective’ optical constant of the NP environment [30, 43, 78, 79].

2.15. Temperature. Temperature (T) increase is associated to SPR redshift and broadening (that means bleaching at SPR maximum) [55, 56, 81]. For NPs embedded in solid matrices or dispersed in liquids, these effects are much less relevant than modifications of the dielectric environment or structural NP modifications at high T, which are induced by local plasmon heating (see section 4.3). In spherical Au NPs embedded in a silica matrix, this change is ca. +0.3% in redshift and ca. +5% in band broadening for every 100 K of temperature increase [81]. However, in open-air configurations, the actual T of the NPs is important for appropriate modelling of experimental results [55].

The redshift is due to thermal dilatation of the lattice, which means a decrease of electron density (n, see figure 6(I)) [82, 83]. In fact, in noble metals the LSP frequency (ω_LSP) is proportional to the bulk plasma frequency (ω_p) [84], and ω_p is proportional to n^{1/2} according to its expression in free electron metals [30, 56, 81]:

\[
\omega_p(T) = \sqrt{\frac{e^2 n_e(T)}{m_{\text{eff}}(T)}}
\]

(9)

where e is the electron charge, m_{eff} the electron effective mass, and ε_0 the vacuum permittivity.

SPR broadening means that \( \Gamma_{m} = \Gamma_{m}(T) \), i.e. that the electron distribution near the Fermi level and the associated increased electron scattering rate both increase with T, ultimately leading to an increase in Im[ε_Au] and a consequent decrease of Q_LSP [55, 81]. On the other hand, this means that Q_LSP can be slightly improved by decreasing T [83].

The effect of temperature on the SPR also depends on the heating modality [55]. In the case of transient heating such as during pump-probe ultrafast experiments, the electron-electron scattering frequency is the main parameter affected by T, because the tail of the Fermi–Dirac electron distribution increases with temperature, and 1/\tau_{ee} depends on the square of the difference between the free-electron energy E and the Fermi energy E_F [51, 56]:

\[
\frac{1}{\tau_{ee}} \propto (E - E_F)^2.
\]

(10)

Transient SPR extinction spectra show the bleaching and broadening of the plasmon band already in the first picoseconds, as a consequence of the higher electronic temperature and higher electron–electron scattering rate [51, 56].

In steady-state heating conditions, the change in the electron–phonon scattering rate is the dominating contribution, while the electron–electron scattering rate remains almost constant [55, 81, 83].

2.16. Pressure. Pressure up to 1.2 GPa has no appreciable effect on the SPR of Au NPs [85], while for larger values plastic deformation of NPs occurs [86].

2.2. Size.

2.2.1. Absorption and scattering cross-section. The SPR band detected in the optical extinction spectra of Au NP dispersions is originated by the sum of scattered and absorbed photons, with a proportion strongly dependent on particle size [15, 30, 37]. We can express the extinction cross-section of an Au NP as the sum of the absorption (\( \sigma_{\text{Abs}} \)) and scattering (\( \sigma_{\text{Sca}} \)) terms [15, 30, 37]:

\[
\sigma_{\text{Ext}} = \sigma_{\text{Abs}} + \sigma_{\text{Sca}}.
\]

(11)

Assuming a homogeneous sample composed of N identical Au NPs in a volume V, the extinction cross-section is related to the measured transmittance (Tras) and absorbance (Abs) by [43]:

\[
\text{Tras}(\omega) = -\log_{10}\left[\exp\left(-\frac{N V}{V_{\text{NP}}} \sigma_{\text{Ext}}(\omega)\right)\right] = -\log_{10}\left[\exp\left(-\frac{N V}{V_{\text{NP}}} (\sigma_{\text{Abs}}(\omega) + \sigma_{\text{Sca}}(\omega))\right)\right]
\]

(12)

where I_0 and I are, respectively, the incident and transmitted light intensity, and I is the optical path within the sample. Since Tras exponentially depends on σ_{Ext}, even a moderate increase in the cross-section leads to a huge enhancement of light extinction.

For Au NPs with size \( d \ll \lambda \), where \( \lambda \) is the wavelength of the electromagnetic radiation, the absorption dominates over scattering [15, 30]. However, for NPs smaller than light wavelength, scattering and absorption scale, respectively, with the 6th and 3rd power of the particle’s size [15, 37]. Therefore, the two effects become comparable for Au NPs of about 50 nm, and scattering prevails above 70–100 nm (see figure 7(A)) [87].

The size dependence of σ_{Abs} and σ_{Sca} is relevant for applications related to optical extinction and near-field enhancement, described in sections 4 and 5. In fact, light scattering is an elastic process consisting in the modification of the photon propagation direction. Therefore, NPs with a large σ_{Sca} are preferentially exploited for biolabelling and sensing up to single-particle sensitivity (see section 4.1), as well as for nano-lensing and the enhancement of nonlinear optical properties in nearby objects (see sections 5 and 6). Instead, light absorption consists in the transfer of photon energy to the plasmonic nanostructure, where it is rapidly converted to heat [35, 88–90].

2.2.2. Extrinsic size effects. The extrinsic size effect is a retardation effect due to the excitation of multipolar plasmon modes when NP size increases with respect to the resonant electromagnetic wavelength [30], i.e. when the size parameter \( x \) is close to 1, where \( x \) is defined as [37, 91]:

\[
x = \pi d / \lambda.
\]

(14)

When Au NP size is small compared to the light wavelength (quasistatic regime, \( x \ll 1 \)), the electric field distribution along the particle is essentially uniform, electron cloud polarization is coherent in each point of the metal, and dipolar plasmon oscillations are excited [15, 30]. Conversely, when Au NP size
Topical Review

is comparable to or larger than the resonant electromagnetic wavelength, the electric field distribution along the particle is non-uniform, electron cloud polarization is no longer coherent in each point of the metal, and multipolar plasmon oscillations are excited [15, 30]. This is a bare electromagnetic phenomenon accounted from the electrodynamic theory such as the Mie model, in contrast to the intrinsic size effect described in the next section [30].

The extrinsic size effect appears in the optical absorption spectrum as broadening and redshift of the SPR for increasing Au NP size [15, 30]. The retardation effects are dominant for Au NPs larger than 60 nm, whereas pure dipolar oscillations dominate for particles of 25 nm or smaller [30, 87]. In Au nanospheres, extrinsic size effects allow the tuning of SPR wavelengths over 60 nm by varying the particle size between 10 and 100 nm [87].

2.2.3. Intrinsic size effects. Intrinsic size effects are due to the modification of the metal optical constant when Au NP size is below 30 nm [30]. The optical constant changes, because of additional contributions to the free electron relaxation rate when the NP size is reduced [30]. In particular, the free electron scattering at the particle surface is no longer negligible when the conduction electron mean free path (~30 nm for Au) becomes comparable to particle size [30]. Therefore, the intrinsic size effect is responsible for the increase of $\Gamma_{nr}$ and $\text{Im}[\varepsilon_{Au}]$, and thus the decrease of $\Omega_{LSP}$, and it appears as a damping of the SPR band for decreasing particle size (figure 7(C)) [43, 92, 93]. SPR quenching is almost complete in Au NPs smaller than about 2 nm, when this effect encompasses all the other scattering mechanisms including electron–electron, electron–phonon, and defect interactions [47].

The Au optical constant can be corrected for intrinsic size effects using a size-dependent relaxation frequency [30, 43]:

$$\Gamma_{nr}(L_{\text{eff}}) = \Gamma_{nr}^{\text{bulk}} + A \frac{v_F}{L_{\text{eff}}}$$

(15)

where $L_{\text{eff}}$ is the effective NP size, $\Gamma_{nr}^{\text{bulk}}$ is the bulk Au value, $v_F$ is the Fermi speed, and $A$ is an empirical parameter. In NPs with arbitrary shape, $L_{\text{eff}}$ is often expressed as the radius of a sphere with the same volume ($V_{NP}$) [94, 95]:

$$L_{\text{eff}} = \left( \frac{3V_{NP}}{4\pi} \right)^{1/3}$$

(16)

However, another expression for $L_{\text{eff}}$ has been proposed on the basis of a geometrical probability approach for electron scattering at the surface of NPs with arbitrary convex shape [92]:

$$L_{\text{eff}} = \frac{4V_{NP}}{S_{NP}}$$

(17)

where $S_{NP}$ is the surface area of the NPs.

$A$ is an empirical parameter, indispensable to account for all factors affecting the electron scattering at the NP surface, such as the CID effect due to strongly interacting ligands, or other types of surface defectivity [30, 43, 78]. According to the literature, $A$ spans the 0.1–2 range [43, 47, 96], and for a specific system can be obtained from the comparison of optical extinction spectra with electron microscopy size analysis [43, 47]. This simple calibration procedure allows the evaluation of spherical Au NP size and concentration based on the fitting of the optical extinction spectra with the Mie model (see section 3.2.1), with an average error of 6% (figure 6(D)) [43].
To introduce the size correction into the bulk Au optical constant, one must refer to the relatively simple Drude–Lorentz model for optical permittivity [30, 43, 94], as described in section S1 of S.I. (stacks.iop.org/JPhysCM/29/203002/mmedia). This model provides high versatility in the correction of Au optical constant and also as a function of other factors such as temperature [55].

2.2.4. Quantum size effects on the SPR. Quantum effects already influence the LSP for NPs smaller than ~10 nm [47], although they become more relevant for a size smaller than ~1.5–2 nm (depending on the surface coating), when the SPR is in the regime of strong quenching due to the surface damping effects [80]. This happens because of the optical constant modification when approaching the quantum regime, known as ‘non-local’ effects (see section 3.1). Indeed, for NPs with size between 2 and 10 nm, lattice contraction occurs, with a consequent increase in electron density, that pushes the resonance towards higher frequencies [47]. For instance, accurate EELS measurement in ‘pure’ (i.e. not passivated by ligands or chemicals) metal NPs with diameter decreasing from 20 to 2 nm evidenced SPR blueshift of ~0.5 eV [47]. The blueshift, not predicted by classical models, is well reproduced with quantum mechanical models accounting for the quantum confinement of the free electron gas by the NP surface [47]. This surface confinement effect is appreciable in naked metal NPs, while CID dominates in ligand-passivated particles [47, 97].

In Au NPs with size below 2 nm, the Au(6sp) states are delocalized over the whole particle in analogy to the free electron gas in bulk gold metal [80, 97–100]. However, the quantum confinement effects in NPs create discrete energy bands with specific symmetries, and these bands are well described by the model of ‘superatom’ [97]. In fact, monolayer-protected 1–2 nm Au NPs are known to have molecular-like electronic structure, and they represent the link between ‘molecular’ gold clusters and ‘metal’ gold NPs [80, 97–100]. For instance, a well-defined SPR is predicted in a monolayer-protected cluster with a 2.0 nm metal core (314 Au atoms), while in a smaller cluster with 1.5 nm gold core (144 Au atoms), the SPR is quenched and confined in the metal core (figure 7(E)) [80]. These results suggest a threshold size between 1.5 and 2 nm for the emergence of SPR in Au NPs [101]. A recent study identified three states corresponding to different size ranges in phenylethanethiolate-protected Au nanoclusters: metallic (size larger than Au133, i.e. 2.3 nm), transition regime (between Au133 and Au144, i.e. 2.3–1.7 nm), and non-metallic or excitonic state (smaller than Au144, i.e. 1.7 nm) [102].

The discrimination of SPR in these systems is indeed difficult [103, 104]. It was recently suggested that the plasmonic state consists of a linear combination of many singly-excited configurations that contribute additively to the transition dipole moment, whereas other excited states show significant cancellation among the configurations leading to weak absorption [104]. Recently, the ‘plasmonic index’ has been proposed as a mean to quantify the plasmonic character of optical excitations in small metal NPs [103]. The plasmonic index is based on the concept that plasmonic excitations should locally enhance the applied electromagnetic radiation, and is extracted from theoretical atomistic models for optical extinction properties in metal clusters [103].

2.3. Assembly

Plasmons on distinct NPs can reciprocally influence each other, depending on particle distance, geometry, and relative light polarization, with the generation of ‘hybrid’ plasmon modes [105, 106].

The simplest case of assembly is the nanosphere dimer in the quasistatic regime, where end-to-tail coupling of dipolar plasmon modes is possible, with consequent decrease of the overall SPR frequency (redshift) for excitation along the dimer axis [105]. Conversely, for electric field perpendicular to the dimer axis, the dipolar plasmon modes couple head-to-head, with a slight blueshift of the SPR [105, 106]. In the case of dimer size comparable to light wavelength, quadrupolar or higher-order plasmon modes are possible, with different effects on the SPR frequency [105, 106].

In more complex systems, the hybrid plasmon modes can be analyzed by applying group theory to the LSP of individual NPs [105]. For instance, according to group theory, a trimer of NPs arranged in the form of an equilateral triangle (point group D3h) supports nine dipolar plasmon modes [105]. Three of these modes can be classified as ‘bonding’ modes (see the hybridization theory described in section 3.2.2.6), and three are non-bonding (or ‘dark’), with energies lower and higher than that of an individual particle, respectively. The mode with the lowest energy has a ring-like arrangement of dipoles, meaning that it is dark for excitation with linearly polarized light, but can be excited with radially polarized light [105, 107].

On the other hand, by referring to the analogy between the LSP and a mass-spring harmonic oscillator, LSP hybridization can be seen as a serial coupling of two or more springs [32, 108, 109]. Multipolar LSP can be modelled as springs oriented along the interaction direction set by charge oscillation in the NPs [109, 110].

The redshift due to SPR hybridization in Au NP dimers decays near-exponentially with the interparticle gap over a distance that is roughly 0.2 times the particle size, independent of the NP size, shape, material, and the medium dielectric constant [111, 112]. This universal decaying behaviour of the SPR in NP pairs originates from the distance decay of the interparticle local field that couples the particles together [111, 112]. When NPs are in touch through a conductive junction, the hybridization effects disappear and the SPR abruptly blueshifts to that of a particle with a necklace shape (figure 8(A)) [46, 112].

This behaviour is rather general and a ‘plasmon ruler’ equation was proposed to estimate with good accuracy the distance between dimers from the measured fractional SPR shift [111]:

$$\frac{\Delta \lambda_{\text{SPR}}}{\lambda_{\text{SPR}}} = K \exp\left(\frac{r/d}{s}\right)$$

where $K$ is a constant depending on particle geometry and dielectric environment, $r$ is the edge-to-edge NP distance, $d$ is the particle diameter, and $s$ is the decay length close to 0.2
and almost independent of particle type, shape and dielectric environment. The same expression can be used to estimate the position of core–shell SPR for different core-to-shell ratios, just replacing \( r \) with the shell thickness and \( d \) with the core radius [113]. In fact, plasmon modes couple in any metal structure, regardless of whether they are spheres, concentric metal layers, or mixed shapes [106, 111, 113].

Agglomerates with fractal structure made by tens of particles have two main bands, one close to the original sphere position and another redshifted [106, 114, 115]. Both are sensibly broader than single-particle SPR and are originated by the convolution of a multitude of plasmon modes supported in each part of the fractal aggregate [114]. In aggregates with a fractal number sensibly lower than three (meaning low density and highly ramified structure), the largest contributions come from pseudo-linear NP assemblies aligned to the light-polarization direction [116]. When particles in the aggregates are several hundred, only one very broad redshifted band is present [106, 114].

Assembly in disordered superclusters is exploited for sensing or for photothermal effects (section 4), and, assembly of plasmonic NPs is also crucial for all the effects related to local-field enhancement, as discussed in section 5.

### 2.3.1. Fano resonances

For specific NP assembly geometries, typically associated to well-defined NP disposition and homogeneous nanometric gaps between particles, the mutual interaction between plasmon oscillations can originate constructive and destructive interference phenomena yielding to asymmetric SPR band shapes and sharp dips or spikes in the optical extinction spectrum, known as Fano resonances (figure 8(B)) [16, 117]. Also, in this case, the analogy between the LSP and a mass-spring harmonic oscillator allows for the convenient modelling of Fano resonances [16]. As Fano resonances arise from the interference between two or more oscillators, they are sensitive to changes in geometry or local environment, with the effect that small perturbations can induce dramatic resonance or line shape shifts up to 600 nm per matrix refractive-index unit [16]. Besides, at those frequencies where constructive interference occurs, optical extinction and local-field enhancement are larger [16].

### 2.3.2. Magnetic plasmonic resonances (MPR)

In principle, both the electric and magnetic components of light can excite LSP modes in Au NPs [118]. Charge currents associated to electric SPR have a dipolar character (i.e. the NPs behave as an electric dipole), while MPR are associated to a circulating displacement current and hence the ring of NPs behaves as a magnetic dipole. \( E_{\text{inc}} \) and \( H_{\text{inc}} \) represent the incident electric and magnetic fields, respectively. Colours indicate the charge distribution. The ring shape and interparticle gap determine the relative intensity and spectral position of the electric and magnetic resonances. For instance, symmetry breaking (c) induces interference between the electric dipole (p) and magnetic dipole (m) modes, which gives rise to a pronounced Fano resonance in the scattering spectrum. Reprinted by permission from Macmillan Publishers Ltd: Nanotechnology [119], copyright (2013).
In isolated NPs, MPR are weak or located outside the range of optical frequencies [119, 121]. However, in assemblies of NPs, MPR at optical frequencies can be intense and even dominate the extinction spectrum [119–121]. This occurs especially when non-touching Au NPs are assembled in rings or shells (figure 8(C)) [119–121]. For specific configurations, the mutual interaction between electric and magnetic LSP modes may also generate Fano resonances [119, 121].

The symmetry of charge displacement in isolated or assembled Au NPs is accessible by the Mie theory and its generalizations (section 3), providing a quantitative way for the identification of electric and magnetic LSP modes [119, 120].

Interestingly, MPR are associated to the enhancement of the oscillating magnetic field, especially in the case of magnetic Fano resonances, in analogy to the well-known local electric field enhancement [119, 121].

The main interest in MPR is due to their exploitability to obtain metamaterials with negative refractive indexes, because close to the MPR frequency both magnetic permeability and electric permittivity can become negative [118]. For this reason, the assemblies of NPs showing MPR are often defined ‘metamolecules’ composed by ‘meta-atoms’ [121, 122].

2.4. Shape

The work on shape, position, and number of SPRs are also determined by the shape of the Au NPs [39]. The advances in synthesis and characterization of plasmonic nanostructures made it possible to realize NPs with many different shapes, such as nanoshells (NSs), nanowires, nanocubes, nanostars, nanotriangles, and nanocones, just to mention a few (figure 9) [38, 39, 123–129]. Notable examples of this are the LSP resonances of core–shells and NRs, that can be tuned away from the lossy IB transitions of gold, improving the SPR quality factor [36, 40, 67, 87].

In general, NP symmetry reduction is an effective method to modify the position, number, and intensity of SPR [39, 42, 94]. A common feature of these new SPRs is that they are located at lower energy compared to the sphere. For instance, Au nanospheres with the size of 2–50 nm show only one plasmon band centred at about 520nm, while two SPR bands appear when the symmetry is reduced from spherical to cylindrical, i.e. in Au NRs [130, 131]. The first band, corresponding to the excitation along the minor axis, is slightly blueshifted with respect to the SPR in an equivalent sphere, while the second band, corresponding to the excitation along the major axis, is redshifted and more intense, since \( Q_{\text{LSP}} \) increases with wavelength. By increasing the aspect ratio \( D \) of the NR (i.e. the main to minor axis ratio), the second SPR can be shifted from the visible to the NIR range [130–132]. The wavelength of the longitudinal plasmon absorption (\( \lambda_{\text{LSP}} \)) is almost linearly dependent on the aspect ratio and the matrix dielectric constant [133]:

\[
\lambda_{\text{LSP}} = (K_D - K_e)\frac{\epsilon_m}{K_3} + K_1
\]

(19)

However, the aspect ratio alone does not uniquely determine the extinction spectrum of a NR even for a monodisperse sample of rods, and the optical properties are very different between ellipsoids and cylinders with hemispherical, hemiellipsoidal, or flat ends [131].

By referring to the analogy between LSP and a mechanical harmonic oscillator, NP shape modification can be seen as a change in the elastic constant of the spring, with the strongest restoring force belonging to nanospheres, and the weakest force to NRs with high aspect ratio [31–33].

For specific geometries, such as concentric NSs with alternating layers of Au and dielectrics, Fano resonances are also observed, because of the mutual interaction of plasmon modes in distinct metal components of the composite NPs [16, 110].

In most Au nanostructures, especially when \( x < 1 \), the absorption bandwidth is limited to a small portion of the visible–NIR range owing to the resonant nature of the plasmon excitation [38, 39, 42]. Recently, asymmetric networks of Au NPs, also called nanocorals (NCs), have been proposed as an interesting system for obtaining versatile and multimodal plasmonic responses [88, 134, 135]. Networks of partially fused Au NPs show very low-energy surface plasmon modes capable of supporting long-range and spectrally tunable propagation in nanoscale waveguides [134]. These Au nanonetworks belong to the C1 point group, the one with the lowest symmetry for an isolated object; hence the number of allowed SPR is larger compared to NPs with higher symmetry [88, 134]. In fact, Au NC dispersions exhibit flat broadband plasmon absorption ranging from the visible to the NIR and unitary light-to-heat conversion (figure 9) [88].

2.5. Composition

The plasmonic properties of any material, such as \( Q_{\text{LSP}} \) and SPR width, intensity, and position, are fully described by its complex optical constant [36]. Therefore, any chemical modification to the Au lattice (such as doping or alloying) induces a remarkable change in \( \epsilon \) and LSPs [35, 36]. This means that Au alloying and doping are other methods for tuning the optical response of plasmonic systems, in addition to the conventional modification of NP size, shape, assembly, and environment [35, 36, 136].

However, composition has seldom been considered as a parameter for tuning the plasmonic response of Au NPs. This is often motivated by the general assumption that other metals cannot perform better than pure Au nanostructures, either in terms of plasmonic response, ease of synthesis, physical–chemical stability, or biocompatibility [35, 36, 40]. The study of alloys is also complicated by the thermodynamic limitations to miscibility of Au with other metals, often yielding to phase-segregated compounds [36].

Indeed, there is a relatively low number of elements with appreciable plasmonic properties (mostly Au, Ag, and Al) [36, 40, 137]. Materials with partially occupied d-states perform poorly as plasmonic materials due to the probability of low-frequency IB transitions and consequent increase of the SPR relaxation frequency due to the enhanced electron–electron scattering rate, ultimately leading to larger \( \text{Im}[\epsilon] \) and lower \( Q_{\text{LSP}} \) [36, 40]. Additional contributions to \( \text{Im}[\epsilon] \) come from the larger probability of electron–electron and electron–defect
scattering in doped crystals and disordered alloys [36, 40, 136, 138, 139].

On the other hand, alloying is frequently desired for the combination of Au properties with that of the other elements, such as magnetism [138, 140], catalytic activity, or lower production costs.

Au alloys with Ag have been frequently studied, because of the ease of synthesis and of the superior plasmon properties of silver [141–143]. In fact, IB transitions in silver are at a shorter wavelength than in gold, meaning that the alloy has larger Re[ε] and smaller Im[ε], leading to higher Q_LSP [36, 94, 137]. In Au–Ag NPs, the SPR frequency and width varies almost linearly from the elemental Ag value to the elemental Au value as the stoichiometry is varied [141–143]. In Cu, the onset of IB transitions is shifted to the visible range, thus Au–Cu alloys have lower Q_LSP [36]. In fact, the metal with IB transitions at lower frequency dominates the plasmon response of the alloy. For a similar reason, Au alloys with Pt and Pd showed poor SPR [144–146]. Disordered Au alloys with Co and Ni also have low Q_LSP and depressed SPR, while SPR blueshift and moderate damping was observed in AuZn NPs [36, 137, 147]. Extreme Q_LSP depression is calculated from thin-film measurements of optical permittivity in Au–Si and Au–Sn alloys, due to the insufficiency of the constituents and consequent amorphous film structure, while for AuAl alloys the effect is similar, but associated to SPR redshift [36, 137, 148].

The case of Fe-doped Au alloy NPs was investigated in detail thanks to the ease of synthesis by laser ablation in liquid [35, 136, 138]. In these nanoalloys, SPR damping and blueshift of ~15 nm is observed after the introduction of ~11at% of Fe (figure 10(A)) [136, 138]. Also, the local-field enhancement rapidly decreases by ~20 times, while increasing the amount of iron in the Au lattice up to ~13 at% [136]. Conversely, the absorption cross-section of Au NPs with size above 70 nm is sensibly increased when iron is included in the lattice [35]. The increase of σ_Abs is size and shape dependent, with the higher increment up to 90%–190% predicted in NSs with size above ~70 nm, which is also the optimum size for practical applications (figure 10(B)) [35]. The augmented plasmon absorption in iron-doped Au nanoalloys is prevalently observed in the red and NIR frequencies, which is actually the working window for most photothermal applications [6, 149].

The change of σ_Abs originates from the modification of the optical constants of gold after doping with iron [35]. Doping Au with Fe introduces new single-electron transitions, which are generated by electrons lying in the iron d-states below the Fermi surface of the metal [150]. In general, low-frequency IB transitions are observed when noble metals and transition metals with partially occupied d-states are alloyed together [36]. The effect is the decrease of the Re[ε] and the increase of Im[ε] compared to pure Au [35]. While this is detrimental for extinction and local-field enhancement, absorption is set by the following expression [40, 151, 152]:

\[ \sigma_{Abs} = \text{const} \times \frac{\exp(\alpha L) - 1}{\exp(\alpha L) + 1} \]

where \( \alpha \) is the absorption coefficient and \( L \) is the sample length.

Figure 9. Au NPs with different shape and corresponding optical extinction (transmission) or scattering (dark-field) spectra. Images adapted with permission from the following references: nanospheres [93] (Copyright (2013) American Chemical Society), porous nanospheres [123] (Copyright The Royal Society of Chemistry), NCs [88] (Copyright The Royal Society of Chemistry), nanostars (or nanourchins) [126] (Copyright (2010) American Chemical Society), NRs [245] (Macmillan Publishers Ltd: Nature [245], copyright (2009)), nanotriangles (or nanoprisms) [127] (Copyright The Royal Society of Chemistry), NSs and nanorice [201] (Copyright (2007) American Chemical Society), nanocubes (or rhombic) nanododecahedra [128] (Copyright (2010) American Chemical Society), nanocages (or nanorattles) [129] (Copyright (2016) American Chemical Society).
The optical extinction spectra for Au$_{1-x}$Fe$_x$ alloy nanospheres in water, with $0 < x < 0.13$.

Reproduced from [136] with permission from The Royal Society of Chemistry.

(B) Integral in the 400–1200 nm range of the cross-section for Au–Fe alloy NS (SiO$_2$ core with radius of 60 nm, metal shell with thickness of 16 nm, calculated with the Mie model) versus composition.

Reproduced from [35] with permission from The Royal Society of Chemistry.

$$\sigma_{\text{Abs}} = \frac{k}{\varepsilon_0 E_0} \int_{\text{NP}} \text{Im}[\varepsilon_{\text{NP}}] \cdot E_{\text{NP}}^2 dV_{\text{NP}}$$

where $k$ is the wave vector, $E_0$ is the modulus of the electric field of the incident light, measured in the medium surrounding the NP of volume $V_{\text{NP}}$, and $E_{\text{NP}}$ is the modulus of the electric field inside the NP. On the one hand, $\sigma_{\text{Abs}}$ is proportional to $\text{Im}[\varepsilon]$, which is augmented by iron doping. On the other hand, it depends on the integral of $E_{\text{NP}}^2$ over $V_{\text{NP}}$ that is maximized when $Q_{LSP}$ is maximum, and it is size dependent. From the balance between these two factors, the $\sigma_{\text{Abs}}$ in Au–Fe nanoalloys results larger than in pure Au NPs when particles size exceeds 70–100 nm [35].

These findings are unexpected, according to the common belief and previous experimental observations that alloys of Au with transition metals show a depressed plasmonic response [36, 137], thus suggesting that the scarcely investigated field of plasmonic nanoalloys can be a source of new, yet unforeseen solutions for the improvement of plasmonic performance [36].

An alternative case to alloys is that of nanograined materials. Plasmonic properties in heterostructures correspond to a linear combination of the properties of the constituent metals, weighted by their respective stoichiometries, with a larger damping contribution to account for scattering by grain boundaries [36]. However, pure nanograined NPs are quite rare, because doping and alloying during the mixing procedure at the nanoscale is highly probable [153].

2.5.1 Electric charge. A small change in the SPR of Au NPs is observed when the charge density is modified, typically through the application of an external voltage bias. This change is of the order of a few % and a few nanometres in SPR intensity and position, respectively [154–156]. In fact, charge variation in common electrochemical experiments is limited to less than 1% of the total number of electrons in the NPs, corresponding to negligible changes in the $\varepsilon$ of the metal [154]. At larger applied potentials, chemical reactions or modifications occur [154, 155].

SPR blue-shift is observed for negative applied potential, and redshift for positive potential, as a consequence of, respectively, the increase and decrease of the electron density of the metal [154–156]. SPR intensity decreases by increasing the free electron density [154, 155]. In general, this behaviour is well reproduced with the simple Drude model for free electrons, although in real experimental conditions other contributions to SPR modifications must also be considered, such as changes in the electrolyte double layer, surface chemical reactions, and variation of adsorbate density and type [154, 155].

3. Modelling the SPR of Au NPs

A full theoretical understanding of the optical behaviour of Au NPs is fundamental to optimize their applications and to account for the many different shapes and structures (see section 2.4). This implies the need for accurate techniques capable of computing the optical properties of nonspherical or aggregated NPs [157–159]. To this end, several analytical and numerical methods have been proposed in the literature and actually there is no single universal method providing the best results for all nanostructure types and targeted physical phenomena. In particular, approximated models are often used to gain insight into the physics of the problem, such as in the case of the mass-spring model, but they may hide important effects and the lack of quantitatively reliable results. In such situations, accurate computational approaches are required to get a good agreement with experiments and a correct understanding of the electromagnetic processes at the nanoscale [157–159].

3.1 Optical constant

Appropriate modelling of LSP requires the knowledge of the Au NP optical constant [157]. Although corrections are often required for size effects, surface coating, temperature, or compositional modifications, as discussed in section 2, the starting point is the optical constant of bulk gold that is experimentally accessible with good precision. The most widely used values are those reported by Johnson and Christy [160], or in the handbook edited by Palik [161]. Their values can also be accessed from online databases such as http://refractiveindex.info/.

However, some inconsistencies exist in the dielectric functions found in the literature, typically due to deviation from ideal flatness and the density of bulk Au [162, 163]. Therefore, precise spectroscopic ellipsometry measurements have been recently repeated on samples with controlled
surface roughness and density, and compared to the literature values [162, 163].

3.1.1. Non-locality and quantum size effects. The standard description of optical properties of Au NPs exploits a ‘local’ bulk dielectric function, i.e. \( \varepsilon(\omega) \) only depends on frequency but not on NP size, shape, and structure [30]. However, this approach fails for very small diameters [47, 80, 164]. Such an example of ‘non-locality’ of \( \varepsilon(\omega) \) was already shown in sections 2.2.3 and 2.2.4 concerning size effects. However, non-locality also has relevant implications when metal NPs are in close proximity [165], irrespective of their size, and when their shape includes sharp features [46, 157, 166–169]. In these cases, an accurate description should also consider electron–electron repulsion due to Pauli exclusion and Coulomb repulsion, which manifest as a pressure in an electron gas resisting the compression induced by the external electromagnetic field [170]. As a consequence, the ‘longitudinal’ dielectric function becomes non-local along the photon-propagation direction, while the transverse dielectric function remains local and equal to the bulk dielectric function [170]. The main effect of the non-local response, thus, is that the electron gas cannot be squeezed into an infinitesimally small thickness on the particle surface, as proposed by a classical local electromagnetic treatment, but rather it spreads out by a minimum distance of the order of 0.25 nm, putting an upper limit to the field enhancement achievable by metallic nanostructures [157].

To account for the electron pressure, a linearized hydrodynamical approach for the electron collective motion in the metal has been proposed [170, 171]. Such an approach in a uniform medium predicts a spatially non-local longitudinal dielectric function \( (\varepsilon_L) \) depending on the modulus \( (k) \) of the propagation vector in addition to the frequency [170]:

\[
\varepsilon_L(\omega, k) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega - \beta^2k^2}
\]  

where \( \gamma \) is the damping coefficient and \( \beta \) is the pressure coefficient proportional to the Fermi velocity [172]:

\[
\beta = \sqrt{3S/v_p}.
\]

A weakness of the hydrodynamical model is that it ignores the possible charge density spill-out outside the metal particle boundaries. This effect stems from the smooth transition of the electron density due to the finite length of the electron waves, generating a negative charge density outside the electronic body [173]. The charge density spill-out is essential for incorporating quantum tunnelling effects between the particles when their separation distance reaches the sub-nanometre scale [46, 166].

To go beyond the hydrodynamical model into the quantum tunnelling regime, a first-principles quantum treatment is required. The time-dependent density functional theory (TDDFT) appears to be a good approach, describing the plasmonic optical response at the quantum level and taking account of non-local effects [168]. The drawback is its computational complexity, so that it is indicated for particles containing only a few thousand electrons. This problem can be solved by using a classical local model capable of incorporating the quantum tunnelling effects, the so-called quantum-corrected model (QCM), which was recently implemented [157, 174]. The QCM can be included within any standard model for the description of SPR in Au NPs, and with excellent agreement to full quantum mechanical calculations, because the junction between two NPs is modelled as a fictitious material with dynamical conductivity adjusted to mimic the effects of electron tunnelling [169]. Therefore, the correction to the metal optical constant is actually essential to the setup of an effective optical constant for the medium at the junction between NPs (see figure 11). In the case of curved surfaces such as a sphere dimer, this can be accounted for as a shell of fictitious material [157, 169].

3.2. Analytical and numerical methods

3.2.1. Mie theory. For homogeneous spherical particles embedded in a non-absorbing medium, Mie theory provides the optical properties for any particle size and optical constant [37]. Indeed, the seminal paper by Gustav Mie deals exactly with colloidal Au NPs [28]. The approach is based on Maxwell equations and on the multipole expansion of the electromagnetic fields. The incident and internal (within the particle) fields are expanded in multipole fields that are regular inside the particle, while the external scattered field is expanded in multipole fields that behave as outgoing spherical waves at infinity. By applying the boundary conditions across the surface of the particle, i.e. the requirement of continuity of the tangential components of the electric and magnetic fields, the unknown coefficients in the expansions of the internal and scattered fields are determined from the known expansion coefficients of the incident plane wave [37, 158]. This solution for spherical particles is sometimes referred to as the Lorenz–Mie theory, since Lorenz also derived, independently, the solution in 1890. Over the years, the theory was extended to core–shell spheres [175], and radially inhomogeneous spheres [176]. The analytical expression for the Mie model is fully reported in section S2 of S.I.

An accurate solution is obtained when convergence of the multipole field expansion is carefully checked. When dealing with metallic NPs, there is no general formula to estimate the number of significant coefficients, but convergence is generally expected to be reached at higher multipole orders compared with dielectric particles of the same size [173, 177]. As particle size increases, higher-order multipole modes appear and a description in terms of dipole contributions becomes inaccurate. However, for size below ~20 nm, i.e. in the quasistatic regime, the dipolar LSP dominates, and the Mie model can be reduced to the simple expression of equation (3) [30, 34, 37].

3.2.2. Non-spherical shapes. In many situations of real interest, particles are far from exhibiting a spherical symmetry. For ellipsoids in the quasistatic regime, the Gans model still provides an analytical solution to the problem (see section S3 in S.I.). However, for more complex shapes and assembly of NPs, other models are required. Currently, the most commonly used numerical approaches for describing the
3.2.2.1. DDA. The DDA, also known as the coupled dipole method, was originally introduced by Purcell and Pennybacker for describing light scattering by interstellar dust grains [179], and was subsequently developed by Draine et al., who also created the popular DDSCAT code [180–182]. The DDA simulates the metal particle as an array of \( N \) point dipoles of known polarizability tensor organised on a cubic lattice to represent the NP shape. Each dipole interacts with the incident electromagnetic wave and with the waves re-radiated by all the other dipoles. This method has found many applications in modelling plasmonic NPs [42, 67, 94, 95]. The accuracy of DDA calculations critically depends on the discretization step. In order to approximate a given particle adequately, dipoles used in the simulation must be significantly smaller than the light wavelength [183]. Moreover, the inter-particle distance, \( r \), must satisfy the condition \( n_{\text{NP}}k \cdot r \leq 1 \), where \( n_{\text{NP}} \) is the particle refractive index and \( k \) is the light wave number in the medium [177, 184]. A great advantage of the DDA approach is that it can be applied to arbitrarily shaped structures. Another remarkable advantage is that target optical constants are introduced directly from experimental data, independently of composition or geometry, and without any need for the interpolation with analytical models of the optical constants [94, 95, 182].

The main drawback of this method is that it can produce artefacts when the number of dipoles is not large enough, and it can become time consuming and very demanding in terms of computing resources for large \( N \) [159, 183]. The theoretical basis for the DDA is reported in section S4 of S.I.

3.2.2.2. FDTD. Another numerical approach that has been widely used to study the optical properties of metal nanostructures is the FDTD method [182–187]. The method is based on the numerical integration of the Maxwell equations in the time domain within a finite space, where fields will be calculated, containing the object of arbitrary geometry and composition [164, 186, 188]. In practice, space is discretized by a grid mesh (Yee cells). The space and time derivatives of the electric and magnetic fields are approximated using a finite-difference scheme with space and time discretizations selected to minimize computational errors and ensure numerical stability [158]. At the initial time, a plane wave source is turned on. The wave excited by the source propagates towards the scattering particle, eventually interacting with it [173]. The fields are specified at spatial grid points, and values at the grid points for the previous and current time steps are used to calculate the values at the next time step.

Advantages of the FDTD method come from its simple implementation, flexibility, and versatility. Moreover, the computational demand of FDTD grows only linearly with the number of parameterization points [164]. Like the DDA, the FDTD method can be applied to any particle shape. Disadvantages may be due to some limitations in terms of efficiency and accuracy when mesh spacing is large compared to NP features (on the other hand, FDTD computations may be very time consuming when mesh size is very dense), and in terms of the maximum particle size parameter \( x \) [158]. The most widely used FDTD codes are commercial, such as the Lumerical FDTD Solutions™, although free codes are also available (see table 1).

3.2.2.3. BEM. Another popular and efficient approach is the BEM, based on vector diffraction theory [189], in which the electromagnetic field is expressed in terms of charges and currents distributed on the surfaces and interfaces of the particle [173]. By imposing the boundary conditions for the continuity of the tangential components of the electric and magnetic fields, a system of surface-integral equations is obtained. The solution is obtained by discretization of the integrals using a set of \( N \) representative points distributed at the boundaries. This ends up with a set of linear equations that are solved numerically by linear algebra techniques [164, 190]. The main advantages offered by BEM are a low computational and
storage demand and the need for discretizing only the particle surface, which allows calculations with a number of non-spherical NPs that would not be feasible with the other models [191]. In fact, particle contour is discretized through a grid of points on the surfaces between different regions, with a variable frame that must be defined with the appropriate density to obtain accurate results [164].

3.2.2.4. FEM. In FEM, the total simulation volume is discretized into a set of finite elements (tetrahedra or triangular prisms) chosen to best describe the geometry of the target. The unknown functions are represented by simple interpolation functions defined on each element with unknown coefficients. These functions provide an approximation to the solution within a finite element, which is obtained by recursive solving the corresponding system of equations. The region of computation is terminated using some artificial absorbing boundary, as in FDTD.

3.2.2.5. T-matrix. A powerful approach, especially when dealing with dispersions of randomly oriented particles and aggregates, is the transition matrix (T-matrix) technique [158, 192]. The method, originally introduced by Waterman [193], is based on the multipole expansions of the electromagnetic fields, so mainly the same framework in which the Lorenz–Mie theory develops. As a matter of fact, the T-matrix method reduces to the Lorenz–Mie theory when the scattering particle is a single isolated (homogenous or layered) sphere [158]. However, the T-matrix approach has proved to be very suitable to solve the light scattering problem by aggregates of spherical particles [158, 192]. Often in the literature the aggregates of spherical NPs are handled within the generalized Mie theory (GMT), which is based on the same kind of approach [173].

In many cases the T-matrix allows a rigorous description of the scattering process, surpassing other commonly used techniques in terms of efficiency and x range that is possible to explore [194, 195]. A great advantage of the method results from the transformation properties under rotation of the T-matrix and concerns the possibility of performing an analytical evaluation of the scattering characteristics averaged over particle orientation [196–198]. This unique feature of the T-matrix method has relevant effects in saving computational time. Given a particle reference frame, the T-matrix needs to be computed only once, and then the average scattering characteristics of particle dispersion can be computed through simple analytical formulas [158, 192]. This interesting property makes the computational effort required by the T-matrix method much lighter than the one required by other approaches, like the DDA and the FDTD, which need ex novo calculation of the scattered field whenever the orientation of the scattering particle changes. Importantly, the T-matrix is a rigorous method for describing light scattering and the results are obtained with high accuracy; DDA, FDTD, and effective medium theories (see section 3.2.3), on the other hand, involve approximations in the numerical simulations and so have to be considered as approximate methods [199]. The drawback of the T-matrix approach is that it is practically limited to spherical NPs and their assemblies [158, 192]. Additional details about the T-matrix method are reported in section S5 of S.I.

3.2.2.6. Hybridization model (HM). This model accounts for hybrid plasmon modes appearing in NP assemblies, or complex structures such as core–shell or multilayers [200, 201]. In the HM, the new LSPs are expressed as linear combinations of non-interacting dipolar plasmons, in analogy to molecular orbital theory, justifying the concept of ‘plasmonic molecules’ [201]. For instance, in an Au NP dimer, the two non-interacting LSP modes originate two hybrid modes corresponding to the bonding and antibonding combination [200]. Only the lower-energy mode can be excited by electromagnetic radiation and is defined as a bright or bonding state, while the other one is a dark or antibonding state, non-optically active (i.e. not emitting in the far field). By exploiting the analogy with the mass-spring harmonic oscillator, dark modes are antiphase
oscillations in which the ‘centre of mass’ is fixed, i.e. there is no net displacement of the electronic charge in the far field [200]. These modes can be experimentally probed by EELS [202].

According to the HM, the plasmon modes of a core–shell Au-dielectric NP are originated from the plasmon of a metal sphere and that of a cavity in a metal matrix, whose interaction produces two new plasmonic states with energy higher and lower than pristine plasmons [201]. The physical basis of HM is the interaction between free electrons that are modelled as a charged incompressible liquid bound to the positive Au ion cores, in close analogy to the mass-spring model.

3.2.3. Effective medium theories (EMTs). EMTs provide an alternative description of the light-scattering properties of inhomogeneous, irregularly shaped particles or nanocomposite media with weakly interacting NPs, i.e. where NPs are well separated [173, 199, 203]. The real particle is approximated by a homogeneous one, e.g. a sphere, with an effective dielectric function obtained from a mixture of the dielectric functions of the surrounding matrix and of the particle inclusions. The resulting dielectric function is used in place of the pure metal one to reproduce the optical properties of Au NPs, for instance, in the Mie or the T-matrix models.

Well-known examples of EMT mixing rules are the Maxwell–Garnett and the Bruggeman ones (see section S6 in S.I. for the analytical expressions). They both come from the same integral equation, but with different approximations [204]. Although both theories provide similar results in most cases, the Bruggeman effective dielectric function generally applies to a randomly inhomogeneous medium, which is a medium in which no distinguishable inclusions, embedded in a matrix, appear [37].

The simplicity of the method resulted in the EMTs being widely used. However, strong concerns exist about their accuracy. The most limiting assumption of EMTs is that they do not take into account the real sample composition, hence EMTs fail when large voids and inclusions (compared with the wavelength of light) are present [173, 199, 203].

4. Applications related to SPR optical extinction

4.1. Sensing and imaging with plasmon resonance

4.1.1. Sensing. The high $\sigma_{Ext}$ and the possibility to modulate the SPR in response to a change of the surrounding chemical environment (see section 2.1) makes the Au NPs an excellent signal transducer, widely used for the development of sensors [2, 34]. Sensing of chemical and biological species using plasmonic Au NPs has received considerable scientific attention with important implications in the field of environmental sciences, diagnostics, and medicine [205–207]. In addition to their optical properties, Au NPs hold several attributes that make them an ideal sensing platform, including [208]:

(i) ease of synthesis;
(ii) chemical stability, photostability and biocompatibility;
(iii) high surface-to-volume ratio, to enhance the sensitivity, since the detection events between the analyte and the receptors occur on the particle surface;
(iv) functionalization of the surface with multiple organic and biological ligands to allow the interaction with the target analyte;
(v) large extinction cross-sections, allowing single NP sensors or single-molecule assay in the best cases.

Besides, optical extinction in NP ensembles can be probed with UV–vis spectrometers that are present in most laboratories, without altering the sample, and the registration of the spectrum requires short times [34].

The ability to tune the optical properties, that depends on the particle size, shape, and aggregation [208], and to control the surface-binding properties by suitable functionalization with proper ligands [209], have provided much insight into the fabrication of sensitive and selective sensors with numerous applications in clinical diagnostics.

In order to generate a detectable response signal, the analyte-receptor event has to produce changes of the SPR. This signal transduction event has been achieved through analyte-induced alterations in the interparticle distance, size, and the dielectric constant of the surrounding solution (figure 12). The two main classes of optical sensors based on Au NPs are colorimetric or connected to the SPR spectral shift [34, 208, 210].

4.1.1.1. Colorimetric sensing with assemblies of NPs. The binding of the analyte on the NP surface can induce aggregation of the NPs resulting in interparticle surface plasmon coupling (see section 2.3) that translates into a visible change of colour of the colloidal solution from red to blue (in the case of Au nanospheres) [211]. During the last two decades, several colorimetric sensors have been developed for the detection of a variety of compounds, such as metal ions [212, 213], small organic molecules [214, 215], proteins [216–218], DNA (deoxyribonucleic acid) [219–222], and living cells [223]. For instance, DNA-mediated assembly of Au NPs has been widely used to develop sensors for the detection of the genetic mutation of DNA, which has important implications for the early diagnosis of many diseases including cancer [224]. In this approach, two Au NP probes were functionalized with two single-stranded DNA, complementary to the target oligonucleotide. The formation of double-stranded DNA occurred in the presence of the target DNA, inducing the Au NP aggregation and concomitant colour changes of the solution. By using this strategy, the selective and highly sensitive (at subnanomolar level) detection of DNA was achieved [219, 225], as a result of the high specificity of the base-pair hybridization along with the intense absorption of Au NPs. The readout of the signal for these assays, which in some configurations result in a visible colour change of the colloidal solution, can be performed with the naked eye or with UV–vis spectrophotometers, allowing DNA detection at low cost.

Colorimetric assays for the detection of proteins of clinical interest have been developed using Au NPs coated with specific antibodies. The NP aggregation and the corresponding
colour change of the colloidal solution are triggered by the target antigen through the antigen–antibody interaction. An important application of this colorimetric immunoassay is the detection of β-hCG, a hormone released by pregnant women, which resulted in the well-known easy, rapid, and low-cost pregnancy test [208, 226].

Plasmon coupling in nearby Au NPs is also exploited in molecular rulers based on the SPR dependence on the distance between two metal NPs [227]. Plasmon molecular rulers have been applied to the real-time sensing of DNA hybridization processes as well as to DNA folding in the presence of different saline buffers. In particular, the SPR sensitivity on the coupling distance of two metal NPs is so high that each step of the dimer formation is measurable, including elastic recoil after the first contact [227]. Au NPs of 40 nm in diameter allow for monitoring distances up to 70 nm by far-field extinction microscopy of a single dimer [227]. In contrast to organic fluorophores, which suffer from photobleaching, plasmon rulers are photostable, which allows for measurement down to a single NP dimer.

4.1.1.2. SPR shift sensing. Another efficient strategy to monitor the binding of the analyte on the surface of functionalized Au NPs is based on the local change of the refractive index of the medium surrounding the NP surface that does not require changes of NPs assembly in response to the analyte. Starting from the Frollich condition (equation (4)), it is possible to find an approximated linear relationship between the SPR maximum ($\lambda_{\text{max}}$) and environment refractive index $n_m = \sqrt{\varepsilon_m}$ [34]:

$$\lambda_{\text{max}} = \frac{2\pi c}{\omega_p} \sqrt{2n_m^2 + 1}$$

(23)

where $c$ is the light speed. Although the SPR wavelength is not strictly linear with $n_m$, this trend agrees with more accurate theoretical predictions and experimental results over small ranges of $n$. Equation (23) provides the basis for expressing the refractive index sensitivity of a NP in nanometres of wavelength ($\lambda_{\text{max}}$) change, without including the linewidth:

$$S = \frac{d\lambda_{\text{max}}}{dn_m}$$

(24)

In general, the precision for change of $n_m$ depends on both $S$ and the peak line-width ($\Delta\lambda_{\text{max}}$). Therefore, a figure of merit (FOM) for LSP sensing can be obtained by dividing the sensitivity by the resonance line-width [34]:

$$\text{FOM} = \frac{S}{\Delta\lambda_{\text{max}}}$$

(25)

An alternative FOM ($\text{FOM}^*$) exists [228], which considers the change in light-scattered intensity ($dI/I_0$) at a given wavelength ($\lambda_0$) versus $n_m$ change, without including the linewidth:

$$\text{FOM}^* = \frac{1}{I(\lambda_0)} \frac{dI(\lambda)}{dn_m}$$

(26)

This is useful when it is difficult to define a consistent SPR linewidth, such as in the case of NPs lacking a single plasmon band. $\text{FOM}^*$ measured at $\lambda_0 = \lambda_{\text{max}}$ can also be expressed as a function of $S$ [34]:

$$\text{FOM}^* = \frac{1}{I(\lambda_{\text{max}})} \frac{dI(\lambda_{\text{max}})}{d\lambda_{\text{max}}} \frac{d\lambda_{\text{max}}}{dn_m} = \frac{S}{I(\lambda_{\text{max}})} \frac{dI(\lambda_{\text{max}})}{d\lambda_{\text{max}}}$$

(27)

In this way, sensors based on changes in intensity and those based on peak shifts can be directly compared.

The performances of the sensors are greatly enhanced when the NPs are fixed on substrates such as glass and metal films, rather than in solution. In these cases, the detection relies in UV–vis spectroscopy or in far-field extinction microscopy [34]. This sensing approach can be easily implemented in microfluidic chips and also allows for detection with a single Au NP [229].

This type of SPR sensor allowed for the detection of proteins by using biotin–streptavidin [230] or antigen–antibody interactions in microfluidic channels [231]. Immobilized Au NPs on a thin metal film have been also employed for the amplification of the signal of a propagating SPR, allowing the development of highly sensitive Au NP-based SPR sensors [8]. The enhancement of the SPR signal in the presence of Au NPs relies on the electronic coupling between the LSP of the Au NPs and the surface plasmon wave generated on the Au sensing film [8]. Immunoassays have been developed using this principle to detect a variety of proteins and hormones in biological samples, demonstrating a signal enhancement of several orders when comparing to conventional propagating SPR sensors [232–235].

Recently, an advanced SPR sensing scheme was developed by coupling the resonance of Au NRs to whispering gallery mode microresonators, and the detection of single atomic ions (Zn or Hg) in aqueous medium was demonstrated [236].
4.12. **Dark-field imaging.** Isolated and aggregated Au NPs with size >30 nm possess a large Rayleigh-scattering cross-section that is ideal for cellular imaging using conventional dark-field microscopy, where the signal comes from the intense light scattering from the label [4]. This is possible without any staining and also in living cells [4]. Several studies showed the possibility of monitoring Au NPs localization in specific cell compartments (figure 13(A)) [237], penetration through specific cell barriers, or specific receptor recognition [3, 4, 238]. All these features are connected to the surface coating of NPs or to the presence of targeting functions such as peptides or antibodies, as discussed below.

4.13. **Role of surface functionalization.** A key consideration in the development of a sensing or imaging platform based on Au NPs is their surface functionalization with recognition units, which allows the specific interaction with the target molecule, yet avoiding nonspecific interactions (see figure 13(B)). The nature of these NP ligands also has a primary role in the stabilization of the particle itself, providing the interface between the NP core and the surrounding environment. Indeed, the chemical synthesis of Au NPs involves the use of capping ligands, such as surfactants, which need to be removed for modification with a specific recognition unit, but are not present in NPs obtained by laser ablation in liquids [18, 88, 239]. In the latter case, the sensing of surface bioconjugation by monitoring the SPR redshift upon binding is possible [239], and exploitable for controlling NP sequential multi-functionalization [237].

The most common and versatile surface chemistry performed on Au NPs uses thiol ligands, thanks to the formation of the strong gold–thiol interaction [234, 240]. Self-assembled monolayer of alkanethiols provides a simple and convenient system to tailor the interface properties of the Au NPs by using a whole gamut of terminal functional groups [19, 241]. For sensing and imaging applications in biological environments, the compact layer of alkanethiols on the Au NPs is important to improve

(i) the biocompatibility;
(ii) the resistance to nonspecific adsorption of biological molecules, by using for example the thiol-terminated polyethylene glycol chains [242]; and
(iii) the stability of NPs in different environments [34, 208, 210].

In addition, these functional groups provide suitable anchoring units for the immobilization of biomolecules, such as proteins, antibodies, nucleic acids, or other receptors for the specific recognition of the target analyte [1].

4.2. **Staining, information storage, and photochromism**

The large extinction cross-section, bright tunable colours and physical and chemical stability of Au NPs have for centuries motivated their use in staining (see section 1). These properties are now being integrated with advanced technologies such as ink-jet printing [26], or as new dyes for old tissues such as merino wool [243]. Importantly, the sensitivity of SPR to dielectric and compositional changes is exploitable for dynamic real-time colour tuning, for instance, for camouflage purposes (figure 14(A)) [244].

Also, optical information storage with the possibility of multiplexed optical recording is possible by exploiting the SPR tunability with the length of Au NRs and the anisotropy of their optical extinction [245]. Optical recording can be made non-permanent by exploiting the reversible aggregation of Au NPs with appropriate surface functionalization (figure 14(B)) [246].

4.3. **Photothermal effects**

The conversion of light into heat is extremely efficient in Au NPs due to the combination of the following features [6, 89, 247]:

(i) efficient plasmon absorption in the visible and NIR regions;
(ii) excellent photostability compared to organic compounds;
(iii) low luminescence yield;
(iv) rapid relaxation of the SPR.

In particular, the absorption cross-section of Au NPs is several orders of magnitude larger than even the strongest absorbing organic chromophores [6, 248], and the SPR can be tuned to the most suitable spectral regions, such as the ‘water transparency windows’, where body tissues are more optically transparent (700–950 nm and 1000–1350 nm) [249, 250], also making it possible to heat Au NPs in vivo [6].
The photothermal heating mechanism after SPR excitation has been investigated intensively with ultrafast spectroscopies, and is well modelled with the TTM [51, 251] (see section 2.2). These studies indicated that energy transfer from light to the environment, i.e. heating of the surrounding medium, occurs by phonon–phonon scattering already on a time scale of hundreds of picoseconds after SPR excitation [51].

Although the process is relatively simple in the case of a single LSP excitation, in photothermal experiments each NP absorbs multiple photons in order to increase the surrounding temperature as much as possible, meaning that multiple LSPs are continuously excited during the irradiation period [251]. Therefore, with increasing intensity of the light source, the Au NP lattice temperature can increase more and more, passing through the following steps (figure 15) [251]:

(i) the threshold for acoustic vibration of the lattice, due to transient thermal expansion;
(ii) the melting threshold, which induces an irreversible shape transformation (for instance NRs are melted into nanospheres);
(iii) the vaporization threshold, which induces size reduction of the original NPs and the formation of smaller NPs in the surrounding medium by nucleation and growth of the Au vapours;
(iv) fragmentation of the NPs into smaller particles due to either boiling or Coulomb explosion, with the latter due to electron ejection by photoionization or thermoelectric effect.

Similarly, the surrounding medium can be heated, melted, vaporized, or deteriorated depending on the temperature reached by the Au NPs. In particular, vaporization is associated to cavitation, i.e. the formation of a vapour bubble with larger pressure than the surrounding medium, which expands until cooling and collapsing (figure 15). In all cases, a stress wave due to the medium thermal expansion propagates in the surroundings of the heated NPs.

This remarkable number of phenomena associated to photothermal heating depends on NP absorption efficiency (i.e. particle size, shape, aggregation state, and composition) as well as on the incident light parameters (i.e. intensity, wavelength, pulse duration, and polarization) [6, 248, 251]. However, there are some general criteria for maximizing photothermal effects in Au NPs. First of all, photons exciting plasmons are either absorbed or scattered, with the probability of the two events determined by the respective \( \sigma_{\text{Abs}} \) and \( \sigma_{\text{Sca}} \) (see section 2.2.1). In particular, there is a size threshold above which scattering prevails over absorption, which depends on the shape, structure, and composition of NPs [4, 6, 37]. For Au NPs it falls approximately at 80–100 nm, while Au NPs with size smaller than ~25 nm behave as pure plasmon absorbers, because of negligible \( \sigma_{\text{Sca}} \) compared to \( \sigma_{\text{Abs}} \) (figure 7) [87, 88, 137]. This means that absorption for unit mass (\( \sigma_{\text{Abs}}/V_{\text{NP}} \)) is maximized by reducing the particle size [87, 151, 252]. Since the cross-section classically corresponds to the geometrical section of an ideally opaque object (\( \text{Tras} = 100\% \)) extinguishing the same number of photons of the NP (figure 16(A)), another useful FOM for plasmon absorption is \( \sigma_{\text{Abs}}/S_{\text{NP}} \) [87], where \( S_{\text{NP}} \) is the geometrical NP cross-section. For instance, in the case of an isolated Au nanosphere in water, the maximum \( \sigma_{\text{Abs}}/V_{\text{NP}} \) and \( \sigma_{\text{Abs}}/S_{\text{NP}} \) are reached at, respectively, 50 and 70 nm (figure 16).

The importance of \( \sigma_{\text{Abs}} \) for local heating is well explained by the expression of the heat (\( q_{\text{NP}} \)) generated inside the NP [152, 253]:

\[
q_{\text{NP}} = \sigma_{\text{Abs}}(\omega) I(\omega) = \frac{1}{2} \omega \varepsilon_0 \int \text{Im} \left[ \varepsilon(\omega) \right] E_{\text{NP}}^2(\omega) dV_{\text{NP}}.
\]

A similar trend is found for the local temperature around a single NP in the steady-state regime [40, 152, 253]:
The measurement of local temperature at the surface of NPs is very challenging, and can be made through monitoring phase transformations of the surrounding matrix [89, 90] or with photothermal optical probes [254].

Despite the $\sigma_{\text{Abs}}/V_{\text{NP}}$ being maximum for small NPs, equation (29) provides the important information that the absolute capacity of light-to-heat conversion for a single NP is proportional to NP volume. Therefore, the most obvious way to increase $\Delta T$ is by increasing the number of NPs in the point of interest [89]. Besides, one can choose the shape and composition to maximize $\sigma_{\text{Abs}}$ at the excitation wavelength [87, 151, 252]. For instance, at equal volumes, Au NRs have larger $\sigma_{\text{Abs}}$ than Au NSs composed of a silica core coated with a gold layer [87], and Fe-doped Au NSs have up to 100% larger $\sigma_{\text{Abs}}$ than the pure Au ones [35].

A long list of applications is possible for Au NPs with efficient absorption in the visible and NIR regions (figure 17), such as photothermal therapy (PT) [6, 132], light-triggered drug release [255, 256], antimicrobial systems [257, 258], photoacoustic imaging [259], photothermal contrast imaging [260], and photothermal phase transformations [261, 262]. Another consequence of photon absorption is the alteration of the equilibrium electron Fermi distribution in the metal NPs, which allows charge injection in the conduction band of nearby materials, and it is exploited for plasmon-enhanced catalysis and photocurrent generation [60].

In analogy to sensing and labelling applications (see section 4.1), the biocompatibility and ability to conjugate Au NPs with functional organic molecules is very important for most of the photothermal applications. For instance, surface functionalization is required for the colloidal stability in biological fluids or in liquid solution, the inclusion in polymeric matrices, the addition of selectivity for biomolecules or other chemical species, and the formation of surface patterns with multiple applications [6, 88, 132, 248].

4.3.1. PT and cell killing. PT offers a gentler alternative for cancer treatment by using optical heating for ablation of tumours [6, 248]. PT is mainly based on protein denaturation and cellular membrane disruption, with initiation of apoptotic mechanisms, when tissue temperature exceeds 42 °C–44 °C [6, 248, 263].

PT requires that strong photoabsorbers are located selectively in the tumour region to reduce nonspecific injury to adjacent healthy tissue [264]. The absorption cross-section of Au NPs ($\sigma_{\text{Abs}} \approx 2.9 \times 10^{-15} \text{ m}^2$ for 40 nm spheres with an absorption band around 530 nm) is five orders of magnitude larger than that of indocyanine green ($\sigma_{\text{Abs}} \approx 1.7 \times 10^{-20} \text{ m}^2$ around 800 nm), a dye used in earlier demonstrations of laser PT tumour therapy, thus promising higher efficacy at much lower irradiation energy [132]. SPR in the NIR region is useful for biological applications, because of the transparency peak of skin, tissues, haemoglobin, and blood in that spectral region [249, 250], thus pointing to shapes such as nano-rods, -stars, -corals and -shells (see figure 9) [6, 132]. Besides, guiding in vivo the PT with the same plasmonic NPs is possible by using photoacoustic (see section 4.3.5) or surface-enhanced Raman scattering (SERS, see section 5.2.4.2) imaging techniques. Although tissue penetration is limited to tens of millimetres, the use of optical fibres is under investigation for PT in deep tissues, and Au NSs are currently under clinical validation for therapy in humans [6].

The same principle of PT can be used for the realization of photothermal antimicrobial surface or substrates that destroy bacteria by light-triggered temperature increase [257, 258]. Antimicrobial activity was also demonstrated by photothermal effects under pulsed CO$_2$ laser irradiation ($\lambda_c \approx 10.5 \mu$m) of Au NP agglomerates [265].

4.3.2. Photothermal drug release and diffusion. The diffusion coefficient D of any molecular compound in a
fluid medium is described by the Einstein–Smoluchowski law [266]:

\[ D = \frac{f_{\text{geom}} k_B T}{\eta_m} \approx T e^{-a/T} \]  

where \( k_B \) is the Boltzmann constant, \( f_{\text{geom}} \) is a geometrical factor depending on molecule shape, and \( \eta_m \) is the medium viscosity, that scales approximately as \( e^{-a/T} \) with \( T \). Therefore, the local increase of \( T \) is a way to activate the diffusion of molecules near the NP surface [267]. In the most sophisticated cases, Au NPs can be included in polymeric cargo loaded with drugs that open after \( T \) increases to release their payload [268], or hydrogel matrices [269]. Perfusion and oxygenation of tissues are also favoured by moderate heating, which justifies the use of Au NPs for photothermal improvement of the delivery of cytostatic drugs [255, 256].

### 4.3.3. Photothermal contrast imaging

In photothermal imaging, Au NPs are heated by a laser beam, while a second weaker probe beam is exploited to locally measure the changes in refractive index due to the temperature gradient [260]. This technique allows for the monitoring of very small single Au NPs (i.e. below 10 nm) inside cells [270].

#### 4.3.4. Nanobubbling

Nanoscale bubble generation is exploitable for photoacoustic imaging [271] (see section 4.3.5), gene therapy treatments [272], or direct suppression of tumour cells by cell membrane perforation [273]. Repeated and effective bubble formation without particle fragmentation requires the use of optimal Au NP structure and laser parameters. Interestingly, this occurs relatively far from SPR in the case of single Au NSs [272]. In analogy with any photothermal application, the assembly of multiple small Au NPs into large aggregates is very efficient for bubble formation, as demonstrated with self-assembled gold NRs in lipid bilayer microcapsules [273].

The vapour layer forms around the surface of the Au NPs already tens of picoseconds after SPR excitation, although nanoscale bubbles appear after \( 10^2 \)–\( 10^4 \) ps (figure 18).
operative tumour detection and the surgical elimination of stable [259, 278, 279]. A key empowering feature in this field is the sufficiently high to promote bubble formation around the Au NPs [259, 277]. However, in the most common version, the laser intensity is able for in vivo imaging [276]. There are several PA variants.

The PA signal obtained is proportional to the Au NP concentration [4]. The PA resolution is set by the laser spot size at the focal plane, which is of the order of 20–50 μm [4, 259]. PA can provide depth penetration of 10–50 mm, which is suitable for in vivo imaging [266]. There are several PA variants. However, in the most common version, the laser intensity is sufficiently high to promote bubble formation around the Au NPs [259, 277]. A key empowering feature in this field is the development of red-NIR contrast agents, which remain photo-stable [259, 278, 279].

Recently, the PA ability of Au NPs was exploited for intraoperative tumour detection and the surgical elimination of microscopic malignant lesions in vivo [271]. The selectivity for tumour tissues exploits two properties of Au NPs, (i) surface conjugation with antibodies, (ii) threshold energy for nanobubble generation significantly lower for large clusters of NPs, which are self-assembled by cancer cells through endocytosis of the NPs, compared to isolated or small clusters of NPs, which are non-specifically accumulated by normal cells. Importantly, the whole procedure exploits clinically-validated gold colloids (conjugated to clinical antibodies against cancer-specific receptors) [271].

4.3.6. Photothermal activation of phase transformation. Au NPs are suitable for releasing controlled amounts of heat in nanoscopic regions. This allows controlled nanoscale phase separation and phase transitions, such as the formation of gold-polymer core–shell structures from polymer aqueous solution [280], or the reversible gel-fluid transformation in phospholipid membranes [281], or controlled chemical modifications [282]. The photothermal effect was exploited to induce a ferroelectric–paraelectric phase transition in a poly(vinylidene fluoride) thin-film nanocomposite loaded with Au nanocages, useful for the generation of patterned ferroelectric domains in a few seconds [283].

Heating Au NPs in fluid media is also a way to control their velocity and to guide the NPs to specific locations [281, 282]. High-intensity laser irradiation of Au NPs on borosilicate glass allowed substrate modification, with the formation of nanometric craters, associated to NP fragmentation and spread over the surface [284]. Another application related to phase transition concerns light-induced vapour generation [266, 285]. Broadband light-absorbing Au NPs are well suited for sunlight photothermal heaters and the generation of steam in stand-alone solar autoclaves, useful for the sanitation of instruments or materials in resource-limited, remote locations [285]. The same principle was also exploited for water–ethanol distillation, yielding fractions significantly richer in ethanol content than simple thermal distillation [286].

4.3.7. Au NP welding, alloying, and shape transformation. The heating of Au NP assemblies at T close to the melting threshold allows the formation of interparticle connections, resulting in nanobelts and nanochains [287]. At higher fluence, NP size can be reduced by photofragmentation (above vaporization threshold), or increased by the melting of NP agglomerates into single objects (below vaporization threshold) [18, 251]. Laser pulses are usually preferred to CW sources for obtaining the selective and rapid delivery of energy to Au NPs. Laser irradiation also allows size reduction or increase [18, 239, 251], shape transformation from low symmetry shapes into spheres [51, 251], or growth into NCs supporting broadband SPR from visible to NIR [88]. Photofragmentation in the presence of various metal NPs is a way to obtain intermetallic or alloy NPs [288].

4.3.8. Photothermal activation of chemical reactions. Heating is exploitable for nanoscale thermal activation of reactant molecules. A wide series of examples exist, including the...
growth of semiconductor nanowires and carbon nanotubes by chemical vapour deposition (CVD) assisted by local heating of nanoscale metallic catalysts, thermal decomposition reactions, cross-linking reactions, decomposition reactions in the solid state, recrystallization of amorphous TiO$_2$ to anatase, radical polymerization, and thermal curing of polymers such as PDMS (polydimethylsiloxane) [289]. The synthesis of polymer nanostructures on the nanometre scale due to SPR-induced photothermal chemical reactions allows the precise positioning of polymer layers with subdiffraction-limited spatial resolution [289]. Although theoretical calculations suggest that the origin of heat generation is not uniform over anisotropic Au NP volume [151, 253], these experiments allowed us to identify that the steady-state temperature profile of photothermally heated NPs is uniform, because thermal equilibrium within the metal lattice occurs just after hundreds of picoseconds [89, 90, 289].

A powerful advantage brought from the plasmon properties of Au NPs, is the ability of tracking chemical modifications at the particle surface by SERS in real time (section 5.2.4.3). For instance, this was demonstrated with a Diels–Alder cycloaddition reaction photothermally activated in a nanometre-volume cavity [290].

### 4.4. Plasmon-induced hot-carrier effects

The relaxation of LSP yields to the alteration of the equilibrium electron Fermi distribution in the metal and the formation of ‘hot electrons’ (see section 2.2). By definition, electrons are ‘hot’ when they have larger energies than the thermal excitation at room temperature [60, 289]. The excitation of electrons in a solid is always associated to the formation of holes. Therefore, hot electrons imply the presence of ‘hot holes’ with lower energies than at room temperature [60, 291, 292]. Due to their excess kinetic energy, hot electrons can transfer into unoccupied levels of acceptor molecules or materials in contact with the Au NP surface (figure 19). In fact, the activation enthalpy of electron transfer reactions catalysed by Au NPs is significantly reduced under visible light photoexcitation [293].

Similarly, electron transfer from occupied adsorbate orbitals to hot holes (i.e. transiently unoccupied states below Fermi energy in the metal) has been demonstrated [60].

The geometry of NPs can be engineered to control the transfer of hot carriers to nearby species, a process that occurs preferentially from hot spots at NP junctions, spikes, points, or edges [294]. Size [291, 295] and surface coating [292] of Au NPs are crucial parameters for the efficiency of the process.

The probability of hot-carrier transfer is lowered by their rapid relaxation and conversion into heat, and the difficulty of matching their energy with the donors/acceptor levels [60, 296]. In general, the process is possible only for acceptor or donor electronic levels with energy close to the metal Fermi level [60, 296].

When the light intensity is large enough, the photoelectric effect is possible. In this case, angle-resolved photoemission spectroscopy can directly probe preferential photoemission from hot spots and subsequent charge acceleration by the evanescent plasmon field [297].

Despite these challenges, hot carriers are exploitable for multiple applications such as in light harvesting, photodetection, doping, and photochemical reactions [60]. For instance, room-temperature dissociation of H$_2$ at the Au NP surface was reported [298]. The best performances are observed by coupling the Au NPs to other catalytic materials, such as Pt, TiO$_2$, MoS$_2$, or semiconductor quantum dots, forming heterostructures in which each component has direct contact with the other, to facilitate the photo-induced hot-carrier transfer [291, 292, 299–301]. For instance, femtosecond pump-probe spectroscopy demonstrated that plasmon-induced hot-electron transfer takes place in the Au NP/MoS$_2$ heterostructure on a time scale of 200 fs [302]. These heterostructures allow artificial photosynthesis experiments on the photoelectrochemical water splitting by combining both plasmon-induced hot electrons and hole generation in the same integrated device [303]. Also, the generation of ammonia from atmospheric nitrogen and water using sunlight was possible with a strontium titanate (SrTiO$_3$) photoelectrode loaded with Au NPs and a zirconium/zirconium oxide (Zr/ZrO$_2$) thin film [304]. An alternative to heterostructures, the alloying of Au with catalytically active metals such as Pd or Pt was also reported [144–146].

Beyond catalysis, hot electrons can be emitted over a Schottky barrier to produce a photocurrent in photodetectors with high responsivity [60], while their application in plasmonic solar cells is more difficult due to the low internal quantum efficiency [296].

### 5. Applications related to local-field enhancement

#### 5.1. Local-field enhancement

One of the main reasons for the interest in Au NPs is their unique ability to channel far-field radiation to subwavelength dimensions, thus amplifying the electromagnetic field near the particle surface, i.e. to act as nanolenses [15]. The nanolensing behaviour has been exploited to enhance several types of optical phenomena in nearby molecules or materials, such as Raman scattering [305], fluorescence [306], visible [71] and IR extinction [307], coherent anti-Stokes Raman scattering (CARS) [308, 309], hyper-Raman scattering (HRS) [310, 311], and a series of other linear and nonlinear optical effects that are discussed in section 6.
In the literature, two different approaches are mainly used to describe the local-field enhancement in plasmonic nanostructures [15]:

(i) A heuristic description based on the mechanical analogy with a mass-spring harmonic oscillator, according to which the plasmon-induced near-field is directly proportional to the mass displacement, which corresponds to the charge density accumulated at the edge of the nanoantenna [32, 33]. Therefore, the local field is due to the instantaneous electrostatic field of the dipole generated by the charge density displacement [32, 33].

(ii) An electromagnetic approach, which refers to the radiation generated by the radiative decay of the SPR (i.e. light scattering), associated to time-dependent electromagnetic fields that extend beyond the NP surface in the near field by some nanometres, and transform into propagating plane waves in far-field distance (i.e. at a distance larger than photon wavelength) [10, 34]. One can observe that the typical scattering cross-section of a 100 nm Au nanosphere in water at the SPR maximum is $3.6 \times 10^{-14}$ m$^2$, which is 4.6 times the geometric cross-section. It must be noted that the crossover between $\sigma_{\text{Sca}}$ and the geometric cross-section occurs in NPs larger than ~30–40 nm (see figure 16 for Au nanospheres).

The local-field enhancement factor (EF) at any point $r$ can be expressed as the ratio of the moduli of the local electric field $E_{\text{loc}}$ to the incident electric field $E_0$ [15, 157, 174]:

$$\text{EF}(r) = \frac{E_{\text{loc}} (r)}{E_0}.$$  \hspace{1cm} (31)

EF is dramatically affected by the NP structural parameters and position around the surface, and can range from less than 1 up to $10^2$–$10^3$. The points with the largest EF in a single NP or a group of them are called electromagnetic ‘hot spots’ [157]. On the other hand, some points on the NP surface can have EF < 1 due to destructive interference between incident and scattered light [15, 312].

In isolated NPs, the EF is larger in shapes with edges (nanocubes) or tips (NRs, nanostars, nanotriangles, nanococones), as shown in figures 20(A) and (B) [42]. However, the largest EFs are possible at the junctions between NPs, such as in dimers, trimers, etc [313]. In the simple case of an NP dimer, the EF at the junction between the particles increases monotonically as the distance between the two particles is reduced to approximately 1 nm [105]. This is a consequence of the gradual increase in the coupling between the particles, while reducing their distance. In fact, the enhancement of the local electric field is limited to the near-field zone, i.e. that zone at a distance smaller than incident light wavelength. In individual nanospheres in the quasistatic regime, the local field scales as $1/r^3$, where $r$ is the distance from the NP surface [15]. This is obtained by approximating the LSP in the Au nanosphere to an oscillating dipole with dipole moment $\vec{p}$, to which corresponds a local electric field [15]:

$$\vec{E}_{\text{loc}} (r) = \vec{E}_0 + \frac{3\hbar (\hat{n} \cdot \vec{p}) - \vec{p}}{4\pi \varepsilon_0 \varepsilon_m} \frac{1}{r^3} \hspace{1cm} (32)$$

where $\vec{n}$ is the unit vector normal to the surface and pointing to the direction of interest. The $\sim 1/r^3$ decay of $E_{\text{loc}}$ explains why LSP hybridization and hot-spot formation strongly depends on interparticle distance [105, 111, 113]. As a rule of thumb, efficient coupling between NPs leading to hot spots is observed for interparticle separation lower than 0.5 times the NP diameter [4].

Below ~1 nm the EF remains constant or, according to recent studies, it decreases again, due to the appearance of quantum effects in the interaction between the electronic density of the two NPs, and to the possibility of electron tunnelling from surface to surface (see section 3.1.1 about the non-locality of the optical constant). This is the reason for an estimated maximum EF in Au NPs of $\sim 10^2$–$10^3$ [314].

The remarkable dependence of EF on the geometrical arrangement of the NPs [315], is well described by the comparison of the maximum field enhancement in isolated Au nanospheres, dimers of nanospheres with the same size (homodimers), and dimers with different size (heterodimers) [316]. In this case, the 4th power of the maximum EF ($G_{\text{SERS}}$, see equation (38)) was considered, because of interest for SERS [317] (see section 5.2), and it was plotted versus NP size, while maintaining a dimer gap fixed at 1 nm (figure 20(D)) [316]. The results show that EF$_{\text{max}}$ in the hot spot of dimers is much higher than in isolated spheres. Besides, EF$_{\text{max}}$ increases with NP size and is higher for homodimers than in heterodimers at parity of total NP volume [316].

5.1.1. Near-field redshift. It is worth noting that the maximum of near-field intensity occurs at lower frequency than the SPR optical extinction peak [318, 319], and the entity of redshift depends on the NP structural parameters. Several authors were able to explain this effect with the simple mass-spring model [32, 33]. In fact, when the harmonic oscillator is damped (due to radiative and non-radiative plasmon decay mechanisms), the maximum oscillation amplitude (which corresponds to the near-field amplification) is located at lower frequency than the maximum dissipation (which corresponds to the far-field absorption) [32, 33]. In particular, the special position of the maximum dissipation does not depend on the damping, while the maximum oscillation amplitude shifts to lower energies with increasing damping, meaning that the spectral shifts between near- and far-field peak intensities is larger in strongly scattering NPs (large NPs with large radiative damping) or in poor plasmonic systems (large Im[$\varepsilon$] with large non-radiative damping) [320].

5.2. SERS

Raman scattering is a well-established vibrational spectroscopic technique (figure 21), possessing analyte fingerprint recognition capabilities. The efficiency with which Raman scattering occurs is very low, typically around $10^{-29}$–$10^{-31}$ cm$^2$/molecule [321, 322], but can reach $10^{-23}$ cm$^2$/molecule if the excitation source is resonant with electronic transitions of the molecule [313, 322].

The intrinsic low efficiency of Raman scattering can be strongly improved if molecules are placed close to plasmonic
NPs, in which case we talk about SERS (figure 22(A)) [7, 10]. The Raman and SERS signals can be formally expressed with the power read by the detector (respectively $P_{\text{Raman}}$ and $P_{\text{SERS}}$) [321]:

$$
\sigma = \frac{P_{\text{KNI}}}{N I \sigma_{\text{Raman}}} \quad (33)
$$

$$
G_{\text{SERS}} = \frac{G_{\text{em}} G_{\text{chem}}}{\sigma_{\text{ads}} / \sigma_{\text{Raman}}} \quad (35)
$$

where $N$ is the number of illuminated molecules, $I$ the laser intensity, $\sigma_{\text{Raman}}$ the differential Raman cross-section of the molecule, and $K$ is a proportionality constant accounting for the quantum efficiency of the detector, the transmittance of the spectrograph, the collection geometry, and the collection optics (including the numerical aperture of the objective if a microscope is used).

$G_{\text{SERS}}$ is called the total SERS enhancement factor and represents the effect of the plasmonic structure [7, 10]. $G_{\text{SERS}}$ depends on two terms [7, 10]:

$$
G_{\text{SERS}} = G_{\text{em}} G_{\text{chem}} \quad (35)
$$

that account for the increase of signal due to, respectively, the electromagnetic ($G_{\text{em}}$) and the chemical ($G_{\text{chem}}$) effects.

5.2.1. Chemical enhancement (CE). The CE corresponds to a modification of the Raman cross-section of a molecule, due to the adsorption on a metallic surface [305]. It can be formally expressed as the ratio between the Raman cross-section of the molecule adsorbed on the metal ($\sigma_{\text{ads}}$) and of the ‘free’ molecule ($\sigma_{\text{Raman}}$) [7, 305, 313]:

$$
G_{\text{chem}} = \frac{\sigma_{\text{ads}}}{\sigma_{\text{Raman}}} \quad (36)
$$

$G_{\text{chem}}$ is normally considered to be $<10^2$ [7, 305]. The exact nature of the CE is still debated in the literature. However, the most established and investigated case of the chemical effect is the formation of a charge-transfer state between the metal and the molecule, because this state can be resonant at the excitation laser wavelength, leading to a resonantly-enhanced Raman signal [323, 324].
5.2.2. Electromagnetic enhancement. The $G_{em}$ term can reach values as high as $10^2$–$10^6$ inside a single hot spot [157], and it strongly depends on the gap size, as demonstrated in Au NP dimers connected by a tuneable DNA origami spacer [325]. For instance, in the 2 nm gap of a dimer formed by two Au spheres with diameters of 50 nm, the maximum $G_{em}$ amounts to about $3 \times 10^6$ [305, 313]. However, if the $G_{em}$ is averaged over the whole dimer surface, its value is reduced by a factor of about 300 [305, 313]. For this reason, the $G_{SERS}$ experimentally measured by averaging over a whole Au NP substrate for SERS purposes, can reach values of about $10^7$–$10^8$ [322, 326]. These results also indicate that the electromagnetic enhancement provides a much stronger contribution than the chemical one [327].

$G_{em}$ can be written in a simplified form, following the so-called $E^4$ approximation described in [313], as:

$$G_{em} = \left( \frac{E_{loc}(\nu_L)}{E_0} \right)^2 \left( \frac{E_{loc}(\nu_{Raman})}{E_0} \right)^2$$

(37)

where $E_0$ is the electric field of the incident light, $\nu_L$ and $\nu_{Raman} = \nu_L + \nu_{Stokes}$ are the laser and the Raman scattering frequencies for the vibrational mode with energy $\nu_{Stokes}$. In the single-molecule case, $E_{loc}$ [2] refers to the value of the local field at the specific point where the molecule resides. Instead, if $G_{em}$ refers to the average value obtained from a large number of molecules adsorbed on the SERS substrate, $E_{loc}$ [2] should be intended as the surface average of the local-field square modulus. Equation (37) indicates that, by local-field enhancement, the metallic substrate plays two roles: amplifying the light intensity at the metallic surface (first factor, excitation) and increasing the Raman scattering rate from molecules (second factor, emission), similar to the case of modified spontaneous emission (see section 5.3). The above formula can be further simplified in the zero Stokes-shift limit of the $E^4$ approximation, by considering $E_{loc}(\nu_L) \approx E_{loc}(\nu_{Raman})$ [317]:

$$G_{em} \approx \left( \frac{E_{loc}(\nu_L)}{E_0} \right)^4.$$  

(38)

Clearly, this approximation is more reliable for $\nu_L$ in the visible region than in the NIR, and for low-frequency vibrational modes [10].

As a rule of thumb, the $G_{em}$ is expected to be maximum when both the excitation and the SERS photon wavelength fall within the SPR profile of the NPs, matching the condition $\lambda_L < \lambda_{SPR} < \lambda_{Raman}$ (Wokaun’s rule) [328].

Equation (37), or its zero Stokes-shift approximation, provides a good estimation of the magnitude of the SERS electromagnetic enhancement in most situations. However, they fail in predicting the polarization properties of the SERS radiation, for example the depolarization ratios, i.e. $I_{\perp}/I_{\parallel}$, where $I_{\perp}$ and $I_{\parallel}$ are the intensity of the Raman scattering polarized perpendicularly and parallel to the incident laser polarization [313, 329]. This stems from the approximations adopted to carry out equation (37), which neglect some issues related to the polarization of the emitted Raman scattering and to the relative orientation of the molecule with respect to the near field [313, 329].

As mentioned in section 5, the local field rapidly decays with distance from the NP surface as $1/r^4$ [15]. Therefore, the efficiency of the electromagnetic enhancement quickly drops from the surface, making SERS highly selective towards molecules located in the first layers above the surface [330–332]. For instance, the distance dependence of $G_{em}$ can be described by considering the simple case of a metallic sphere of radius $R$ in the quasistatic approximation as [321]:

Figure 22. SERS is exploited for ultrasensitive detection of analytes by Raman spectroscopy (A) or for ultra-bright labelling of target samples (B). In (A), the analyte emits intense Raman signals when deposited on the Au NP substrate. In (B), Au NPs are loaded with a Raman-active dye (reporter) and a targeting function, so that the target analyte is detected by the intense Raman signal after binding of the SERS label to it.
The fabrication of suitable plasmonic substrates for SERS is crucial for successful results [7, 338]. The sensitivity of the equipment is moving SERS towards real-world applications [338, 339]. The fabrication of suitable plasmonic substrates for SERS is crucial for successful results [7, 338]. In general, vibrations with a change of polarizability perpendicular to the surface are enhanced, whereas Raman modes oriented parallel to the metal surface are weakly or not enhanced [7].

5.2.3. Analyte contribution to SERS. SERS signals also depend on the properties of the analyte, since each molecule is characterized by its Raman tensor and can have different orientation relative to the metal surface [7]. For instance, the orientation of the molecule on the metal surface can significantly change the coupling efficiency with the local field [333, 334], which is determined by specific surface selection rules [7, 333]. In general, vibrations with a change of polarizability perpendicular to the surface are enhanced, whereas Raman modes oriented parallel to the metal surface are weakly or not enhanced [7].

Importantly, the brightest Raman signals are observed when both resonant Raman and SERS occur, a condition known as surface-enhanced resonant Raman scattering or SERRS. In resonant Raman scattering, the excitation frequency coincides with that of the electronic transitions in the analyte. In this case, the $P_{\text{SERS}}$ is large, because both the $G_{\text{SERS}}$ and $P_{\text{Raman}}$ terms are very large (see section S7 for the full justification) [316, 335]. The optical absorption bands of the analyte tell in most cases which are the optimal excitation lines to obtain both resonant Raman scattering and SERS conditions [316, 335].

5.2.4. Applications. SERS is a well-established vibrational spectroscopic technique that simultaneously provides fingerprint recognition capabilities and extremely high detection sensitivity, down to single-molecule level [336, 337]. These features have triggered the application of SERS in many fields such as analytical and bioanalytical chemistry, chemistry, nanomedicine, and biolabelling. Notably, the progress made in the engineering of the substrates, miniaturization, and sensitivity of the equipment is moving SERS towards real-life applications [7, 338]. The fabrication of suitable plasmonic substrates for SERS is crucial for successful results [7, 339–342].

5.2.4.1. Fundamental studies. Due to the ultra-sensitive molecular recognition allowed by SERS, single-molecule Raman spectroscopy has been the subject of in-depth investigations. What is a reliable proof of single-molecule SERS, or what information can be extracted from single-molecule Raman spectra, is still debated in the literature [337].

Moreover, the possibility of quantifying the near-field intensity has made SERS a valuable tool to investigate fundamental plasmonic issues. Since SERS is an indirect probe of the near-field intensity, wavelength-scanned SERS has been used to carry out fundamental structure-to-property studies aimed at investigating the connection between the morphology of the plasmonic substrate and its near- and far-field properties [318, 319, 343–346]. In fact, the spectral gap between the near- and far-field properties (see section 5.1.1) is a crucial issue for analytical applications. The near-field wavelength dispersion is not easily predictable on the basis of the far-field spectra in complex plasmonic substrates [318, 319, 343–346].

5.2.4.2. Analytical and bioanalytical applications. SERS detection can follow two conceptually different approaches, which are direct detection [7] (in which the SERS signal is generated from the target species, see figure 22(A)) and indirect detection [347] (in which the SERS signal comes from a Raman reporter molecule that is bound to a larger nanostructure, which can selectively recognize the target species, see figure 22(B)).

Direct detection has been exploited for biological species [348, 349], antineoplastic drugs [350], chemical warfare agents, toxic industrial chemicals, pesticides, food additives, and in the fields of art preservation and forensic science [338, 350, 351]. Recently, direct SERS detection was demonstrated with glucose at physiologically relevant concentrations [352], or with volatile tumour biomarkers in the breath of patients, with the capability of distinguishing early and advanced gastric cancer patients from healthy persons [353]. Indirect detection is more common in complex environments, like those often encountered in the medical field [347]. Indirect detection relies on ‘SERS tags’: they are composed of one or more plasmonic NPs, a Raman reporter molecule anchored to their surface, a stabilizing layer to prevent coalescence and fouling, and one or more targeting functions for the selective binding of analytes [316, 347, 354]. To achieve the largest possible brightness, these tags are built with a Raman reporter capable of SERRS at the expected excitation wavelength [316]. SERS tags have been used for ionic (i.e. Hg$^{2+}$, Cd$^{2+}$, As$^{3+}$), biomolecular (i.e. glutathione, glucose), pathogenic (i.e. Salmonella bacteria) detection [355, 356] as well as in in vivo studies aimed at the identification of cancer by passive accumulation [140, 357], or active targeting of cancer markers [357–359]. Most of these studies exploit the multifunctionality of Au NPs for combined imaging techniques or guiding the therapeutic follow-up [140, 360, 361].

5.2.4.3. Monitoring of chemical reactions. Real-time monitoring of chemical reactions is also possible by SERS, when Au NPs do not act as substrates for the reaction [10]. Due to the SERS effect, chemical reactions inducing changes in the electronic structure of reagents are especially easy to monitor. SERS can be performed at specific points of a reaction environment [362]. For instance, when SERS is coupled with a microfluidic reaction chamber, reaction kinetics can be easily controlled [362]. SERS methodologies are also well suited to study electron transfer reactions, because the Au NPs act both as plasmonic substrate and a metal-conducting electrode [363]. On the other hand, the contribution from photothermal and photochemical effects due to SPR excitation must be considered in these experiments [362].

5.2.5. Coherent anti-Stokes Raman scattering. CARS is a third-order nonlinear process in which a pump and a Stokes beam at frequency $\nu_p$ and $\nu_{\text{Stokes}}$ are crossed, with a suitable geometry, in the sample (figure 21). When $\nu_p = \nu_{\text{Stokes}}$ matches the frequency of a molecular vibrational mode

\[
\frac{G_{\text{SERS}}(r)}{G_{\text{SERS}}(0)} = \left( \frac{R}{R + r} \right)^{12}. \tag{39}
\]

Considering a typical Au nanosphere with $R = 30$ nm, the $G_{\text{SERS}}(r)/G_{\text{SERS}}(0)$ goes from 100% at $r = 0$, to 10% at $r \sim 6$ nm.
(\nu_{\text{Stokes}}), a strong anti-Stokes signal is generated at \nu_{\text{AStokes}} = 2 \nu_p - \nu_{\text{Stokes}} [364]. This is a coherent process in which the generated beam is directional and governed by the phase-matching conditions, which is the opposite to normal Raman in which the scattering is normally distributed over the whole solid angle. CARS intensity depends linearly on the Stokes beam intensity and quadratically on the pump beam intensity. In practice, CARS is also significantly more sensitive than normal Raman scattering, in the case of molecules with an intrinsically low cross-section (~10^{-30} \text{cm}^2/\text{sr}), for which resonant Raman is not possible [308, 309]. By coupling CARS with SERS substrates, single-molecule sensitivity was also demonstrated for this type of analyte [309].

5.2.6. Hyper Raman scattering. HRS is a second-order nonlinear process in which two incident photons are simultaneously scattered from a medium (figure 21) [364]. When high-power lasers are used, the molecular polarizability (\hat{\alpha}) is not linearly dependent on the electric field and more terms have to be included in its Taylor expansion:

\[ \hat{\alpha} = \alpha + \hat{\beta} \hat{E} + \hat{\gamma} \hat{E} \hat{E} + \ldots \]  

(40)

where \alpha is the linear polarizability tensor, \beta and \gamma the first and second hyper-polarizabilities. HRS is due to the modulation of \beta, induced by the vibrational normal modes of the molecule. This modulation gives rise to scattering components at frequency 2\nu_L - \nu_{\text{Stokes}} or 2\nu_L + \nu_{\text{AntiStokes}} where \nu_L and \nu_{\text{Stokes}} are the laser and vibrational mode frequencies, respectively. HRS allows the experimental investigation of specific molecular information such as the frequency of vibrational modes, which is neither Raman nor IR active [310]. However, HRS suffers from fluorescence background, low signal intensity, and averaged signal over all molecules in the sample [310, 311]. Coupling molecules with Au NPs proved to be an effective way to simultaneously reduce the background signal and enhance the HRS signal, in some cases up to single-molecule level [310, 311, 365].

5.3. Fluorescence modulation

Fluorescence emission from a molecule [306] or a fluorescent NP (such as a semiconductor quantum dot [366] or a rare-earth luminescent nanocrystal [366, 367]) is strongly influenced by the nearby presence of Au NPs. The fluorescence cross-section (\sigma_{\text{Fluo}}) can be expressed as the product of the fluorophore absorption cross-section (\sigma_{\text{Abs}}) and its quantum yield (Q_{\text{Fluo}}) in free space:

\[ \sigma_{\text{Fluo}} = \sigma_{\text{Abs}} Q_{\text{Fluo}} \]  

(41)

leading to the following definition of the fluorescence EF (EF_{\text{Fluo}}) [313]:

\[ \text{EF}_{\text{Fluo}} = \frac{\sigma_{\text{Fluo}}^\text{Au}}{\sigma_{\text{Fluo}}} = \frac{\sigma_{\text{Abs}}^\text{Au} Q_{\text{Fluo}}^\text{Au}}{\sigma_{\text{Abs}} Q_{\text{Fluo}}} \]  

(42)

The superscript ‘Au’ pinpoints that the quantities refer to a fluorophore near the Au NPs. The absorption cross-section may be written as [313, 367]:

\[ \sigma_{\text{Abs}} \propto \omega \Im [\alpha] \left( \frac{E_{\text{loc}}}{E_0} \right)^2 \cos^2 \theta \]  

(43)

where \alpha is the fluorophore linear polarizability and \theta is the angle between the direction of the induced dipole moment in the fluorophore and the incident electric field \hat{E}. Therefore, the fluorophore absorption cross-section is proportional to the square of the local-field enhancement:

\[ \frac{\sigma_{\text{Abs}}^\text{Au}}{\sigma_{\text{Abs}}} = \left( \frac{E_{\text{loc}}}{E_0} \right)^2. \]  

(44)

However, the metal surface acts on fluorescence by influencing both the absorption cross-section and the fluorescence quantum yield (see figure 23(A)) [7, 306].

Concerning Q_{\text{Fluo}}, it depends on the relative entity of radiative (\Gamma_{\text{Rad}}) and non-radiative (\Gamma_{\text{NRad}}) relaxation rates as [306, 368]:

\[ Q_{\text{Fluo}} = \frac{\Gamma_{\text{Rad}}}{\Gamma_{\text{Rad}} + \Gamma_{\text{NRad}}}. \]  

(45)

and in proximity of a metal surface there are additional contributions entering in the expression of Q_{\text{Fluo}} [306, 368]:

\[ Q_{\text{Fluo}}^\text{Au} = \frac{\Gamma_{\text{Rad}} + \Gamma_{\text{NRad}}^\text{Au}}{\Gamma_{\text{Rad}} + \Gamma_{\text{Rad}} + \Gamma_{\text{NRad}} + \Gamma_{\text{NRad}}^\text{Av}}. \]  

(46)

From one side, the Au substrate increases the emission rate of the molecule through the \Gamma_{\text{Rad}} term, by stimulating photon emission due to the local electromagnetic field enhancement, analogously to what happens to the stimulation of Raman scattered radiation (see section 5.2). In fact, according to Poynting’s theorem, the power (P_{\text{Fluo}}^\text{Au}) emitted radiatively from a fluorophore near an Au NP depends on the local field as [369, 370]:

\[ P_{\text{Fluo}}^\text{Au} = \frac{\sigma_{\text{Abs}}}{12 \pi \varepsilon_m} + \frac{\omega}{2} \Im [\hat{p} \cdot \hat{E}_{\text{loc}}] = P_{\text{Fluo}} + \frac{\omega}{2} \Im [\hat{p}^* \cdot \hat{E}_{\text{loc}}], \]  

(47)

where \hat{p} and \hat{p}^* are the quantum mechanical transition dipole of the fluorophore (treated phenomenologically as a classical dipole) and its complex conjugate.

In addition, electromagnetic energy transfer may occur from the fluorophore to the metal due to the image charges in the NP induced by the fluorophore dipole (\Gamma_{\text{NRad}}^\text{Av}) [371, 372].

Since EF_{\text{Fluo}} depends on the enhancement of the absorption cross-section and on the enhancement/quenching undergone by the quantum yield, EF_{\text{Fluo}} can reach values up to 1000, but can also be \textless 1 [306, 373].

The effects on fluorescence modulation depends on the type of fluorophore and its orientation [306, 368, 369]. Considering a good fluorophore in free space, \Gamma_{\text{Rad}} \gg \Gamma_{\text{NRad}} and Q_{\text{Fluo}} \approx 1, \Gamma_{\text{Rad}}^\text{Au} will play a limited role in the quantum yield (that cannot be larger than 1). Conversely, in low-quantum-yield fluorophores (i.e. \Gamma_{\text{Rad}} \ll \Gamma_{\text{NRad}} and Q_{\text{Fluo}} \ll 1), \Gamma_{\text{Rad}}^\text{Au} can strongly increase Q_{\text{Fluo}}^\text{Au} with respect to Q_{\text{Fluo}} [306, 368]. Clearly, this is valid only if the weight of \Gamma_{\text{NRad}}^\text{Au} with respect to \Gamma_{\text{Rad}}^\text{Au} is negligible, otherwise Q_{\text{Fluo}}^\text{Au} will be smaller than Q_{\text{Fluo}}. Quenching...
effects prevail on the radiative enhancement in small NPs (i.e., with low local-field enhancement), and at short distance (typically below 5–10 nm) [369] and vice versa [7, 306, 368, 374]. This leads to an optimum distance of the dye at which EF\textsubscript{FRET} is maximized, which is normally assumed to be in between 5 and 20 nm [7, 374].

Fluorescence quenching in dyes close to Au NPs occurs at a distance longer than in conventional Förster intermolecular energy transfer processes such as fluorescence resonance energy transfer (FRET) [375]. The distance dependence of quenching has been studied in the specific case of a dye attached to a 2 nm Au NP [373, 376]. The NP-dye distance was set to 7, 12, and 17 nm by using three DNA strands with different lengths as spacers (figure 23(B)). The study of the PL emission, as a function of the distance showed that the quantum efficiency of energy transfer follows a 1/r\textsuperscript{4} distance dependence both in the case of a fluoresceine derivative and Cyanine 5 (figure 23(C)). Notably, the authors showed that the Au NP does not modify the radiative emission of the dyes (Γ\textsubscript{Rad, Au} ≪ Γ\textsubscript{Rad}) and hence the measured distance dependence arises only from an additional non-radiative decay pathway, due to the so-called nanosurface energy transfer process (NSET).

Concerning applications, fluorescence modulation has been used in the detection of metal ions, small molecules, proteins, pathogens, and mammal cells [1]. For example, β-cyclodextrin (β-CD) functionalized Au NPs can work as a FRET cholesterol sensor [377]. When fluorescein is included into the cavity of β-CD, its fluorescence is quenched by FRET towards the NP: due to its higher binding affinity to β-CD, cholesterol can replace fluorescein, releasing it from the cavity and restoring its fluorescence. In this way, cholesterol at nanomolar concentration can be detected [377]. In a different approach, fluorescence enhancement was achieved by positioning the fluorophores at the optimal distance from plasmonic NPs, such as on the surface of Au nanotriangles coated with a silica layer of well-defined thickness [378]. In this case, displacement of the label by interaction with the analyte originated a measurable decrease of the fluorescence signal [378].

5.3.1. Active plasmonic devices. The incorporation of fluorophores as gain material in suitably engineered Au NP assemblies (such as Au core/silica shell or porous silica capsules embedding Au NPs) is often sought for the realization of active plasmonic devices, because it makes it possible to induce resonant energy transfer processes from gain units to plasmonic NPs to compensate losses [379, 380]. This concept allows the realization of surface plasmon amplification by stimulated emission of radiation (SPASER) [381, 382]. A SPASER is composed by a medium with optical gain in close vicinity to a plasmonic NP (see figure 23(D)), so that resonant energy transfer from excited molecules to the LSP of the cavity and restoring its fluorescence. In this way, cholesterol at nanomolar concentration can be detected [377]. In a different approach, fluorescence enhancement was achieved by positioning the fluorophores at the optimal distance from plasmonic NPs, such as on the surface of Au nanotriangles coated with a silica layer of well-defined thickness [378]. In this case, displacement of the label by interaction with the analyte originated a measurable decrease of the fluorescence signal [378].

Figure 23. (A) Simplified Jablonski diagram for a fluorophore in free space (black arrows and labels) and in the presence of the metallic substrate (red and yellow arrows and labels). Γ\textsubscript{Rad} and Γ\textsubscript{NRad} are the radiative and non-radiative decay rates without metal; Γ\textsubscript{Rad, Au} and Γ\textsubscript{NRad, Au} are the additional contributions brought about by the metal. σ\textsubscript{Abs} and σ\textsubscript{Abs, Au} represent the absorption cross-sections of the molecule in free space and in the presence of the metal. Note that Γ\textsubscript{Rad, Au} and Γ\textsubscript{NRad, Au} are additive contributions to the corresponding quantities in free space; σ\textsubscript{Abs, Au} instead is the enhanced cross-section and not an additive contribution to σ\textsubscript{Abs}. (B) In a fluorescence quenching experiment, DNA strands of different lengths were used as spacers to vary the distance between the dyes (fluoresceine and Cyanine 5) and Au NPs. (C) Quantum efficiency of energy transfer (Q\textsubscript{eff}) follows a 1/r\textsuperscript{4} distance dependence for both dyes. (B) and (C) Reprinted with permission from [376]. Copyright (2006) American Chemical Society. (D) Sketch of a typical SPASER architecture composed by dye molecules embedded in a silica shell surrounding an Au NP. (E) Normalized extinction (1), excitation (2), spontaneous emission (3), and stimulated emission (4) spectra of the SPASER shown in (D), (D) and (E) Reprinted by permission from Macmillan Publishers Ltd: Nature [382], copyright (2009).
5.4. Surface-enhanced infrared absorption (SEIRA)

In SEIRA, two mechanisms contribute to enhance the IR absorption: (i) the electromagnetic mechanism causes an increase of the absorption cross-section for the same reason discussed about fluorescence enhancement and in the same way described by equation (43); (ii) the chemical mechanism corresponds to a change of the absorption cross-section upon adsorption of the molecule on the metal substrate, by a similar mechanism discussed about CE in SERS [7, 321].

The absorption cross-section for vibrational modes can be written as [7, 384]:

\[
\sigma_{\text{Abs}} \propto \left( \frac{\partial \mu}{\partial Q_i} \right) E^2 \cos^2 \theta
\]

(48)

where \(\partial \mu/\partial Q_i\) is the first derivative of the dipole transition moment with respect to a normal vibrational coordinate \(Q_i\), and \(\theta\) is the angle between \(\partial \mu/\partial Q_i\) and the oscillating electric field \(E\). Therefore, similar to equation (42), the increase of the molecule absorption cross-section is due to the electric field enhancement generated by the plasmonic substrate, that is:

\[
\frac{\sigma^{\text{Au}}_{\text{Abs}}}{\sigma_{\text{Abs}}} = \left( \frac{E_{\text{loc}}}{E_0} \right)^2.
\]

(49)

It was suggested that surface-enhanced scattering, scaling with \(E_{\text{loc}}[4]\) due to the contribution of the nearby nanoantenna, can also contribute to the IR extinction measured in ordinary SEIRA experiments [174]. This was experimentally verified by measuring the scattering of a Si tip placed in proximity of an Au dimer nanoantenna [174]. In this case, the apparent IR extinction cross-section of the analyte extracted from SEIRA experiments can show a mixed dependence on \(E_{\text{loc}}[7, 174]\):

\[
\frac{\sigma^{\text{Au}}_{\text{Ext}}}{\sigma_{\text{Abs}}} = k_1 \left( \frac{E_{\text{loc}}}{E_0} \right)^2 + k_2 \left( \frac{E_{\text{loc}}}{E_0} \right)^4.
\]

(50)

Experimental SEIRA enhancement factors are normally in the range \(10–10^3\) [384], although they can exceed \(10^3\) in the hot spots of optimized substrates [385], where Fano resonance effects involving the interference of a broadband plasmon with the narrowband vibration from adsorbates are possible [386, 387].

SEIRA is most efficient within 5 nm of the surface, where the effect of the two mechanisms of enhancement is larger, since the absorption enhancement decays as \(1/r^3\), where \(r\) is the distance between the analyte and metal surface [7].

In SEIRA, the local-field enhancement is required at IR frequencies. Therefore, best hot spots are achieved at the junction between linear Au nanoantennas with high aspect ratio (up to 10) and micrometer length, using illumination with light that is polarized parallel to the antenna axis (figures 24(A) and (B)) [385, 387]. Interestingly, appropriate engineering of the Au nanoantennas allows simultaneous SERS and SEIRA on the same substrate, by endowing it with both visible and infrared SPRs (figure 24(A)) [388].

As for applications, SEIRA has been used for the characterization of ultrathin films in several contexts, to study catalytic reactions and electrochemical processes with improved sensitivity, and in cultural heritage studies [7, 321, 389].

Recently, the photothermal-induced resonance imaging (PTIR) technique emerged for the investigation of SEIRA with 30–100 nm of spatial resolution [390]. In PTIR, samples are illuminated with a tunable IR laser in a total internal reflection configuration. The absorption of laser light by the sample results in local heating, sample expansion, and thus in a mechanical excitation, which can be detected with an atomic force microscope (AFM) cantilever in contact with the sample (figure 24(C)). AFM tip displacement will be proportional to the absorbance of the probed area at each specific IR wavelength used. Therefore, PTIR provides an IR absorption spectrum, directly comparable with IR spectral libraries, but collected with 30–100 nm of spatial resolution, which is compatible with plasmonic features of several Au nanostructures acting as SEIRA substrates [390, 391].

5.5. Enhanced optical absorption and photovoltaic applications

Surface-enhanced absorption is possible in molecules with electronic transitions in the same spectral range of the SPR in the Au NPs, according to equation (43). The enhancement of light absorption in materials near the Au NP surface finds application in the field of photovoltaics [392, 393]. Conventional silicon [392] or bulk heterojunction [393, 394] solar cells are fabricated in order to meet two opposite requirements, which are good absorption of the sunlight and efficient collection of the generated charge carriers. An increase of the cell thickness would improve the former, but reduce the latter, since charge carriers generated far from the p–n junction (in Si cells) or the acceptor–donor junction (in bulk heterojunction cells) have higher probability of charge recombination. Improving the absorption efficiency of the photovoltaic layer would allow one to fabricate thinner cells, with a reduction of the production costs and an increase of charge-carrier collection efficiency. Plasmonic NPs can be used to this end, following two different schemes (figure 25) [392, 395–398]:

(i) Light scattering. Metal NPs placed above the photovoltaic layer drive the sunlight preferentially into the photovoltaic layer itself, introducing an angular spread that increases the effective light path and, therefore, the absorption.

(ii) Light concentration. Metal NPs are embedded in the photovoltaic layer; sunlight absorption is increased due to the intense local field present at the surface of the metal NPs.

6. Other applications and advanced phenomena

6.1. Optical trapping and manipulation

Optical forces and torques stem from the conservation of linear and angular momentum during the light–matter interaction [177]. Such mechanical effects of light are the enabling principles of the so-called optical tweezers (OT) [177, 399], tools based on highly focused laser spots that can trap and
manipulate particles over a broad size range, from atoms to cells. Capable of applying and detecting extremely small forces (at the femtonewton range) and torques, OT find applications in many research fields ranging from life sciences, to spectroscopic sensing, and quantum technologies [399]. In this context, the plasmonic response of gold has been exploited for two main classes of OT applications: (i) optical trapping and manipulation of colloidal Au NPs [400], aggregates [115, 401], and composites [402, 403], where the particles’ large polarizability as well as their localized plasmonic response enhances optical forces; (ii) the so-called plasmonic tweezers [404], where particles are trapped by the enhanced near fields associated with the plasmonic response of gold nanostructures on a substrate [405].

6.1.1. Optical trapping of Au NPs. Optical trapping of colloidal Au NPs is generally achieved by tuning the light on the long wavelength side of any plasmon resonance, i.e. typically in the NIR where the optical response of individual metal NPs is dictated by the free-electron plasma resulting in increased dipolar polarizability [406]. Thus, a tenfold enhancement of the mon enhanced radiation force that can be exploited for optical injection in living cells [419].

In Raman tweezers (RT), OT, and Raman spectroscopy are performed with the same laser line and optical setup, to collect Raman signals from the trapped object (figure 26).

6.1.2. Plasmonic tweezers with Au NPs. Plasmonic tweezers based on Au NPs exploit the enhanced field associated with localized hot spots generated by gold structures (pads, holes, nanoantennas) fixed on a substrate [405, 420]. The localized hot spots provide 3D optical trapping at the nanoscale [405, 420]. Changing the shape and size of the nanostructures, results in a wide tunability of the optomechanical interaction. This enables the optical trapping and SERS up to single-molecule level [421].

6.2. Plasmonic chiroptical effects

Any object is chiral if its image in a plane mirror cannot be brought to coincide with itself and, consequently, chiral objects can have left- or right-handedness [422]. This means that the inversion symmetry is broken, i.e. the object does not have a mirror and rotation-reflection symmetry [423]. In nature, chirality is associated to chiroptical effects, due to the fact that the refractive index and the extinction coefficient of chiral objects (or enantiomers) differ for left- and right-hand circularly polarized light. The difference in refractive index causes a rotation of the plane of linearly polarized light (optical rotation (OR) or optical activity), while the difference of extinction coefficient causes a difference in transmission for left- and right-hand circularly polarized light (circular dichroism or CD) [422]. When OR is probed as a function of wavelength, it is called optical rotatory dispersion (ORD).

OR and CD also have nonlinear optical counterparts such as second harmonic generation (SHG) OR and SHG-CD, although nonlinear chiroptical effects are sensitive to different structural parameters and selection rules [422]. Chiroptical effects are at the basis of several applications such as optical modulation, the characterization of molecular enantiomers (biomolecules, organic compounds, etc), and have the potential to induce asymmetric synthesis and catalysis (chiral photochemistry) [422, 423].
6.2.1 Intrinsic chiroptical effects in Au NPs. Chiroptical effects in Au NPs can have different origins [422]:

(i) The kink atoms of high Miller index surfaces, such as one at which the (0 0 1), (0 1 1), and (1 1 1) surfaces of a cubic lattice intersect (not related to the SPR).

(ii) The relaxation of surface atoms due to surface patterning with adsorbed molecules (chiral footprinting, not related to the SPR).

(iii) The shape or the assembly of Au NPs into chiral geometry. In fact, the same symmetry requisites of molecules showing chiroptical effects are also valid for plasmonic nanostructures [423]. However, chiroptical effects in molecules are small, because the chiral arrangement of molecular bonds occurs over a much shorter distance than the helical pitch of circularly polarized light. Instead, the shape or assembly of Au NPs can be optimized to increase the chiroptical effects several orders of magnitude higher than those for common biomolecules [424], for instance by increasing the chiral pitch of the material to match that of circularly polarized light [422]. Typical chiral shapes are 2D and 3D spirals, also obtained by the superposition of achiral objects (figure 27). In particular, chirality can be obtained from the assembly of achiral Au NPs onto chiral molecules and nanostructures, such as organic fibres or DNA scaffolds [425, 426].

This is exploitable for designing elegant chiroplasmonic sensors. For instance, Au–Ag NPs conjugated with aptamers were assembled into chiral structures capable of intense CD signals only when the human epidermal growth factor receptor 2 (HER2) antigen of specific cancer cells is present, due to the bioaffinity for the aptamer coating [427].

On the other hand, chiroptical effects can lead to negative refractive index, which is of interest for the realization of metamaterials (i.e. materials with optical properties not found in nature) and the related wide range of possible photonic applications [422].

6.2.2 Enhancement of chiroptical effects in nearby molecules. Au NPs can increase the chiroptical effects in nearby molecules, for example when they are used as trapping or plasmonic nanoaggregates in the SERS [428].

Figure 25. Two different mechanisms and arrangements can be exploited to improve the efficiency of a solar cell with plasmonic nanoparticles. (a) Light scattering; (b) light concentration. The blue and red areas represent, for instance, the p- and n-doped layers of a Si cell. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials [392], copyright (2010).

Figure 26. (A) Simplified sketch of the RT. (B) Raman signals from the molecules adsorbed on the trapped Au NPs are collected through the same objective used for trapping. In this spectra, pyridine and bovine serum albumin vibrational peaks, adsorbed on the surface of a trapped aggregate of Au NPs, were detected. Reprinted with permission from [401]. Copyright (2011) American Chemical Society.
Figure 27. Helical structures are the most intuitive examples for a chiral plasmonic nanostructure, and they can be obtained by a single helical object (A), or by assembling nonchiral Au NPs along a chiral path, such as the DNA helix (B) and (C). (A) Optical chirality enhancement ($\tilde{C}$) in a nearby chiral molecule for a left-handed Au helix with left-handed circularly polarized light (left) and its enantiomer (right). For helix diameter and height of the helix of 400 nm and Au thickness of 80 nm, the enhancement is observed for an excitation at 2030 nm. The sign of $\tilde{C}$ flips in different points of the helices. (B) The same as in (A) but for a helix obtained by assembling Au nanodisks (50 nm diameter, 40 nm thick, excitation at 900 nm). (C) and (D) Sketch of helical Au NP structures assembled on DNA scaffolds (C) and CD spectra corresponding to the left-handed and right-handed helices. Reproduced from [424]. CC BY 3.0 ((A) and (B)), and reprinted with permission from [426]. Copyright (2016) American Chemical Society. (C).

nearby molecules in several ways. In general, the chiroptical effects are related to the optical chirality $C_{\text{co}}$ [424]:

$$C_{\text{co}} = -\frac{e_{\text{out}}}{2} \operatorname{Im} \{ \mathbf{E}_{\text{loc}} \cdot \mathbf{B}_{\text{loc}} \}. \quad (51)$$

Thus, the chiroptical effects scale linearly with the local electric-field enhancement, and chiral enhancement in a molecule close to the Au NPs can be expressed as [372, 424]:

$$\tilde{C} = \frac{C_{\text{co}}(E_{\text{loc}}, B_{\text{loc}})}{C_{\text{co}}(E_{\text{co}}, B_{\text{co}})}. \quad (52)$$

It was calculated that $C_{\text{co}}$ of molecules near chiral Au NPs can be about 20 times higher than in the absence of the NPs (figure 27) [424]. Therefore, the same plasmonic NPs possessing intrinsic chiroptical properties can also enhance the chiroptical effects of nearby molecules, in principle allowing the identification of enantiomers with higher sensitivity [424], or significantly increasing the enantiomeric excess of direct asymmetric synthesis and catalysis [422].

A more detailed expression can be used for $C_{\text{co}}$ [372]:

$$C_{\text{co}} = a_{\text{co}} \operatorname{Im} \{ \langle \tilde{P} \tilde{\mu}_{1z} \rangle \cdot \tilde{m}_{2z} \} + b_{\text{co}} F(\tilde{\mu}_{1z}, \tilde{m}_{2z}) \quad (53)$$

where $\tilde{\mu}_{1z}$ and $\tilde{m}_{2z}$ are the electric and magnetic dipole moments of a molecule, $a_{\text{co}}$, $b_{\text{co}}$ and $F(\tilde{\mu}_{1z}, \tilde{m}_{2z})$ are coefficients depending on the geometry, material, and incident light frequency, $\tilde{P}$ is the electric-field enhancement matrix. For increasing distance between the molecule and NP, $\tilde{P}$ tends to unit matrix and $b$ tends to 0. The first term in equation (53) shows that $\tilde{P}$ can change the angle between $\tilde{P} \tilde{\mu}_{1z}$ and $\tilde{m}_{2z}$, which allows the creation of a non-zero CD signal also in molecules with a mirror-symmetry plane and orthogonal dipole moments [372]. This means that the interaction with a NP may lower the symmetry of a molecule and create a CD signal. The second term in equation (53) accounts for mutual interactions between molecules and the NP, such as the chiral currents inside a NP induced by the dipole of a chiral molecule. Both the first and second term of equation (53) must be considered to properly reproduce the observed Fano resonance effects in CD spectra [372].

6.3. Magneto-plasmonic effects

The literature refers to magneto-plasmonics in Au NPs in two distinct cases [428]:

(i) when magnetic and plasmonic properties are combined in a single nanosystem, resulting in additive magnetic-plasmonic effects, without reciprocal influence on the magnetic or plasmonic responses;

(ii) when the magnetic properties influence the plasmonic response or vice versa, resulting in new magneto-plasmonic performances or phenomena.

A consequence of this definition is that ‘magnetic-plasmonic’ devices require the combination of a ferro-, ferri- or para-magnetic material with a plasmonic one, whereas ‘magneto-plasmonic’ phenomena can in principle also be observed in traditionally dia-magnetic plasmonic materials such as pure Au. Since, external magnetic fields must be applied to enable magneto-plasmonic activity, the presence of ‘magnetic’ elements such as Fe, Co, or Ni is generally preferred to obtain stronger or new combined effects [428]. However, magnetic materials have damped plasmon resonance and limited chemical stability in ordinary operating conditions [36], which justifies the combination with good plasmonic materials such as Au to obtain appreciable optical properties [35, 138, 428].

Magnetic-plasmonic NPs are exploited for a variety of applications, taking advantage of the coexistence of the two
For instance, magnetism allows localization of NPs in a specific area for collection and enhanced detection of analytes, for localized drug delivery, or for the realization of remotely-assembled and reconfigurable plasmonic devices, including arrays of SERS substrates [428–430]. Magneto-optics is also exploited in nanomedicine for adding multimodal imaging and therapeutic properties to Au NPs [140, 431–433].

Magneto-plasmonics is an emerging research field including some well-established physical phenomena such as magneto-optic Kerr effect (MOKE) and the Faraday effect (figure 28(A)), and new phenomena that are still under debate, such as photoswitchable magnetism [428]. MOKE consists in the rotation of the polarization plane of light reflected from a magnetized material [364]. The Faraday effect is the equivalent of MOKE for transmitted light [364]. The rotation of the plane of polarization is linearly proportional to the component of the magnetic field in the direction of light propagation. The Faraday effect can be seen as a magnetic-field-induced circular birefringence, meaning that left and right circularly polarized waves propagate at slightly different speeds in the medium [364].

Essential devices in photonics technology such as light polarization rotators and non-reciprocal optical isolators are based on MOKE or Faraday rotation, and magneto-plasmonics is a promising route to bring these devices to the nanoscale [434]. Besides, magneto-optical SPR (MOSPR) sensors, which employ the MOKE signal as the sensing magnitude instead of the reflectivity, theoretically allow much higher sensitivity than the pure plasmonic equivalents for gas and biosensing detection [428, 429]. As discussed below, the MOKE signal is enhanced when the probe frequency is in resonance with the LSP modes, and the SPR is influenced by the refractive index of the surroundings (see sections 2.1 and 4.1), thus providing the sensing principle of the MOSPR sensors [435].

The physics of magneto-plasmonics can actually be divided into two parts. Concerning the magnetic response, MO activity is observed, because the optical constant of any material, that is a tridimensional tensor in the general case, becomes non-diagonal when an external magnetic field \( B \) is present. In the case of an isotropic material like Au, \( \varepsilon \) is [428]:

\[
\varepsilon(B) = \begin{pmatrix}
\varepsilon_x & k_i \Pi_x & k_i \Pi_y \\
-k_i \Pi_x & \varepsilon_x & -k_i \Pi_z \\
-k_i \Pi_y & -k_i \Pi_z & \varepsilon_x
\end{pmatrix}
\]

(54)

where \( k_i \Pi_i \) are the MO constants of the material and \( \Pi_i \) are the \( B \)-dependent components. In dia- and para-magnetic materials, \( \Pi_i \) are proportional to \( B \), while in ferro-magnetic materials \( \Pi_i \) are set by material magnetization and are orders of magnitude larger than those of dia- and para-magnetic materials, thus justifying the use of ferro-magnetic materials for magneto-plasmonics [428].

Like all noble metals, Au is dia-magnetic, and MO effects can be observed only for large enough applied \( B \). In particular, MO effects are possible when the SPR is excited by circularly polarized light in the presence of a static magnetic field parallel to the direction of light propagation [428, 436, 437]. The MO effect can be well described by considering a Drude model and the Lorentz force induced by the \( B \) field on the circular collective movement of conduction electrons under circularly polarized light illumination, that for the single electron is [436, 437]:

\[
\vec{F}_L = -e\vec{E}_0 - e\vec{v}_e \times \vec{B}
\]

(55)

with \( e \) the electron charge and \( v_e \), the electron speed. The effect is a collective circular charge motion more or less confined depending on the helicity of the circular plasmonic mode that corresponds to splitting, i.e. to a positive or negative shift of the SPR frequency, roughly proportional to \( B \) [436]:

![Figure 28](image-url)
where the sign depends on light helicity (figure 28(B)). The entity of this shift is of about 0.01 nm per applied Tesla, observable by ordinary magnetic circular dichroism (MCD) spectroscopy [436].

On the other hand, MO effects also benefit the plasmon resonance and the associated local-field enhancement. For instance, when linear p-polarized light is reflected from a sample, it is possible to express the MOKE performance by the complex Kerr rotation \( \Phi \) [428]:

\[
\Phi = \frac{r_{ps}}{r_{pp}}
\]

(57)

where \( r_{pp} \) and \( r_{ps} \) are the polarization conversion fraction of p- and s- polarized light, respectively. \( r_{pp} \) scales with the reflectivity of the material, meaning that at the SPR, where light absorption is maximum, the MOKE performance is larger. \( r_{ps} \) scales with the MO ability of the material, and can be expressed as [428]:

\[
r_{ps} \propto \langle E_p E_s \rangle k d
\]

(58)

where \( \langle E_p E_s \rangle \) is the mean value of the two components of the electric field, and \( d \) is the thickness of the material. The \( \langle E_p E_s \rangle \) term is greatly increased when the magnetic material is in proximity of a plasmonic structure and incident light is in resonance with its LSP modes.

Therefore, the excitation of an LSP increases the MOKE performance both by decreasing reflectivity and increasing the MO term [428].

There are several examples of surface plasmon resonance-enhanced magneto-optics (SuPREMO) in composite magnetic-plasmonic nanosystems [428, 429, 438]. Plasmon-enhanced Faraday rotation was observed in Au-coated maghemite (\( \gamma \)-Fe$_2$O$_3$) NPs and attributed to the near-field enhancement resulting from the spectral overlap of the SPR in the gold with the electronic transition in maghemite [438]. SPR enhancement of the MO activity was also observed in Au/Co/Au nanosandwiches, Au/CoPt/Au nanodisks, and colloidal Au–Fe$_3$O$_4$ NPs [428, 429]. Interestingly, the tunability of the SPR by acting on the Au NP structure is also exploitable for the spectral tunability of the MO effects.

An open point in magneto-plasmonics is the possibility of using the SPR to change the magnetic properties of NPs. For instance, it was observed that a reversible optically-induced variation of the magnetic moment was possible in Fe-doped Au NPs, opening interesting perspectives for the realization of photoswitchable nanomagnets that can be controlled and monitored by light [439]. One major problem of Au:Fe alloys is the presence of segregated domains of the two elements, with no ‘true’ alloying taking place [439]. Indeed, these studies require the coupling of magnetic and plasmonic elements at the atomic level and have been limited in the past by the lack of effective ways for the production of stable Au–X alloy NPs, where X is a magnetic element such as Fe, Co, or Ni, that have been developed only recently [136, 138]. Overall, due to the limited number of nanosystems with magnetic and plasmonic properties coexisting in the same phase, such as the recently developed Fe-doped plasmonic nanoalloys [136, 138, 139, 430], the realm of magneto-plasmonic effects still has to be fully investigated.

### 6.4. Nonlinear optical applications

Au NPs have highly polarizable electrons, which ensure a strong nonlinear optics (NLO) response, i.e. a large nonlinear susceptibility [13]. However, by definition, NLO depends on light intensity and requires high fields [364], which poses the problem of heating and NP degradation [251]. Besides, the nonlinear response of Au NPs cannot be predicted from the knowledge of the linear optical constant alone [440]. Therefore, several aspects related to plasmonic NLO (PNLO) are still under debate.

There are two types of PNLO:

(i) PNLO effects originated from the Au NPs, i.e. depending on the electric field inside the NPs;

(ii) PNLO effects originated by nearby structures, i.e. depending on local-field enhancement at electromagnetic hot spots. To date, these are less frequent and mostly concern the effects mentioned in section 5.

#### 6.4.1. Optical Kerr effect (OKE)

The OKE is a third-order phenomenon consisting in the light-intensity-dependent variation of the refractive index of a material. Au NPs have large third-order susceptibility (\( \chi^{(3)} \)), especially at frequencies close to the SPR. When embedded in dielectric matrices, Au NPs are of interest in all ultrafast optical switching devices based on OKE [441, 442]. The magnitude of the nonlinear response varies with size and shape as well as volume fraction of metal nanoclusters in the dielectric matrix [441, 442]. Three mechanisms contribute to \( \chi^{(3)} \) [443]: (i) a fast mechanism (~500 fs) due to electron–electron scattering after SPR excitation, leading to electron thermalization, (ii) a contribution from IB transition, which occurs on the same time scale as the former and (iii) a hot electron mechanism on a time scale of picoseconds or longer. Only the first two mechanisms are fast enough for optical switching applications.

#### 6.4.2. Multiple harmonic generation (MHG)

In MHG, two, three, or more photons with the same frequency are simultaneously annihilated by exciting the material to a virtual electronic state, from which it decays generating a single photon with a frequency sum of the incoming ones, resulting in second, third, or higher harmonic generation. Au NPs exhibit significant MHG conversion efficiencies [444], with best performances achieved for excitation or emission wavelength resonant with particle SPR [440]. In fact, Miller’s rule predicts that the nonlinear conversion is maximum when the linear optical properties exhibit resonances either at the fundamental or harmonic frequencies [364]. As for the linear plasmonic response, MHG in Au NPs can also be qualitatively described by the anharmonic oscillator model [440].

Several advances were recently reported about the engineering of Au NPs for MHG. For instance, SHG is a second-order process occurring in objects without an inversion centre,
Figure 29. (A) Simplified Jablonski diagram for SHG (a), sketch of an Au nanostructure satisfying the requirements described in the text for optimal SHG (b), and (c) calculated scattering spectra of the coupled V-shaped antenna (grey line) and of the coupled antenna (open black circles). Blue and red lines represent the scattering spectra of the coupled antenna when illuminated with light polarization parallel and orthogonal to the long axis of the NR, respectively, showing overlap with the fundamental (red stripe) and the SH (blue stripe) lines. Reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnology [445], copyright (2015). (B) The principle of linear and nonlinear plasmonic sensing based on a refractive index difference and orthogonal to the long axis of the NR, respectively, showing overlap with the fundamental (red stripe) and the SH (blue stripe) lines. Reprinted by permission from Macmillan Publishers Ltd: Nature Nanotechnology [445], copyright (2015). (C) In 2PPL, the first photon (1) induces an sp–sp intraband transition, and the second photon (2) induces a d–sp IB transition to the empty state generated in the conduction band, then the e–h couple relaxes radiatively. (D) Au NPs are recognized for their excellent ability to limit the intensity of transmitted light when a critical threshold is exceeded. (E) Au NP fragmentation, which occurs during OL, can be avoided by a self-repair mechanism in the presence of phthalocyanine (PCs): the PCs promote the assembly of photofragmented Au NPs into larger aggregates, which are photomelted to reform bigger Au NPs ready to efficiently limit light again. Reprinted with permission from [14, 457]. Copyright The Royal Society of Chemistry and (2012) American Chemical Society. (C) (D)
possible method for measuring nanoscale distances with high spectral accuracy and signal-to-noise ratio [450].

Although SHG is not allowed in isotropic dispersions of non-centrosymmetric particles, a weak frequency doubling phenomenon is still possible, called hyper Rayleigh scattering [451]. This is a nonlinear second-order light scattering phenomenon. Compared to 2PPL, the 4PPL is favoured with ultrashort pulse duration [454]. Independent of the mechanism, two- and four-photon PL processes are more efficient than three- and five-photon processes [454]. Two-photon PL (2PPL) in gold is the result of two sequential single-photon absorption steps mediated by a real state, where the first photon excites an electron via an intraband transition within the sp conduction band, while the second photon excites an electron from the d band to recombine with an sp hole in the conduction band (figure 29(C)) [454]. In 4PPL, the first step is a three-photon sp $\rightarrow$ sp direct IB transition followed by a single-photon transition. Compared to 2PPL, the 4PPL is favoured with ultrashort (<100 fs) laser pulses, providing a way to switch between the two mechanisms by acting on pulse duration [454].

Although 2PPL is a third-order effect, associated with two-photon absorption, whereas SHG is a second-order nonlinear optical effect, both depend on the second power of laser intensity, making the discrimination of the two contributions non-trivial [125, 455].

6.4.4. Optical limiting (OL). In OL materials, their transmittance decreases rapidly when incident light exceeds a threshold fluence, due to the increased light absorption and/or scattering (figure 29(D)) [364]. Au NPs are excellent optical limiters due to free-carrier multiphoton absorption and nonlinear scattering [456–458]. Independent of the mechanism, all the investigations on OL properties of Au NPs pointed out the following aspects [456–458]: (i) the OL performances are amongst the best ever measured; (ii) big NPs are better optical limiters than small ones; (iii) NPs lose limiting efficiency after a few laser pulses due to their fragmentation, which is more rapid and has a lower threshold when particle size is big; (iv) NPs have appreciable OL performance only at frequencies close to the SPR or IB transitions. In several cases, the OL properties were enhanced by blending Au NPs with organic molecules [457]. An extremely long durability under laser irradiation was observed in the case of Au NPs blended with zinc phthalocyanines (PCs). The origin of the enhanced OL performance resides in the ability of the Au NPs to self-heal during the laser pulse irradiation by interaction with the PCs (figure 29(E)), via a mechanism mediated by SPR absorption and photo-induced melting of NP aggregates [457]. The Au NPs/PCs blend represents the first reported example of a functional nanomaterial that self-heals during use [14, 457].

7. Conclusions

Exploited for centuries for their intense colouration, in the last two decades Au NPs have been the subject of a growing number of scientific investigations related to their SPR properties. Plasmon physics is rich and intriguing, and LSPs of Au NPs enter into countless applications. Although the ‘traditional’ research about optical sensing, SERS, and photothermal phenomena are the lion’s share of the literature, new fields are rapidly emerging, such as NLOs, optical trapping, chiroptical effects, magneto-plasmonics, and plasmon-enhanced catalysis. At the same time, the control over the SPR of Au NPs is no longer restricted to shape, size, assembly, and surface chemistry, but is now expanding towards new frontiers such as alloying. With the continuous progress in modelling and the understanding of plasmon physics, and the parallel advancement in the realization of Au NPs with precisely controlled structure and composition, in the near future one can easily expect a further increase in the number of technological and scientific applications.

Acknowledgments

R Saïja is gratefully acknowledged for useful discussions. VA acknowledges financial support from the University of Padova (PRAT no. CPDA114097/11 and Progetto Strategico STPD11RYPT_001). RP thanks the Italian Ministero dell’Università e della Ricerca (MIUR) for financial support through the PRIN project Prot. 2012T9XHH7. This work was performed in the context of the European COST Action MP1302 Nanospectroscopy.

Certain images in this publication have been obtained by the author(s) from the Wikipedia/Wikimedia website, where they were made available under a Creative Commons licence or stated to be in the public domain. Please see individual figure captions in this publication for details. To the extent that the law allows, IOP Publishing disclaims any liability that any person may suffer as a result of accessing, using, or forwarding the image(s). Any reuse rights should be checked and permission should be sought if necessary from Wikipedia/Wikimedia and/or the copyright owner (as appropriate) before using or forwarding the image(s).

References