Plasmonic Purcell factor and coupling efficiency to surface plasmons. Implications for addressing and controlling optical nanosources

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Abstract
The Purcell factor $F_p$ is a key quantity in cavity quantum electrodynamics (cQED) that quantifies the coupling rate between a dipolar emitter and a cavity mode. Its simple form $F_p \propto Q/V$ unravels the possible strategies to enhance and control light–matter interaction. Practically, efficient light–matter interaction is achieved thanks to either (i) high quality factor $Q$ at the basis of cQED or (ii) low modal volume $V$ at the basis of nanophotonics and plasmonics. In the last decade, strong efforts have been done to derive a plasmonic Purcell factor in order to transpose cQED concepts to the nanoscale, in a scale-law approach. In this work, we discuss the plasmonic Purcell factor for both delocalized (SPP) and localized (LSP) surface-plasmon-polaritons and briefly summarize the expected applications for nanophotonics. On the basis of the SPP resonance shape (Lorentzian or Fano profile), we derive closed form expression for the coupling rate to delocalized plasmons. The quality factor factor and modal confinement of both SPP and LSP are quantified, demonstrating their strongly subwavelength behavior.

Keywords: Purcell factor, surface plasmon, localized plasmon, lossy cQED

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

1. Introduction
Nanophotonics permits light–matter interaction at the nanoscale, down to the single photon/single atom level. The motivations are notably sensitive sensing with applications such as nano-optical imaging (surface analysis), environmental health (air pollutants, infectious agents detection), security (explosive detection) or healthcare (cancer early diagnosis, theranostics) and the miniaturization of photonics components for on chip integrated ultrafast devices. The optical cross-section is a simple way to characterize the efficiency of light–matter interaction. For a molecule, it is typically $\sigma \approx 10^{-20} \text{m}^2$, that has to be compared to the focus area of a diffraction limited beam, of the order of $(\lambda/2)^2 \approx 10^{-13} \text{m}^2$ in the visible domain. This unsuitability between the light confinement and the active size of the molecule points out the difficulty of so-called nanoscopy [1]. In the last decades, several strategies have been proposed to increase the efficiency of light–matter interaction. (i) Increasing the absorption cross-section by working at low temperature; indeed, in the limit of very low temperature ($T < 10 \text{ K}$), the molecular absorption cross-section increases up to the diffraction limit $\sigma_0 = 3\lambda^2/2\pi$ revealing that the molecule absorbs almost all the incoming light of a focused beam [2, 3]. (ii) Increasing the duration of the interaction by placing the molecule inside an optical microcavity presenting...
a high quality factor $Q$ [4]. (iii) Confining the excitation beam below the diffraction limit thanks to near-field optics [5–9] or plasmonics [10, 11].

Quantitatively, the efficiency of light–matter interaction can be inferred from the so-called cooperativity parameter $C$. The meaning of this parameter is easily understood from a classical point of view [12, 13]. In free-space, the cooperativity can be expressed as the ratio between the resonant atomic cross-section $\sigma_0$ and the effective area $A_{\text{eff}} = \pi w_0^2$ of a gaussian beam with a beam waist $w_0$; $C_0 \approx \sigma_0/A_{\text{eff}}$. Therefore, the cooperativity quantifies the suitability between the focused spot and the molecule active area. In an optical Fabry–Perot cavity, it increases to $C = 4C_0 F/\pi$ where $F$ is the finesse of the cavity. The cavity enhances the free-space cooperativity by the number of wave round trips $F/\pi$ inside the cavity and an additional factor of four accounting for the intensity enhancement at a mode antinode. In cavity quantum electrodynamics (cQED), the cooperativity writes for a single atom

$$C = \frac{g^2}{2\kappa_{\text{cav}}n_1\Gamma_0},$$

where $g$ is the coupling rate between the atom and the cavity mode. $\kappa_{\text{cav}}$ and $\Gamma_0$ refers to the cavity losses rate and the atom decay rate in vacuum, respectively ($n_1\Gamma_0$ is the decay rate in the homogeneous medium of optical index $n_1$). The strong coupling regime, $g \gg \kappa_{\text{cav}}$, $\Gamma_0$ ($C \gg 1$) leads to a reversible energy exchange between the cavity and the atom. In the weak coupling regime, the cavity opens a new channel for the atom (irreversible) relaxation with a decay rate $\Gamma = (1 + 2C)\Gamma_0$. The Purcell factor quantifies the effect of the cavity on the atom decay rate and writes

$$F_p = \frac{\Gamma_{\text{cav}}}{n_1\Gamma_0} = 2C$$

with $\Gamma_{\text{cav}} = \Gamma - n_1\Gamma_0$ the modification of the decay rate due to the optical microcavity. It also expresses [14]

$$F_p = \frac{\Gamma_{\text{cav}}}{n_1\Gamma_0} = \frac{3}{4\pi^2} \left( \frac{\lambda_{\text{em}}}{n_1} \right)^3 \frac{Q}{V_{\text{eff}}},$$

where $Q$ is the quality factor of the cavity and $V_{\text{eff}}$ the effective volume of the cavity mode involved in the coupling. $\lambda_{\text{em}}$ is the emission wavelength of the atom. This expression is equivalent to the classical description with the finesse for a Fabry–Perot cavity.

Remarkably, the Purcell factor expression (3) points out that spontaneous emission can be efficiently controlled in an optical cavity presenting a high quality factor and/or a strongly confined mode. However, high $Q$ cavities are obtained at the price of low modal (diffraction limited) confinement [4]. In this context, molecular plasmonics proposes a new strategy for light–matter interaction [15, 17, 16]. The strong confinement of surface plasmon polaritons insures efficient coupling at a deeply subwavelength scale whereas cQED increases the duration of interaction. At this point, we have to mention that the $Q$ factor entering the Purcell factor is the lower of the cavity factor and the atomic resonance. Actually, $1/Q = 1/Q_{\text{at}} + 1/Q_{\text{cav}}$ where $Q_{\text{at}}$ and $Q_{\text{cav}}$ are the quality factor of the atom emission spectrum and cavity, respectively [18]. That is why cQED generally works at low temperature where atomic resonance is sufficiently narrow so that cavity modifies the spontaneous emission ($Q_a \gg Q_{\text{cav}}$ and $Q \approx Q_{\text{cav}}$). On the contrary, a low $Q$ factor of plasmon resonance permits it to work at room temperature and allows one to envision high-speed optical devices [19, 20]. This paves the way to ultrafast control at the nanoscale.

The Purcell factor describes the emitter–cavity coupling as a function of the optical cavity properties, independently of the emitter properties. Particularly, the best coupling efficiency is achieved for a high $Q/V$ ratio, that occurs either for a narrow resonance, or a deeply confined mode. The Purcell factor is therefore a key parameter to transpose cQED concepts to quantum plasmonics [15, 21–28].

In this article, we first summarize the derivation of the Purcell factor in an optical microcavity with particular attention to the underlying hypothesis (section 2). In section 3, we briefly discuss some expected applications of efficient emitter-SPP coupling. Then we study the concepts of plasmonic Purcell factor. Since the mode confinement is the crucial parameter for achieving a high Purcell factor near a plasmonic nanostructures, we follow the progress of extended metal film (section 4) and plasmonic waveguide (section 5) supporting delocalized surface plasmon polaritons (SPP) towards nanoparticles sustaining localized surface plasmons (LSP, section 6).

2. Purcell factor

2.1. Purcell factor in an optical microcavity: generalities

The spontaneous emission at the angular frequency $\omega_{\text{em}} = 2\pi c/\lambda_{\text{em}}$ from the excited state $|b\rangle$ to the ground state $|a\rangle$ of an excited atom presents a decay rate that follows Fermi’s golden rule

$$\Gamma(r) = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}_s} (\langle a, \mathbf{k}_s | H | b, 0 \rangle)^2 \delta (\omega_{\text{em}} - \omega_{kn})$$

$H_I = \mathbf{p} \cdot \mathbf{E}(r)$ is the interaction hamitonian describing the coupling of an atom to an electromagnetic field within the dipolar approximation, taken at the position $r$ of the atom. The operators $\mathbf{p}$ and $\mathbf{E}$ refer to the atomic transition dipole moment and the electric field, respectively. In the following, we are interested in the effect of the cavity on the spontaneous emission rate. Therefore, we separate the decay rate into the free-space contribution (in an homogeneous medium of optical index $n_1$) and the cavity contribution

$$n_1\Gamma_0 = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}_s} (\langle a, \mathbf{k}_s | H | b, 0 \rangle)^2 \delta (\omega_{\text{em}} - \omega_{kn}),$$

$$= n_1 \frac{\hbar^2 \omega_{\text{em}}^3}{3\pi\epsilon_0 hc^3}, \text{ and}$$

$$\Gamma_{\text{cav}} = \frac{2\pi}{\hbar^2} \sum_{\mathbf{k}_s} (\langle a, \mathbf{k}_s | H_{\text{cav}} | e, 0 \rangle)^2 \delta (\omega_{\text{em}} - \omega_{kn}).$$
In addition, we assume a single-mode cavity, resonant at $\omega_c$, therefore
\[ \Gamma_{\text{cav}} = \frac{2\pi}{\hbar^2} |\langle a, 1|H_{\text{cav}}|b, 0 \rangle|^2 \delta(\omega_{\text{em}} - \omega_c) \] (8)
$I$ indicates a photon into the cavity mode. The coupling rate $\gamma$ between the atom and the cavity mode (see equation (1)) obeys $\gamma = |\langle a, 1|H_{\text{cav}}|b, 0 \rangle|$. The electric-field operator associated to the single-mode cavity writes [12, 29]
\[ \hat{E}_{\text{cav}}(r) = i \frac{\hbar \omega_c}{2\varepsilon_0 \varepsilon_1 V} \hat{f}(r) \hat{a} + \text{h.c.}, \] (9)
where $V$ is the quantization volume, $\hat{a}$ the boson operator and $\hat{f}(r)$ describes the spatial variations of the mode into the cavity $[|f(r)| = 0 \text{ at a node and } |f(r)| = 1 \text{ at an antinode}]$. To achieve this expression, the classical electric field is expressed
\[ E_{\text{cav}}(r, t) = i \frac{\hbar \omega_c}{2\varepsilon_0 \varepsilon_1 V} f(r) e^{-i\omega_{\text{cav}} t} + \text{c.c.} \] (10)
and is normalized with respect to the energy
\[ \hbar \omega_c = \frac{1}{2} \int [\varepsilon_0 \varepsilon(r) E^2(r, t) + \mu_0 H^2(r, t)] \text{d}r, \] (11)
\[ \frac{\hbar \omega_c}{\varepsilon_1 V} \int \varepsilon(r) |f(r)|^2 \text{d}r, \] (12)
where we assumed a non-dispersive medium. Finally, the mode obeys
\[ V = \frac{1}{\varepsilon_1} \int \varepsilon(r) |f(r)|^2 \text{d}r. \] (13)

Spectral shape of the resonance. In the case of a lossy cavity, the dirac distribution in (8) is replaced by the density of modes per unit angular frequency $N(\omega)$ (unit: s·rad$^{-1}$). Moreover, the profile of the mode resonance is assumed to be Lorentzian
\[ \delta(\omega - \omega_c) \rightarrow N(\omega) = \frac{1}{\pi} \frac{\kappa_{\text{cav}}^2 / 2}{(\omega - \omega_c)^2 + \kappa_{\text{cav}}^2 / 4}. \] (14)
Defining the resonance quality factor $Q = \omega_c / \kappa_{\text{cav}}$, we can rewrite
\[ N(\omega) = \frac{Q}{\pi \omega_c} \frac{1}{1 + 4Q^2 \left(\frac{\omega - \omega_c}{\omega_c}\right)^2}. \] (15)

Spatial profile. Inserting the electric field operator (equation (9)) into the interaction hamiltonian, we achieve
\[ |\langle g, 1|H_{\text{cav}}|e, 0 \rangle|^2 = \frac{\hbar^2 \omega_c}{2\varepsilon_0 \varepsilon_1 V} |\mathbf{u} \cdot \mathbf{f}(r)|^2 \] (16)
where we introduced the dipole moment orientation $\mathbf{u}$ (i.e. $p = pu$).

Purcell factor Finally, using equations (15) and (16) the cavity contribution to the decay rate (equation (8)) simplifies to
\[ \Gamma_{\text{cav}} = \frac{2\pi^2}{\hbar \omega_c} |\mathbf{u} \cdot \mathbf{f}(r)|^2 \frac{Q}{V} \frac{1}{1 + 4Q^2 \left(\frac{\omega_{\text{em}} - \omega_c}{\omega_c}\right)^2}, \] (17)
so that the normalized decay rate writes (using equation (6)) and $\lambda_{\text{em}} = 2\pi c / \omega_{\text{em}}$
\[ \frac{\Gamma_{\text{cav}}}{\tau_{\text{cav}}} = \frac{3}{4\pi^2} \left(\frac{\lambda_{\text{em}}}{n_1}\right)^3 \frac{Q}{1 + 4Q^2 \left(\frac{\omega_{\text{em}} - \omega_c}{\omega_c}\right)^2}, \] (18)

2.1.1. Summarize. The cavity contribution to the decay rate obeys
\[ \frac{\Gamma_{\text{cav}}}{\tau_{\text{cav}}} = F_p \frac{|\mathbf{u} \cdot \mathbf{f}(r)|^2}{1 + 4Q^2 \left(\frac{\omega_{\text{em}} - \omega_c}{\omega_c}\right)^2}, \] (19)
where $F_p$ is the so-called Purcell factor, $\mathbf{f}(r)$ reveals the position dependency (from cancellation at a node to maximum effect at an antinode) and the denominator factor $[1 + 4Q^2 (\omega_{\text{em}} / \omega_c - 1)^2]$ shows the effect of the detuning between the emission frequency and the cavity resonance. Finally, the emitter couples to modes presenting a polarization along the dipole moment [quantified by the term $|\mathbf{u} \cdot \mathbf{f}(r)|$].

In the following, we are interested in defining the Purcell factor for a dipolar emitter coupled to a plasmonic nanostructure. It is therefore useful to recall the hypothesis done to demonstrate the Purcell factor expression (3):

- the Purcell factor is associated to a given mode of the cavity
- the cavity resonance follows a Lorentzian shape
- the mode volume can be estimated from expression (13), assuming a non-dispersive medium. It equivalently writes
\[ V = \frac{\int \varepsilon(r) |\mathbf{E}(r)|^2 \text{d}r}{\text{Max} |\varepsilon| |\mathbf{E}(r)|^2}, \] (20)
where $\mathbf{E}(r)$ is the electric field associated to the cavity mode $[\mathbf{f}(r) = \mathbf{E}(r)/\text{Max}|\mathbf{E}(r)|]$ describes the mode profile.

2.1.2. Purcell factor near a nanofiber. The full control of spontaneous emission in 3D optical cavities are a technological challenge and is bandwidth limited, so simpler configurations have been proposed. In particular, fluorescence emission into photonic nanowires can be enhanced over a large spectrum range; this has been widely studied over the last decade [30, 31]. To derive the Purcell factor near a waveguide, we define an arbitrary quantization length $L$. The electric-field operator and the density of mode
write, respectively \[32\]

\[\mathbf{E}(r) = \frac{i}{\hbar c \sqrt{2\varepsilon_0\varepsilon_f}} \mathbf{f}(r) \hat{a} + \text{h.c., with} \]

\[A_{\text{eff}} = \int \frac{\varepsilon(x, z) \left| \mathbf{E}(r_c) \right|^2 \text{d}x \text{d}z}{\text{Max} \left[ \varepsilon \left| \mathbf{E}(x, z) \right|^2 \right]}, \]

\[N(\omega) = \frac{L}{\pi v_g}, \quad \text{with} \quad v_g = \frac{d\omega}{dk_g} \]

\[A_{\text{eff}} \text{ defines the mode effective area and } v_g \text{ is the group velocity of the guided mode. We then proceed as previously and the Purcell factor for the guided mode simplifies to} \]

\[F_p = \frac{\Gamma_{\text{guided}}}{n_1 \Gamma_0} = \frac{3}{4} \frac{\left( \lambda_{\text{em}}/n_1 \right)^2 n_g}{\pi \lambda_{\text{em}}}, \]

\[L_{\text{eff}} = \frac{\int \varepsilon(z) \left| \mathbf{E}(z) \right|^2 \text{d}z}{\text{Max} \left[ \varepsilon \left| \mathbf{E}(z) \right|^2 \right]} \]

where \(L_{\text{eff}}\) is the mode effective length and characterizes its confinement.

2.1.3. Purcell factor in a Fabry–Pérot cavity. We finally consider the one-dimensional (1D) planar waveguide. The density of guided modes obeys \(N^{1D} = \omega^2/2\pi n_\text{eff} n_g\) where \(n_\text{eff}\) refers to the mode effective index. The Purcell factor becomes

\[F_p = \frac{\Gamma_{\text{guided}}}{n_1 \Gamma_0} = \frac{3}{4} \frac{\left( \lambda_{\text{em}}/n_1 \right)^2 n_\text{eff} n_g}{\pi \lambda_{\text{em}}}, \]

\[L_{\text{eff}} = \frac{\int \varepsilon(z) \left| \mathbf{E}(z) \right|^2 \text{d}z}{\text{Max} \left[ \varepsilon \left| \mathbf{E}(z) \right|^2 \right]} \]

so that equations (4) and (28) are fully equivalent in a non-absorbing medium. The P-LDOS also writes from cQED considerations

\[\rho_\text{g}(r, \omega_{\text{em}}) = \frac{k_\text{d}}{\pi \omega} \text{Im}[G_{uu}(r, r, \omega_{\text{em}})] \]

2.2. Decay rate near lossy and dispersive materials

In presence of a lossy and dispersive medium, the modification of the decay rate can be described either within classical Lorentz model of an oscillating dipole \[36-38\] or within the full quantum description \[39\]. In both cases, this leads to the following expression for the rate modification

\[\frac{\Gamma(r)}{n_1 \Gamma_0} = \frac{6\pi}{n_1 \kappa_0} \text{Im}[G_{uu}(r, r, \omega_{\text{em}})], \]

where \(G\) is the Green’s tensor associated to the emitter surroundings and \(G_{uu}\) refers to its diagonal components along the dipolar direction \(u\). This expression quantifies the modification of the decay rate in a complex surroundings and will be our starting point to determine the effect of plasmonic nanostructures on the fluorescence decay rate. The expression (28) is a generalization of the Fermi’s golden rule to dispersive and lossy surroundings. Indeed, the Fermi’s golden rule (4) can be recast in the form

\[\Gamma(r) = 2\pi \omega^2 (r, \omega_{\text{em}}) N(\omega_{\text{em}}), \]

\[\rho_\text{g}(r, \omega_{\text{em}}) = \left| \langle a, 1 \vert H_{\text{cav}} \vert b, 0 \rangle \right|, \]

\[= \frac{\hbar c \varepsilon_0}{\sqrt{2\varepsilon_0\varepsilon_f}} \mathbf{p} \cdot \mathbf{f}(r), \]

where we introduced the coupling strength \(g\) and density of modes \(N(\omega)\), as discussed above. It is well-known from scattering formalism that the partial local density of states (P-LDOS) is related to the Green’s dyad (unit: s m\(^3\)) \[38, 40\]

\[\rho_\text{g}(r, \omega_{\text{em}}) = \frac{k_\text{d}}{\pi \omega} \text{Im}[G_{uu}(r, r, \omega_{\text{em}})] \]

3. Plasmonic addressing and control of optical nanosources

Before discussing the plasmonic Purcell factor, it is worthwhile to briefly introduce some expected applications of coupled emitter-SPP configurations. Here, we indicate the main applications and refer the reader to the literature for more complete descriptions.

3.1. Surface enhanced spectroscopies

Surface enhanced Raman spectroscopy (SERS) is probably among the first application of molecular material coupled to plasmonics nanostructures \[41\] and is now available at the single molecule level \[42\] so that ultrasensitive chemicals or...
biosensors are expected [43]. In the context of Purcell factor, we would like to mention that the SERS efficiency follows a $\propto Q^2/V$ law with the LSP properties [44].

Following SERS, metal enhanced fluorescence leads to enhancement factors of the order of tens [45–50] with possible applications to nanotheranostics [51, 52]. The fluorescence increase results from excitation field enhancement and emission rate modification (Purcell effect). However, due to the non-radiative energy transfer to metal nanostructures, it is crucial to distinguish the radiative from non-radiative rates. At the end, the critical parameter is the quantum yield of the emitter so that stimulated emission of plasmon occurs. The efficiency of the stimulated emission strongly depends on the Purcell factor up to 1000 keeping a reasonable enhancement (Purcell effect). Remarkably, coupling an emitter to a plasmonic nanostructure opens the way to the control of the photophysical processes [57], notably blinking effect [58–60] and photobleaching [61], but also to modify the ratio between magnetic and electric allowed dipolar transitions [62, 63].

3.2. Nano-optical antennas

Since a plasmonic nanostructure efficiently interfaces a single molecule to far-field radiation [64–67] the concept of optical nano-antenna has emerged a decade [68–70]. Optical nano-antennas rely on plasmonics nanostructures to efficiently redirect the fluorescence emission and cQED-like description gives an insight of the coupling mechanism [15, 71]. Recently, a Purcell factor up to 1000 keeping a reasonable quantum yield and with a collection efficiency of 84% was demonstrated [72]. Moreover, optical nano-antenna could efficiently interface molecular fluorescent emission and a nanophotonic waveguide [73] with possible applications to realize a platform for quantum optics. In addition, coupling a single photon source to an optical nano-antenna permits control of its emission cadency [74–83]. Realization of indistinguishable single photons is also a major issue [84, 85].

3.3. SPP amplification and SPASER

Taking advantage of the analogy between optical microcavities and plasmonic nanostructures, the concepts of plasmon nanolaser and amplifier were proposed [86–88]. It consists of a gain medium in contact to a metal nanostructure so that stimulated emission of plasmon occurs. The efficiency of the stimulated emission strongly depends on the Purcell factor [89–92].

3.4. Dipole–dipole coupling

Finally, since an emitter can be efficiently coupled to a surface plasmon, it has been proposed to use plasmon to couple two emitters for applications such as long range resonant energy transfer (above 10 nm) [93–97] or qubits entanglement [98, 99].

In the following, we discuss the plasmonic Purcell factor for typical configurations. We first consider the well-known case of extended metal film that is the simplest case of delocalized SPP enabling to clearly identify the coupling mechanisms [100, 101].

![Figure 1. Decay rate as a function of the distance to a gold or PEC surface. (a) Dipole moment parallel to the surface. (b) Dipole moment perpendicular to the surface. The emission wavelength is $\lambda_{em} = 670$ nm. The gold permittivity is taken from tabulated data [102].](image)

4. Quantum emitter decay rate near a metal mirror

4.1. Thick mirror

Figure 1 presents the dipolar total decay rate as a function of the distance to a gold surface [103]. The perfect mirror (PEC) case is also shown for comparison [104]. Far from the surface, we observe a typical interference pattern since the driving reflected field has to be in phase with the dipolar oscillation to enhance the emission rate. When the emitter touches the surface, the decay rate presents a finite value for the perfect mirror. It fully cancels for a dipole parallel to the surface (figure 1(a)) whereas it doubles for a perpendicular dipole (figure 1(b)), in agreement with the image dipole induced into the conductor. In case of real metal, the behavior is rather different close to the surface due to the apparition of new decay channels such as excitation of SPP and non-radiative energy transfer to the metal film [100, 101].
The emission wavelength is \( \lambda_{\text{em}} = 670 \text{ nm} \). Direct (free-space) dipolar emission is not included in \( P(k_i) \).

### 4.1.1. Relaxation channels

The various contributions to the total decay rate are easily determined from the Sommerfeld expansion of the dipolar emission, represented in figure 2 [101, 103]. Indeed, since the metal/air interface is invariant along \( r_1 = (x, y) \), it is possible to expand the Green’s dyad over the wavenumber \( k_{\parallel} \) so that the total decay rate (equation (28)) obeys (see also appendix A.1)

\[
\Gamma_{\parallel}(d) = \int_0^{\infty} P(k_i)dk_i, \quad \text{with} \quad P(k_i) = \frac{P(k_i)}{m P_0},
\]

\[
\Gamma_{\parallel}(d) = \frac{\pi}{n_i n_0} \frac{\lambda_{\text{em}}^3}{2 L_{\text{SPP}}} P(k_{0})^2 \Leftrightarrow \Gamma_{\parallel}(d) = \frac{\pi}{n_i n_0} \frac{\lambda_{\text{em}}^3}{2 L_{\text{SPP}}} \text{Purcell factor},
\]

where \( u = ||, \perp \) represents the orientation of the emitter and \( d \) is the distance to the metal surface. \( P_0 = \omega_{\text{em}}^4 |p|^2 / 12 \pi \epsilon_0 c^3 \) is the power radiated by the oscillating dipole in vacuum. \( P(k_i) \) is the dipolar emission power spectrum (in the \( k_{\parallel} \)-space) and represents the dipolar emission at a surface wavevector \( k_{\parallel} \). \( P(k_i) \) is \( P(k_i) \), normalized with respect to \( P_0 \) (unit of \( P :- \)) meter).

It is useful to distinguish the radiative waves for which \( k_{\parallel} < n_i k_0 \) that contributes to the radiative rate \( \Gamma_{\parallel}\) and the evanescent waves \( k_{\parallel} > n_i k_0 \). Evanescent waves corresponds to either SPP or lossy waves (LSW) [100, 101]. Particular attention has to be paid to SPP contribution, shown in figure 2(b). It presents a Lorentzian profile that permits to derive a closed form expression for the Purcell factor as we will discuss in details later. Finally, the large wavevectors are associated to electron scattering losses. These so called lossy waves are responsible for fluorescence inhibition close to the metal surface. Let us mention that an additional non-radiative energy transfer, namely electron–hole pair creation in the metal, could also occur at very short separation distances \( d < 1 \text{ nm} \) but is not included in this model since it involves non-local description of the metal dielectric constant [100].

Eventually, we present in figure 3 the radiative, SPP and lossy waves contribution to the total decay rate. The radiative decay rate is the main channel for large separation distances whereas lossy waves dominate very close to the metal surface. The SPP contribution is practically negligible for a parallel dipole (figure 3(a)) since Au/air SPP is TM polarized (that is the electric field is perpendicular to the metal surface), hence low \( \beta_{\parallel} \) factor (figure 3(c)). At the opposite, we observe that a perpendicular dipole is efficiently coupled to a SPP (figure 3(b)). About 90% of the dipolar emission couples to the Au/air SPP for a separation distance of \( d = 200 \text{ nm} \), see figure 3(c). This high \( \beta_{\parallel} \) factor originates from a low radiative rate due to a destructive interference between the direct and reflected dipolar fields (figure 3(b)). At shorter distances where the SPP rate is higher, we achieve \( \beta_{\parallel} = 70\% \) for \( d = 40 \text{ nm} \), see figure 3(c).

At this point, a closed form expression of the plasmonic Purcell factor is achievable. Since the emitted power follows a Lorentzian profile near the SPP resonance, the integration over the SPP contribution leads to [105]

\[
\Gamma_{\parallel}(d) = \frac{\pi}{n_i n_0} \frac{\lambda_{\text{em}}^3}{2 L_{\text{SPP}}} P(k_{0})^2,
\]

This extends the Purcell factor definition to a (lossy) SPP. Care has to be taken when interpreting plasmonic Purcell factor, in particular the role of losses. We derive in appendix A.2 the SPP contribution assuming a lossless metal. It perfectly matches the SPP contribution calculated for a real lossy metal (see green dots in figure 3(b)). So the plasmonic Purcell factor does not depend on the propagation length [105, 106], although it explicitly appears in the denominator of expression (36). Mathematically, the integral of the Lorentzian resonance gives the number of supported modes and does not depend on ohmic losses [107]. This is finally not surprising since SPP rate defines the coupling efficiency to the propagating SPP, no matter of how energy is dissipated afterward.

As a consequence, the Purcell factor as well as the coupling efficiency to a SPP can be high, even in presence of strong losses. We plot in figure 4 the different contributions to the decay rate at \( \lambda_{\text{em}} = 525 \text{ nm} \). Due to strong losses in gold,
it is difficult to separate the SPP and LSW contributions to the total decay rate. This behavior is discussed in detail in appendix A.3. For simplicity, we estimate the SPP decay rate from the emitter power integrated over \( k_{||}/k_0 < 1.4 \). All decay channels present a behavior very similar to the \( \lambda_{em} = 670 \text{ nm} \) case (compare with figure 3). Although we expect strong losses in the metal due to interband transitions, we still observe \( \beta_{\perp} = 80\% \) for \( d = 100 \text{ nm} \), see figure 4(b). The SPP has an effective index \( n_{SPP} = 1.10 \) (effective wavelength \( \lambda_{SPP} = 477 \text{ nm} \)) but an extremely short propagation length \( L_{SPP} = 640 \text{ nm} \). Therefore, the SPP presents only a single spatial oscillation over its propagation length. This quasi-mode, although efficiently excited would not be of interest for the control of a dipolar emission.

So far, we only discussed the emission process of the dipolar emitter. Another quantity of interest is the collection

\[ \beta_{\perp} = \frac{n_{SPP}}{n_{tot}} \]

\[ \beta_{\parallel} \]

\[ \beta \]

\[ \lambda_{em} = 670 \text{ nm} \]

\[ \lambda_{SPP} = 477 \text{ nm} \]

\[ L_{SPP} = 640 \text{ nm} \]
efficiency. We plot in figure 5 the scattering rate $G_{scatt}$, defined as the dipolar power dissipated in the far-field zone. The difference with the radiative rate $G_{rad}$ is due to absorption in the metal but does not depend on the distance to the metal surface $[103]$ (see also appendix A.4). We observe in figure 5(b) that absorption becomes negligible above $\lambda > 650$ nm.

As the last quantity, we plot in figure 6 the collection efficiency $\eta = G_{scatt}(NA)/G_{rad}$ as a function of the detection numerical aperture (NA). $G_{scatt}(NA)$ refers to the power scattered in a given NA. A NA = 0.6 air objective collects 10% of the emitted signal so that strategies has to be developed to improve this efficiency such as surface plasmon coupled emission (SPCE) $[46]$ or grating decoupler $[108–110]$.

4.1.2. Quality factor and mode confinement. Micro-optical cavities are generally characterized by their mode confinement and quality factor. For comparison purposes, it is therefore convenient to estimate also SPP confinement and quality factor.

Firstly, the SPP quality factor is estimated from the resonance Lorentzian profile (figure 3(b)). At $\lambda_{em} = 670$ nm it comes $Q = k_{SPP}/\Delta k_{SPP} = n_{SPP}/2n_{SPP}^2 = 192$.

Secondly, we would like to characterize the mode confinement. For this purpose, we identify the SPP rate $G_{SPP}$ to the Purcell factor (equation (25)). Remembering the hypothesis done to achieve the Purcell factor expression, we calculate $G_{SPP}$ at the gold/air interface where the SPP field amplitude is the highest and sum the contributions for dipoles along the three directions (so that $|u \cdot l| = 1$). Indeed, the decay rate obeys then

$$\frac{\Gamma_{SPP}}{n_1 I_0} + \frac{\Gamma_{SPP}}{n_1 I_0} \frac{\Gamma_{SPP}}{n_1 I_0} = F_p,$$

$$\equiv \frac{3 (\lambda_{em}/n_1) n_{eff}n_g}{4 L_{eff}}.$$

We estimate the SPP effective and group indices $n_{eff} = 1.036$ and $n_g = 1.16$, respectively, from the dispersion relation. From identification to the Purcell factor (equation (38)), we can attribute the effective length $L_{eff} = 203$ nm $\approx 0.6(\lambda_{SPP}/2)$ to the gold/air SPP (Purcell factor of $F_p = 2.9$).

This effective length is similar to the SPP penetration depth in air $\delta/2 = \lambda/2k_0 \sqrt{n_{SPP}^2 - 1} = 196$ nm. Indeed, neglecting the mode extension in gold, its effective length can be estimated as (assuming the validity of this expression in presence of the absorbing and dispersive gold mirror)

$$L_{eff} = \frac{\int |E(z)|^2 dz}{Max[|E(z)|^2]} = \int_0^\infty e^{-z^2/\delta}dz = \frac{\delta}{2}$$

and $\delta$ is a good parameter to estimate the SPP confinement.

For $\lambda_{em} = 525$ nm, we achieve $Q = 8$ and $L_{eff} = 223$ nm $\approx (\lambda_{SPP}/2)$ (and $\delta/2 = 235$ nm). However,
plasmonic Purcell factor is meaningless in this spectral range as pointed out in the previous section.

4.2. Thin metal film

4.2.1. Relaxation channels. We now turn to the thin metal film case. We consider a 50 nm gold film deposited on a glass substrate, and an emission wavelength $\lambda_{em} = 670$ nm. The Au/air and Au/glass SPP modes couple and to form a leaky and a bound SPP. We determine their characteristics using the reflection pole method [111]. The leaky mode is confined at the gold/air interface and has an effective index $n_{eff} = 1.0375$ and a propagation length $L_{SPP1} = 8.8 \mu m$ ($n_{eff} = 6.07 \times 10^{-3}$). The bound SPP is confined at the gold/glass interface ($n_{SPP2} = 1.663$, $n_{eff2} = 1.45 \times 10^{-2}$ corresponding to $L_{SPP2} = 3.7 \mu m$).

Figure 7(a) presents the dipolar emitted power $P(k_\beta)$. We observe a similar behavior than above a gold mirror with three different contributions; the radiative waves ($k_\beta \leq n_1 k_0$), the two SPP contributions and the lossy waves for high wavenumbers $k_\beta$. Note that the leaky plasmon also contributes to the radiative waves via leakage into the glass substrate (so-called SPCPE) [112]. We again observe the strong increase of LSW for a dipole emitter close to the metal film. Finally, the two peaks near $k_\beta = 1.04 k_0$ and $k_\beta = 1.66 k_0$ reveal the SPP contributions. Their resonance profiles are shown in details on figures 7(b) and (c). These two modes result from the coupling of the (leaky) Au/air and (bound) Au/glass SPP of a single interface. Therefore their resonant behavior does not follow a Lorentzian profile anymore but rather a Fano profile [113, 114]. Fano profile expresses

$$P(k_\beta) = \frac{P(k_{SPP}) (x + q)^2 + b}{q^2 + 1 + x^2},$$

with

$$x = \frac{k_\beta}{k_0 - n_{SPP}}.$$

This expression is a generalization of the Fano formula to lossy materials according to [114]. $q$ is the ratio between the optical response of the mode of interest and the second mode and $b$ introduces an offset due to losses. The Fano fits perfectly match the two SPP resonances (figure 7(b)). The leaky mode presents a high $q$ parameter ($q = 50$) so that it closely follows a Lorentzian profile. However, the bound mode resonance cannot be fitted with a Lorentzian profile since it is coupled to a leaky mode that can be treated as a continuum, hence the Fano behavior [18]. The SPP contribution is therefore estimated from the integral of the Fano resonance. If we remove the continuum background contribution, we obtain (see appendix B)

$$\frac{\Gamma_{SPP}}{n_1 I_0} = \frac{p(k_{SPP}) q^2 + b - 1 \pi}{L_{SPP} q^2 + b - 2},$$

with

$$p(k_{SPP}) = \frac{P(k_{SPP})}{n_1 P_0}.$$

We plot in figures 8(a) and (b), the different contributions to the total decay rate for a dipolar emitter oriented parallel or perpendicular to the metal surface. The radiative rate refers to the power integrated over $0 \leq k_\beta \leq n_1 k_0$ (radiative waves in medium 1). Note that leakages of SPP1 into the substrate contribute to the scattering rate but not to the radiative rate. We discuss this point later. The contribution of surface plasmon to the decay rate remains small for a dipole parallel to the surface. Differently, for a perpendicular dipole, we observe strong excitation of the gold/glass SPP (figure 8(b)) whereas the gold/glass SPP2 contribution remains small due to poor overlap with the dipolar emission since the emitter is located in air. This is quantified by the coupling efficiency $\beta$ represented on figures 8(c) and (d). Up to $\beta = 93\%$ coupling efficiency is achieved for a vertical dipole $d = 200$ nm above the gold film. This high $\beta$ factor originates from the small radiative rate at this distance due to an interference effect between the direct emission and the reflected field. Note that the SPP rate is equal to the free-space rate at this distance ($\Gamma_{SPP}/n_1 I_0 \approx 1$). Therefore the power coupled into the SPP guide is the same as the power emitted in the whole space ($4\pi$ str) by an isolated radiator. Since the gold/air SPP is leaky into the substrate ($n_{SPP} < n_{sub}$), it is worthwhile to estimate leakage radiation that are of interest for e.g. leakage radiation microscopy [92, 115, 116] or surface enhanced fluorescence [45, 117]. In order to determine the leakage contribution, we first estimate the leakage and Ohmic losses of the gold/air SPP. Indeed, the
finite propagation length of the leaky plasmon originates from (i) intrinsic (Ohmic) losses with the rate per unit length \( \alpha_i \) and (ii) radiative losses into the substrate with the rate per unit length \( \alpha_{\text{leak}} \). The propagation length expresses

\[
L_{\text{SPP leakage}} = \frac{1}{\alpha_i + \alpha_{\text{leak}}}. \tag{43}
\]

The leakage rate is estimated by cancelling the ohmic losses \([\text{Im}(\varepsilon_{\text{Au}})\] put to zero\) to \( \alpha_{\text{leak}} = 6.1 \times 10^{-2} \text{ m}^{-1} \). Therefore SPP leakage contributes for

\[
\int_0^\infty \alpha_{\text{leak}} e^{-r_{\text{L}}/L_{\text{SPP}}} dr_{\text{L}} = \alpha_{\text{leak}} L_{\text{SPP}} = 53\% \text{ to the SPP rate.}
\]

Figure 9(a) presents the power emitted in the far field \( \Gamma_{\text{scatt}} \) as well as the radiative rate and SPP leakage \( \Gamma_{\text{leak}} = 53\% \Gamma_{\text{SPP}} \). We also estimate the absorption in the metal \( \Gamma_{\text{abs}} = \Gamma_{\text{rad}} + \Gamma_{\text{leak}} - \Gamma_{\text{scatt}} \). Only a small part of the radiative emission is absorbed in the metal and does not contribute to the far-field emission. This rate practically does not depend on the distance to the metal film as in the mirror case (see figure 5). Last, the collection efficiency into the substrate using an oil immersion objective (NA > \( \eta_{\text{SPP}} \)) is estimated as \( \beta_{\text{SPP}} = \Gamma_{\text{tot}} / \Gamma_{\text{leak}} \) and is shown in figure 9(b). It reaches 50% at 200 nm.

4.2.2. Quality factor and mode confinement. We proceed as previously (see section 4.1.2) to estimate the SPPs quality factor and effective length. We gather the values achieved for the leaky and bound SPPs in table 1. Although the leaky SPP is delocalized into the substrate, we can estimate an effective length according to the Purcell factor definition. It is again close to the penetration depth in air, indicating that the confinement entering the Purcell factor corresponds to the near-field behavior of the SPP mode. We will observe a similar behavior for localized surface plasmons (see section 6.2).

4.3. In-plane plasmonic cavity

SPP is a surface wave, intrinsically confined near the metal film. It can be further laterally confined by distributed Bragg reflectors, forming an in-plane plasmonic cavity as schemed in figure 10 [119–121]. Such an open in-plane plasmonic cavity would further increase the plasmonic Purcell factor, with the possibility to access the fluorescent emitter. This enables an external control or manipulation of the emitter position (optical trapping, AFM manipulation, ...) or emission properties (Stark effect using a STM tip, ...).

The two-dimensional dipolar emission can be numerically achieved using the 2D-Green’s dyad technique. It expresses [105, 122]

\[
\frac{\Gamma_\text{d}(x, z)}{n_1 F_0} = \frac{6}{n_1 k_0} \int_{0}^{+\infty} \text{Im} G_{uu}^{2D}(r_c, r_x, k_y) dk_y, \tag{44}
\]

Figure 8. Contributions to the total decay rate as a function of the distance to the 50 nm gold film for a dipole parallel (a) or perpendicular (b) to the surface. (c) and (d) Coupling efficiency to the leaky (c) and bound (d) SPP. The emission wavelength is \( \lambda_{\text{em}} = 670 \text{ nm} \).
The penetration depth calculated at the gold plane $Oxz = \frac{\gamma}{|k_y|}$, where $\gamma$ is the propagation constant, is invariant to the grating structure. Since the 2D-Green dyad $G_{kk'}$, we numerically compute, we can define the normalized dipolar emission power $P(k_y) = \frac{6}{n_f k_0} \text{Im} G_{kk'}(\mathbf{r}_{\text{em}}, \mathbf{r}_{\text{em}}, k_y)$ as a function of the propagation constant $k_y$. This makes a direct analogy between the dipolar emission in 1D and 2D geometries and all the above discussion near a flat metal film is easily extended to this configuration.

Figure 10 compares the behavior of a (2D) planar plasmonic cavity and a (1D) Fabry–Perot cavity. The 2D dipolar emission $P(k_y)$ and 1D dipolar emission $P(k_0)$ are calculated for a dipolar emitter parallel to the mirrors and located at the center of the cavity. The dipolar emission significantly increases for cavity size $L_{\text{cav}} = (2p + 1)\lambda_{\text{eff}}/2$ with $p$ an integer and $\lambda_{\text{eff}}$ the mode effective wavelength ($\lambda_{\text{SPP}}$ or $\lambda_{\text{em}}/n_1$ in the plasmonic and Fabry–Perot cavities, respectively). This corresponds to the emission into the even modes of the cavity that presents an antinode at the cavity center. We observe a cut-off for cavity size below $\lambda_{\text{eff}}/2$. The normalized decay rate, calculated as a function of the cavity size, presents very similar behavior for these two cavities. This demonstrates the strong analogy between the in-plane plasmonic cavity and the micro-optical cavity. However, some distinct features appear in the planar cavity. First, since SPP are polarized perpendicular to the metal film, we do not observe polarization degeneracy (TE/TM) in the planar cavity. We also note the permanent contribution of the planar SPP mode at $k_y/k_0 = n_{\text{SPP}} = 1.04$. The gold/glass SPP at $k_y/k_0 = 1.66$ contribution is very weak (not shown). Finally, a planar plasmonic cavity relies on the confinement of the SPP surface waves instead of confining a bulk mode for an optical micro-cavity. This additional mode confinement leads to a significant increase of the decay rate inside the cavity [121]. This is however at the price of strong losses.
As discussed above, SPP Purcell factor into extended metal film can be increased by an in-plane cavity that confines laterally the delocalized SPP. However, the lateral confinement is still limited to about $\lambda_{SPP}/2$. Stronger lateral mode confinement can be achieved in plasmonic waveguides. For instance, metal nanowires does not present a cut-off and the lateral mode confinement is not diffraction limited but given by the nanowire cross-section [123]. Therefore, we expect high coupling efficiency of a dipolar emitter to a metal nanowire [124–130]. Metal nanowires define 1D plasmonic waveguides with a great potential for integrated optical routing [131]. They can be chemically synthesized with high crystallinity hence supporting SPP with reduced losses [132–136]. SPP propagation can be controlled by a single emitter, leading to the concept of single photon transistor [137]. Reciprocally, two distant emitters can be interfaced via surface plasmons, with applications such as SPP mediated resonant energy transfer [94, 122], remote qubits entanglement [99, 138] or nano-optical logical gates [98]. SPP gain amplification has also been shown when dipolar emitters play the role of gain medium [139–141].

On the basis of expression (44) the different decay channels near a plasmonic waveguide are easily estimated. In order to specifically discuss the contributions of the guided modes, we rewrite the expression (44) in the equivalent form

$$\Gamma(x, z) \approx \frac{\pi}{n_1} \Gamma_0 + \frac{3\pi}{n_1 k_0} \int_{0}^{\infty} \Delta\rho_{2D}(r_{zc}, k_y) \frac{dk_y}{k_y}$$

where we have introduced the 2D-LDOS [105, 122]

$$\Delta\rho_{2D}(r_{zc}, k_y) = \frac{2\pi k_y}{\pi} \text{Im} \frac{\Delta G_{2D}^{2D}(r_{zc}, r_{zc}, k_y)}{G_0^{2D}}$$

and $\Delta G^{2D} = G^{2D} - G_0^{2D}$ is the difference between the total Green’s tensor of the 2D-structure and the free-space Green’s tensor $G_0^{2D}$. It describes the role of the waveguiding structure only.

Figure 11(a) represents the variation of the 2D-LDOS near a silver nanowire as a function of the propagation constant $k_y$. It behaves very similarly to the mirror case (figure 2). In particular, we can again distinguish three contributions to the decay rate. (i) Radiative waves for $k_y < n_1 k_0$, (ii) SPP peaked near the plasmon propagation constant (here $k_{SPP} = 2.28k_0$) and (iii) lossy waves at large $k_y$. The corresponding decay channels are calculated by numerical integrations over the different wave domains.

We first discuss the SPP rate. The SPP contribution follows a Lorentzian profile as above a thick plasmon film. It is peaked on the plasmon propagation constant $k_{SPP} = 2.28k_0$ and with a FWHM inversely proportional to the propagation length ($l_{SPP} = 1.2 \mu m$; see the inset of figure 11(a)). This again leads to a closed form expression of the plasmonic...
Figure 12. Purcell factor near a circular or pentagonal silver nanowire ($\lambda_{\text{em}} = 1 \, \mu\text{m}$). $d$ is the distance to the nanowire surface or edge. Reproduced with permission from [105]. APS, copyright 2011.

Purcell factor [105, 122]

\[
\frac{\Gamma_{\text{SPP}}}{n_1 \Gamma_0} = \frac{3\pi \lambda}{4n_1^2 k_{\text{SPP}}} \frac{\Delta_{2D}(\mathbf{r}_c, k_{\text{SPP}})}{L_{\text{SPP}}} = \pi \frac{p(k_{\text{SPP}})}{2} \frac{P(k_{\text{SPP}})}{L_{\text{SPP}}}, \quad \text{with} \quad p(k_{\text{SPP}}) = \frac{P(k_{\text{SPP}})}{n_1 P_0}. \tag{47}
\]

It is worth to compare this expression to the lossless case for which the coupling rate to the guided mode expresses [142, 143]

\[
\frac{\Gamma_{\text{SPP}}}{n_1 \Gamma_0} = \frac{3\pi \epsilon_0 c}{n_1 k_0^2} \int_{A_\lambda} \left| \mathbf{E} \wedge \mathbf{H}^* \right|^2 \, \mathbf{d}A, \tag{48}
\]

where $(\mathbf{E}, \mathbf{H})$ is the electromagnetic field associated with the guided SPP mode. For a circular waveguide, an analytical expression is readily obtained (see supplementary information of [122]). Figure 11(b) compares the SPP rate obtained using the 2D-LDOS formalism in the lossy nanowire (equation (74)) and the lossless ideal system (equation (48)). Lossy and lossless rates perfectly superimpose, revealing that the coupling rate to the guided mode does not depend on the propagation losses [105].

The equivalence between the lossy and lossless Purcell factors for a guided mode can be understood as follows. The dispersion relation $\omega = f(k_{\text{SPP}})$ governs the guided mode excited by an emitter near the emission angular frequency $\omega_{\text{em}}$. Therefore, the dirac distribution in the decay rate equation (8) becomes

\[
\delta (\omega - \omega_c) = \frac{1}{v_g} \delta [k_{\text{SPP}} - k_{\text{SPP}}(\omega_{\text{em}})] \tag{49}
\]

introducing the group velocity $v_g = \partial \omega / \partial k_{\text{SPP}}$ and assuming a weak dispersion around the emission wavelength. The dirac distribution $\delta [k_{\text{SPP}} - k_{\text{SPP}}(\omega_{\text{em}})]$ is again replaced by a Lorenzian profile for a lossy waveguide so that we achieve

\[
F_p = \frac{3}{4\pi^2} \frac{(\lambda_{\text{em}}/n_1)^3 Q_{\text{SPP}} \omega_{\text{em}}}{V v_g k_{\text{SPP}}}. \tag{50}
\]

Moreover, the quality factor and effective volume of the guided mode are expressed, respectively by

\[
Q_{\text{SPP}} = \frac{k_{\text{guide}}}{\Delta k_{\text{guide}}} = k_{\text{SPP}} L_{\text{SPP}} \tag{51}
\]

and

\[
V = \frac{\int \varepsilon (\mathbf{r}) |\mathbf{E}(\mathbf{r})|^2 \mathbf{d}x \mathbf{d}y \mathbf{d}z}{\text{Max} \left[ |\varepsilon (\mathbf{r})|^2 \right]} = \frac{\int \varepsilon (x, z) |\mathbf{E}(x, z)|^2 \mathbf{d}x \mathbf{d}z}{\text{Max} \left[ |\varepsilon (x, z)|^2 \right]} \times \int_{-\infty}^{\infty} e^{-|x|/\lambda_{\text{eff}}} \mathbf{d}y = A_{\text{eff}} 2L_{\text{SPP}}. \tag{52}
\]

$A_{\text{eff}}$ defines the mode effective area (see equation (22) and we assume again a non-dispersive medium. Finally, the Purcell factor simplifies to the nanofiber expression (24)

\[
F_p = \frac{\Gamma_{\text{SPP}}}{n_1 \Gamma_0} = \frac{3}{4\pi} \frac{(\lambda_{\text{em}}/n_1)^2 n_g}{A_{\text{eff}} n_1}. \tag{54}
\]

and does not depend on the propagation length. Moreover, the guided SPP mode volume obeys $V_{\text{SPP}} = 2A_{\text{eff}} L_{\text{SPP}}$ that becomes strongly confined for short propagation distances $L_{\text{SPP}}$. It makes a bridge between delocalized and localized SPP, notably in the quasi-static regime where they present very similar behavior [122]. This discussion also points out that the role of losses in the plasmonic Purcell factor must be carried out carefully.

Eventually, the Purcell factor is identical considering a real lossy or an ideal non-lossy plasmonics waveguide, so that we can identify the Purcell factor expressions (24) and (48) to estimate the SPP confinement. As previously, we identify at the nanowire surface

\[
\frac{\Gamma_x}{n_1 \Gamma_0} + \frac{\Gamma_y}{n_1 \Gamma_0} + \frac{\Gamma_z}{n_1 \Gamma_0} = F_p, \tag{55}
\]

\[
\equiv \frac{3}{4\pi} \frac{(\lambda_{\text{em}}/n_1)^2 n_g}{A_{\text{eff}} n_1}. \tag{56}
\]

The effective surface of the guided SPP is shown on figure 11(c) as a function of the wire radius. This reveals that quantum plasmonics relies on strongly subwavelength mode confinement with huge Purcell factor (up to $10^3$ see inset of figure 11(c)) [21, 144]. We achieve similar values for $\lambda_{\text{em}} = 670 \, \text{nm}$ and a gold nanowire (not shown). The small SPP effective area permits to decrease the threshold for SPP amplification compared to a photonic nanowire of similar cross-section [145].

Finally, the radiative and non-radiative contributions are presented in figures 11(d) and (e). Above $d = 20 \, \text{nm}$, the only contribution to the non-radiative rate is SPP, due to losses along the propagation. At short distances, electron scattering are responsible of the additional losses, leading to
fluorescence quenching. Last, a coupling efficiency into the guided plasmon of $\beta = 83\%$ is achieved at 20 nm from the nanowire (not shown) [105].

For a nanowire above a glass substrate, the guided SPP becomes leaky. The 2D-LDOS again follows a Fano profile (or a Lorentzian profile for weak leakage) and the leakage rate is easily estimated as done in the case of thin metal film. For instance, $\beta_{\text{leak}} = 70\%$ of the emission is collected into the substrate for a 100 nm silver wire 50 nm above the glass substrate [105].

Since the 2D-Green’s dyad associated to a plasmonic waveguide can be numerically computed, this formalism can be applied to arbitrary geometries [107, 146–148]. Specifically, crystalline silver nanowires present a pentagonal cross-section shape leading to strong mode confinement at the corners (see figure 12) [134, 149]. This mode confinement significantly increases the Purcell factor near the edge of the nanowire compared to a circular nanowire [105].

6. Localized plasmon

This last section is devoted to localized plasmon for which we expect full 3D subwavelength confinement. For the sake of clarity, we focus on a spherical metal nanoparticle (MNP) that constitutes a canonical configuration for LSP. We first consider the quasi-static approximation for which we derive analytical expressions for the mode volume and quality factor of each mode (section 6.1). In section 6.2, we extend the discussion to the retarded regime using the Mie theory.

6.1. Quasi-static regime

6.1.1. Dipolar LSP. Let us consider a spherical MNP of radius $R$ small compared to the wavelength. For clarity, we first discuss the dipolar response of the particle. It is characterized by the effective polarizability

$$\alpha_{\text{eff}}^\text{dip} (\omega) \sim \frac{\omega^2}{\omega^2 - \omega_p^2},$$

$$\kappa_{\text{dip}} \sim \frac{2 (k R)^3 \omega_1}{3}, \quad (\kappa_1 = \kappa_{\text{dip}}/c).$$

$\kappa_{\text{dip}}$ is the decay rate of the particle dipolar mode, and includes both the Joule ($\kappa_{\text{abs}}$) and radiative ($\kappa_{\text{rad}}$) losses. We can therefore define the quality factor of the dipolar mode $Q_1 = \omega_1/\kappa_1$ that typically ranges from 10 to 25 for gold or silver nanoparticles [151].

The decay rate of a dipolar emitter located in the very near-field of a spherical metal particle approximates to [154–156]

$$\frac{\Gamma_1}{\Gamma_0} \sim \frac{6}{k^3} \text{Im} (\alpha_1),$$

$$\frac{\Gamma_1}{\Gamma_0} \sim \frac{6 \omega_1 R^3}{k^3 c} \text{Im} (\alpha_1).$$

$$\frac{\Gamma_1}{\Gamma_0} \sim \frac{3}{2 k^3 c} \text{Im} (\alpha_1).$$

for a dipole emitter oriented perpendicularly or parallel to the nanoparticle surface and an emission tuned to the dipolar particle resonance ($\lambda_{\text{em}} = \lambda_1 = 2 \pi c/\omega_1$). In order to determine the dipolar mode effective volume, we now identify the coupling rate $\Gamma_1/\Gamma_0$ to the Purcell factor (equation (3)). It is worthwhile to note that the Purcell factor is obtained assuming a single mode cavity. Since the dipolar mode is three-fold degenerated, the SPP rate writes $\Gamma_1/\Gamma_0 = 3 F_{\text{p}}$ so that we can identify the Purcell factor to the SPP rate of a randomly oriented dipolar emitter at the particle surface ($\zeta_0 = R$). The average decay rate writes

$$\frac{\Gamma_1}{\Gamma_0} = \frac{\Gamma_1^+ + 2 \Gamma_1^-}{3 \Gamma_0} \sim \frac{3}{4 \pi^2} \lambda_1^3 \frac{1}{2 \pi R^3} Q_1,$$

$$\frac{\Gamma_1}{\Gamma_0} = \frac{3}{4 \pi^2} \lambda_1^3 Q_1 V_1,$$

where we define the dipolar LSP mode volume $V_1 = 2 \pi R^3 = 3/2 V_0$, $V_0 = 4 \pi R^3/3$ is the volume of the MNP. As a consequence, although the dipolar LSP is radiative in the far-field, it is possible to assign a finite mode volume within the quasi-static approximation. As expected, it is strongly subwavelength for small MNP [69, 151, 157, 158].

6.1.2. High order modes. The Purcell factor associated to the dipolar mode can be generalized to each LSP mode. Due to the $(2n + 1)$ degeneracy, the coupling rate to the $n$th mode ($n = 1$, dipolar LSP, $n = 2$, quadrupolar LSP, ...) obeys

$$\frac{\Gamma_n}{\Gamma_0} = (2n + 1) F_{\text{p}}, \quad \text{with}$$

$$F_{\text{p}} = \frac{3}{4 \pi^2} \lambda_1^3 Q_1 V_n,$$

We use a different definition for the mode volume in [151], assuming a randomly oriented dipole. The definition used here, that includes the mode degeneracy is more consistent with usual Purcell factor definition.
\[ Q_n = \frac{\omega_n}{\kappa_n} = \frac{\omega_n}{\kappa_{\text{abs}} + \kappa_{\text{rad}}} \]  
(68)

\[ V_n = \frac{3}{n + 1} V_0, \]  
(69)

\[ \kappa_{\text{rad}} = \omega_n \frac{(n + 1)(k_n R)^{2n+1}}{n(2n - 1)!!(2n + 1)!!} \left( k_n = \omega_n / c \right). \]  
(70)

The quality factor is governed by ohmic losses \( \kappa_{\text{abs}} \) in the MNP, identical for all the modes, and radiative losses that slightly decreases for high order modes \( \propto (k_n R)^{2n+1} \). Quality factor therefore slightly increases from a few 10 for a dipolar LSP \((n = 1)\) to about 50 to 100 for high order modes. In addition, the high order modes are more confined than the dipolar LSP \((V_1 = 1.5V_0, V_2 = V_0, V_n \to 0)\). This quantifies the mode confinement and reveals that although having low \( Q \) factor, LSP presents sub diffraction mode volume that ensures efficient coupling to a nearby emitter at the origin of surface enhanced spectroscopies.

Last, we can again define a coupling efficiency \( \beta \)-factor to a given mode. It strongly depends on the distance to the MNP but also of the emission wavelength. For an emission wavelength matching the dipolar LSP, the coupling efficiency reaches \( \beta_1 = 90\% \) into the \( n = 1 \) mode at a distance \( d = 10 \text{ nm} \). It can be as high as \( \beta_2 = 87\% \) into the quadrupolar mode at \( d = 15 \text{ nm} \) if the wavelength emission matches the \( n = 2 \) LSP resonance (not shown, see [151]).

### 6.1.3. Energy confinement

In cQED, the mode volume is defined as the energy confinement (see equation (20)). For dispersive materials, this *extrapolates* to

\[ V_{n}^{\text{eff}} = \frac{\int U_n(r) dr}{\max_{\omega}[\mathcal{E}_n(\omega)]}, \]

\[ U_n(\omega) = \frac{\partial}{\partial \omega} \left[ \omega \mathcal{E}_n r, \omega \right] \mathcal{E}_n(\omega) + \mu_0 |\mathbf{H}_n(\omega)|^2, \]  
(71)

where \((\mathcal{E}_n, \mathbf{H}_n)\) is the electromagnetic field of the \( n \)th mode. In the quasi-static regime, the magnetic contribution is negligible and the electric field is confined near the particle surface. This definition then leads to \( V_{n}^{\text{eff}} = 6/(n + 1)^2 V_0 \) [159]. The effective volumes of the \((2n+1)\) degenerated \( n \)th LSP modes are represented on figure 13 (see appendix C for details). We observe that the \((2n + 1)\) degenerated modes present the same volume (note that the energy confinement of the \((l, m)\) mode is normalized with respect to the \((l, m = 0)\) mode maximum intensity).

The ratio between the mode volume deduced from Purcell factor \((V_{\text{Purcell}})\) and the mode volume estimated from energy mode confinement assuming a lossless metal \((V_{\text{energy}})\)

\[ \frac{V_{\text{Purcell}}}{V_{\text{energy}}} = \frac{n + 1}{2} \]  
(72)

depends on the mode number \( n \) only. We attribute this difference to the (Joule and radiative) losses that are neglected in the energy confinement but taken into account in the Purcell volume derivation. Unlike delocalized SPP for which Purcell factor does not depend on Joule losses, Purcell factor for a localized LSP is strongly affected by losses in the metal. In addition, we observe that both Purcell and energy confinement derivations leads to identical values for the dipolar mode volume. This again shows that the mode volume entering in the Purcell factor is governed by the mode near-field behavior, even for a leaky mode (see also section 4.2.2). In addition, it is worth noticing that the LSP volume derived from the Purcell factor, taking into account losses, does not depends on the losses in the quasi-static approximation. As for cQED, the effect of losses on the Purcell factor are fully included in the quality factor (equation (68)).

### 6.2. Retarded regime

So far, we have discussed the Purcell factor within the quasi-static regime. In this section, we generalize it to spherical MNP of arbitrary size using the Mie expansion. Particular attention is again devoted to the definition of the mode volume as the energy confinement, in analogy with cQED definition. Dipolar emission near a spherical particle of arbitrary size is exactly solved using the Mie (modal) expansion [160]. We can therefore define a mode volume by identifying the contribution to the total decay rate of the \( n \)th mode to the Purcell expression (3) [161]. In the following, we define this volume as the Purcell effective volume. We compare it to the mode energy confinement (see equation (71)). However, the application of definition (71) is difficult in the retarded regime since LSPs leak in the far-field. As far as light–matter coupling is concerned, the pertinent parameter is the confinement of the mode energy stored inside the cavity. Following the work of Koenderink [162], the intrinsic mode volume is estimated from the energy confinement, excluding radiative leaks (i.e., ordinate at the origin in figures 14(a) and (b)).

In figure 14, we compare the mode volume estimated from the Purcell factor and energy definition as a function of

![Figure 13. Energy confinement mode volume \( V_{n} \) as a function of the mode number \( l \) and \( m = 0, 1, \ldots \). The curve is the Purcell volume estimated identifying the decay rate to a given mode and Purcell factor \( V_{\text{Purcell}} = 3V_0/(l + 1) \).](image-url)
the MNP size. This again reveals sub diffraction mode volume ensuring efficient light–matter interaction. For small particles, we recover the quasi-static limit. For large particles, the energy definition is in qualitative agreement with the Purcell factor definition. However, large MNP supports quasi-mode with lifetime shorter than the collective oscillation so that the concept of Purcell factor fails to describe this regime.

6.3. Generalization of the Purcell factor concept

6.3.1. Complex mode volume. Recently, Sauvan and coworkers define a complex mode volume [164]

\[ V_n = \frac{1}{2} \int \mathbf{E}_n \cdot \frac{\partial \mathbf{H}_n}{\partial t} - \mathbf{E}_n \cdot \mu_0 \mathbf{H}_n^2 \, d\mathbf{r} \max_{\|\mathbf{E}_n\|} \left[ \mathbf{E}_n(\mathbf{r}) \right]^2 , \]

(73)

where \((\mathbf{E}_n, \mathbf{H}_n)\) is the quasi-normal \(n\)th mode. The convergence of the volume integral is ensured thanks to phase matching layers. This generalizes the Purcell factor to dissipative cavities such that

\[ F_p = \frac{\Gamma_n}{n_1 \Gamma_0} = \frac{3}{4 \pi^2} \left( \frac{\lambda}{n_1} \right)^3 \frac{\text{Re} \left( \frac{Q_n}{V_n} \right)}{\text{Re} \left( \frac{Q_0}{V_0} \right)} , \]

(74)

This definition is consistent with the Purcell volume definition (figure 14) and reconciles the Purcell factor with the energy-like confinement definition of the mode volume [165, 166]. Similar definitions should work for the effective mode area or length.

Moreover, detuning between the emission wavelength and the mode resonance \(\omega_n\) leads to a Fano-like behavior [164, 167]. Taking into account the \((2n + 1)\) LSPs degeneracy, the decay rate for a randomly oriented emitter obeys

\[ \frac{\langle \Gamma_n \rangle}{n_1 \Gamma_0} = \frac{(2n + 1)}{3} \frac{\text{Re} \left( \frac{Q_n}{V_n} \right)}{\text{Re} \left( \frac{Q_0}{V_0} \right)} \left[ 1 + 2Q \delta \omega \frac{\text{Im} \left( \frac{Q_n}{V_n} \right)}{\text{Re} \left( \frac{Q_n}{V_n} \right)} \right] \]

(75)

and generalizes expression (19) to lossy cavities. Figure 15 presents the dipolar and quadrupolar LSP contributions to the decay rate near a gold MNP. We observe an excellent agreement with the Fano-like behavior. From the fitting parameters, we extract the Purcell factor, quality factor and effective volume of the dipolar mode: \(F_{p1} = 41, Q_1 = 6\) and \(V_1 = 6.4 \times 10^{-2} \mu m^3 = 0.01 (\lambda_1/n_1)^3\) respectively. Similarly, for the quadrupolar mode: \(F_{p2} = 34, Q_2 = 8.4\) and \(V_2 = 8.2 \times 10^{-4} \mu m^3 = 0.02 (\lambda_2/n_2)^3\).

6.3.2. Decay channels. The Purcell factor quantifies the coupling efficiency into a given LSP mode but does not distinguish radiative from Joule losses, as for delocalized SPPs. Figure 16(a) presents the radiative and non-radiative contributions to the decay rate near a gold MNP. At very short distances, the decay rate is enhanced by several orders of magnitude. For distances below a few nanometers, the non-local response of the metal permittivity (not included in this work) could lead to different values [168–170] but without significant change in the behavior. In the very near-field, the...
main coupling mechanism is non-radiative energy transfer, responsible for fluorescence quenching [171]. Above $d = 20 \text{ nm}$, the total decay rate is still enhanced by a factor of about ten but is mainly radiative. In figure 16(b), we show the contribution of the dipolar, quadrupolar and high order LSP mode to the total decay rate. At short distances, high order modes play a dominant role since they are strongly confined near the particle surface, as revealed by their extremely small effective volume (figure 14) [55, 151, 156, 172]. For distances of a few tens of nanometer, the radiative dipolar mode is responsible for the decay rate enhancement. This is summarized in figure 16(c) where the coupling efficiency to the dipolar mode reaches $\beta_1 = 85\%$ at $d \approx 20 \text{ nm}$. The apparent quantum yield $\eta = \Gamma_{\text{rad}}/\Gamma_{\text{tot}}$ is governed by the dipolar mode in the near-field of the MNP as revealed by the two superimposed curve in figure 16(c).

7. Conclusion

In this work, we transposed the cQED Purcell factor to plasmonics. The Purcell factor characterizes the capability of a structure to modify and control the emission of a nearby emitter. Both optical cavity and plasmon modes present high Purcell factors that favor efficient excitation by a dipolar emitter. However it originates from high quality factors in case of optical cavities (but diffraction limited confinements) and on strongly subwavelength confinements for plasmonics (but low quality factors). Therefore the Purcell factor reveals the new paradigm opened by quantum plasmonics for achieving efficient light–matter interaction at the nanoscale. This permits a scale law approach profiting from the strong maturity of cQED concepts and adapt them to nanophotonics. We also discussed the presence of losses that are inevitable at the nanoscale. The Purcell factor includes Ohmic losses that are inherent to the excitation of plasmon in real metal so that it has to be manipulated with care. In the particular case of plasmonic waveguides, the coupling efficiency to a guided mode is not affected by propagation losses. Obviously, only low loss systems such that crystalline nanowires or nanoplatelets would permit realistics applications. Finally, hybrid plasmonic/nanophotonic configurations would profit from the concept of Purcell factor through a common description of the coupling mechanism.

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Appendix A. Decay rate above a flat mirror

A.1. Green's tensor and total decay rate

The Green’s tensor above a mirror writes $G = G_0 + G_{\text{refl}}$ where $G_0$ is the Green’s tensor of the infinite homogeneous medium of optical index $n_1$ and $G_{\text{refl}}$ describes the reflection on the mirror. It can be expressed thanks to Weyl expansion

$$G_{\text{refl}}(\mathbf{r}, \mathbf{r}_0) = \frac{i}{4\pi k_0} \int_0^{\infty} [g^s + g^p] e^{k_1 z_1 + z_2} dk_1$$

with $k_1 = n_1 k_0$, $k_{1z} = (k_1^2 - k_0^2)^{1/2}$, $[\text{Im}(k_{1z}) \geq 0]$.

(A.1)
and, writing \( \mathbf{r} - \mathbf{r}_0 = (\rho, \varphi, z - z_0) \) in cylindrical coordinates:

\[
\begin{align*}
g_{xx}' &= k_1^2 k_{z1} \sin^2 \varphi J_0(k_1\rho) + \cos(2\varphi) J_1(k_1\rho) \\
g_{xx}^p &= -k_1 k_{z1} r^p \cos^2 \varphi J_0(k_1\rho) - \cos(2\varphi) J_1(k_1\rho) \\
g_{xy}' &= -k_1^2 k_{z1} r^p \sin \varphi \cos \varphi \left[ J_0(k_1\rho) - 2 \frac{J_1(k_1\rho)}{k_1\rho} \right] \\
g_{yy}' &= w_1 k_{z1} r^p \sin \varphi \cos \varphi \left[ J_0(k_1\rho) - 2 \frac{J_1(k_1\rho)}{k_1\rho} \right] \\
g_{xx}^s &= 0, \quad g_{xy}^s = g_{yx}^s = g_{yy}^p = g_{yx}^p = g_{yy}^p \\
g_{xy}^s &= k_1^2 k_{z1} r^p \left[ \cos^2 \varphi J_0(k_1\rho) - \cos(2\varphi) \frac{J_1(k_1\rho)}{k_1\rho} \right] \\
g_{yy}^s &= -k_1 k_{z1} r^p \left[ \sin^2 \varphi J_0(k_1\rho) + \cos(2\varphi) \frac{J_1(k_1\rho)}{k_1\rho} \right] \\
g_{xx}^s &= 0, \quad g_{xy}^s = -i k_1^2 r^p \sin \varphi J_1(k_1\rho) \\
g_{yx}^s &= 0, \quad g_{xy}^s = i k_1^2 r^p \cos \varphi J_1(k_1\rho) \\
g_{yy}^s &= 0, \quad g_{yy}^s = i k_1^2 r^p \sin \varphi J_1(k_1\rho) \\
g_{xx}^s &= 0, \quad g_{xy}^s = 0, \quad g_{yx}^s = -k_1^3 k_{z1} r^p J_0(k_1\rho)
\end{align*}
\]

\( r^p \) (or \( r^p \)) refer to the fresnel reflection coefficient on the slab for TE (TM) polarized light and \( J \) are the cylindrical Bessel function.

The total decay rate of a dipolar emitter above follows equation (28) and writes above a slab:

\[
\Gamma_{e}(d) = \frac{3}{2 n_1^{3/2} k_0} \text{Re} \int_0^\infty [g_{uu}^s + g_{uu}^p] e^{2ki_1d} \, dk_1
\]

with

\[
\begin{align*}
g_{xx}^s &= g_{yy}^s = k_1^2 k_{z1} r^s \\
g_{xx}^p &= g_{yy}^p = -\frac{1}{2} k_1 k_{z1} r^s g_{zz}^s = 0, \\
g_{zz}^s &= k_1^3 k_{z1} r^p
\end{align*}
\]

so that the total decay rate writes

\[
\Gamma_{e}(d) = \int_0^\infty \mathcal{P}_{uu}(k_1) \, dk_1,
\]

with

\[
\mathcal{P}_{uu}(k_1) = \frac{3}{2 n_1^{3/2} k_0} \text{Re} \left[ (g_{uu}^s + g_{uu}^p) e^{2ki_1d} \right]
\]

that defines the dipolar emission power spectrum used in equation (35).

### A.2. SPP contribution near a lossless mirror

In this section, we consider a metal(\( \varepsilon_2 \))/dielectric(\( \varepsilon_1 \)) single interface, and assume a lossless metal [\( \text{Im}(\varepsilon_2) = 0 \)]. The coefficient of reflection writes

\[
r^p = \frac{\varepsilon_2 k_1 - \varepsilon_1 k_2}{\varepsilon_2 k_1 + \varepsilon_1 k_2} \quad (A.4)
\]

and presents a pole for \( \varepsilon_2 k_1 - \varepsilon_1 k_2 = 0 \) leading to the (real) SPP wavector

\[
k_{\text{SPP}} = k_1 \left( \frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2}. \quad (A.5)
\]

The dipolar emission power spectrum near the SPP resonance can be assessed from an expansion of \( r_p \) near its pole

\[
r^p(k_1) \sim \frac{2 \varepsilon_1 \varepsilon_2}{k_1^2 - \varepsilon_1^2 - \varepsilon_2^2 k_1 - k_{\text{SPP}}} \quad (A.6)
\]

so that the SPP contribution to the decay rate is determined from the residu. We achieve [100]

\[
\begin{align*}
\Gamma_{e}(d) &= \frac{3 \pi n_{\text{SPP}}^5}{n_1 \Gamma_0} \left[ \frac{1}{|\varepsilon_1 - \varepsilon_2|^2} e^{-2|\varepsilon_1 - \varepsilon_2|^2/k_{\text{SPP}} d} \right] \\
\Gamma_{e}(d) &= \frac{3 \pi n_{\text{SPP}}^5}{n_1 \Gamma_0} \left[ \frac{1}{|\varepsilon_1 - \varepsilon_2|^2} e^{-2|\varepsilon_1 - \varepsilon_2|^2/k_{\text{SPP}} d} \right].
\end{align*} \quad (A.7)
\]

### A.3. SPP contribution near a strongly lossy mirror

We now consider the strong lossy configuration at the emission wavelength \( \lambda_{\text{em}} = 525 \text{ nm} \). Figure A1 (a) presents the dipolar emitter spectrum as a function of the in-plane wavector. Due to strong losses in the metal, lossy waves cannot be separated from the SPP resonance (compare to figure 2). Indeed, the power spectrum presents a very broad resonance-like power spectrum at high \( k_1 \). Therefore the dipolar emitter can couple to either the SPP or LSW, hence a Fano behavior. In order to determine the SPP contribution to the total decay rate, we numerically integrate the emitted power in the range \( 1 < k_1/k_0 < 1.4 \) (continuous line in figure A1(c)). We also estimate the SPP behavior assuming a Fano resonance as described in the next section (dots in figure A1(c)). Finally, the SPP contribution assuming a lossless metal and the total decay rate are also represented. We observe that the lossless model overestimates the SPP rate and could be even larger than the total decay rate (around \( d \approx 100 \text{ nm} \)). The SPP rate estimated from Fano profile or by direct numerical integration are in qualitative agreement but show some discrepancies, illustrating the difficulty to separate the SPP and LSW contributions.

### A.4. Scattering rate

The scattering rate is achieved from the power scattering in the far-field zone. It can be estimated from asymptotic
behavior of the Green’s tensor. We achieve

$$\frac{\Gamma_{\text{scan}}}{n_1T_0} = \int_0^{\pi/2} \sin \theta \sigma^{11}(\theta)d\theta + \frac{n_1}{n_1} \int_0^{\pi} \sin \theta \sigma^{13}(\theta)d\theta,$$

where the differential scattering cross-section expresses

$$\sigma^{11}_s(\theta) = \frac{3}{8} - \frac{3}{8} \sin^2 \theta + \frac{3}{2} |r_p|^2 \cos^2 \theta + |r_s|^2$$

$$+ \frac{3}{4} Re \left\{ (-r_p \cos \theta + r_s) e^{2ik_s d} \right\}, \quad \text{(A.8)}$$

$$\sigma^{11}_p(\theta) = \frac{3}{4} + \frac{3}{4} |r_p|^2 + \frac{3}{2} Re \left\{ r_p e^{2ik_s d} \right\} \quad \text{(A.9)}$$

above the film, for a dipole parallel or perpendicular to the surface, respectively and

$$\sigma^{13}_s(\theta) = \frac{3}{8} e^{2ik_s d} \left( |r_p|^2 + \frac{k_{1\parallel}}{k_{1\perp}} \right)^2 \cos^2 \theta \quad \text{(A.10)}$$

$$\sigma^{13}_p(\theta) = \frac{3}{4} e^{2ik_s d} |r_p|^2 + \frac{k_{1\parallel}}{k_{1\perp}}^2 \cos^2 \theta \sin^2 \theta \quad \text{(A.11)}$$

in the substrate. $t_p$ and $t_s$ refer to the Fresnel transmission coefficients for $p$ and $s$ polarized light, respectively. This generalizes the expression achieved for a thick mirror [103] to a finite metal slab or multilayer system. The difference between the radiative and scattering rates originates from the part of the radiative waves absorbed before achieving the far-field (see e.g. figure 5) and/or from SPCE leakage (see figure 9).

Appendix B. Fano profile

Assuming a Fano profile of the emitted power $P(k||)$ (see e.g. Figure 1(b)), it follows [114]

$$P(k||) = \frac{P(k_{app}) (q \kappa_{app} + k|| - k_{app})^2 + b \kappa_{app}^2}{q^2 + b} \quad \text{(B.1)}$$

$$= P(k_{app}) (x + q)^2 + b \quad \text{(B.2)}$$

$$= \frac{q^2 + b}{1 + x^2} \quad \text{(B.3)}$$

with $x = k|| - k_{app} / \kappa_{app} = k||/k_0 - n_{app} \kappa_{app} / n_{app}$. The SPP rate is then estimated from the integral of the emitted power. We first estimate the integral of the Fano resonance (the term $-1$ removes the background contribution)

$$I = \int_{-\infty}^{+\infty} \left[ \frac{(x + q)^2 + b}{1 + x^2} - 1 \right] \frac{dx}{x^2}$$

$$= (q^2 + b - 1) \left[ \frac{1}{1 + x^2} \right]_{-\infty}^{+\infty} \quad \text{(B.4)}$$

$$+ 2q \left[ \frac{1}{1 + x^2} \right]_{-\infty}^{+\infty} \quad \text{(B.5)}$$

$$= (q^2 + b - 1) \pi \quad \text{(B.6)}$$
and the SPP rate simplifies to
\[
\Gamma_{\text{SPP}} = \int_{-\infty}^{+\infty} P(k_{\text{SPP}}) dk_{\text{SPP}}
\]
\[
= \frac{1}{2L_{\text{SPP}}} \int_{-\infty}^{+\infty} P(x) dx,
\]
\[
P(k_{\text{SPP}}) = \frac{P(k_{\text{SPP}})}{2L_{\text{SPP}}} \frac{q^2 + b - 1}{q^2 + b} \frac{1}{2}
\]
so that we recover the expression (36) for a Lorentzian profile \((q \rightarrow \infty)\).

### Appendix C. Energy confinement of LSPs

The electrostatic potential associated to the \(nth\) LSP mode of a spherical MNP follows [150]
\[
\Phi_{n,m} = \sum_{m=-n}^{n} C_{n,m} \left( \frac{R}{r} \right)^{n+1} P^m_n(\cos \theta)e^{im\varphi}, r < R
\]
\[
\Phi_{n,m} = \sum_{m=-n}^{n} C_{n,m} \left( \frac{R}{r} \right)^{n+1} P^m_n(\cos \theta)e^{im\varphi}, r \geq R
\]
with the normalization constant
\[
C_{n,m} = (-1)^m \sqrt{\frac{2l+1}{4\pi} \frac{(n-m)!}{(n+m)!}}
\]
and \(P^m_n\) is the associated Legendre polynomial. The boundary conditions imposes
\[
n\varepsilon_m + (n+1)\varepsilon_l = 0
\]
that fixes the resonances of the \(nth\) LSP. If the dielectric constant of the metal \(\varepsilon_m\) follows a Drude behavior, the resonance angular frequency obeys \(\omega_n = \omega_p \sqrt{n/n + (n+1)\varepsilon_l}\). The \(nth\) LSP presents a degeneracy \(\delta_m = (2n+1)\) and the electric field of the \((m,n)\) mode writes
\[
E_{\text{nm}} = C_{n,m} \left( \frac{r}{R} \right)^{n+1} P^m_n(\cos \theta)e^{im\varphi}\hat{e}_r
\]
\[
\frac{1}{\sin \theta} \left[ (n+1) \cos \theta P^m_n(\cos \theta) \right]
\]
\[
-(n-m+1)\sin \theta P^m_n(\cos \theta) e^{im\varphi}\hat{e}_\theta,
\]
\[
\frac{im}{\sin \theta} P^m_n(\cos \theta)e^{im\varphi}\hat{e}_\varphi.
\]
\((r < R)\)

\[
E_{\text{nm}} = C_{n,m} \left( \frac{R}{r} \right)^{n+2} P^m_n(\cos \theta)e^{im\varphi}\hat{e}_r
\]
\[
\frac{1}{\sin \theta} \left[ (n+1) \cos \theta P^m_n(\cos \theta) \right]
\]
\[
-(n-m+1)\sin \theta P^m_n(\cos \theta) e^{im\varphi}\hat{e}_\theta,
\]
\[
\frac{im}{\sin \theta} P^m_n(\cos \theta)e^{im\varphi}\hat{e}_\varphi.
\]
\((r \geq R)\)

The effective volume is expressed extrapolating the cQED description to a dispersive medium
\[
V_{n,m} = \int U_{n,m}(\mathbf{r}) d\mathbf{r}
\]
\[
= \max \left\{ \varepsilon_m \left| E_{n,m=0}\right|^2 \right\}
\]
\[
U_{n,m}(\mathbf{r}) = \frac{\partial \left[ \omega_0 \Phi_{n,m}(\mathbf{r}, \omega) \right]}{\partial \omega} \left| E_{n,m}(\mathbf{r}) \right|^2.
\]
\(\)Note, since the mode is degenerated, we normalized the field with respect to maximum of the field considering all the degenerated modes \((\max \left| E_{n,m}(\mathbf{r}) \right|^2)\) and not \((\max \left| E_{n,m}(\mathbf{r}) \right|^2)\) in the denominator of equation (C.7). Assuming a lossless Drude metal, it comes
\[
\frac{\partial \left[ \omega_0 \Phi_{n,m}(\omega) \right]}{\partial \omega} \left| E_{n=m}(\mathbf{r}) \right|^2 = 2 + \frac{n + 1}{n} \varepsilon_l
\]
\(\)so that the effective volume is for \(m = 0\) [159]
\[
V_{n,0} = \frac{6V_0}{(2n+1)\left(1 + \frac{n}{(n+1)\varepsilon_l}\right)}.
\]
For \(m \neq 0\), the integration over \(\theta\) is numerically evaluated (see figure 13). We note a discrepancy between the mode volume deduced from Purcell factor \((V_{\text{Purcell}})\) and the mode volume estimated from energy mode confinement assuming a lossless metal \((V_{n,m})\). Indeed, we have [151]
\[
V_{n,m}^{\text{Purcell}} = \frac{3V_0}{(2n+1)\left(1 + \frac{n}{(n+1)\varepsilon_l}\right)}
\]
so that the ratio
\[
\frac{V_{n,m}^{\text{Purcell}}}{V_{n,m}^{\text{Energy}}} = \frac{n + 1}{2}
\]
depends on the mode number \(n\) only.

### References

[1] Hell S W 2007 Science 316 1153
[2] Celebroano M, Kukura P, Renn A and Sandoghdar V 2011 Nat. Photonics 5 95–8
[3] Tamrat P, Maali A, Lounis B and Orrit M 2000 J. Phys. Chem. A 104 1–6
[4] Vahala K J 2003 Nature 424 839–46
[5] Betzig E and Chichester R J 1993 Science 262 1422–5
[6] Veerman J A, Garcia-Parajo M F, Kuipers L and van Hulst N F 1999 J. Microsc. 194 477–82
[7] Sick B, Hecht B, Wild U P and Novotny L 2001 J. Microsc. 202 365–73
[8] Molenda D, Colas des Francs G, Fischer U, Rau N and Naber A 2005 Opt. Express 13 10688
[9] Wenger J and Rigneault H 2010 Int. J. Mol. Sci. 11 206–21
[10] Brun M, Drezet A, Mariette H, Chevalier N, Woelfl J C and Huant S 2003 Europhys. Lett. 64 634–40
[11] Bharadwaj P, Anger P and Novotny L 2007 Nanotechnology 18 044017
[12] Grynbeg G, Aspect A and Fabre C 2010 Quantum Optics (Paris: Cambridge University Press)
[13] Tanji-Suzuki H, Leroux I, Schleier-Smith M, Cetina M, Grier A, Simon J and Vuletic V 2011 Adv. At. Mol. Opt. Phys. 60 201–40
[14] Purcell E 1946 Phys. Rev. 69 681
[83] Nerkararyan K and Bozhevolnyi S 2014 *Opt. Lett.* **39** 1617–20
[84] Beveratos A, Gerard I A A and Robert-Philip I 2014 *Eur. Phys. J. D* **68** 377
[85] Grange T, Hornecker G, Hunger D, Poizat J, Gerard J, Senellart P and Augraves A 2015 *Phys. Rev. Lett.* **114** 193601
[86] Bergman D J and Stockman M I 2003 *Phys. Rev. Lett.* **90** 027402
[87] Protsenko I E, Uskov A V, Zaimidgora O A, Samoilov N V and O’Reilly E 2005 *Phys. Rev. A* **71** 063812
[88] Berini P and Leon I D 2012 *Nat. Photonics* **6** 16–24
[89] Winter G, Wedge S and Barnes W L 2006 *New J. Phys.* **8** 125
[90] De Leon I and Berini P 2008 *Phys. Rev. B* **78** 161401
[91] Colas des Francs G, Bramant P, Grandidier J, Bouthelier A, Weeber J C and Dereux A 2010 *Opt. Express* **18** 16327–34
[92] Grandidier J, Colas des Francs G, Massenot S, Bouthelier A, Weeber J C, Markey I and Dereux A 2010 *J. Microsc.* **239** 167–72
[93] Andrew P and Barnes W L 2000 Science **290** 785–8
[94] Martin-Cano D, Martin-Moreno L, Garcia-Vidal F and Moreno E 2010 *Nano Lett.* **10** 3129–34
[95] Gonzaga-Galeana J and Zurita-Sanchez J 2013 *J. Phys. Chem.* **139** 244302
[96] Karanikolas V, Marocico C and Bradley A L 2014 *Phys. Rev. A* **89** 063817
[97] Boucheït D, Cao D, Carminati R, Wilde Y D and Krachmalnicoff V 2015 arXiv:1507.04235
[98] Dzotian J, Sorensen A S and Fleischhauer M 2010 *Phys. Rev. B* **82** 075427
[99] Gonzalez-Tudela A, Martin-Cano D, Moreno E, Martin-Moreno L, Tejedor C and Garcia-Vidal F J 2011 *Phys. Rev. Lett.* **106** 020501
[100] Ford G W and Weber W H 1984 *Phys. Rep.* **113** 195–287
[101] Barnes W 1998 *J. Mod. Opt.* **45** 661–99
[102] Johnson P and Christy R 1972 *Phys. Rev. B* **6** 4370–9
[103] Chance R R, Brock A F and Silbey R 1975 *J. Chem. Phys.* **62** 2245–53
[104] Hinds E 1991 *Adv. At. Mol. Opt. Phys.* **28** 237–89
[105] Barthes J, Colas des Francs G, Bouthelier A, Weeber J C and Dereux A 2011 *Phys. Rev. B* **84** 073403
[106] Siahpoush V, Sondergaard T and Jung J 2012 *Phys. Rev. B* **85** 075035
[107] Colas des Francs G, Grandidier J, Massenot S, Bouthelier A, Weeber J C and Dereux A 2009 *Phys. Rev. B* **80** 151459
[108] Aouani H, Mahboub O, Bonod N, Devaux E, Popov E, Rigneault H, Ebbesen T W and Wenger J 2011 *Nano Lett.* **11** 637–44
[109] Choy J T, Bulu I, Hausmann B M, Janitz E, Huang I C and Loncar M 2013 *Appl. Phys. Lett.* **103** 161101
[110] Kumar A, Weeber J C, Bouthelier A, Eliot F, Buil S, Quelin X, Naslowski M, Dubertret B, Hermier J and Colas des Francs G 2015 *Sci. Rep.* **5** 16796
[111] Anemogiannis E, Glytsis E N and Gaylord T K 1999 *J. Lightwave Technol.* **17** 929–41
[112] Møller O, Huant S, Dantelle G, Gacoin T and Drezet A 2012 *Phys. Rev. B* **86** 045401
[113] Miroshnichenko A E, Flach S and Kivshar Y S 2010 *Rev. Mod. Phys.* **82** 2257–98
[114] Gallinet B and Martin O 2011 *Phys. Rev.* **B** **83** 235427
[115] Drezet A, Hohenau A, Koller D, Stepant A, Ditlbacher H, Steinberger B, Aussenegg F, Leitner A and Krenn J 2008 *Mater. Sci. Eng.* B **149** 230–9
[116] Bouthelier A, Colas des Francs G and Grandidier J 2012 Surface plasmon imaging *Plasmonics, From Basics to Advanced Topics* (Springer Series in Optical Sciences vol 167) (Berlin: Springer) pp 225–268
[117] Lakowicz J R 2005 *Anal. Biochemistry* **337** 171–94
[118] Raether H 1986 *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* (Berlin: Springer)
[153] Grigoriev V, Bonod N, Wenger J and Stout B 2015 ACS Photonics 2 263
[154] Carminati R, Grefet J, Henkel C and Vigoureux J 2006 Opt. Commun. 261 368–75
[155] Colas des Francs G, Girard C, Juan M and Dereux A 2005 J. Chem. Phys. 123 174709
[156] Colas des Francs G, Bouhelier A, Finot E, Weeber J C, Dereux A, Girard C and Dujardin E 2008 Opt. Express 16 17654–17666
[157] Deeb C et al 2010 ACS Nano 4 4579–86
[158] Zhou X et al 2014 Appl. Phys. Lett. 104 023114
[159] Khurgin J B and Sun G 2009 J. Opt. Soc. Am. B 26 B83–95
[160] Kim Y S, Leung P T and George T F 1988 Surf. Sci. 195 1–4
[161] Colas des Francs G, Derom S, Vincent R, Bouhelier A and Dereux A 2012 Int. J. Opt. 2012 175162
[162] Koenderink A F 2010 Opt. Lett. 35 4208–10
[163] Derom S, Vincent R, Bouhelier A and Colas des Francs G 2012 Europhys. Lett. 98 47008
[164] Sauvan C, Hugonin J P, Maksymov I S and Lalanne P 2013 Phys. Rev. Lett. 110 237401
[165] Zambrana-Puyal X and Bonod N 2015 Phys. Rev. B 91 195422
[166] Kristensen P, Ge R C and Hughes S 2015 Phys. Rev. A 92 053810
[167] Yang J, Perrin M and Lalanne P 2015 Phys. Rev. X 5 021008
[168] Leung P T 1990 Phys. Rev. B 42 7622
[169] Castanie E, Boffety M and Carminati R 2010 Opt. Lett. 35 291–3
[170] Girard C, Cuche A, Dujardin E, Arbouet A and Mlayah A 2015 Opt. Lett. 40 2116–9
[171] Anger P, Bharadwaj P and Novotny L 2006 Phys. Rev. Lett. 96 113002
[172] Kim J, Song J H, Jeong K Y, Ee H S and Seo M K 2015 Opt. Express 9 11080–91