Quantification des ondes de surface
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Sommaire

Dans ce chapitre, à partir d'une expression du champ des ondes de surface sous forme de somme de modes obtenue dans le chapitre 1, on détermine l'énergie associée à chacun de ces modes, puis on les quantifie canoniquement, chacun d'entre-eux étant analogue à un oscillateur harmonique – comme les modes du champ électromagnétique du vide (Loudon 2000). On obtient alors une expression des opérateurs associés au champ des ondes de surface, qui permet, dans le chapitre 5, de modéliser l'émission et l'absorption de phonons-polaritons de surface par transitions inter- et intrasousbandes des électrons d'un puits quantique.

Nous serons amenés au cours de ce chapitre à définir un facteur de Purcell associé à l'émission d'ondes de surface. Nous donnerons une expression de ce facteur de Purcell à partir du formalisme quantique que l'on développera, ainsi qu'à partir de l'expression du champ des ondes de surface dans le cas d'une fréquence complexe, obtenue au chapitre 1. Le traitement quantique négligeant les pertes des ondes de surface, une comparaison des deux facteurs de Purcell permettra d'estimer dans quelle mesure ce traitement quantique s'applique en présence de pertes.

La suite de ce chapitre et l'annexe F qui l'accompagne correspondent au contenu de (Archambault et al. 2010), auquel le lecteur peut se reporter s'il le souhaite.

4.1   Introduction originale

Quantum theory of light is a useful tool to describe microscopic interactions between light and matter. The electromagnetic state is represented by photon number states and the electromagnetic field becomes an operator(Loudon 2000). Such a description of light provides a quantitative description of absorption, spontaneous and stimulated emission of photons by a two-level system. In particular, it allows to derive a quantitative treatment of light amplification. It also predicts pure quantum effects, such as photon coalescence or antibunching. Quantum theory of light can be extended to non-dispersive and non-lossy media. Each photon in the material corresponds to the excitation of a mode characterized by a wave vector **k** and circular frequency ω, such as $k = n\omega/c$, where n is the refractive index of the medium and c the light velocity in a vacuum. It is the purpose of this paper to introduce a quantification scheme for surface waves propagating along an interface.

It is well known that electromagnetic surface waves called surface plasmons exist at interfaces between metals and dielectrics(Raether 1988). Their quantum nature has been demonstrated by energy loss spectroscopy experiments on thin metallic films reported by Powell and Swan(Powell et Swan 1959). Single optical plasmons have been excited recently along a metallic nanowire(Akimov et al. 2007 ; Kolesov et al. 2009) Surface plasmons are associated with collective oscillation of free electrons in the metal at the surface. Similar electromagnetic fields exist also on polar materials and are called surface phonon-polariton. Both surface plasmon-polaritons and surface phonon-polaritons propagate along the interface and decrease in the direction perpendicular to the surface. Such a resonance is therefore called surface wave in a more general way. Most studies deal with a plane interface between air or vacuum and a non-lossy material. In this case, it is well known(Raether 1988) that a surface wave can exist if the dielectric constant $\epsilon(\omega)$ has a real part lower than -1.

Losses are often a serious limitation for many practical applications envisionned for surface plasmons. This problem could be circumvented by introducing gain in the system. Studies have been made in such a way with metallic nanoparticles embedded in a gain medium both numerically with dye molecules (Smuk et Lawandy 2006) or quantum dots Bergman et Stockman 2003 ; Li et al. 2005 and experimentally Noginov et al. 2007. Seidel et al. reported the first experiment demonstrating the amplification of surface plasmons on a flat silver film surrounded by a solution of dye molecules Seidel et al. 2005. Since then, a few studies have dealt with stimulated emission of surface plasmons on flat interfaces both experimentally (Ambati et al. 2008b ; Noginov et al. 2008) and theoretically De Leon et Berini 2008. Such works have paved the way to active plasmonics (Ambati et al. 2008a ; MacDonald et al. 2008 ; Cao et Brongersma 2009) and nanolasers (Protsenko et al. 2005 ; Bergman et Stockman 2004) or more precisely to spasers (Bergman et Stockman 2003 ; Zheludev et al. 2008), or surface plasmon amplification by stimulated emission introduced by Bergman and Stockman and demonstrated experimentally recently(Noginov et al. 2009 ; Oulton et al. 2009).

It is clear that a quantum treatment of surface plasmon could be useful for many applications. For instance an efficient single photon emitter could be optimized(Barnes et al. 2002). A quantum treatment allows to

model stimulated emission and therefore to specify gain conditions and laser operation. It could also allow to analyse pure quantum effects for surface plasmons such as single plasmon interferences, quantum correlationsFasel et al. 2006, bunching, strong coupling regimeChang et al. 2006 ; Gong et Vuckovic 2007 or single photon excitation of surface plasmonAltewischer et al. 2002 ; Moreno et al. 2004 ; Fasel et al. 2005 ; Tame et al. 2008. To our knowledge, the first quantization scheme for surface plasmon on a metallic surface has been reported by Elson and Ritchie Elson et Ritchie 1971. In their work, the metal is characterized by a non-lossy Drude model so that real optical properties cannot be included. Using Green's approach, Gruner and Welsch introduce a quantization scheme for electromagnetic fields in dispersive and absorptive materials (Gruner et Welsch 1996). It should hence be possible to quantize the field associated with surface waves using their model. Note that due to losses, they cannot obtain operators for modes but only local operators : one recovers the usual creation/annihilation operators in the limit of zero losses. A related work, reported in the early nineties by Babiker et al., dealt with the quantization of interface optical phonons in quantum well, which could appear also as a confined surface phonon in a heterostructureBabiker et al. 1993.

In this paper, a quantization scheme that is not based on a specific model of the dielectric constant is introduced. The aim is to quantize the field by accounting for the experimental dispersion properties of the medium. The procedure follows the quantization scheme for photons in a vacuum. We will first introduce a classical mode description of the surface waves and discuss the dispersion relation. A key issue for quantization is the definition of the energy of surface waves for dispersive lossy media. The problem of electromagnetic energy in a dispersive and lossy medium has been recently addressed in a paper by Stallinga (Stallinga 2006). The third section addresses the problem of the electromagnetic energy associated with surface waves in a simpler case following Landau and Lifchitz for non-lossy dielectric material Landau et Lifshits 1984. The quantization scheme is finally described in the fourth section. In order to check our results, we apply our formalism in the fifth section to the calculation of the spontaneous emission of a two-level system in the presence of surface plasmons. The Purcell factor (i.e. the local density of states normalized by the vacuum density of states) and Einstein's coefficients are also derived using this model.

4.2 Modal description of surface waves

Let us consider surface waves propagating on a plane interface at $z = 0$ separating two semi-infinite media (Fig. 4.1). One of them is a vacuum or air and the second is a metal or a polar material. A surface mode is characterized by its circular frequency ω and the projection of the wave vector $\mathbf{K}$ on the plane perpendicular to the z-axis. The material has a dielectric constant $\epsilon(\omega)$. We use Coulomb's gauge (div$\mathbf{A}(\mathbf{r}, t) = 0$) to write the magnetic and electric fields :

$$\mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A}(\mathbf{r}, t) \tag{4.1}$$

$$\mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{A}(\mathbf{r}, t)}{\partial t} \tag{4.2}$$

The field produced by any distribution of sources in the presence of an interface can be computed using
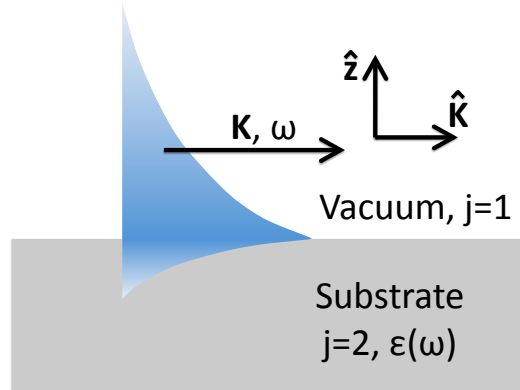
FIGURE 4.1 – Surface wave on a plane interface. The surface mode is characterized by its circular frequency ω and the projection of the wave vector along the interface **K**. $\hat{\mathbf{K}}$ and $\hat{\mathbf{z}}$ are unit vectors along and perpendicular to the plane interface respectively.

Green's tensor. By extracting the pole contribution, it is possible to derive the general form of the surface plasmon field. The details of this procedure can be found in (ARCHAMBAULT et al. 2009). The corresponding vector potential can be cast in the form :

$$\mathbf{A}(\mathbf{r}, t) = \int \frac{\mathrm{d}^2\mathbf{K}}{(2\pi)^2} \, \alpha_{\mathbf{K}} \mathbf{u}_{\mathbf{K}}(z) \, \exp(i\mathbf{K}.\mathbf{r}) \exp(-i\omega_{sp}t) + c.c. \tag{4.3}$$

where $c.c.$ stands for complex conjugate. In this equation, **K** is a real wave vector parallel to the interface and the circular frequency ω_{sp} is a complex root of the equation :

$$K = \frac{\omega}{c} \sqrt{\frac{\epsilon(\omega)}{\epsilon(\omega) + 1}} \tag{4.4}$$

The term $\alpha_{\mathbf{K}}$ is an amplitude associated with wave vector **K** in the decomposition. The vectors $\mathbf{u}_{\mathbf{K}}(z)$ are given by :

$$\mathbf{u}_{\mathbf{K}}(z) = \frac{1}{\sqrt{L(\omega_{sp})}} \exp(i\gamma_j z) \left(\hat{\mathbf{K}} - \frac{K}{\gamma_j} \hat{\mathbf{z}} \right) \tag{4.5}$$

where $L(\omega_{sp})$ has the dimension of a length and will be fixed later by Eq. (F.66) to normalize the energy of each mode. γ_j is the projection of the wave vector along the z-axis, $j = 1$ in the region $z > 0$, and $j = 2$ in the region $z < 0$, so that $\gamma_j^2 = \epsilon_j(\omega_{sp})\omega_{sp}^2/c^2 - K^2$. The sign of γ_j is then chosen such as the field goes to zero when z goes to $\pm\infty$. Let us note that in the non-lossy case, γ_1 and γ_2 are purely imaginary, so that the electric field decays exponentially along the z-axis. $\hat{\mathbf{K}}$ and $\hat{\mathbf{z}}$ are unit vectors directed along **K** and the z-axis respectively.

Figure 4.2 shows the dispersion relation of surface plasmons as well as the variation of the imaginary part
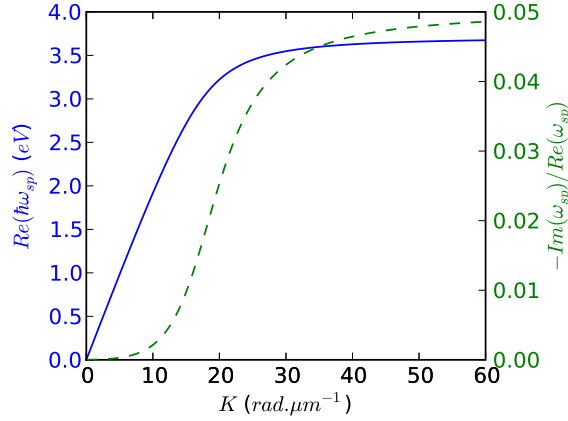
FIGURE 4.2 – (Color online). Dispersion relation of a surface plasmon on a plane interface between air and silver (solid line, left axis) and variation of the imaginary part of ω (dashed line, right axis). The dispersion relation has been obtained using the silver dielectric constant given in Appendix F.1

of the frequency with K on a plane interface of silver. To perform the calculations when a complex frequency is needed, it has been useful to fit the experimental values of the dielectric constant $\epsilon(\omega)$ given by (PALIK et GHOSH 1998) with an analytical model. The real part of the silver dielectric constant is very well represented by a Drude model given in (AMBATI et al. 2008a). For the imaginary part we add to this Drude model a conductivity term, so that the modelized dielectric constant is in very good agreement with the experimental data. The model we used is given in appendix F.1. In this example, $\text{Im}(\omega_{sp})$ is small, less than 5%, comparing to $\text{Re}(\omega_{sp})$. In other words, the lifetime of the surface mode is long enough to have a few tens of periods for the oscillating electromagnetic field on the asymptotic part of the dispersion relation and hundreds of periods on the linear part, close to the light cone. Note that this point seems to be rather general. Indeed we found similar ratios for many other materials supporting surface waves.

From the dispersion relation, it is possible to derive the density of states. To this aim, it is convenient to introduce a virtual box, which is in fact a virtual square in the $x - y$ plane of sides L_x and L_y and size $S = L_x \times L_y$. Born-Von Karman's conditions yields a quantized value of the wave vector $K_x = n_x 2\pi/L_x, K_y = n_y 2\pi/L_y$, where $n_{x,y}$ are relative integers. Let us note that a different expansion of the surface plasmon field can be used with a complex wave vector and a real frequency as discussed in (ARCHAMBAULT et al. 2009). We stress here that the Born-von Karman procedure imposes a real wave vector. It follows that the relevant dispersion relation has no backbending as seen in Fig. 4.2. The reader is refered to (ARCHAMBAULT et al. 2009) for more details. Substituting the discrete sum $\frac{1}{S}\sum_{\mathbf{K}}$ over the quantized wave vector $\mathbf{K}$ and the discrete amplitude $SA_{\mathbf{K}}$ to $\int \frac{\mathrm{d}^2\mathbf{K}}{(2\pi)^2}$ and $\alpha_{\mathbf{K}}$ respectively, the vector potential can be cast as

$$\mathbf{A}(\mathbf{r}, t) = \sum_{\mathbf{K}} A_{\mathbf{K}} \mathbf{u}_{\mathbf{K}}(z) \exp(i\mathbf{K}.\mathbf{r}) \exp(-i\omega t) + c.c. \tag{4.6}$$

where we have omitted the subscript sp for the circular frequency ω. We can insert this form in Eqs. (4.1) and (4.2) to obtain the electric and magnetic fields. Introducing the notations $\mathbf{k}_j = \mathbf{K} + \gamma_j \hat{\mathbf{z}}$ and $\mathbf{b}_{\mathbf{K}}(z) =$

$\mathbf{k}_j \times \mathbf{u_K}(z)$, we have :

$$
\begin{aligned}
\mathbf{E}(\mathbf{r}, t) &= i \sum_{\mathbf{K}} \omega A_{\mathbf{K}} \mathbf{u_K}(z) \exp(i\mathbf{K}.\mathbf{r}) \exp(-i\omega t) + c.c. & \text{(4.7a)} \\
\mathbf{B}(\mathbf{r}, t) &= i \sum_{\mathbf{K}} A_{\mathbf{K}} \mathbf{b_K}(z) \exp(i\mathbf{K}.\mathbf{r}) \exp(-i\omega t) + c.c. & \text{(4.7b)}
\end{aligned}
$$

4.3 Energy of a surface wave

The quantization procedure is based on the fact that the energy of the field has the structure of a sum of harmonic oscillators. It is thus a key issue to derive the energy of the surface plasmon field. In this section, we give a brief outline of the derivation and leave the details to appendix F.2 and F.5. In a vacuum, the energy density is given by(JACKSON 1999) :

$$
u_1 = \frac{\epsilon_0}{2}\mathbf{E}^2(\mathbf{r}, t) + \frac{1}{2\mu_0}\mathbf{B}^2(\mathbf{r}, t) \tag{4.8}
$$

The electromagnetic energy in a lossy dispersive material is a more subtle issue. This problem has been addressed for the first time by Brillouin(BRILLOUIN 1960). He considered a very simple case, with two perfectly monochromatic waves in the material. Landau and Lifchitz analysed(LANDAU et LIFSHITS 1984) the energy of an electromagnetic field in a non-lossy dispersive medium, whose frequencies form a narrow continuum around the mean frequency ω_0. They dealt with fields such as $\mathbf{E} = \mathbf{E}_0(t) \exp(-i\omega_0 t)$, $\mathbf{E}_0(t)$ varying slowly over the period $2\pi/\omega_0$. In the appendix, we follow this method. The main idea is to derive the work done by an external operator to build adiabatically the field amplitude. This work is equal to the total amount of electromagnetic energy of the surface waves for a non-lossy medium. Note that more recently, Stallinga derived an expression of the energy for dispersive and lossy materials(STALLINGA 2006). The result is the same provided that ϵ is replaced by $\text{Re}(\epsilon)$. This suggests that it is possible to neglect losses in the calculation of the energy. Actually, it is essential to deal with a non-lossy medium to have well-defined modes. A key issue regarding this approximation is whether the dispersion relation is modified by the presence of losses. Indeed, the density of states critically depends on the dispersion relation. We compared the dispersion relation obtained using $\text{Re}(\omega_{sp})$ for a lossy medium with the dispersion relation with a non-lossy medium in the case of silver. We found a relative difference between the two dispersion relations always less than 1.5×10^{-3}.

We will thus neglect the losses of the medium in the derivation of the energy. The calculation outlined in appendix F.2 gives the total energy of the surface waves :

$$
U = \sum_{\mathbf{K}} \epsilon_0 \omega^2 S \left[A_{\mathbf{K}} A_{\mathbf{K}}^* + A_{\mathbf{K}}^* A_{\mathbf{K}} \right]. \tag{4.9}
$$

We emphasize that this convenient expression for the energy is obtained using the right normalization condi-

tion on $L(\omega)$ or equivalently on $\mathbf{u_K}(z)$ given respectively by Eqs. (F.66) and (F.69).

4.4 Quantization of surface waves

We now turn to the quantization of the electromagnetic field of surface plasmons. We first notice that the expression $\epsilon_0\omega^2 S\left[A_\mathbf{K}A_\mathbf{K}^* + A_\mathbf{K}^* A_\mathbf{K}\right]$ of the energy for each mode $\mathbf{K}$, has the structure of the energy of a harmonic oscillator, hence the quantized hamiltonian :

$$\hat{H} = \sum_\mathbf{K} \frac{\hbar\omega}{2}\left[\hat{a}_\mathbf{K}\hat{a}_\mathbf{K}^\dagger + \hat{a}_\mathbf{K}^\dagger\hat{a}_\mathbf{K}\right] \tag{4.10}$$

with the equivalence

$$A_\mathbf{K} \rightarrow \sqrt{\frac{\hbar}{2\epsilon_0\omega S}}\,\hat{a}_\mathbf{K} \tag{4.11}$$

$$A_\mathbf{K}^* \rightarrow \sqrt{\frac{\hbar}{2\epsilon_0\omega S}}\,\hat{a}_\mathbf{K}^\dagger. \tag{4.12}$$

The surface wave field is thus quantized by association of a quantum-mechanical harmonic oscillator to each mode $\mathbf{K}$. We introduce $\hat{a}_\mathbf{K}^\dagger$ and $\hat{a}_\mathbf{K}$ which are respectively the creation and annihilation operators for the mode $\mathbf{K}$. As in the harmonic oscillator theory, $\hat{a}_\mathbf{K}^\dagger$ and $\hat{a}_\mathbf{K}$ act on surface wave number states $|n_\mathbf{K}\rangle$ which are eigenvectors associated with eigenvalues $(n_\mathbf{K} + 1/2)\hbar\omega$ of the Hamiltonian ($n_\mathbf{K}$ is an integer). Operators $\hat{a}_\mathbf{K}^\dagger$ (respectively $\hat{a}_\mathbf{K}$) allow to create (respectively destroy) a quantum of energy $\hbar\omega$ according to the operating rules(LOUDON 2000) :

$$\hat{a}_\mathbf{K}^\dagger|n_\mathbf{K}\rangle = \sqrt{n_\mathbf{K}+1}|n_\mathbf{K}+1\rangle \tag{4.13}$$

$$\hat{a}_\mathbf{K}|n_\mathbf{K}\rangle = \sqrt{n_\mathbf{K}}|n_\mathbf{K}-1\rangle \tag{4.14}$$

Different surface modes are independent so that their associated operators commute :

$$[\hat{a}_\mathbf{K}, \hat{a}_{\mathbf{K}'}^\dagger] = \delta_{\mathbf{K},\mathbf{K}'}. \tag{4.15}$$

We can now write the fields as operators acting on the surface plasmon number quantum states $|n_\mathbf{K}\rangle$:

$$\hat{\mathbf{E}}(\mathbf{r}, t) = i\sum_\mathbf{K} \sqrt{\frac{\hbar\omega}{2\epsilon_0 S}}\mathbf{u_K}(z)\,\hat{a}_\mathbf{K}\exp(i\mathbf{K}.\mathbf{r})\exp(-i\omega t) + h.c. \tag{4.16}$$

$$\hat{\mathbf{B}}(\mathbf{r}, t) = i\sum_\mathbf{K} \sqrt{\frac{\hbar}{2\epsilon_0\omega S}}\mathbf{b_K}(z)\,\hat{a}_\mathbf{K}\exp(i\mathbf{K}.\mathbf{r})\exp(-i\omega t) + h.c. \tag{4.17}$$

where $h.c.$ denotes the hermitian conjugate.

4.5 Emission rates : comparison with the classical case, Einstein's coefficients

4.5.1 Spontaneous emission of a dipole above a metallic interface

The quantization scheme that we have introduced allows to derive an expression of the electromagnetic field using operators. Hence, we can write interaction hamiltonians and describe the coupling between light and matter. In order to test this quantization procedure, we performed the calculation of the lifetime of a two-level system placed in the vicinity of a metal-vacuum interface so that surface plasmons can be excited. This result is interesting as the lifetime can also be computed using a classical approach as shown for instance by Ford and Weber (FORD et WEBER 1984). More specifically, they showed how to find the surface plasmon contribution to the lifetime by extracting the pole contribution. By comparing both results, we can assess the validity of the quantum theory of surface plasmon within the approximation of a dispersive but non-lossy medium.

4.5.1.1 Quantum calculation

In the quantum approach, we first derive the decay rate associated to the spontaneous emission of surface plasmons of a two-level quantum system close to an interface, using Fermi's golden rule. This gives the surface plasmon spontaneous emission rate as a function of the matrix element $\langle 2|\hat{\mathbf{D}}|1\rangle = \mathbf{D}_{12}$ of the dipole moment operator $\hat{\mathbf{D}}$. The details of the calculation are given in appendix F.3.

We obtain the following expression for the spontaneous emission rate :

$$\gamma_{spont}(\mathbf{D}_{12}, \omega_0, z) = \frac{\omega_0|\mathbf{D_{12}}|^2}{2\epsilon_0\hbar} K \frac{\mathrm{d}K}{\mathrm{d}\omega} \frac{1}{L_{eff}(z, \mathbf{d}_{12}, \omega_0)} \tag{4.18}$$

in which $\mathbf{d}_{12} = \mathbf{D}_{12}/|\mathbf{D}_{12}|$ is the (possibly complex) polarization of the dipole, $d_{12,z} = \mathbf{d}_{12}.\hat{\mathbf{z}}$, $\mathbf{d}_{12,//} = \mathbf{d}_{12} - d_{12,z}\hat{\mathbf{z}}$. We introduced the effective length of the surface plasmon mode $L_{eff}(z, \mathbf{d}_{12}, \omega_0)$,

$$\frac{1}{L_{eff}(z, \mathbf{d}_{12}, \omega_0)} = \frac{\exp(2i\gamma_1 z)}{L(\omega_0)} \left[\frac{1}{2}|\mathbf{d}_{12,//}|^2 - \epsilon(\omega_0)|d_{12,z}|^2\right]. \tag{4.19}$$

It will be seen later that this length allows to define an effective volume of the plasmon mode.

For comparison with the classical calculation, we normalize $\gamma_{spont}(\mathbf{D}_{12}, \omega_0, z)$ with the spontaneous emission rate of the same two-state quantum system in a vacuum, given by(LOUDON 2000) $\gamma_{spont}^0 = \frac{\omega_0^3|\mathbf{D}_{12}|^2}{3\pi\epsilon_0\hbar c^3}$. This gives the Purcell factor associated to the emission of surface plasmons :

$$F_P(\mathbf{d}_{12}, \omega_0, z) = \frac{3\pi c^3}{2\omega_0^2} K \frac{\mathrm{d}K}{\mathrm{d}\omega} \frac{1}{L_{eff}(z, \mathbf{d}_{12}, \omega_0)} \tag{4.20}$$

which does not depend anymore on the amplitude of $\mathbf{D}_{12}$, but only on its polarization $\mathbf{d}_{12}$, its frequency ω_0 and its distance to the interface z. As expected, the Purcell factor decreases exponentially as the dipole goes farther from the interface, and can have rather high values (see Fig. 4.3 and comments below) as ω_0 gets closer

to the asymptotic frequency of surface plasmons if the dipole is not too far from the interface.

This Purcell factor can also be cast under the form :

$$F_P(\mathbf{d}_{12}, \omega_0, z) = \omega_0 \, g(\omega_0) \, \frac{\lambda_0^3}{V_{eff}(z, \mathbf{d}_{12}, \omega_0)} \, \frac{3}{8\pi} \tag{4.21}$$

where the (global) density of states of surface plasmons $g(\omega)$ is given by $g(\omega) = S\frac{K}{2\pi}\frac{\mathrm{d}K}{\mathrm{d}\omega}$ and $V_{eff}(z, \mathbf{d}_{12}, \omega_0) = SL_{eff}(z, \mathbf{d}_{12}, \omega_0)$ is the volume of the surface plasmon modes of frequency ω_0 for a dipole polarization $\mathbf{d}_{12}$ in which the emission occurs. Eq. (4.21) is thus similar to the Purcell factor F_P of a dipole interacting with a single damped mode(PURCELL et al. 1946). ($F_P = Q\frac{\lambda^3}{V}\frac{3}{4\pi^2}$, or equivalently $F_P = \omega g(\omega)\frac{\lambda^3}{V}\frac{3}{8\pi}$ using the density of states of the single mode at resonance, $g(\omega) = \frac{2}{\pi}\frac{Q}{\omega}$.)

When dealing with an isotropic distribution of dipoles, the average of the rate of spontaneous emission (4.18), over the orientations of the dipole $\mathbf{D}_{12}$, should be considered. Let us first introduce the total effective length of the surface plasmon mode, defined as the inverse of the average of $\frac{1}{L_{eff}(z,\mathbf{d}_{12},\omega_0)}$ over the directions of $\mathbf{d}_{12}$:

$$\frac{1}{L_{eff,total}(z, \omega_0)} = \frac{1}{3}\frac{\exp(2i\gamma_1 z)}{L(\omega_0)}\left[1 + |\epsilon(\omega_0)|\right], \tag{4.22}$$

Calculating the averaged rate of spontaneous emission then amounts to replacing $L_{eff}(z, \mathbf{d}_{12}, \omega_0)$ by $L_{eff,total}(z, \omega_0)$ in Eq. (4.18) :

$$\gamma_{spont,total}(|\mathbf{D_{12}}|, \omega_0, z) = \frac{\omega_0|\mathbf{D_{12}}|^2}{2\epsilon_0\hbar}K\frac{\mathrm{d}K}{\mathrm{d}\omega}\frac{1}{L_{eff,total}(z, \omega_0)}. \tag{4.23}$$

More details are given in appendix F.3.

4.5.1.2 Classical approach

In the previous section, we considered a two-level quantum system having a given polarization $\mathbf{d}_{12}$ and Bohr circular frequency ω_0, and we normalized its spontaneous emission rate by its value in a vacuum. The power radiated by a classical harmonic dipole having the same polarization $\mathbf{d}_{12}$ and a circular frequency ω_0 can also be normalized by its value in a vacuum. Both expressions give the normalized local density of states, which is a classical quantity. They are therefore equal, that is the normalized radiated power gives the normalized spontaneous emission rate. The normalized radiated power can be expressed as a function of Green's tensor $\overleftrightarrow{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega)$ of the system :

$$F_{P,cl}(\mathbf{d}_{12}, \omega_0, z) = \frac{6\pi c}{\omega_0}\mathrm{Im}\left[\mathbf{d}_{12}^*.\overleftrightarrow{\mathbf{G}}(z\hat{\mathbf{z}}, z\hat{\mathbf{z}}, \omega_0)\mathbf{d}_{12}\right]. \tag{4.24}$$

Following the steps detailed in (ARCHAMBAULT et al. 2009), the pole contribution $\overleftrightarrow{\mathbf{G}}_{sp}$ of Green's tensor of a plane interface can be derived, and inserted in Eq. (4.24). We use here the pole contribution of the surface plasmon with a complex frequency (see (ARCHAMBAULT et al. 2009)). The details of the calculation are given

in appendix F.4. One finds for the normalized radiated power in the non-lossy case :

$$F_{P,cl}(\mathbf{d}_{12}, \omega_0, z) = \frac{3\pi c^3}{\omega_0^3} K^3 \frac{\mathrm{d}K}{\mathrm{d}\omega} R(K, \omega_0) \exp(2i\gamma_1 z) \left[\frac{1}{2} |\mathbf{d}_{12,//}|^2 - \epsilon(\omega_0)|d_{12,z}|^2 \right]. \qquad (4.25)$$

Using Eq. (F.71) and comparing Eq. (4.25) to Eq. (4.20), we see easily that $F_P(\mathbf{d}_{12}, \omega_0, z) = F_{P,cl}(\mathbf{d}_{12}, \omega_0, z)$. We thus recover the quantum spontaneous emission rate in the non lossy limit of the above classical approach. This result is not surprising. Indeed the normalized spontaneous emission rate yields the local density of states. The latter is a classical quantity. In the quantum approach, it has been calculated using the dispersion relation. In the classical approach, it has been calculated using the Green's tensor. We have thus checked that the mode approach and the Green's formalism approach are equivalent. We now go one step further and compare the quantum approach (without losses) with the Green's tensor approach that accounts for losses. We compute the spontaneous emission rate for both cases in order to assess the role of losses.

4.5.1.3   Comparison with the lossy case

The lossy and non lossy emission rates are compared using Eqs. (4.20) and (F.40). The result is seen on Fig. 4.3 for a dipole located at three different distances of a silver surface (10, 75 and 250 nm). It appears that the differences between both curves in this case are still very small as long as the frequency is not too close from the asymptote of the dispersion relation. This is not surprising considering the fact that at this asymptotic value the losses are the most important. Moreover, when the distance between the dipole and the interface increases, the part of the electromagnetic field due to the higher surface plasmons wave vector decreases, so that the part due to the surface plasmons lying on the linear part of the dispersion relation is more important. As seen in Fig.4.2, these surface waves have less losses and the quantum approach is thus more accurate. It follows the important conclusion that the non-lossy medium approximation in the quantum treatment is reasonable to deal with surface waves provided that the frequency is not too close to the asymptotic value.

Note that (FORD et WEBER 1984) provides an expression for the surface plasmon emission rate of a dipole close to an interface, which can be compared to ours (details not given here). In the non lossy case, it can be proved analytically that their results lead to the same normalized emission rate as Eq. (4.20). In the lossy case, one finds a normalized emission rate close to the one used here (Eq. (F.40)), although they are not rigorously equal. Our method gives an expression of the normalized surface plasmon emission rate as a sum over the modes **K** (see Eq. (F.36)), which provides a better understanding of the difference between the lossy and the non lossy cases.

4.5.2   Einstein's coefficients

A quantum approach for surface waves allows us also to derive easily Einstein's coefficients for spontaneous and stimulated emission. The same example of a dipole above the interface is taken. Once again, it is possible to follow the approach described for photons in (LOUDON 2000) for instance. Einstein's coefficient for surface plasmon spontaneous emission has already been calculated : $A_{21} = \gamma_{spont}(\mathbf{D}_{12}, \omega_0, z)$ (see Eq. (4.18)). In
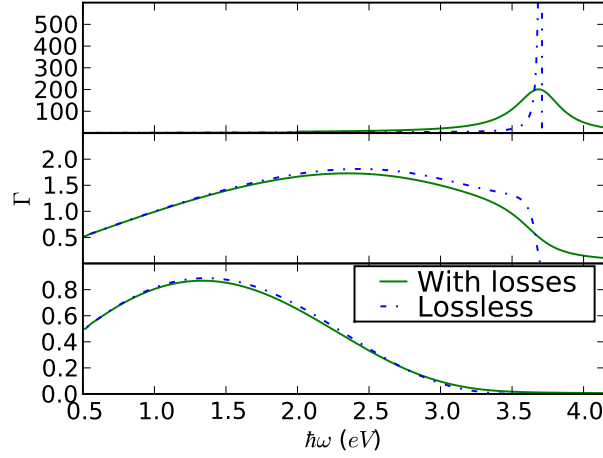
FIGURE 4.3 – (Color online). Normalized emission rate F_P of a vertical dipole located at 10 nm (top), 75 nm (center) and 250 nm (bottom) from the surface when taking into account losses (solid lines) comparing to the non-lossy cases (dashdotted lines).

order to obtain Einstein's coefficient for stimulated emission, one needs to start from Eq. (F.28). In this equation, the term proportional to $n_{\mathbf{K}}$ is the matrix element for stimulated emission. We note $\langle W(\omega) \rangle$ the energy density of the radiation per unit surface and we assume that it varies slowly for frequencies near ω_0. The total energy in the single mode $n_{\mathbf{K}}$ is now replaced by :

$$n_{\mathbf{K}} \hbar \omega \to S \int \mathrm{d}\omega \langle W(\omega) \rangle \tag{4.26}$$

The transition rate due to stimulated emission can thus be written :

$$\gamma_{stim}(\mathbf{D}_{12}, \omega_0, z) = \frac{2\pi}{\hbar^2} \int \mathrm{d}\omega \langle W(\omega) \rangle \frac{1}{2\epsilon_0} \left| \mathbf{D}_{12} . \mathbf{u}_{\mathbf{K}}(\mathbf{r}) \right|^2 \ \delta(\omega - \omega_0) \tag{4.27}$$

It follows that Einstein's coefficient for stimulated emission in mode $\mathbf{K}$, $B_{21} = \gamma_{stim}(\mathbf{D}_{12}, \omega_0, z)/\langle W(\omega_0) \rangle$, is given by :

$$B_{21} = \frac{\pi |\mathbf{D}_{12}|^2}{\epsilon_0 \hbar^2} \frac{\exp(2i\gamma_1 z)}{L(\omega_0)} \left| d_{12,//} \cos \phi - \frac{K}{\gamma_1} d_{12,z} \right|^2 \tag{4.28}$$

where $d_{12,//}$ and $d_{12,z}$ are defined above, and ϕ is the angle between the projection of $\mathbf{D}_{12}$ on the interface and $\mathbf{K}$. When dealing with an isotropic distribution of dipoles, B_{12} should be averaged over the directions of $\mathbf{D}_{12}$, in the same way as in Sec. (4.5.1.1). We get the total Einstein coefficient for stimulated emission in mode $\mathbf{K}$

$$B_{21,total} = \frac{\pi |\mathbf{D}_{12}|^2}{3\epsilon_0 \hbar^2} \frac{\exp(2i\gamma_1 z)}{L(\omega_0)} \left[1 - \epsilon(\omega_0) \right] \tag{4.29}$$

To describe the amplification of a surface plasmon beam by an amplifying medium, it is interesting to derive the ratio $r(\omega_0, z) = A_{21}^{(i)}(|\mathbf{D}_{12}|, \omega_0, z)/B_{21,total}(|\mathbf{D}_{12}|, \omega_0, z)$, where $A_{21}^{(i)}(|\mathbf{D}_{12}|, \omega_0, z) = \gamma_{spont}^0 \langle F_{P,cl}^{(i)}(\mathbf{d}_{12}, \omega_0, z) \rangle$ stands for the total spontaneous emission rate of the dipole close to the interface ((i) denotes interface), and

γ^0_{spont} is given above. It can be computed with Eq. (4.24), using Green's tensor of a plane interface (this rate includes all the waves that can be emitted, not only surface plasmons). $\langle \cdot \rangle$ stands for average over the orientations $\mathbf{d}_{12}$ of the dipole. $r(\omega_0, z)$ gives the threshold energy per unit surface $W_c(\omega_0)$ at which the stimulated emission rate equals the spontaneous one. It can be written as :

$$r(\omega_0, z) = r^0(\omega_0) \frac{\langle F^{(i)}_{P,cl}(\mathbf{d}_{12}, \omega_0, z) \rangle}{\exp(2i\gamma_1 z)\left[1 - \epsilon(\omega_0)\right]} L(\omega_0) \tag{4.30}$$

where $r^0(\omega_0) = \frac{\hbar \omega^3}{\pi^2 c^3}$ is the ratio of the Einstein's coefficients in a vacuum. Fig. 4.4 shows $r(\omega, z)$ as a function of ω. From 0 to approximately 35 nm, the ratio decreases, mainly because the (total) spontaneous emission rate $A^{(i)}_{21}$ decreases. Above 35 nm, the ratio increases, as B_{21} decreases, because of the exponential decay of the surface plasmon field away from this interface. Note that for a given frequency ω, $r(\omega_0, z)$ rises at lower distances for ω closer to the surface plasmon asymptote frequency.
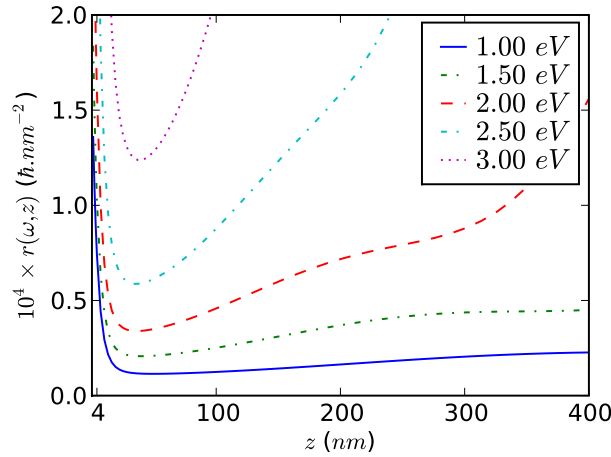

FIGURE 4.4 – (Color online). Ratio of Einstein's coefficients $r(\omega, z)$ for (total) spontaneous emission and stimulated emission of surface plasmons as a function of the distance to the interface, for several values of ω (see legend).

These results can be used to calculate the amount of power that undergoes stimulated emission of surface plasmons in a gain medium in close vicinity of the silver interface. We consider a parallel beam of surface plasmons. and suppose that they are excited via a grating or a prism by a He-Ne laser whose emission has a linewidth of about $\Delta\omega = 10$ MHz centered around $\omega_0 = 2$ eV, and that they carry $P = 1$ mW of power per μm. The spectral power at maximum, assuming a lorentzian profile, is given by $P_\omega(\omega_0) = P/\pi\Delta\omega$, and the associated spectral energy per unit surface is $W(\omega_0) = P_\omega(\omega_0)/v_g = \frac{P}{\pi\Delta\omega\, v_g}$ where $v_g = \frac{dK}{d\omega}$ is the group velocity of surface plasmons, close to c below the asymptote frequency. The spectral energy per unit surface at maximum of these surface plasmons is then $W(\omega_0) \approx \frac{P}{\pi\Delta\omega\, c} \approx 10^3\ \hbar.\text{nm}^2$. This value is far above those of Fig. 4.4 : stimulated emission in a freely propagating surface plasmon beam is several orders of magnitude higher than spontaneous emission.

4.6   Conclusion

In this paper, we have extended previous work on quantization of surface plasmons by introducing a formalism that can use experimental values of the dielectric constant instead of using a specific model for the free electron gas. The key step is the derivation of the energy of a surface plasmon in a dispersive non-lossy medium. The standard quantization scheme in Coulomb's gauge yields the quantum form of the field. This scheme can be extended in a straigthforward way to thin metallic films. To illustrate the formalism, we have derived the spontaneous emission rate of surface plasmons by a two-level system placed close to an interface supporting surface waves as well as Einstein's coefficients. This quantized theory of surface plasmon will be useful to analyse specific quantum effects such as antibunching, single plasmon interference, quantum coherence properties, but also to derive the interactions of surface waves with other quantum objects, as quantum wells for example.