2. Surface Plasmons on Smooth Surfaces

In this chapter the fundamental properties of SPs are reviewed and thus give the background for Chaps. 3–7.

2.1 Fundamental Properties: Dispersion Relation, Extension and Propagation Length for the Electromagnetic Fields of the Surface Plasmons

Dispersion Relation

The electron charges on a metal boundary can perform coherent fluctuations which are called surface plasma oscillations, *Ritchie* [2.1]. Their existence has been demonstrated in electron energy-loss experiments by *Powell* and *Swan* [2.2]. The frequency ω of these longitudinal oscillations is tied to its wave vector k_x by a dispersion relation $\omega(k_x)$. These charge fluctuations, which can be localized in the z direction within the Thomas-Fermi screening length of about 1 Å, are accompanied by a mixed transversal and longitudinal electromagnetic field which disappears at $|z|\to\infty$, Fig. 2.1, and has its maximum in the surface $z = 0$, typical for surface waves. This explains their sensitivity to surface properties. The field is described by

$$E = E_0^{\pm}\exp\left[+i(k_x x \pm k_z z - \omega t)\right] \tag{2.1}$$

with + for $z\geq 0$, − for $z\leq 0$, and with imaginary k_z, which causes the exponential decay of the field E_z. The wave vector k_x lies parallel to the x direction; $k_x = 2\pi/\lambda_p$, where λ_p is the wavelength of the plasma oscillation. Maxwell's

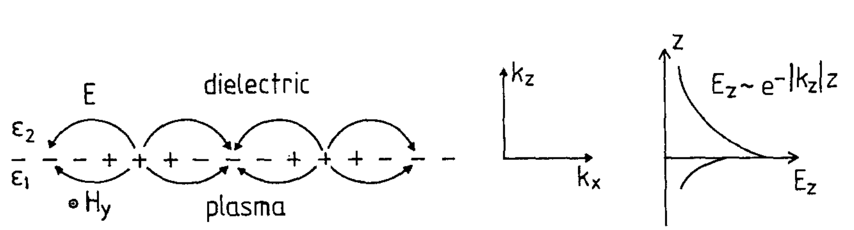

Fig. 2.1. The charges and the electromagnetic field of SPs propagating on a surface in the x direction are shown schematically. The exponential dependence of the field E_z is seen on the right. H_y shows the magnetic field in the y direction of this p-polarized wave

equations yield the retarded dispersion relation for the plane surface of a semi-infinite metal with the dielectric function ($\varepsilon_1 = \varepsilon_1' + i\varepsilon_1''$), adjacent to a medium ε_2 as air or vacuum:

$$D_0 = \frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0 \qquad \text{together with} \tag{2.2}$$

$$\varepsilon_i \left(\frac{\omega}{c}\right)^2 = k_x^2 + k_{zi}^2 \quad \text{or} \tag{2.3}$$

$$k_{zi} = \left[\varepsilon_i \left(\frac{\omega}{c}\right)^2 - k_x^2\right]^{1/2} \quad , \quad i = 1, 2 \ .$$

The wave vector k_x is continuous through the interface (for the derivation see Appendix I). The dispersion relation (2.2) can be written as

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right)^{1/2} \ . \tag{2.4}$$

If we assume besides a real ω and ε_2 that $\varepsilon_1'' < |\varepsilon_1'|$, we obtain a complex $k_x = k_x' + ik_x''$ with

$$k_x' = \frac{\omega}{c}\left(\frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2}\right)^{1/2} \tag{2.5}$$

$$k_x'' = \frac{\omega}{c}\left(\frac{\varepsilon_1' \varepsilon_2}{\varepsilon_1' + \varepsilon_2}\right)^{3/2} \frac{\varepsilon_1''}{2(\varepsilon_1')^2} \ . \tag{2.6}$$

For real k_x' one needs $\varepsilon_1' < 0$ and $|\varepsilon_1'| > \varepsilon_2$, which can be fulfilled in a metal and also in a doped semiconductor near the eigen frequency; k_x'' determines the internal absorption, see below. In the following we write k_x in general instead of k_x'.

The dispersion relation, see Fig. 2.2, approaches the light line $\sqrt{\varepsilon_2}\omega/c$ at small k_x, but remains larger than $\sqrt{\varepsilon_2}\omega/c$, so that the SPs cannot transform into light: it is a "nonradiative" SP, see below. At large k_x or

$$\varepsilon_1' \rightarrow -\varepsilon_2 \tag{2.7}$$

the value of ω approaches

$$\omega_{\mathrm{sp}} = \left(\frac{\omega_{\mathrm{p}}}{1 + \varepsilon_2}\right)^{1/2} \tag{2.8}$$

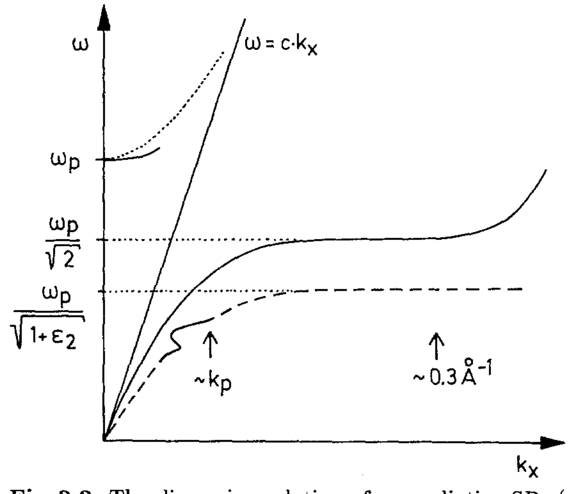

Fig. 2.2. The dispersion relation of nonradiative SPs (——), right of the light line $\omega = ck_x$; the retardation region extends from $k_x = 0$ up to about $k_p = 2\pi/\lambda_p$ (λ_p plasma wavelength). The dashed line, right of $\omega = ck_x$, represents SPs on a metal surface coated with a dielectric film (ε_2). Left of the light line, $\omega(k_x)$ of the radiative SPs starts at ω_p (——). (The *dotted line* represents the dispersion of light in a metal: $\omega/k_x = c/|\varepsilon_1'|^{1/2}$ or in the case of free electrons $\omega^2 = \omega_p^2 + c^2k_x^2$.) The slight modulation in the dashed dispersion curve comes from an eigen frequency in a monomolecular dye film deposited on a Langmuir-Blodgett film (ε_2). The latter depresses $\omega_p/\sqrt{2}$ to $\omega_p/\sqrt{1+\varepsilon_2}$

for a free electron gas where ω_p is the plasma frequency $\sqrt{4\pi ne^2/m}$, with n the bulk electron density. With increasing ε_2, the value of ω_{sp} is reduced.

At large k_x the group velocity goes to zero as well as the phase velocity, so that the SP resembles a localized fluctuation of the electron plasma.

Spatial Extension of the SP Fields

Wave vectors k_{z2} and k_{z1} are imaginary due to the relations $\omega/c<k_x$ and $\varepsilon_1'<0$, see (2.3), so that, as mentioned above, the field amplitude of the SPs decreases exponentially as $\exp(-|k_{zi}||z|)$, normal to the surface. The value of the (skin) depth at which the field falls to 1/e, becomes

$$\hat{z} = \frac{1}{|k_{zi}|} \quad \text{or} \tag{2.9}$$

$$\begin{aligned} &\text{in the medium with } \varepsilon_2: \quad \hat{z}_2 = \frac{\lambda}{2\pi}\left(\frac{\varepsilon_1' + \varepsilon_2}{\varepsilon_2^2}\right)^{1/2} \\ &\text{in the metal with } \varepsilon_1: \quad \hat{z}_1 = \frac{\lambda}{2\pi}\left(\frac{\varepsilon_1' + \varepsilon_2}{\varepsilon_1'^2}\right)^{1/2} . \end{aligned} \tag{2.10}$$

For $\lambda = 6000$ Å one obtaines for silver $\hat{z}_2 = 3900$ Å and $\hat{z}_1 = 240$ Å, and for gold 2800 Å and 310 Å, respectively.

At large k_x, $\hat{z}_i$ is given by about $1/k_x$ leading to a strong concentration of the field near the surface in both media.

At low k_x or large $|\varepsilon_1'|$ values, the field in air has a strong (transverse) component E_z compared to the (longitudinal) component E_x, namely $E_z/E_x = -i|\varepsilon_1'|^{1/2}$ and extends far into the air space; it resembles thus a guided photon field (Zenneck-Sommerfeld wave). In the metal, E_z is small against E_x since $E_z/E_x = i|\varepsilon_1'|^{-1/2}$. These relations are derived from div$\boldsymbol{E} = 0$, valid outside the surface air/metal. At large k_x both components E_x and E_z become equal: $E_z = \pm iE_x$ (air: $+i$, metal: $-i$).

Propagation Length of the SPs

The intensity of SPs propagating along a smooth surface decreases as $e^{-2k_x''x}$ with k_x'' from (2.6). The length L_i after which the intensity decreases to $1/e$ is then given by

$$L_i = (2k_x'')^{-1} \ . \tag{2.11}$$

In the visible region, L_i reaches the value of $L_i = 22\,\mu$ in silver at $\lambda = 5145\,\text{Å}$ and $L_i = 500\,\mu$ (0.05 cm) at $\lambda = 10\,600\,\text{Å}$. The absorbed energy heats the film, and can be measured with a photoacoustic cell, see Sect. 2.3.

Instead of regarding the spatial decay of the SPs along the coordinate x, the temporal decay time T_i can be of interest. The values of L_i and T_i are correlated by $L_i = T_i v_g$ with v_g the group velocity. Assuming a complex $\omega = \omega' - i\omega''$ and real k_x', with $T_i = 2\pi/\omega''$, we obtain from (2.4)

$$\omega'' = k_x' c \frac{\varepsilon_1''}{2(\varepsilon_1')^2} \frac{\varepsilon_1' \cdot \varepsilon_2}{\varepsilon_1' + \varepsilon_2}$$

$$\omega' = k_x' c \frac{\varepsilon_1' + \varepsilon_2^{1/2}}{\varepsilon_1' \varepsilon_2} \ . \tag{2.12}$$

More detailed information on SPs can be found in [2.3–5].

2.2 Excitation of Surface Plasmons by Electrons and by Light

Excitation by Electrons

Electrons penetrating a solid transfer momentum $\hbar q$ and energy ΔE_0 to the electrons of the solid. The projection of q upon the surface of the film k_x determines the wave vector and, together with the dispersion relation, the energy loss of the scattered electron $\Delta E = \hbar\omega$, see Fig. 2.3. Since the electrons are scattered at different angles θ, they transfer different momenta $\hbar k_x = \hbar k_{\text{el}}' \sin\theta \cong \hbar k_{\text{el}}\theta$ with $k_{\text{el}} = 2\pi/\lambda_{\text{el}}$. If one observes the energy loss $\Delta E = \hbar\omega$ at an increasing angle θ (or smaller λ_{el}) the dispersion relation of the SPs can be measured up to large k_x beyond the Brillouin zone. The physics of SPs has thus been studied intensively with electrons, especially with fast electrons, and the fundamen-