Plasmon resonance

1. What is plasmon ?

Plasmons are explained in the classical picture using the Drude model of metals. The metal is treated as a three dimensional crystal of positively charged ions, and a delocalized electron gas is moving in a periodic potential of this ion grid.

and, consequently, χ must be expressed as a tensor. We shall find that the χ tensor of a crystal summarizes most of its optical properties.

6.3 The General Wave Equation

In our study of solid-state optics we shall be concerned only with nonmagnetic, electrically neutral media. Hence **M** and ρ are both zero. Maxwell's equations, in the form expressed by Equations (6.1) to (6.4), then reduce to the following:

$$\nabla \times \mathbf{E} = -\mu_0 \frac{\partial \mathbf{H}}{\partial t} \tag{6.10}$$

$$\nabla \times \mathbf{H} = \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \frac{\partial \mathbf{P}}{\partial t} + \mathbf{J} \tag{6.11}$$

$$\nabla \cdot \mathbf{E} = -\frac{1}{\epsilon_0} \nabla \cdot \mathbf{P} \tag{6.12}$$

$$\nabla \cdot \mathbf{H} = 0 \tag{6.13}$$

The general wave equation for the **E** field is obtained by taking the curl of Equation (6.10) and the time derivative of Equation (6.11) and eliminating **H**. The result is

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} = -\mu_0 \frac{\partial^2 \mathbf{P}}{\partial t^2} - \mu_0 \frac{\partial \mathbf{J}}{\partial t} \tag{6.14}$$

The two terms on the right-hand side of the above equation are called *source terms*. They stem from the presence of polarization charges and conduction charges, respectively, within the medium. The way in which the propagation of light is affected by the sources is revealed by the solution of the wave equation when the source terms are included. In the case of nonconducting media the polarization term $-\mu_0\, \partial^2\mathbf{P}/\partial t^2$ is of importance. It turns out that this term leads to an explanation of many optical effects, including dispersion, absorption, double refraction, and optical activity to mention only a few. In the case of metals it is the conduction term $-\mu_0\, \partial\mathbf{J}/\partial t$ that is important, and the resulting solutions of the wave equation explain the large opacity and high reflectance of metals. Both source terms must be taken into account in the case of semiconductors. The result is a rather complicated wave equation and the solutions are somewhat difficult to interpret. Nevertheless, a qualitative description of many of the optical properties of semiconductors is furnished by classical theory. A rigorous treatment of semiconductor optics must await the application of quantum theory.

6.4 Propagation of Light in Isotropic Dielectrics. Dispersion

In a nonconducting, isotropic medium, the electrons are permanently bound to the atoms comprising the medium and there is no preferential direction. This is what is meant by a simple isotropic dielectric such as glass. Suppose that each electron, of charge $-e$, in a dielectric is displaced a distance **r** from its equilibrium position. The resulting macroscopic polarization **P** of the medium is given by

$$\mathbf{P} = -Ne\mathbf{r} \tag{6.15}$$

where N is the number of electrons per unit volume. If the displacement of the electron is the result of the application of a static electric field **E**, and if the electron is elastically bound to its equilibrium position with a force constant K, then the force equation is

$$-e\mathbf{E} = K\mathbf{r} \tag{6.16}$$

The *static* polarization is therefore given by

$$\mathbf{P} = \frac{Ne^2}{K} \mathbf{E} \tag{6.17}$$

However, if the impressed field **E** varies with time, the above equation is incorrect. In order to find the true polarization in this case, we must take the actual motion of the electrons into account. To do this we consider the bound electrons as classical damped harmonic oscillators. The differential equation of motion is

$$m \frac{d^2\mathbf{r}}{dt^2} + m\gamma \frac{d\mathbf{r}}{dt} + K\mathbf{r} = -e\mathbf{E} \tag{6.18}$$

The term $m\gamma\,(d\mathbf{r}/dt)$ represents a frictional damping force that is proportional to the velocity of the electron, the proportionality constant being written as $m\gamma$.[1]

Now suppose that the applied electric field varies harmonically with time according to the usual factor $e^{-i\omega t}$. Assuming that the motion of the electron has the same harmonic time dependence, we find that Equation (6.18) becomes

$$(-m\omega^2 - i\omega m\gamma + K)\mathbf{r} = -e\mathbf{E} \tag{6.19}$$

Consequently, the polarization, from Equation (6.15), is given by

$$\mathbf{P} = \frac{Ne^2}{-m\omega^2 - i\omega m\gamma + K} \mathbf{E} \tag{6.20}$$

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[1] The magnetic force $e\mathbf{v}\times\mathbf{B}$ is neglected here. For electromagnetic waves, this force is normally much smaller than the electric force $e\mathbf{E}$.

It reduces to the static value, Equation (6.17), when $\omega = 0$. Thus for a given amplitude of the impressed electric field, the amount of polarization varies with frequency. The phase of **P**, relative to that of the electric field, also depends on the frequency. This is shown by the presence of the imaginary term in the denominator.

A more significant way of writing Equation (6.20) is

$$\mathbf{P} = \frac{Ne^2/m}{\omega_0{}^2 - \omega^2 - i\omega\gamma}\mathbf{E} \tag{6.21}$$

in which we have introduced the abbreviation ω_0 given by

$$\omega_0 = \sqrt{\frac{K}{m}} \tag{6.22}$$

This is the *effective resonance frequency* of the bound electrons.

The polarization formula (6.21) is similar to the amplitude formula for a driven harmonic oscillator, as indeed it should be, since it is the displacement of the elastically bound electrons that actually constitutes the polarization. We should therefore expect to find an optical resonance phenomenon of some kind occurring for light frequencies in the neighborhood of the resonance frequency ω_0. As we shall presently see, this resonance phenomenon is manifest as a large change in the index of refraction of the medium and also by a strong absorption of light at or near the resonance frequency.

To show how the polarization affects the propagation of light, we return to the general wave equation (6.14). For a dielectric there is no conduction term. The polarization is given by Equation (6.21). Hence we have

$$\nabla \times (\nabla \times \mathbf{E}) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{-\mu_0 N e^2}{m}\left(\frac{1}{\omega_0{}^2 - \omega^2 - i\gamma\omega}\right)\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{6.23}$$

Also, from the linear relationship between **P** and **E**, it follows from (6.12) that $\nabla \cdot \mathbf{E} = 0$. Consequently, $\nabla \times (\nabla \times \mathbf{E}) = -\nabla^2 \mathbf{E}$, and the above wave equation reduces to the somewhat simpler one

$$\nabla^2 \mathbf{E} = \frac{1}{c^2}\left(1 + \frac{Ne^2}{m\epsilon_0}\cdot\frac{1}{\omega_0{}^2 - \omega^2 - i\gamma\omega}\right)\frac{\partial^2 \mathbf{E}}{\partial t^2} \tag{6.24}$$

after rearranging terms and using the relation $1/c^2 = \mu_0\epsilon_0$.

Let us seek a solution of the form

$$\mathbf{E} = \mathbf{E}_0\, e^{i(\mathscr{K} z - \omega t)} \tag{6.25}$$

This trial solution represents what are called *homogeneous* plane harmonic waves. Direct substitution shows that this is a possible solution provided that

$$\mathscr{K}^2 = \frac{\omega^2}{c^2}\left(1 + \frac{Ne^2}{m\epsilon_0}\cdot\frac{1}{\omega_0{}^2 - \omega^2 - i\gamma\omega}\right) \tag{6.26}$$

The presence of the imaginary term in the denominator implies that the wavenumber $\mathscr{K}$ must be a complex number. Let us inquire as to the physical significance of this. We express $\mathscr{K}$ in terms of its real and imaginary parts as

$$\mathscr{K} = k + i\alpha \tag{6.27}$$

This amounts to the same thing as introducing a complex index of refraction

$$\mathscr{N} = n + i\kappa \tag{6.28}$$

where

$$\mathscr{K} = \frac{\omega}{c}\mathscr{N} \tag{6.29}$$

Our solution in Equation (6.25) can then be written as

$$\mathbf{E} = \mathbf{E}_0 e^{-\alpha z}\, e^{i(kz - \omega t)} \tag{6.30}$$

The factor $e^{-\alpha z}$ indicates that the amplitude of the wave decreases exponentially with distance. This means that as the wave progresses, the energy of the wave is absorbed by the medium. Since the energy in the wave at a given point is proportional to $|\mathbf{E}|^2$, then the energy varies with distance as $e^{-2\alpha z}$. Hence 2α is the *coefficient of absorption* of the medium. The imaginary part κ of the complex index of refraction is known as the *extinction index*. The two numbers α and κ are related by the equation

$$\alpha = \frac{\omega}{c}\kappa \tag{6.31}$$

The phase factor $e^{i(kz-\omega t)}$ indicates that we have a harmonic wave in which the phase velocity is

$$u = \frac{\omega}{k} = \frac{c}{n} \tag{6.32}$$

From Equations (6.26) and (6.29) we have

$$\mathscr{N}^2 = (n + i\kappa)^2 = 1 + \frac{Ne^2}{m\epsilon_0}\left(\frac{1}{\omega_0{}^2 - \omega^2 - i\gamma\omega}\right) \tag{6.33}$$

Equating real and imaginary parts yields the following equations:

$$n^2 - \kappa^2 = 1 + \frac{Ne^2}{m\epsilon_0}\left(\frac{\omega_0{}^2 - \omega^2}{(\omega_0{}^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{6.34}$$

$$2n\kappa = \frac{Ne^2}{m\epsilon_0}\left(\frac{\gamma\omega}{(\omega_0{}^2 - \omega^2)^2 + \gamma^2\omega^2}\right) \tag{6.35}$$

from which the optical parameters n and κ may be found.

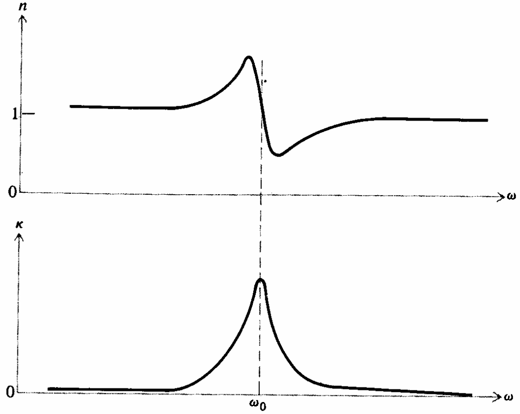


Figure 6.1. Graphs of the index of refraction and extinction coefficient versus frequency near a single resonance line.

Figure 6.1 shows the general way in which n and κ depend on frequency. The absorption is strongest at the resonance frequency ω_0. The index of refraction is greater than unity for small frequencies and increases with frequency as the resonance frequency is approached. This is the case of "normal" dispersion, which is exhibited by most transparent substances over the visible region of the spectrum, the principal resonance frequencies being in the ultraviolet region. At or near the resonance frequency, however, the dispersion becomes "anomalous" in the sense that the index of refraction *decreases* with increasing frequency.

Anomalous dispersion can be observed experimentally if the substance is not too opaque at the resonance frequency. For instance, certain dyes have absorption bands in the visible region of the spectrum and exhibit anomalous dispersion in the region of these bands. Prisms made of these dyes produce a spectrum that is reversed; that is, the longer wavelengths are refracted more than the shorter wavelengths.

Now, in the above discussion it has been tacitly assumed that all of the electrons were identically bound, and hence all had the same resonance frequencies. In order to take into account the fact that different electrons may be bound differently, we may assume that a certain fraction f_1 has an associated resonance frequency ω_1, a fraction f_2 has the resonance frequency ω_2, and so on. The resulting formula for the square of the complex index of refraction is of the form

$$\mathcal{N}^2 = 1 + \frac{Ne^2}{m\epsilon_0} \sum_j \left(\frac{f_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega} \right) \tag{6.36}$$

The summation extends over all the various kinds of electrons indicated by the subscript j. The fractions f_j are known as *oscillator strengths*. The damping constants associated with the various frequencies are denoted by γ_j. Figure 6.2 shows graphically the general dependence of the real and imaginary parts of $\mathcal{N}$ as determined by Equation (6.36). This graph is intended to show qualitatively the case for a substance, such as glass, which is transparent in the visible region and has absorption bands in the infrared and ultraviolet regions of the spectrum. In the limit of zero frequency, the square of the index approaches the value $1 + (Ne^2/m\epsilon_0)\ \Sigma f_j/\omega_j^2$. This is just the static dielectric constant of the medium.

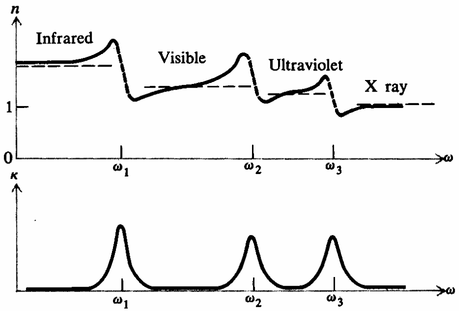


Figure 6.2. Index of refraction and extinction index for a hypothetical substance with absorption bands in the infrared, visible, and ultraviolet regions of the spectrum.

In the high-frequency region, the theory predicts that the index should dip below unity and then approach unity from below as ω becomes infinite. This effect is actually seen experimentally. The case of quartz is shown in Figure 6.3. Here the measured index of refraction of quartz is plotted as a function of wavelength for the appropriate region of the spectrum (x-ray region).

If the damping constants γ_j are sufficiently small so that the terms $\gamma_j\omega$ can be neglected in comparison to the quantities $\omega_j^2 - \omega^2$ in Equation (6.36), then the index of refraction is essentially real and its square is given by

$$n^2 = 1 + \frac{Ne^2}{m\epsilon_0} \sum_j \left(\frac{f_j}{\omega_j^2 - \omega^2} \right) \tag{6.37}$$

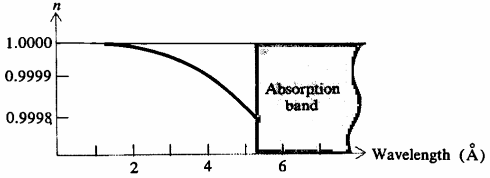


Figure 6.3. Measured index of refraction of quartz in the x-ray region.

It is possible, by an impirical curve-fitting procedure, to make a formula of the above type match the experimental data quite well for many transparent substances. When expressed in terms of wavelength instead of frequency, the equation is known as *Sellmeier's formula.*

6.5 Propagation of Light in Conducting Media

The effects of conduction on the propagation of light through a medium can be treated in much the same manner as the effects of polarization were treated in the preceding section. The difference is that we are now interested in the conduction term in the general wave equation, not the polarization term. Again, owing to the inertia of the conduction electrons, we cannot merely put $\mathbf{J} = \sigma\mathbf{E}$ for the current density where σ is the static conductivity. We must consider actual motion of the electrons under the action of the alternating electric field of the light wave.

Since the conduction electrons are not bound, there is no elastic restoring force as there was in the case of polarization. The differential equation of motion of the electron is therefore of the form

$$m\frac{d\mathbf{v}}{dt} + m\tau^{-1}\mathbf{v} = -e\mathbf{E} \qquad (6.38)$$

where $\mathbf{v}$ is the velocity of the electron. The frictional dissipation constant is expressed in the form $m\tau^{-1}$. This constant is related to the static conductivity as we shall presently see. Since the current density is

$$\mathbf{J} = -Ne\mathbf{v} \qquad (6.39)$$

where N is now the number of conduction electrons per unit volume, then Equation (6.38) can be expressed in terms of $\mathbf{J}$ as follows:

$$\frac{d\mathbf{J}}{dt} + \tau^{-1}\mathbf{J} = \frac{Ne^2}{m}\mathbf{E} \qquad (6.40)$$

The decay of a transient current is governed by the associated homogeneous equation

$$\frac{d\mathbf{J}}{dt} + \tau^{-1}\mathbf{J} = 0 \qquad (6.41)$$

whose solution is $\mathbf{J} = \mathbf{J}_0 e^{-t/\tau}$. Thus a transient current will decay to e^{-1} of its initial value in a time τ. This is called the *relaxation time.* Now for a static electric field, Equation (6.40) becomes

$$\tau^{-1}\mathbf{J} = \frac{Ne^2}{m}\mathbf{E} \qquad (6.42)$$

The static conductivity σ is therefore given by

$$\sigma = \frac{Ne^2}{m}\tau \qquad (6.43)$$

Let us now assume a harmonic time dependence $e^{-i\omega t}$ for both electric field $\mathbf{E}$ and the resulting current $\mathbf{J}$ in our differential Equation (6.40). It follows that

$$(-i\omega + \tau^{-1})\mathbf{J} = \frac{Ne^2}{m}\mathbf{E} = \tau^{-1}\sigma\mathbf{E} \qquad (6.44)$$

Solving for $\mathbf{J}$, we find

$$\mathbf{J} = \frac{\sigma}{1 - i\omega\tau}\mathbf{E} \qquad (6.45)$$

When $\omega = 0$, the above equation reduces to $\mathbf{J} = \sigma\mathbf{E}$, which is the correct equation for the static case.

Using the dynamic expression for $\mathbf{J}$, we find that the general wave Equation (6.14) reduces to

$$\nabla^2\mathbf{E} = \frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2} + \frac{\mu_0\sigma}{1 - i\omega\tau}\frac{\partial\mathbf{E}}{\partial t} \qquad (6.46)$$

For a trial solution we take a simple homogeneous plane-wave solution of the type

$$\mathbf{E} = \mathbf{E}_0\, e^{i(\mathscr{K}z - \omega t)} \qquad (6.47)$$

where, as in Equation (6.26), $\mathscr{K}$ is assumed to be complex. It is easily found that $\mathscr{K}$ must then satisfy the relation

$$\mathscr{K}^2 = \frac{\omega^2}{c^2} + \frac{i\omega\mu_0\sigma}{1 - i\omega\tau} \qquad (6.48)$$

For very low frequencies the above formula reduces to the approximate formula

$$\mathscr{K}^2 \approx i\omega\mu_0\sigma \qquad (6.49)$$

so that $\mathcal{K} \approx \sqrt{i\omega\mu_0\sigma} = (1 + i)\sqrt{\omega\mu_0\sigma/2}$. In this case the real and imaginary parts of $\mathcal{K} = k + i\alpha$ are equal and are given by

$$k \approx \alpha \approx \sqrt{\frac{\omega\sigma\mu_0}{2}} \tag{6.50}$$

Similarly the real and imaginary parts of $\mathcal{N} = n + i\kappa$ are equal and are given by

$$n \approx \kappa \approx \sqrt{\frac{\sigma}{2\omega\epsilon_0}} \tag{6.51}$$

The so-called "skin depth" δ of a metal is that distance at which the amplitude of an electromagnetic wave drops to e^{-1} of its value at the surface. Thus

$$\delta = \frac{1}{\alpha} = \sqrt{\frac{2}{\omega\sigma\mu_0}} = \sqrt{\frac{\lambda_0}{c\pi\sigma\mu_0}} \tag{6.52}$$

where λ_0 is the vacuum wavelength. This shows why good conductors are also highly opaque. A high value of the conductivity σ gives a large coefficient of absorption α and a correspondingly small skin depth. For example, the skin depth in copper ($\sigma = 5.8 \times 10^7$ mho/m) for 1-mm microwaves is about 10^{-4} mm.

Let us return to the more accurate expression for $\mathcal{K}$ given in Equation (6.48). The equivalent form of this equation written in terms of the complex index of refraction, as defined by Equation (6.29), is

$$\mathcal{N}^2 = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\tau^{-1}} \tag{6.53}$$

Here we have introduced *plasma frequency* for the metal. It is defined by the relations

$$\omega_p = \sqrt{\frac{Ne^2}{m\epsilon_0}} = \sqrt{\frac{\mu_0\sigma c^2}{\tau}} \tag{6.54}$$

By equating real and imaginary parts in Equation (6.53), we find

$$n^2 - \kappa^2 = 1 - \frac{\omega_p^2}{\omega^2 + \tau^{-2}} \tag{6.55}$$

$$2n\kappa = \frac{\omega_p^2}{\omega^2 + \tau^{-2}}\left(\frac{1}{\omega\tau}\right) \tag{6.56}$$

from which the optical "constants" n and κ may be obtained. An explicit algebraic solution of the above pairs of equations is very cumbersome, hence the equations are usually solved numerically for n and κ. According to the above theory, these are determined entirely by the plasma frequency ω_p, the relaxation time τ, and the frequency ω of the light wave.

Typical relaxation times for metals, as deduced from conductivity measurements, are of the order of 10^{-13} s, which corresponds to frequencies in the infrared region of the spectrum. On the other hand plasma frequencies of metals are typically around 10^{15} s^{-1}, corresponding to the visible and near ultraviolet regions. Figure 6.4 shows the behavior of n and κ plotted as functions of ω-from Equations (6.55) and (6.56). As seen from the figure, the index of refraction n is less than unity for a wide range of frequencies in the region of the plasma frequency. The extinction coefficient κ is very large at low frequencies (long wavelengths). It decreases monotonically with increasing frequency, becoming very small for frequencies greater than the plasma frequency. The metal thus becomes transparent at high frequencies. Qualitative agreement with these predictions of classical theory is obtained in the case of the alkali metals and some of the better conductors such as silver, gold, and copper.

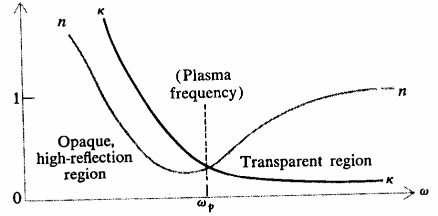


Figure 6.4. Index of refraction and extinction index versus frequency for a metal.

For poor conductors and semiconductors, both free electrons and bound electrons can contribute to the optical properties. Classical theory would, accordingly, yield an equation of the type

$$\mathcal{N}^2 = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\tau^{-1}} + \frac{Ne^2}{m\epsilon_0}\sum_j\left(\frac{f_j}{\omega_j^2 - \omega^2 - i\gamma_j\omega}\right) \tag{6.57}$$

for the complex index of refraction. It turns out that quantum theory gives a similar relation and, in addition, can predict the values of the various parameters f_j, γ_j, and so forth. The theoretical calculations are difficult, however, as are also the experimental measurements. The optics of semiconductors is one of the most active areas of current experimental and theoretical research.

$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2}$$

Plasma resonances for various geometries

Material	Resonance condition	Resonance Frequency
Bulk Metal	$\varepsilon_{eff} = 0$	ω_p
Planar Surface	$\varepsilon_{eff} = -\varepsilon_d$	$\frac{\omega_p}{\sqrt{2}}$
Sphere	$\varepsilon_{eff} = -2\varepsilon_d$	$\frac{\omega_p}{\sqrt{3}}$
Ellipsoid	$\varepsilon_{eff} = -\frac{1-L_M}{L_M}$	$\omega_p L_M$

Optical Properties of Metal Clusters
Kreibig and Vollmer,1995

$$K_i^2 = k^2 - \frac{\varepsilon_i \omega^2}{c^2}$$

We now have enough information to determine the fields to within a scale factor. In the dielectric (medium 1), we define

$$E_{1x} = Ae^{-K_1 x} e^{i(kz - \omega t)}$$

The scalar quantity A represents a scale factor to be determined. From Gauss' s Law we may derive E_z

$$E_{1z} = \frac{K_1}{ik} E_{1x} = A \frac{K_1}{ik} e^{-K_1 x} e^{i(kz - \omega t)}$$

Likewise for the conductor, we may derive E_x and E_z. In this case, we set the scale factor to unity, as only the relative scale factor carries importance.

$$E_{2x} = e^{-K_2 x} e^{i(kz - \omega t)}$$

$$E_{2z} = \frac{K_2}{ik} e^{-K_2 x} e^{i(kz - \omega t)}$$

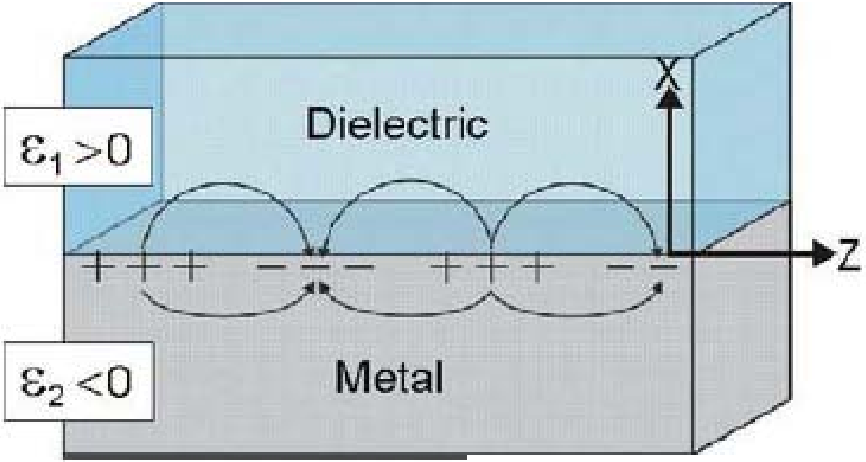
Applying the electromagnetic boundary conditions at the interface allows one to then solve for A. The continuity of E_z and D_z yield

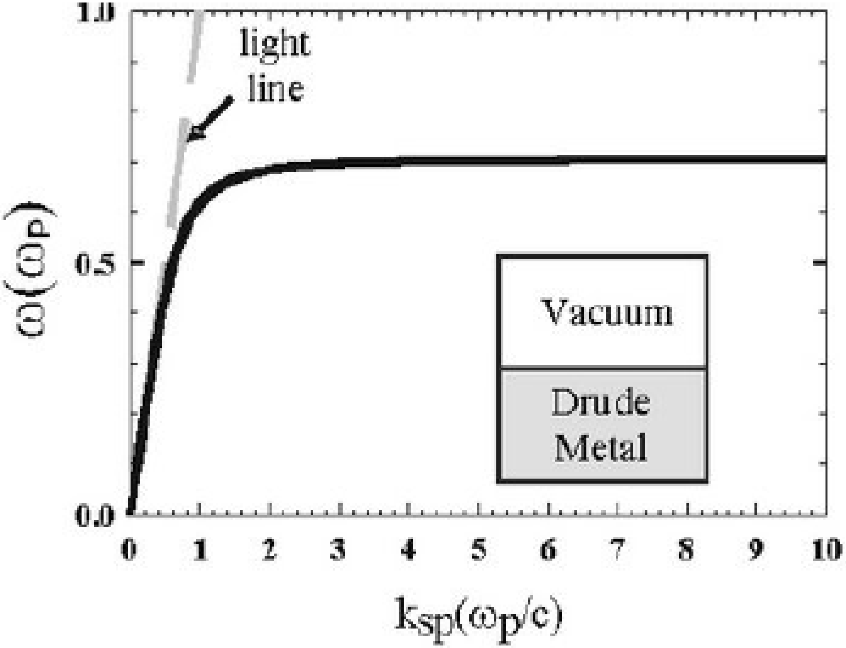
$$A = \frac{\varepsilon_2}{\varepsilon_1} = -\frac{K_2}{K_1}$$

Some simple algebra may then be used to solve for k, finally generating the dispersion relation for these simple surface plasmon modes[x].

$$k = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$

The wave-vector is no longer a linear function of permittivity as in standard dielectrics. Because we have the sum of dielectrics of opposite sign in the denominator, very large wave-vectors are possible.


ε₁ > 0
Dielectric
X
Z
+ + + − − − + + + − −
ε₂ < 0
Metal


1.0
0.5
0.0
light line
ω(ωp)
Vacuum
Drude Metal
0 1 2 3 4 5 6 7 8 9 10
ksp(ωp/c)