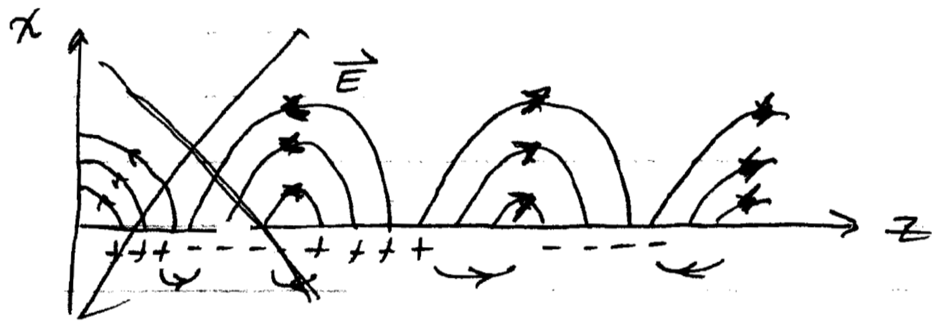
Lecture 16-1

Field configurations of surface plasmons



$\vec{H} = H\hat{y}$

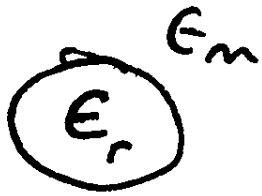
Applications of surface plasmons

1. explain anomalies in diffraction efficiency of diffraction gratings ("Wood's anomalies ")
2. Surface plasmon waveguides (e.g . in mid-IR "quantum cascade lasers ")
3. optical modes of metal nanostructures

- local field enhancements (up to $10^3\times$)
- surface – enhanced Raman scattering :
  Single-molecule spectroscopy

See W.L.Bornes, et al .Nature 424,824(2003)

Spherical particles



ε_r : Relative dielectric constant of particle

ε_m : Relative dielectric constant of surrounding medium

Induced dipole $\vec{P} = \varepsilon_m \alpha \vec{E}$

$$\alpha = 4\pi a^3 \frac{\varepsilon_r - \varepsilon_m}{\varepsilon_r + 2\varepsilon_m} \quad \text{in electrostatics approximation (ok if } a \ll \lambda \text{)}$$

For a metal nanoparticle $\varepsilon_r = \varepsilon_r(\omega)$ plasma dielectric const.

$$\sim \varepsilon_L (1 - \frac{\omega_p^2}{\omega^2}) \quad \text{Neglecting damping}$$

A pole of the response function (polarizability) is the natural oscillation frequency:

$$\varepsilon_r = -2\varepsilon_m$$

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

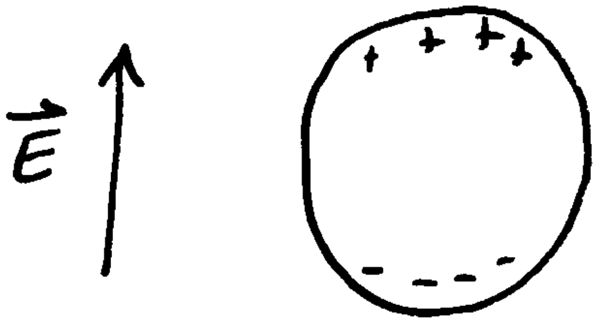
$$1-\frac{\omega_p^2}{\omega^2} = -2\frac{\varepsilon_m}{\varepsilon_L}$$

$$\omega^2\left(1+2\frac{\varepsilon_m}{\varepsilon_L}\right) = \omega_p^2$$

$$\omega = \frac{\omega_p}{\sqrt{1+2\frac{\varepsilon_m}{\varepsilon_L}}} \qquad \text{or} \qquad \boxed{\omega = \frac{\omega_p}{\sqrt{3}}} \quad \text{for common case of } \varepsilon_m = \varepsilon_L = 1$$

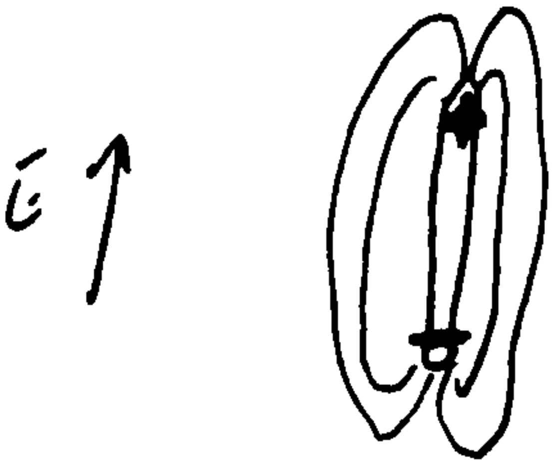
Physically

$\frac{\omega_p}{\sqrt{3}}$ = natural osc. Freq. of spatial charge oscillations
(induced charge is on the surface of the sphere => this is also referred to as a surface plasmon)



• Small (sub-λ) metal particles show absorption is scattering resonances in the visible region of the spectrum (=> strongly colored)

- metal nanoparticles finding many applications in biotechnology/nanotechnology
- collide suspensions of nanoparticles were used in ancient times to make colored glazes
- field enhancement:



Linear Response and Kramers – Kronig Relations

Returning to our expression an page 99 for the linear electric susceptibility

$$\chi(\omega) = -\chi_0'' \left[\frac{\Delta y}{1+(\Delta y)^2} + i\frac{1}{1+(\Delta y)^2} \right]$$

It seems that the functional forms of the real and imaginary parts are related somehow. It turns out there is a precise general relationship between the real and imaginary parts of any physical susceptibility, which we will prove here.

This can be important in some instances, since the relationship means that if one (real or imaginary) part is known, then the other is determined.

The consequence is that of if you can measure the absorption spectrum of a sample (I.e. the imaginary part), then you can calculate from that the spectrum of the index of refraction (I.e. the real part).

We need to note two features of our CEO model in particular:

(1) the response is linear in the field : P $\propto$ E

(2) the response is causal: consider an impulsive excitation $E = E_0\delta(t)$.The dipole must be zero before the impulse arrived ,and will be a damped oscillation for t>0.

What we shall show is that, for any system which is both linear and causal, the real and imaginary parts of χ are related. (Of course, not all physical systems are linear, but they are causal!)

Let's first look at the consequence of causality in a linear system. The most general expansion for the polarization induced in a medium by a field E is

$$\vec{P}(t) = \varepsilon_0 \int_{-\infty}^{\infty} \chi(t,t')\vec{E}(t')dt'$$

Where $\chi(t,t')$ is the response function in the first term. In general, the polarization induced depends on the absolute time it is excited by E, but only on the time difference $t-t'$ (i.e. χ is "time-shift invariant")

$$\vec{P}(t) = \varepsilon_0 \int_{-\infty}^{\infty} \chi(t-t')\vec{E}(t')dt'$$

We also know the response is causal, which means that the response P. cannot before the stimulus, i.e.

$$\chi(t-t') = 0 \quad \text{for} \quad t' > t$$

Then we can write

(*) $$\vec{P}(t) = \varepsilon_0 \int_{-\infty}^{t} \chi(t-t')\vec{E}(t')dt'$$

Now let us see what this looks like in the frequency domain. Following the notation convention in Guenther chap 6, the Fourier transform $F(\omega)$ of a function f(t) is

$$F\{f(t)\} = F(\omega) = \int_{-\infty}^{\infty} f(t)e^{-i\omega t}dt$$

And the inverse transform relation is

$$F^{-1}\{F(\omega)\} = f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} F(\omega)e^{i\omega t}d\omega$$

Thus we can introduce the Fourier transforms of the different functions in (*)

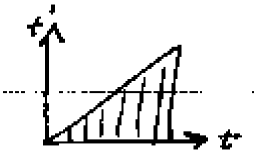
$$\vec{P}(\omega) = \int_{-\infty}^{\infty} \vec{P}(t)e^{-i\omega t}dt$$

$$\vec{E}(\omega) = \int_{-\infty}^{\infty} \vec{E}(t)e^{-i\omega t}dt$$

$$\chi(\omega) = \int_{-\infty}^{\infty} \chi(t-t')e^{-i\omega(t-t')}dt$$

We insert (*) into the above eqn, for $\vec{P}(\omega)$:

$$\vec{P}(\omega) = \int_{-\infty}^{\infty} dte^{-i\omega t}\int_{-\infty}^{t} \varepsilon_0\chi(t-t')\vec{E}(t')dt' = \varepsilon_0\int_{-\infty}^{\infty} dte^{-i\omega t}\int_{-\infty}^{t}\chi(t-t')\vec{E}(t')dt'$$



Since $\chi(t-t') = 0$ for $t' > t$

Trick: introduce $1 = e^{i\omega t'}e^{-i\omega t'}$ in the integral and rearrange:

$$\vec{P}(\omega) = \varepsilon_0 \underbrace{\int_{-\infty}^{\infty} dt'e^{-i\omega t'}\vec{E}(t')}_{\vec{E}(\omega)} \underbrace{\int_{-\infty}^{\infty} dte^{-i\omega(t-t')}\chi(t-t')}_{\chi(\omega)}$$

Or $\boxed{\vec{P}(\omega) = \varepsilon_0\chi(\omega)\vec{E}(\omega)}$

This is just what we found for our specific CEO model. However, the general conclusion is that, for any physical system (i.e. one obeying causality and time-shift invariance) in the linear response regime, the response of the system may be written as above. The polarization induced at one frequency depends only in the amplitude of the driving field at that frequency.

Note that in the frequency domain, and simply multiplied the response function χ by the driving field E to get the resulting polarization.

In the time domain, the polarization is a convolution of the response of the response function with the driving field.

Note also that sometimes $\chi(t-t')$ is called the impulse response of the system. This is for the simple reason that if the dipoles are given a δ - function “kick” at time t_0, then

$$\vec{P}(t) = \varepsilon_0\int_{-\infty}^{\infty}\chi(t-t')\vec{E}(t')dt' = \varepsilon_0\int_{-\infty}^{\infty}\chi(t-t')\vec{E}_0\delta(t'-t_0)dt' = \varepsilon_0\chi(t-t_0)\vec{E}_0$$

Example; harmonic oscillator (CEO) model impulse response

We have (see P.90)

$$\chi(\omega)=\frac{\omega_p^2}{\omega_0^2-\omega^2+i\omega\gamma}$$

Where we have defined (as in Guenther notation)

$$\omega_p^2=\frac{Ne^2}{\varepsilon_0 m}$$

And γ is really $\gamma+\frac{2}{T'}$, but I've left it as γ for convenience.

We want

$$\chi(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\chi(\omega)e^{i\omega t}d\omega$$

$$\chi(t)=\frac{\omega_p^2}{2\pi}\int_{-\infty}^{\infty}\frac{e^{i\omega t}}{\omega_0^2-\omega^2+i\omega\gamma}d\omega$$

It is useful to factorize the denominator "

$$-(\omega-\omega_1)(\omega-\omega_2)=-\omega^2+(\omega_1+\omega_2)\omega-\omega_1\omega_2=\omega_0^2-\omega^2+i\omega\gamma \quad \text{Required}$$

=> $-\omega_1\omega_2=\omega_0^2$ and $\omega_1+\omega_2=i\gamma$

$$\omega_1=-\frac{\omega_0^2}{\omega_2}\Rightarrow-\frac{\omega_0^2}{\omega_2}+\omega_2=i\gamma$$

$$\omega_2{}^2-i\gamma\omega_2-\omega_0^2=0$$

$$\omega_2=\frac{i\gamma\pm\sqrt{-\gamma^2+4\omega_0^2}}{2}=i\frac{\gamma}{2}\pm\sqrt{\omega_0^2-\gamma^2/4}$$

--in fact ω_1 is the same, but $\pm$, so the two roots are

$$\omega_{1,2}=i\frac{\gamma}{2}\pm\sqrt{\omega_0^2-\gamma^2/4} \quad \text{def. } \upsilon_0^2=\omega_0^2-\gamma^2/4$$

$$(*) \qquad \chi(t)=-\frac{\omega_p^2}{2\pi}\int_{-\infty}^{\infty}\frac{e^{i\omega t}}{(\omega-\omega_1)(\omega-\omega_2)}d\omega$$

Crucial note: notice that ω_1 and ω_2 are complex quantities now! They are like complex frequencies, with an imaginary part arising from the damping.

As a result of expressions like this, it is clear that it can be very useful, then, to consider the possibility of the angular frequency being considered to be a complex variable, rather than the real variable we have always considered it to be .

In other words, we can write a field

$$E(t) = E_0 e^{i\omega t}$$

Where now, not only are E and E_0 complex (which we do in order to account for phase), but ω is complex, too.

This extension of the definition of E is often called the "complex analytic signal" associated with the physical electric field.

Note how damping naturally comes in this formulation.

Decompose ω into its real and imaginary parts

$$\omega = \omega_r + i\Gamma$$

=> $$E(t) = E_0 e^{i(\omega_r + i\Gamma)t} = E_0 e^{-\Gamma t} e^{i\omega_r t}$$

As usual, the physically significant (i.e. measurable) part of E is the real part

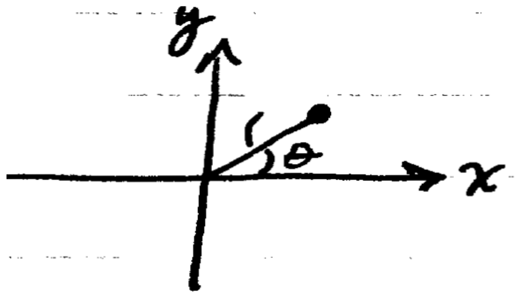
$$\mathrm{Re}(E) = (\mathrm{Re}\, E_0) e^{-\Gamma t} \cos(\omega_r t + \phi)$$

Clearly the real part of ω corresponds to the frequency of the harmonic oscillation, and the imaginary part corresponds to the temporal damping of the field. (or polarization)

Now that we are free to consider ω as a complex variable, we can go back to our integral (*) p.114. It will be instructive to use complex-variable integration methods to evaluate the integral.

Digression: A review of some important results in complex-function theory.

Complex variable $z = x + iy = re^{i\theta}$



Complex function f(z)

Derivative: as usual

$$\frac{df}{dz} = \lim_{\Delta z \to 0} \frac{f(z + \Delta z) - f(z)}{\Delta z} = f'(z)$$

If the derivative exists in a region R of the complex plane, f is said to be analytic in R.

$f(z_0)$ is analytic at z_0 if there is neighborhood $|z - z_0| < \delta$ at all points of which $f'(z)$ exist.

Quite often, functions we are interested in fail to be analytic in a very specific way.

A point at which f fails to be analytic is called a singularity.

z_0 is called an isolated singularity of f if we can find $\delta > 0$ such that the circle $|z - z_0| = \delta$ encloses no singular point other than z_0

A specific functional form containing an isolated singularity is $f(z)=\dfrac{g(z)}{z-z_0}$

Where $g(z)$ is analytic in a region containing z_0

A function of this form is said to have a <u>simple pole</u> of $z=z_0$

Def.: if $\lim\limits_{z\to\Delta z}(z-z_0)^n f(z)=A\neq 0$

Then $z=z_0$ is called a <u>pole of order n.</u>

Ex. $f(z)=\dfrac{1}{(z-z_0)\left(z-z_0'\right)^3}$

Has a simple pole at z_0 and a third order pole at $z=z_0'$

It should be clear why functions like this are interesting in linear response theory. Look at the integrand in (*) p.114

$\dfrac{e^{i\omega t}}{(\omega-\omega_1)(\omega-\omega_2)}$ has simple poles at ω_1 and ω_2 .