10. Optics of metals - plasmons

Drude theory at higher frequencies

The Drude scattering time corresponds to the frictional damping rate

The ultraviolet transparency of metals

Interface waves - surface plasmons

Plasmon excitations of metal nanoparticles
A few announcements

• Problem set 4 will be posted on Friday. It will include a note reminding you to sign up for an exam time slot.

• It will be due on Monday Feb. 25th (not on a Friday!).

• **Sign-up for Exam 1** will be posted with the problem set. AFTER it is posted:
  - You will need to email Dr. Mittleman to sign up for a time slot.
  - Email only. No other method is acceptable.
  - Include both a 1st choice AND a 2nd choice.
  - Time slots assigned on a first-email, first-allocated basis.
  - Sign-up deadline is Friday Feb. 22, before class.
  - **IF YOU WILL BE UNAVAILABLE ON THOSE DATES:** contact Dr. Mittleman **IMMEDIATELY** to arrange an alternative.
Our ‘guess’ from the last lecture…

Recall the inhomogeneous wave equation:

$$\frac{\partial^2 E}{\partial z^2} - \frac{1}{c_0^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2}$$

As a guess, we replaced $dP/dt$ with the current density $J(t)$, and then used Ohm’s Law to replace $J(t)$ with $\sigma_0 E(t)$:

$$\frac{\partial^2 E}{\partial z^2} - \frac{1}{c_0^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial J}{\partial t} = \mu_0 \sigma_0 \frac{\partial E}{\partial t}$$

from which we found the complex refractive index:

$$n = \sqrt{1 + j \frac{\sigma_0}{\varepsilon_0 \omega}} \approx e^{j\pi/4} \sqrt{\frac{\sigma_0}{\varepsilon_0 \omega}} \quad \rightarrow n \approx \kappa = \text{large}$$
When is this guess likely to be wrong?

Because $\sigma_0$ is REAL, Ohm's Law $J(t) = \sigma_0 E(t)$, implies that the current is always in phase with the incident wave!

Recall: in the Drude model, the electrons are free to move - they are not bound to atoms by “springs”. So, for low or moderate frequencies, our guess is ok.

But at a high enough frequency, it MUST fail. Even without springs, the electrons must take some time to respond, so a very high frequency oscillation must leave them lagging: $J$ must eventually become out of phase with $E$.

So, we are back to the inhomogeneous wave equation.

$$\frac{\partial^2 E}{\partial z^2} - \frac{1}{c_0^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2}$$
The “polarization” when there is current

Let’s go back to our forced oscillator model. Newton’s law $F=ma$ gave us:

$$ \frac{d^2 x_e(t)}{dt^2} = -\omega_0^2 x_e(t) + 2\Gamma \frac{dx_e(t)}{dt} + \frac{eE_0}{m_e} e^{-j\omega t} $$

$\omega_0^2 = \frac{\text{spring constant}}{m_e}$

resonant frequency of the spring

frictional damping

force due to the incident light field

From this, we found the polarization:

$$ P(t) = \left[ \frac{Ne^2 / m_e}{\omega_0^2 - \omega^2 - j2\omega\Gamma} \right] E(t) $$

(see lecture 7)

For a Drude metal, there is no spring holding some of the electrons. So what if we simply take $\omega_0 = 0$?
The plasma frequency

\[ P(t) = -\left[ \frac{N e^2 / m_e}{\omega^2 + j2\omega\Gamma} \right] E(t) \]

Define a new constant, the “plasma frequency” \( \omega_p \):

\[ \omega_p^2 = \frac{N e^2}{\varepsilon_0 m_e} \]

Thus \( P(t) = -\varepsilon_0 \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma} E(t) \)

We could use this as a ‘new and improved’ guess: plug this in for the polarization term in the wave equation.
Back to the wave equation

\[
\frac{\partial^2 E}{\partial z^2} - \frac{1}{c_0^2} \frac{\partial^2 E}{\partial t^2} = \mu_0 \frac{\partial^2 P}{\partial t^2} = -\mu_0 \varepsilon_0 \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma} \frac{\partial^2 E}{\partial t^2}
\]

But this is similar to a problem we solved several times already:

\[
\frac{\partial^2 E}{\partial z^2} - \frac{1}{c_0^2} \left( 1 - \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma} \right) \frac{\partial^2 E}{\partial t^2} = 0
\]

This is the wave equation for a wave propagating in a medium, if we define the refractive index of the medium as:

\[
n_{metal}^2(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma}
\]

This is our new result for the (complex) refractive index of a metal.
Summary of our new and improved result

Instead of making a ‘guess’ that \( \frac{dP}{dt} = \sigma_0 E(t) \),
we make the better guess that \( P(t) = -\varepsilon_0 \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma} E(t) \)

and then, this modified Drude model (plus the wave equation) predict the optical properties of metals as:

\[
n_{metal}(\omega) = \sqrt{1 - \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma}} \quad \text{or} \quad \varepsilon_{metal}(\omega) = \varepsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma}\right)
\]

Recall the relation between the refractive index and dielectric function of a material:

\[ n(\omega) = \frac{\sqrt{\varepsilon(\omega)}}{\varepsilon_0} \]

It is instructive to compare the ‘guess’ from last lecture to this new result, and see where they are similar.
How does this compare to our earlier result?

For this new result, consider the low-frequency limit, $\omega << \Gamma$:

$$\varepsilon(\omega) = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma} \right) \approx \varepsilon_0 \left( 1 + j \frac{\omega_p^2}{2\omega\Gamma} \right)$$

But in the last lecture, our naïve guess gave this result:

$$n \approx \sqrt{1 + j \frac{\sigma_0}{\varepsilon_0 \omega}} \quad \rightarrow \quad \varepsilon(\omega) = \varepsilon_0 \left( 1 + j \frac{\sigma_0}{\varepsilon_0 \omega} \right)$$

In the Drude model, we have $\sigma_0 = \frac{Ne^2\tau}{m_e}$, so thus:

$$\frac{\sigma_0}{\varepsilon_0 \omega} = \frac{Ne^2}{\varepsilon_0 \omega m_e} \cdot \tau$$

With our earlier definition of $\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m_e}$, we find:

$$\frac{\omega_p^2}{2\omega\Gamma} = \frac{Ne^2}{\varepsilon_0 \omega m_e} \cdot \frac{1}{2\Gamma}$$

The two results are consistent at low frequency!
High frequency dielectric of metals

How does this dielectric function behave at higher frequencies, e.g., $\omega >> \Gamma$?

For high frequencies we find: $\varepsilon(\omega) \approx \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2} \right)$

The dielectric function becomes purely a real number.
And, it is negative below the plasma frequency and positive above the plasma frequency.

Some numbers:

Recall from Drude theory, that $\tau \sim 10^{-14}$ sec, so $\Gamma \sim 1/\tau \sim 10^{14}$ Hz.
(corresponding to the frequency of infrared light)

For a typical metal, $\omega_p$ is 100 or even 1000 times larger.
(corresponding to the frequency of ultraviolet light)
Dielectric function of metals

\[ \varepsilon(\omega) = \varepsilon_0 \left(1 - \frac{\omega_p^2}{\omega^2 + j2\omega\Gamma}\right) \]

A plot of Re(\(\varepsilon\)) and Im(\(\varepsilon\)) for some example values:

- imaginary part gets very small for high frequencies
- real part has a zero crossing at the plasma frequency
- real and imaginary parts are equal in magnitude at \(\omega = \Gamma\)
A comparison of the two results

A plot of $\kappa$ and $n$ for the same example values:

- the two results are equivalent for frequencies much less than $\Gamma$
- the Lecture 10 result predicts interesting behavior near $\omega_p$, which the Lecture 9 result cannot account for.
Drude theory: it works pretty well…

large and negative (below $\omega_p$)

small and positive
… but not perfectly

For silver, the plasma frequency is about 9 eV (i.e., $1.44 \times 10^{-18}$ joules, corresponding to $\lambda = 138$ nm). So the stuff at ~4 eV is not due to $\omega_P$.

It is due to inter-band (valence-to-conduction band) transitions of the bound electrons (our Drude model analysis ignored bound electrons).
High frequency optical properties

In the regime where \( \omega \gg \Gamma \), we find: 
\[
 n(\omega) = \sqrt{1 - \frac{\omega_p^2}{\omega^2}}
\]

For frequencies below the plasma frequency, \( n \) is complex, so \( \kappa > 0 \). The wave is attenuated and does not propagate very far into the metal.

For high frequencies above the plasma frequency, \( n \) is real. The metal becomes transparent! It behaves like a non-absorbing dielectric medium.

reflectivity drops abruptly at the plasma frequency

This is why x-rays can pass through metal objects.
Another example: the ionosphere

The ionosphere is the uppermost part of the atmosphere, where many of the atoms are ionized. There are a lot of free electrons floating around here...

For $N \sim 10^{12} \text{ m}^{-3}$, the plasma frequency is:

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m_e}} = 2\pi \times 9 \text{ MHz}$$

Radiation at frequencies above 9 MHz is transmitted, while radiation at lower frequencies is reflected back to earth.

That’s why AM radio broadcasts can be heard very far away.
An observation

For real metals, there is a very broad range of frequencies for which $\text{Im}(\varepsilon) \sim 0$ and $\text{Re}(\varepsilon)$ is negative.

$\omega_p = 15000 \text{ cm}^{-1}$

$\Gamma = 20 \text{ cm}^{-1}$

This has interesting implications.
Waves trapped at an interface

Consider a wave at the interface between two semi-infinite media.

Is there a solution to Maxwell’s equations describing a wave that propagates along the surface?

We can guess a solution of the form:

$$
\begin{align*}
\vec{E}_1 &= \left( E_{1x}, 0, E_{1z} \right) e^{-\kappa_1 |z|} e^{j(\kappa x - \omega t)} \\
\vec{B}_1 &= \left( 0, B_{1y}, 0 \right) e^{-\kappa_1 |z|} e^{j(\kappa x - \omega t)}
\end{align*}
$$

This propagates along the interface, and decays exponentially into both media.

(Note: this is not a transverse wave… but that’s ok!)
Interface waves

In order to exist, the wave must satisfy Maxwell’s equations:

\[ j \kappa_1 B_{1y} = \frac{\omega}{c_0} \varepsilon_1 E_{1x} \quad j \kappa_2 B_{2y} = -\frac{\omega}{c_0} \varepsilon_2 E_{2x} \]

and also the continuity boundary conditions at \( z=0 \):

\[ B_{1y}^{z=0} = B_{2y}^{z=0} \quad E_{1x}^{z=0} = E_{2x}^{z=0} \]

It is easy to show that these conditions can only be satisfied if:

\[ \frac{\varepsilon_1}{\kappa_1} + \frac{\varepsilon_2}{\kappa_2} = 0 \]

Since \( \kappa_1 \) and \( \kappa_2 \) are always positive, this shows that these interface waves only exist if \( \varepsilon_1 \) and \( \varepsilon_2 \) have opposite signs.

We just showed: in a metal, \( \varepsilon < 0 \) for frequencies less than \( \omega_p \).
Surface plasmon polaritons (SPP) - a surface wave moving along the interface between a metal and a dielectric (e.g., air)

The electrons in the metal oscillate in conjunction with the surface wave, at the same frequency. In fact, an SPP is both an electromagnetic wave and a collective oscillation of the electrons.
Surface plasmon sensors

Surface plasmons are very sensitive to molecules on the metal surface.

A commercial SPP-based biosensor
Surface plasmons on small objects

Instead of considering a semi-infinite piece of metal, what if the metal object is small?

e.g., a metal nanosphere

We can still excite a plasmon, but in this case it does not propagate! The electrons just collectively slosh back and forth.

There is a restoring force on the electron cloud! Once again, we encounter something like a mass on a spring, with a resonance...
The sloshing electrons interact with light most strongly at the resonant frequency of their oscillation.

Surface plasmon resonance


2.8 nm copper nanoparticles

gold nanoparticles give rise to the red colors in stained glass windows
Controlling the surface plasmon resonance

The frequency of the plasmon resonance can be tuned by changing the geometry of the metal nano-object.

Changing the color by changing only the shell thickness!

Halas group, Rice Univ.