Another modern technique to determine the optical constants of samples is ellipsometry. Here changes in polarization are measured when a light beam is reflected from or transmitted through a sample. For reflected light, this change in polarization, ρ, is often described with two values, Ψ and Δ:

$$\tilde{\rho} = \tan(\Psi)\, e^{-i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s}$$

(complex reflectivity; amplitude and phase)

where Ψ is the ratio of the reflected amplitudes and Δ is the phase difference produced upon reflection. Polarization changes arise from the reflectivity difference between electric field components oriented parallel (p-) and perpendicular (s-) to the plane of incidence (slide). In general, light reflection produces a change in amplitude ratio and phase difference between the p- and s-components. Ellipsometry measures this change in polarization in order to determine the sample properties. slide

For the case of metals and semiconductors, the optical properties are heavily influenced by the presence of free electrons. In principle, these can be treated as Lorentz oszillators with $\omega_0 = 0$. In the following, we will look in detail at the consequences from this model. We can treat metals (and doped semiconductors) as <u>plasmas</u> because they contain equal numbers of fixed positive ions and free electrons. The free electrons experince no restoring forces when they intract with elektromagnetic waves. The model we will discuss here combines the <u>Drude model</u> of free electron conductivity with the Lorentz model of dipole oscillators, and is therefore known as the <u>Drude-Lorentz-model</u>. In analogy to the treatment above, we write:

$$m_0 \frac{d^2x}{dt^2} + m_0 \gamma \frac{dx}{dt} = -e E_0 e^{-i\omega t},$$

where we only leave out the term for the restoring force. With the ansatz

$$x = x_0 e^{-i\omega t}$$

we obtain:

$$x = \frac{e E}{m_0 (\omega^2 + i\gamma\omega)},$$

and, as above:

$$\begin{aligned} D &= \varepsilon_r \varepsilon_0 E \\ &= \varepsilon_0 E + P \\ &= \varepsilon_0 E - N e x \\ &= \varepsilon_0 E - \frac{N e^2 E}{m_0 (\omega^2 + i\gamma\omega)} \end{aligned}$$

Finally:

$$\varepsilon_r = 1 - \frac{N_e^2}{\varepsilon_0 m_0} \frac{1}{(\omega^2 + ij\omega)}$$

$$= 1 - \frac{\omega_p^2}{(\omega^2 + ij\omega)} \quad \text{with } \omega_p = \sqrt{\frac{N_e^2}{\varepsilon_0 m_0}}$$

↗ Plasma frequency

This is again the same result as above only with $\omega_0 = 0$.

For the case of weak damping ($\gamma = 0$) we have: $\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$

We get the reflectivity via $\tilde{n} = \sqrt{\varepsilon_r}$

$\tilde{n}$ is imaginary for $\omega < \omega_p$ and real for $\omega > \omega_p$, with $\tilde{n} = 0$ for $\omega = \omega_p$. The reflectivity is $R = \left| \frac{\tilde{n} - 1}{\tilde{n} + 1} \right|^2$.

For $\omega \ll \omega_p$ we have:

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

$$\Rightarrow R = \left| \frac{\sqrt{-\frac{\omega_p^2}{\omega^2}} - 1}{\sqrt{-\frac{\omega_p^2}{\omega^2}} + 1} \right|^2 \approx \left| \frac{\sqrt{-\frac{\omega_p^2}{\omega^2}}}{\sqrt{-\frac{\omega_p^2}{\omega^2}}} \right|^2 = 1$$

For $\omega = \omega_p$ we have:

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2} = 0$$

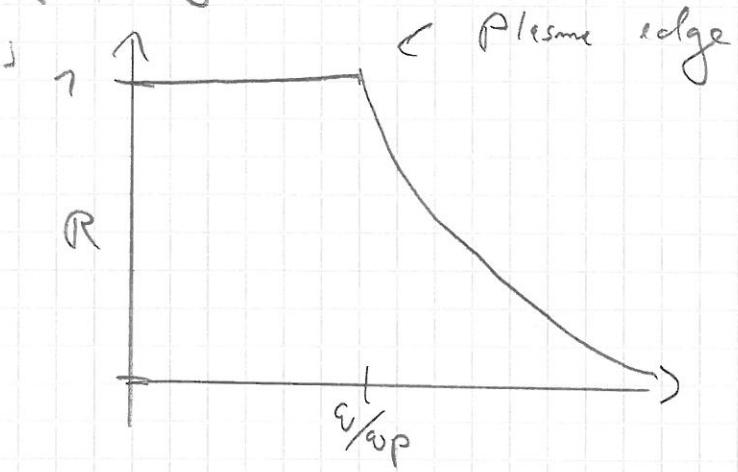
$$\Rightarrow R = \left| \frac{\sqrt{0} - 1}{\sqrt{0} + 1} \right|^2 = |-1|^2 = 1$$

For $\omega \gg \omega_p$ we have:

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

$$\Rightarrow \quad R = \left| \frac{\sqrt{\eta} - 1}{\sqrt{\eta} + 1} \right|^2 = 0$$

This frequency dependance is shown below:



A metal is thus completely reflecting up to the plasma edge. As this is usually beyond the visible part of the spectrum, metals appear shiny.

We will now explicitely include damping in our model. Therefore, we rewrite the equation of motion, this time using the electron velocity v:

$$m_0 \frac{dv}{dt} + m_0 \gamma v = -eE$$

For the case of free electrons, it is often more intuitive to think of the damping time τ instead of the damping rate: $\tau = 1/\gamma$

$$m_0 \frac{dv}{dt} + m_0 \cdot \frac{1}{\tau} \cdot v = -eE$$

The solution for v must have a similar form as the solution for x. With the ansatz $v = v_0 e^{-i\omega t}$, one obtains:

$$v(t) = -\frac{e\tau}{m_0} \frac{1}{1-i\omega\tau} E(t)$$

For the case of free electrons, one can also use the <u>current</u> and the <u>conductivity</u> to describe the behaviour of the electrons. We have Ohm's law: $j = -Nev = \sigma E$

(j: current, σ: conductivity)

$$\Rightarrow \quad j = \underbrace{\frac{Ne^2\tau}{m_0} \frac{1}{1-i\omega\tau}}_{\sigma(\omega)} E(t)$$

<u>AC conductivity</u>
<u>(optical conductivity)</u>

We can define $\sigma(\omega) = \sigma_0 \cdot \frac{1}{1-i\omega\tau}$

with $\sigma_0 = \frac{Ne\tau}{m_0}$

The optical conductivity and the dielectric function are related to each other by

$$\varepsilon_r(\omega) = 1 + \frac{i\sigma(\omega)}{\varepsilon_0 \omega}$$

slide

Roughly speaking, ε_r is used for high frequencies and σ for low frequencies where the relation to the DC conductivity σ_0 becomes very obvious.

To further understand the optical properties of metals, let us look at some numbers. The plasma frequency depends on the number density of free electrons: $\omega_p = \sqrt{\frac{N_e^2}{\varepsilon_0 m_0}}$

The slide shows an overview of selected values for N, ω_p, and λ_p. It is apparent that very large values of N lead to plasma frequencies in the ultraviolet spectral region. Above this frequency, metals become transparent. An example is Aluminium [slide].

An important mechanism of absorption in metals are <u>interband transitions</u>. Here, a photon moves an electron from an occupied to an unoccupied band. Let us discuss this for our example of Al. The [slide] shows the band diagram (we have already encountered this before. When you look closely, you can see the back folded free-electron bands).

The absorption rate is proportional to the density of states in the final state

in [illegible]. This is Fermi's golden rule:

$$W_{i\to f} = \frac{2\pi}{\hbar} |\langle f|H'|i\rangle|^2 S$$

DOS in final state

We thus have strong adsorption for energies corresponding to a transition between a initial state with a high density and a final state with a high density.
This is the case if the bands are parallel (only direct transitions have to be considered due to the small k of the photon).
Two such transitions are marked in the diagram. They cause the dip in the reflectivity of Al at 1.5 eV. The overall slightly decreased reflectivity above 1.5 eV is caused by higher inter band transitions which are not so pronounced due to the absence of the parallel band effect.
Our second example is copper. Here, in addition to the s-bands found in Al, the d-bands are important [slide]. The 3d band has a pronounced and narrow maximum as the overlap between the d-orbitals is small. Consequently, absorption will increase significantly for energies where intra band transitions from the 3d band are allowed. This can be also seen in the full band structure. [slide]. The experimental curve for the reflectivity thus drops significantly now well before the plasma

edge [slide]. The onset of the intraband transition above 2eV explains the red color of copper. The same argument explains the yellow color of gold [slide].

Now we consider the behavior of the free electrons right at the plasma frequency. Remember, that a plasma consists of a gas of charged particles in dynamic equilibrium. The particles are in constant motion, and this can create local charge fluctuations. When by such a fluctuation a small region with an excess charge is created, a force is acting on these electrons with the goal of reaching a homogeneous distribution again. The velocity acquired by the electrons can lead to overshooting and in consequence to an oscillatory motion, the <u>plasma oscillation</u> which have their characteristic frequency right at the plasma frequency. The corresponding quasiparticle is called <u>plasmon</u> [slide]. As the plasmon is a longitudinal wave, it cannot couple with photons, which are described by a transversal wave. In the next lecture we will see that they can be detected by inelastic scattering of photons instead. This situation changes for a special plasmon mode localized at the surface

of a metal, the surface plasmon. [slide].
The associated wave propagates along the interface. The amplitude of the electric field decays exponentially on either side of the interface. It is obvious that the surface plasmon contains also transverse components of the electric field that allow coupling to photons. In the case of strong coupling it is appropriate to speak of a polariton which is a coupled electric polarization – photon wave. The most clear manifestation of surface plasmon effects is found in the optical properties of metal nanoparticles. The color of a suspension of such clusters is dominated by the plasmon resonance. This is exploited since antiquity to produce colored windows by embedding metal nanoparticles.