Content of this lecture

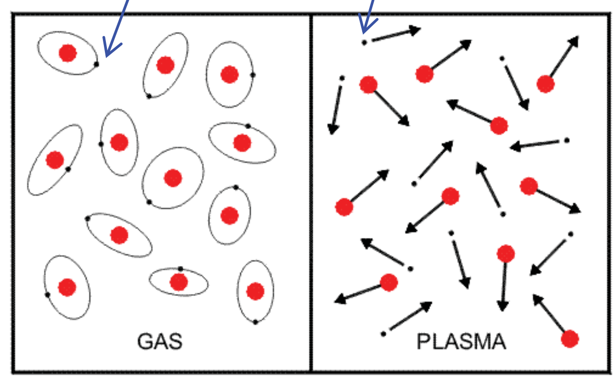
1. What is plasmon?
   – Plasmons (plasma) in universe
   – Plasmons in metal
2. Metal optics
   – Drude model
   – Permittivity ε at plasma frequency
3. Volume plasmons
   – Physical nature of volume plasmons
   – Properties of volume plasmons
   – Application of volume plasmons in nanophotonics

1. What is plasmon?

How many states of matter?

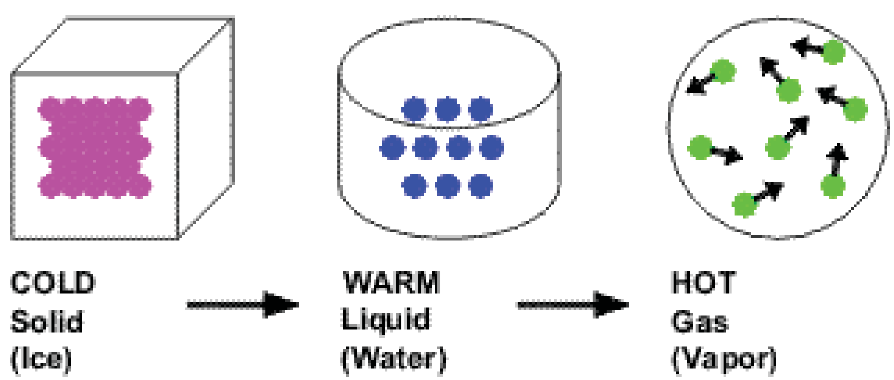
- Solid
- Liquid
- Gas
- Plasma – hot ionized gas with free charges

bound electron free electron



Ionization

Temperature



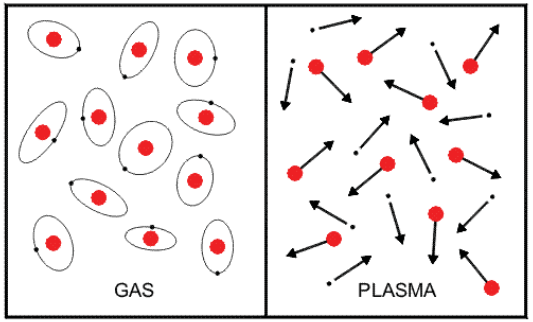
ionization: 电离化，bound electron: 束缚电子，free electron: 自由电子

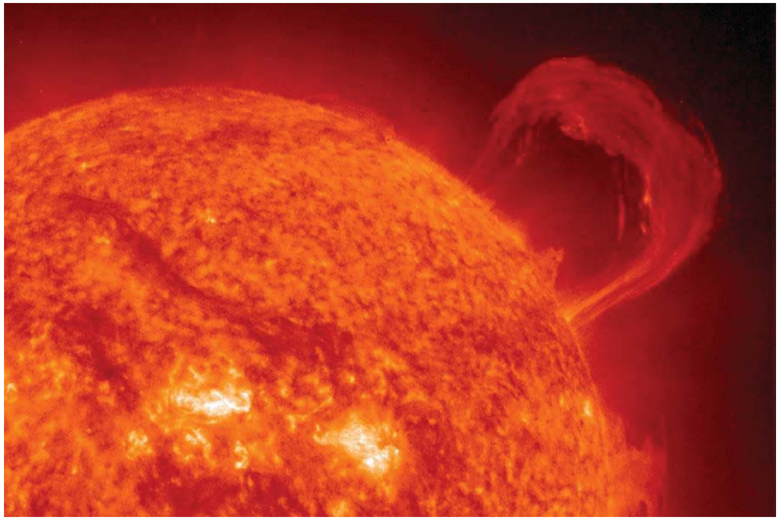
Plasmons (plasma) in universe

- Plasma: the 4th state of matter

99% of the matter in universe is in plasma state

- Different from ordinary neutral gas: strong interaction with EM fields

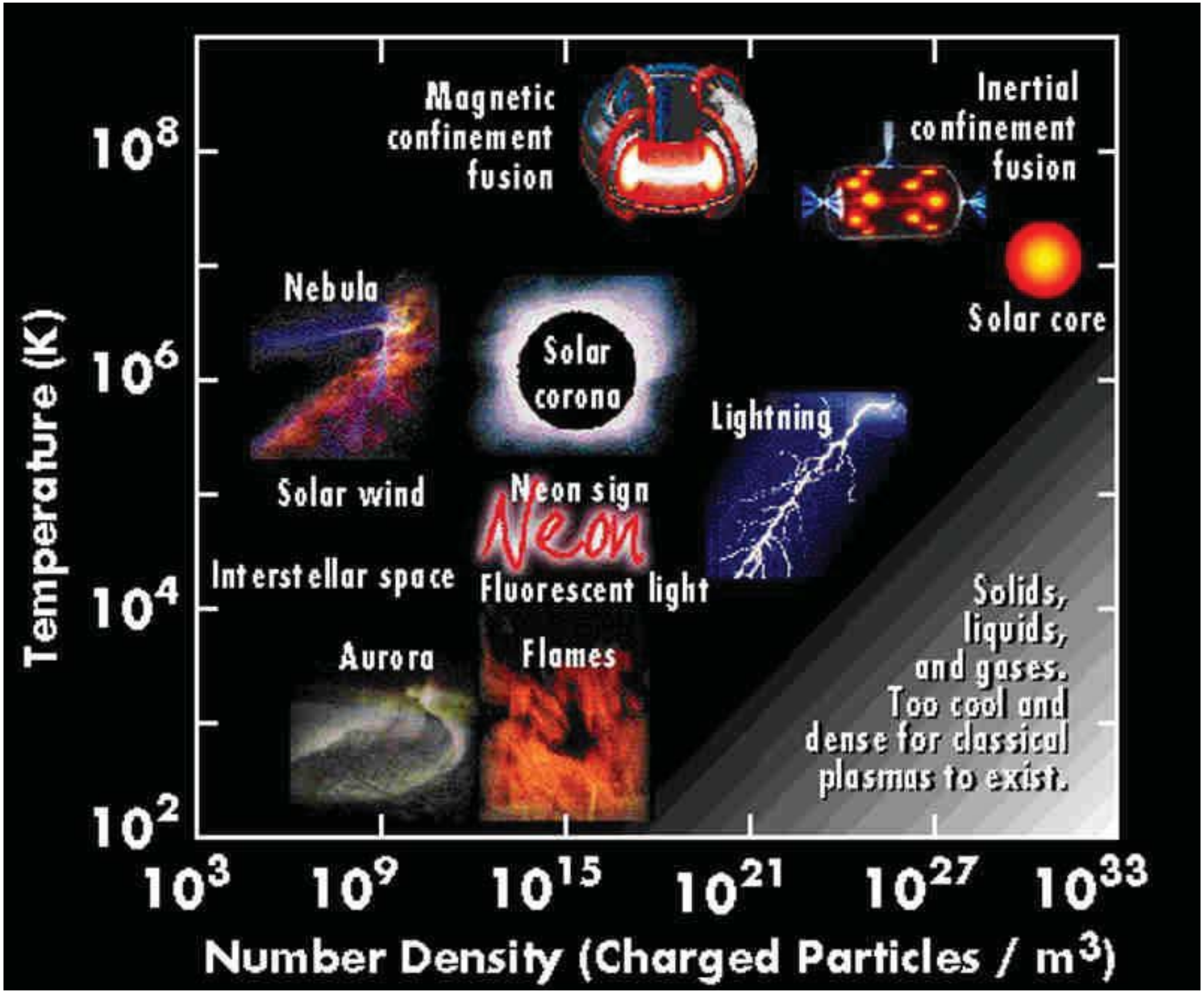




Solar corona with hot plasma

neutral: 电中性的， solar corona: 日冕

Types of plasma according to temperature and density of charged particles



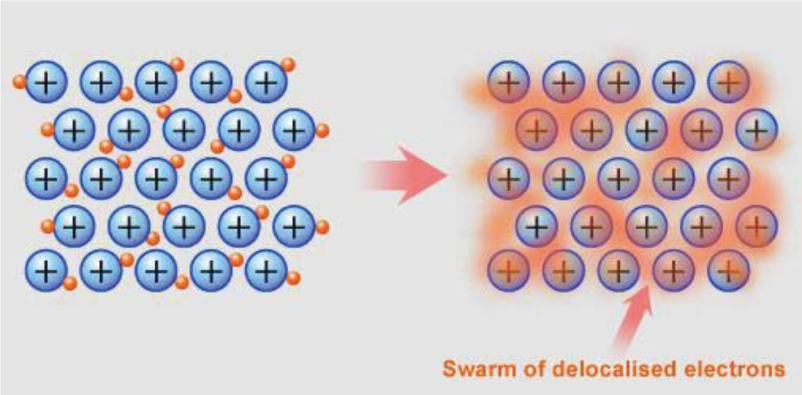
aurora: 极光，nebula: 星云，fluorescent light: 荧光，inertial confinement fusion: 惯性约束核聚变

Plasmons in metal

- Solids, liquids, and gases are usually too cold and dense for classical plasma to exist.

- Can we get plasmons at room temperature?

- Let's think about metal:
  free electrons + ions
  → plasmons?

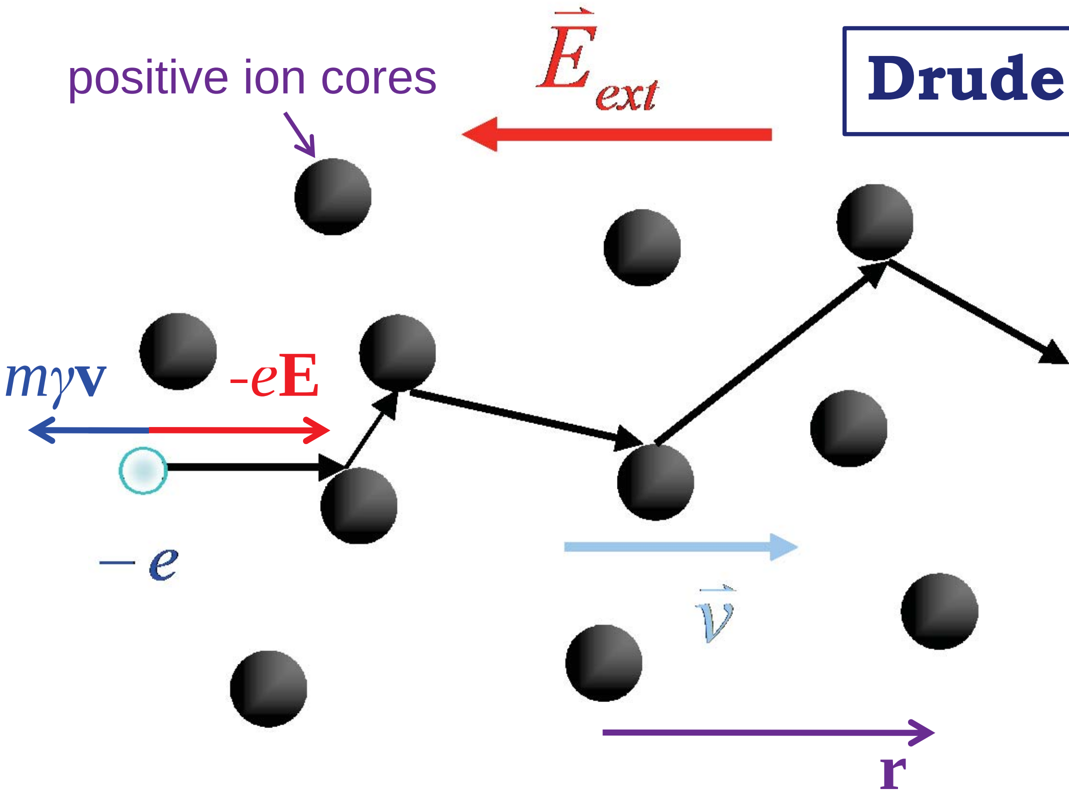


- Yes (but not in its classical meaning), three types of plasmons:
  - Volume plasmons
  - Surface plasmon polaritons
  - Localized surface plasmons

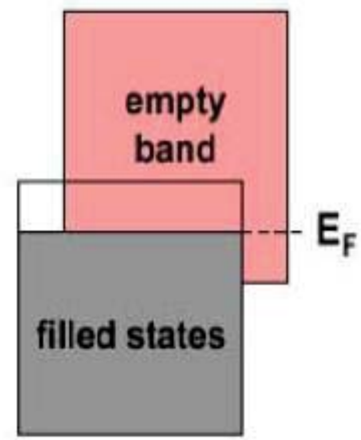
ion: 离子，surface plasmon polariton: 表面等离激元，localized surface plasmons: 局域表面等离子体

2. Metal optics

- Metal response is determined by the behavior of free electrons.
- Under external field **E**, free electrons can be treated as harmonic oscillators <u>without restoring force</u>



Drude model



Forces on electrons:

- Electric field force $-e\mathbf{E}$
- Damping force $m\gamma\mathbf{v}$
  (γ – damping frequency)

damping: 阻尼，ion: 离子，Drude model: 杜德模型

Equation of motion of free electrons:

$$m\ddot{\mathbf{r}} + m\gamma\dot{\mathbf{r}} + \cancel{K\mathbf{r}} = -e\mathbf{E}$$

m – mass of electron
γ – damping frequency (~100 THz)

Can be solved similarly as the Lorentz model

For a time-harmonic stimulus $\mathbf{E}(t) = \mathbf{E}_0 \exp(-i\omega t)$, there is a time-harmonic solution $\mathbf{r}(t) = \mathbf{r}_0 \exp(-i\omega t)$, which is solved as:

$$\mathbf{r} = \frac{e/m}{\omega^2 + i\omega\gamma}\mathbf{E}$$

Then we can get the **macroscopic** polarization vector:

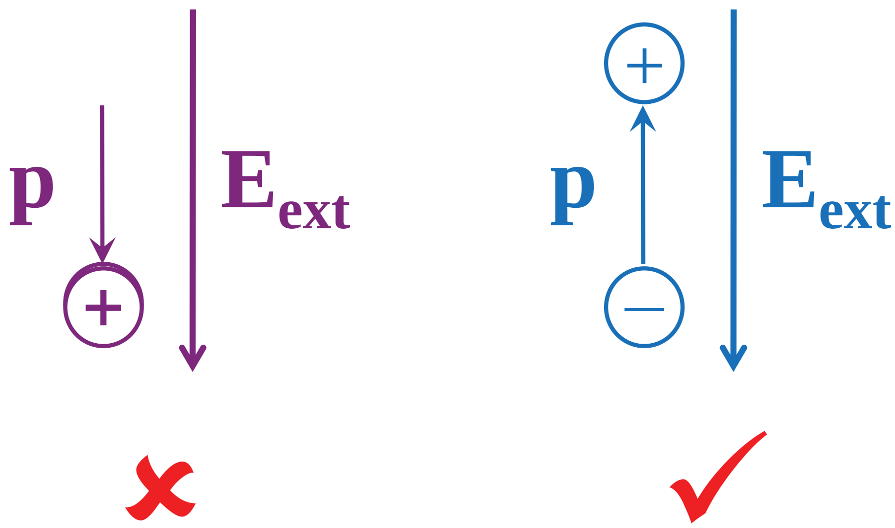
$$\mathbf{P} = -Ne\mathbf{r} = -\frac{Ne^2/m}{\omega^2 + i\omega\gamma}\mathbf{E}$$

N – density of electrons

Any problem???

polarization vector: 极化矢量

Let's think about the polarization process:



Which one is correct?

However, $\mathbf{P} = -Ne\mathbf{r} = -\dfrac{Ne^2/m}{\omega^2 + i\omega\gamma}\mathbf{E}$

Question: $\mathbf{E}$ is out of phase with $\mathbf{P}$ by π (a depolarizing force!), why? – discussion topic

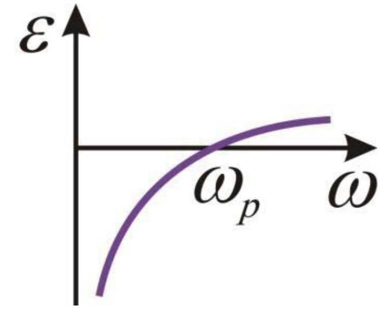
Then we can derive the permittivity:

$$\mathbf{P} = -Ne\mathbf{r} = -\frac{Ne^2/m}{\omega^2 + i\omega\gamma}\mathbf{E} \quad \Rightarrow \quad \mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0\varepsilon\mathbf{E}$$

$$\Rightarrow \quad \boxed{\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}} \qquad \omega_p = \sqrt{\frac{Ne^2}{\varepsilon_0 m}}$$ **(plasma frequency)**

At optical frequency $\omega >> \gamma$, $\varepsilon(\omega)$ can be simplified as

$$\boxed{\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}}$$



Let's discuss ε for different ω …

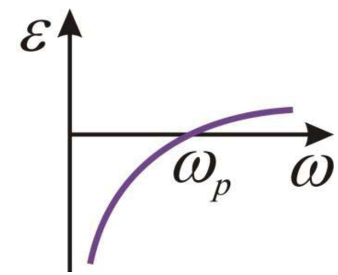
plasma frequency: 等离子体频率

General:

$$\boxed{\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}}$$

High frequency ($\omega >> \gamma$):

$$\boxed{\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}}$$

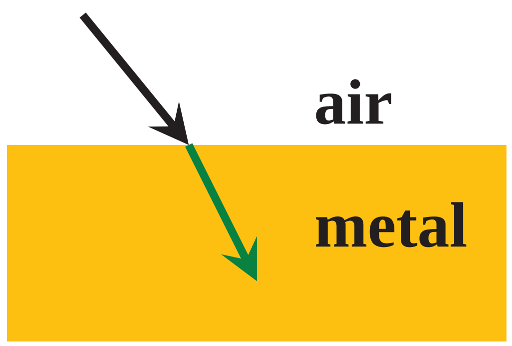


① For very high frequency $\omega > \omega_p$:

→ $\varepsilon > 0$

→ **refractive index** $n = \sqrt{\varepsilon} = n' + in''$ **is *real*** **($n' > 0$, $n'' = 0$)**

→ **metal is *transparent* (like dielectric)**



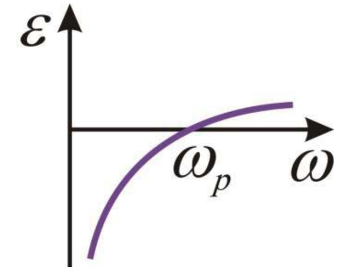
refractive index: 折射率， transparent: 透明的， dielectric: 电介质

General:

$$\boxed{\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}}$$

High frequency ($\omega >> \gamma$):

$$\boxed{\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}}$$



② For optical frequency $\gamma << \omega < \omega_p$:

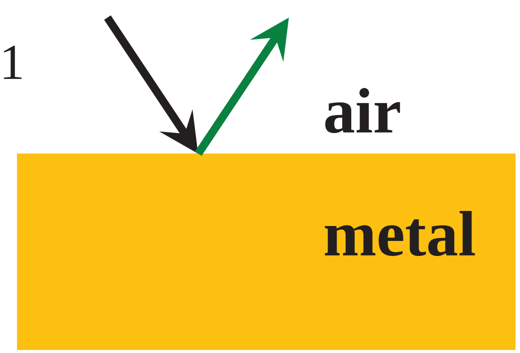
→ $\varepsilon < 0$

→ **refractive index** $n = \sqrt{\varepsilon} = n' + in''$ **is *complex*** **($n' \approx 0$, $n'' > 0$)**

Electric field in metal: $\mathbf{E} = \mathbf{E}_0 \exp(-n''\mathbf{k}_0 \cdot \mathbf{r})$, skin depth $\delta = c/n''\omega$

→ **Fields *decay exponentially* in metal**

Reflectance (normal incidence): $R = \dfrac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2} \approx 1$



→ ***High reflectance*** **on metal surface**

→ **When $\gamma = 0 \rightarrow$ ideal metal, $R = 1$**

skin depth: 趋肤深度，reflectance: 反射率，normal incidence: 垂直入射，ideal metal: 理想金属

General:

$$\boxed{\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}}$$

High frequency ($\omega \gg \gamma$):

$$\cancel{\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}}$$

③ For very low frequency $\omega \ll \gamma$: $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$

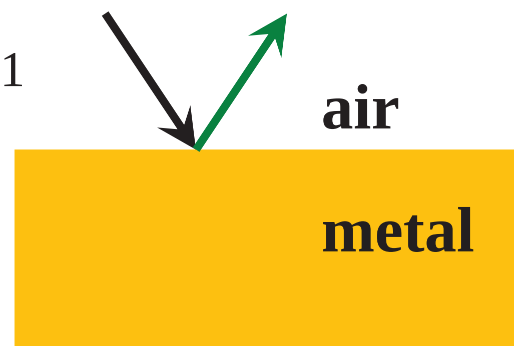
→ $\varepsilon'' \gg \varepsilon'$ (derive it by yourself)

→ **refractive index** $n' \approx n'' \approx \sqrt{\dfrac{\varepsilon''}{2}}$ (derive it by yourself)

Electric field in metal: $\mathbf{E} = \mathbf{E}_0 \exp(in'\mathbf{k_0}\cdot\mathbf{r})\exp(-n''\mathbf{k_0}\cdot\mathbf{r})$, skin depth $\delta = c/n''\omega$

→ **Fields *decay rapidly* in metal**

Reflectance (normal incidence): $R = \dfrac{(n'-1)^2 + n''^2}{(n'+1)^2 + n''^2} \approx 1$



→ ***High reflectance* on metal surface**

→ **When ω is very low → perfect conductor**

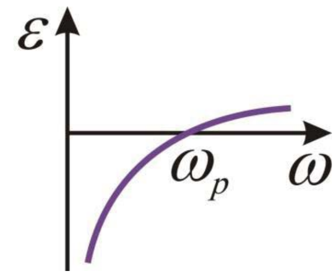
perfect conductor: 理想导体

General:

$$\boxed{\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}}$$

High frequency ($\omega >> \gamma$):

$$\boxed{\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}}$$



④ At plasma frequency $\omega \approx \omega_p$:

→ $\varepsilon \approx 0$

→ **Refractive index** $n = (\varepsilon\mu)^{1/2} \approx 0$

→ **Wave number** $k = nk_0 \approx 0$

What does this mean??? No wave propagation?

Let's review the *wave equation* in Lecture 2…

plasma frequency: 等离子体频率

Harmonic field

Solution to wave equation:

$$\nabla(\nabla\cdot\mathbf{E})-\nabla^2\mathbf{E}=-\frac{\varepsilon\mu}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}$$

Henceforth, we consider only nonmagnetic media ($\mathbf{M}$=0, μ=1)

→ time- and spatial-harmonic field:

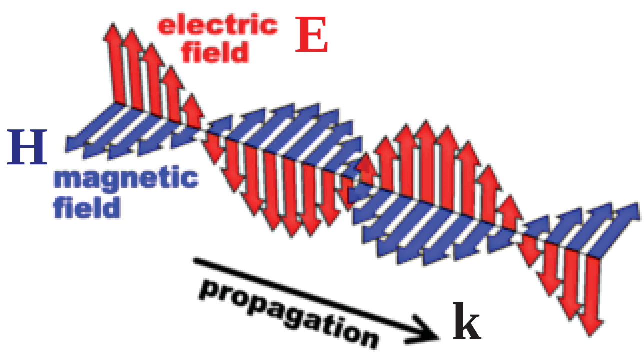
$\mathbf{k}$ – wave vector

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t)$$ (check this is a solution)

In this case, $\nabla\rightarrow i\mathbf{k},\quad \partial/\partial t\rightarrow -i\omega$ (derive by yourself)

Therefore, the wave equation turns to

$$\mathbf{k}(\mathbf{k}\cdot\mathbf{E})-k^2\mathbf{E}=-\varepsilon\frac{\omega^2}{c^2}\mathbf{E}$$



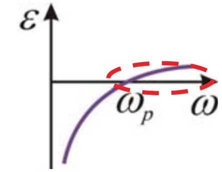
- If transverse wave → $\mathbf{k}\cdot\mathbf{E}$ = 0 →

$$k=\sqrt{\varepsilon}\frac{\omega}{c}\equiv nk_0$$

- If **longitudinal wave** → $\mathbf{k}(\mathbf{k}\cdot\mathbf{E})$ = $k^2\mathbf{E}$ → ε = 0

harmonic field: 简谐场，transverse wave: 横波，longitudinal wave: 纵波

Let's have a closer look at $\omega \geq \omega_p$:

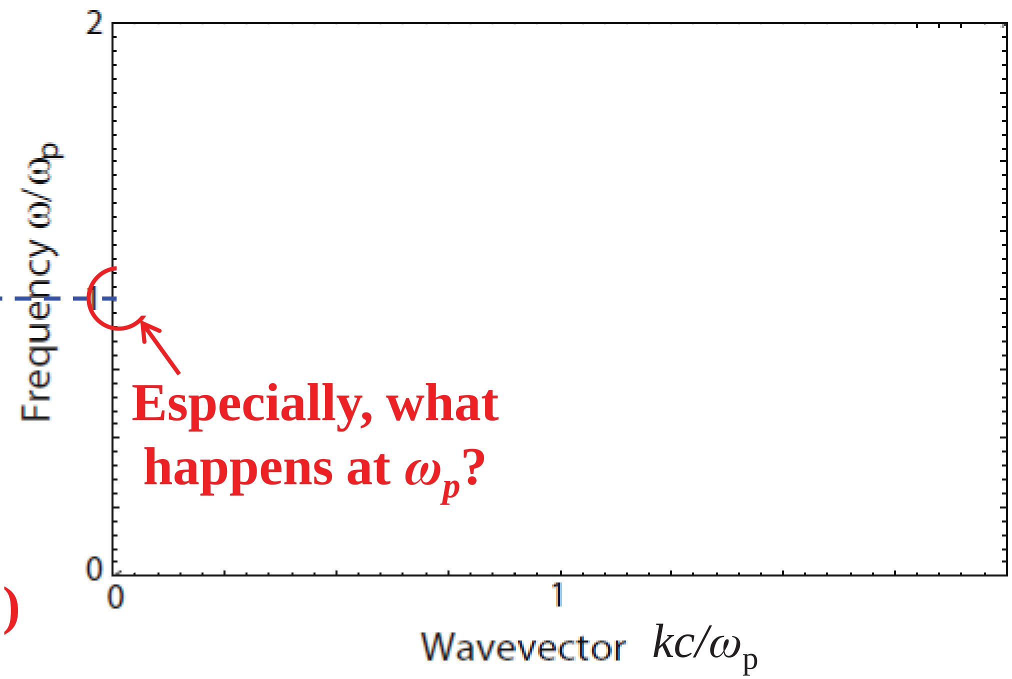


$$\boxed{\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}} \longrightarrow \boxed{\text{for transverse wave: } k = \sqrt{\varepsilon}\,\frac{\omega}{c}} \longrightarrow \boxed{\omega^2 = \omega_p^2 + k^2c^2}$$

Draw the k-ω plot (dispersion relation):

$\omega > \omega_p$: transverse propagating wave allowed

$\omega < \omega_p$: transverse propagating wave forbidden



(Any longitudinal wave?)

transverse wave: 横波， dispersion relation: 色散关系， longitudinal wave: 纵波

ε at plasma frequency ($\omega=\omega_p$)

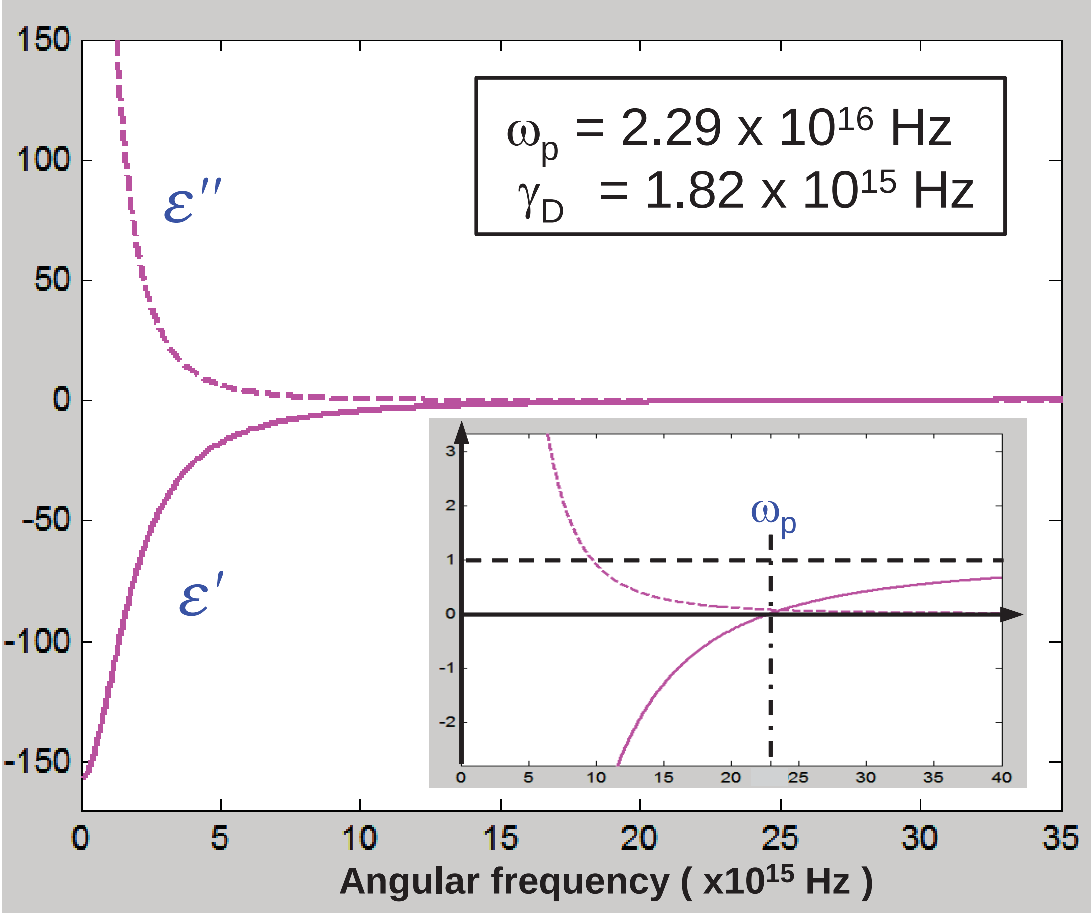
Example: permittivity of Sb

$$\varepsilon(\omega)=\varepsilon'(\omega)+i\varepsilon''(\omega)$$

$$\varepsilon'(\omega)\approx 1-\frac{\omega_p^2}{\omega^2}=0$$

$$\varepsilon''(\omega)\approx \frac{\omega_p^2\gamma}{\omega^3}$$

$$\therefore n'=n''=\sqrt{\frac{\varepsilon''(\omega)}{2}}$$

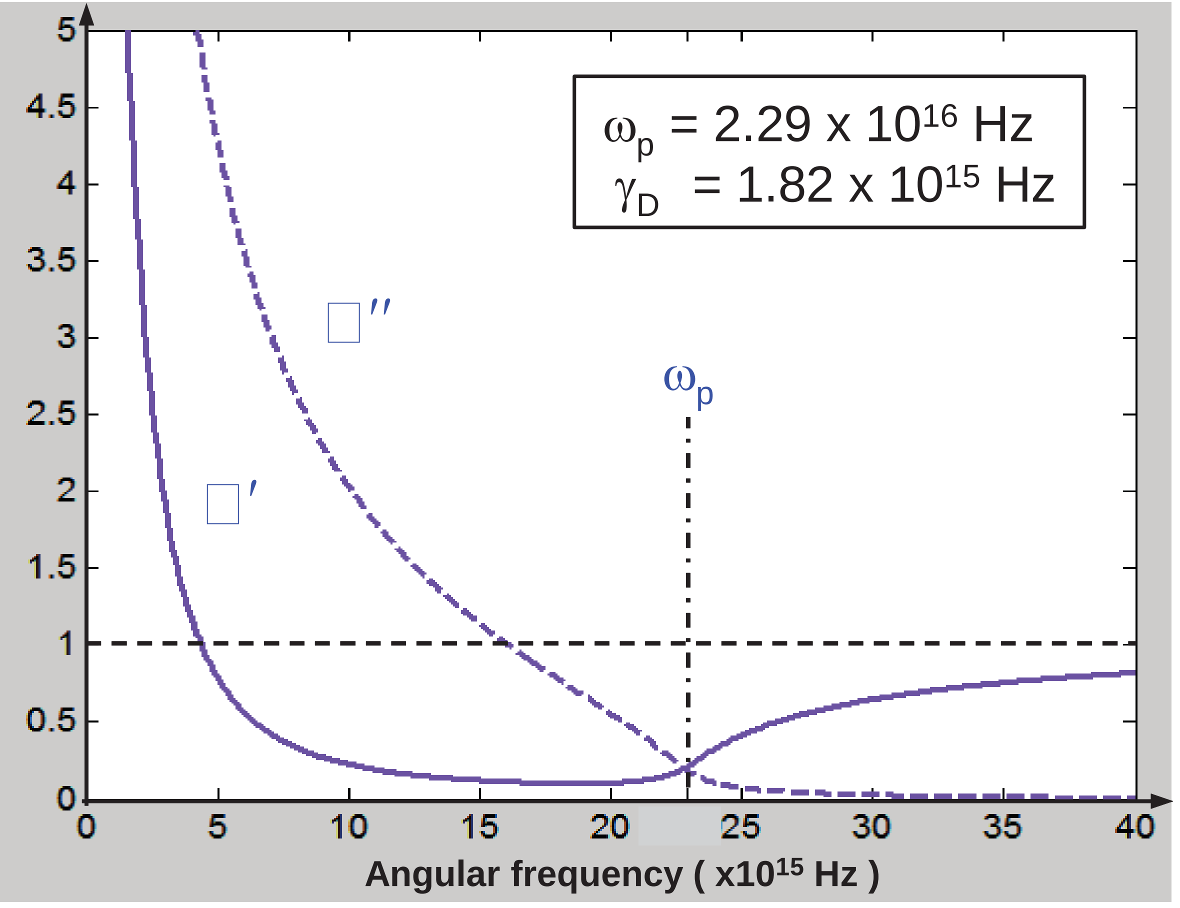


Check these by yourself

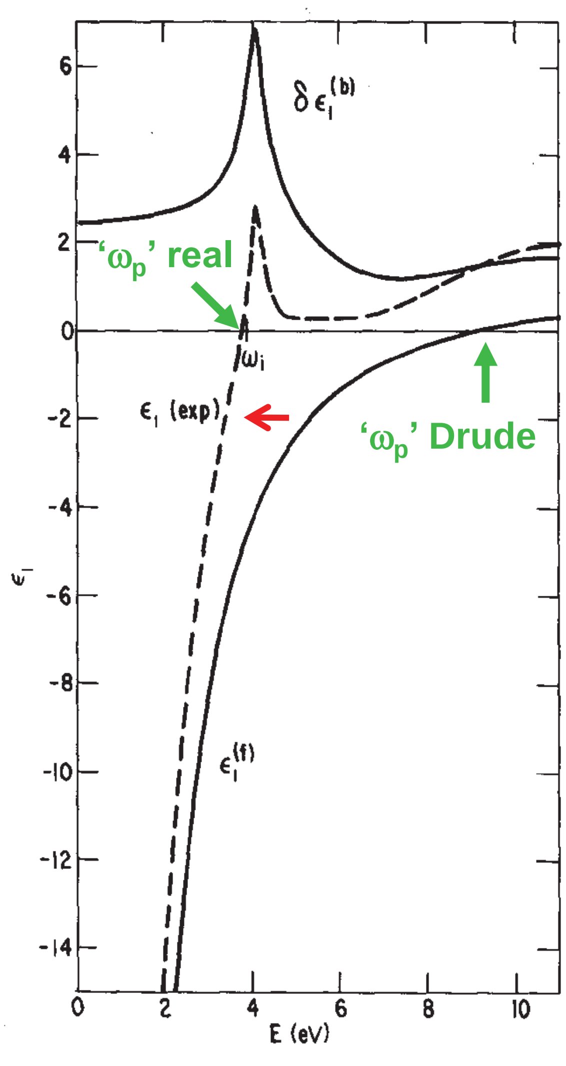
plasma frequency: 等离子体频率， Sb: 锑

Example: refractive index of Sb

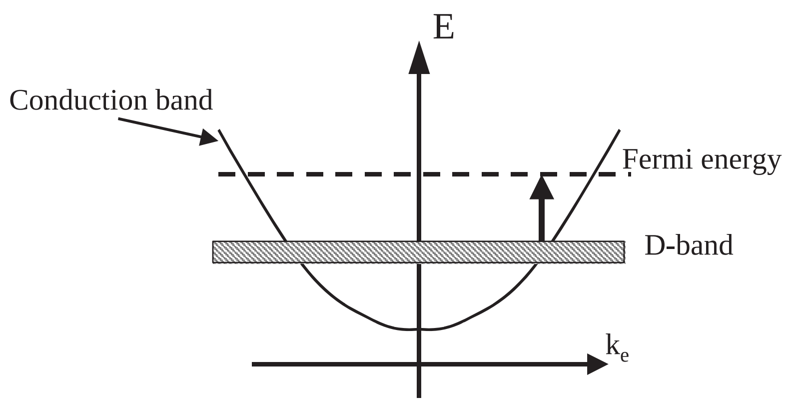
$$n' = n'' = \sqrt{\frac{\varepsilon''(\omega)}{2}}$$

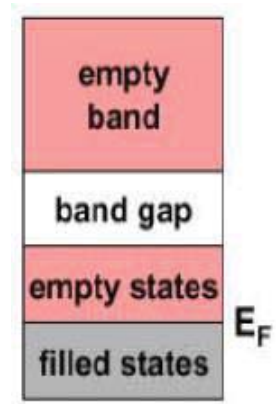


For real metals, especially noble metals (e.g., Ag):



- Measurement shows a peak in ε' and ω_p is shifted, why?
- **Interband transition** (excitation of bound electrons)



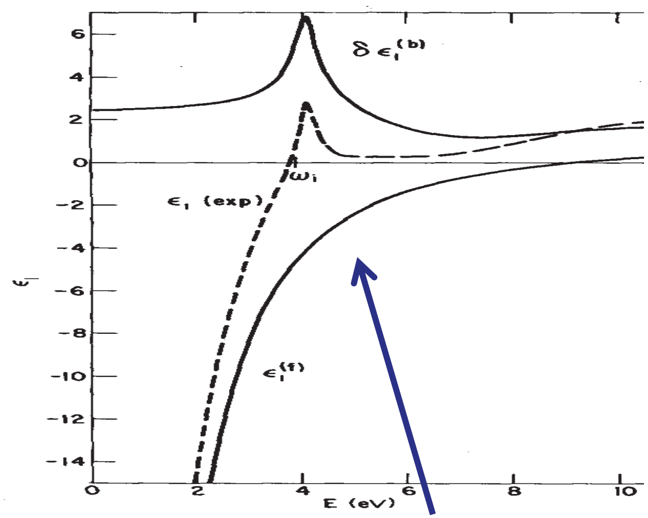


- Drude model should be modified with additional **Lorentz-oscillator terms**:

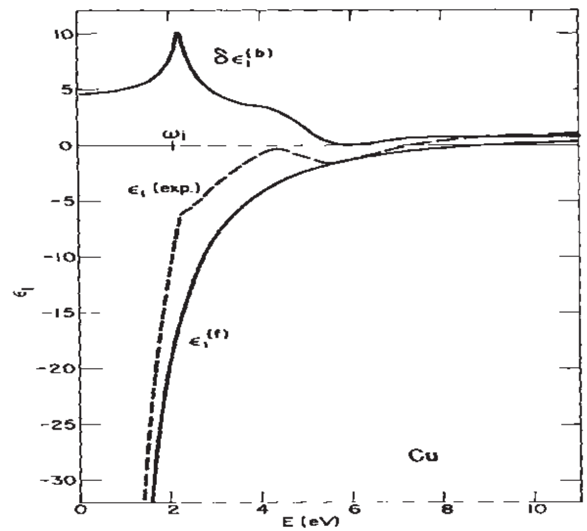
$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} + \sum_j \frac{\omega_{jp}^2}{\omega_{j0}^2 - \omega^2 - i\gamma_j\omega}$$

interband transition: 能带间跃迁，bound electron: 束缚电子

Ag

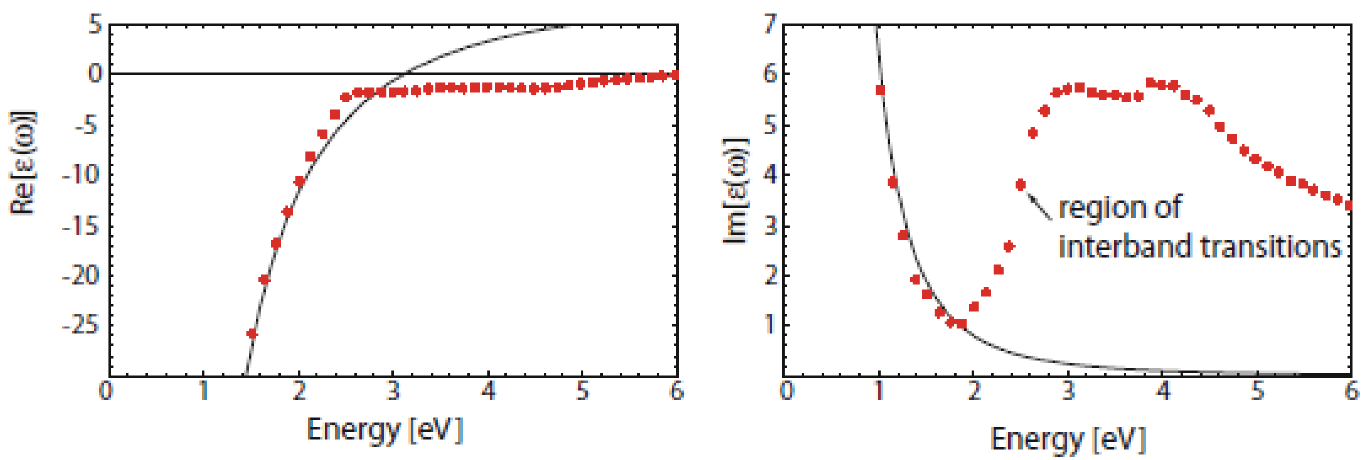


Cu



A consequence is that ω_p is red-shifted
(to λ~330 nm that we could utilize)

Au



3. Volumn plasmons

What happens at plasma frequency ω_p?

- **At plasma frequency $\omega = \omega_p$, we have $\varepsilon(\omega_p) \approx 0$**
- **Let's see the wave equation:** $\mathbf{k}(\mathbf{k}\cdot\mathbf{E}) - k^2\mathbf{E} = -\varepsilon\dfrac{\omega^2}{c^2}\mathbf{E}$
  - If transverse wave, $\mathbf{k}\cdot\mathbf{E} = 0 \rightarrow k = \sqrt{\varepsilon}\dfrac{\omega}{c},\ \varepsilon \neq 0$
  - If longitudinal wave, $\mathbf{k} // \mathbf{E} \rightarrow \mathbf{k}(\mathbf{k}\cdot\mathbf{E}) = k^2\mathbf{E} \rightarrow \varepsilon = 0$

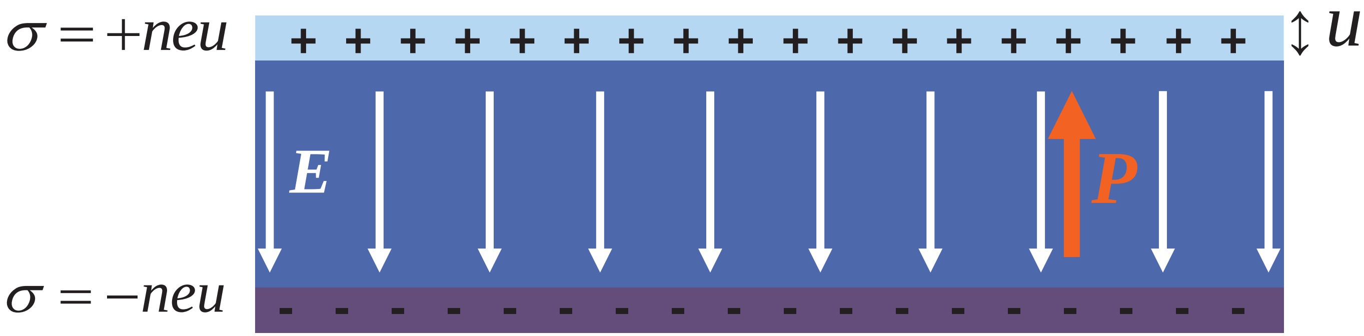
So, at ω_p, only collective longitudinal oscillations of free electrons exist!

– which are called volume plasmons!

volume plasmon: 体等离子体，collective: 集体的

The physical meaning of ω_p

Let's consider a thin slab in the bulk metal at ω_p:



Electron displacement u normal to surface $\rightarrow$ surface charge σ

$\rightarrow$ a homogeneous electric field $E = neu / \varepsilon_0$

$\rightarrow$ restoring force

Then the motion equation of electrons: $nm\ddot{u} = -ne\mathbf{E}$

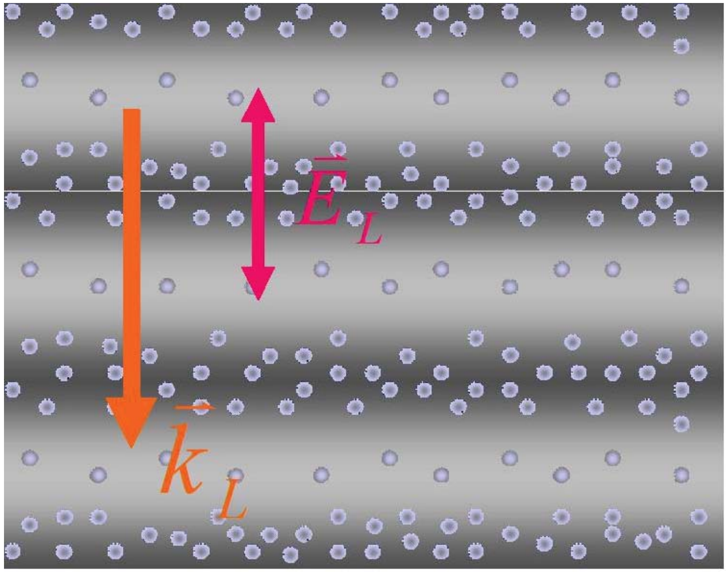
$$\longrightarrow \quad nm\ddot{u} = -\frac{n^2e^2u}{\varepsilon_0} \quad \longrightarrow \quad \ddot{u} + \underline{\omega_{\mathrm{p}}^2} u = 0$$

So, ω_p is the natural frequency of volume plasmons!

bulk metal: 大块金属，restoring force: 回复力，natural frequency: 固有频率

Properties of volume plasmons

(1) Longitudinal wave
k//**E**



(2) No interplay between **E** and **H** → no EM field

$$\because \nabla\times\mathbf{E}=-\partial\mathbf{B}/\partial t \rightarrow 0=\mathbf{k}\times\mathbf{E}=\omega\mu\mathbf{H}$$

(3) Decay of oscillation occurs only via energy transfer to single electrons, known as Landau damping

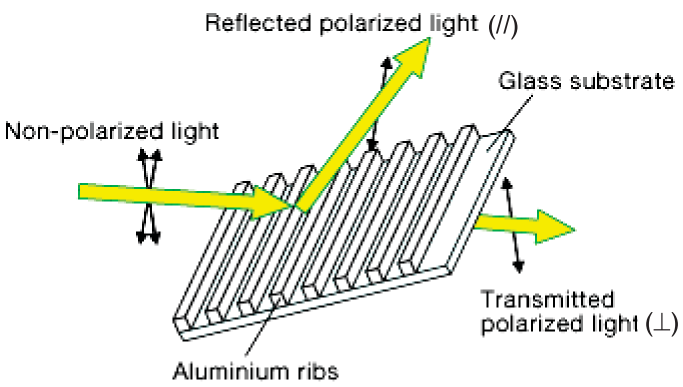
interplay: 相互作用，Landau damping: 朗道衰减

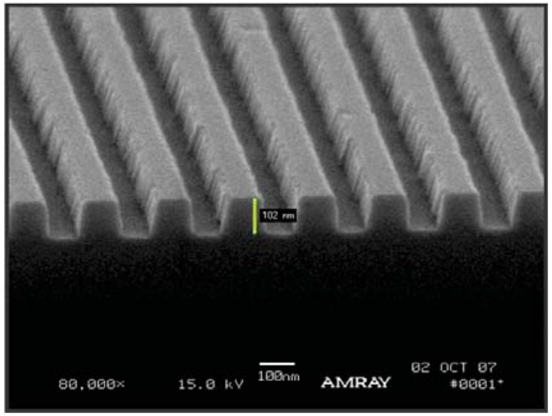
Application of volume plasmons in nanophotonics

Example: Inverse metal wire-grid polarizer

Normal (classical) wire-grid polarizer:

- $E_{//}$ reflected, $E_{\perp}$ transmitted (form birefringence in Lecture 2)



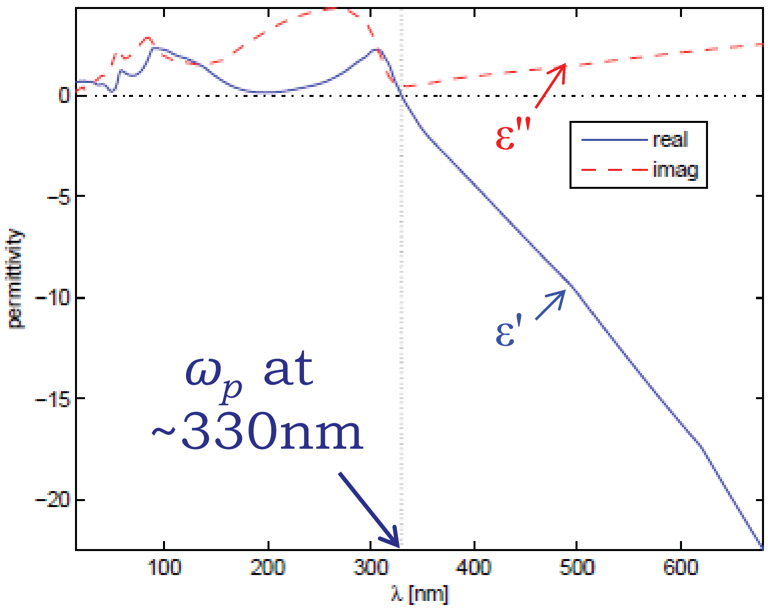


Inverse wire-grid polarizer:

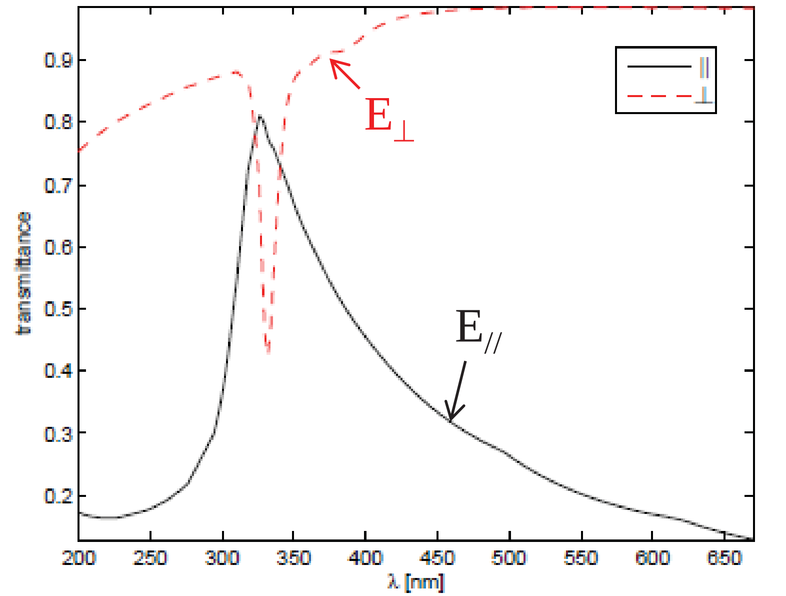
- $E_{//}$ transmitted, $E_{\perp}$ reflected

wire-grid polarizer: 栅格偏振器

Permittivity of Ag



Transmittance of $E_{//}$ and $E_{\perp}$

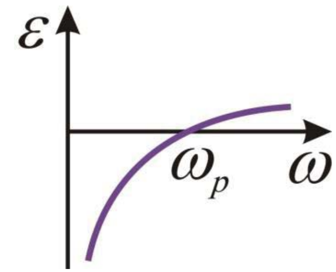


Why the dual behavior?
Analyze it by yourself (by considering the form birefringence).

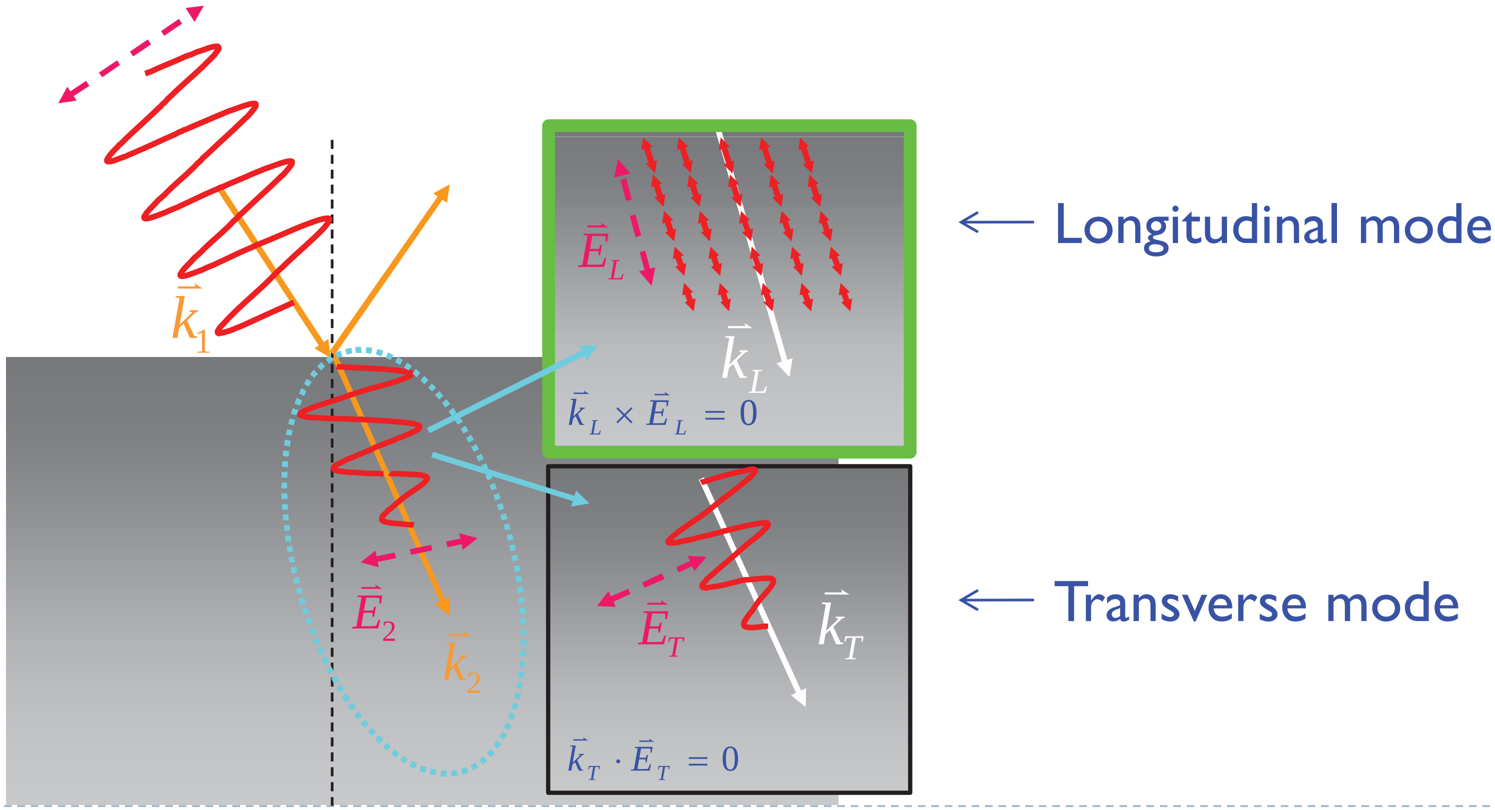
Reference:

A. Lehmuskero, B. Bai, P. Vahimaa, and M. Kuittinen , “Wire-grid polarizers in the volume plasmon region,” Opt. Express **17**, 5481-5489 (2009).

Light-matter interaction in bulk metal



- When $\omega > \omega_p$, **transverse mode** (EM wave)
- When $\omega = \omega_p$, **longitudinal mode** (volume plasmons, non-EM wave)
- When $\omega < \omega_p$, **no propagating wave** (rapid drop of field, skin depth δ)



Summary

- Plasmons (plasma):
  Ionized gas with free charges
- Plasmons in metal:
  Density waves of free electrons, three types
- Understand the EM response of metal with Drude model
- Volume plasmons:
  Longitudinal wave, physical meaning of ω_p, non-EM wave, inverse wire-grid polarizer, two propagating modes in bulk metal