Scuola di Dottorato in Ingegneria Leonardo da Vinci – a.a. 2009/10

PROPRIETÀ MECCANICHE, OTTICHE, ELETTRONICHE DEI MATERIALI ALLE PICCOLE E PICCOLISSIME SCALE

Versione 1 – Ottobre 2010 – http://www.df.unipi.it/~fuso/dida

Parte 8

Proprietà ottiche dei metalli (conduttori): dalla scale macroscopiche alle risonanze plasmoniche

Me 13.10 13-16 aula S1 DF

Outlook

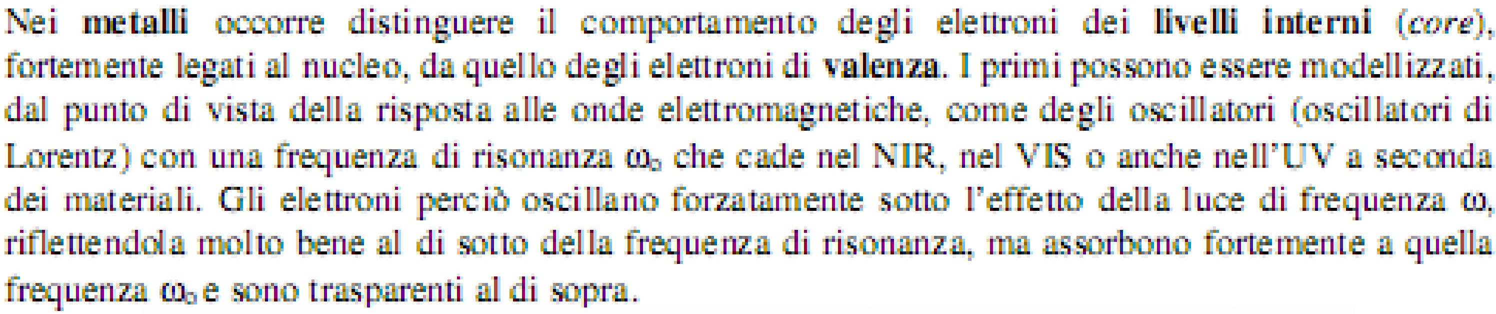
- Metals often do not require the use of quantum electronics to understand the main optical properties!

- Qualitative description of optics with metals: free electrons and their oscillation (in bulk)

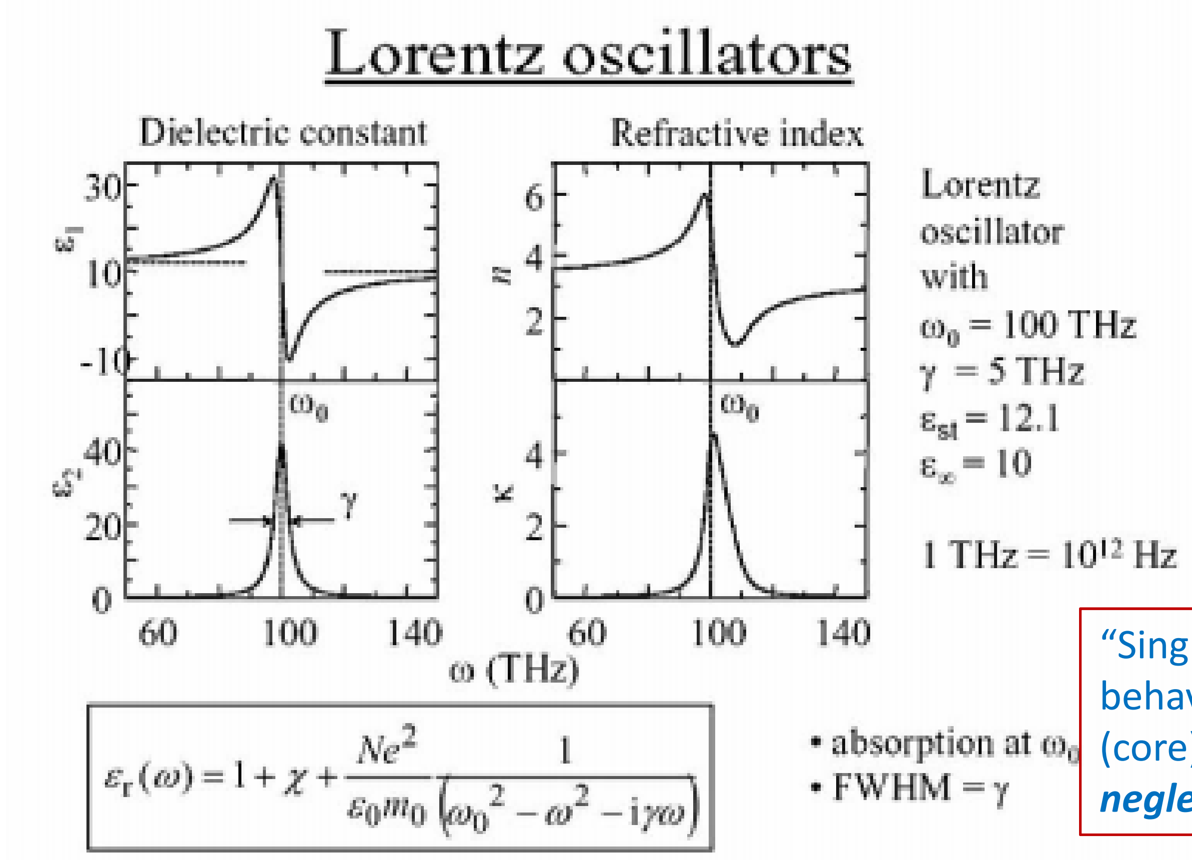
- The astonishing features associated with metals at the small scale:
  - Surface Plasmons
  - Localized Plasmons

- A few words on possible (future) applications

Optical behavior of metals: core levels



Nei **metalli** occorre distinguere il comportamento degli elettroni dei **livelli interni** (*core*), fortemente legati al nucleo, da quello degli elettroni di **valenza**. I primi possono essere modellizzati, dal punto di vista della risposta alle onde elettromagnetiche, come degli oscillatori (oscillatori di Lorentz) con una frequenza di risonanza ω_0 che cade nel NIR, nel VIS o anche nell'UV a seconda dei materiali. Gli elettroni perciò oscillano forzatamente sotto l'effetto della luce di frequenza ω, riflettendola molto bene al di sotto della frequenza di risonanza, ma assorbono fortemente a quella frequenza ω_0 e sono trasparenti al di sopra.



Lorentz oscillator with
ω_0 = 100 THz
γ = 5 THz
ε_{st} = 12.1
ε_∞ = 10

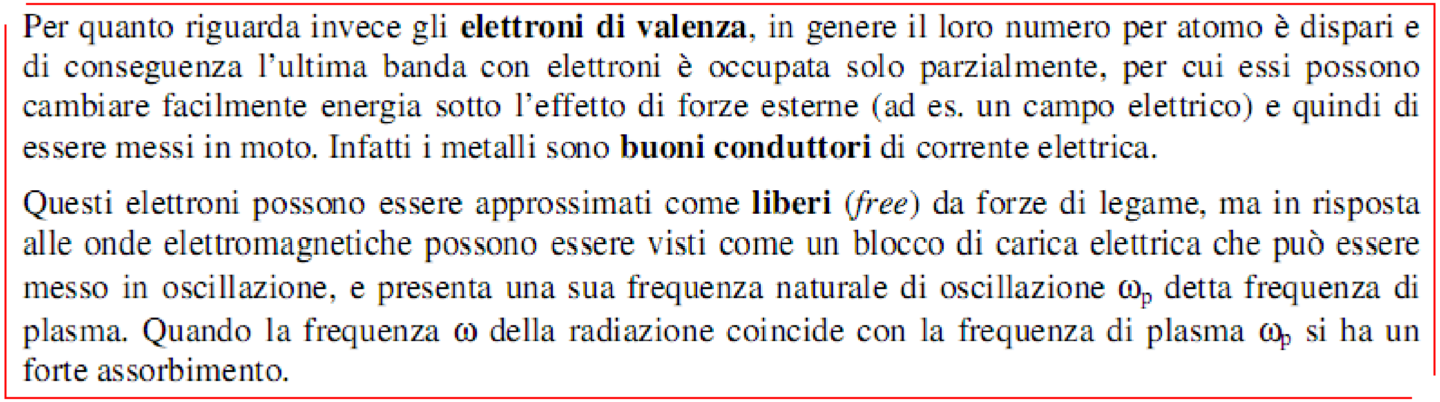
1 THz = 10^{12} Hz

$$\varepsilon_r(\omega) = 1 + \chi + \frac{Ne^2}{\varepsilon_0 m_0} \frac{1}{\left(\omega_0^2 - \omega^2 - i\gamma\omega\right)}$$

- absorption at ω_0
- FWHM = γ

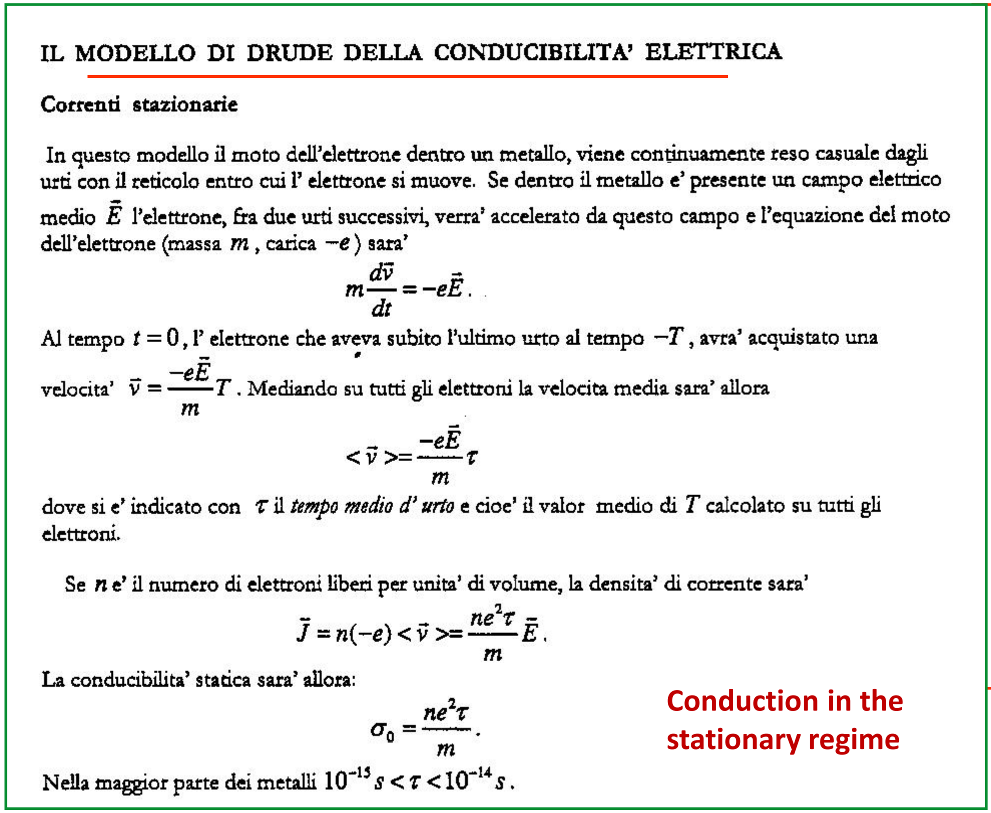
“Single-atom”-like behavior for the inner (core) levels: ***we will neglect it***

Optical behavior of metals: free (valence) electrons



Per quanto riguarda invece gli **elettroni di valenza**, in genere il loro numero per atomo è dispari e di conseguenza l'ultima banda con elettroni è occupata solo parzialmente, per cui essi possono cambiare facilmente energia sotto l'effetto di forze esterne (ad es. un campo elettrico) e quindi di essere messi in moto. Infatti i metalli sono **buoni conduttori** di corrente elettrica.

Questi elettroni possono essere approssimati come **liberi** (*free*) da forze di legame, ma in risposta alle onde elettromagnetiche possono essere visti come un blocco di carica elettrica che può essere messo in oscillazione, e presenta una sua frequenza naturale di oscillazione ω_p detta frequenza di plasma. Quando la frequenza ω della radiazione coincide con la frequenza di plasma ω_p si ha un forte assorbimento.



IL MODELLO DI DRUDE DELLA CONDUCIBILITA' ELETTRICA

Correnti stazionarie

In questo modello il moto dell'elettrone dentro un metallo, viene continuamente reso casuale dagli urti con il reticolo entro cui l' elettrone si muove. Se dentro il metallo e' presente un campo elettrico medio $\vec{E}$ l'elettrone, fra due urti successivi, verra' accelerato da questo campo e l'equazione del moto dell'elettrone (massa m, carica $-e$) sara'

$$m\frac{d\vec{v}}{dt} = -e\vec{E}.$$

Al tempo $t = 0$, l' elettrone che aveva subito l'ultimo urto al tempo $-T$, avra' acquistato una velocita' $\vec{v} = \frac{-e\vec{E}}{m}T$. Mediando su tutti gli elettroni la velocita media sara' allora

$$<\vec{v}> = \frac{-e\vec{E}}{m}\tau$$

dove si e' indicato con τ il *tempo medio d' urto* e cioe' il valor medio di T calcolato su tutti gli elettroni.

Se n e' il numero di elettroni liberi per unita' di volume, la densita' di corrente sara'

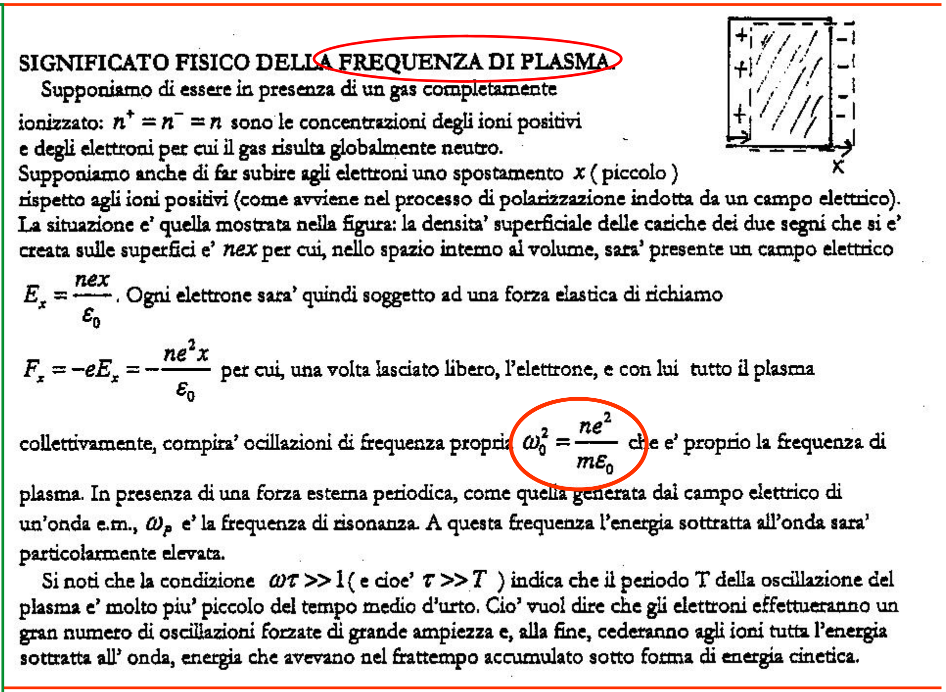
$$\vec{J} = n(-e) <\vec{v}> = \frac{ne^2\tau}{m}\vec{E}.$$

La conducibilita' statica sara' allora:

$$\sigma_0 = \frac{ne^2\tau}{m}.$$

Nella maggior parte dei metalli $10^{-15}s < \tau < 10^{-14}s$.

Conduction in the stationary regime



SIGNIFICATO FISICO DELLA FREQUENZA DI PLASMA

Supponiamo di essere in presenza di un gas completamente ionizzato: $n^+ = n^- = n$ sono le concentrazioni degli ioni positivi e degli elettroni per cui il gas risulta globalmente neutro.

Supponiamo anche di far subire agli elettroni uno spostamento x (piccolo) rispetto agli ioni positivi (come avviene nel processo di polarizzazione indotta da un campo elettrico). La situazione e' quella mostrata nella figura: la densita' superficiale delle cariche dei due segni che si e' creata sulle superfici e' nex per cui, nello spazio interno al volume, sara' presente un campo elettrico $E_x = \frac{nex}{\varepsilon_0}$. Ogni elettrone sara' quindi soggetto ad una forza elastica di richiamo

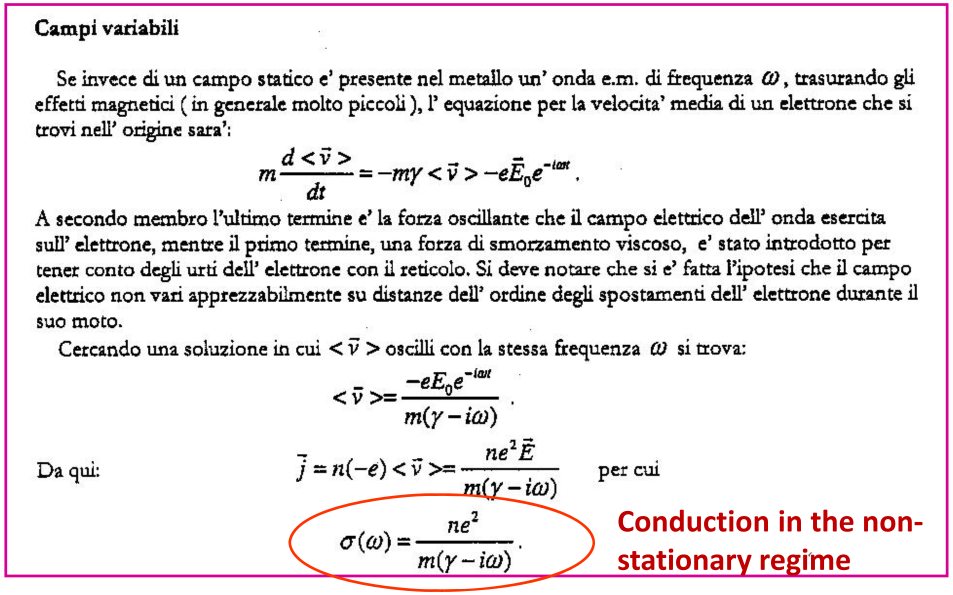
$F_x = -eE_x = -\frac{ne^2x}{\varepsilon_0}$ per cui, una volta lasciato libero, l'elettrone, e con lui tutto il plasma collettivamente, compira' ocillazioni di frequenza propria $\omega_0^2 = \frac{ne^2}{m\varepsilon_0}$ che e' proprio la frequenza di plasma. In presenza di una forza esterna periodica, come quella generata dal campo elettrico di un'onda e.m., ω_p e' la frequenza di risonanza. A questa frequenza l'energia sottratta all'onda sara' particolarmente elevata.

Si noti che la condizione $\omega\tau >> 1$ (e cioe' $\tau >> T$) indica che il periodo T della oscillazione del plasma e' molto piu' piccolo del tempo medio d'urto. Cio' vuol dire che gli elettroni effettueranno un gran numero di oscillazioni forzate di grande ampiezza e, alla fine, cederanno agli ioni tutta l'energia sottratta all' onda, energia che avevano nel frattempo accumulato sotto forma di energia cinetica.

Plasma frequency as signature of "restoring" forces

P.L. Braccini, Lezioni di Fisica II
Per ing. TLC (Pisa, 2001)

Free electrons in the presence of variable electric fields



Campi variabili

Se invece di un campo statico e' presente nel metallo un' onda e.m. di frequenza ω, trasurando gli effetti magnetici (in generale molto piccoli), l' equazione per la velocita' media di un elettrone che si trovi nell' origine sara':

$$m\frac{d<\vec{v}>}{dt}=-m\gamma<\vec{v}>-e\vec{E}_0e^{-i\omega t}.$$

A secondo membro l'ultimo termine e' la forza oscillante che il campo elettrico dell' onda esercita sull' elettrone, mentre il primo termine, una forza di smorzamento viscoso, e' stato introdotto per tener conto degli urti dell' elettrone con il reticolo. Si deve notare che si e' fatta l'ipotesi che il campo elettrico non vari apprezzabilmente su distanze dell' ordine degli spostamenti dell' elettrone durante il suo moto.

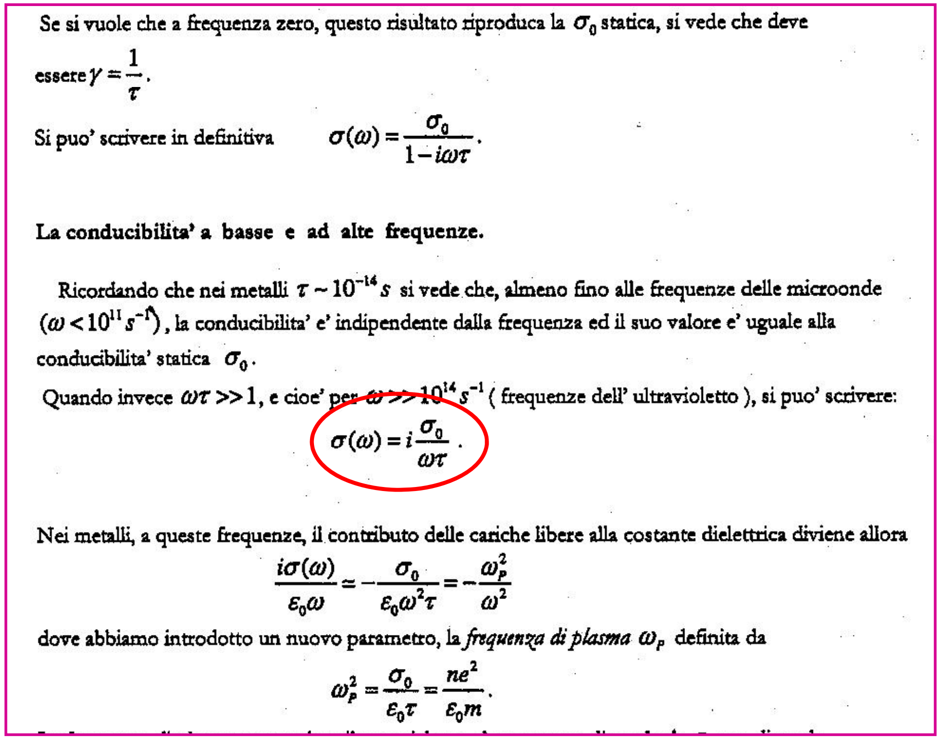
Cercando una soluzione in cui $<\vec{v}>$ oscilli con la stessa frequenza ω si trova:

$$<\vec{v}>=\frac{-eE_0e^{-i\omega t}}{m(\gamma-i\omega)}.$$

Da qui: $\vec{j}=n(-e)<\vec{v}>=\frac{ne^2\vec{E}}{m(\gamma-i\omega)}$ per cui

$$\boxed{\sigma(\omega)=\frac{ne^2}{m(\gamma-i\omega)}}.$$

Conduction in the non-stationary regime



Se si vuole che a frequenza zero, questo risultato riproduca la σ_0 statica, si vede che deve essere $\gamma=\frac{1}{\tau}$.

Si puo' scrivere in definitiva $\sigma(\omega)=\frac{\sigma_0}{1-i\omega\tau}$.

La conducibilita' a basse e ad alte frequenze.

Ricordando che nei metalli $\tau\sim10^{-14}s$ si vede che, almeno fino alle frequenze delle microonde ($\omega<10^{11}s^{-1}$), la conducibilita' e' indipendente dalla frequenza ed il suo valore e' uguale alla conducibilita' statica σ_0.

Quando invece $\omega\tau>>1$, e cioe' per $\omega>>10^{14}s^{-1}$ (frequenze dell' ultravioletto), si puo' scrivere:

$$\boxed{\sigma(\omega)=i\frac{\sigma_0}{\omega\tau}}.$$

Nei metalli, a queste frequenze, il contributo delle cariche libere alla costante dielettrica diviene allora

$$\frac{i\sigma(\omega)}{\varepsilon_0\omega}\simeq-\frac{\sigma_0}{\varepsilon_0\omega^2\tau}=-\frac{\omega_p^2}{\omega^2}$$

dove abbiamo introdotto un nuovo parametro, la *frequenza di plasma* ω_p definita da

$$\omega_p^2=\frac{\sigma_0}{\varepsilon_0\tau}=\frac{ne^2}{\varepsilon_0 m}.$$

Upon interaction with variable fields one gets:

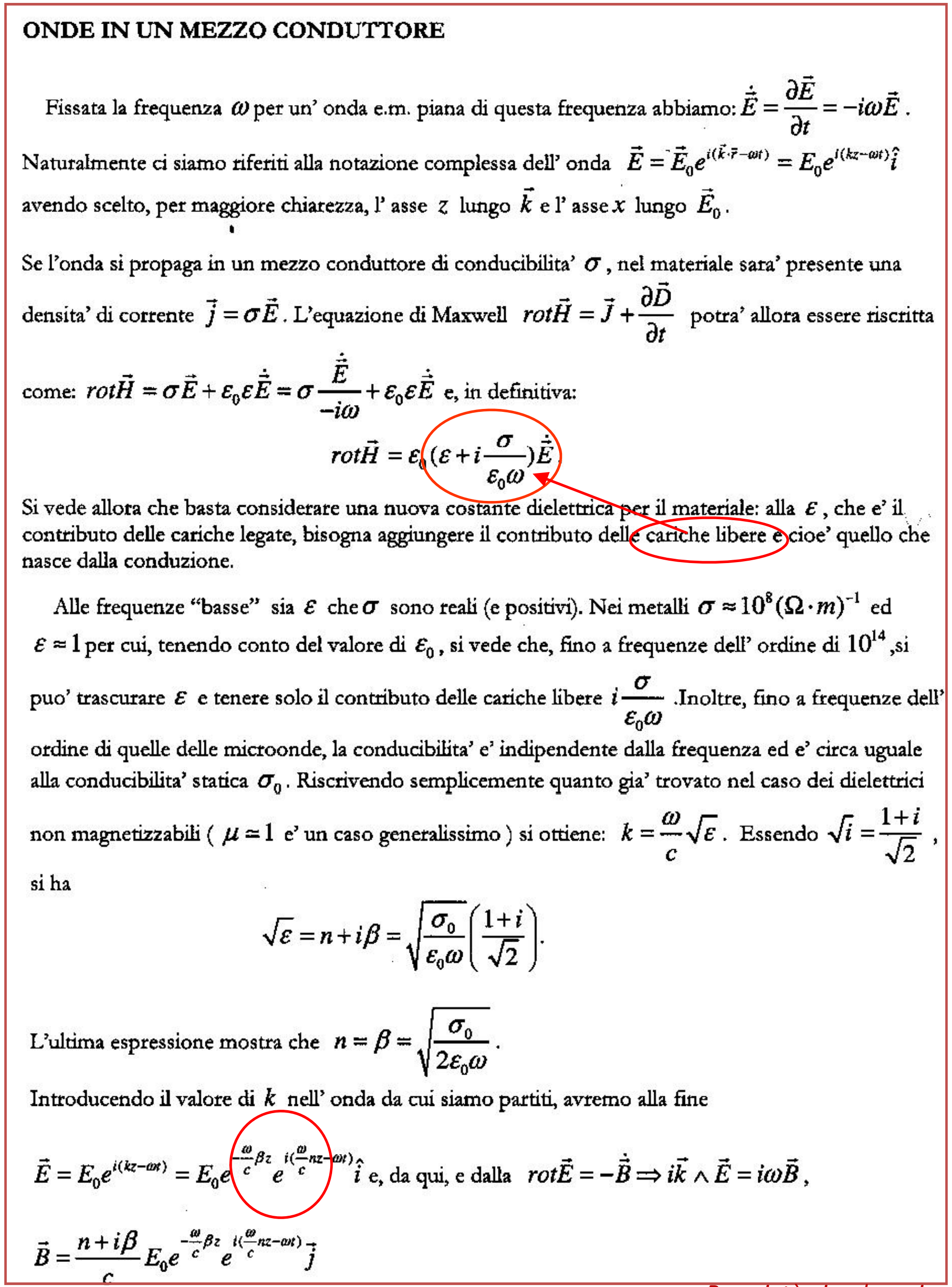
$$\sigma(\omega)=\frac{\sigma_0}{1-i\omega\tau}$$

$$\omega_P^2=\frac{ne^2}{\varepsilon_0 m}=\frac{\sigma_0}{\varepsilon_0\tau}\rightarrow\tau=\frac{\sigma_0}{\varepsilon_0\omega_P^2}$$

$$\sigma(\omega)=\frac{\sigma_0}{1-i\frac{\omega}{\omega_P^2}\frac{\sigma_0}{\varepsilon_0}}$$

Conducibility depends on the frequency (and the "dynamical" material properties are in the plasma frequency)

Reminders of Maxwell equations



ONDE IN UN MEZZO CONDUTTORE

Fissata la frequenza ω per un' onda e.m. piana di questa frequenza abbiamo: $\dot{\vec{E}} = \frac{\partial \vec{E}}{\partial t} = -i\omega\vec{E}$.

Naturalmente ci siamo riferiti alla notazione complessa dell' onda $\vec{E} = \vec{E}_0 e^{i(\vec{k}\cdot\vec{r}-\omega t)} = E_0 e^{i(kz-\omega t)}\hat{i}$ avendo scelto, per maggiore chiarezza, l' asse z lungo $\vec{k}$ e l' asse x lungo $\vec{E}_0$.

Se l'onda si propaga in un mezzo conduttore di conducibilita' σ, nel materiale sara' presente una densita' di corrente $\vec{j} = \sigma\vec{E}$. L'equazione di Maxwell $rot\vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}$ potra' allora essere riscritta come: $rot\vec{H} = \sigma\vec{E} + \varepsilon_0\varepsilon\dot{\vec{E}} = \sigma\frac{\dot{\vec{E}}}{-i\omega} + \varepsilon_0\varepsilon\dot{\vec{E}}$ e, in definitiva:

$$rot\vec{H} = \varepsilon_0(\varepsilon + i\frac{\sigma}{\varepsilon_0\omega})\dot{\vec{E}}$$

Si vede allora che basta considerare una nuova costante dielettrica per il materiale: alla ε, che e' il contributo delle cariche legate, bisogna aggiungere il contributo delle cariche libere e cioe' quello che nasce dalla conduzione.

Alle frequenze "basse" sia ε che σ sono reali (e positivi). Nei metalli $\sigma \approx 10^8(\Omega\cdot m)^{-1}$ ed $\varepsilon \approx 1$ per cui, tenendo conto del valore di ε_0, si vede che, fino a frequenze dell' ordine di 10^{14}, si puo' trascurare ε e tenere solo il contributo delle cariche libere $i\frac{\sigma}{\varepsilon_0\omega}$. Inoltre, fino a frequenze dell' ordine di quelle delle microonde, la conducibilita' e' indipendente dalla frequenza ed e' circa uguale alla conducibilita' statica σ_0. Riscrivendo semplicemente quanto gia' trovato nel caso dei dielettrici non magnetizzabili ($\mu \approx 1$ e' un caso generalissimo) si ottiene: $k = \frac{\omega}{c}\sqrt{\varepsilon}$. Essendo $\sqrt{i} = \frac{1+i}{\sqrt{2}}$, si ha

$$\sqrt{\varepsilon} = n + i\beta = \sqrt{\frac{\sigma_0}{\varepsilon_0\omega}}\left(\frac{1+i}{\sqrt{2}}\right).$$

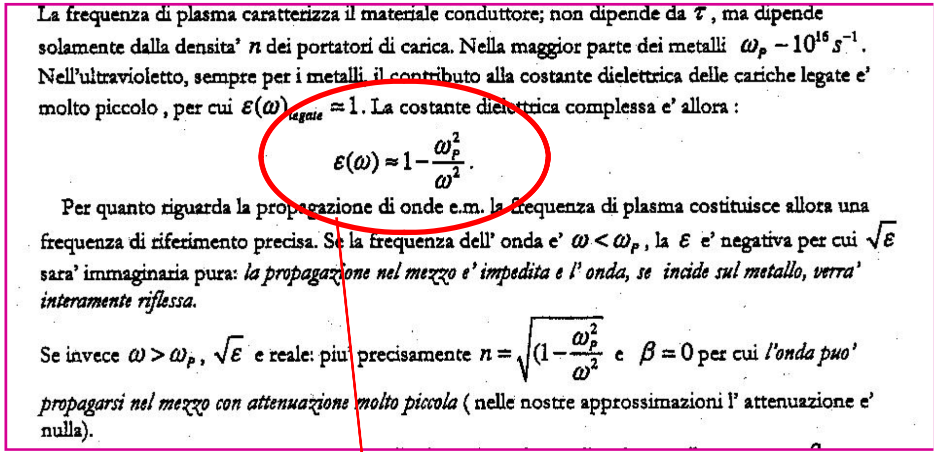
L'ultima espressione mostra che $n = \beta = \sqrt{\frac{\sigma_0}{2\varepsilon_0\omega}}$.

Introducendo il valore di k nell' onda da cui siamo partiti, avremo alla fine

$\vec{E} = E_0 e^{i(kz-\omega t)} = E_0 e^{-\frac{\omega}{c}\beta z} e^{i(\frac{\omega}{c}nz-\omega t)}\hat{i}$ e, da qui, e dalla $rot\vec{E} = -\dot{\vec{B}} \Rightarrow i\vec{k}\wedge\vec{E} = i\omega\vec{B}$,

$$\vec{B} = \frac{n+i\beta}{c}E_0 e^{-\frac{\omega}{c}\beta z} e^{i(\frac{\omega}{c}nz-\omega t)}\vec{j}$$

Effective dielectric constant for a metal

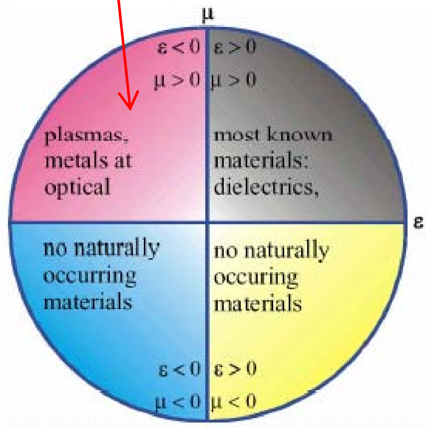


La frequenza di plasma caratterizza il materiale conduttore; non dipende da τ, ma dipende solamente dalla densita' n dei portatori di carica. Nella maggior parte dei metalli $\omega_p - 10^{16}s^{-1}$. Nell'ultravioletto, sempre per i metalli, il contributo alla costante dielettrica delle cariche legate e' molto piccolo, per cui $\varepsilon(\omega)_{legate} \approx 1$. La costante dielettrica complessa e' allora :

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

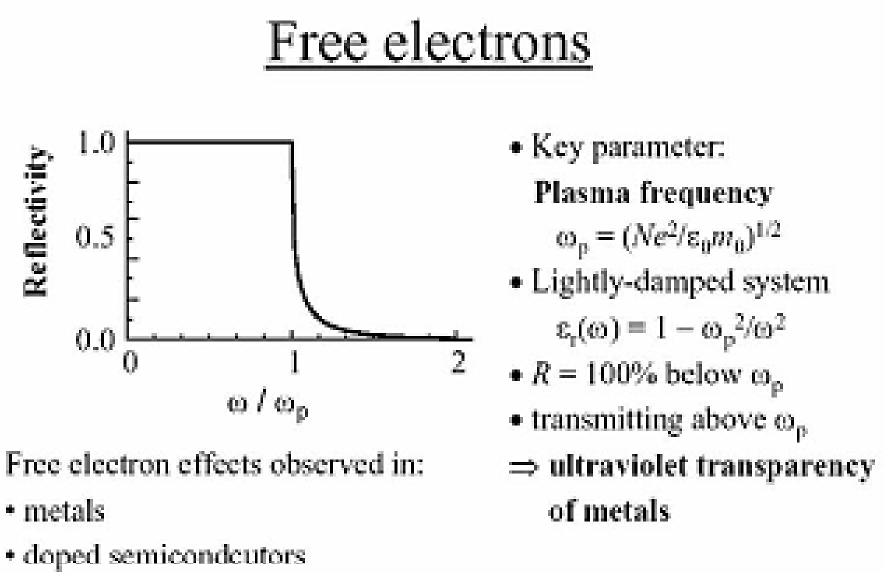
Per quanto riguarda la propagazione di onde e.m. la frequenza di plasma costituisce allora una frequenza di riferimento precisa. Se la frequenza dell' onda e' $\omega < \omega_p$, la ε e' negativa per cui $\sqrt{\varepsilon}$ sara' immaginaria pura: *la propagazione nel mezzo e' impedita e l' onda, se incide sul metallo, verra' interamente riflessa.*

Se invece $\omega > \omega_p$, $\sqrt{\varepsilon}$ e reale: piu' precisamente $n = \sqrt{(1 - \frac{\omega_p^2}{\omega^2}}$ e $\beta = 0$ per cui *l'onda puo' propagarsi nel mezzo con attenuazione molto piccola* (nelle nostre approssimazioni l' attenuazione e' nulla).



Negative dielectric constant means absorption

Qualitative optical behavior of metals



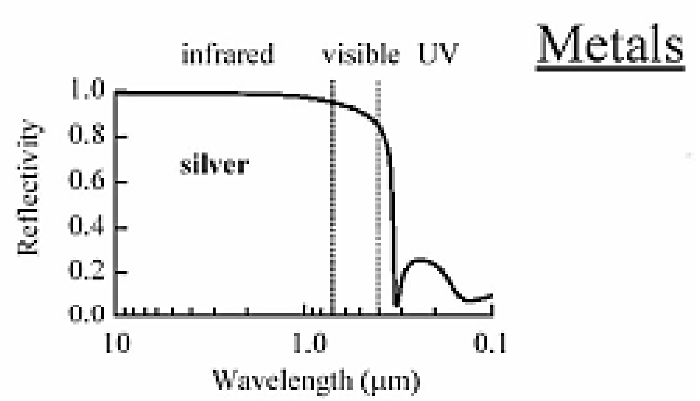
Free electrons

- Key parameter:
  Plasma frequency
  $\omega_p = (Ne^2/\varepsilon_0 m_0)^{1/2}$
- Lightly-damped system
  $\varepsilon_r(\omega) = 1 - \omega_p^2/\omega^2$
- R = 100% below ω_p
- transmitting above ω_p

⇒ **ultraviolet transparency of metals**

Free electron effects observed in:
- metals
- doped semicondcutors

modello teorico



Per $\omega >> \omega_p$:
$\varepsilon = 1$,
$n = 1$,
materiale trasparente;

Per $\omega < \omega_p$:
$\varepsilon < 0$,
n complesso,
materiale riflettente.

Quindi anche gli elettroni liberi contribuiscono alla riflettività dei metalli.

A sinistra è mostrato un reale spettro di Riflettività di un metallo, ed è evidenziato l'assorbimento alla frequenza di plasma.

La trasmettività è molto bassa (se non per strati molto sottili) perché il metallo essenzialmente riflette, sia nell'IR che nel visibile.

Surface plasmons at a metal/dielectric interface I

Now consider a more complicated situation than that in simple homogeneous and isotropic material, namely, a plane boundary between two such regions, as is shown in Fig. 1. The dielectric constant of medium 1, ε_1 is assumed real and positive. For the time being assume ε_2 to be real, but make no assumption about its sign.

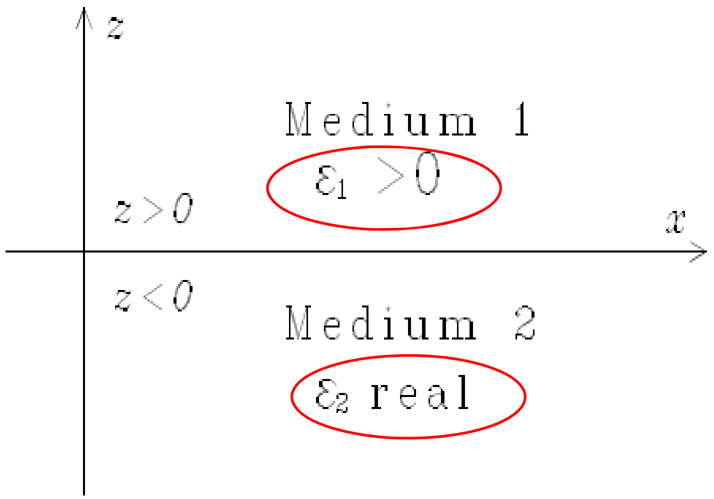
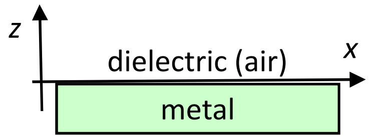
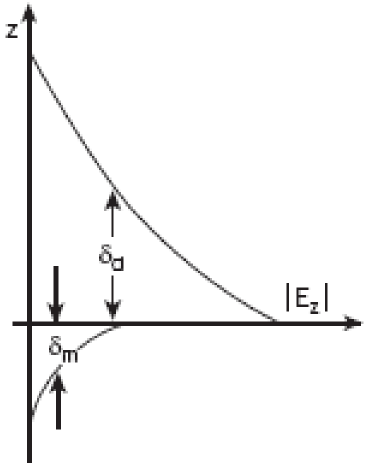


Figure 1: Interface between di



Waves at an interface between materials with different dielectric constants



Solution of the wave equation with the above boundary conditions:

There are a set of solutions called "surface waves" which exist at the boundary between medium 1 and 2. These waves propagate along the surface $z = 0$. One set of such waves which has no y component may be written in complex form as follows:

For medium 1, $z \geq 0$,

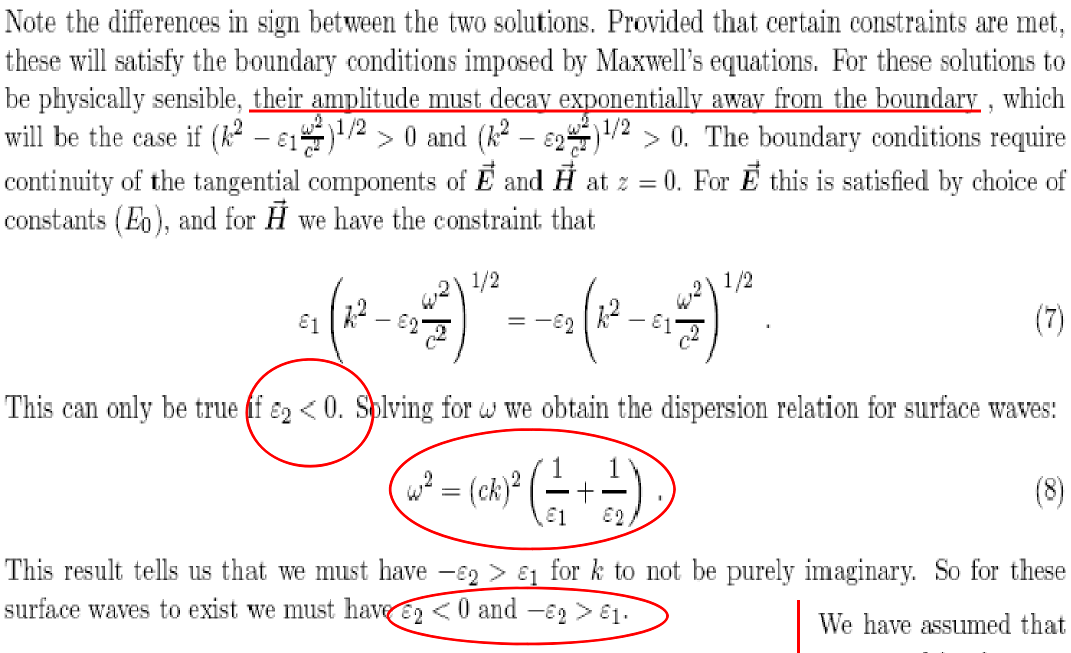
$$\left.\begin{array}{rcl} E_x & = & E_0 \\ E_y & = & 0 \\ E_z & = & ikE_0\left(k^2 - \varepsilon_1\frac{\omega^2}{c^2}\right)^{-1/2} \end{array}\right\} e^{i(kx-\omega t)} e^{-\left(k^2-\varepsilon_1\frac{\omega^2}{c^2}\right)^{1/2} z}. \qquad (5)$$

For medium 2, $z \leq 0$,

$$\left.\begin{array}{rcl} E_x & = & E_0 \\ E_y & = & 0 \\ E_z & = & -ikE_0\left(k^2 - \varepsilon_2\frac{\omega^2}{c^2}\right)^{-1/2} \end{array}\right\} e^{i(kx-\omega t)} e^{+\left(k^2-\varepsilon_2\frac{\omega^2}{c^2}\right)^{1/2} z}. \qquad (6)$$

http://courses.washington.edu/phys431/spr.pdf

Surface plasmons at a metal/dielectric interface II



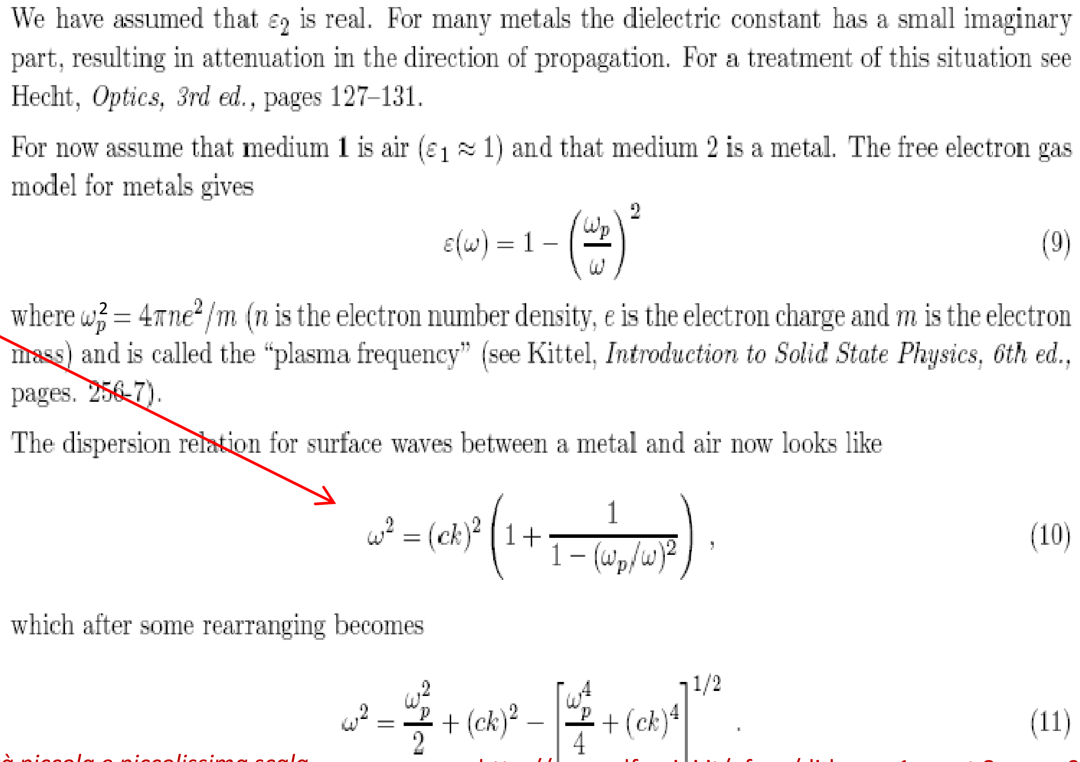
Note the differences in sign between the two solutions. Provided that certain constraints are met, these will satisfy the boundary conditions imposed by Maxwell's equations. For these solutions to be physically sensible, their amplitude must decay exponentially away from the boundary, which will be the case if $(k^2-\varepsilon_1\frac{\omega^2}{c^2})^{1/2}>0$ and $(k^2-\varepsilon_2\frac{\omega^2}{c^2})^{1/2}>0$. The boundary conditions require continuity of the tangential components of $\vec{E}$ and $\vec{H}$ at $z=0$. For $\vec{E}$ this is satisfied by choice of constants (E_0), and for $\vec{H}$ we have the constraint that

$$\varepsilon_1\left(k^2-\varepsilon_2\frac{\omega^2}{c^2}\right)^{1/2}=-\varepsilon_2\left(k^2-\varepsilon_1\frac{\omega^2}{c^2}\right)^{1/2} . \tag{7}$$

This can only be true if $\varepsilon_2<0$. Solving for ω we obtain the dispersion relation for surface waves:

$$\omega^2=(ck)^2\left(\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}\right) . \tag{8}$$

This result tells us that we must have $-\varepsilon_2>\varepsilon_1$ for k to not be purely imaginary. So for these surface waves to exist we must have $\varepsilon_2<0$ and $-\varepsilon_2>\varepsilon_1$.



We have assumed that ε_2 is real. For many metals the dielectric constant has a small imaginary part, resulting in attenuation in the direction of propagation. For a treatment of this situation see Hecht, *Optics, 3rd ed.*, pages 127–131.

For now assume that medium 1 is air ($\varepsilon_1\approx 1$) and that medium 2 is a metal. The free electron gas model for metals gives

$$\varepsilon(\omega)=1-\left(\frac{\omega_p}{\omega}\right)^2 \tag{9}$$

where $\omega_p^2=4\pi ne^2/m$ (n is the electron number density, e is the electron charge and m is the electron mass) and is called the "plasma frequency" (see Kittel, *Introduction to Solid State Physics, 6th ed.*, pages. 256-7).

The dispersion relation for surface waves between a metal and air now looks like

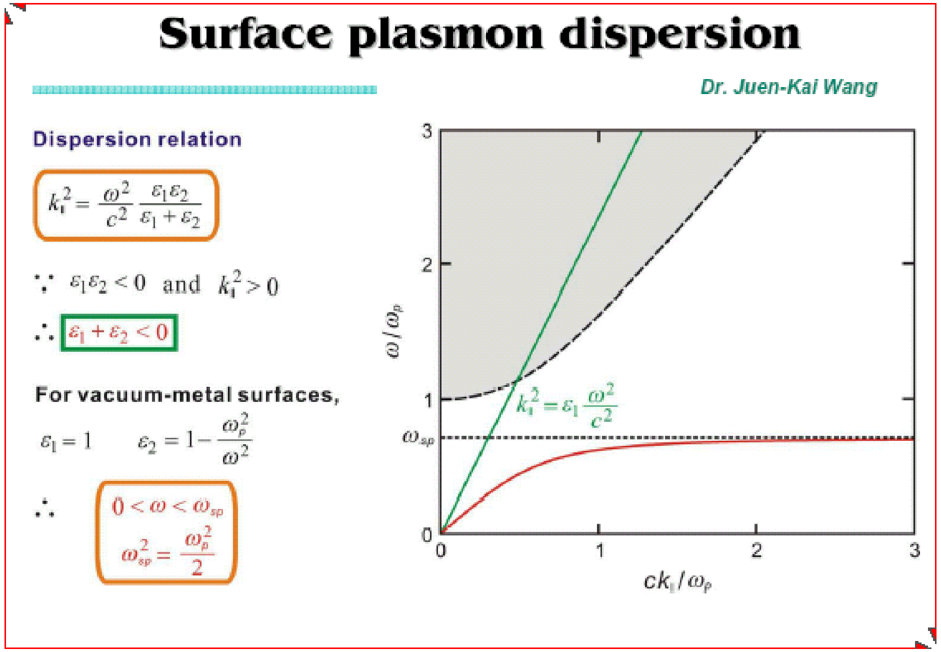
$$\omega^2=(ck)^2\left(1+\frac{1}{1-(\omega_p/\omega)^2}\right) , \tag{10}$$

which after some rearranging becomes

$$\omega^2=\frac{\omega_p^2}{2}+(ck)^2-\left[\frac{\omega_p^4}{4}+(ck)^4\right]^{1/2} . \tag{11}$$

Peculiar dispersion relation (with a resonance condition)

Dispersion relations



Surface plasmon dispersion

Dr. Juen-Kai Wang

Dispersion relation

$$\boxed{k_\parallel^2 = \frac{\omega^2}{c^2}\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}}$$

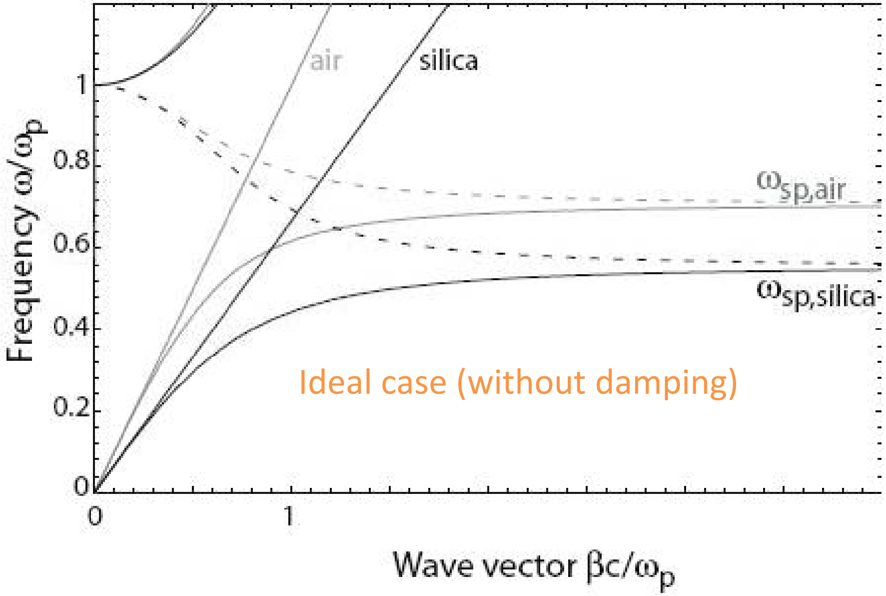
∵ $\varepsilon_1\varepsilon_2 < 0$ and $k_\parallel^2 > 0$

∴ $\boxed{\varepsilon_1+\varepsilon_2 < 0}$

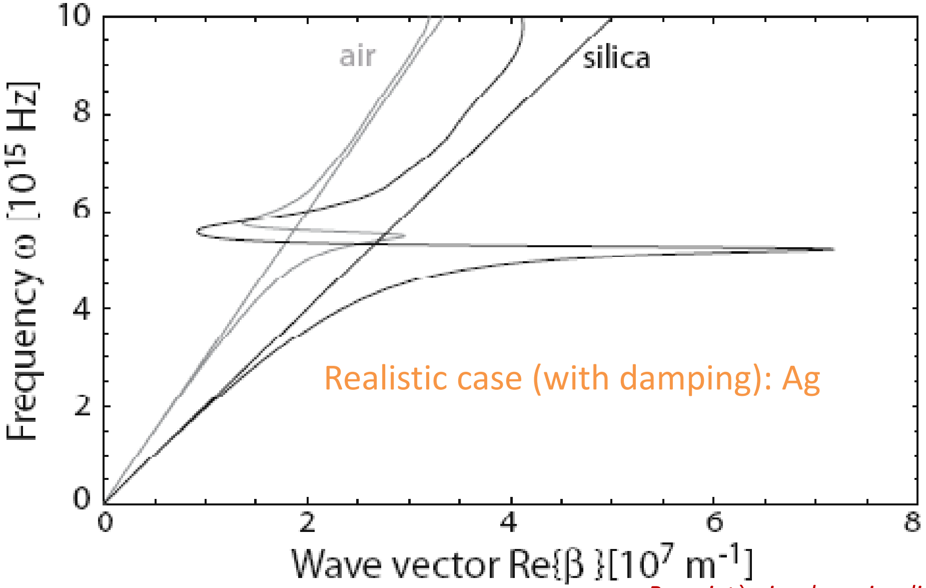
For vacuum-metal surfaces,

$\varepsilon_1 = 1 \qquad \varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2}$

∴ $\boxed{\begin{array}{c} 0 < \omega < \omega_{sp} \\ \omega_{sp}^2 = \frac{\omega_p^2}{2} \end{array}}$



Ideal case (without damping)



Realistic case (with damping): Ag

Per un metallo ideale (senza smorzamento) alla risonanza β diverge e la velocità di gruppo tende a zero: fenomeno puramente elettrostatico

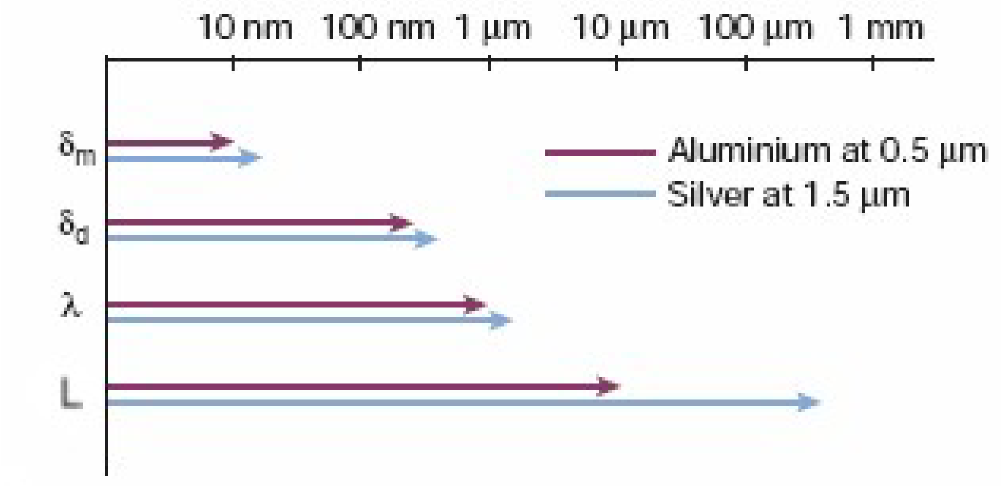
Materiale da Simone Birindelli
Tesi di Laurea in Fisica, 2008

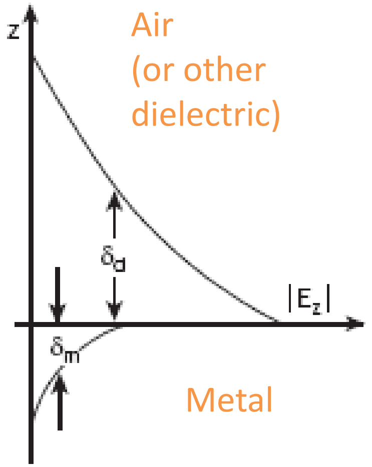
Realistic case

METALLO REALE

- Funzione dielettrica e vettore d'onda β complessi
- Il plasmone si propaga ma viene smorzato con lunghezza di attenuazione $L = (2 \text{ Im } (\beta))^{-1}$, tipicamente compresa fra i 10 e i 100μm nel visibile
- Alla risonanza β raggiunge un valore limite finito, e quindi esiste un limite inferiore alla lunghezza d'onda del plasmone
- Vicino alla risonanza si ha confinamento migliore (subdiffrattivo) ma minore lunghezza propagazione
- Esempi numerici: interfaccia fra aria e argento,

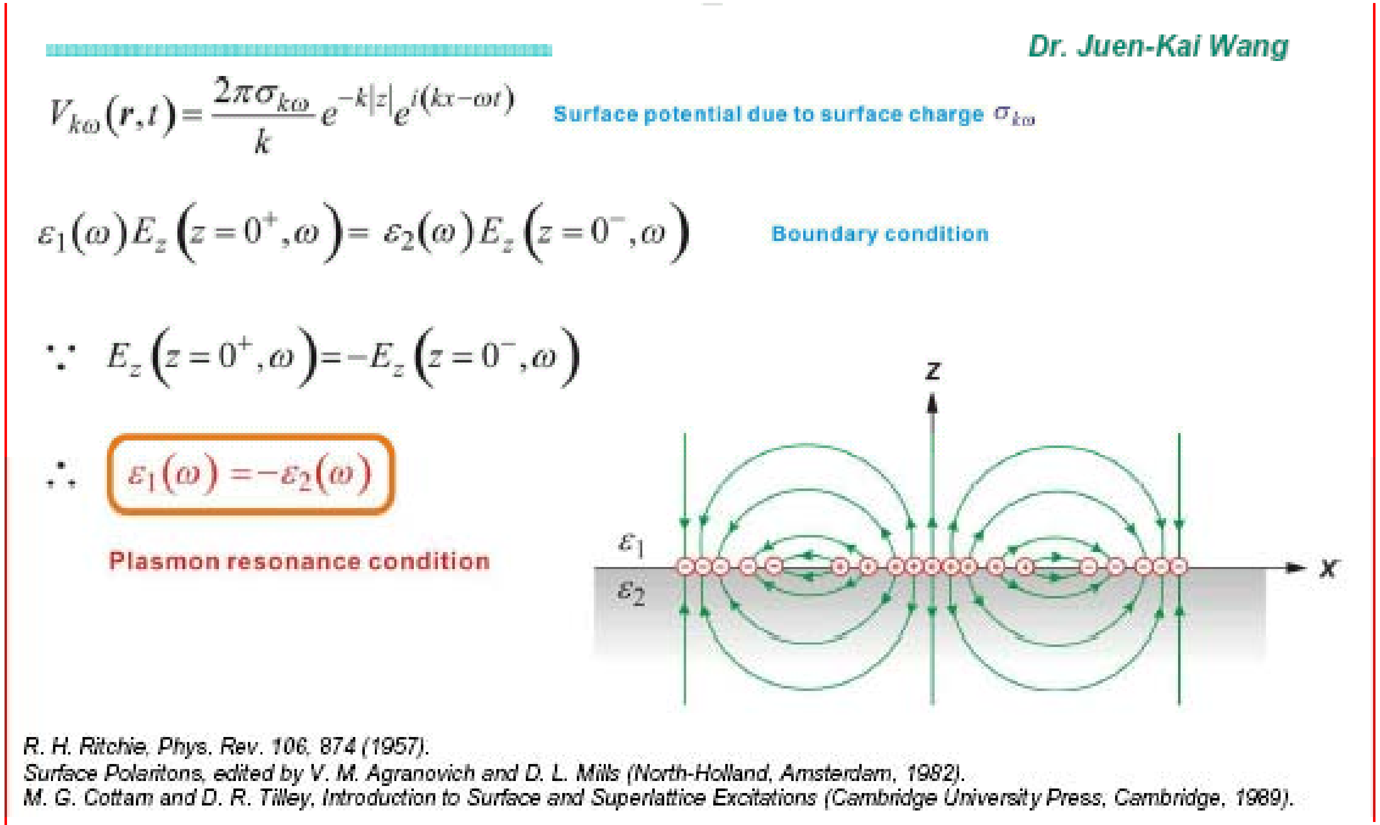
  con λ_0 = 450 nm si ha L = 16 μm e δ_d = 180 nm, invece con λ_0 = 1.5 μm si ha L = 1080 μm e δ_d = 2.6 μm
- In generale, migliore è il confinamento, minore è la lunghezza di propagazione, e viceversa





Sub-diffraction confinement
Possibility of propagation

Summary of surface plasmons



Dr. Juen-Kai Wang

$$V_{k\omega}(\mathbf{r},t)=\frac{2\pi\sigma_{k\omega}}{k}e^{-k|z|}e^{i(kx-\omega t)}$$

Surface potential due to surface charge $\sigma_{k\omega}$

$$\varepsilon_1(\omega)E_z\left(z=0^+,\omega\right)=\varepsilon_2(\omega)E_z\left(z=0^-,\omega\right)$$

Boundary condition

$$\because\ E_z\left(z=0^+,\omega\right)=-E_z\left(z=0^-,\omega\right)$$

$$\therefore\ \boxed{\varepsilon_1(\omega)=-\varepsilon_2(\omega)}$$

Plasmon resonance condition

R. H. Ritchie, Phys. Rev. 106, 874 (1957).
Surface Polaritons, edited by V. M. Agranovich and D. L. Mills (North-Holland, Amsterdam, 1982).
M. G. Cottam and D. R. Tilley, Introduction to Surface and Superlattice Excitations (Cambridge University Press, Cambridge, 1989).

Summarizing:

✓plasmon oscillations can be seen as space and time modulations of free charges at the surface of the metal/dielectric interface

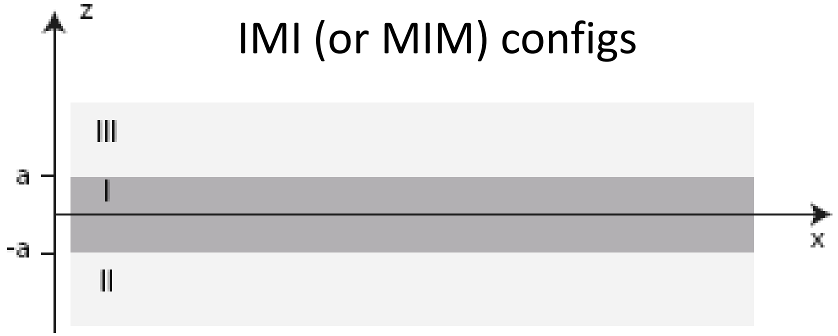
✓a resonance frequency exists (depending on material properties) where oscillation effects are enhanced

✓plasmons exhibit a longitudinal character

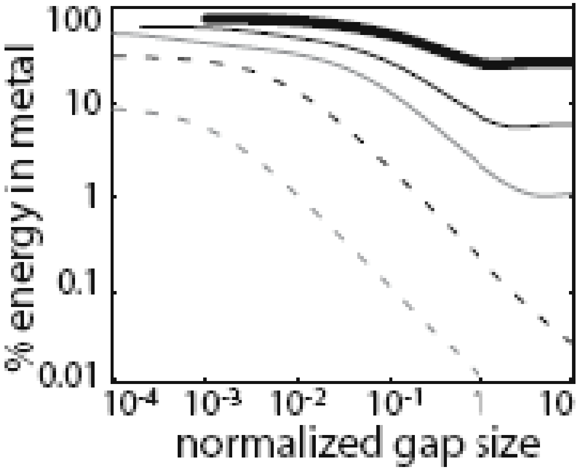
Note: plasmons are evident with noble metals (charges should be free as more as possible, metal should be pure, interfaces well defined, without surface oxidization or similar effects)

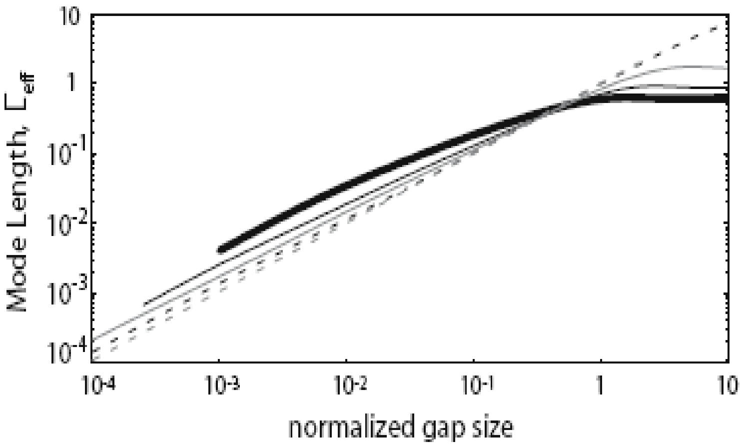
Using surface plasmons as waveguides

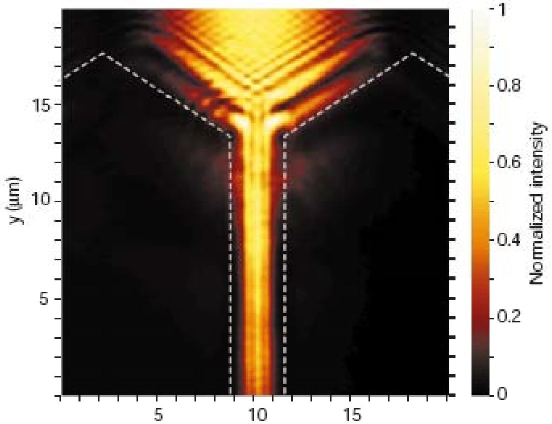
IMI (or MIM) configs



Sistemi di film sottili dielettrici e conduttori alternati danno luogo a modi accoppiati, con parità definita se substrato e superstrato sono dello stesso materiale



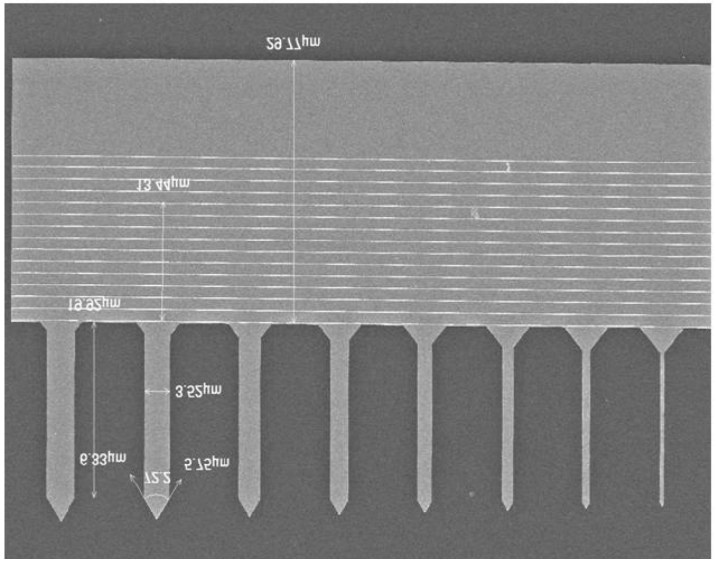




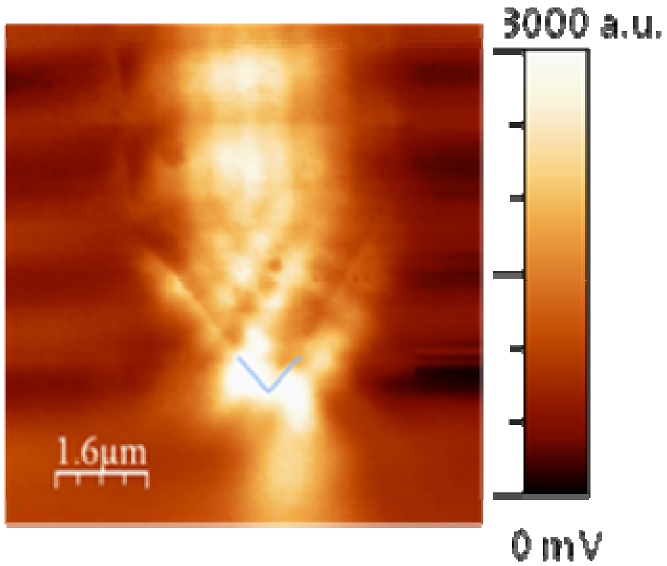
- *Oscillazioni plasmoniche possono essere utilizzate per il trasporto di energia (guide d'onda)*
- *Grandi potenzialità applicative: plasmoni superficie consentono di confinare e guidare segnali luminosi in regioni di dimensioni inferiori a limite diffrazione, e lungo percorsi fortemente angolati, impossibile in sistemi basati su guide d'onda dielettriche (fibre ottiche)*

Surface plasmon concentrators

Array of “concentrators” made of Gold



Map of the electromagnetic field local intensity(acquired in the near-field)



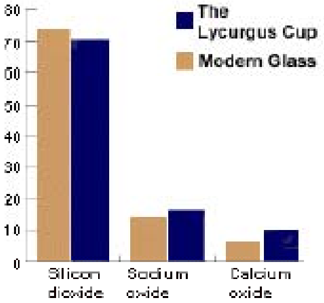
Efficient propagation of radiation (energy) accomplished in a device with small dimensions, much smaller (thickness) than the wavelength

Courtesy: F.Tantussi, A.Bouhelier

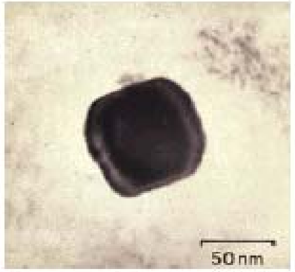
Optical behavior of metal nanoparticles I

Mysterious red color in Lycurgus Cup

Dr. Juen-Kai Wang



The same composition as modern glass



X-ray analysis:
70% Ag + 30% Au

These Ag-Au nanoparticles (~300 ppm) scatter the light, rather in the same way that fine particles in the atmosphere cause a 'red sky at night' effect. They cause the color effects shown by the Cup.

The Lycurgus Cup, Roman (4th century AD), British Museum (www.thebritishmuseum.ac.uk)

See: http://www.ndhu.edu.tw /~nano/93041702.pdf

Au nanoparticles in solution

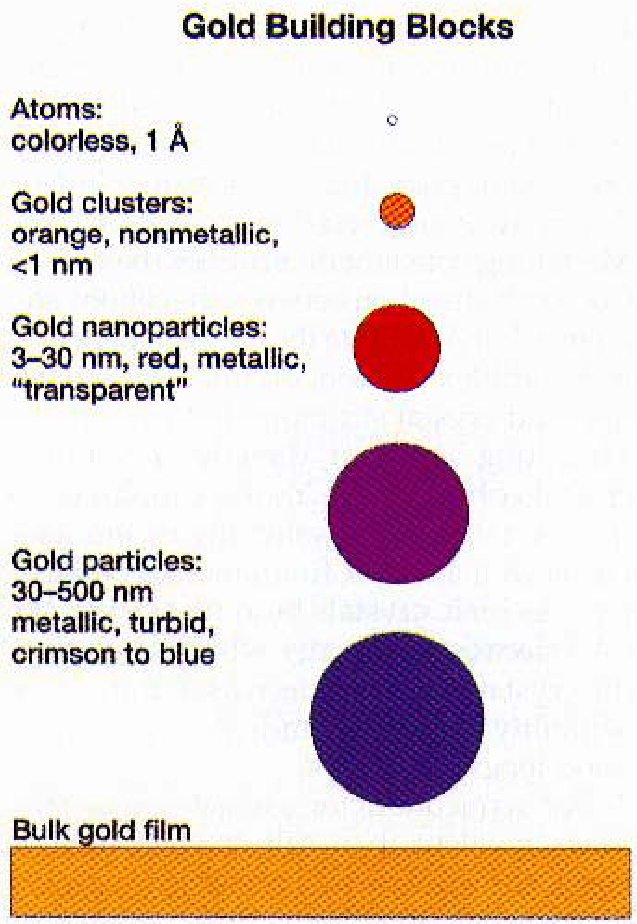


Figure 1. Gold building blocks, from the atomic to the mesoscopic, and their changing colors.

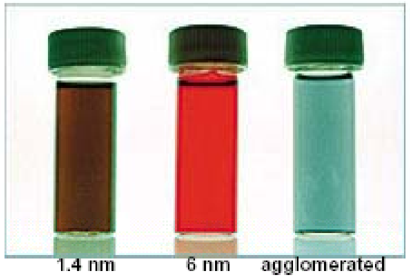
Metal vs semiconductors

In nanosized semiconductors (and dielectrics) the optical behavior is ruled by quantum confinement

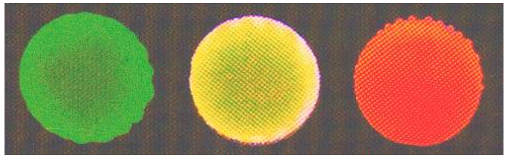
Quantum wells (in 1, 2, 3 dimensions) are created due to the spatial confinement of **single** electron and hole wavefunctions
→ Sets of discrete (or quasi-discrete) energy levels appears
→ Exciton states play a role

Due to the absence of electron transitions from the valence to the conduction bands, electron excitation in metals gets a profoundly different character, e.g.:
-Excitation is **collective (plasma oscillations)**, not single:
-**No excitons** are practically produced;
-Electron distribution tends to be enhanced close to surface → **weak confinement** realized;
-**Diffusive** (e.g., Joule) effects play a role in damping the excitation

Quantum confinement is not relevant in ruling optical properties (but it governs transport properties)



Au nanoparticles in solution

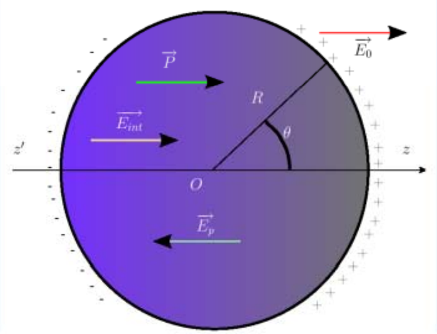


Semiconductive quantum dots in solution

In metal nanoparticles, classical (not quantum) models are enough

Polarization of a (dielectric) sphere I

Here we study a dielectric material made sphere. It is polarized by a polarization vector $\vec{P}$ and we can decompose its internal electric field $\overrightarrow{E_{\mathrm{int}}}$ in a sum of contributions from the external surrounding electric field and the induced electric field.



Schematic of a dielectric polarized sphere

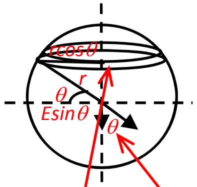
“Total” electric field given by the superposition of “local” and “external” fields

In the space commmon to both spheres, charges compensate so that the electrical field is not affected. In the infinitely small space at the end of each sphere that is not shared with the other one, we have:

a : distance between sphere centers
dS : surface element
so: *acosθ : “volume height”*

$$dq = \rho\, d\tau$$
with $d\tau = a.\cos\theta\, dS$

$$dq = \rho a \cos\theta\, dS$$



and then we have:

$$\sigma = \frac{dq}{dS} = \rho a \cos\theta$$

$\mathbf{E} = \mathbf{z}\left(\int \sigma\, 2\pi r^2 \cos\theta \sin\theta\, d\theta\right)/(4\pi r^2\, \varepsilon_0) =$

Applying the Gauss theorem to each sphere and then the supeposition theorem give, for the common part:

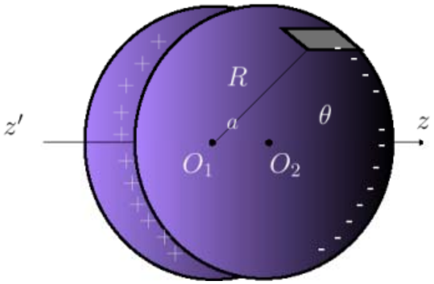
Induced field

$$\boxed{\vec{E_d} = -\frac{\vec{P}}{3\varepsilon_0}}$$

$= \mathbf{z}\, \rho\, a/(3\varepsilon_0) = -\mathbf{P}/(3\varepsilon_0)$

Depolarizing electric field

We must calculate the contributions from the different phenomena. The induced field $\vec{E_d}$ is calculated by decomposing the sphere in two virtual spheres separated by an infinitesimal space we will note a along O_z so that the sphere 1 has a $-\rho$ volume density charge and the sphere 2 has a $+\rho$ volume density charge. You can easily prove that these spheres together are equivalent to a single polarized one.



The polarization induced electric field is colinear but in the opposite direction to the external field. It is called *depolarizing field*.

Knowing the relation between the polarization vector and the electric field, we can deduce a global relation:

$$\mathbf{P} = \varepsilon_0 \chi\, \mathbf{E}_{int}$$

$$\overrightarrow{E_{\mathrm{int}}} = \vec{E_0} + \vec{E_d}$$

$$\chi = \varepsilon/\varepsilon_0 - 1$$

$$\overrightarrow{E_{\mathrm{int}}} = \vec{E_0} - \frac{\chi_r \overrightarrow{E_{\mathrm{int}}}}{3}$$

So, for a linear homogeneous isotropic material, we get:

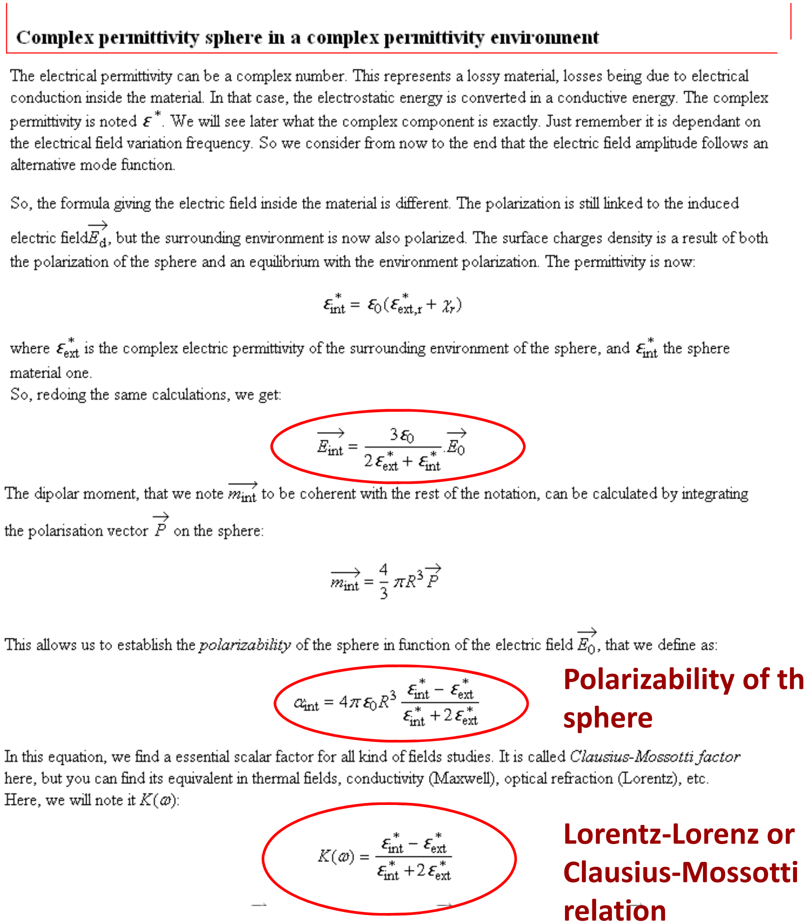
(in a vacuum)

Internal field

$$\boxed{\overrightarrow{E_{\mathrm{int}}} = \frac{3\varepsilon_0}{2\varepsilon_0 + \varepsilon}\vec{E_0}}$$

Internal field linearly depends on the external field

Polarization of a (dielectric) sphere II



Complex permittivity sphere in a complex permittivity environment

The electrical permittivity can be a complex number. This represents a lossy material, losses being due to electrical conduction inside the material. In that case, the electrostatic energy is converted in a conductive energy. The complex permittivity is noted ε^*. We will see later what the complex component is exactly. Just remember it is dependant on the electrical field variation frequency. So we consider from now to the end that the electric field amplitude follows an alternative mode function.

So, the formula giving the electric field inside the material is different. The polarization is still linked to the induced electric field$\overrightarrow{E_d}$, but the surrounding environment is now also polarized. The surface charges density is a result of both the polarization of the sphere and an equilibrium with the environment polarization. The permittivity is now:

$$\varepsilon^*_{\text{int}} = \varepsilon_0(\varepsilon^*_{\text{ext},r} + \chi_r)$$

where $\varepsilon^*_{\text{ext}}$ is the complex electric permittivity of the surrounding environment of the sphere, and $\varepsilon^*_{\text{int}}$ the sphere material one.
So, redoing the same calculations, we get:

$$\overrightarrow{E_{\text{int}}} = \frac{3\varepsilon_0}{2\varepsilon^*_{\text{ext}} + \varepsilon^*_{\text{int}}}.\overrightarrow{E_0}$$

The dipolar moment, that we note $\overrightarrow{m_{\text{int}}}$ to be coherent with the rest of the notation, can be calculated by integrating the polarisation vector $\overrightarrow{P}$ on the sphere:

$$\overrightarrow{m_{\text{int}}} = \frac{4}{3}\pi R^3 \overrightarrow{P}$$

This allows us to establish the *polarizability* of the sphere in function of the electric field $\overrightarrow{E_0}$, that we define as:

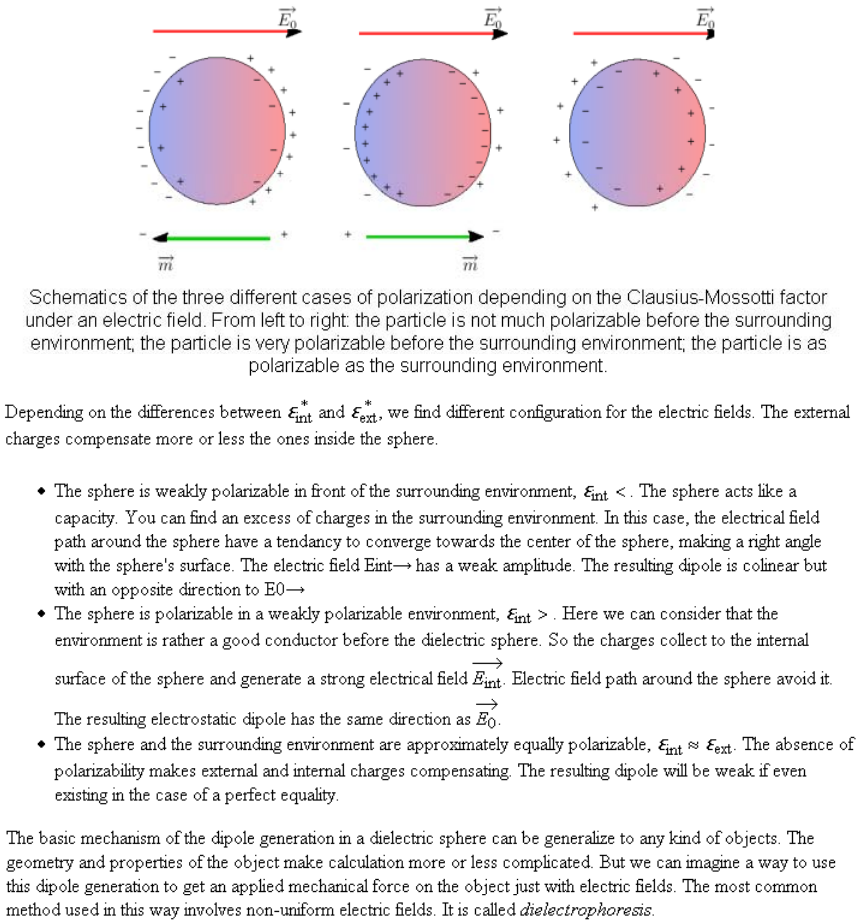
$$\alpha_{\text{int}} = 4\pi\varepsilon_0 R^3 \frac{\varepsilon^*_{\text{int}} - \varepsilon^*_{\text{ext}}}{\varepsilon^*_{\text{int}} + 2\varepsilon^*_{\text{ext}}}$$

Polarizability of the sphere

In this equation, we find a essential scalar factor for all kind of fields studies. It is called *Clausius-Mossotti factor* here, but you can find its equivalent in thermal fields, conductivity (Maxwell), optical refraction (Lorentz), etc.
Here, we will note it $K(\omega)$:

$$K(\omega) = \frac{\varepsilon^*_{\text{int}} - \varepsilon^*_{\text{ext}}}{\varepsilon^*_{\text{int}} + 2\varepsilon^*_{\text{ext}}}$$

Lorentz-Lorenz or Clausius-Mossotti relation



Schematics of the three different cases of polarization depending on the Clausius-Mossotti factor under an electric field. From left to right: the particle is not much polarizable before the surrounding environment; the particle is very polarizable before the surrounding environment; the particle is as polarizable as the surrounding environment.

Depending on the differences between $\varepsilon^*_{\text{int}}$ and $\varepsilon^*_{\text{ext}}$, we find different configuration for the electric fields. The external charges compensate more or less the ones inside the sphere.

- The sphere is weakly polarizable in front of the surrounding environment, $\varepsilon_{\text{int}} <$. The sphere acts like a capacity. You can find an excess of charges in the surrounding environment. In this case, the electrical field path around the sphere have a tendancy to converge towards the center of the sphere, making a right angle with the sphere's surface. The electric field Eint⟶ has a weak amplitude. The resulting dipole is colinear but with an opposite direction to E0⟶
- The sphere is polarizable in a weakly polarizable environment, $\varepsilon_{\text{int}} >$. Here we can consider that the environment is rather a good conductor before the dielectric sphere. So the charges collect to the internal surface of the sphere and generate a strong electrical field $\overrightarrow{E_{\text{int}}}$. Electric field path around the sphere avoid it. The resulting electrostatic dipole has the same direction as $\overrightarrow{E_0}$.
- The sphere and the surrounding environment are approximately equally polarizable, $\varepsilon_{\text{int}} \approx \varepsilon_{\text{ext}}$. The absence of polarizability makes external and internal charges compensating. The resulting dipole will be weak if even existing in the case of a perfect equality.

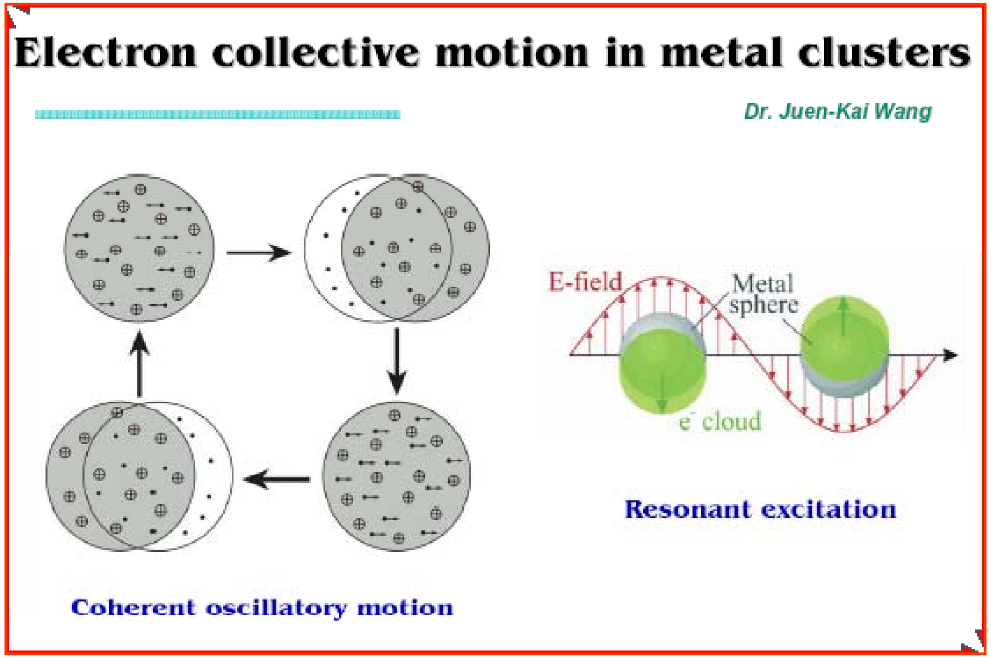
The basic mechanism of the dipole generation in a dielectric sphere can be generalize to any kind of objects. The geometry and properties of the object make calculation more or less complicated. But we can imagine a way to use this dipole generation to get an applied mechanical force on the object just with electric fields. The most common method used in this way involves non-uniform electric fields. It is called *dielectrophoresis*.

$$K(\omega) = \frac{\varepsilon_{int} - \varepsilon_{ext}}{\varepsilon_{ext} + 2\varepsilon_{int}}$$

Polarizability depends on internal and external dielectric constants (for a sphere, the dependence is given by Clausius-Mossotti)

http://matthieu.lagouge.free.fr/elecstq/sphere.xhtml

Surface plasmons and nanoparticles



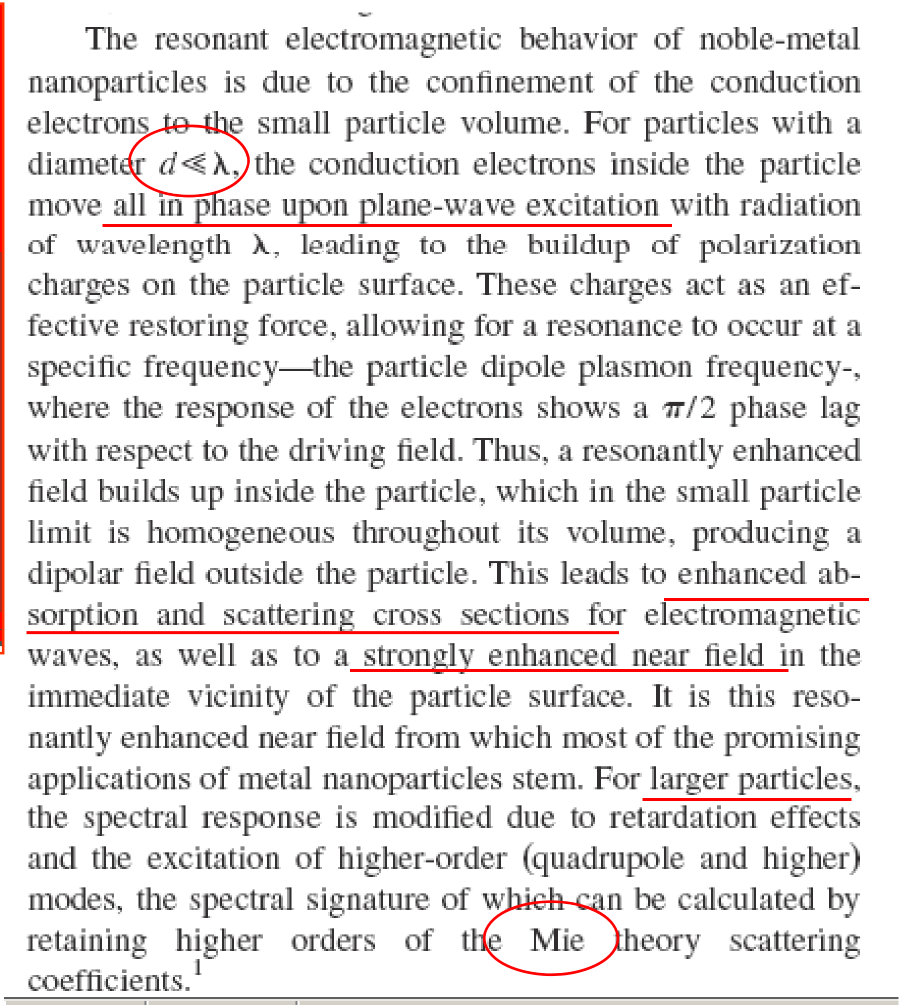
Electron collective motion in metal clusters

Dr. Juen-Kai Wang

Coherent oscillatory motion

Resonant excitation

- ✓ Geometrical restrictions are relaxed (the interface layer gets a spherical shape, in case of a spherical nanoparticle)
- ✓ **Excitation can be achieved with conventional (propagating) waves**
- ✓ Collective plasma oscillations occur, with a "coherent" character if particle size is (much) smaller than the wavelength



The resonant electromagnetic behavior of noble-metal nanoparticles is due to the confinement of the conduction electrons to the small particle volume. For particles with a diameter $d \ll \lambda$, the conduction electrons inside the particle move all in phase upon plane-wave excitation with radiation of wavelength λ, leading to the buildup of polarization charges on the particle surface. These charges act as an effective restoring force, allowing for a resonance to occur at a specific frequency—the particle dipole plasmon frequency-, where the response of the electrons shows a $\pi/2$ phase lag with respect to the driving field. Thus, a resonantly enhanced field builds up inside the particle, which in the small particle limit is homogeneous throughout its volume, producing a dipolar field outside the particle. This leads to enhanced absorption and scattering cross sections for electromagnetic waves, as well as to a strongly enhanced near field in the immediate vicinity of the particle surface. It is this resonantly enhanced near field from which most of the promising applications of metal nanoparticles stem. For larger particles, the spectral response is modified due to retardation effects and the excitation of higher-order (quadrupole and higher) modes, the spectral signature of which can be calculated by retaining higher orders of the Mie theory scattering coefficients.[1]

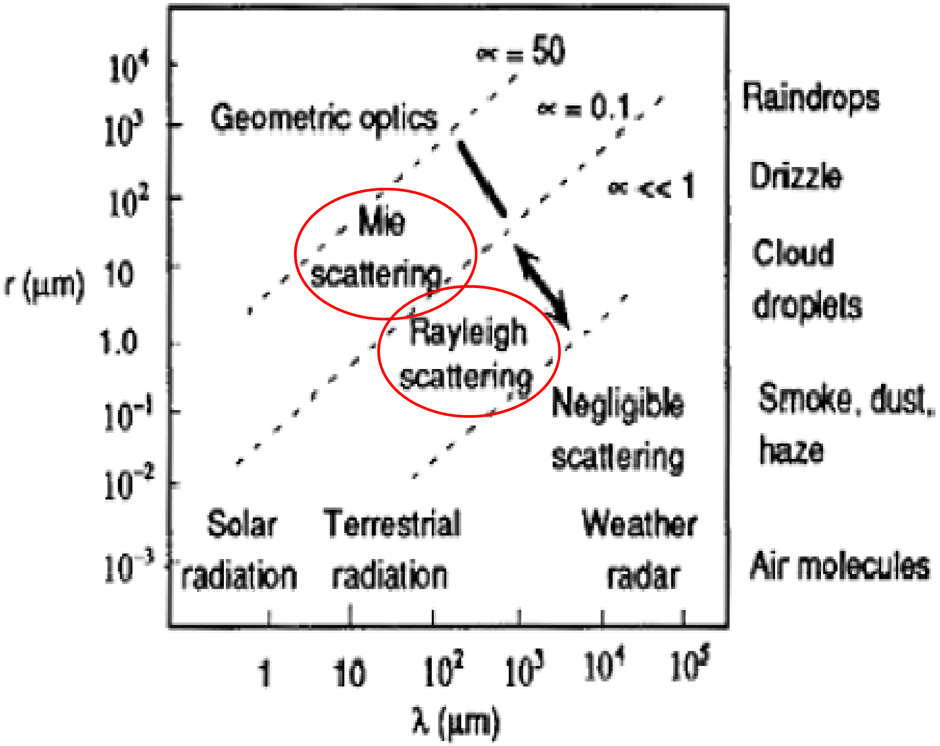
JOURNAL OF APPLIED PHYSICS **98**, 011101 (2005)

APPLIED PHYSICS REVIEWS–FOCUSED REVIEW

Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures

Stefan A. Maier[a] and Harry A. Atwater

Far-field scattering by a small particles



For the dielectrics: well investigated problem (colour of the sky, of the clouds), e.g., in atmospherics

Two main regimes are usually recongnized:

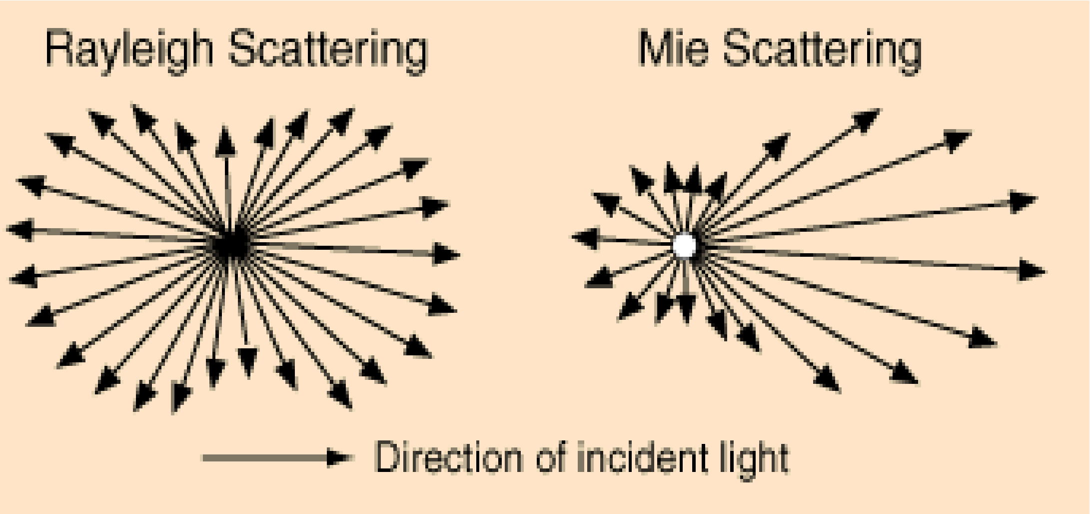
- Rayleigh (for $d << \lambda$)
- Mie (for $d \sim< \lambda$)

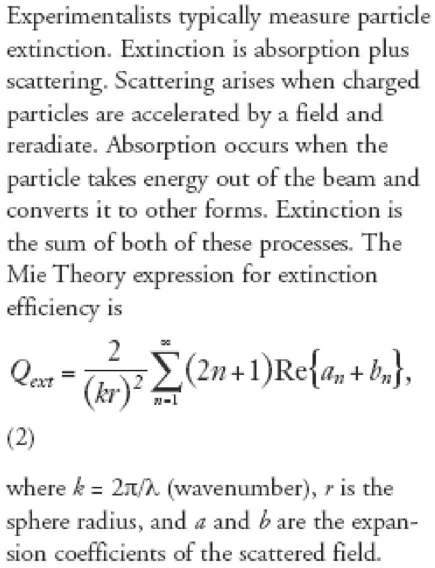
Qualitatively: in Rayleigh any retardation effect is neglected (pure small-sized dipoles); In Mie retardation effects are considered to account for the finite size of the particles

Rayleigh can be retrieved from Mie in the small size limit

Mie scattering and metal nanoparticles

Mie scattering: elastic process with anisotropic character and rather independent of wavelength (contrary to Rayleigh)





Experimentalists typically measure particle extinction. Extinction is absorption plus scattering. Scattering arises when charged particles are accelerated by a field and reradiate. Absorption occurs when the particle takes energy out of the beam and converts it to other forms. Extinction is the sum of both of these processes. The Mie Theory expression for extinction efficiency is

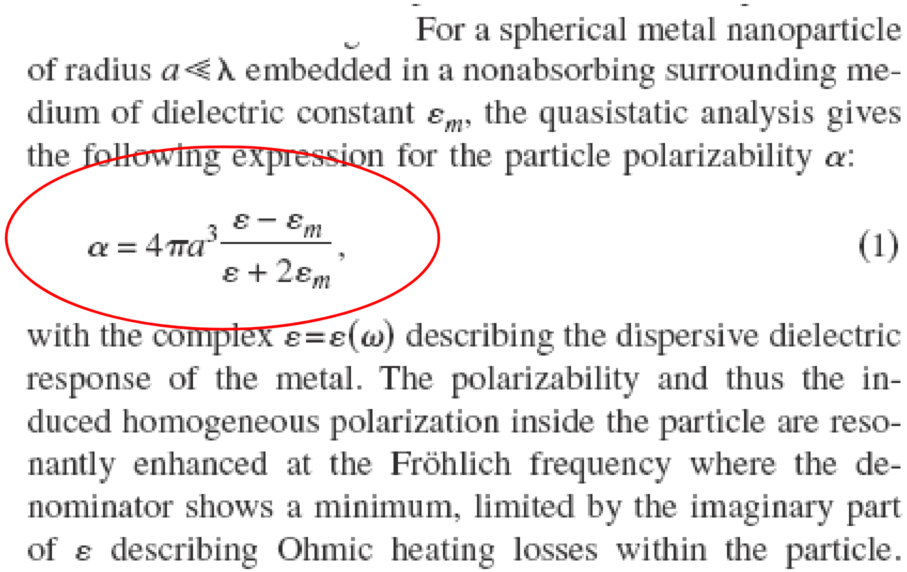
$$Q_{ext} = \frac{2}{(kr)^2}\sum_{n=1}^{\infty}(2n+1)\mathrm{Re}\{a_n + b_n\},$$

(2)

where $k = 2\pi/\lambda$ (wavenumber), r is the sphere radius, and a and b are the expansion coefficients of the scattered field.

For small particles, only the first term(s) of the expansion must be retained!

This corresponds to a "quasi-static" approximation, that is retardation effects can be beglected, i.e., electrons do follow almost completely the driving force



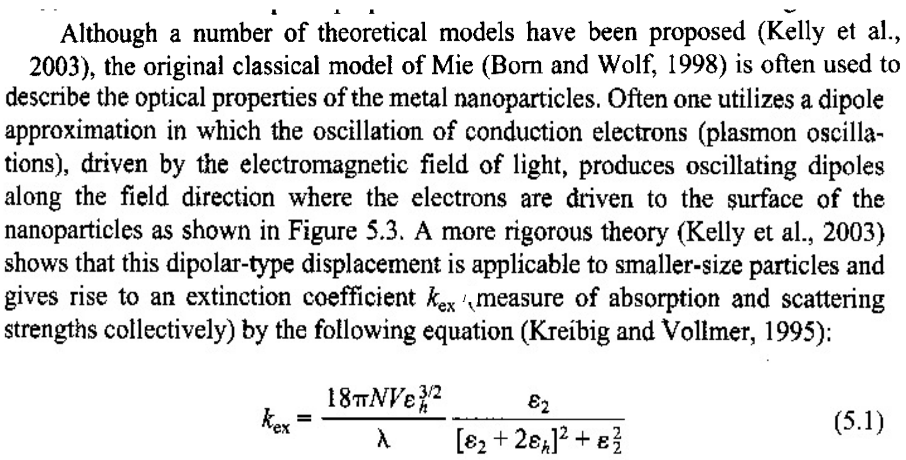
For a spherical metal nanoparticle of radius $a \ll \lambda$ embedded in a nonabsorbing surrounding medium of dielectric constant ε_m, the quasistatic analysis gives the following expression for the particle polarizability α:

$$\alpha = 4\pi a^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}, \qquad (1)$$

with the complex $\varepsilon = \varepsilon(\omega)$ describing the dispersive dielectric response of the metal. The polarizability and thus the induced homogeneous polarization inside the particle are resonantly enhanced at the Fröhlich frequency where the denominator shows a minimum, limited by the imaginary part of ε describing Ohmic heating losses within the particle.

Maier, Atwater, JAP (2005)

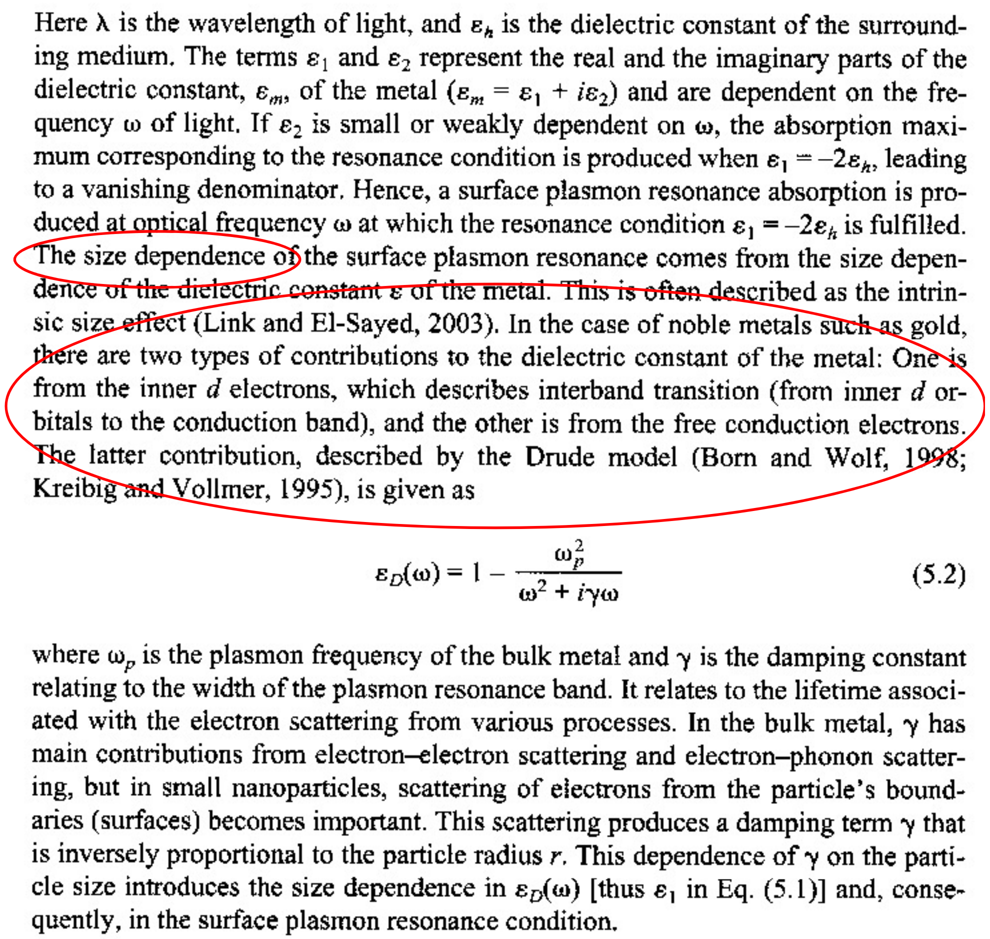
Scattering by small metal particles I



Although a number of theoretical models have been proposed (Kelly et al., 2003), the original classical model of Mie (Born and Wolf, 1998) is often used to describe the optical properties of the metal nanoparticles. Often one utilizes a dipole approximation in which the oscillation of conduction electrons (plasmon oscillations), driven by the electromagnetic field of light, produces oscillating dipoles along the field direction where the electrons are driven to the surface of the nanoparticles as shown in Figure 5.3. A more rigorous theory (Kelly et al., 2003) shows that this dipolar-type displacement is applicable to smaller-size particles and gives rise to an extinction coefficient k_{ex} (measure of absorption and scattering strengths collectively) by the following equation (Kreibig and Vollmer, 1995):

$$k_{\mathrm{ex}} = \frac{18\pi N V \varepsilon_h^{3/2}}{\lambda} \frac{\varepsilon_2}{[\varepsilon_2 + 2\varepsilon_h]^2 + \varepsilon_2^2} \qquad (5.1)$$

Extinction coeff for metal nanoparticles



Here λ is the wavelength of light, and ε_h is the dielectric constant of the surrounding medium. The terms ε_1 and ε_2 represent the real and the imaginary parts of the dielectric constant, ε_m, of the metal ($\varepsilon_m = \varepsilon_1 + i\varepsilon_2$) and are dependent on the frequency ω of light. If ε_2 is small or weakly dependent on ω, the absorption maximum corresponding to the resonance condition is produced when $\varepsilon_1 = -2\varepsilon_h$, leading to a vanishing denominator. Hence, a surface plasmon resonance absorption is produced at optical frequency ω at which the resonance condition $\varepsilon_1 = -2\varepsilon_h$ is fulfilled. The size dependence of the surface plasmon resonance comes from the size dependence of the dielectric constant ε of the metal. This is often described as the intrinsic size effect (Link and El-Sayed, 2003). In the case of noble metals such as gold, there are two types of contributions to the dielectric constant of the metal: One is from the inner d electrons, which describes interband transition (from inner d orbitals to the conduction band), and the other is from the free conduction electrons. The latter contribution, described by the Drude model (Born and Wolf, 1998; Kreibig and Vollmer, 1995), is given as

$$\varepsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \qquad (5.2)$$

where ω_p is the plasmon frequency of the bulk metal and γ is the damping constant relating to the width of the plasmon resonance band. It relates to the lifetime associated with the electron scattering from various processes. In the bulk metal, γ has main contributions from electron–electron scattering and electron–phonon scattering, but in small nanoparticles, scattering of electrons from the particle's boundaries (surfaces) becomes important. This scattering produces a damping term γ that is inversely proportional to the particle radius r. This dependence of γ on the particle size introduces the size dependence in $\varepsilon_D(\omega)$ [thus ε_1 in Eq. (5.1)] and, consequently, in the surface plasmon resonance condition.

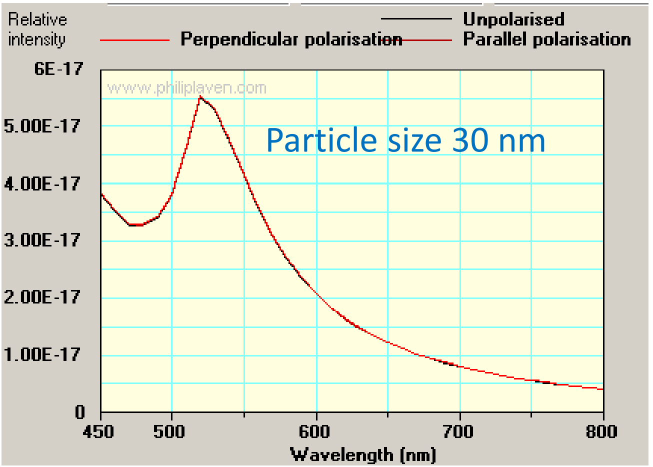
Scattering by metal nanoparticles can be described in terms of Mie extinction coefficient

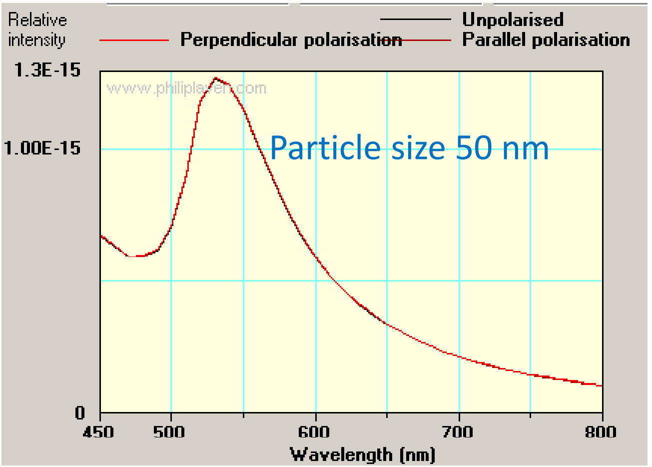
Size effects can be accounted for by considering the contributions from higher multiipolar orders

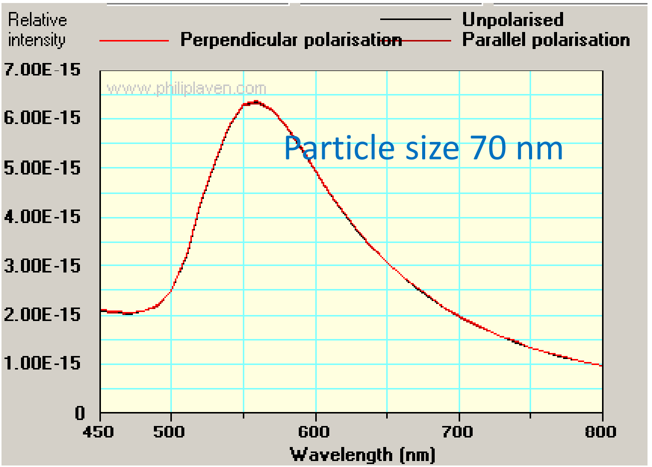
Simulation of the scattered intensity

System: gold in a vacuum
Scattering angle: 175 degrees
Scattering model: Mie

http://www.philiplaven.com/mieplot.htm

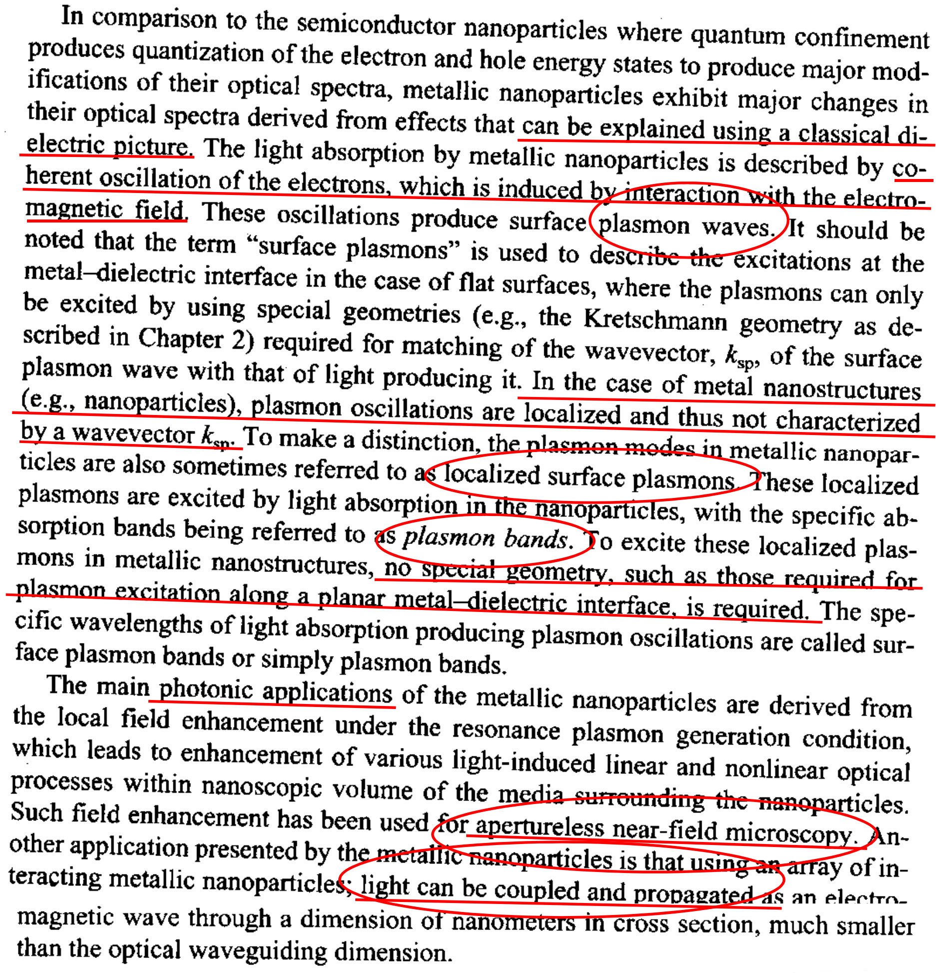






Mie scattering from a metal nanoparticle can be efficiently simulated
Spectral features (peak position and width) depend on the particle size

Optical behavior of small metal particles II



In comparison to the semiconductor nanoparticles where quantum confinement produces quantization of the electron and hole energy states to produce major modifications of their optical spectra, metallic nanoparticles exhibit major changes in their optical spectra derived from effects that can be explained using a classical dielectric picture. The light absorption by metallic nanoparticles is described by coherent oscillation of the electrons, which is induced by interaction with the electromagnetic field. These oscillations produce surface plasmon waves. It should be noted that the term "surface plasmons" is used to describe the excitations at the metal–dielectric interface in the case of flat surfaces, where the plasmons can only be excited by using special geometries (e.g., the Kretschmann geometry as described in Chapter 2) required for matching of the wavevector, k_{sp}, of the surface plasmon wave with that of light producing it. In the case of metal nanostructures (e.g., nanoparticles), plasmon oscillations are localized and thus not characterized by a wavevector k_{sp}. To make a distinction, the plasmon modes in metallic nanoparticles are also sometimes referred to as localized surface plasmons. These localized plasmons are excited by light absorption in the nanoparticles, with the specific absorption bands being referred to as *plasmon bands*. To excite these localized plasmons in metallic nanostructures, no special geometry, such as those required for plasmon excitation along a planar metal–dielectric interface, is required. The specific wavelengths of light absorption producing plasmon oscillations are called surface plasmon bands or simply plasmon bands.

The main photonic applications of the metallic nanoparticles are derived from the local field enhancement under the resonance plasmon generation condition, which leads to enhancement of various light-induced linear and nonlinear optical processes within nanoscopic volume of the media surrounding the nanoparticles. Such field enhancement has been used for apertureless near-field microscopy. Another application presented by the metallic nanoparticles is that using an array of interacting metallic nanoparticles, light can be coupled and propagated as an electromagnetic wave through a dimension of nanometers in cross section, much smaller than the optical waveguiding dimension.

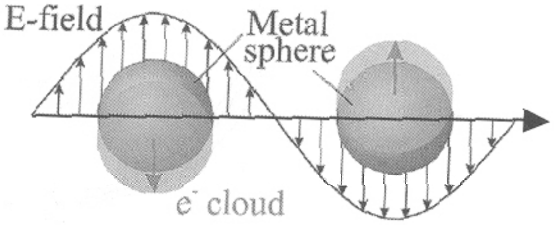
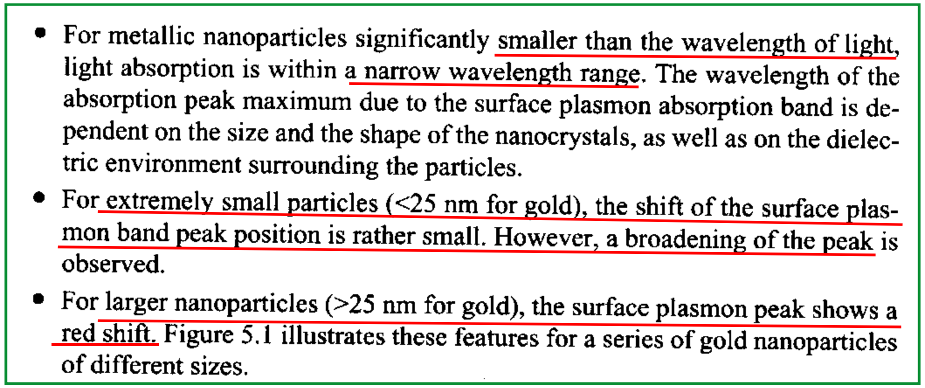


Figure 5.3. Schematic of plasmon oscillation in a metal nanosphere. From Kelly et al. (2003), reproduced with permission.



- For metallic nanoparticles significantly smaller than the wavelength of light, light absorption is within a narrow wavelength range. The wavelength of the absorption peak maximum due to the surface plasmon absorption band is dependent on the size and the shape of the nanocrystals, as well as on the dielectric environment surrounding the particles.
- For extremely small particles (<25 nm for gold), the shift of the surface plasmon band peak position is rather small. However, a broadening of the peak is observed.
- For larger nanoparticles (>25 nm for gold), the surface plasmon peak shows a red shift. Figure 5.1 illustrates these features for a series of gold nanoparticles of different sizes.

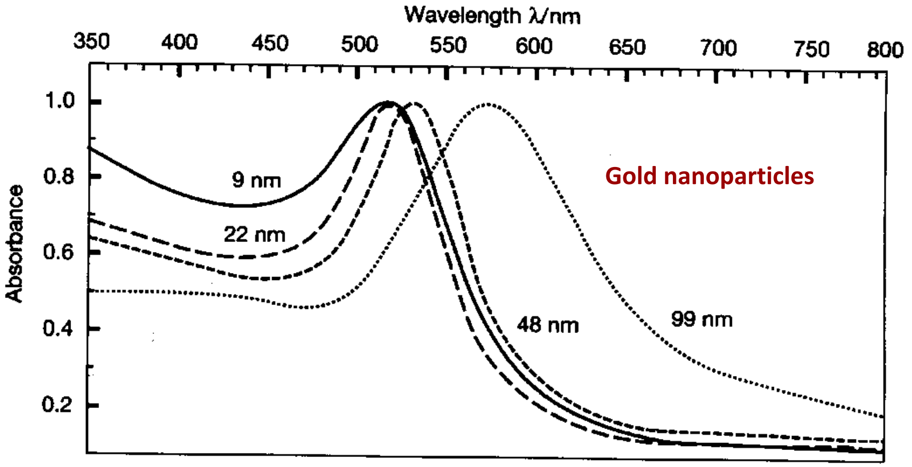
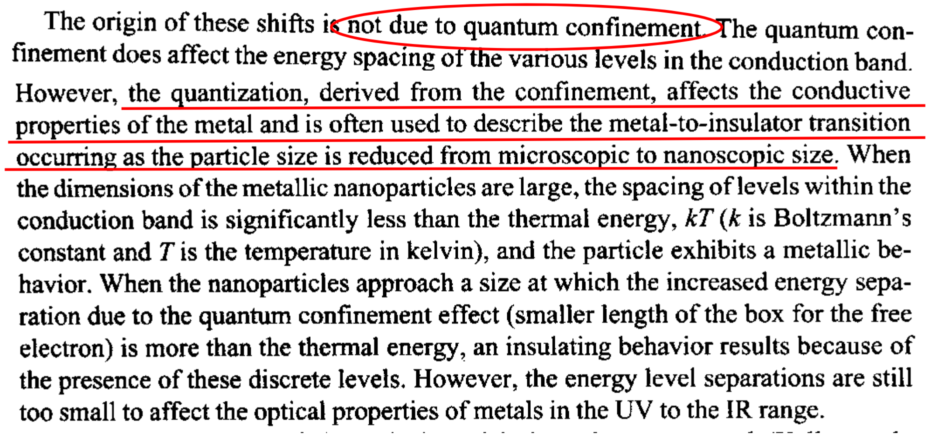


Figure 5.1. Optical absorption spectra of gold nanoparticles of different sizes. From Link and El-Sayed (1999), reproduced with permission.

Red-shift of the absorption peak observed as particle size increases

Optical behavior of small metal particles III



The origin of these shifts is not due to quantum confinement. The quantum confinement does affect the energy spacing of the various levels in the conduction band. However, the quantization, derived from the confinement, affects the conductive properties of the metal and is often used to describe the metal-to-insulator transition occurring as the particle size is reduced from microscopic to nanoscopic size. When the dimensions of the metallic nanoparticles are large, the spacing of levels within the conduction band is significantly less than the thermal energy, kT (k is Boltzmann's constant and T is the temperature in kelvin), and the particle exhibits a metallic behavior. When the nanoparticles approach a size at which the increased energy separation due to the quantum confinement effect (smaller length of the box for the free electron) is more than the thermal energy, an insulating behavior results because of the presence of these discrete levels. However, the energy level separations are still too small to affect the optical properties of metals in the UV to the IR range.

Red shift observed also as a function of the environment dielectric constant

Au nanoparticle core surrounded by SiO_2 shell

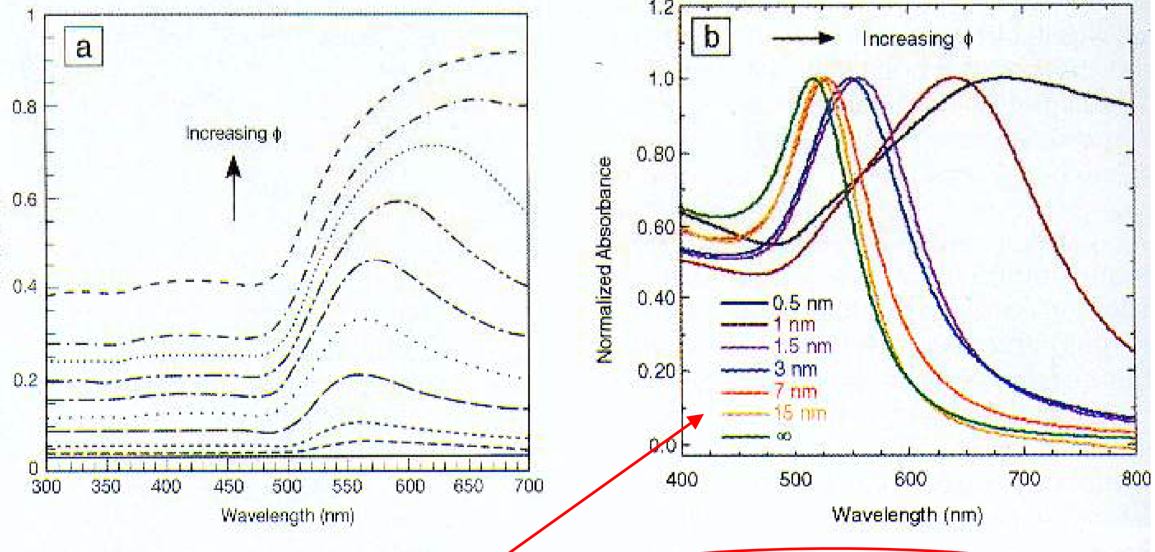
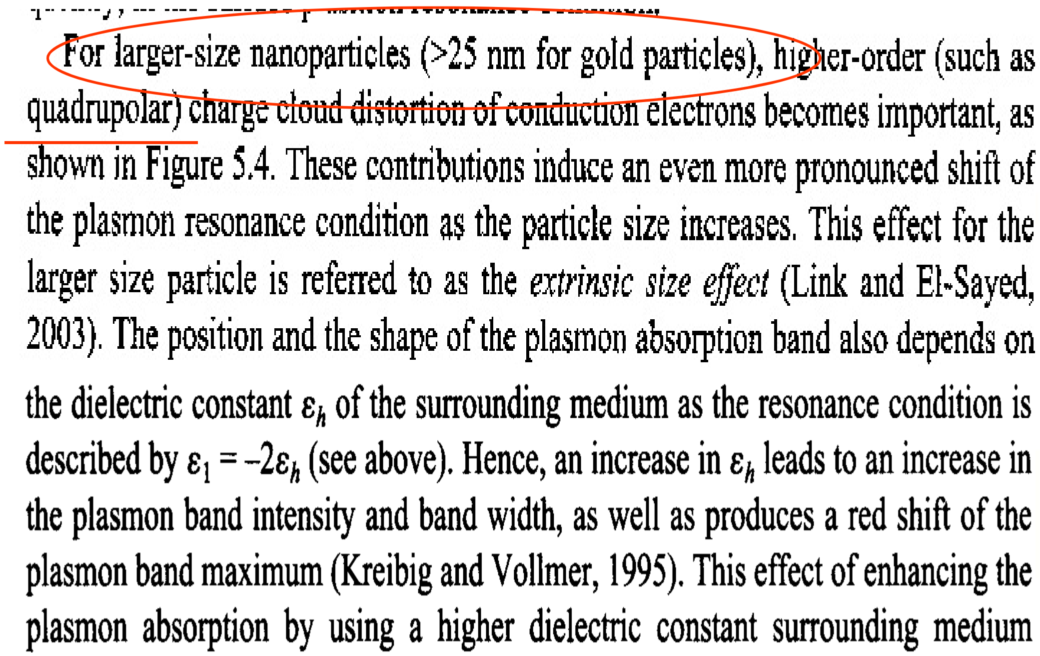


Figure 6. (a) Normalized reflectance spectra for Au@SiO$_2$ (gold concentrically coated by silica) films as a function of the volume fraction ϕ of Au. From the bottom curve upward, ϕ for each curve, respectively, is 0.01, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, and pure Au. (b) The normalized absorbance of a series of Au@SiO$_2$ films as a function of particle spacing.

Color depends on particle size, features of the sorrounding dielectric and interparticle spacing (collective interparticle effects!)

The Lycurgus cup



For larger-size nanoparticles (>25 nm for gold particles), higher-order (such as quadrupolar) charge cloud distortion of conduction electrons becomes important, as shown in Figure 5.4. These contributions induce an even more pronounced shift of the plasmon resonance condition as the particle size increases. This effect for the larger size particle is referred to as the *extrinsic size effect* (Link and El-Sayed, 2003). The position and the shape of the plasmon absorption band also depends on the dielectric constant ε_h of the surrounding medium as the resonance condition is described by $\varepsilon_1 = -2\varepsilon_h$ (see above). Hence, an increase in ε_h leads to an increase in the plasmon band intensity and band width, as well as produces a red shift of the plasmon band maximum (Kreibig and Vollmer, 1995). This effect of enhancing the plasmon absorption by using a higher dielectric constant surrounding medium

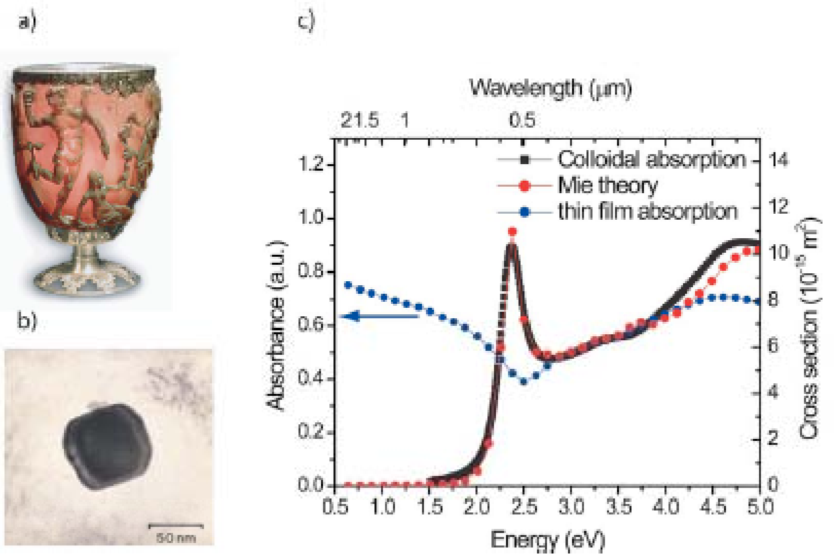


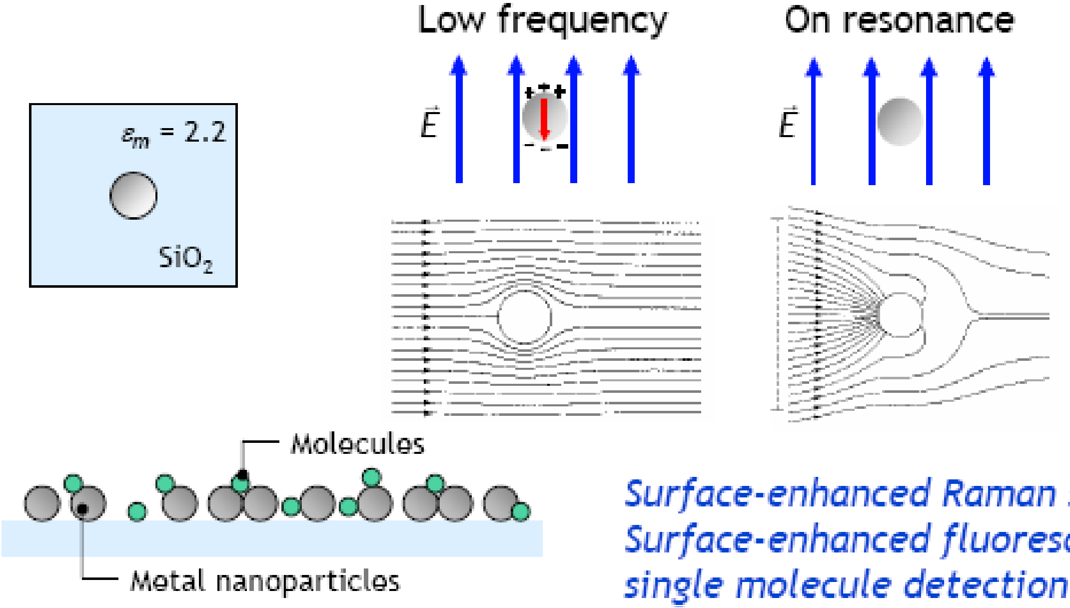
FIG. 1. (Color online) (a) The Lycurgus glass cup, demonstrating the bright red color of gold nanocrystals in transmitted light. (b) scanning electron microscopy (SEM) image of a typical nanocrystal embedded in the glass (courtesy of the British museum). (c) Calculated absorption spectrum of a thin gold film (blue dots) and of 30-nm Au nanoparticles in water (red dots) using classical electromagnetic theory. A measured absorption spectrum of an aqueous solution of 30-nm Au colloids (black dots) shows good agreement with the theory.

Calculations based on Mie scattering and accounting for the effective dielectric constant do fit well the observations (e.g., Lycurgus cup)

(Envisioned) nano-optics applications for plasmonics I

Isolated metal nanoparticles act as localized near-field sources (as already seen), with applications also in field enahncement

The ultimate confinement of light:
surface plasmons in metal nanoparticles



Surface-enhanced Raman scattering
Surface-enhanced fluorescence
single molecule detection

Other possible exploitations in modification/enhancement of photonics performance of various devices

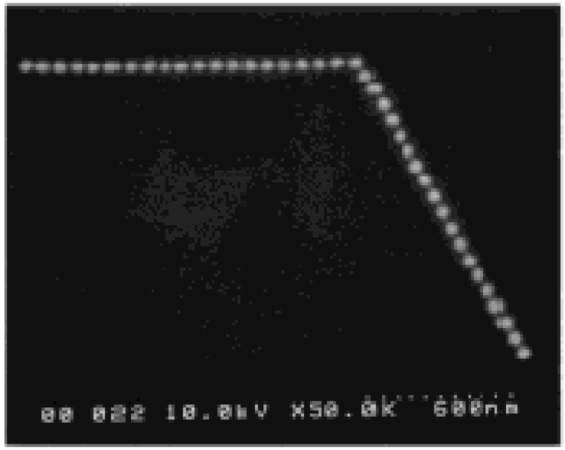
See, e.g.,

Surface plasmon nanophotonics:
optics below the diffraction limit

Albert Polman

Center for *nano*photonics
FOM-Institute AMOLF, Amsterdam

(Envisioned) nano-optics applications for plasmonics II

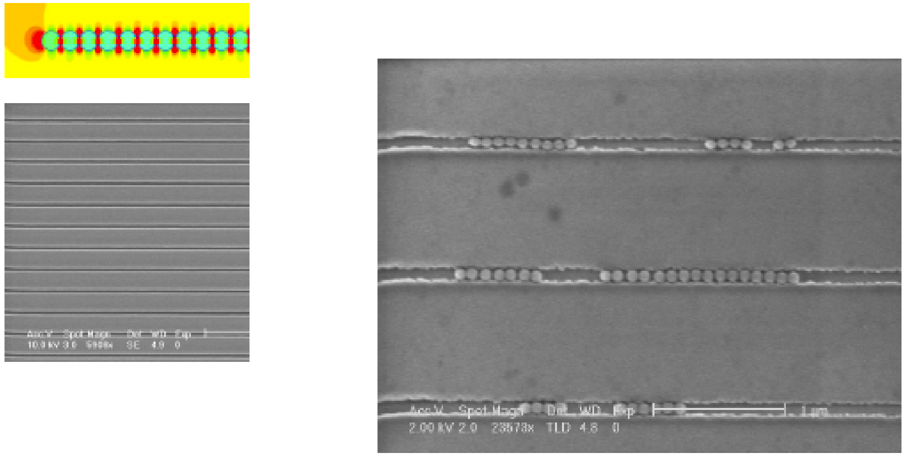


Guida d’onda costituita da catena di nanoparticelle, spaziate di poche decine di nm, che interagiscono mediante campo prossimo: perdite dovute solo a dissipazione ohmica, alte velocità di gruppo, confinamento subdiffrattivo e possibilità di guidare segnali su percorsi fortemente angolati

Plasmon resonances localized in contiguous nanoparticles can behave in a cooperative fashion allowing for radiation transport on arbitrary patterns with macroscopic lengths

(Envisioned) nano-optics applications for plasmonics III

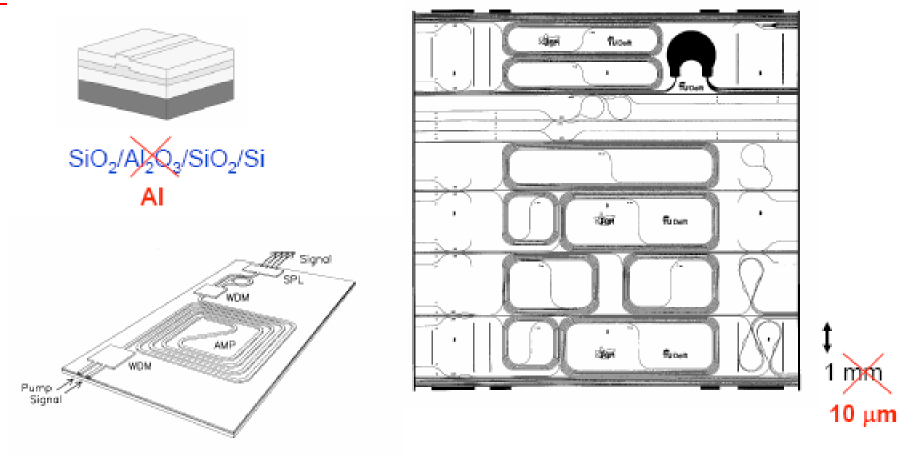
Final goal: surface plasmon nanophotonic waveguides



Plasmonics: energy transfer and confinement of light below the diffraction limit

Collective excitation of plasmon resonances in ordered arrays of metal nanoparticles can lead to optical guiding in a transverse size range below the diffraction limit
→Extreme miniaturization
(and integration) achieved

~~Photonic~~ integrated circuits on silicon
Plasmonic



Opto-electronic integration, (e.g. interconnects)
Plamonic nanolithography

Plasmon waveguides can break the miniaturization limits imposed by optics (with the side advantage of integrability)

Metal nanoparticle preparation (a few words)

A huge variety of methods exists to produce (noble) metal nanoparticles *with relatively controlled shape and size* (issue well established for catalyst fabrication!)

Most of them exploits solution-based techniques leading to colloidal dispersion of nanoparticles

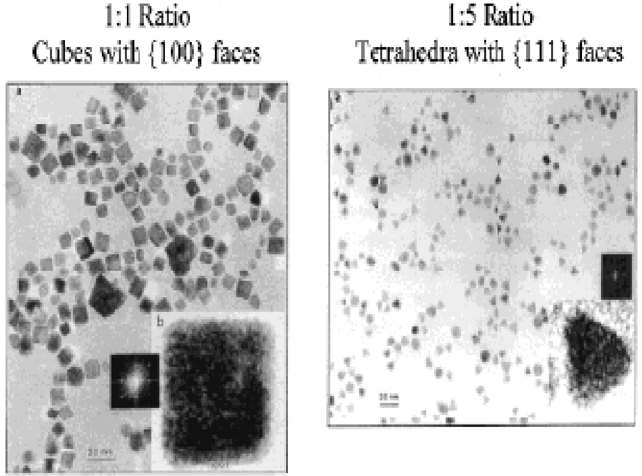
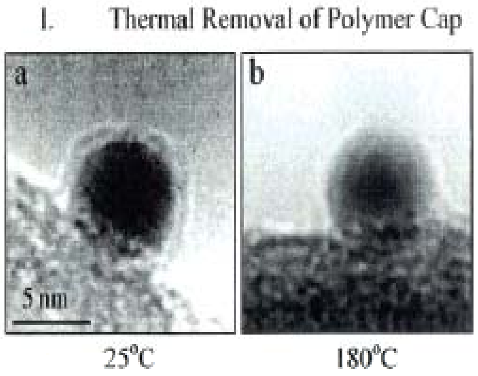


FIGURE 1. Platinum nanoparticles synthesized in colloidal solution and having different shapes (11-nm cubes on the left and ~7-nm tetrahedrons on the right).[27] The potential use of these nanoparticles for different types of catalyses drives our research interest in these particles. Do these different shapes have different catalytic properties?



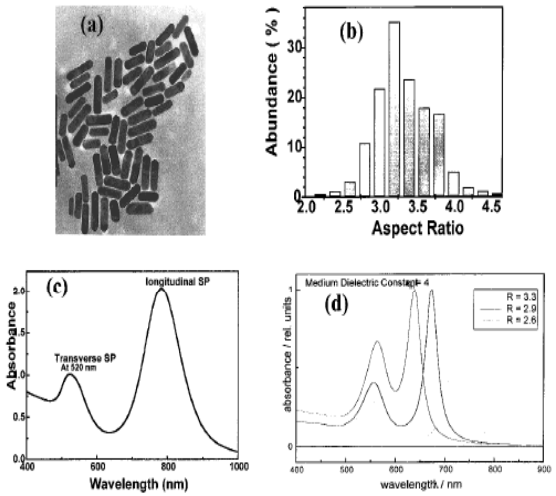


FIGURE 3. (a) TEM image of gold nanorods synthesized electrochemically in micellar solution[38] under the best conditions. (b) Size distribution of the nanorods. (c) Absorption spectrum of these nanorods. (d) Simulated spectra of nanorods of different aspect (length to width) ratios.

For details see, e.g.,:

Some Interesting Properties of Metals Confined in Time and Nanometer Space of Different Shapes

MOSTAFA A. EL-SAYED*

VOLUME 34 NUMBER 4

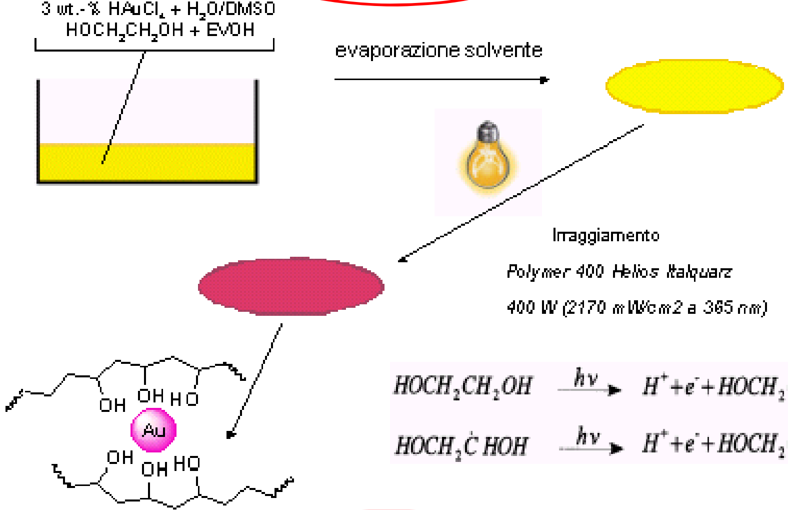
ACCOUNTS of CHEMICAL RESEARCH®

APRIL 2001

An example of preparation method

Materiale tratto dal seminario di
M. Barnabò, Apr. 2004

FOTORIDUZIONE



3 wt.-% $HAuCl_4 + H_2O/DMSO$
$HOCH_2CH_2OH$ + EVOH

evaporazione solvente

Irraggiamento

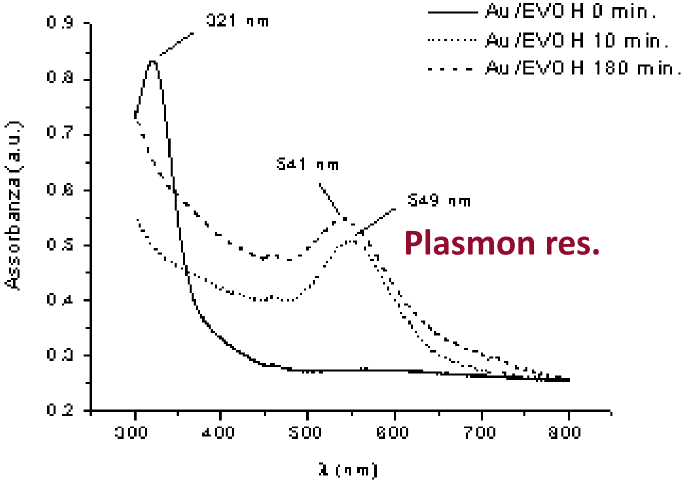
Polymer 400 Helios Italquarz

400 W (2170 mW/cm2 a 365 nm)

$$HOCH_2CH_2OH \xrightarrow{h\nu} H^+ + e^- + HOCH_2\dot{C}HOH$$

$$HOCH_2\dot{C}HOH \xrightarrow{h\nu} H^+ + e^- + HOCH_2CH{=}O$$

SPETTRO UV RELATIVO A CAMPIONI IRRAGGIATI
A TEMPI DIFFERENTI



Plasmon res.

PREPARAZIONE DI NANOPARTICELLE D'ORO STABILIZZATE DA AMMINA O DA TIOLO:

$$mAuCl_4^-{}_{(aq.)} + mN(C_8H_{17})_4^+{}_{(toluene)} \longrightarrow m[N(C_8H_{17})_4^+AuCl_4^-]_{(toluene)}$$

CON AMMINA

$$m[N(C_8H_{17})_4^+AuCl_4^-]_{(toluene)} + n(\text{alchilammina})_{(toluene)} + 3me^-{}_{(aq.)} \longrightarrow$$

$$\longrightarrow 4mCl_{(aq.)} + (Au_m)(\text{alchilammina})_{(dx)(toluene)} + x(\text{alchilammina})_{(toluene)}$$

$$+ m[N(C_8H_{17})_4^+]_{(toluene\ aq.)}$$

CON TIOLO

$$m[N(C_8H_{17})_4^+AuCl_4^-]_{(toluene)} + nC_{12}H_{25}SH_{(toluene)} + 3me^- \longrightarrow$$

$$\longrightarrow 4mCl^-{}_{(aq.)} + (Au_m)(C_{12}H_{25}SH)_{n(toluene)}$$

In order to avoid undesired large-scale coalescence of metal atoms into large fragments, surfactant agents (e.g., ammines) must be used

Frequently, thiol molecules (**SAM**) are used to stabilize Au nanoparticles in solution

Conclusions

- ✓ Optical properties in metals are mostly ruled by free-electrons oscillations driven by the electromagnetic field
- ✓ Classical descriptions (Drude+Maxwell) are generally adequate: plasma frequency is the key parameter ruling absorption
- ✓ Collective oscillations of surface charge (electrons) can be used to transport electromagnetic energy such as in Surface Plasmons
- ✓ Efficient Surface Plasmons effects are seen in thin films (small systems in one direction)
- ✓ Striking optical properties, radically different from bulk behavior, are observed in metal nanoparticles, i.e., systems showing small dimensions (in all three directions)