Lecture 34. Localized Plasmons

Quasi-Static Regime

Consider the situation when the fields are confined within volume $V \sim a^3$ that is sub-wavelength, $a << \lambda_0/n$ as shown in Fig.34.1

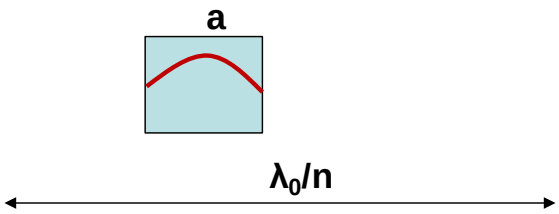

Figure 34.1 Subwavelength mode

Let us write Maxwell equation

$$\nabla \times \mathbf{H} = -j\omega\varepsilon_0\varepsilon_r \mathbf{E} = -jk_0 n\varepsilon_0 cn\mathbf{E} = -j\frac{2\pi n}{\lambda_0}\frac{\mathbf{E}}{\eta} \tag{34.1}$$

Where the impedance in the medium is $\eta = \eta_0 / n$ .Start with the relation between two fields in free space, where

$$\left|\nabla \times \mathbf{H}_0\right| = \frac{2\pi n}{\lambda_0} H_0 \tag{34.2}$$

and, of course from (34.1) $H_0 = E/\eta$. In a small sub-wavelength volume, however the field can be written as

$$H \sim \sin(\pi x / a) \tag{34.3}$$

so that

$$\left|\nabla \times \mathbf{H}\right| \sim \pi H / a \tag{34.4}$$

Substituting it into (34.1) we immediately obtain

$$\frac{\pi}{a} H \sim \frac{2\pi n}{\lambda_0}\frac{E}{\eta} = \frac{2\pi n}{\lambda_0} H_0, \tag{34.5}$$

and

$$H \sim \frac{a}{\lambda_0 / 2n} H_0 << H_0 \tag{34.6}$$

Therefore, magnetic field becomes vanishingly small when the electric field is confined to sub-wavelength volumes. Furthermore, from the second Maxwell's equation it follows that

$$\nabla \times \mathbf{E} = j\omega\mu\mathbf{H} \to 0, \tag{34.7}$$

i.e. the field is irrotational, hence one can introduce scalar potential as

$$\mathbf{E} = -\nabla\Phi \tag{34.8}$$

Taking divergence of both sides in (34.8) we obtain the Poisson equation

$$\nabla \cdot \mathbf{E} = -\nabla^2\Phi = \rho / \varepsilon_0\varepsilon_r \tag{34.9}$$

where ρ is the free charge density. Therefore, the potential behaves as an electrostatic potential, even though it is of course time dependent

$$\Phi(\mathbf{r},t) = \Phi(\mathbf{r})e^{-j\omega t} \tag{34.10}$$

In the absence of free charges one is left with Laplace equation

$$\nabla^2\Phi(\mathbf{r}) = 0 \tag{34.11}$$

Polarized sphere in the external electric field.

Consider a small sphere with relative permittivity ε_{r1} and radius a placed in another material (usually a dielectric) with relative permittivity ε_{r2} as shown in Fig.34.2 a

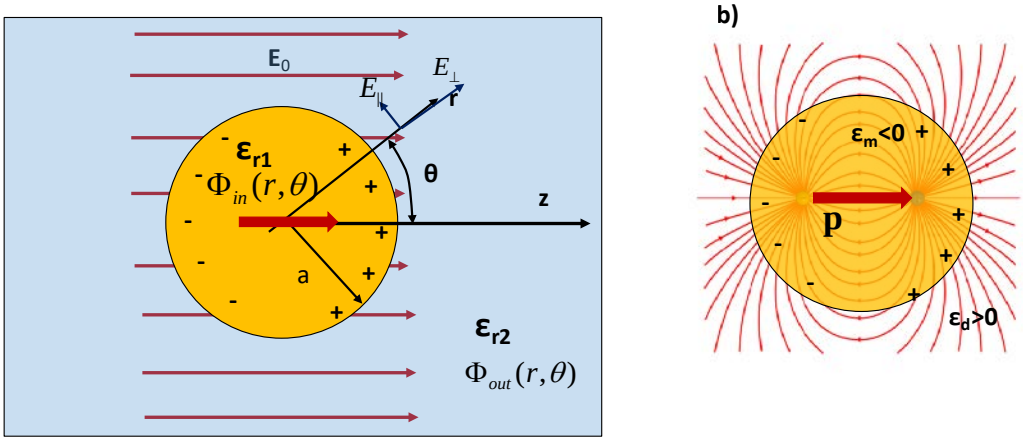

Figure 34.2 (a) polarizable sphere in external electric field (b) electric field of the metal sphere at resonance

When the external field $\mathbf{E}_0$ is introduced the surface charged is induced as the medium in the sphere becomes polarized. Since the sphere is sub-wavelength we can use quasi-static approximation and solve the Poisson equation for the potential inside and outside the sphere

$$\Phi_{in}(r,\theta) = -\frac{3E_0\varepsilon_{r2}}{\varepsilon_{r1}+2\varepsilon_{r2}} r\cos\theta = -\frac{3E_0\varepsilon_{r2}}{\varepsilon_{r1}+2\varepsilon_{r2}} z$$
$$\Phi_{out}(r,\theta) = -E_0 r\cos\theta + E_0 \frac{\varepsilon_{r1}-\varepsilon_{r2}}{\varepsilon_{r1}+2\varepsilon_{r2}} \frac{a^3}{r^2}\cos\theta \quad (34.12)$$

At the same time, we know that electro-static potential of a dipole $\mathbf{p}$ placed in the origin (center of sphere) is

$$\Phi_{dipole}(r,\theta) = \frac{1}{4\pi\varepsilon_0\varepsilon_{r2}} \frac{\mathbf{p}\cdot\mathbf{r}}{r^3} \quad (34.13)$$

If the dipole is oriented along z axis,

$$\Phi_{dipole}(r,\theta) = \frac{1}{4\pi\varepsilon_0\varepsilon_{r2}} \frac{p\cos\theta}{r^2} \quad (34.14)$$

Therefore, the potential outside of the sphere can be represented as the sum of external potential $\Phi_0 = -E_0 r\cos\theta$ and the potential of the induced dipole $\mathbf{p}$,

$$\Phi_{out}(r,\theta) = \Phi_0 + \Phi_{dipole}(r,\theta), \quad (34.15)$$

where

$$\mathbf{p} = 4\pi\varepsilon_0\varepsilon_{r2}a^3 \frac{\varepsilon_{r1}-\varepsilon_{r2}}{\varepsilon_{r1}+2\varepsilon_{r2}} \mathbf{E}_0 \quad (34.16)$$

The electric field can be found as

$$\mathbf{E} = -\nabla\Phi, \quad (34.17)$$

yielding

$$\mathbf{E}_{in}(r,\theta) = \frac{3E_0\varepsilon_{r2}}{\varepsilon_{r1}+2\varepsilon_{r2}} \hat{\mathbf{z}}$$
$$\mathbf{E}_{out}(r,\theta) = \mathbf{E}_0 + \mathbf{E}_{dipole} = \mathbf{E}_0 + \frac{1}{4\pi\varepsilon_0\varepsilon_{r2}} \frac{3\hat{\mathbf{r}}\left(\mathbf{p}\cdot\hat{\mathbf{r}}\right)-\mathbf{p}}{r^3} E_0, \quad (34.18)$$

as shown in Fig. 34.2 b. This filed can be split into radial (normal to surface) and tangential components as

$$E_{dipole,\perp} = \mathbf{E}_{dipole}\cdot\hat{\mathbf{r}} = \frac{1}{4\pi\varepsilon_0\varepsilon_{r2}} \frac{3\left(\mathbf{p}\cdot\hat{\mathbf{r}}\right)-\mathbf{p}\cdot\hat{\mathbf{r}}}{r^3} = \frac{p\cos\theta}{2\pi\varepsilon_0\varepsilon_{r2}r^3}$$
$$E_{dipole,\parallel} = \frac{p\sin\theta}{4\pi\varepsilon_0\varepsilon_{r2}r^3} \quad (34.19)$$

The field inside is then

$$E_{in} = \frac{3E_0\varepsilon_{r2}}{\varepsilon_{r1} + 2\varepsilon_{r2}} = \frac{3\varepsilon_{r2}}{\varepsilon_{r1} - \varepsilon_{r2}} \frac{p}{4\pi\varepsilon_0\varepsilon_{r2}a^3} \tag{34.20}$$

Localized surface plasmon (LSP)

Consider now what happens when the denominator in (34.16) diverges, i.e.

$$\varepsilon_{r1} + 2\varepsilon_{r2} \to 0 \tag{34.21}$$

That means that the dipole exists even in the absence of the applied field and one has self-sustained oscillations. For that one has to have $\varepsilon_{r1} < 0$, or, more precisely $\mathrm{Re}(\varepsilon_{r1}) < 0$, i.e.e the sphere should be made from metal. Introduce $\varepsilon_{r1} = \varepsilon_m(\omega)$ and $\varepsilon_{r2} = \varepsilon_d$, and now we have resonance condition

$$\mathrm{Re}(\varepsilon_m) + 2\varepsilon_d \to 0 \tag{34.22}$$

Since

$$\varepsilon_m(\omega) = \varepsilon_{rb} - \frac{\omega_p^2}{\omega^2 + j\omega\gamma} = \varepsilon_{rb}\left(1 - \frac{\omega_{ps}^2}{\omega^2 + j\omega\gamma}\right) \tag{34.23}$$

the resonant frequency of LSP can be found from

$$\varepsilon_{rb}\left(1 - \frac{\omega_{ps}^2}{\omega_0^2}\right) + 2\varepsilon_d = 0 \tag{34.24}$$

as

$$\omega_0 = \frac{\omega_{ps}}{\sqrt{1 + 2\varepsilon_d / \varepsilon_{rb}}} = \frac{\omega_p}{\sqrt{\varepsilon_{rb} + 2\varepsilon_d}} \tag{34.25}$$

The resonant frequency is less than for propagating SPP on the surface because the field spreads out of metal more, hence the restoring force acting on electrons in the metal is less for the same surface charge. If the metal nanoparticle is not spherical, then

$$\omega_0 = \frac{\omega_{ps}}{\sqrt{1 + 2l\varepsilon_d / \varepsilon_{rb}}}; \tag{34.26}$$

Where depolarization factor l is larger than 1 for prolate (elongated) spheroid and less than 1 for the oblate one.

Excitation of LSPs

So, what happens when external field $\mathbf{E}(t) = \mathbf{E}_0 e^{-j\omega t}$ is applied to the metal nanoparticle with frequency ω near resonance ω_0? The induced dipole moment is $\mathbf{p}(t) = \mathbf{p}_0 e^{-j\omega t}$ and since $\varepsilon_m \approx -2\varepsilon_d$

$$\mathbf{p}_0 = 4\pi\varepsilon_0\varepsilon_d a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\mathbf{E}_0 \approx 3\varepsilon_0\varepsilon_d V \frac{-3\varepsilon_d}{\varepsilon_{rb} - \dfrac{\omega_p^2}{\omega^2 + j\omega\gamma} + 2\varepsilon_d}\mathbf{E}_0 \tag{34.27}$$

Take $1/\left(\varepsilon_{rb} + 2\varepsilon_d\right)$ outside the denominator and use (34.25)

$$\begin{aligned}\mathbf{p}_0 &= \frac{3\varepsilon_0\varepsilon_d V}{\varepsilon_{rb} + 2\varepsilon_d}\frac{3\varepsilon_d}{\dfrac{\omega_p^2}{(\omega^2 + j\omega\gamma)(\varepsilon_{rb} + 2\varepsilon_d)} - 1}\mathbf{E}_0 = \\ &= \frac{9\varepsilon_0\varepsilon_d^2 V}{\varepsilon_{rb} + 2\varepsilon_d}\frac{\omega_p^2}{\omega_p^2}\frac{1}{\dfrac{\omega_0^2}{(\omega^2 + j\omega\gamma)} - 1}\mathbf{E}_0 = 9\varepsilon_0\varepsilon_d^2 V\frac{\omega_0^2}{\omega_p^2}\frac{\omega^2 + j\omega\gamma}{\omega_0^2 - \omega^2 - j\omega\gamma}\mathbf{E}_0\end{aligned} \tag{34.28}$$

Finally, since $\omega \approx \omega_0 >> \gamma$

$$\mathbf{p}_0 = 9\varepsilon_0\varepsilon_d^2 V\frac{\omega_0^2}{\omega_p^2}\frac{\omega_0^2}{\omega_0^2 - \omega^2 - j\omega\gamma}\mathbf{E}_0 = \alpha\mathbf{E}_0, \tag{34.29}$$

where polarizability is

$$\alpha = 9\varepsilon_0\varepsilon_d^2 V\frac{\omega_0^2}{\omega_p^2}\frac{\omega_0^2}{\omega_0^2 - \omega^2 - j\omega\gamma} = \alpha_0\frac{\omega_0^2}{\omega_0^2 - \omega^2 - j\omega\gamma} \tag{34.30}$$

Obviously

$$\alpha_0 = 9\varepsilon_0\varepsilon_d^2 V\frac{\omega_0^2}{\omega_p^2} = \frac{9\varepsilon_0\varepsilon_d^2 V}{\varepsilon_{rb} + 2\varepsilon_d} \tag{34.31}$$

Is DC polarizability that gets resonantly enhanced and

$$\mathbf{p}(t) = \alpha_0\frac{\omega_0^2}{\omega_0^2 - \omega^2 - j\omega\gamma}\mathbf{E}(t) \tag{34.32}$$

It is easy to see that this is the solution of equation for a driven oscillator \,

$$\frac{d^2\mathbf{p}}{dt^2} = -\omega_0^2\mathbf{p} - \gamma\frac{d\mathbf{p}}{dt} + \alpha_0\omega_0^2\mathbf{E} \tag{34.33}$$

It is interesting to note that

$$\alpha_0\omega_0^2 = 9\varepsilon_0\varepsilon_d^2 V\frac{\omega_0^4}{\omega_p^2} = \frac{9\varepsilon_0\varepsilon_d^2 V}{\left(\varepsilon_{rb} + 2\varepsilon_d\right)^2}\frac{Ne^2}{\varepsilon_0 m_0} = \frac{9}{\left(\varepsilon_{rb}/\varepsilon_d + 2\right)^2}\frac{N_{total}e^2}{m_0} \tag{34.34}$$

The presence of total number of carriers inside the metal shows that one simply sums up polarizabilities of all individual free carriers.

LSP field enhancement near resonance

Let us re-write (34.32) as

$$\mathbf{p}(t) = \alpha_0 \frac{\omega_0^2}{\omega_0^2 - \omega^2 - j\omega\gamma}\mathbf{E}(t) \approx \frac{\alpha_0}{2}\frac{\omega_0}{\omega_0 - \omega - j\frac{\gamma}{2}} = \alpha_0 \frac{Q}{\frac{\omega_0 - \omega}{\gamma/2} - j}, \qquad (34.35)$$

where $Q = \omega/\gamma$. The normal to surface electric field of the dipole is given by (34.19) and the maximum filed near the surface and at $\theta = 0$ is

$$E_{dipole,\max} = \frac{p}{2\pi\varepsilon_0\varepsilon_d a^3} = \frac{3\varepsilon_0\varepsilon_d^2 \times 4\pi a^3}{(\varepsilon_{rb} + 2\varepsilon_d)}\frac{Q}{\frac{\omega_0 - \omega}{\gamma/2} - j}\frac{E_0}{2\pi\varepsilon_0\varepsilon_d a^3} = \frac{6\varepsilon_d}{\varepsilon_{rb}/\varepsilon_d + 2}\frac{Q}{\frac{\omega_0 - \omega}{\gamma/2} - j}E_0$$

(34.36)

On resonance, therefore

$$E_{dipole,\max}(\omega_0) = \frac{6\varepsilon_d}{\varepsilon_{rb}/\varepsilon_d + 2} jQE_0 \qquad (34.37)$$

If $\varepsilon_{rb} = \varepsilon_d$ $E_{dipole,\max} = 2\,jQE_0$.

Note that The field enhancement and linewidth of extinction spectrum do not depend on the size of nanoparticle (as long as it is sub-wavelength). The field is enhanced in the so-called "hot spots" near the surface as shown in Fig.34.3 a

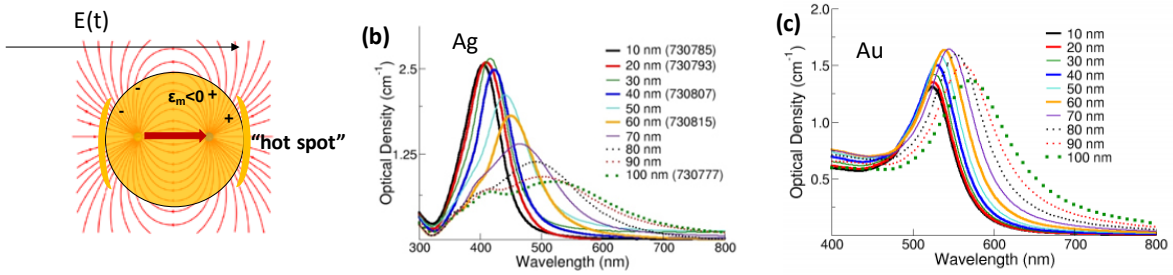

Figure 34.3 (a) "hot spots" in LSP (b,c) Extinction spectra of Ag and Au nanospheres of different sizes

Plasmonic colors

One can calculate the absorption coefficient as simply

$$\alpha_{abs}(\omega) = \frac{\omega}{c}N_p\,\mathrm{Im}(\alpha)/\varepsilon_0 = \frac{N_p\alpha_0}{4c\varepsilon_0}\frac{\omega_0\omega\gamma}{(\omega_0 - \omega)^2 + \gamma^2/4} = \frac{\pi}{2\lambda}\frac{9\varepsilon_d^2 N_p V}{\varepsilon_{rb} + 2\varepsilon_d}\frac{\omega_0\gamma}{(\omega_0 - \omega)^2 + \gamma^2/4}, \qquad (34.38)$$

where N_p is the volume density of nanoparticles. On resonance

$$\alpha_{abs}(\omega_0) = \frac{2\pi}{\lambda}\frac{9\varepsilon_d^2 N_p V}{\varepsilon_{rb}+2\varepsilon_d}Q \tag{34.39}$$

Note that $N_p V$ is the fraction of total volume occupied by the nanoparticles

One can see that the quasi-static approximation is not exact and for larger particles there is a red shift fo the extinction spectrum and also broadening of the spectrum. The broadening has to do with the radiation damping as oscillating dipoles emit – i.e. the suspension of nanospheres not only absorbs but also scatters. This is shown in Fig.34.4 (a) where gold spheres suspended in water have different coloration depending on size. One can also functionalize the nanospheres – covering tehm with a layer of molecules that change their properties (dielectric constant) depending on surrounding. This way one can make pH-sensor as shown in Fig.34.4(b)

(a) **(b)**

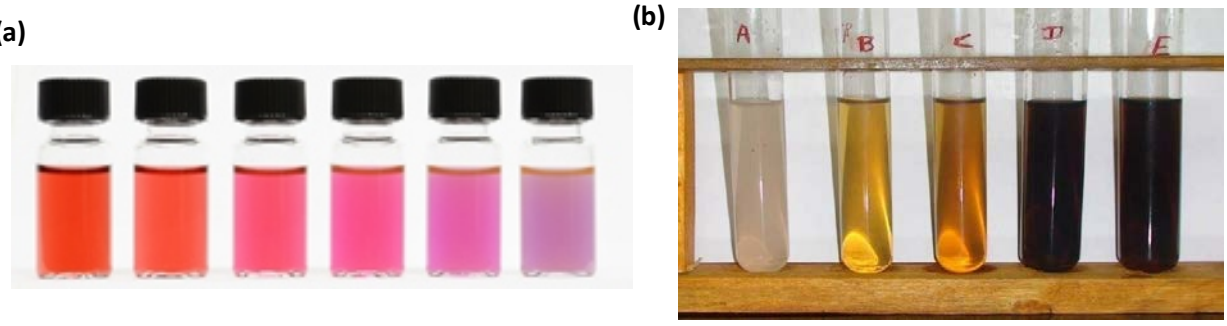

Figure 34.4 (a) Plasmonic colors- suspensions of Au nanospheres of different sizes (b) Color change due to pH variation on biosynthesized silver nanoparticles A: pH 2, B: pH 4, C:pH 6, D:pH 8, E:pH 10

Energy in LSP

Let us find the energy contained inside LSP. The outside fields are given by (34.19), so the total field squared is

$$\left|E_{out,\perp}\right|^2 = \left|E_{out,\perp}\right|^2 + \left|E_{out,\parallel}\right|^2 = \left(\frac{p\cos\theta}{2\pi\varepsilon_0\varepsilon_d r^3}\right)^2 + \left(\frac{p\sin\theta}{4\pi\varepsilon_0\varepsilon_d r^3}\right)^2 = \frac{\sin^2\theta + 4\cos^2\theta}{(4\pi\varepsilon_0\varepsilon_d)^2 r^6}p^2 \tag{34.40}$$

The energy (considering the dielectric non-dispersion) is

$$U_{out} = \frac{1}{4}\varepsilon_0\varepsilon_d\int\left|E_{out}\right|^2 dV = \frac{1}{4}\varepsilon_0\varepsilon_d 2\pi p^2\int_a^\infty\int_0^\pi \frac{\sin^2\theta+4\cos^2\theta}{(4\pi\varepsilon_0\varepsilon_d)r^6}\sin\theta d\theta r^2 dr = \frac{p^2}{8\pi\varepsilon_0\varepsilon_d}\int_a^\infty\frac{dr}{r^4} = \frac{p^2}{24\pi\varepsilon_0\varepsilon_d a^3} \tag{34.41}$$

where we have used

$$\int_0^\pi\left(\sin^2\theta+4\cos^2\theta\right)\sin\theta d\theta = \int_0^1(1+3x^2)dx = 4 \tag{34.42}$$

Inside metal we must use the expression for energy density in the metal that includes dispersion (ie.e kinetic energy of electrons)

$$U_{in} = \frac{1}{4}\varepsilon_0 \frac{d(\omega\varepsilon_m)}{d\omega} V \left|E_{in}\right|^2 \tag{34.43}$$

where E_{in} is composition-independent according to (34.20).

$$E_{in} = \frac{3\varepsilon_d}{\varepsilon_d - \varepsilon_m} \frac{p}{4\pi\varepsilon_0\varepsilon_{r2}a^3} = \frac{p}{4\pi\varepsilon_0\varepsilon_{r2}a^3} \tag{34.44}$$

(where $\varepsilon_m = -2\varepsilon_d$ we have used

From (34.23) neglecting damping we get

$$\frac{d\left(\omega\varepsilon_m\right)}{d\omega} = \varepsilon_{rb} - \frac{\omega_p^2}{\omega^2} + 2\frac{\omega_p^2}{\omega^2} = \frac{\omega_p^2}{\omega^2} - \varepsilon_{rb} + 2\varepsilon_{rb} = \mid \varepsilon_m \mid + 2\varepsilon_{rb}, \tag{34.45}$$

and substituting it into (34.43) we get

$$U_{in} = \frac{1}{4}\varepsilon_0 \left(\mid \varepsilon_m \mid + 2\varepsilon_{rb}\right)\frac{4}{3}\pi a^3 \frac{p^2}{\left(4\pi\varepsilon_0\varepsilon_d a^3\right)^2} = \frac{\mid \varepsilon_m \mid + 2\varepsilon_{rb}}{\varepsilon_d}\frac{p^2}{48\pi\varepsilon_0\varepsilon_d a^3} \tag{34.46}$$

Finally, since at resonance $\varepsilon_m = -2\varepsilon_d$

$$U_{in} = (1 + \varepsilon_{rb}/\varepsilon_d)\frac{p^2}{24\pi\varepsilon_0\varepsilon_d a^3} \tag{34.47}$$

Total energy is then (34.43) obtained by adding (34.41) and (34.47)

$$U_{LSP} = (2 + \varepsilon_{rb}/\varepsilon_d)\frac{p^2}{24\pi\varepsilon_0\varepsilon_d a^3} \tag{34.48}$$

Let us now find the energy dissipation in the metal

$$P = \frac{1}{2}\varepsilon_0\varepsilon_{m,im}\omega V \left|E_{in}\right|^2 \tag{34.49}$$

Where imaginary part of metal dielectric constant can be found from (34.23) (this time obviously including damping) as

$$\varepsilon_{m,im} \approx \frac{\gamma}{\omega}\frac{\omega_p^2}{\omega^2} = \frac{\gamma}{\omega}\left(\left|\varepsilon_m\right| + \varepsilon_{rb}\right) \tag{34.50}$$

Substituting (34.50) and into (34.49) one gets

$$P = \frac{1}{2}\gamma\varepsilon_0 \left(\mid \varepsilon_m \mid + \varepsilon_{rb}\right)\frac{4}{3}\pi a^3 \frac{p^2}{\left(4\pi\varepsilon_0\varepsilon_d a^3\right)^2} = \gamma\frac{\mid \varepsilon_m \mid + \varepsilon_{rb}}{\varepsilon_d}\frac{p^2}{24\pi\varepsilon_0\varepsilon_d a^3} = \gamma(2 + \varepsilon_{rb}/\varepsilon_d)\frac{p^2}{24\pi\varepsilon_0\varepsilon_d a^3} = \gamma U_{LSP}$$

(34.51)

The decay rate of LSP is the same as the scattering rate γ in the metal – no matter what is the shape or size of the nanoparticle (as long as a<<λ).

Another approach to LSP

Let us find the density of kinetic energy of electrons

$$u_k(t)=\frac{1}{2}Nm_0v^2(t)=\frac{1}{2}Nm_0\left(\frac{eE_{in}^2}{m_0\omega}\sin\omega t\right)^2=\frac{1}{2}\frac{Ne^2}{m_0\omega^2}E_{in}^2\sin^2\omega t=\frac{1}{2}\varepsilon_0\frac{\omega_p^2}{\omega^2}E_{in}^2\sin^2\omega t \quad (34.52)$$

The time averaged value of it is

$$\left\langle u_k(t)\right\rangle_t=\frac{1}{4}\varepsilon_0\frac{\omega_p^2}{\omega^2}E_{in}^2=\frac{1}{4}\varepsilon_0\left(|\varepsilon_m|+\varepsilon_{rb}\right)E_{in}^2 \quad (34.53)$$

Therefore, the total time-average kinetic energy (oscillating in quadrature with electric field) is

$$U_K=\frac{1}{4}\varepsilon_0\left(|\varepsilon_m|+\varepsilon_{rb}\right)\frac{4}{3}\pi a^3\frac{p^2}{\left(4\pi\varepsilon_0\varepsilon_d a^3\right)^2}=\frac{|\varepsilon_m|+\varepsilon_{rb}}{\varepsilon_d}\frac{p^2}{48\pi\varepsilon_0\varepsilon_d a^3}=(2+\varepsilon_{rb}/\varepsilon_d)\frac{p^2}{48\pi\varepsilon_0\varepsilon_d a^3}=\frac{1}{2}U_{LSP}$$

(34.54)

This of course makes perfect sense – one half of energy oscillates in phase with electric field (potential energy) and the other half oscillates in quadrature (kinetic energy) – just like in the case of pendulum or loaded spring oscillator. In fact, we can determine the oscillating condition in the following way. Assume that we do not know that we ar eat LSP resonance an d $\varepsilon_m=-2\varepsilon_d$, and

$$U_K=\frac{|\varepsilon_m|+\varepsilon_{rb}}{\varepsilon_d}\frac{p^2}{48\pi\varepsilon_0\varepsilon_d a^3} \quad (34.55)$$

The total energy is according to (34.46) and (34.41) is

$$U_{LSP}=\frac{p^2}{24\pi\varepsilon_0\varepsilon_d a^3}+\frac{|\varepsilon_m|+2\varepsilon_{rb}}{\varepsilon_d}\frac{p^2}{48\pi\varepsilon_0\varepsilon_d a^3}=\left(2+\frac{|\varepsilon_m|+2\varepsilon_{rb}}{\varepsilon_d}\right)\frac{p^2}{48\pi\varepsilon_0\varepsilon_d a^3} \quad (34.56)$$

Self-sustained oscillation is possible when $U_K=\frac{1}{2}U_{LSP}$, or

$$2(|\varepsilon_m|+\varepsilon_{rb})=2\varepsilon_d+|\varepsilon_m|+2\varepsilon_{rb} \quad (34.57)$$

The oscillation condition is $|\varepsilon_m|=2\varepsilon_d$.

Kinetic inductance and circuit approach to LSP

Let us consider a simple wire with diameter significantly less than skin depth $a<\lambda_p/2\pi$. Kinetic energy inside the wire is according to (34.53) as shown in Fig.34.5 a

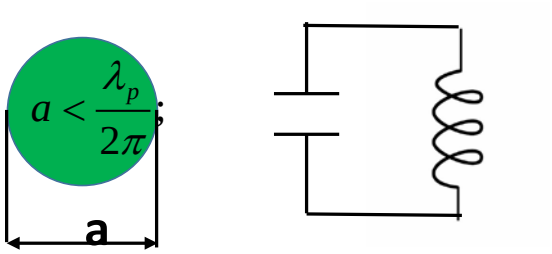

Figure 34.5 (a)Plasmonic nanoparticle and its equivalent circuit

$$U_K = \frac{1}{4}\varepsilon_0 \frac{\omega_p^2}{\omega^2} E^2 S_{eff} l \tag{34.58}$$

where $S_{eff} \le \pi a^2 / 4$ to take into account that the field inside is not exactly uniform and l is the length of the wire. The current inside is

$$I = eNvS_{eff} = \frac{Ne^2}{m_0\omega} E_{in} \sin(\omega t) S_{eff} = \varepsilon_0 \frac{\omega_p^2}{\omega} E_{in} \sin(\omega t) S_{eff} \tag{34.59}$$

and

$$\left\langle I^2 \right\rangle = \frac{1}{2}\varepsilon_0^2 \frac{\omega_p^4}{\omega^2} S_{eff}^2 E_{in}^2 \tag{34.60}$$

Therefore, we can write

$$U_K = \frac{1}{2}\frac{1}{\varepsilon_0 \omega_p^2 S_{eff}} l = \frac{1}{2} L_K \left\langle I^2 \right\rangle \tag{34.61}$$

where we have introduced Kinetic inductance as

$$L_K = \frac{1}{\varepsilon_0 \omega_p^2 S_{eff}} l = \mu_0 \frac{1}{\varepsilon_0 \mu_0 \omega_p^2 S_{eff}} l = \mu_0 \frac{c^2}{\omega_p^2 S_{eff}} l = \mu_0 \frac{\lambda_p^2}{4\pi^2 S_{eff}} l \approx \frac{\lambda_p^2}{\pi^3 a^2} \mu_0 l \tag{34.62}$$

Magnetic inductance of the wire, on the other hand is

$$L_M = \frac{\mu_0}{2\pi} l \tag{34.63}$$

So that

$$L_K = \frac{2\lambda_p^2}{\pi^2 a^2} L_M \tag{34.64}$$

For very thin wire the kinetic inductance becomes very large and dominates the magnetic inductance.

Let us now consider a very simple LC model of a small metal nanosphere. It has kinetic inductance determined by (34.62) under assumption $l \sim a$

$$L_K \sim \frac{4}{\varepsilon_0 \omega_p^2 \pi a^2} a = \frac{4}{\varepsilon_0 \omega_p^2 \pi a} \tag{34.65}$$

At the same time, assuming that the sphere is placed in vacuum, its capacitance is

$$C \sim \varepsilon_0 a \tag{34.66}$$

Now we can find resonant frequency as simply

$$\omega_0 = \left(L_K C\right)^{-1/2} = \omega_p \frac{\sqrt{\pi}}{2} \tag{34.67}$$

This value is not that far from the correct value (34.25)

$$\omega_0 = \frac{\omega_p}{\sqrt{\varepsilon_{rb} + 2\varepsilon_d}} = \frac{\omega_p}{\sqrt{3}} \tag{34.68}$$

The key here that the resonant frequency does not depend on the size of the structure – only on the material (via plasma frequency) and also the shape.

If the sphere is large, much larger than skin depth, magnetic inductance $L_M \sim \frac{\mu_0}{2\pi} a$ dominates, hence

$$\omega_0 = \left(L_M C\right)^{-1/2} = \frac{\sqrt{2\pi}}{a} c \tag{34.69}$$

And the resonant wavelength is

$$\lambda_0 = 2\pi \frac{c}{\omega_0} = a\sqrt{2\pi} \tag{34.70}$$

It is on the scale of the size of the sphere and does not depend on material – just as in any photonic resonator. So, here is the main difference between plasmoncis and photonics. In plasmonics kinetic inductance dominates and the resonances do not depend on size – in photonic normal (magnetic) inductance dominates and resonances scale with the size. Since kinetic inductance dominates, the energy is contained in kinetic motion half of the time – the losses are quite high therefore in plasmonics.

An energy balance approach to diffraction limit and plasmonics.

For most of the applications in plasmonics and metamaterials we want to concentrate optical field on sub-wavelength scale…but are prevented by the diffraction limit, $L_{\min} \sim \lambda / 2n$. This diffraction limit is in fact a manifestation of the Heisenberg's uncertainty principle,

$$\Delta p_x \Delta x \geq \hbar / 2 \tag{34.71}$$

where Δx is the uncertainty of the position and Δp_x is the uncertainty of the projection of momentum of a particle, photon in our case. Momentum of photon is $p = \hbar k = 2\pi n / \lambda_0$. Therefore we can write (34.71) as

$$\Delta k_x \Delta x \geq 1/2 \tag{34.72}$$

The uncertainty of projection of wavevector k cannot be larger than the wavevector itself

$$\Delta k_x \leq k = 2\pi n / \lambda_0 \tag{34.73}$$

and the uncertainty of x is obviously $\Delta x = L_{\min}$. Then from (34.72) we obtain

$$\frac{2\pi n}{\lambda_0} L_{\min} \geq \frac{1}{2}, \tag{34.74}$$

or

$$L_{\min} \sim \lambda_0 / 4\pi n \tag{34.75}$$

which is close enough to the diffraction limit. (In reality, if you assume any reasonable distribution of k_x from $-k$ to k and take Δk_x as mean square deviation you will end up with Δk_x that is a few times less than (34.73). Anyway, form this fundamental point of view the diffraction limit seems unassailable. So how on Earth can it be beaten? The answer lies in the fact that in (34.75) refractive index is real. What if it is imaginary? Seems like then the definition of momentum becomes very "uncertain". Another approach is needed – and we can re-derive the diffraction limit from simple energy-conservation considerations.

Energy balance in a mode.

Consider a simple resonator of a characteristic size $a > \lambda / 2n$ in all three directions. The standing wave mode is then

$$\begin{aligned} \mathbf{E} &= \mathbf{E}_0 \sin(kz)\cos(\omega t) \\ \mathbf{H} &= \mathbf{H}_0 \cos(kz)\sin(\omega t), \end{aligned} \tag{34.76}$$

Where $k = n\omega / c$ So, at times $\omega t = 0, \pi, 2\pi, \ldots$ only electric field is present as shown in Fig.34.6a and at times $\omega t = 0, \pi/2, 3\pi/2, \ldots$ only magnetic field as shown in Fig.34.6b. The relation between two fields is well known. According to Maxwell's equation $\nabla \times \mathbf{H} = \varepsilon \partial \mathbf{E} / \partial t$

$$H_0 = \frac{\omega}{k} \varepsilon E_0 = \frac{c}{n} \varepsilon_0 n^2 E_0 = \frac{n}{\eta_0} E_0 \tag{34.77}$$

The electrical energy is maximum at $\omega t = 0, \pi, 2\pi, \ldots$ and equals

$$U_E = \frac{1}{2} \varepsilon \int E^2(z) dV = \varepsilon \frac{E_0^2}{4} V \tag{34.78}$$

Magnetic energy, by the same considerations

$$U_M = \mu_0 \frac{H_0^2}{4} V = n^2 \frac{\varepsilon_0}{\mu_0} \frac{E_0^2}{4} V = \varepsilon \frac{E_0^2}{4} V \tag{34.79}$$

So, two energies are equal to each other as shown symbolically in Fig.34.6 c and energy oscillates between electric and magnetic energies in way similar to oscillation between potential and kinetic energies for pendulum or weight on a spring as shown in Fig. 34.6 d. Perfect energy balance is achieved.

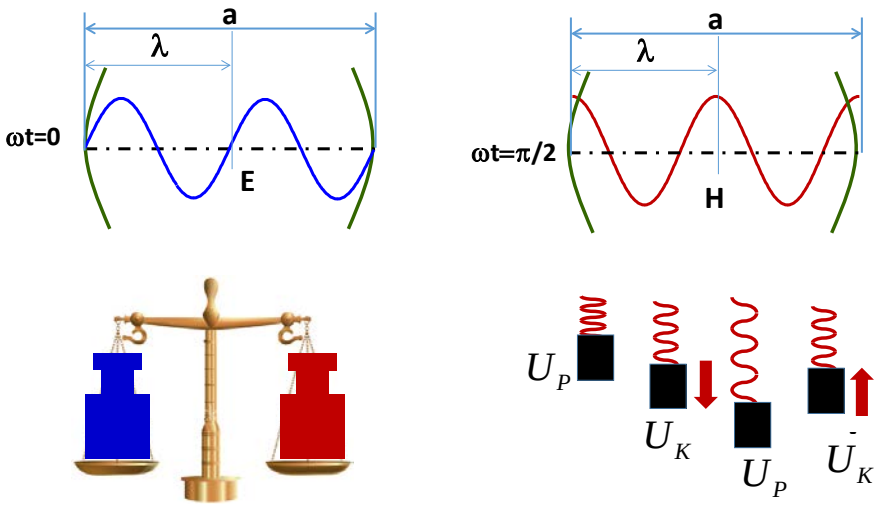

Figure 34.6 a electric and (b) magnetic fields in a larger-than-wavelength cavity (c) energy balance (d) comparison to the oscillation of a weight on a spring.

Lack of energy balance in a sub-λ mode

Let us consider the case when the mode dimension is reduced to

$$a < \frac{\lambda_0}{2n} = \frac{2\pi c}{n\omega} \tag{34.80}$$

as seen in Fig.34.7. The fields, shown in Fig. 34.7 a and b are

$$\mathbf{E} = \mathbf{E}_0 \sin\left(\frac{\pi}{a} z\right) \cos(\omega t)$$
$$\mathbf{H} = \mathbf{H}_0 \cos\left(\frac{\pi}{a} z\right) \sin(\omega t) \tag{34.81}$$

The relation between magnitudes of electric and magnetic fields is(as shown in (34.6)

$$H_0 \approx \frac{\omega a}{\pi} \varepsilon E_0 = \frac{2a}{\lambda_0} c\varepsilon E_0 = \frac{2na}{\lambda_0} \frac{nE_0}{\eta_0} \tag{34.82}$$

The electric energy is still described by (34.78) but magnetic energy is

$$U_M = \mu_0 \frac{H_0^2 V}{4} = \left(\frac{2na}{\lambda_0}\right)^2 \varepsilon \frac{E_0^2 V}{2} = \left(\frac{2na}{\lambda_0}\right)^2 U_E \tag{34.83}$$

So, in quasi-static limit of sub-wavelength (in all directions) mode $U_M << U_E$ - the energy is not conserved as shown in Fig.34. 7c – one simply cannot transform the electric energy into magnetic energy when phase changes by 90 degrees – the energy will simply radiate out as shown by arrows in Fig.34.7a. So, this is how we arrive at the diffraction limit!

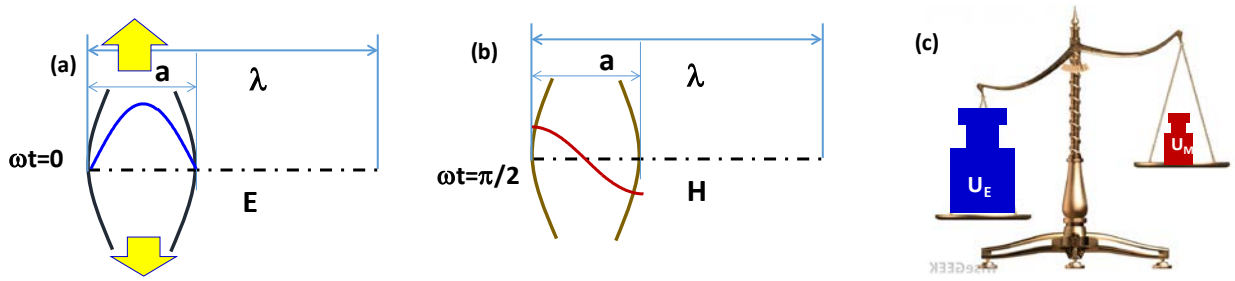

Figure 34.7 a electric and (b) magnetic fields in a smaller than-wavelength cavity (c) lack of energy balance,

How kinetic energy of free carriers restores the balance in subwavelength mode

So, once the problem with the sub-wavelength confinement has been identified- no energy "reservoir" available to store the excess energy at times $\omega t = 0, \pi/2, 3\pi/2, \ldots$, the solution immediately follows. Why do not we introduce the free carriers, so their kinetic energy which is in quadrature with the electric field will augment insufficient magnetic energy. As shown in Fig.34.8 once fee carriers have been introduced, the electric (Fig.34.8a) and magnetic (Fig.34.8 b) fields are still the same as before, (34.81), but now there is also a current density

$$\mathbf{J} = \mathbf{J}_0 \sin(\omega t) \tag{34.84}$$

Therefore, in addition to electric and magnetic energy we have kinetic energy of free carriers that according to (34.58) is

$$U_K = \frac{NV_{met} m v^2}{2} = \varepsilon_0 \frac{\omega_p^2}{\omega^2} \frac{E_0^2 V_{met}}{2} = \frac{\omega_p^2}{\omega^2} \frac{V_{met}}{V} U_E \sim \frac{L_K I^2}{2} \tag{34.85}$$

Now the energy balance can be restored as shown in Fig.34.8c if

$$U_E = U_M + U_K \tag{34.86}$$

or

$$\left(\frac{2na}{\lambda_0}\right)^2 + \frac{\omega_p^2}{\omega^2} F_{met} = 1 \tag{34.87}$$

Here F_{met} is some geometric factor that takes place of V_{met}/V and takes into account exact field distribution in the mode (but the meaning is the same – fraction of the effective volume of the mode taken by the metal) .

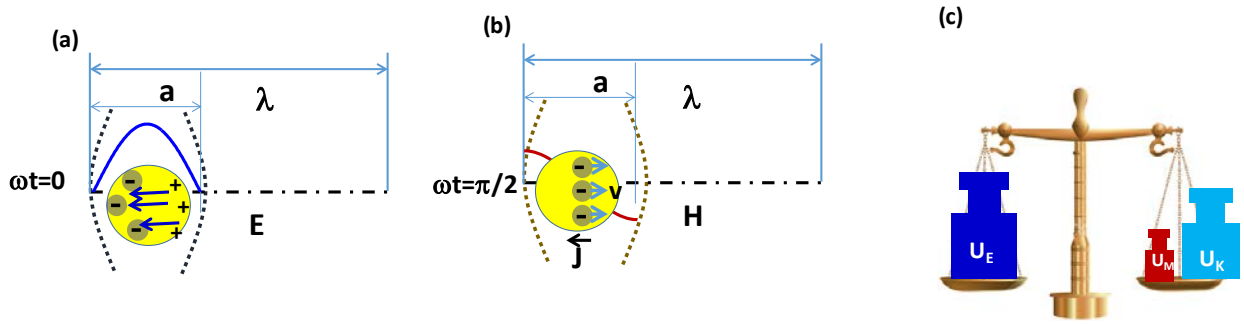

Figure 34.8 a electric and (b) magnetic fields and current in a smaller than-wavelength cavity with free carriers (c) energy balance restored.

At some frequencies ω_0 the balance is achieved. These frequencies are the resonant frequencies of the Surface Plasmon Polariton Modes. It is easy to see that for really small modes $\omega_0 \sim \omega_p / F^{1/2}$ but for larger ones or when $F_{met} << 1$, $a \sim \lambda_0 / 2n$. Note that there usually more than a single solution for different polarizations.

The inevitable loss in plasmonics.

If $a << \lambda_0 / 2n$ there is almost no magnetic field (quasi-static limit) $U_M << U_E$ – hence energy oscillates between electric energy and kinetic energy of free carriers. Therefore, In the sub-wavelength metallic structures (in all three dimensions !) half of the time almost all the energy is stored in kinetic motion of electrons –where it is being lost with the decay rate 2γ of the order of $10^{14} s^{-1}$ (Factor of two is because γ is the decay rate of velocity (momentum) so the square of it, the energy decays twice as fast). Therefore, the rate of energy loss in truly sub-wavelength structure is always of the order of γ.

The loss dependence on the wavelengths

Consider now roughly what is the kinetic and magnetic inductances of a metal nanoparticle. Consider a cylindrical wire of length l and diameter a. Magnetic inductance of a wire is

$$L_M = \frac{\mu_0}{2\pi} l F(l/a) \tag{34.88}$$

where $F(l/a) \sim 1$ that is weakly (logarithmically) dependent on the aspect ratio. For Kinetic inductance, we take into account that the field only penetrates the skin depth, $\lambda_p / 2\pi$ - therefore we can estimate the effective area that conducts current as

$$S_{eff} = \left[\frac{1}{\pi a^2 / 4} + \frac{1}{2\pi a \times \lambda_p / 2\pi} \right]^{-1} = \frac{\pi a^2}{4} \left[1 + \frac{\pi}{4} \frac{a}{\lambda_p} \right]^{-1} \tag{34.89}$$

The Kinetic inductance is (34.62)

$$L_K = \mu_0 \frac{\lambda_p^2}{4\pi^2 S_{eff}} l \tag{34.90}$$

Since the energy stored in the magnetic field is not dissipated and the energy stored in the kinetic energy does get dissipated, the effective loss rate is

$$\gamma_{eff} = \gamma \frac{L_K}{L_K + L_M} = \gamma \frac{1}{1 + L_M / L_K} = \gamma \frac{1}{1 + 2\pi F (l/a) S_{eff} / \lambda_p^2} \tag{34.91}$$

Substituting (34.89) we obtain

$$\frac{\gamma_{eff}}{\gamma} = \frac{1}{1 + F(l/a) \frac{\pi^2 a^2}{2\lambda_p^2} \left[1 + \frac{\pi}{4} \frac{a}{\lambda_p} \right]^{-1}} \tag{34.92}$$

Clearly, the loss decreases with size of the nanoparticle relative to the plasma wavelength as shown in Fig. 34.9

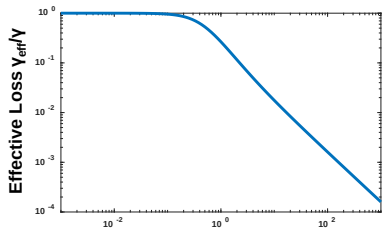

Figure 34.9 Effective loss versus the size of nanoparticle relative to the plasma wavelength

Therefore, at low frequencies (far IR and lower) $\lambda >> \lambda_p \sim 100nm$ the particle can be subwavelength $a << \lambda$ and still much larger than plasma wavelength $a >> \lambda_p$ - the loss will be reduced. One cannot really call this regime plasmonic because the field mostly stays outside of the metal. In Fig. 34.10 we summarize all the relevant regimes in photonics and plasmonics

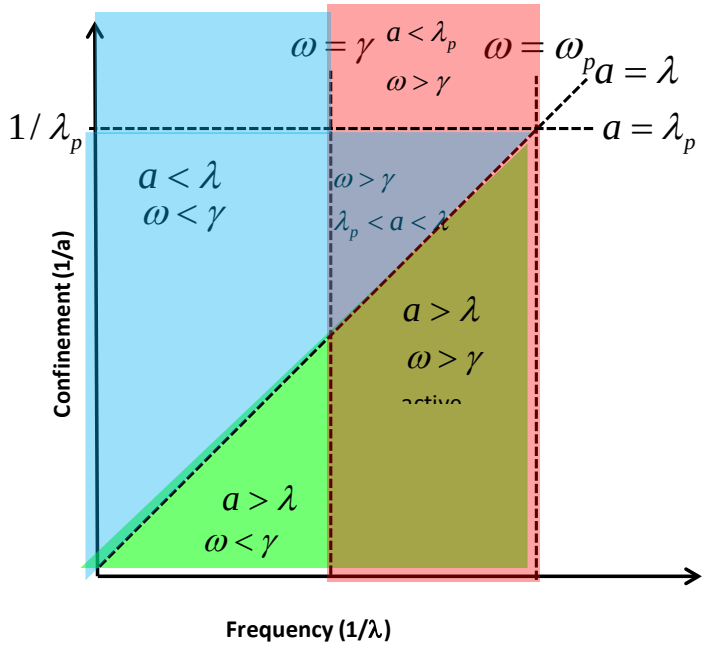

Figure 34.10 Plasmoncis and Photonics. "True Plasmonic Regime" implies that a significant part of energy s stored in motion of charged carriers. This regime is inherently lossy and should be avoided if possible. At lower frequencies one enters the "metal optics" or "nanoantenna" or "microwave" (which extends into THz and mid-IR) regime where magnetic inductance dominates. This low loss regime is highly desirable