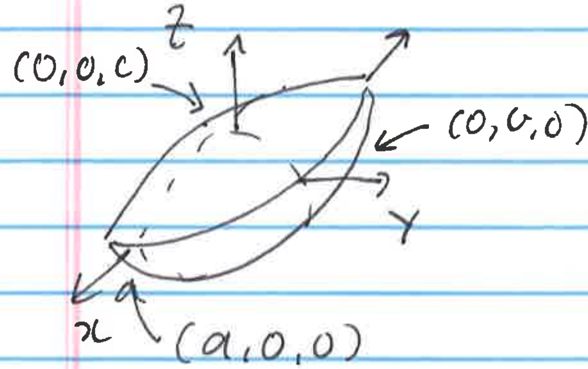
Particles w/ different sizes & shapes

~ analogous formula to "Mie theory" has been developed for ellipsoidal particles
"Gans theory"



$a \geq b \geq c$

$$C_{abs} = \frac{2\pi V}{3\lambda} \epsilon_m^{3/2} \sum_{j=1,2,3} \frac{(1/P_j^2)\,\epsilon_1''}{\left(\epsilon_1' + \frac{(1-P_j)}{P_j}\epsilon_m\right)^2 + \epsilon_1''^2}$$

P_j ~ "depolarization factors"

~ complex for the general case of $a \neq b \neq c$

~ relatively simple form for "spheroids" (2 axes are the same)

Prolate Spheroid $b = c$ ~ cigar

$$P_a = \left(\frac{1-e^2}{e^2}\right)\left\{\frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right)-1\right\}$$

$$P_b = P_c = \frac{1-P_a}{2} \qquad (P_a+P_b+P_c=1)$$

$$e^2 = 1 - b^2/a^2 = 1 - 1/AR^2 \qquad AR = \text{aspect ratio} = a/b$$

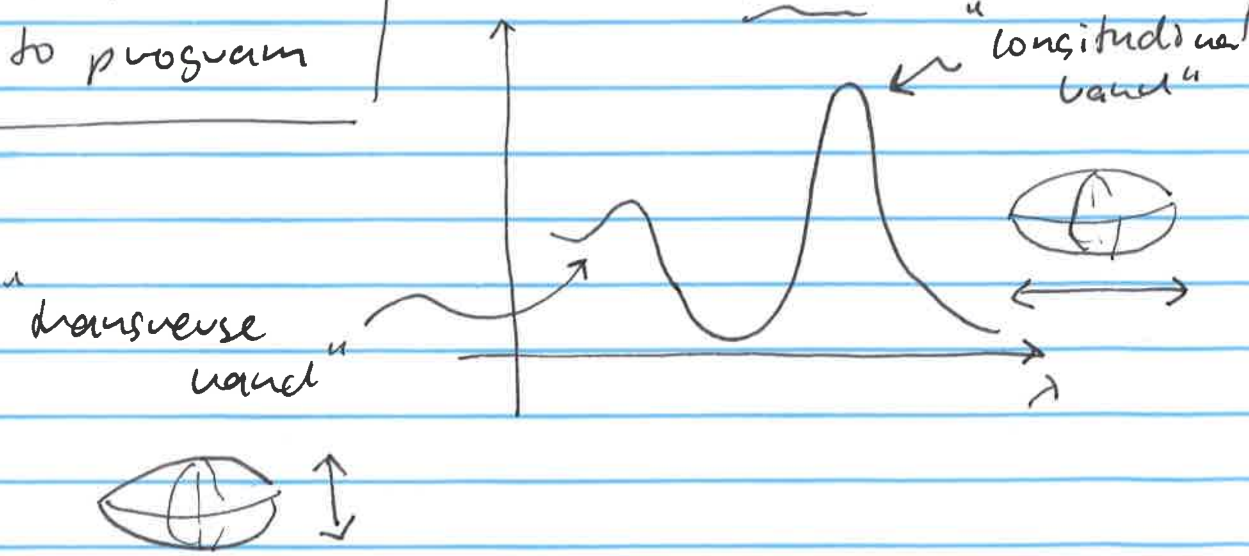
Oblate Spheroid $a = b$ ~ disk

$$P_a = \frac{g(e)}{2e^2}\left[\frac{\pi}{2} - \tan^{-1} g(e)\right] - \frac{g(e)^2}{2}$$

$$g(e) = \left(\frac{1-e^2}{e^2}\right) \qquad e^2 = 1 - c^2/a^2 \qquad P_b = P_a,\ P_c = 1-2P_a$$

$\boxed{\text{expressions are easy to program}}$

Rods

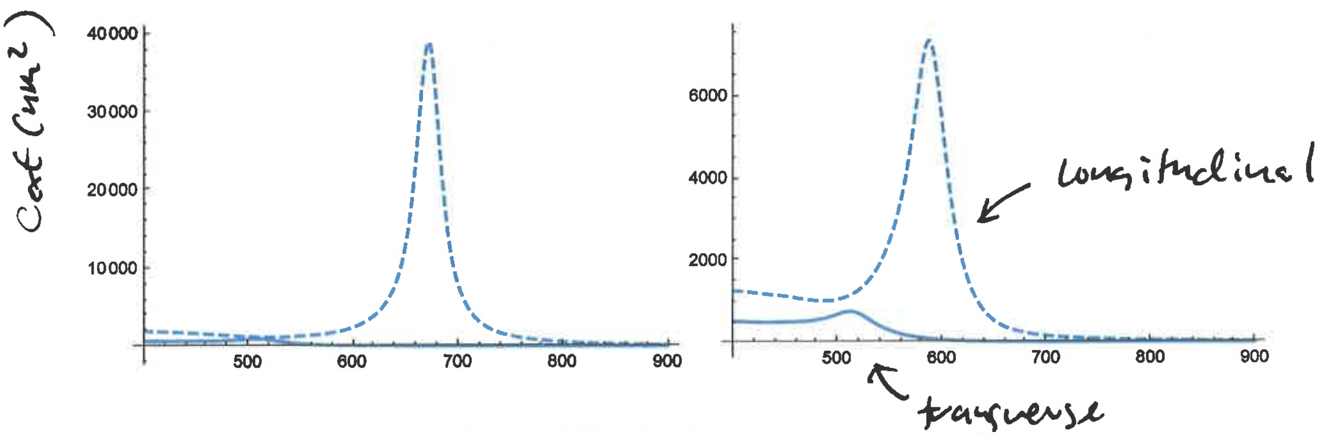


~ Gans theory also in the quasi-static limit

⇒ $|C_{ext}| \propto$ w/ Volume, shape of the spectrum (linewidth) doesn't change w/ size

Gold Nanorods $\epsilon_2 = 1.77$ (water)

L = 90nm, w = 30nm   L = 60nm, w = 30nm



longitudinal resonance is isolated & easy to fit to a Lorentzian function...

$$L(\omega) \propto \frac{(\Gamma/2)}{(\omega-\omega_0)^2 + (\Gamma/2)^2}$$

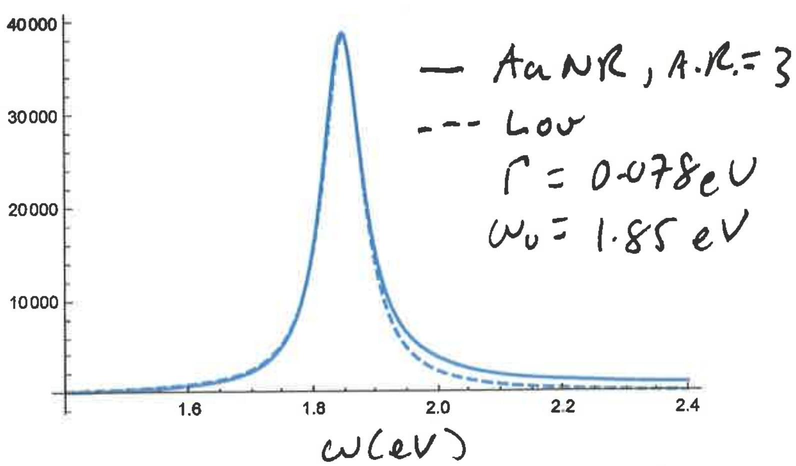
FWHM $= \Gamma$ ~ related to the "dephasing time" for the plasmon

$\Gamma = 2\hbar/T_2$ $\quad$ T_2 = dephasing time

and $1/T_2 = 1/2T_1 + 1/T^*$ ← "pure dephasing"

T_1 = lifetime

T^* ~ loss of coherence w/o loss of energy



$\Gamma = 0.078\,eV \Rightarrow T_2 \simeq 18\,fs.$

General form for ext= cross-section

$$C_{ext} \propto \frac{\epsilon_1''}{(\epsilon_1' + \beta\epsilon_2)^2 + \epsilon_1''^2}$$

~ use a Taylor's expansion for ϵ_1' & ϵ_1'' in the vicinity of the resonance $(\epsilon_1' = -\beta\epsilon_2)$

$$\left.\begin{aligned} \epsilon_1'(\omega) &= \epsilon_1'(\omega_R) + (\partial\epsilon_1'/\partial\omega)\Delta\omega \\ \epsilon_1''(\omega) &= \epsilon_1''(\omega_R) + (\partial\epsilon_1''/\partial\omega)\Delta\omega \end{aligned}\right\} \Delta\omega = \omega - \omega_R$$

$$C_{ext} \propto \frac{\epsilon_1''}{(\epsilon_1'(\omega_R) + (\partial\epsilon_1'/\partial\omega)\Delta\omega + \beta\epsilon_2)^2 + (\epsilon_1''(\omega_R) + (\partial\epsilon''/\partial\omega)\Delta\omega)^2}$$

$$= \frac{\epsilon_1''}{[(\partial\epsilon_1'/\partial\omega)\Delta\omega]^2 + \epsilon_1''^2 + 2\epsilon_1''(\partial\epsilon_1''/\partial\omega)\Delta\omega + [(\partial\epsilon_1''/\partial\omega)\Delta\omega]^2}$$

$$= \frac{\epsilon_1''}{[(\partial\epsilon_1'/\partial\omega)^2 + (\partial\epsilon_1''/\partial\omega)^2]\Delta\omega^2 + \epsilon_1''^2 + 2\epsilon_1''(\partial\epsilon_1''/\partial\omega)\Delta\omega}$$

$$= \frac{\epsilon_1''\,/\,[(\partial\epsilon_1'/\partial\omega)^2 + (\partial\epsilon_1''/\partial\omega)^2]}{\Delta\omega^2 + \dfrac{\epsilon_1''^2 + 2\epsilon_1''(\partial\epsilon_1''/\partial\omega)\Delta\omega}{[(\partial\epsilon_1'/\partial\omega)^2 + (\partial\epsilon_1''/\partial\omega)^2]}}$$

$$|\epsilon_1''|^2 \gg |2\epsilon_1''(\partial\epsilon_1''/\partial\omega)\Delta\omega|$$

$$\Rightarrow C_{ext} \sim \frac{\epsilon_1''(\quad)}{\Delta\omega^2 + \epsilon_1''^2/[(\partial\epsilon_1'/\partial\omega)^2 + (\partial\epsilon_1''/\partial\omega)^2]}$$

c/f Lorentzian

$$\Gamma^2/4 = \frac{\epsilon_1''^2}{[(\partial\epsilon_1'/\partial\omega)^2 + (\partial\epsilon_1''/\partial\omega)^2]}$$

$$\Rightarrow \Gamma = 2\epsilon_1''/[(\partial\epsilon_1'/\partial\omega)^2 + (\partial\epsilon_1''/\partial\omega)^2]^{1/2}$$

Get broad linewidths when ϵ_1'' is large and $(\partial\epsilon_1'/\partial\omega)$ and $(\partial\epsilon_1''/\partial\omega)$ are small

Drude model: $\epsilon_1' = 1 - \omega_p^2/\omega^2$

$$\epsilon_1'' = \omega_p^2\gamma/\omega^3$$

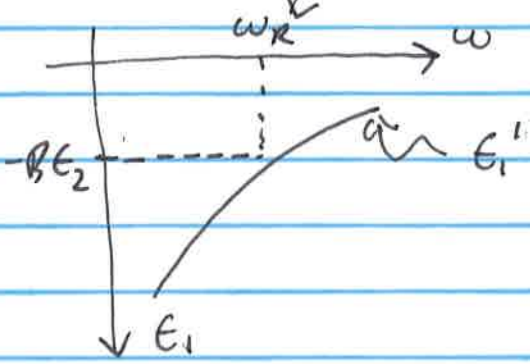
γ small $\Rightarrow \left|\frac{\partial\epsilon_1'}{\partial\omega}\right| \gg \left|\frac{\partial\epsilon_1''}{\partial\omega}\right|$

$$\Rightarrow \Gamma \simeq 2\epsilon_1'' \Big/ \left|\partial\epsilon_1'/\partial\omega\right|$$

Resonance when $\epsilon_1' = -\beta\epsilon_2$

$\Rightarrow$ position of plasmon resonance det^{d} by ϵ_1'

$\Rightarrow$ linewidth determined by ϵ_1'' and $(\partial\epsilon_1'/\partial\omega)$



$\Big\}$ ϵ_1' flat near ω_R, then a range of frequencies give large C_{ext}

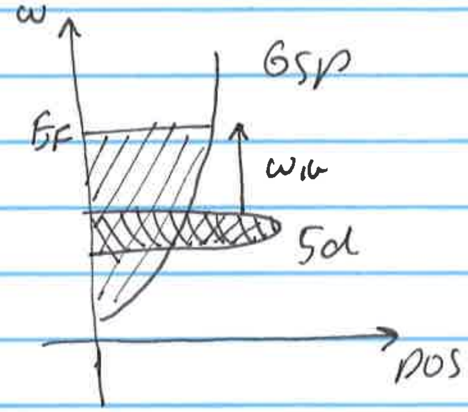
Drude model: $\dfrac{\partial\epsilon_1'}{\partial\omega} = \dfrac{2\omega_p^2}{\omega^3}$

$$\Rightarrow \Gamma = \frac{2\epsilon_1''}{\left|\partial\epsilon_1'/\partial\omega\right|} = \frac{2\omega_p^2\gamma/\omega^3}{2\omega_p^2/\omega^3} = \gamma$$

$\Rightarrow$ linewidth = damping constant in the Drude model!!

~ for metals like Au + Cu, interband transitions make a large contribution to $\epsilon_1(\omega)$ near the LSPR (for spheres at least)

eg Au



$$\epsilon_1(\omega) = \epsilon_1^{ib}(\omega) + \underbrace{1 - \frac{\omega_p^2}{\omega(\omega+i\gamma)}}_{\text{"Drude" cont}^{n}}$$

$$\Rightarrow \quad \epsilon_1' = \epsilon_1^{ib'} + 1 - \omega_p^2/\omega^2$$

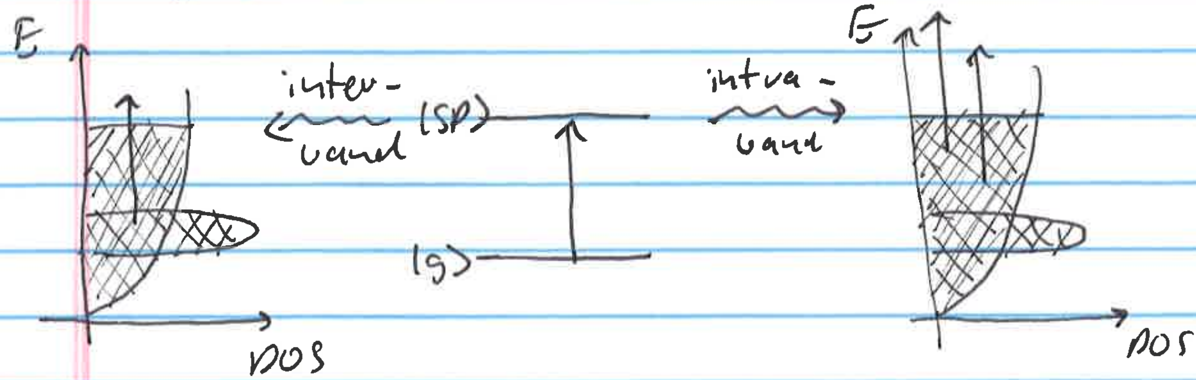
$$\epsilon_1'' = \epsilon_1^{ib''} + \omega_p^2\gamma/\omega^3$$

$$\Rightarrow \quad \Gamma = \frac{2\epsilon_1''}{|\partial\epsilon_1'/\partial\omega|} \simeq \frac{2(\epsilon_1^{ib''} + \omega_p^2\gamma/\omega^3)}{2\omega_p^2/\omega^3}$$

$$= \frac{\omega^3\epsilon_1^{ib''}}{\omega_p^2} + \gamma = \gamma_b \quad \text{"bulk damping"}$$

extra cont^{n} to damping from the presence of interband transitions

~ interpretation



create electrons at higher energy levels in C.B.?

What happens if we change size?

~ decrease size $\gamma_b \to \gamma_b + \frac{A v_F}{R}$ v_F = Fermi velocity

ϵ_1 becomes $\epsilon_1(\omega; R) = \epsilon_1^{ib}(\omega) + 1 - \frac{\omega_p^2}{\omega(\omega + i(\gamma_b + \frac{A v_F}{R}))}$

dielectric function modified by size

$\Gamma = \frac{\omega^3 \epsilon_1^{ib''}}{\omega_p^2} + \gamma + \frac{A v_F}{R}$ ← extra cont. due to damping from the surface

~ increase size?

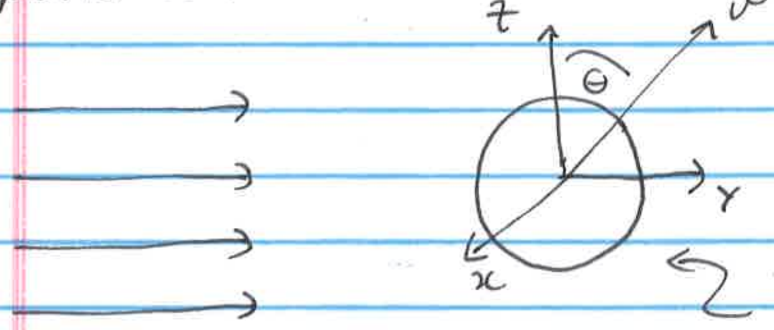
~ need new expressions for C_{ext}, as the "quasi-static" approximation is no longer any good.

Mei theory:

~ analytic expressions for the extinction and scattering of a sphere of arb. size in homogeneous medium

use spherical polar co-ordinates

incident plane wave



$E_i = \vec{E}_0 e^{iky}$

boundary conditions

$$(\vec{E}_i + \vec{E}_s - \vec{E}_e) \times \hat{e}_r$$
$$= (\vec{H}_i + \vec{H}_s - \vec{H}_e) \times \hat{e}_r = 0$$

internal scattered light

E_i / H_i ~ write as an expansion of spherical Bessel functions $j_n(kr)$

E_s / H_s ~ write as an expansion of spherical Hankel functions $h_n^{(1)} / h_n^{(2)}$

different choice determined by physics
~ require the internal field to be finite at the origin
~ require the scattered field to decay as $1/r$ at large r

~ Apply boundary conditions to get equations that relate the expansion coefficient, j_n, $h_n^{(1)}$ & their derivatives

~ calculate extinction cross-section by the optical theorem $\left(\iint_S \frac{1}{2} \mathrm{Re} \{ \vec{E}_i \times \vec{H}_s^* + \vec{E}_s \times \vec{H}_i^* \} \cdot \hat{e}_r \, dA \right)$ and scattering cross-section by integration of the scattered power over a sphere

Result: $\sigma_{scat} = \frac{2\pi R^2}{x^2} \sum_{n=1}^{\infty} (2n+1) \left\{ |a_n|^2 + |b_n|^2 \right\}$

$$\sigma_{ext} = \frac{2\pi R^2}{x^2} \sum_{n=1}^{\infty} (2n+1) \, \mathrm{Re}\left[a_n + b_n \right]$$

where $x = \frac{2\pi R n_{med}}{\lambda}$ ← n_{med} = ref. index of medium

~ the a_n & b_n factors are given by:

$$a_n = \frac{\psi_n'(mx)\psi_n(x) - m\psi_n(mx)\psi_n'(x)}{\psi_n'(mx)\zeta_n(x) - m\psi_n(mx)\zeta_n'(x)} \quad (7a)$$

← $m = \frac{n_p}{n_{med}}$

$$b_n = \frac{m\psi_n'(mx)\psi_n(x) - \psi_n(mx)\psi_n'(x)}{m\psi_n'(mx)\zeta_n(x) - \psi_n(mx)\zeta_n'(x)} \quad (7b)$$

where $\psi_n(z) = (\pi z/2)^{1/2} \times J_{n+1/2}(z)$, $\zeta_n(z) = (\pi z/2)^{1/2} \times (J_{n+1/2}(z) - iY_{n+1/2}(z))$ and $m = n_p/n_m$, where n_p is the refractive index of the particle. The different terms in eqs 6a and 6b correspond to the dipole ($n = 1$), quadrupole ($n = 2$), hexapole ($n = 3$), etc., contributions.

Note: (i) $\sigma_{ext} = \sigma_{scat} + \sigma_{abs}$

⇒ calculate σ_{abs} from the difference b/w σ_{ext} & σ_{scat}

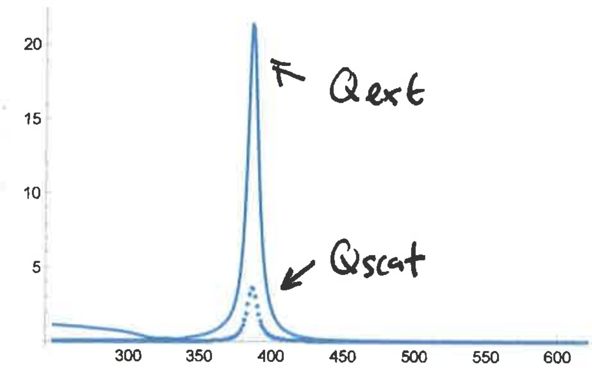
(ii) common (& maybe more useful) to work w/ efficiencies

$Q = \sigma / \pi R^2$ ← cross-section normalized by area

~ spectra of Ag & Au nanoparticles in H_2O

Ag data

a = 10



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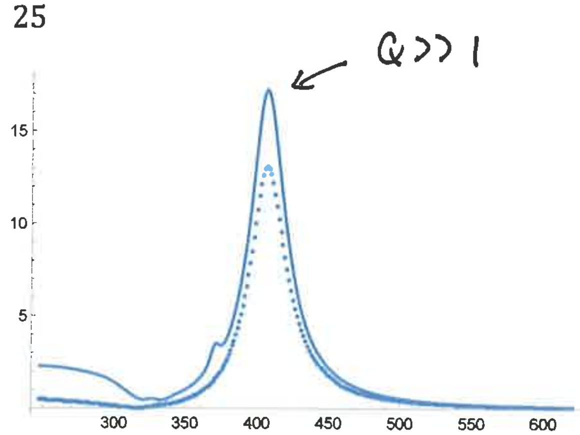

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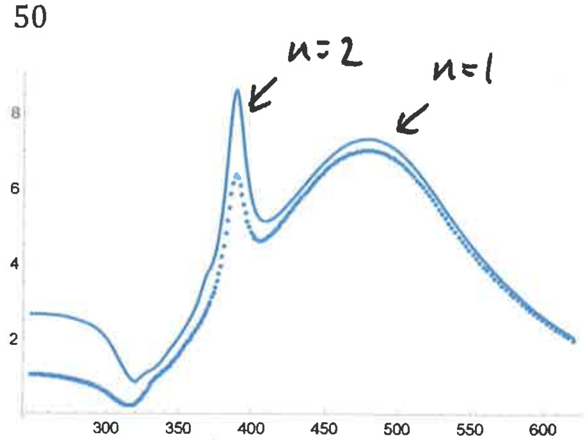
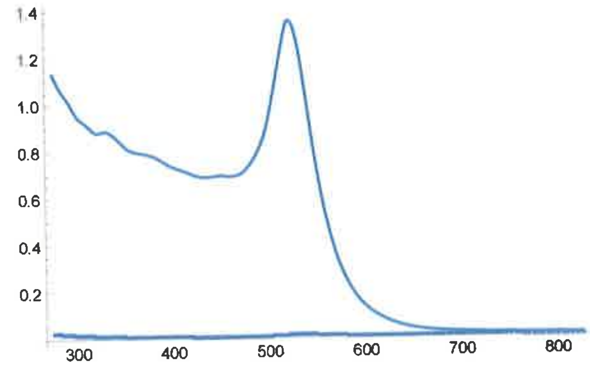


Au data

a = 10



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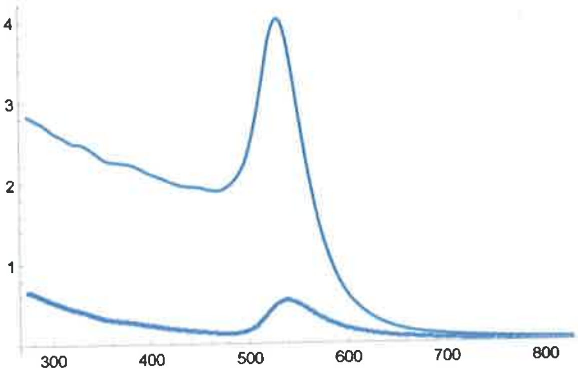

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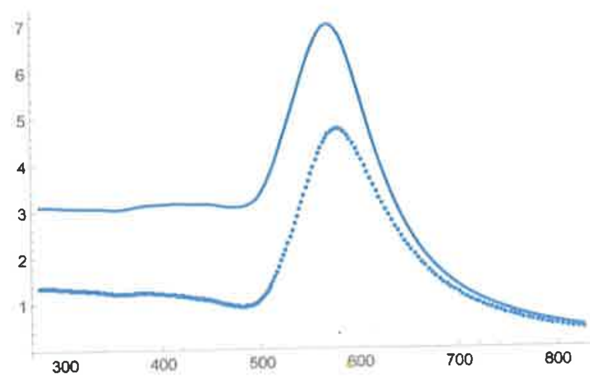


~ spectra for Ag are sharper & more intense than spectra for Au b/c Ag has less damping from interband transitions

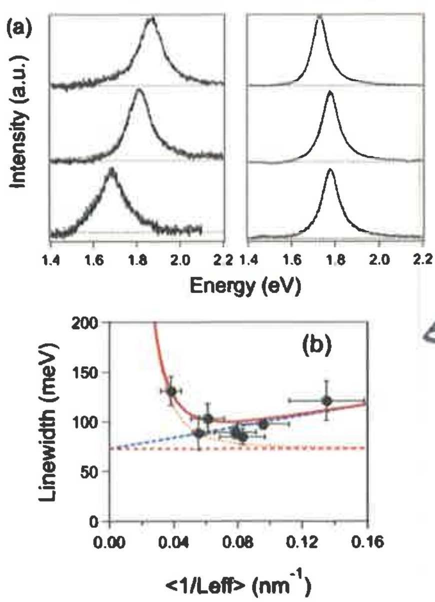
$$\left(\underbrace{\Gamma = \omega^3 \epsilon''_{ib}/\omega_p^2}_{\text{interband}} + \underbrace{\gamma}_{\text{Drude model}} \right)$$

~ spectra become broader at large sizes due to "radiation damping"

$$\Gamma = \gamma_0 + \frac{A v_F}{R} + \underbrace{2\hbar K V}_{\text{Radiation damping term}}$$

Radiation damping term $\propto V$ at not too large sizes

Rayleigh scattering spectra from single Au nanorods



linewidth versus $1/l_{eff}$ ~ minimum @ $w \simeq 14$ nm

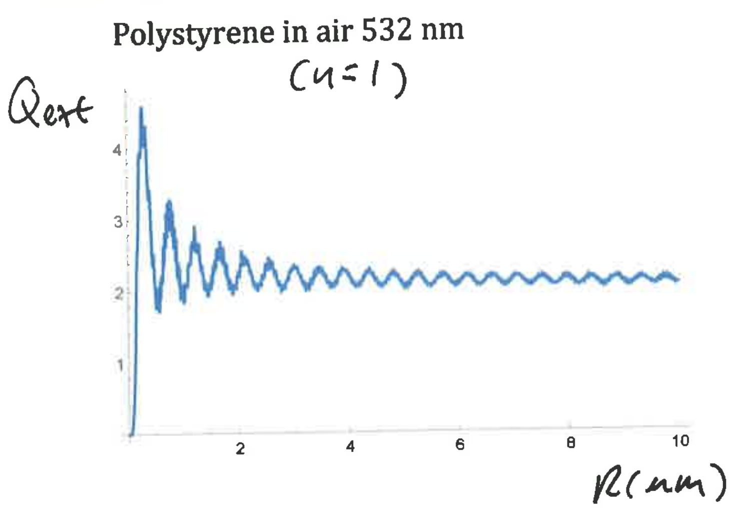
~ competition b/w rad^n damping & surface scattering

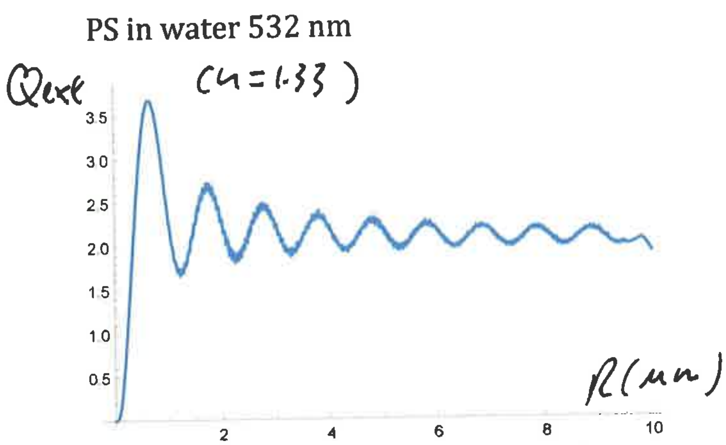
~ it is also useful to plot Q_{ext} at a fixed wavelength as a f^n of size

eg polystyrene

$n = 1.592$ / $\lambda = 0.532\ \mu m$

~plot Q_{ext} versus R (in μm)



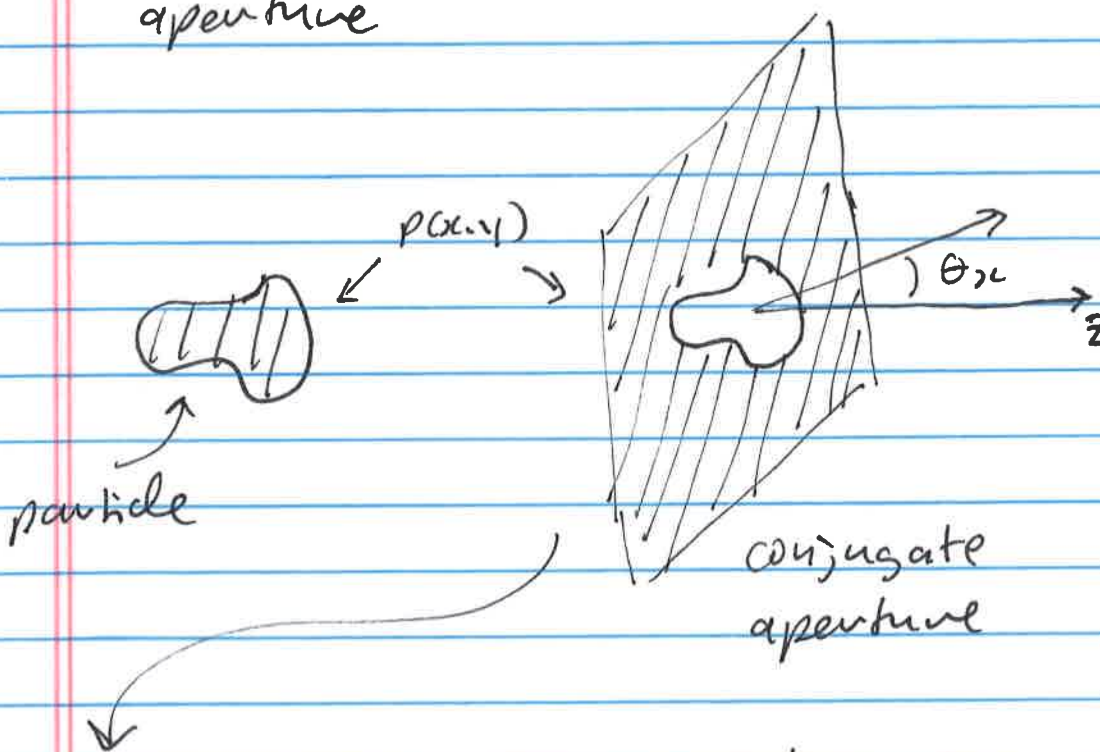


larger resonances when there is a larger dielectric contrast

in both cases $Q_{ext} \to 2$ as $R \to \infty$

Babinet's Principle

- light transmitted around a particle equals the incident field minus the light diffracted by the "conjugate aperture"



diffracted field $g(x,y) = I_0^{1/2} h_0 P\left(\frac{x}{\lambda d}, \frac{y}{\lambda d}\right)$

$$P(\nu_x, \nu_y) = \iint_{-\infty}^{\infty} p(x,y)\, e^{i2\pi(\nu_x x + \nu_y y)}\, dx\,dy$$

$$\nu_x = \frac{x}{\lambda d} = \frac{\theta_x}{\lambda} \; ; \; \nu_y = \frac{y}{\lambda d} = \frac{\theta_y}{\lambda}$$

define $D(\theta_x, \theta_y) = \frac{1}{a} \iint_{-\infty}^{\infty} p(x,y)\, e^{i2\pi(\nu_x x + \nu_y y)}\, dx\, dy$

where $a = \iint p(x,y)\, dx\, dy$ = area of the particle/aperture

$\Rightarrow$ diffracted field $g(x,y) = I_0^{1/2}\, h_0\, a\, D(\theta_x, \theta_y)$

$$h_0 = \frac{i}{\lambda z} e^{-ikr}$$

For the particle

$$g(x,y) = \underbrace{E_0 e^{-ikz}}_{\text{incident field}} - \underbrace{\frac{i E_0 e^{-ikr}}{\lambda z} a\, D(\theta_x, \theta_y)}_{\text{diffracted field from conjugate aperture}}$$

$$g(x,y) = E_0 e^{-ikz}\left(1 - \frac{i e^{-ik(r-z)}}{\lambda z} a\, D(\theta_x, \theta_y)\right)$$

$$r - z \simeq \frac{x^2+y^2}{2z}$$

$$\Rightarrow g(x,y) = E_0 e^{-ikz}\left(1 - \frac{i e^{-ik(x^2+y^2)/2z}}{\lambda z} a\, D(\theta_x, \theta_y)\right)$$

~ compare to the optical theorem

$$E_{tot} = E_0 e^{-ikz}\left(1 + \frac{i S(\theta,\phi)}{\lambda z} e^{ik(x^2+y^2)/(2z)}\right)$$

$$\Rightarrow \quad -a D(\theta_x, \theta_y) \equiv S(\theta,\phi) \Leftarrow$$ function that describes scattering by the particle

~ from the optical theorem $\frac{\Delta I}{I} = 2\,Re(S(0))$

scattering in the forward direction

$$D(\theta_x, \theta_y) = \frac{1}{a}\iint_{-\infty}^{\infty} p(x,y)\, e^{i2\pi\left(\frac{\theta_x}{\lambda}x + \frac{\theta_y}{\lambda}y\right)} dx\,dy$$

$\theta_x, \theta_y \simeq 0$ for forward direction

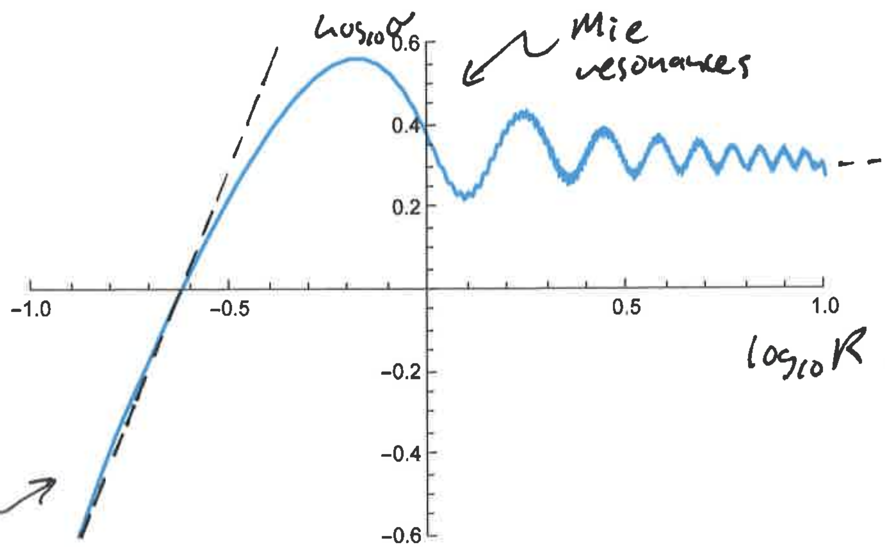
$$\Rightarrow D(\theta_x, \theta_y) \simeq \frac{1}{a}\iint_{-\infty}^{\infty} p(x,y)\, dx\,dy = 1$$

$$\Rightarrow \frac{\Delta I}{I} = -2a \quad \text{or} \quad C_{ext} = 2a$$

"Extinction Paradox"

~ for a large particle extinction is twice the geometrical area

~ extinction is a combination of the light blocked by the object and the light diffracted by the object



extinction paradox
$\sigma_{ext} = 2G$

Rayleigh region
$\sigma_{ext} \propto V$