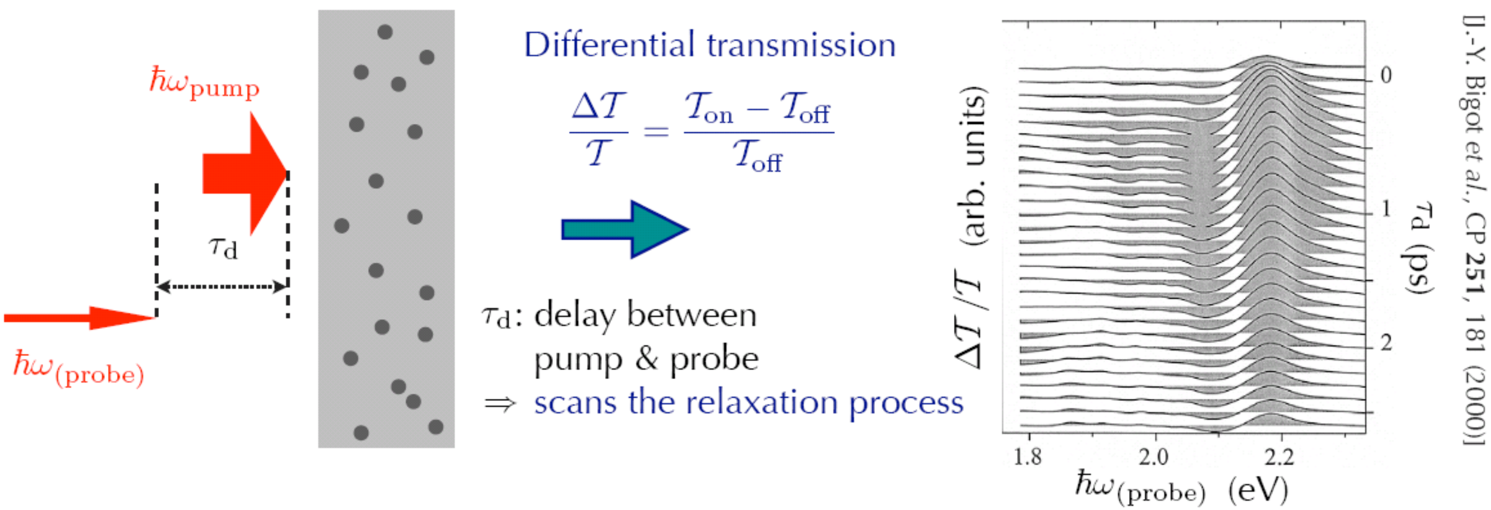
# Plan of the lectures

1. Introductory remarks on metallic nanostructures
   - Relevant quantities and typical physical parameters
   - Applications
2. **Linear electron response: Mie theory and generalizations**
3. Nonlinear response
   - Survey of various models from N-body to macroscopic
   - Mean-field approximation (Hartree and Vlasov equations)
4. Beyond the mean-field approximation
   - Hartree-Fock equations
   - Time-dependent density functional theory (DFT) and local-density approximation (LDA)
5. Macroscopic models: quantum hydrodynamics

   Linear theory and comparison of various models
6. Spin dynamics: experimental results and recent theoretical advances
7. Illustration: the nonlinear electron dynamics in thin metal films

# Electron dynamics — qualitative aspects

- We have seen that the typical timescale of collective phenomena is
  - **$2\pi\omega_p^{-1} \approx 1$ fs**
- We need short laser pulses to probe this timescale.
- **Pump-probe experiments**



# Linear response: driven-damped harmonic oscillator

$$\frac{d^2x(t)}{dt^2} + 2\beta\frac{dx(t)}{dt} + \omega_0^2\,x(t) = F_0\cos(\omega t).$$

damping

Oscillations (plasmon)

Forcing (laser)

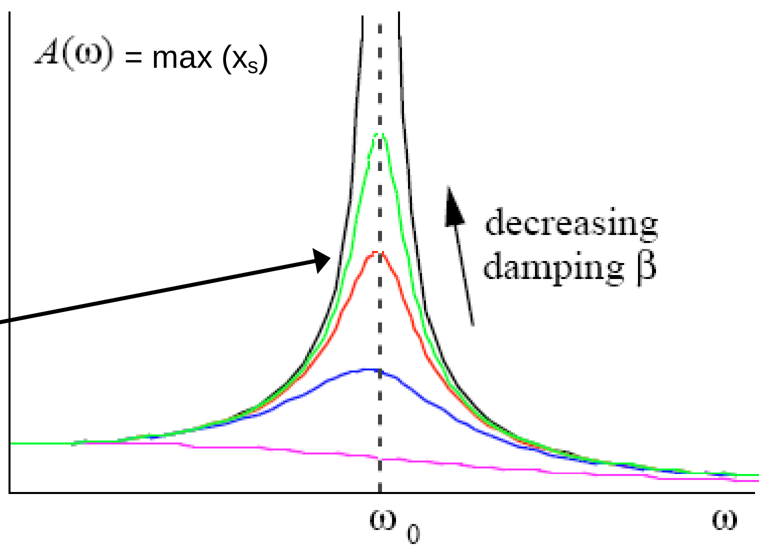
Steady state solution (t→∞):

$$\boxed{x_s(t) = \frac{F_0}{m\sqrt{(\omega^2-\omega_R^2)^2+4\beta^2\omega_1^2}}\cos(\omega t-\delta)}$$

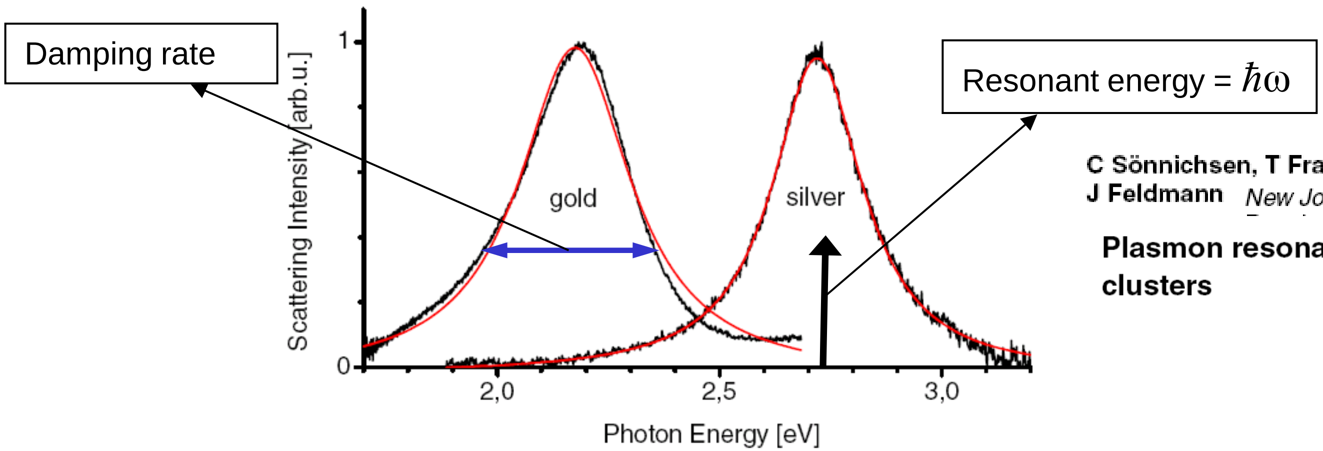
where the *resonant frequency* is given by

$$\boxed{\omega_1 = \sqrt{\omega_0^2-\beta^2}} \qquad \boxed{\omega_R = \sqrt{\omega_0^2-2\beta^2}}$$

Resonance becomes broader with increasing damping



1. **The response is directly proportional to the excitation**
   - For instance, the electron density modulation is proportional to laser field amplitude
2. **When the frequency ω of the excitation is close to the "natural" frequency of the system, we have resonance → enhanced absorption**
   - For electron gas, **natural frequency ~ $\omega_p$**
3. **In the presence of damping, the resonance becomes « broad »**




C Sönnichsen, T Franzl, T Wilk†, G von Plessen‡ and J Feldmann *New Journal of Physics* 4 (2002) 93.1–93.8

**Plasmon resonances in large noble-metal clusters**

**Main purpose of linear theory: determine resonant frequency and damping rate**

# Mie theory — 1D model

$$\langle x \rangle = \frac{\int nx dx}{\int n dx} \equiv d(t)$$

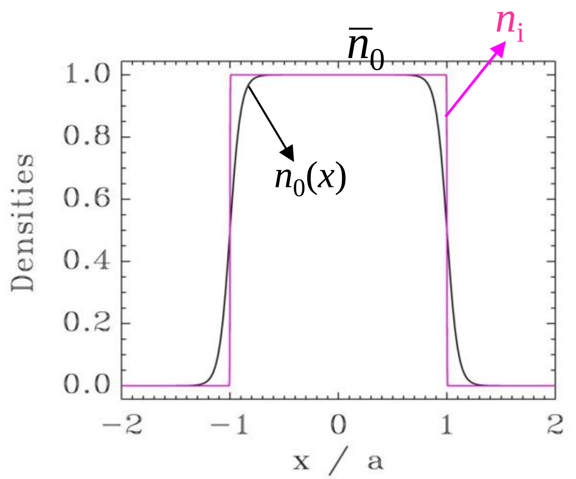
- Def. of electric dipole

$$\frac{d^2\langle x \rangle}{dt^2} = -\frac{e}{m}\langle E \rangle = -\frac{e}{m}\frac{\int nE dx}{\int n dx}$$

- "Ehrenfest theorem"

$$\frac{\partial E}{\partial x} = \frac{e}{\varepsilon_0}[n_i(x) - n(x,t)]$$

- Poisson's equation




- Initial shift of the electron density by a distance *d*(0): $n(x,t) = n_0[x - d(t)] \simeq n_0(x) - n_0' d(t)$ $\boldsymbol{\delta n}$

- Induced change in electric field (from Poisson's equation) $E(x,t) = E_0(x) + \delta E(x,t)$

$$\frac{\partial E_0}{\partial x} = \frac{e}{\varepsilon_0}[n_i(x) - n_0(x)] \qquad \delta E(x,t) = \frac{e n_0(x)}{\varepsilon_0}\, d(t)$$

- We obtain: $\displaystyle\int nE dx \simeq \int (n_0\, \delta E + \delta n E_0) dx = \frac{e}{\varepsilon_0}\, d \int n_0 n_i dx$

***NB***: $\displaystyle\int n_0 E_0 dx = 0$

- Finally the dipole obeys the harmonic oscillator equation:

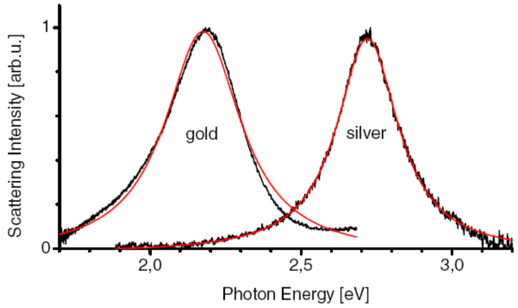
$$\ddot{d} = \underbrace{-\frac{e^2}{m\varepsilon_0}\frac{\int n_0 n_i dx}{\int n_0 dx}}_{\boxed{\omega^2}} d$$

- If $n_0 = n_i = const$ it can be taken out of the integral:

$$\ddot{d} = -\frac{e^2\overline{n}_0}{m\varepsilon_0}\, d = -\omega_p^2\, d,$$

- We obtain oscillations at the plasma frequency.

- **This is the fundamental result of the Mie theory**

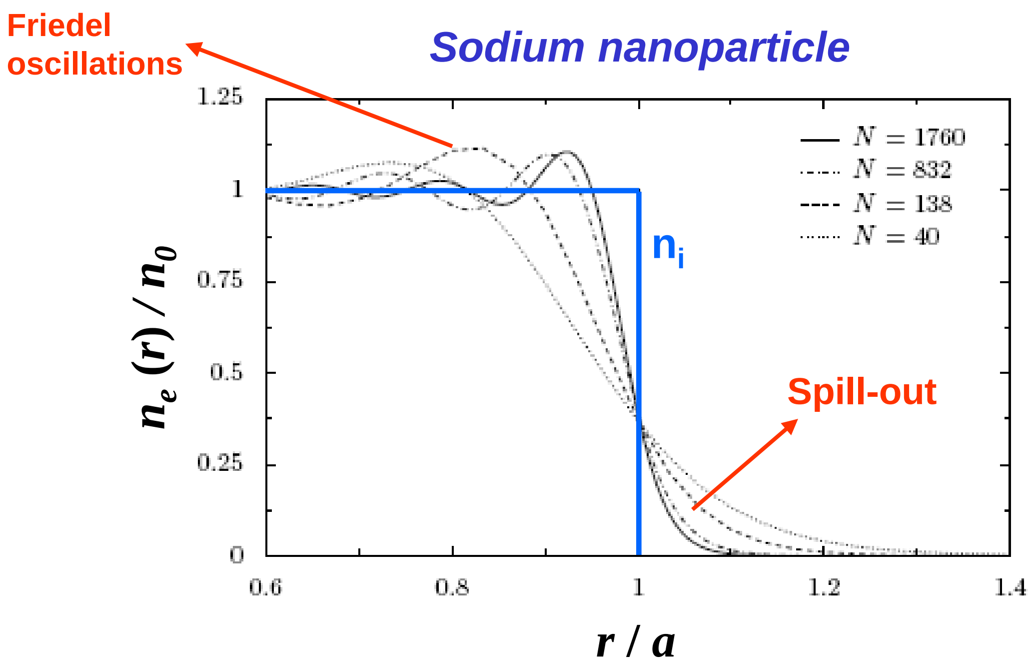



Limitations:

1. No dependence on size, temperature, …
   The metal species (Au, Ag,…) appears only in the plasma frequency, through the electron density.
2. No damping: purely oscillatory mode at a single frequency
3. Derivation in 1D
4. … and, of course, purely linear response

# Spill-out effect: illustration

Numerical computation of the ground state at zero temperature



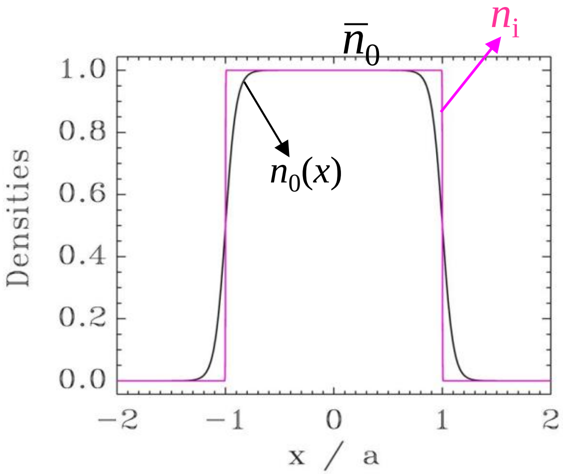

G. Weick, PhD thesis, IPCMS, Strasbourg (2006)

$$\ddot{d} = -\frac{e^2}{m\varepsilon_0}\,\frac{\int n_0 n_i dx}{\int n_0 dx}\; d$$

$$\ddot{d} = -\frac{e^2\overline{n}_0}{m\varepsilon_0}\; d = -\omega_p^2\; d,$$

# Spill-out effect: qualitative picture

- The electron density at equilibrium is not equal to the ion density
- The electrons "spill out" of a length $\boldsymbol{\delta}$
- **This leads to a reduction of the oscillation frequency**




$$\int n_0 n_i dx = \bar{n}_0\, N_{in} = \bar{n}_0 (N - N_{out})$$

$$\int n_0 dx = N$$

$$\omega^2 = \frac{e^2}{m\varepsilon_0} \frac{\int n_0 n_i dx}{\int n_0 dx} = \omega_p^2 \left(1 - \frac{N_{out}}{N}\right)$$

Red shift

- **The correction to the frequency goes as 1/*a***
- This is the first correction we have found to the simple plasmon frequency
- It is true in **any number of dimensions**
  - It's just the surface to volume ratio
- **For instance, in 3D:**

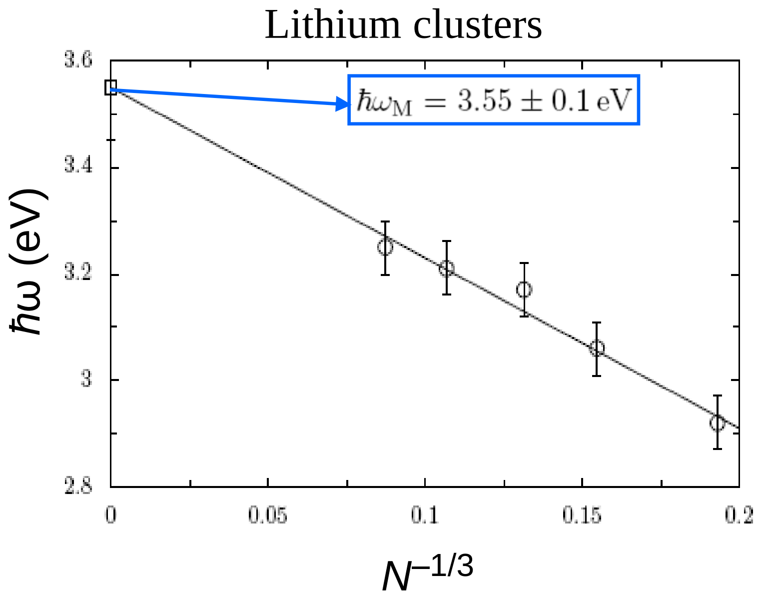
$$\omega = \omega_p \sqrt{1 - \frac{N_{out}}{N}} \simeq \omega_p - \omega_p \frac{N_{out}}{2N}$$

$$N = \frac{4\pi R^3}{3}\,\overline{n}_0$$

$$N_{out} = \delta N = 4\pi R^2 \overline{n}_0 \delta R$$

$$\frac{N_{out}}{N} = \frac{3\delta R}{R} \sim N^{-1/3}$$

Assuming $\delta R$ does not depend on $R$




Data : C. Brechignac et al, PRL **70**, 2036 (1993)

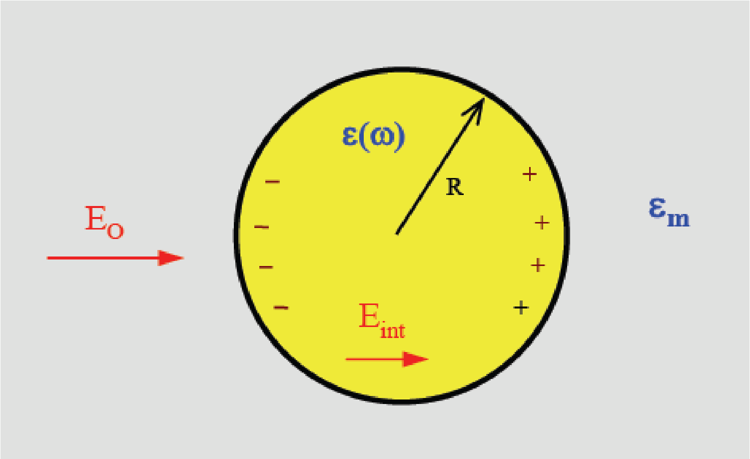
Graph : G. Weick, PhD thesis, IPCMS, Strasbourg (2006)

# General Mie theory of the surface plasmon (1908)

- Spherical nanoparticle immersed in external field $E_0$
- Electrostatic response: free charges tend to shield the external field
  - Inside the sphere the electric field is*

$$\boxed{E_{\text{int}} = E_0 \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} < E_0 \quad \text{if} \quad \varepsilon > \varepsilon_m}$$

- We make the following assumptions:
  - No magnetic field effect (E/B ~ c)
  - Electric field wavelength >> R = radius of nanoparticle; OK for visible-light lasers $\lambda \approx$ 400-800 nm
- Thus, we consider only the time variation of the field
  - $E = E_0 \exp(-i\omega t)$
- The dielectric constant depends on the frequency




* J. D. Jackson, "Classical Electrodynamics"

- The dielectric constant has a real and an imaginary part

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

$$E_{\text{int}} = E_0 \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

- When $\varepsilon_2 << \varepsilon_1$, the **resonance condition** is: $\boldsymbol{\varepsilon_1 = -2\,\varepsilon_m}$
- The dielectric constant also determines the photo-absorption cross-section

$$\sigma(\omega) = \frac{9\omega\epsilon_{\mathrm{m}}^{3/2}\mathcal{V}}{c}\frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + 2\epsilon_{\mathrm{m}}]^2 + \epsilon_2(\omega)^2},$$

- <u>It remains to be determined the frequency dependence of</u> $\boldsymbol{\varepsilon_1(\omega)}$**.**

# Frequency-dependent dielectric constant

**Drude theory for time-dependent electric field**

$$\dot{p} = -\Gamma p - eE\ \exp(-i\omega t)$$ Equation of motion

$$p = \frac{eE}{i\omega - \Gamma}$$ Fourier transform: p → p exp(–iωt)

***j*** = electric current density

$$j = -\frac{nep}{m} = \frac{ne^2}{m}\frac{E}{\Gamma - i\omega} \equiv \sigma(\omega)\ E(\omega)$$ **microscopic Ohm's law** (I = V/R)

$$\boxed{\sigma(\omega) = \frac{ne^2}{m}\ \frac{1}{\Gamma - i\omega}}$$ $\sigma$ (ω) = conductivity

# Maxwell's equations

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \qquad \nabla \times B = \mu_0 J + \mu_0 \varepsilon_0 \varepsilon_b \frac{\partial E}{\partial t}$$

$$\nabla \times (\nabla \times E) = -\frac{\partial}{\partial t}(\nabla \times B) =$$

$$\boxed{\nabla \times (\nabla \times E) = -\frac{\partial}{\partial t}\left(\mu_0 J + \mu_0 \varepsilon_0 \varepsilon_b \frac{\partial E}{\partial t}\right)}$$

$$= i\omega\left(\mu_0 \sigma - i\frac{\omega}{c^2}\varepsilon_b\right)E$$

$$= i\frac{\omega}{c^2}\left(\frac{\sigma}{\varepsilon_0} - i\varepsilon_b \omega\right)E$$

$$= \frac{\omega^2}{c^2}\left(\varepsilon_b + \frac{i\sigma}{\varepsilon_0 \omega}\right)E$$

$$\frac{\partial}{\partial t} \to -i\omega$$

**Use: $J = \sigma$ E**

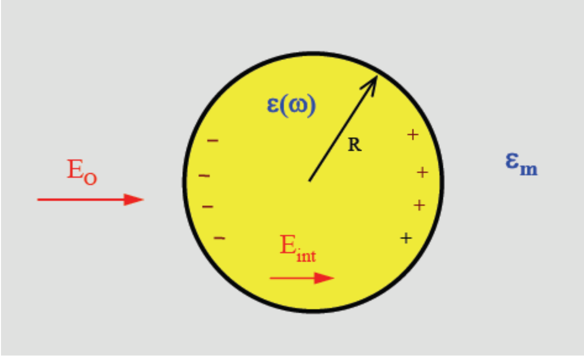
$$\varepsilon_0 \mu_0 = \frac{1}{c^2}$$

$$\varepsilon(\omega) = \varepsilon^b + \varepsilon^f = \varepsilon^b + i\frac{\sigma}{\omega\varepsilon_0} = \boxed{\varepsilon^b - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}}$$

Bound electrons

Free electrons

# Mie resonance




$$E_{\text{int}} = E_0 \frac{3\varepsilon_m}{\varepsilon + 2\varepsilon_m} < E_0 \quad \text{if} \quad \varepsilon > \varepsilon_m$$

- When $\varepsilon_2 << \varepsilon_1$, the **resonance condition** is $\boldsymbol{\varepsilon_1 = -2\,\varepsilon_m}$
- Remember the frequency-dependent dielectric constant

$$\varepsilon(\omega) = \varepsilon^b - \frac{\omega_p^2}{\omega^2 + i\Gamma\omega}$$

$\approx$

If $\Gamma << \omega$ : $\quad \varepsilon_1(\omega) \simeq \varepsilon^b - \dfrac{\omega_p^2}{\omega^2} = -\,2\,\varepsilon_m \qquad \varepsilon_2 \approx \dfrac{\omega_p^2}{\omega^2}\dfrac{\Gamma}{\omega}$

**Mie frequency:** $\boxed{\omega^2 = \dfrac{\omega_p^2}{2\varepsilon_m + \varepsilon^b} \approx \dfrac{\omega_p^2}{3}}$ $\quad$ if $\varepsilon_m \approx \varepsilon^b \approx 1$

**Surface plasmon**

# Mie resonance in 1D, 2D, and 3D

| Dimensionality | Geometry | Resonant frequency |
|---|---|---|
| 1D | Thin film | $\omega_p$ |
| 2D | Planar surface | $\omega_p / \sqrt{2}$ |
| 3D | Sphere | $\omega_p / \sqrt{3}$ |

# Does Mie theory work?

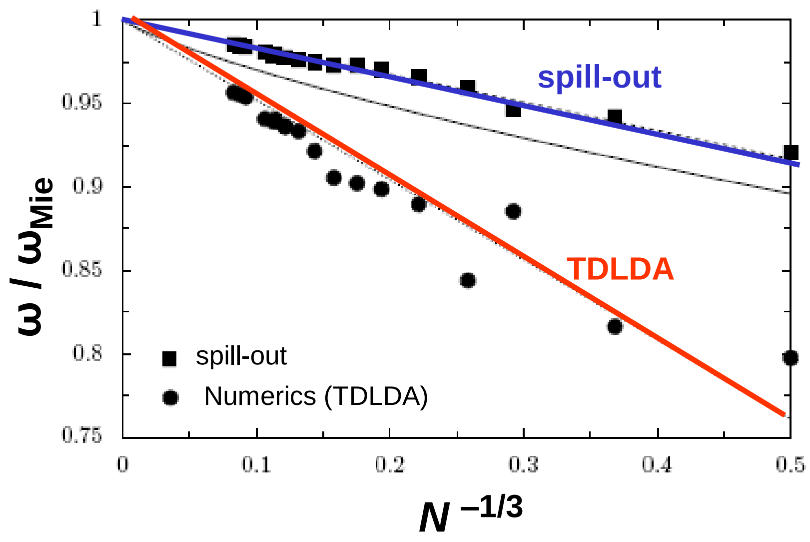
1. **Pure Mie**: $\omega = \omega_p / \sqrt{3} \equiv \omega_{Mie}$

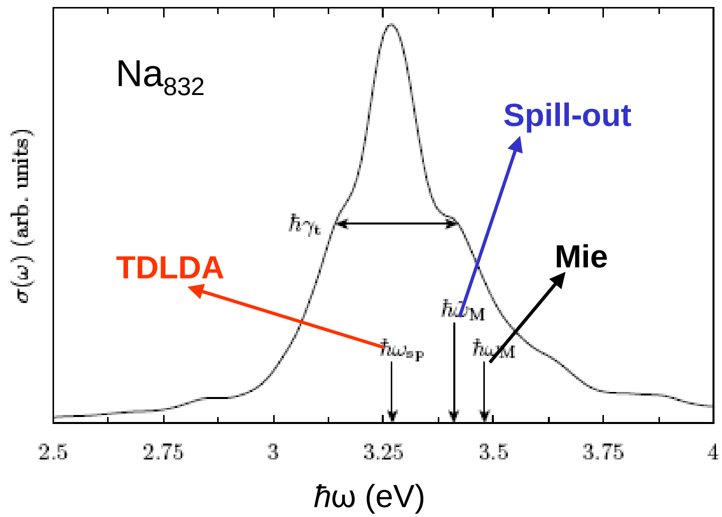
2. **Spill-out correction**

$$\omega \approx \omega_{Mie}\left(1 - K\, N^{-1/3}\right)$$

3. **Self-consistent calculation using TDLDA** (time-dependent local density approximation)

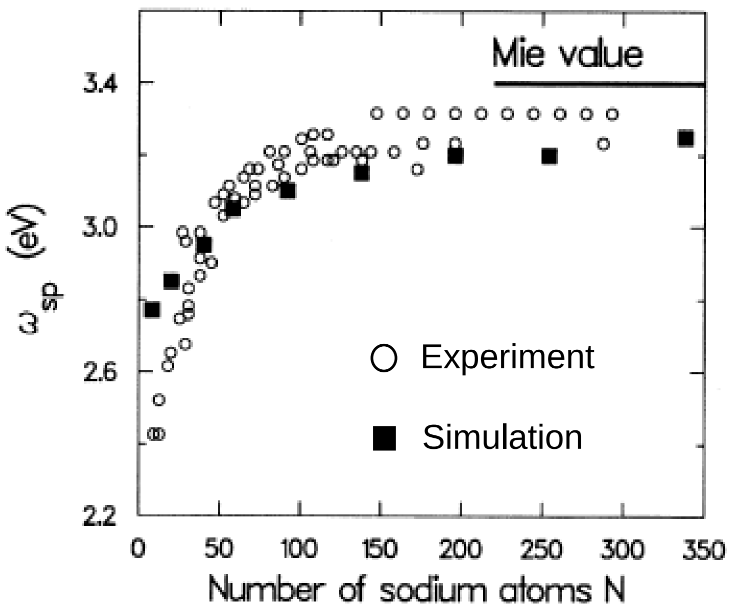
$$\omega \approx \omega_{Mie}\left(1 - K'\, N^{-1/3}\right) \ ; \qquad K' > K$$




G. Weick, PhD thesis, IPCMS, Strasbourg (2006)

# Experiment vs. Mie theory and TDLDA simulations




C. Yannouleas et al., Phys. Rev. B **47**, 9849 (1993)

Recover Mie value
for large N

# Linewidth of the Mie resonance — damping

## Sources of damping

1. Electron-electron collisions (e-e)
2. Electron-phonons collisions (e-ph): interactions with lattice
3. Coupling between collective modes (plasmon) and single-particle modes: “Landau damping”
4. Radiation damping
5. …

$$\Gamma = \frac{1}{\tau_{e-e}} + \frac{1}{\tau_{e-ph}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{Landau}} + \ldots$$

# Linewidth of the Mie resonance — damping

- Collision rate in the bulk material: **$\Gamma_\infty = V_F / L_\infty$**
  - $L_\infty$ is the bulk mean free path: $L_\infty$(Na) = 34 nm; $L_\infty$(Ag) = 52 nm (at T=273K)
- When $L_\infty$ > R (size of the nanoparticle) then one should replace $L_\infty$ with R
  - **Collisions with the particle's surfaces**

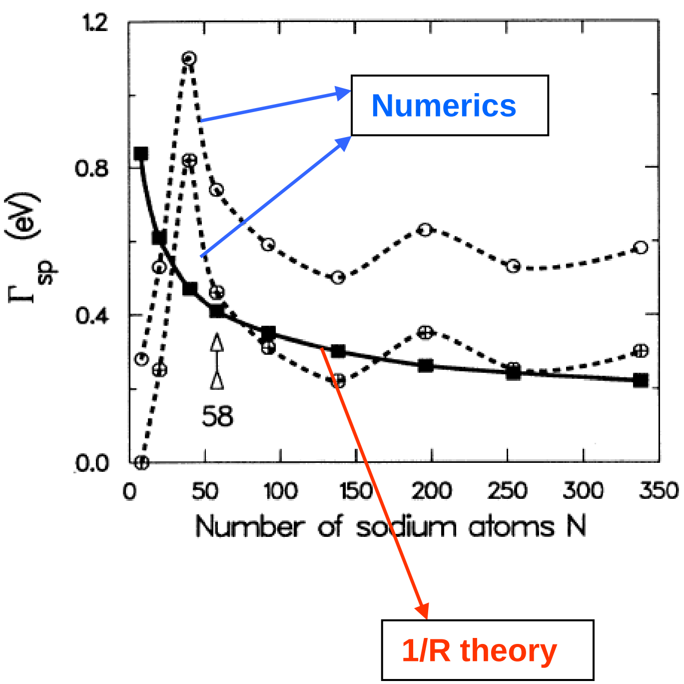
$$\boxed{\Gamma = \Gamma_\infty + A\frac{V_F}{R}}$$

- This picture is not quite correct quantum-mechanically
  - The boundaries determine the shape of the wave functions *everywhere*
- Kawabata and Kubo (1966) computed the quantum damping rate
  - **Still obtain 1/R behavior**.

# Linewidth — experimental and numerical results

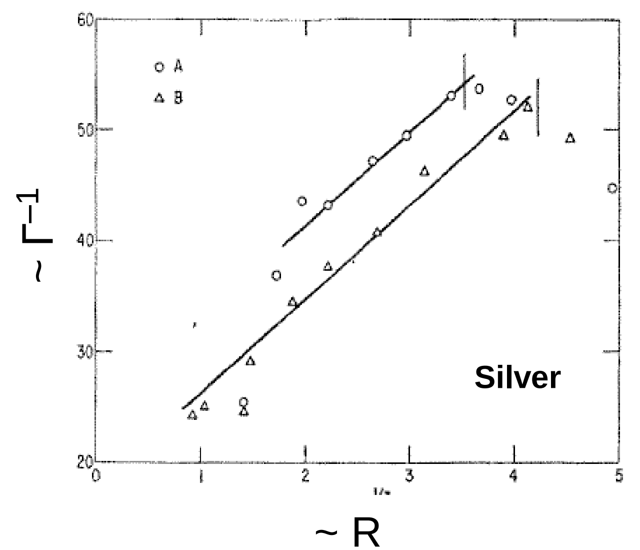
**Num.**

C. Yannouleas et al., Phys. Rev. B **47**, 9849 (1993)




**Exp.**

R. H. Doremus, J. Chem. Phys. **42**, 414 (1965).

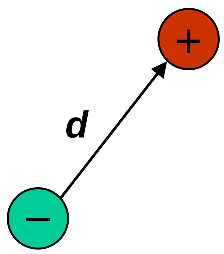


# Radiation damping

- An oscillating electric dipole radiates electromagnetic energy
- This is a source of damping of the electronic energy *W:*

$$W = N\left(\frac{1}{2}mv^2\right) = \frac{1}{2}Nm\frac{p^2}{e^2}\omega_{sp}^2 \qquad v = d\omega_{sp} = \frac{p}{e}\omega_{sp}$$

Electric dipole: *p=ed*



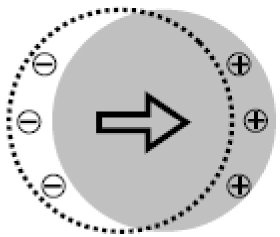

- The total radiated power is (see Jackson, *Classical Electrodynamics*)

$$\boxed{\frac{dW}{dt} = -\frac{1}{4\pi\varepsilon_0}\frac{I^2(kd)^2}{12c}}$$

$I = Q\omega_{sp}$ : current

$k = \omega_{sp}/c$ : wavevector

$$\boxed{\frac{dW}{dt} \propto -\left(\frac{Q}{e}\right)^2 \frac{\omega_{sp}^4 p^2}{4\pi\varepsilon_0 c^3} \propto -\frac{N^2\omega_{sp}^4 p^2}{4\pi\varepsilon_0 c^3}} = -\Gamma_{rad}W$$



- This yields $\boxed{\Gamma_{rad} \propto \frac{e^2}{4\pi\varepsilon_0 mc^3}\omega_{sp}^2\ N \propto R^3}$

- **Proportional to the volume: significant only for large nanoparticles**

$$\frac{\Gamma_{rad}}{\omega_{sp}} \propto \left(\frac{e^2}{2\varepsilon_0 hc}\right)\left(\frac{\hbar\omega_{sp}}{mc^2}\right)N \approx \frac{1}{137}\left(\frac{3\,\text{eV}}{511\,\text{keV}}\right)N \approx (4\times10^{-8})\times N$$