Academia Romana

From biological cells to semiconductor and metallic nanoparticles: the same recipe with different flavors

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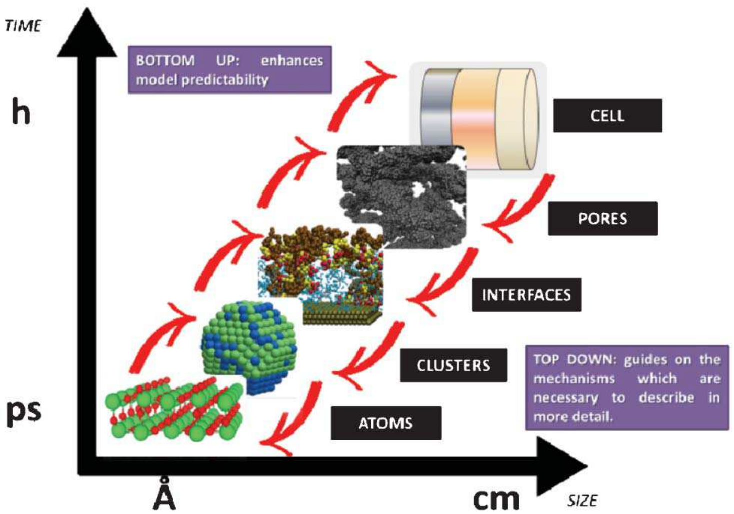
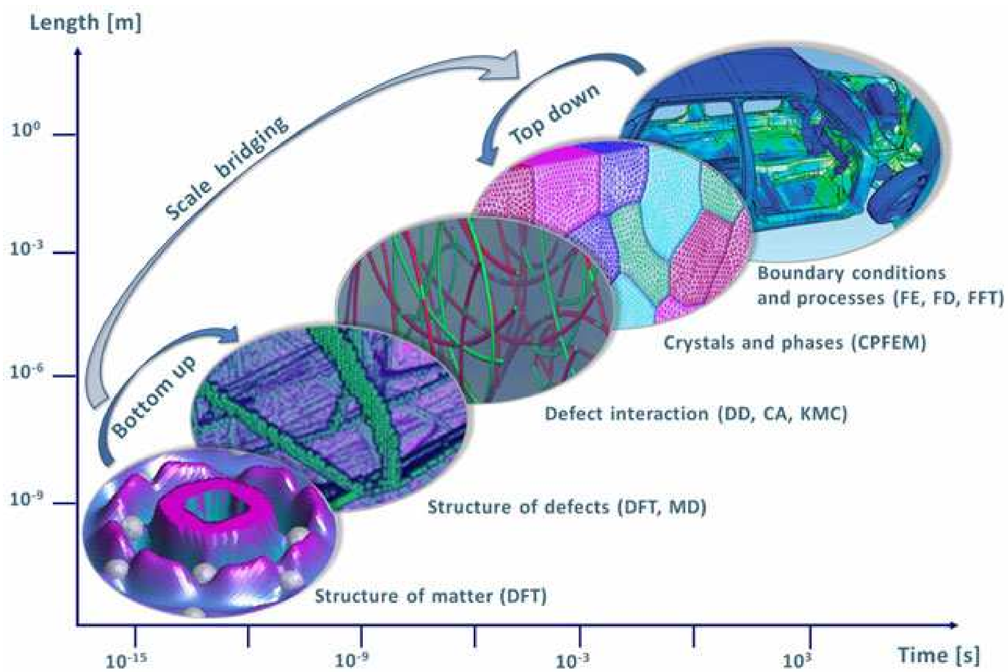
Summary

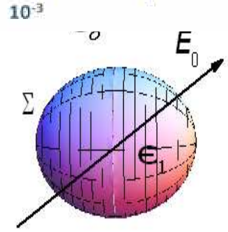
1. Introduction

- Simulation, modeling and theoretical investigation of micro- and nano-systems can be made by a variety of methods starting with continuum models based on classical physics and ending with atomistic models that require principles of quantum mechanics



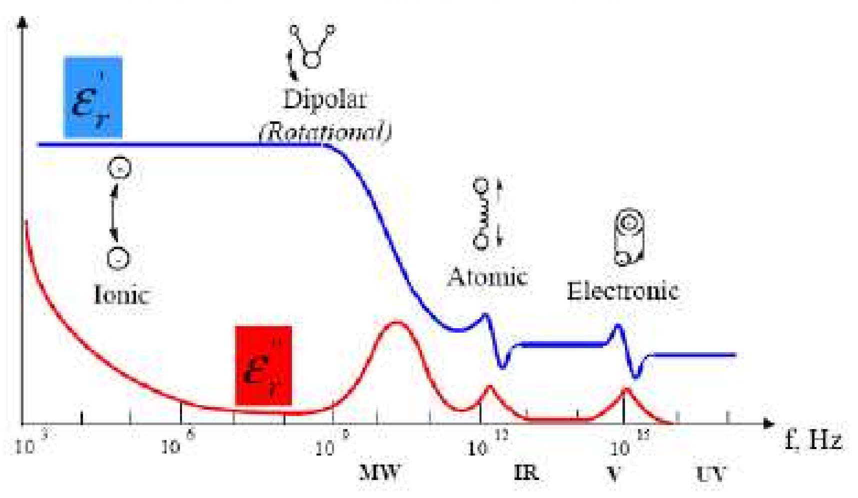


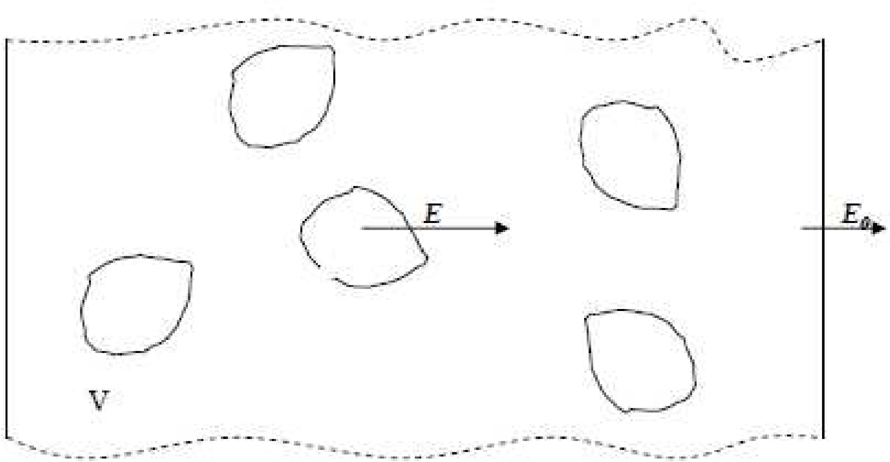
•Many times the response of micro- and nano-particles to electromagnetic radiation can be modeled just by resolution of **Maxwell or Poisson** equations if the response function of materials is known.



1. Introduction

Interaction of electromagnetic fields with matter





Homogeneous systems

$$\epsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$

Heterogeneous systems: additional resonances

•Maxwell-Wagner relaxations- (low frequency)

$$\epsilon = \varepsilon_0 + \sigma / i\omega \quad C = \epsilon_{eff}\varepsilon_0 \frac{S}{d}$$

•Surface phonons (deep infrared)

$$\epsilon(\omega) = \epsilon_\infty \left[1 + \frac{\omega_L^2 - \omega_T^2}{\omega_T^2 - \omega^2 + i\Gamma\omega} \right]$$

•Plasmon resonances (optical frequencies)
Local surface plasmon resonances -LSPRs

$$\epsilon = \varepsilon(\infty) - \frac{\omega_p^2}{\omega(\omega + i\gamma)},$$

2. Heterogeneous systems interacting with electromagnetic fields: Calculation methods

Calculation methods for LSPRs

- discrete-dipole approximation (DDA).[1]
- finite-difference time domain (FDTD).[2]
- hybridization model (HB).[3]
- operator method (quasistatic limit)[4] related to HB[5]

[1] B. T. Draine and P. J. Flatau, J. Opt. Soc. Am. A, **11** (1994) 1491.

[2] C. Oubre and P. Nordlander J. Phys. Chem. B **108** (2004) 17740.

[3] E. Prodan, *et al.* Science, **302** (2003) 419.

[4] D. R. Fredkin and I. D. Mayergoyz, Phys. Rev. Lett. **91** (2003) 253902.

[5] T. J. Davis *et al.* Nanoletters **10** 2618 (2010); T Sandu *et al.* Plasmonics 6, 407, (2011)

Calculation methods for dielectric response of living cells

- finite difference method (FDM) [1]
- finite element method (FEM) [2]
- boundary element method (BEM)[3]
- and boundary integral equation (BIE) [4,5]

[1] K. Asami, J. Phys. D. 39, 492 (2006), E. Tuncer et al, IEEE Trans. Dielectr. Electr. Insul., 9, 809 (2002).

[2] E.C. Fear, M.A. Stuchly, IEEE Trans. Biomed. Eng. 45, 1259 (1998).

[3] K. Sekine, Bioelectrochemistry 52, 1 (2000).

[4] M. Sancho et al., J. Electrostat., 57, 143 (2003).

[5]. T Sandu et al., Phys. Rev E, 81, 021913 (2010).

In the quasistatic limit both phenomena can be described by the same formalism

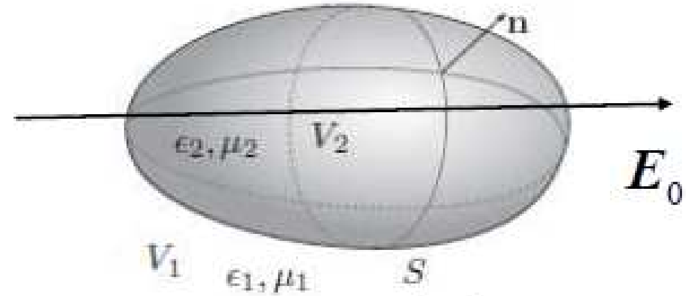
2. Heterogeneous systems interacting with electromagnetic fields: Calculation methods

Boundary Integral Equation Method (BIE): quasistatic

$$\Delta\Phi(\boldsymbol{x}) = 0;\ \boldsymbol{x} \in \Re^3 \setminus S$$

$$\epsilon_0 \frac{\partial\Phi}{\partial \boldsymbol{n}}\Big|_+ = \epsilon_1 \frac{\partial\Phi}{\partial \boldsymbol{n}}\Big|_- ;\ \boldsymbol{x} \in S$$

$$-\nabla\Phi(\boldsymbol{x}) \to \boldsymbol{E}_0,\ |\boldsymbol{x}| \to \infty$$



Σ

Solution in terms of a single-layer potential:

$$\Phi(\boldsymbol{x}) = -\boldsymbol{x}\boldsymbol{E}_0 + \frac{1}{4\pi}\int_{y\in S} \frac{u(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} dS_y.$$

$$\frac{1}{2\lambda} u(\boldsymbol{x}) - \hat{M}[u] = \boldsymbol{n}\boldsymbol{E}_0$$

$$\hat{M}[u] = \frac{1}{4\pi}\int_{y\in S} \frac{u(\boldsymbol{y})\mathrm{n}_x(\boldsymbol{x}-\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|^3} dS_y$$

$$\hat{M}^\dagger[v] = \frac{1}{4\pi}\int_{y\in S} \frac{v(\boldsymbol{y})\mathrm{n}_y(\boldsymbol{x}-\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|^3} dS_y$$

$$u = \sum_k \frac{n_k E_0}{\frac{1}{2\lambda} - \chi_k} \qquad \lambda = \frac{\epsilon_1 - \epsilon_0}{\epsilon_1 + \epsilon_0}$$

$$\hat{S}[u] = \frac{1}{4\pi}\int_{y\in S} \frac{u(\boldsymbol{y})}{|\boldsymbol{x}-\boldsymbol{y}|} dS_y$$

$$v_k = \hat{S}u_k$$

D. R. Fredkin, I. D. Mayergoyz, Phys. Rev. Lett. 91 (2003) 253902;
T. Sandu et al.Phys. Rev. E 81 (2010) 021913; Plasmonics 6 (2011) 407

(T. Sandu, Plasmonics,8,391, 2013)

eigenvectors of M and $M^\dagger$ $\quad \langle v_i | u_j \rangle = \delta_{ij}$

2. Heterogeneous systems interacting with electromagnetic fields: Calculation methods

Polarization Charge: $$u=\sum_k \frac{n_k E_0}{\frac{1}{2\lambda}-\chi_k}$$

T Sandu *et al.* Phys. Rev. E 81 (2010) 021913.

Eigenmode decomposition of:

(a) Specific polarizabiliy-imaginary part is proportional to the extinction spectrum:

$$\alpha=\sum_k \frac{p_k}{\frac{1}{2\lambda}-\chi_k}$$

Drude metals: $\epsilon=\varepsilon_m-\frac{\omega_p^2}{\omega(\omega+i\gamma)}$,

$$\alpha_{plasmon}(\omega)=\sum_k \frac{p_k(\varepsilon_m-\varepsilon_{do})}{\varepsilon_{eff\_k}}-\frac{p_k}{1/2-\chi_k}\frac{\varepsilon_{do}}{\varepsilon_{eff\_k}}\frac{\tilde{\omega}_{pk}^2}{\omega(\omega+i\gamma)-\tilde{\omega}_{pk}^2}$$

$$C_{ext}=\frac{2\pi}{\lambda}\mathrm{Im}(\alpha V)$$

(T Sandu *et al.* Plasmonics 6 (2011) 407)

(b) Near-field Enhancement-tangential and normal components:

$$E_n(\xi_1,\xi_2)=\left(\hat{M}+1/2\right)u=\sum_k \frac{n_k(\chi_k+1/2)}{\frac{1}{2\lambda}-\chi_k}u_k(\xi_1,\xi_2)$$

(T. Sandu, Plasmonics, 8,(2013), 391)

$$E_t(\xi_1,\xi_2)=-\sum_k \frac{n_k}{\frac{1}{2\lambda}-\chi_k}\left[\frac{1}{h_{\xi_1}}\frac{\partial v_k(\xi_1,\xi_2)}{\partial \xi_1}t_{\xi_1}+\frac{1}{h_{\xi_2}}\frac{\partial v_k(\xi_1,\xi_2)}{\partial \xi_2}t_{\xi_2}\right]$$

$$\tilde{\omega}_{pk}^2=\frac{(1/2-\chi_k)\omega_p^2}{\varepsilon_{eff\_k}}$$

$$\varepsilon_{eff\_k}=(1/2+\chi_k)\varepsilon_{do}+(1/2-\chi_k)\varepsilon_m$$

3. Polaritons: plasmons, phonons

Elementary excitations:

•Plasmons

•Phonons

•Excitons(e-h pairs)

Polaritons: coupled states between elementary excitations and photons.
Plasmon polaritons (visible).
Phonon polaritons (deep infrared).

3. Polaritons: plasmons, phonons

Plasmon polaritons

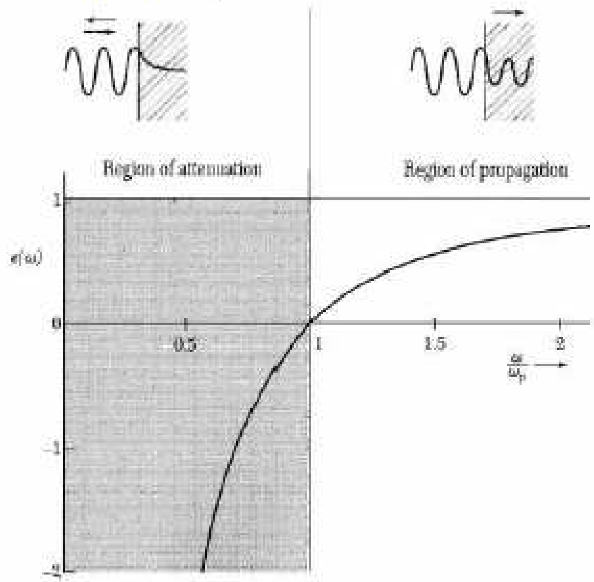
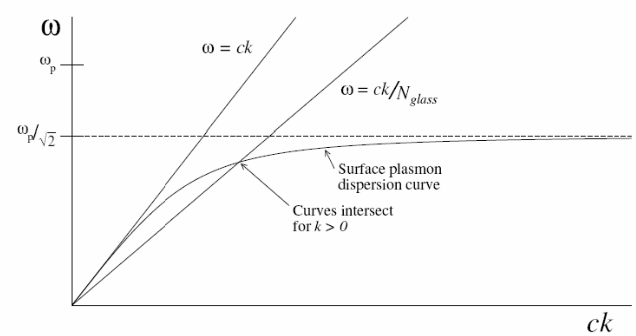


Figure 1 Dielectric function ε(ω) or ε(ω, 0) of a free-electron gas versus frequency in units of the plasma frequency ω_p. Electromagnetic waves propagate without damping only when ε is positive and real. Electromagnetic waves are totally reflected from the medium when ε is negative.

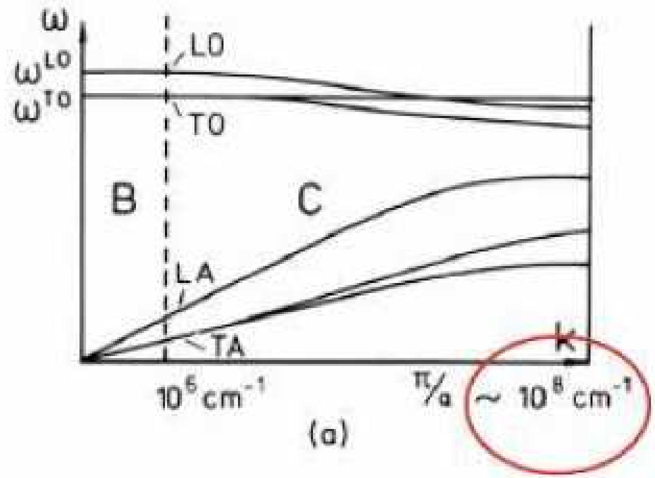


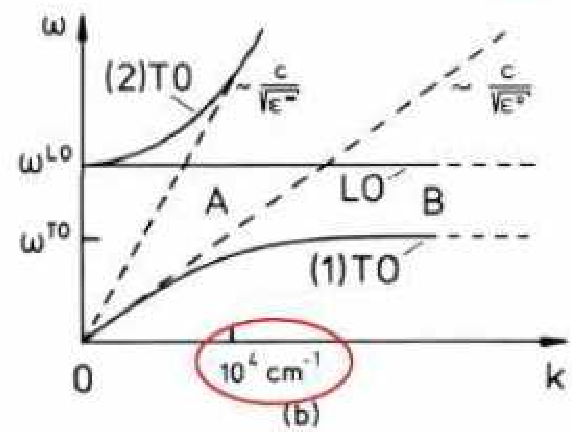
$$\tilde{\omega}_{pk}^2 = \frac{(1/2 - \chi_k)\,\omega_p^2}{\varepsilon_{eff\_k}}$$

ck

Phonon polaritons (deep infrared).

ELECTROMAGNETIC SURFACE MODES

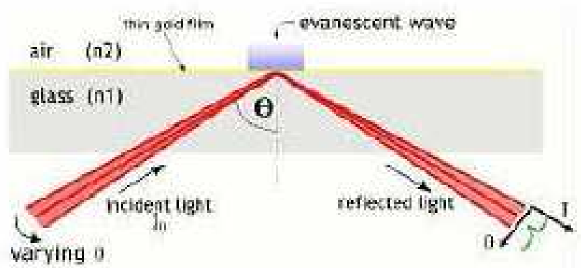




4. Localized Surface Plasmon Resonances (LSPRs)

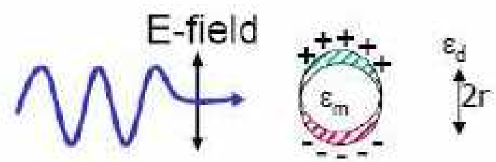
Propagating and localized plasmons: strong field localization at the interface

propagating



$$k_{sp} = k\left(\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}\right)^{1/2} = \frac{\omega}{c}\sqrt{\varepsilon_d}\,\sin\theta$$

localized



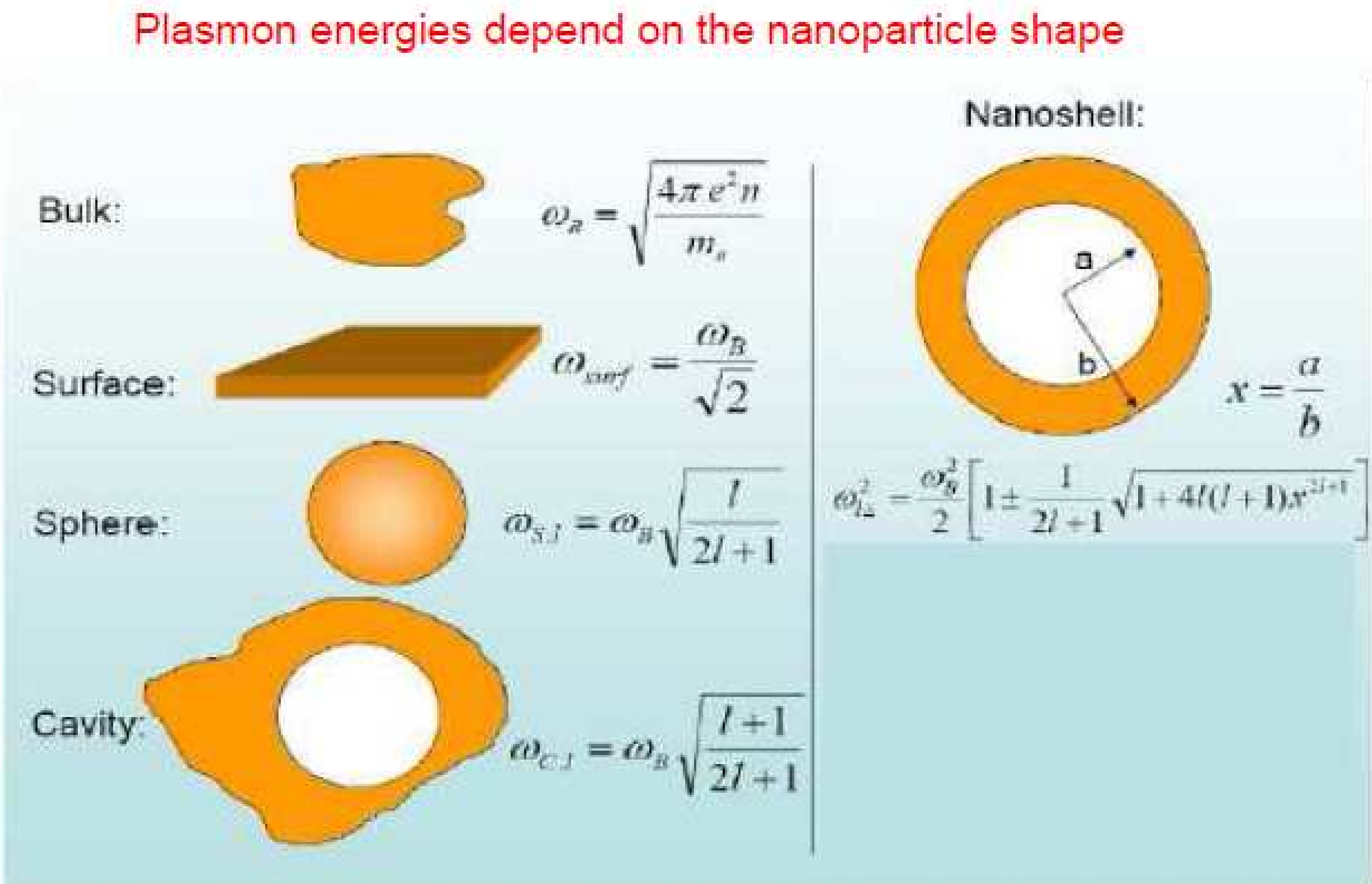
$$\omega_{res} = \frac{\omega_p}{\sqrt{3}}$$ Resonant frequency (geometry considerations)

Localized surface plasmon resonances (LSPRs)

In both cases resonance depends on dielectric permittivity

$$\tilde{\omega}_{pk}^2 = \frac{(1/2 - \chi_k)\,\omega_p^2}{\varepsilon_{eff\_k}}$$

4. Localized Surface Plasmon Resonances (LSPRs)



5. Application of LSPRs

•LSPRs for Nanoscale Imaging and Spectroscopy

Scattering-Based Microscopy-Near-field scanning optical microscopy (NSOM/SNOM)

•*Spectroscopy Based on Local Field Enhancement*

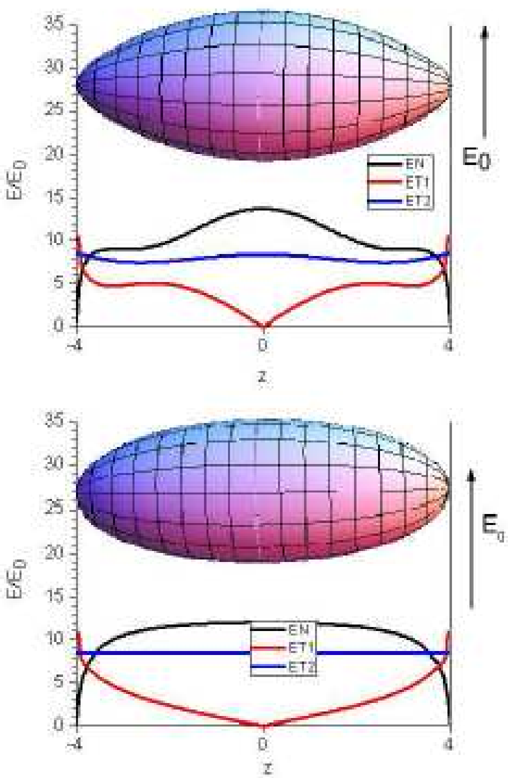
LSPR-enhanced fluorescence, LSPR-enhanced Raman scattering

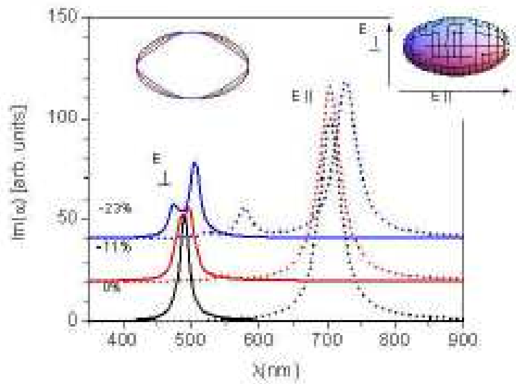
•LSPRs for Photovoltaics

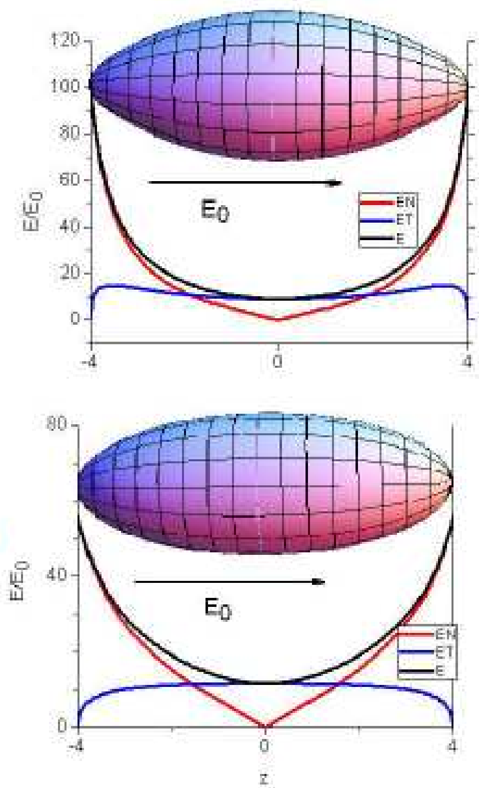
•LSPRs for Light Emission -OLEDs

5. Application of LSPRs

Calculation of the shape-dependent near-fields and far-fields in Localized Surface Plasmon Resonances of metallic Nanoparticles







Shape variations may induce large changes of both the near-field enhancement and the far-field extinction spectrum.

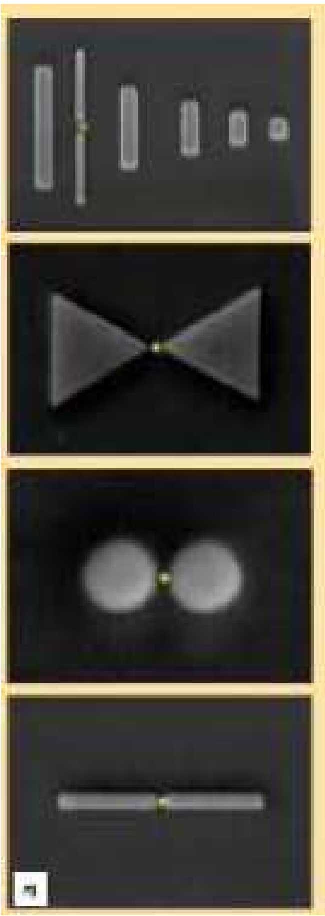
T. Sandu, J. Nanopart. Research, 14, 905 2012
T. Sandu, G. Boldeiu, Digest J. NanoMater. & Biostr., 9, 1255, 2014

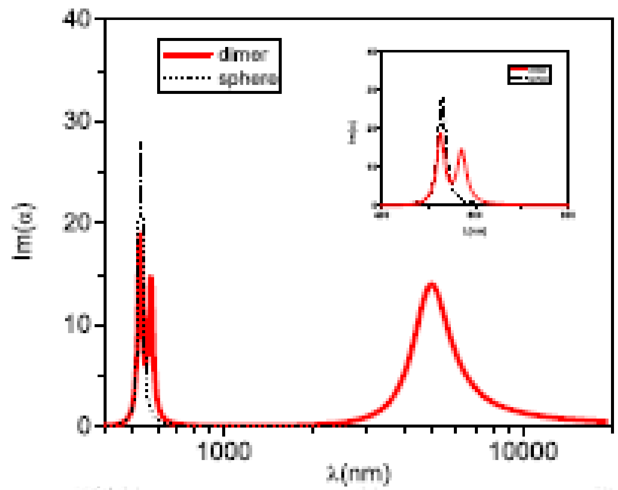
5. Application of LSPRs

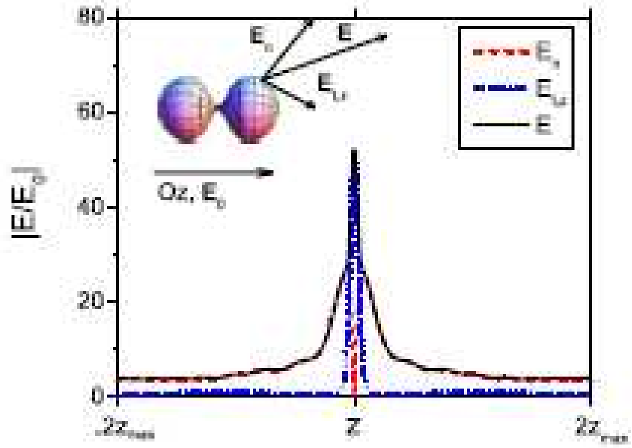
Hot spots in plasmonic structures

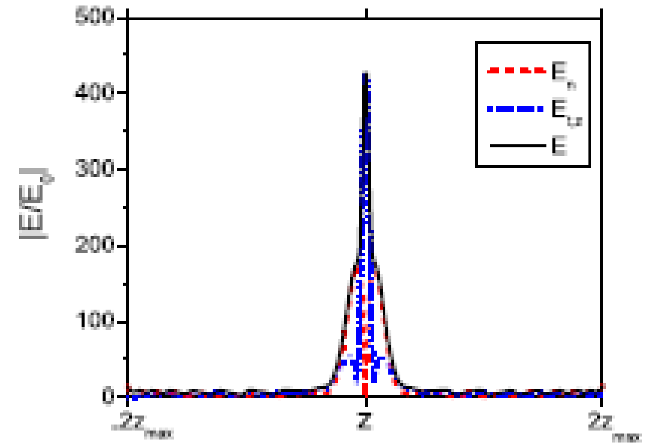
Touching dimers

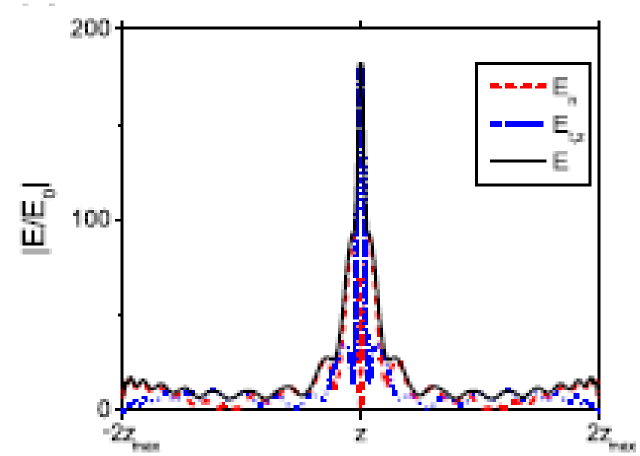
(T. Sandu, Plasmonics,8,391, 2013)











5. Application of LSPRs

Antennas in Plasmonics: Nanoantennas

•Optical antenna: a device designed to efficiently convert free-propagating optical radiation to localized energy, and vice versa. P. Bharadwaj et al., Advances in Optics and Photonics 1, (2009) 438.

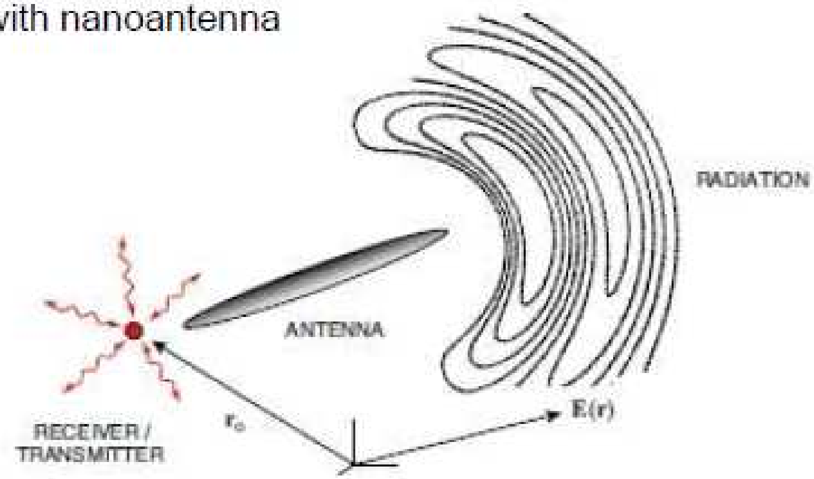
•Skin depth negligible in *rf* but comparable with nanoantenna at optical frequencies.

•The antenna geometry scales differently in visible:

$\lambda_{eff}/2$ Instead of $\lambda/2$

L. Novotny, Phys. Rev. Lett. 98, (2007) 266802.

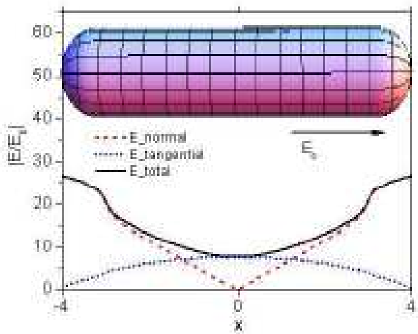
$$\lambda_{eff} = n_1 + n_2\left[\frac{\lambda}{\lambda_p}\right]$$



A receiver/transmiter interacting with free optical waves through optical antenna

5. Application of LSPRs

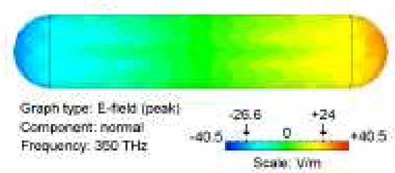
Electrostatic results



Fully Retarded Results-CST

Aspect ratio 4/1, Rod length 100 nm

Longitudinal enhancement



Tangential enhancement

Nanorod Antenna-some results

$$\lambda_{eff} = n_1 + n_2\left[\frac{\lambda}{\lambda_p}\right] \qquad \lambda_{res} = a + bL$$

$$\frac{1}{\sqrt{1/2-\chi_x}} = n + m\frac{L}{d}$$

L. Novotny, Phys. Rev. Lett. 98, (2007) 266802.

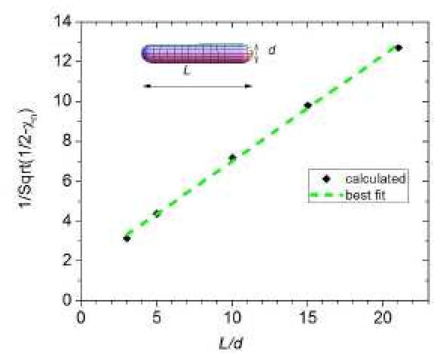


Fig. 1. The scaling law of nanoantenna in the electrostatic limit. The symbols represent the numerical results, while the green dashed line is the best linear fit to numerical calculations. The inset shows the rod antenna and its dimensions.

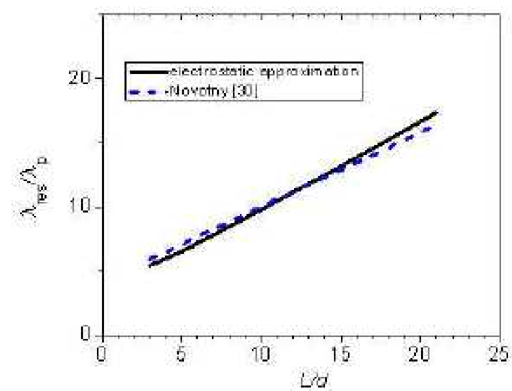


Fig. 2. The ratio of plasmon resonance wavelength and plasma wavelength of the bulk metal with the electrostatic scaling (black solid line) and with the scaling given by Novotny [30].

T. Sandu, Proc. Rom. Acad, Series A, 15(4), 338, 2014
T. Sandu, V Buiculescu, IEEE CAS, 2012

6. Interaction of living cells with (rf) electromagnetic fields

Advantages: Non-invasive and in situ characterization of biological samples

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon + \frac{\kappa}{j\varepsilon_0\omega},$$

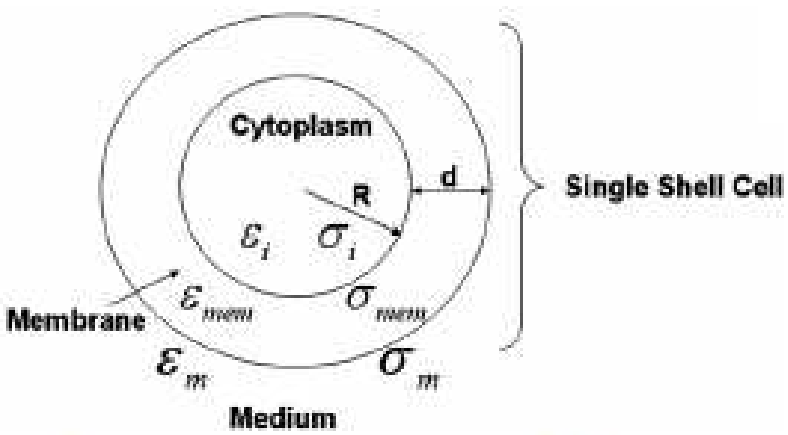
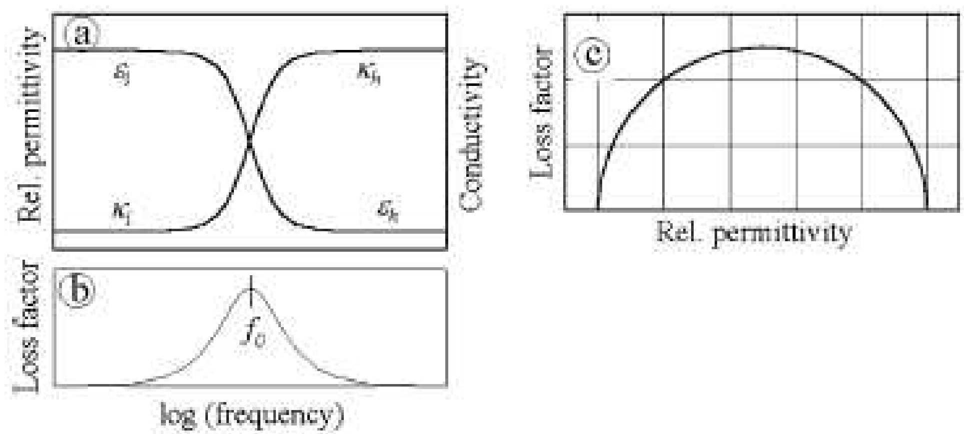


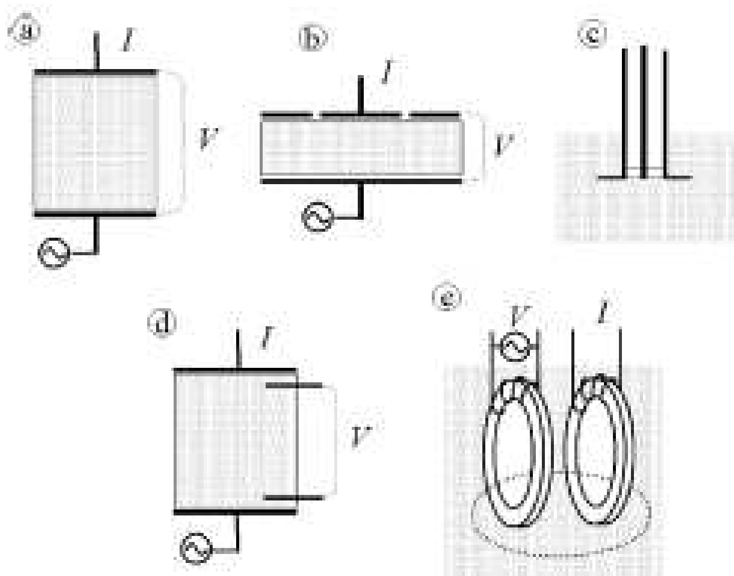
Figure 1. Schematic diagram of a single shelled spherical particle in a homogeneous suspending medium.



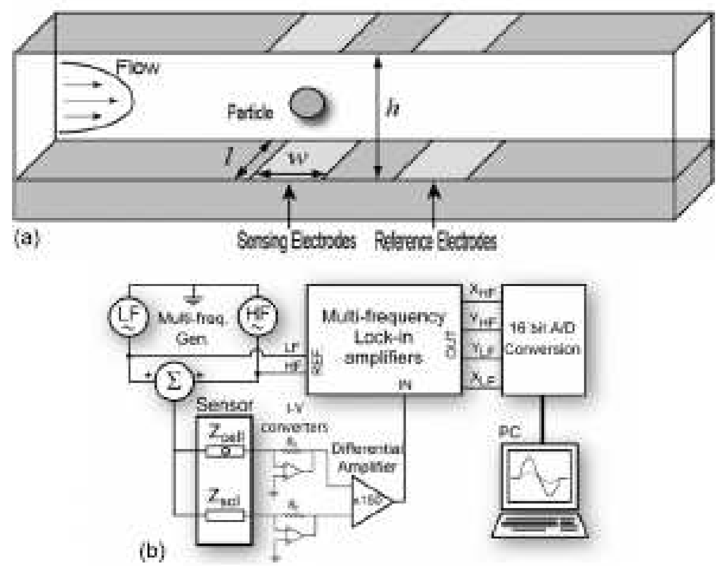
Ideal Debye relaxation

6. Interaction of living cells with (rf) electromagnetic fields

Measurements: in suspension or single cell

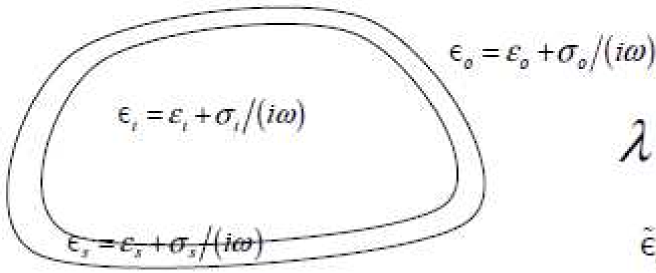


Some measurement setups for suspensions



Single cells dielectric spectroscopy
In microfluidic channel
J.Phys. D Appl. Phys. 40, p. 61, 2007

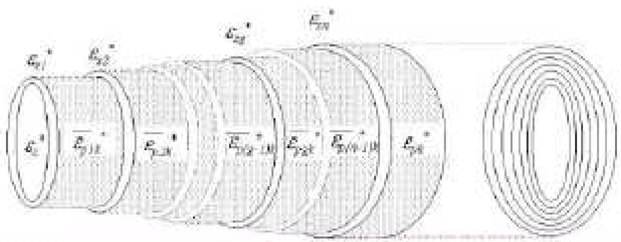
6. Interaction of living cells with (rf) electromagnetic fields



Shelled particles

$$\lambda \to \lambda_k = (\tilde{\epsilon}_k - \epsilon_0)/(\tilde{\epsilon}_k + \epsilon_0)$$

$$\tilde{\epsilon}_k = \epsilon_S \left(1 + \frac{\epsilon_1 - \epsilon_S}{\epsilon_S + \delta(1/2 - \chi_k)\epsilon_1 + \delta(1/2 + \chi_k)\epsilon_S} \right),$$



Homogenization:

- at a single cell level
- for suspension

K. Asami / Prog. Polym. Sci. 27 (2002) 1617–1659

$$\alpha = \sum_k \frac{p_k}{\frac{1}{2\lambda_k} - \chi_k} \qquad \epsilon_{sus} = \epsilon_0 + f\frac{\alpha\epsilon_0}{1 - f\alpha/3},$$

$$\epsilon_{sus} = \epsilon_0 \left(1 + f\sum_k p_k \frac{\tilde{\epsilon}_k - \epsilon_0}{(1/2 + \chi_k)\epsilon_0 + (1/2 - \chi_k)\tilde{\epsilon}_k} \right).$$

Effective complex permittivity of a biological cell or metallic NP suspension

6. Interaction of living cells with (rf) electromagnetic fields

Maxwell-Wagner relaxation of a suspension of biological cells with *n* shells

Each medium has the permittivity $\epsilon_i = \varepsilon_i + \sigma_i / i\omega$

Generally, the Maxwell-Wagner relaxations have a Debye-type form

$$\epsilon = \varepsilon_\infty + \sigma_0 / i\omega + \Delta\varepsilon / (1 + i\omega T)$$

intensity of dielectric relaxation

Relaxation time

- A suspension of living cells with *n* shells has a Debye-type effective permittivity containing (*n+1*) relaxation times for each bright/active eigenmode

$$\epsilon_{sus} = \epsilon_f + \sum_{k,j} \Delta\varepsilon_{kj} / (1 + i\omega T_{kj})$$

Hanai, H. Z. Zhang, K. Sekine, K. Asaka, and K. Asami, Ferroelectrics 86, 191 (1988).

It is possible to express relationships between electric and shape parameters of the cells and the Debye parameters, even though the algebraic equations are quite sophisticated.

6. Interaction of living cells with (rf) electromagnetic fields

Living cell with a non-conductive membrane

First relaxation-relaxation time

$$T_{k1} \approx \frac{\varepsilon_S}{\delta \cdot \sigma_1 (1/2 - \chi_k)}$$

intensity of dielectric relaxation

$$\Delta\varepsilon_{k1} \approx \frac{f \cdot p_k \cdot \varepsilon_S}{\delta (1/2 - \chi_k)(1/2 - \chi_k)^2}$$

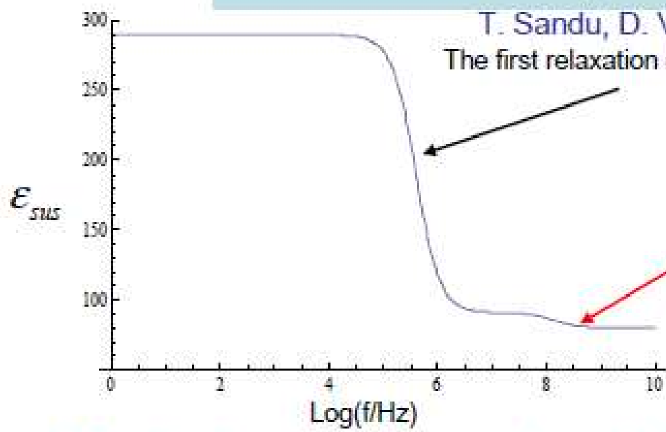
2nd relaxation-relax. time

$$T_{k2} \approx \frac{(1/2+\chi_k)\varepsilon_0 + (1/2-\chi_k)\varepsilon_1}{(1/2+\chi_k)\sigma_0 + (1/2-\chi_k)\sigma_1}$$

intensity of dielectric relaxation

$$\Delta\varepsilon_{k2} \approx f \cdot p_k (1/2-\chi_k) \frac{(\varepsilon_1\sigma_0 - \varepsilon_0\sigma_1)^2}{\left((1/2+\chi_k)\varepsilon_0 + (1/2-\chi_k)\varepsilon_1\right)\left((1/2+\chi_k)\sigma_0 + (1/2-\chi_k)\sigma_1\right)^2}$$

T. Sandu, D. Vrinceanu and E. Gheorghiu, Phys. Rev. E **81**, 021913 (2010).



The first relaxation due to the membrane

2nd relaxation due to the mismatch of electric properties inside vs. outside

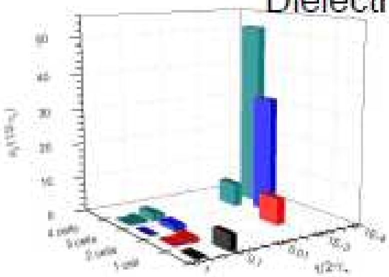
$$\sigma_o \ll \sigma_1$$

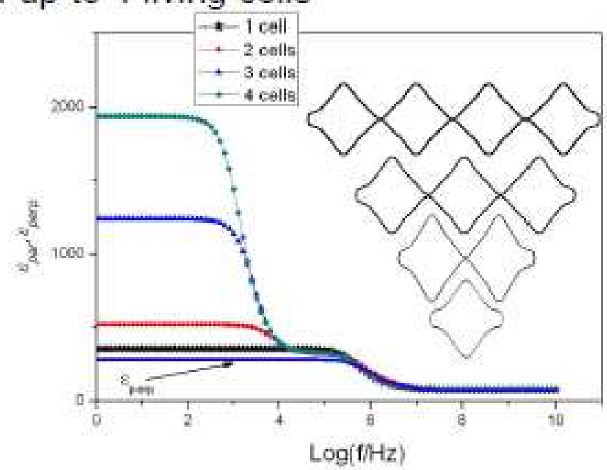
K. Asami, J. Phys. D 39, 492 , (2006).

Different active eigenmodes cannot provide distinct relaxations (large width of each relaxation), UNLESS.....

6. Interaction of living cells with (rf) electromagnetic fields

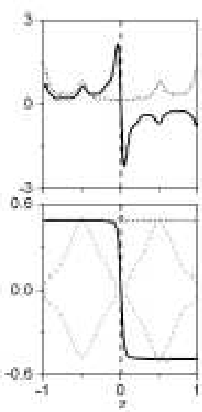
Dielectric behavior of linear clusters of up to 4 living cells





$$p_k/(1/2-\chi_k) \propto \Delta\varepsilon_k$$

$$(1/2-\chi_k) \propto \omega_k : relaxation\ frequency$$



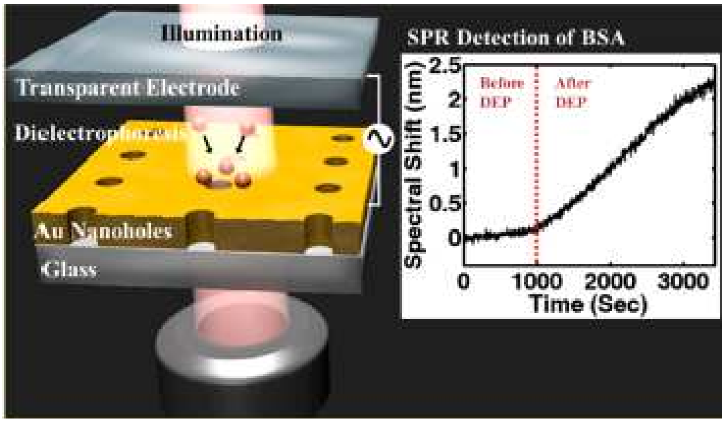
Conjecture: In general, a linear cluster having *m* celule has *m-1* eigenvalues close to ½ ,
And the 2[nd] has the largest contribution to the cell polarization and the effective permittivity.

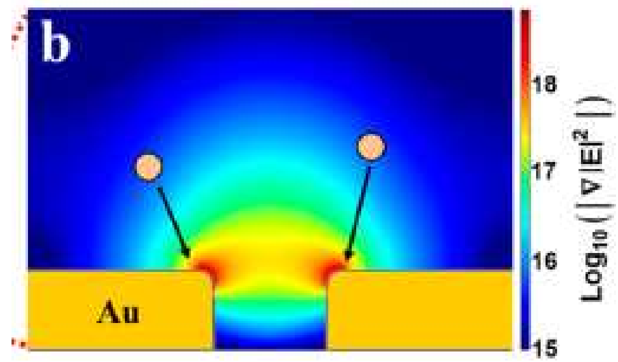
I. Romero, J. Aizpurua, G. W. Bryant, and F. J. Garcia de Abajo, Optics Express 14, 9988 (2006)

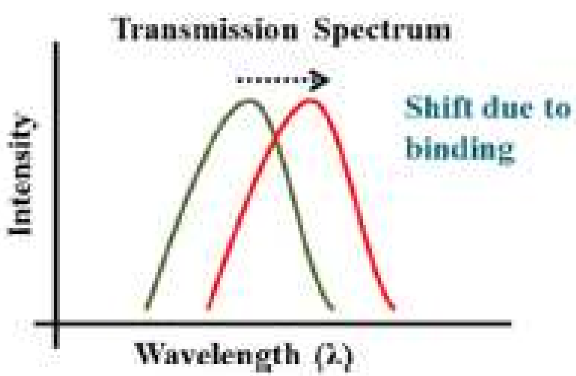
T. Sandu, D. Vrinceanu and E. Gheorghiu, Phys. Rev. E **81**, 021913 (2010).

7. Coupling *rf* response to optical response

Dielectrophoresis-Enhanced Plasmonic Sensing with Gold Nanohole Arrays
A. Barik et al., Nano Lett. 2014, **14**, 2006−2012







$$\vec{F}_{DEP}(\omega) = \pi\varepsilon_m R^3 \cdot \mathrm{Re}(f_{CM}(\omega))\nabla|E|^2$$

8. Conclusions

- Electromagnetic related phenomena in some heterogeneous systems can be unitarily described with the same operator method

- The operator method allows eigenmode decomposition of polarizability for living cells, semiconductor and metallic NPs.

- Oscillator strengths and relaxation intensities depend on shape as $\sim p_k/(1/2-\chi_k)$

- Direct calculation of resonances and field enhancement for localized plasmon/phonon polaritons.

- Direct calculation of Debye parameters for living cells.

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