Nonlinear optics

(the Z-Scan technique)

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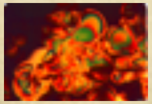

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INCT-FCx (CNPq, FAPESP, CAPES, MCTI)

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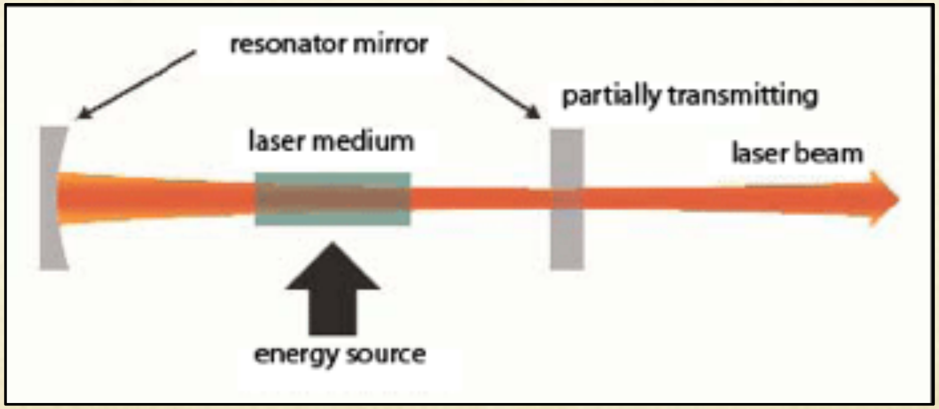
Nonlinear optics

- 1960 ⇨ Maiman obtained a coherent light source of big intensity throughout the stimulated emission in a Rubi crystal.

- LASER (Light Amplification by Stimulated Emission of Radiation).

- Intense light beam with coherence length >> thermal sources.



http://www.fascination-of-light.net/campaign/exhibition/the-laser

- P.A. Franken et al. PRL (1961)

rubi laser (694.2 nm) →  → UV (347.1 nm)

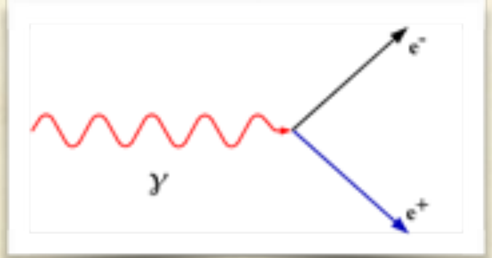
quartz crystal

$$E = 1kV/cm \quad \Leftrightarrow \quad I = 2.5kW/cm^2$$

Second Harmonic Generation

- All the media are nonlinear, even the vacuum!

→ photons interact trough vacuum polarisation



- This high intensity allows to obtain high electric fields to interact with matter, that was possible only in static experiments, far from the VIS or IR spectral region.

- The nonlinear optical effects are those where the electric field of the wave is so intense that promotes a modification in the medium.

- Changes in the optical properties of the medium: index of refraction, absorption coefficient.

- The light that promoted changes in the properties of the medium also has its propagation affected in a nonlinear manner.

- Nonlinear optical process occurs in two steps:
- The presence of a high intensity light in the medium induces a nonlinear polarisation on it that also modifies the optical fields in a nonlinear manner.

- 1st part of the process ⇨ constitutive equations

$$\vec{D} = \vec{D}(\vec{E}, \vec{B}) \qquad \vec{H} = \vec{H}(\vec{E}, \vec{B})$$

- 2nd part of the process ⇨ Maxwell's equations

$$\vec{\nabla}.\vec{D} = \rho_{free} \qquad \vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

$$\vec{\nabla}.\vec{B} = 0 \qquad \vec{\nabla} \times \vec{H} = \vec{J}_{free} + \frac{\partial \vec{D}}{\partial t}$$

- Most of the nonlinear effects ⇨ classical electromagnetic theory, with nonlinear susceptibilities included in the constitutive equations.

- The electric polarisation.

$$\vec{P}(\vec{E}) = \chi(\vec{E})\vec{E}$$

- When the light propagates through a transparent medium the oscillating electromagnetic field exerts a force on the electrons.

- When the light intensity is high in a way that the radiation field is comparable with the interatomic fields, the electrical charges behave as anharmonic oscillators and the induced polarisation depends on the field strength.

$$\frac{d^2x}{dt^2} + \gamma\frac{dx}{dt} + \omega_0^2 x + \alpha x^2 = F$$

- The electric polarisation

$$P^{Total}(\omega) = \chi^{(1)}(\omega)E(\omega) + 2\chi^{(2)}(\omega)E(\omega)E(\omega) + 3\chi^{(3)}(\omega)\left|E(\omega)^{2}\right|E(\omega) + \ldots$$

- $\chi^{(1)}$ is the linear susceptibility, $\chi^{(2)}$, $\chi^{(3)}$,..., $\chi^{(n)}$, are the different susceptibilities of different orders, being determined by the symmetry properties of the medium.

- This is valid for transparent medium where the nonlinear optical response is small.

- The most intense process is related to ⇨ $\chi^{(2)}$.

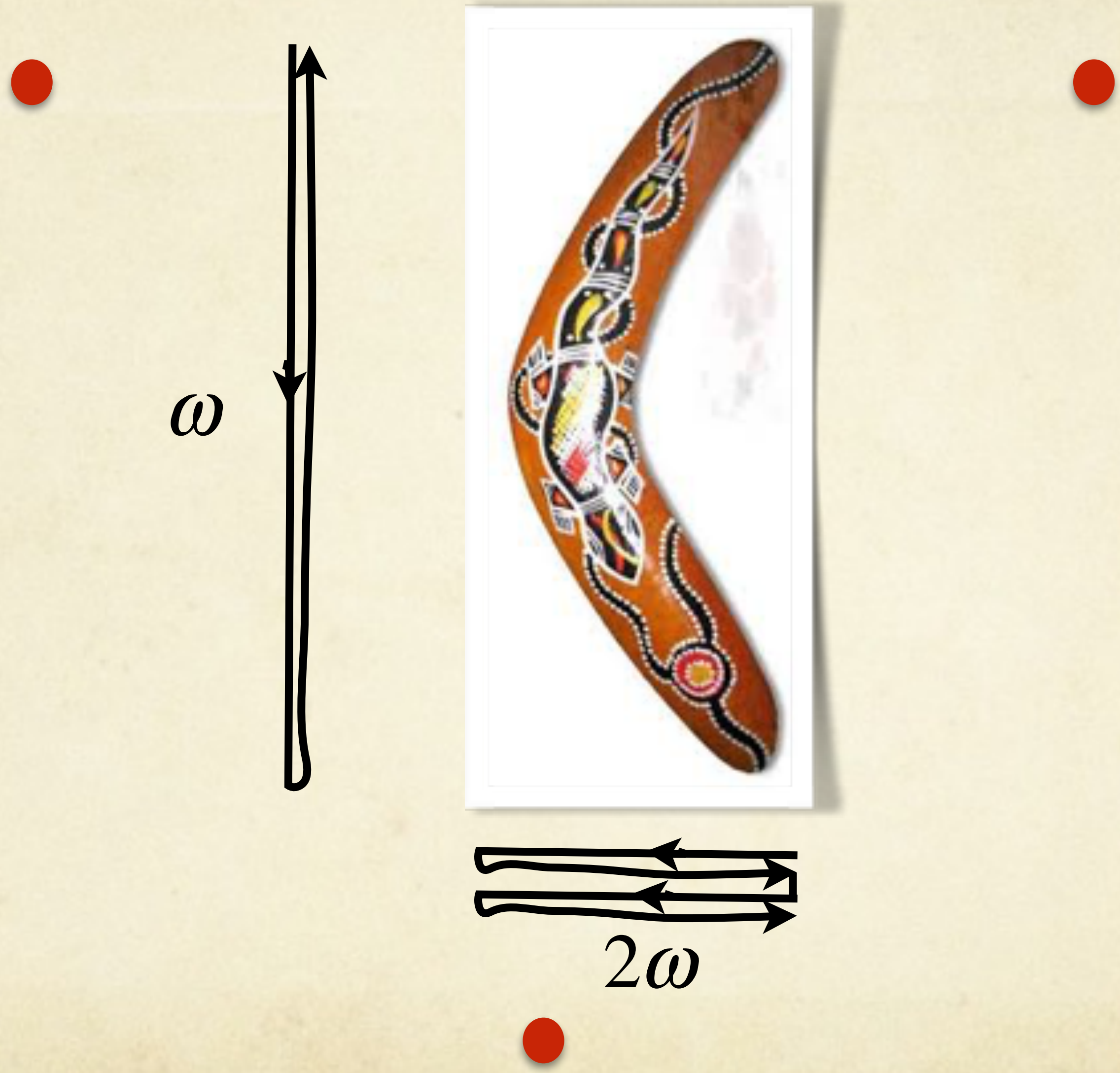
- Second-Harmonic Generation (SHG) ⇨ the light of frequency **ω** is doubled (2**ω**) after the nonlinear medium.

- Occurs in media without inversion symmetry.

- Media with inversion symmetry, the most important nonlinearity is the third-order.

- It is responsible for the changes in the media refractive index.

Medium without inversion symmetry



- Media with $\chi^{(2)} = 0$, the nonlinear polarisation is

$$P^{NL}(\omega) = 3\chi^{(3)}(\omega)\left|E(\omega)^2\right|E(\omega)$$

- The total polarisation is written as

$$P^{Total}(\omega) = \chi^{(1)}(\omega)E(\omega) + 3\chi^{(3)}(\omega)\left|E(\omega)^2\right|E(\omega)$$

- The electrical susceptibility of the material

$$\chi_{eff}(\omega) = \chi^{(1)}(\omega) + 3\chi^{(3)}(\omega)\left|E(\omega)^2\right|$$

- The nonlinear polarisation component corresponds to a small increment in the susceptibility $\Delta\chi$, given by

$$\varepsilon_0 \Delta\chi = \frac{P^{NL}}{E(\omega)} = 3\chi^{(3)} \left| E(\omega)^2 \right| = \frac{6\chi^{(3)}}{n_0 \varepsilon_0 c} I$$

- Intensity of the incident wave

$$I = \frac{\left| E(\omega)^2 \right|}{2} n_0 c \varepsilon_0$$

- As $$n = \sqrt{1 + \chi_{eff}}$$

$$n = \sqrt{1 + \chi_{eff}} \qquad\qquad n_0 = \sqrt{1 + \chi^{(1)}}$$

- $\Delta\chi \longrightarrow \Delta n$

$$\Delta n = \frac{3\chi^{(3)}}{n_0^2 \varepsilon_0^2 c} I = n_2 I$$

- n_2 is the nonlinear refractive index.
- The modification of the refractive index is proportional to the light intensity.

$$n(I) = n_0 + n_2 I$$

- **Optical Kerr effect**

- **Different processes may cause changes in the refractive index due to the light intensity.**

Mechanism	n_2 (cm^2/W)	$\chi^{(3)}$(esu)	Response time (s)
Electronic polarization	10^{-16}	10^{-14}	10^{-15}
Molecular reorientation	10^{-14}	10^{-12}	10^{-12}
Electrostriction	10^{-14}	10^{-12}	10^{-9}
Saturated atomic absorption	10^{-10}	10^{-18}	10^{-8}
Thermal effects	10^{-6}	10^{-4}	10^{-3}

Soret effect ⟷ 1

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Self-focusing

- Phase self-modulation ⇨ self-focusing / self-defocusing.

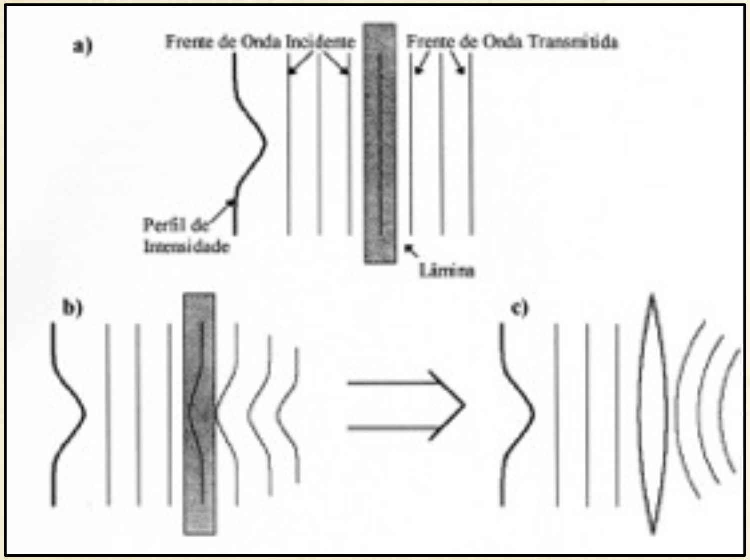
- Intense laser beam transmitted across a nonlinear thin-film sample which exhibts the optical Kerr effect ⇨ the index of refraction changes according to the intensity profile, in the plane perpendicular to the beam.

- Kerr effect

$$n = n_0 + n_2 I$$

- The dependence of the refractive index with the intensity is the responsible for the self-focusing of the beam if the beam has a nonuniform intensity profile.

Self-focusing



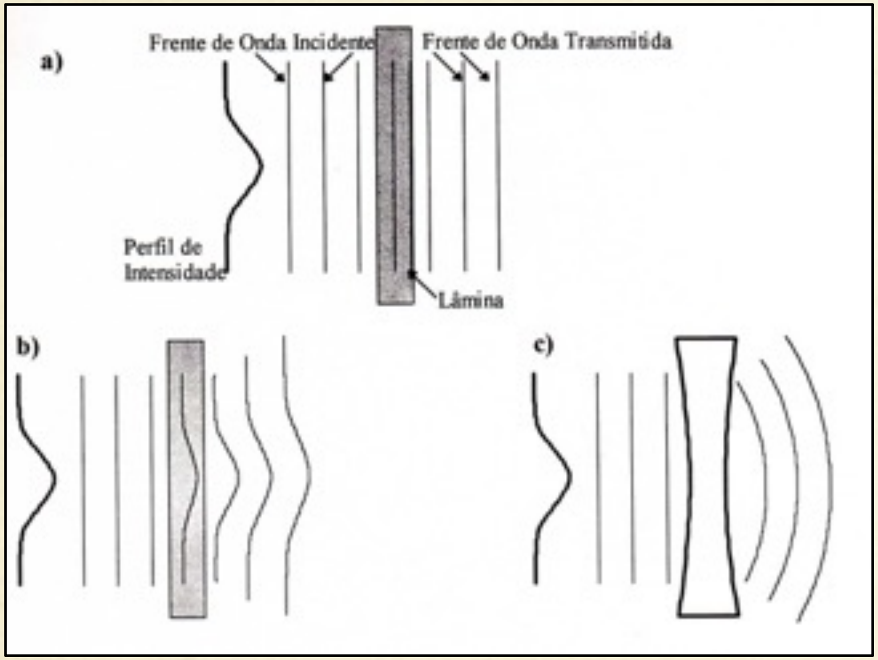
- Self-focusing of a Gaussian beam:

a) Transmission of the Gaussian laser beam through a "linear material".

b) Transmission of the Gaussian laser beam through a nonlinear material, where the refractive index increases with the intensity.

c) The increase of the optical path is equivalent of that from a convergent lens.

Self-defocusing



- Self-defocusing of a Gaussian beam:

a) Transmission of the Gaussian laser beam through a “linear material”.

b) Transmission of the Gaussian laser beam through a nonlinear material, where the refractive index decreases with the intensity.

c) The increase of the optical path is equivalent of that from a divergent lens.

The Z-Scan technique

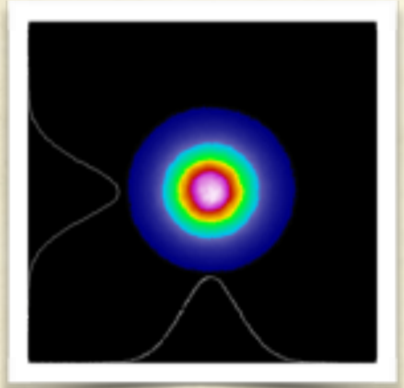
- In 1989 Sheik-Bahae and col. developed a method to measure the sign and magnitude of the nonlinear index of refraction and absorption as a function of the third-order susceptibility.

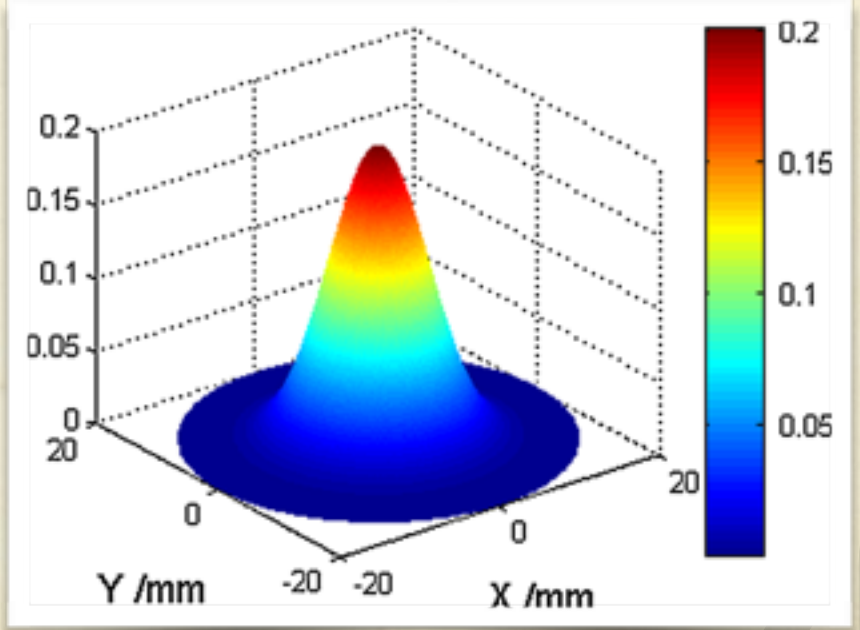
- This technique is named Z-Scan and is based on the principles of spatial distortion of the beam. Is simple and very sensitive.

- Allows to determine the nonlinear refractive index from the measurement of the transmittance through a thin sample.

The Gaussian beam

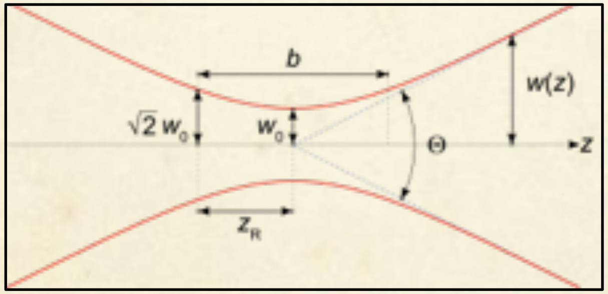
- Pulsed or cw.



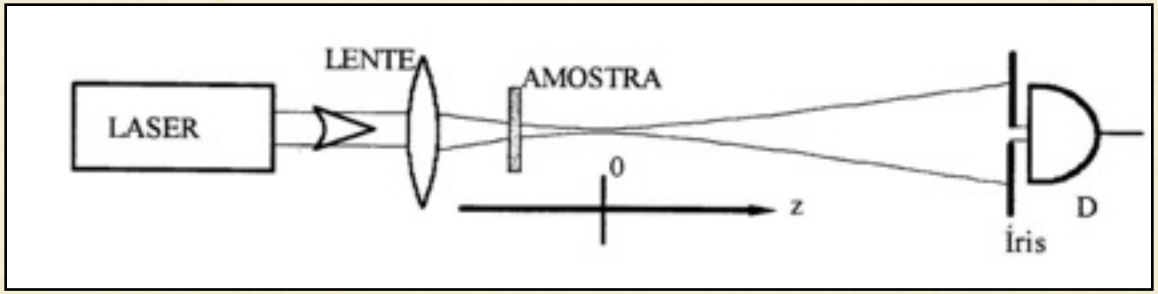


The Z-Scan

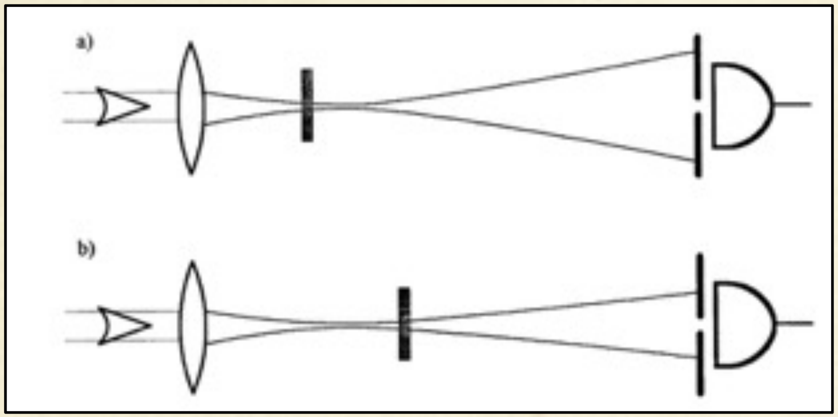
- A convergent lens is placed in the way of the Gaussian beam, that will reach a minimum waist af the focus position. There, the beam intensity is maximum. After that point the beam will diverge as a function of z.

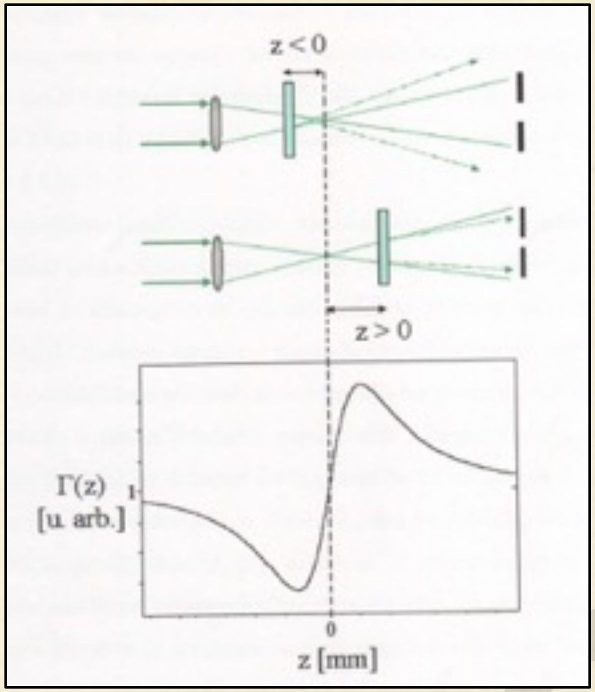


- The transmittance is measured with a photodetector. An iris is placed in the front of the detector.
- The sample is moved along the z-axis and is subjected to different light intensities.

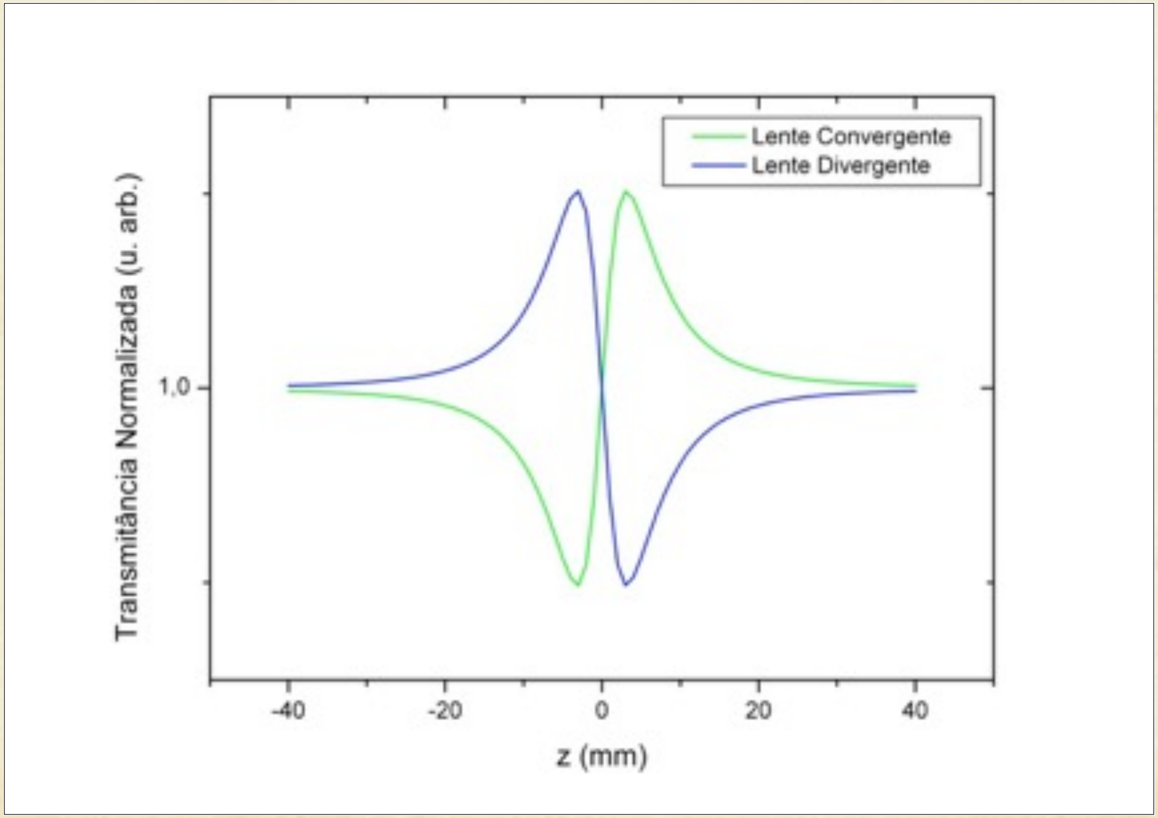


- Kerr-type medium with nonlinear refractive index, $n_2 > 0$.





Characteristic Z-Scan curve



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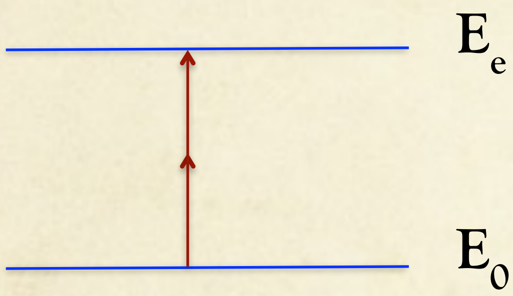
Models

- Electronic effects
  - Response time ~ 10^{-15} s
  - Sheik- Bahae model
    - $n = n_0 + n_2 I$
- Thermal effects
  - Response time ~ 10^{-3} s
  - Thermal Lens model
    - $n = n_0 + (dn/dT)\Delta T$
- Thermodiffusion (Soret effect)
  - Response time ~ seconds
  - Generalised Thermal Lens model
    - $n = n_0 + n_2 I + (dn/dT)\Delta T + (dn/d\Phi)\Delta \Phi$

Nonlinear absorption

Two-fotons absorption (TPA)



$$E_e - E_0 = 2\,\hbar\omega$$

$$\alpha = \alpha_0 + \beta I$$

Free-carrier absorption (FCA)

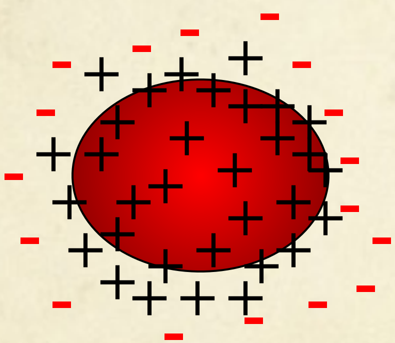
$$E_g < \hbar\omega$$

$$\alpha = \alpha_0 + \sigma N$$

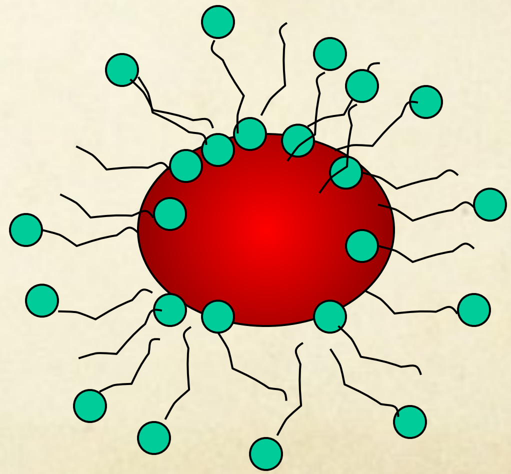
Bulk material
X
nanoparticle
Ferrofluid

Ferrofluids

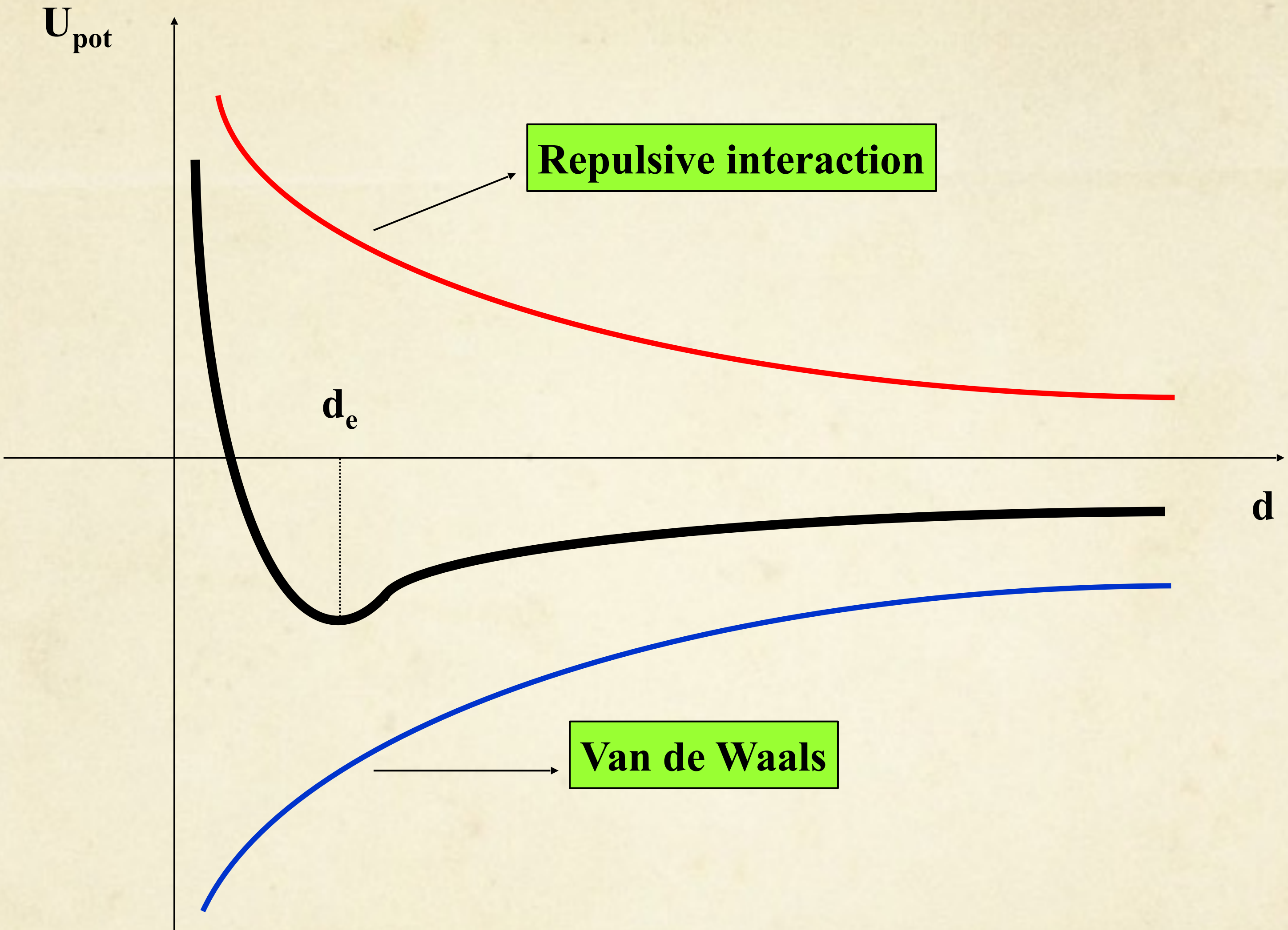
Magnetic nanoparticles dispersed in a fluid carrier



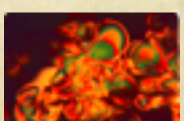
H_2O



IFF SFF

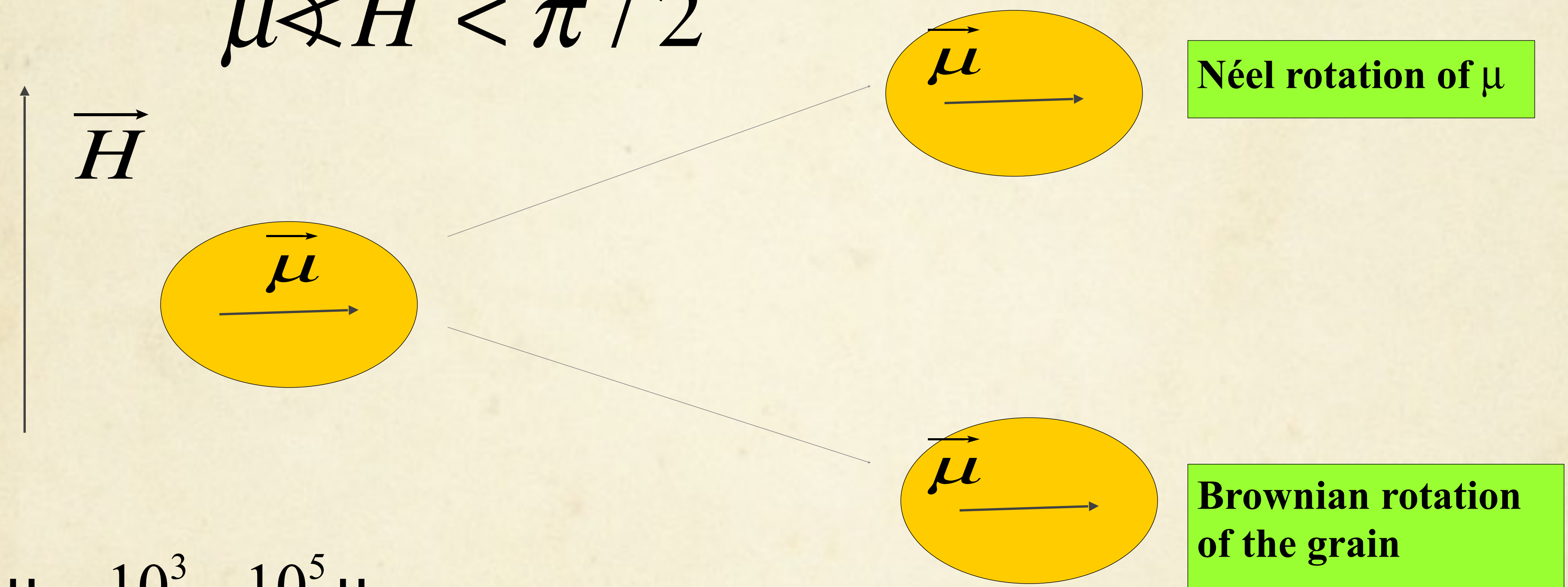


d is the distance between magnetic grains



Behaviour in the presence of the field

$$\vec{\mu} \measuredangle \vec{H} < \pi / 2$$



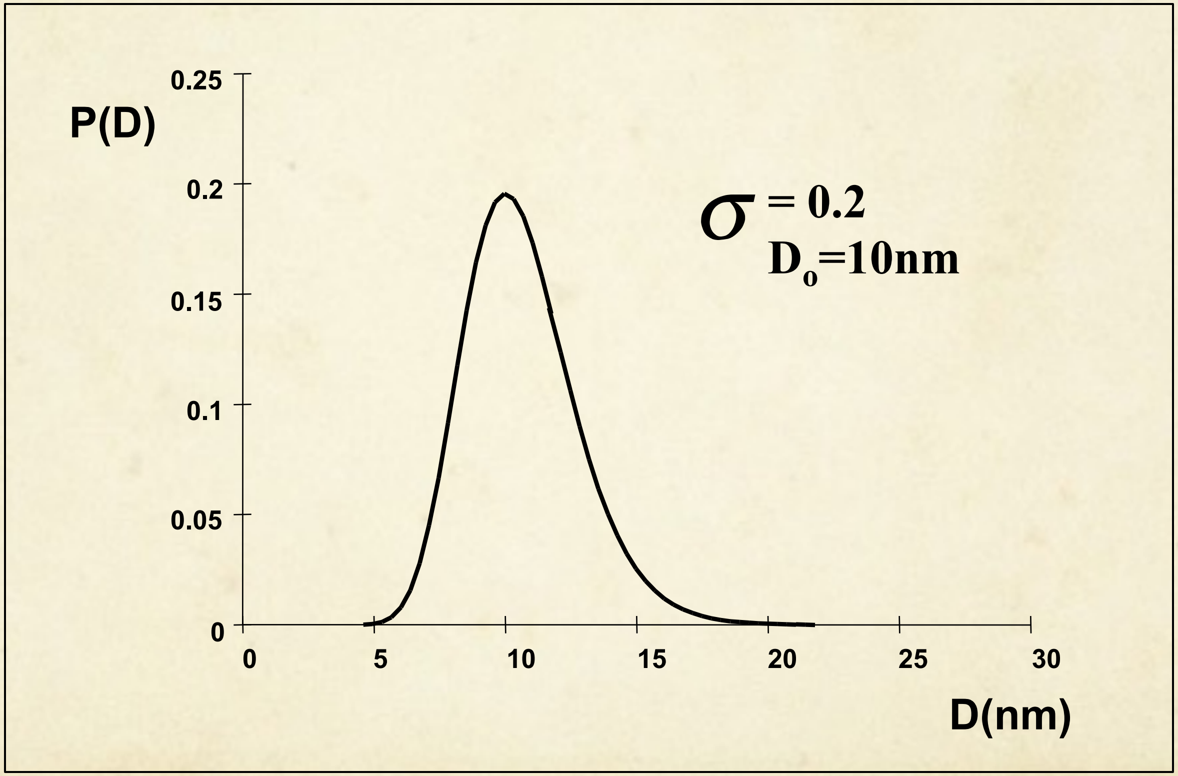
$$\mu \sim 10^3 - 10^5 \mu_B$$

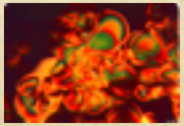
$$1\mu_B = 9.2740154 \times 10^{-24} \text{ J T}^{-1}$$

The size distribution function

$$P(D) = \frac{1}{D_o\sigma\sqrt{2\pi}\,\exp(\sigma^2/2)}\exp\left[-\frac{\ln^2(D/D_o)}{2\sigma^2}\right]$$

Log-normal



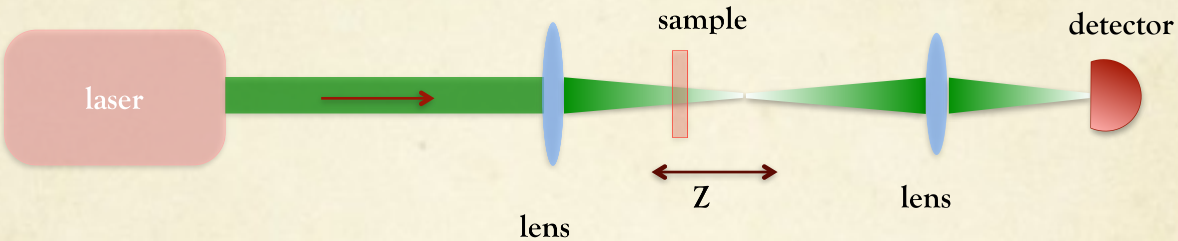


Surfacted ferrofluid
Fe_3O_4, d = 10 nm,
synthetic isoparaffinic oil-based

Volume fraction of magnetic material
0.36% and 0.036%

T = 22°C

Experimental technique
Z-Scan



$$\lambda = 532nm$$

$$cw - Nd:YVO_4$$

$$\tau = 2ms\ (f = 250Hz) \rightarrow 17ms\ (f = 29.4Hz)$$

$$Nd:YAG$$

$$\tau = 100ps\ (f = 20Hz)$$

$$Ti:Sapphire$$

$$\tau = 280fs;\ (f = 3kHz \rightarrow 10kHz)$$

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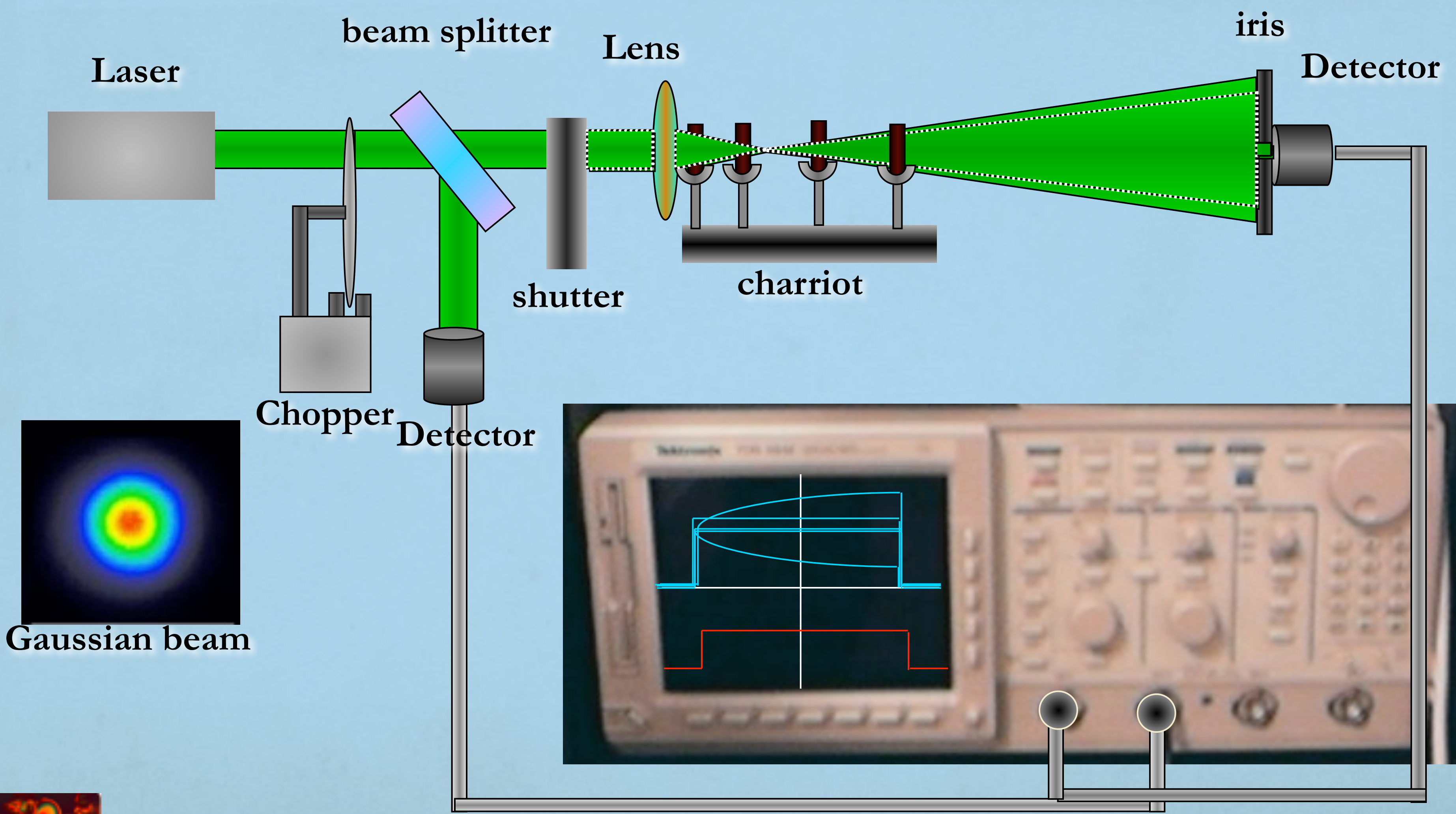
The ZS setup

sample with $n_2 < 0$



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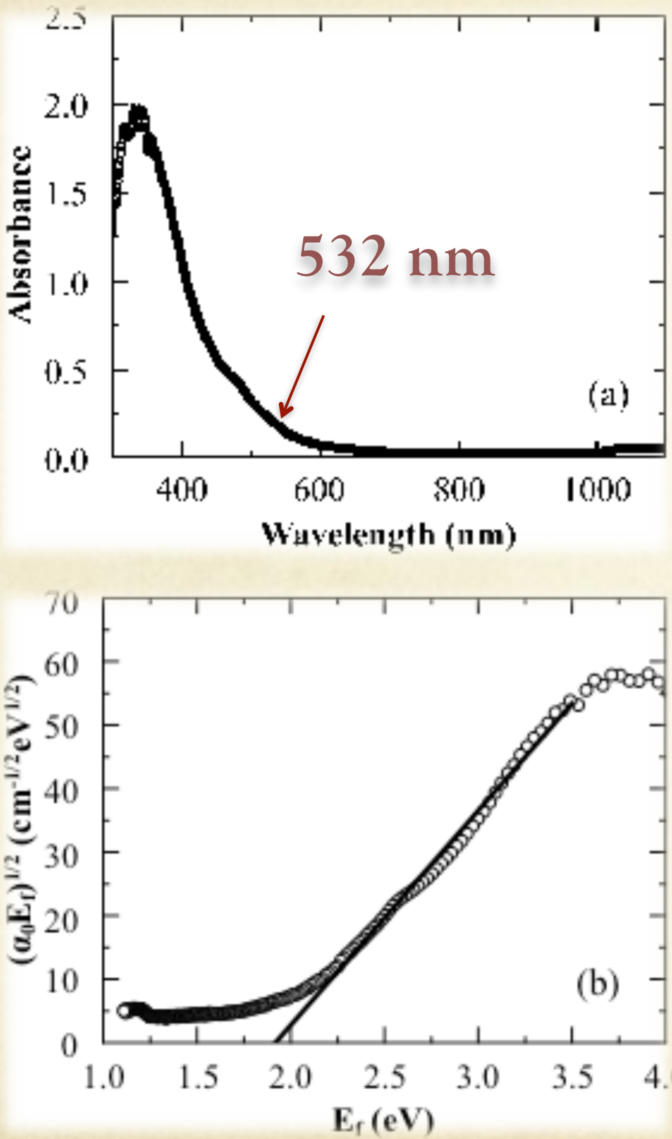


Linear absorbance

Band-gap determination

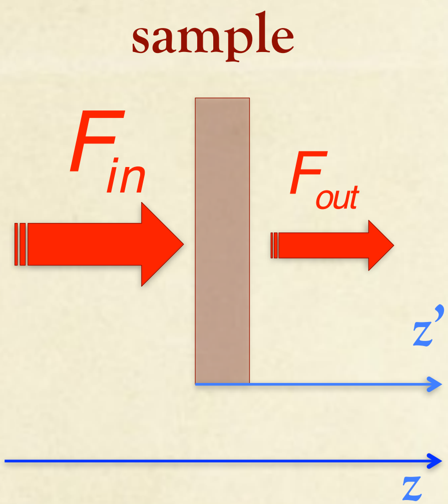
$$\sqrt{E_f \alpha_0} \times E_f$$

$$\sqrt{E_f \alpha_0} \rightarrow 0$$

$$0.95 < E_g < 1.9eV$$

$$E_f \sim 2.3eV \Leftrightarrow \lambda = 532nm$$

The FCA



$$\frac{dI}{dz'} = -(\alpha_0 + \sigma N) I$$

$$\frac{dN}{dt} = \frac{\alpha_0}{h\nu} I(t)$$

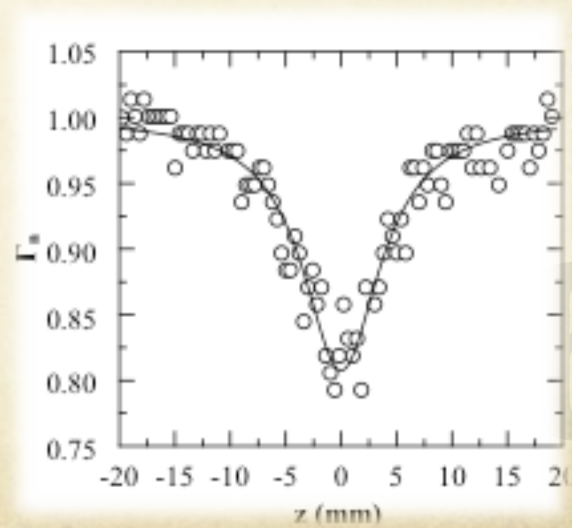
Fluence (J/cm²)

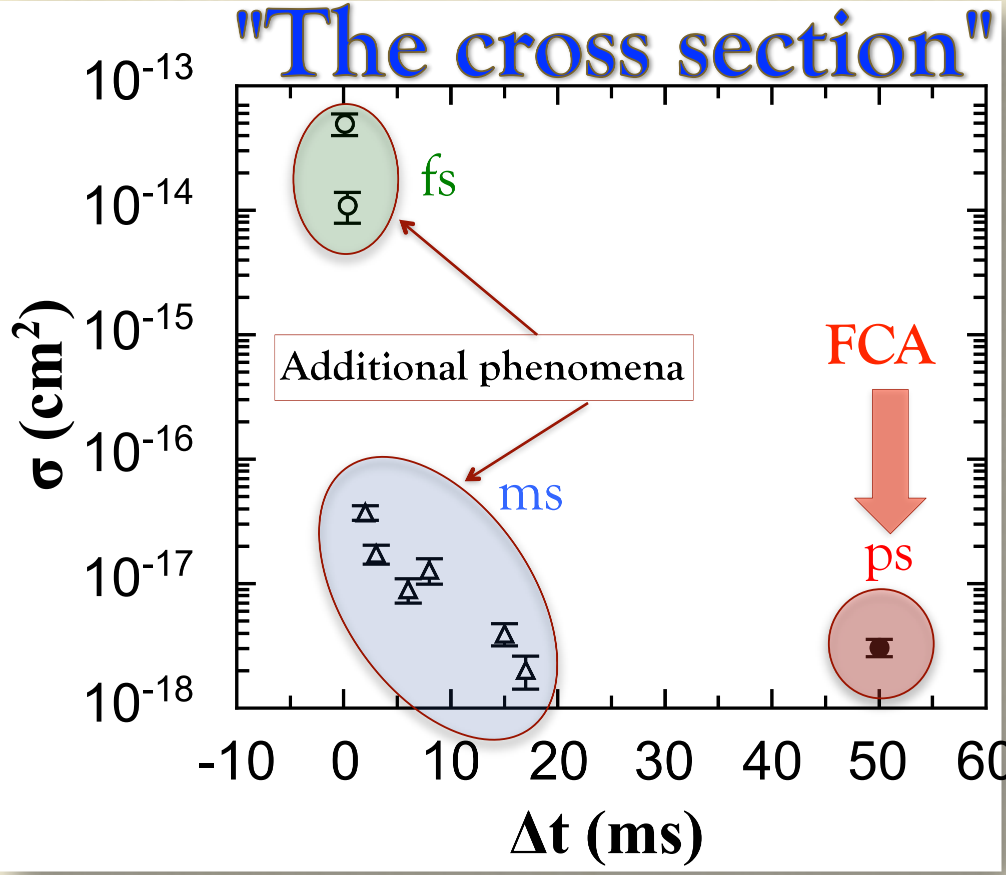
$$\frac{dF}{dz'} = -\left(\alpha_0 + \frac{\sigma\alpha_0}{2h\nu} F\right) F$$

$$F_{out}(z,r) = \frac{F_{in}(z,r)\, e^{-\alpha_0 L}}{1 + \frac{\alpha_0 \sigma}{2h\nu} F_{in}(z,r) L_{eff}}$$

$$\Gamma_n(z) = \frac{\ln[1 + p(z)]}{p(z)}$$

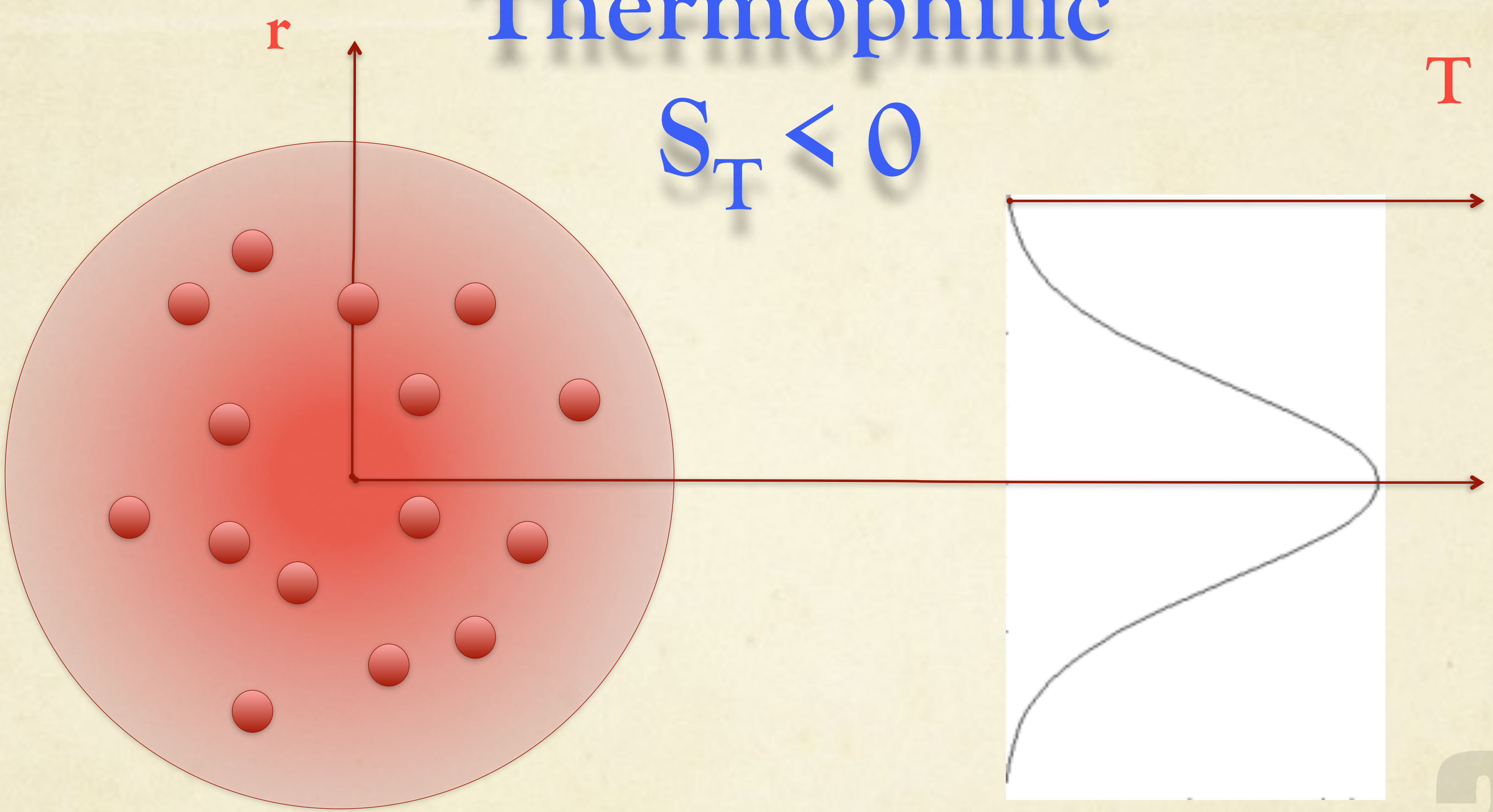
$$p(z) = \frac{\alpha_0 \sigma}{2h\nu} \frac{F_0 L_{eff}}{\left(1 + z^2 / z_0^2\right)}$$



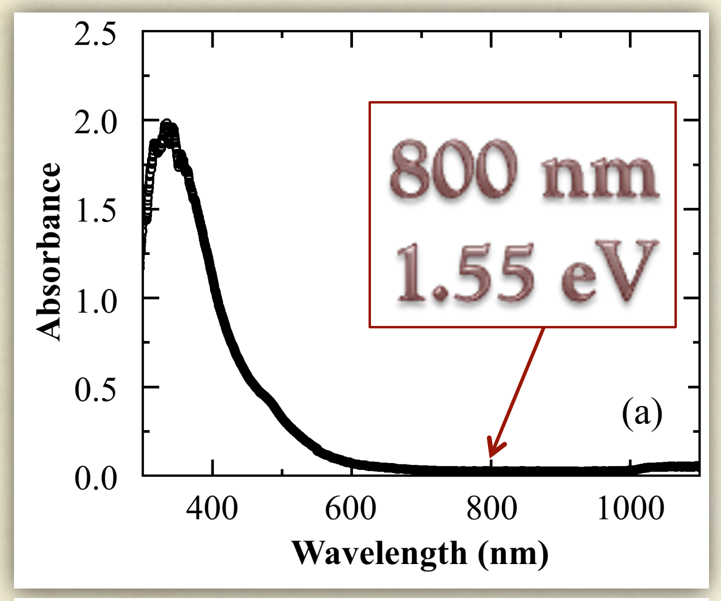


$$\sigma = (3.1 \pm 0.5) \times 10^{-18}\ cm^2$$

Ferrofluid under investigation
Thermophilic
$S_T < 0$



The TPA



$$n = n_0 + n_2 I$$

$$\alpha = \alpha_0 + \beta I$$

CA

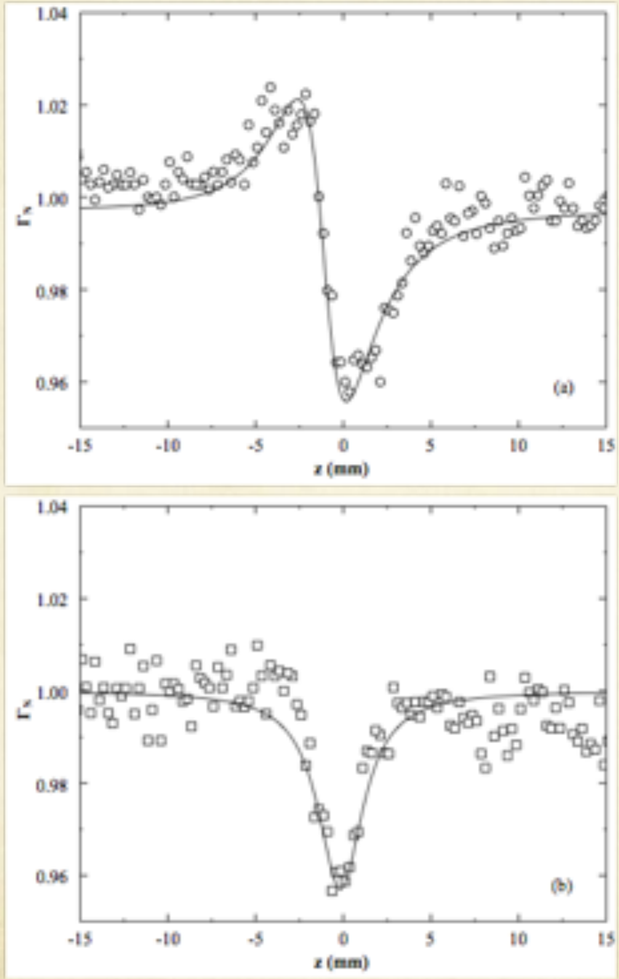
$$\Gamma_N(\gamma) = 1 + \frac{8\pi}{\lambda}\frac{n_2 I_0 L_{eff}\gamma}{(\gamma^2+9)(\gamma^2+1)} - \frac{\beta I_0 L_{eff}(\gamma^2+3)}{(\gamma^2+9)(\gamma^2+1)}$$

OA

$$\Gamma_N(\gamma) = \sum_{m=0}^{\infty}\frac{\left[-\beta I_0 L_{eff}/(\gamma^2+1)\right]^m}{(m+1)^{3/2}}$$

$$\gamma = \frac{z}{z_0}$$

Typical results @ f = 10^2 Hz



CA

OA

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Calculation of $\chi^{(3)}$

$$\mathrm{Re}\,\chi^{(3)} = 2n_0^2\varepsilon_0 c n_2 = -\left(4.1 \pm 1.8\right)\times 10^{-20}\, m^2/V^2$$

$$\mathrm{Im}\,\chi^{(3)} = \frac{\beta n_0^2 \varepsilon_0 c \lambda}{2\pi} = \left(1.2 \pm 0.6\right)\times 10^{-20}\, m^2/V^2$$

$$\left|\chi^{(3)}\right| = \left(4.3 \pm 1.9\right)\times 10^{-20}\, m^2/V^2 \sim 3.1\times 10^{-12}\, esu$$

Thermal lens model

- The label "thermal lens" is used to describe the process where the sample is heated by a spatial nonuniform laser beam
- Nonlocal process. The refractive index of the sample changes due to this heating:

$$\Delta n = \frac{dn}{dT}\Delta T$$

- The intensity measured at the iris position is

$$I(z,t) = \frac{2P}{\pi\omega_2^2}$$

- The focal distance of the thermal lens

$$\frac{1}{f} = -\left.\frac{d^2 l}{dr^2}\right|_{r\to 0} = -b\frac{dn}{dT}\frac{d^2}{dr^2}\Delta T = \frac{\theta}{1+\left(\frac{z}{z_0}\right)^2}\frac{2t}{2t+t_c}$$

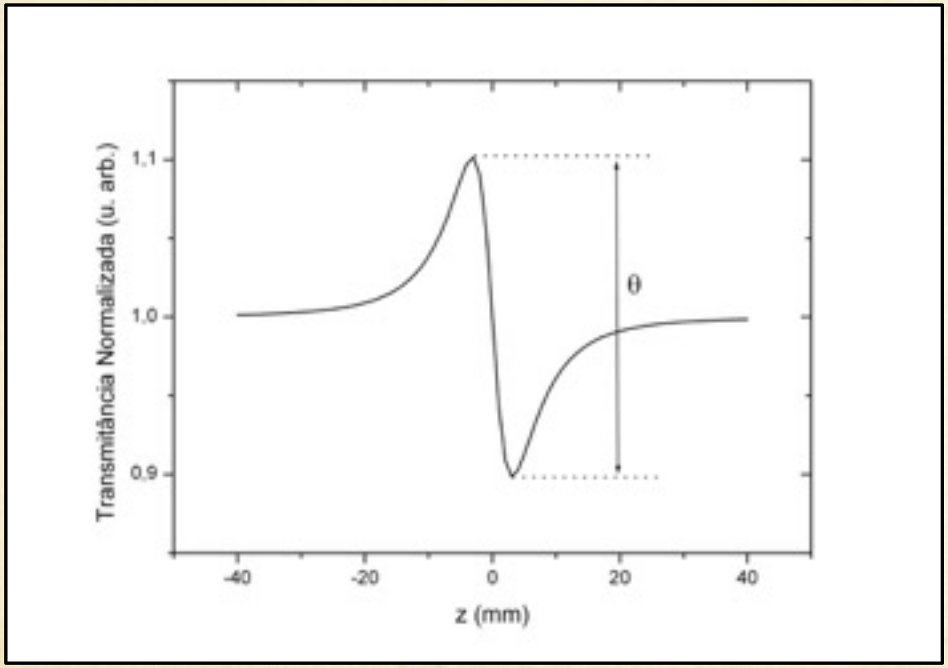
- Where $$\theta = -\frac{\alpha b P}{\pi \omega_0^2}\frac{dn}{dT}$$

- The intensity as a function of z and t

$$I(z,t) = I(z,0)\left\{1+\frac{\theta}{1+{}^{t_c}\!/_{2t}}\left(\frac{2\,{}^{z}\!/_{z_0}}{1+\left({}^{z}\!/_{z_0}\right)^2}\right)+\left(\frac{\theta}{1+{}^{t_c}\!/_{2t}}\right)^2\left(\frac{1}{1+\left({}^{z}\!/_{z_0}\right)^2}\right)\right\}^{-1}$$

The normalised transmittance

$$\Gamma_N(z) = \frac{1}{\left(1+\theta\dfrac{2z/z_0}{1+(z/z_0)^2}+\theta^2\dfrac{1}{1+(z/z_0)^2}\right)}$$



$$\theta = \frac{2.303\,P\,A}{\lambda\,D\,\rho\,c_p}\left(-\frac{\partial n}{\partial T}\right)$$

$$A = -\log_{10}(1-\alpha L)$$

Low-Density Lipoproteins (LDL)

"nonlinear fingerprint"

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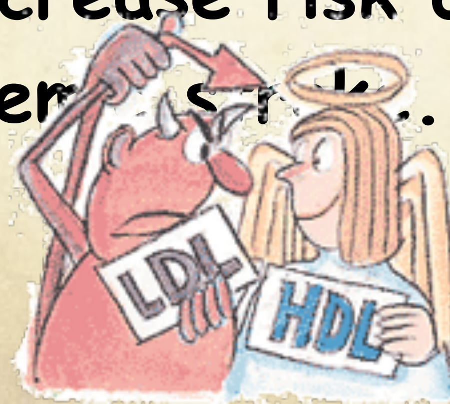
Motivation

World Health Organisation

Risk factor to cardiovascular diseases (atherosclerosis)

- Abnormal blood lipids

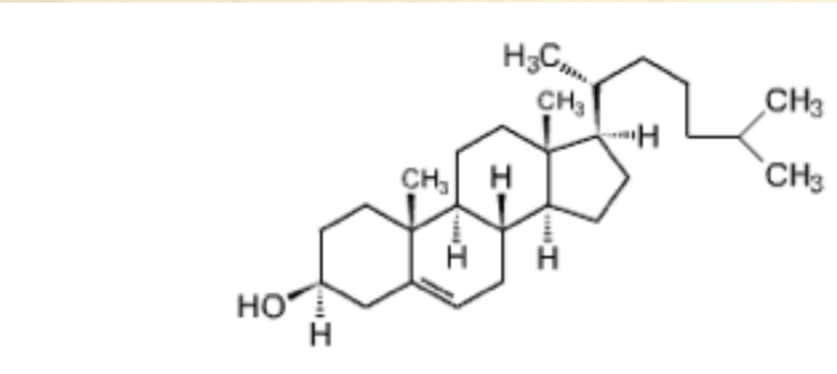
High total cholesterol, LDL-cholesterol and triglyceride levels, and low levels of HDLcholesterol increase risk of coronary heart disease and ischaem[illegible].

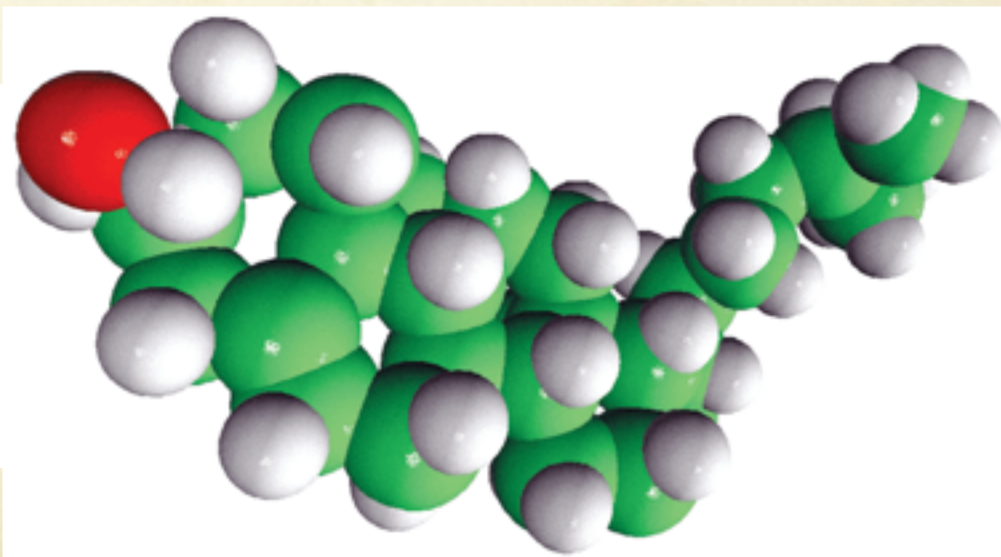


Low-**D**ensity **L**ipoproteins → **LDL**

High-**D**ensity **L**ipoprotein → **HDL**

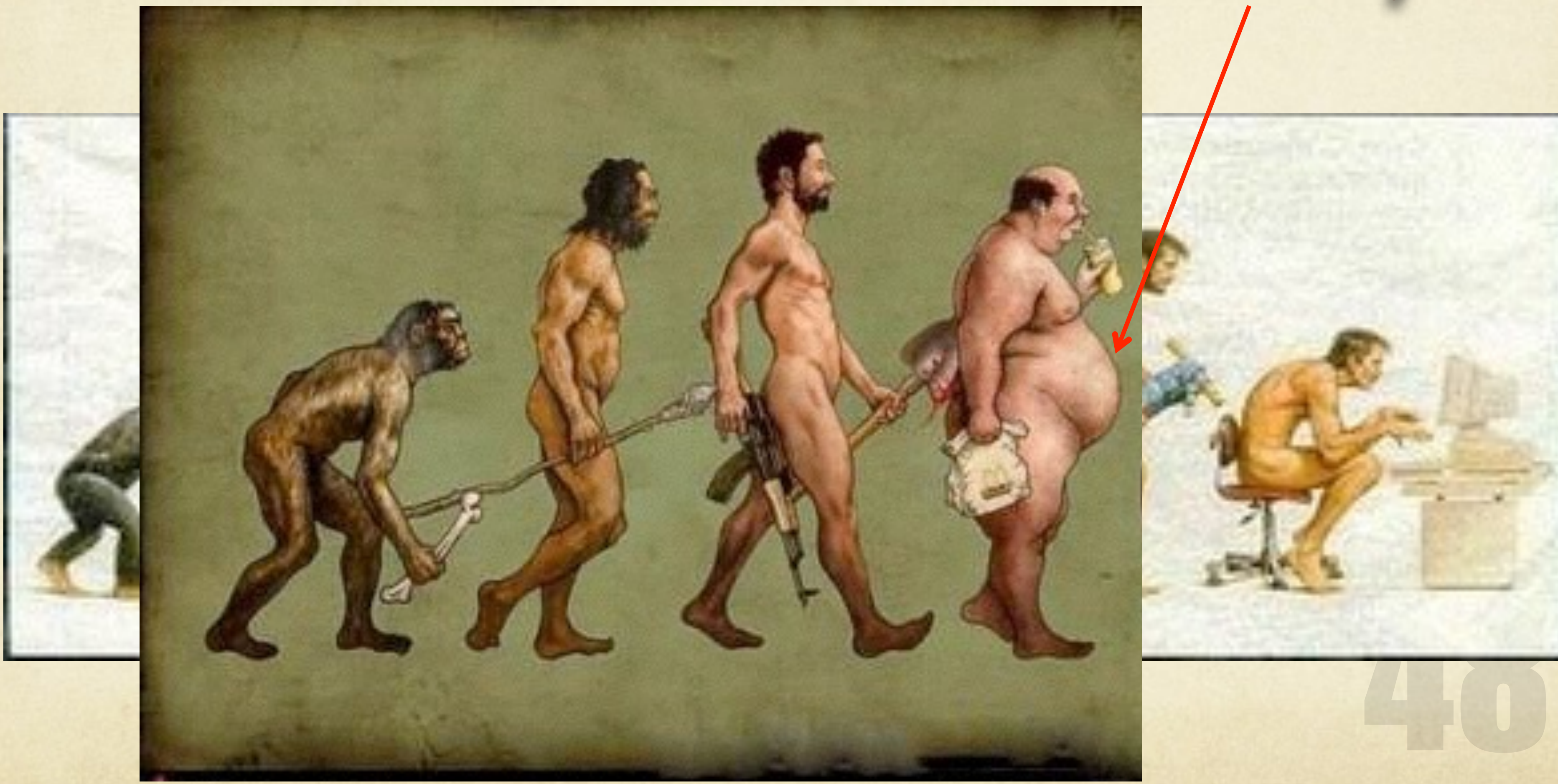
Main carrier of cholesterol, playing a critical role in the human cholesterol metabolism





The life style

Visceral obesity



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The nano submarine

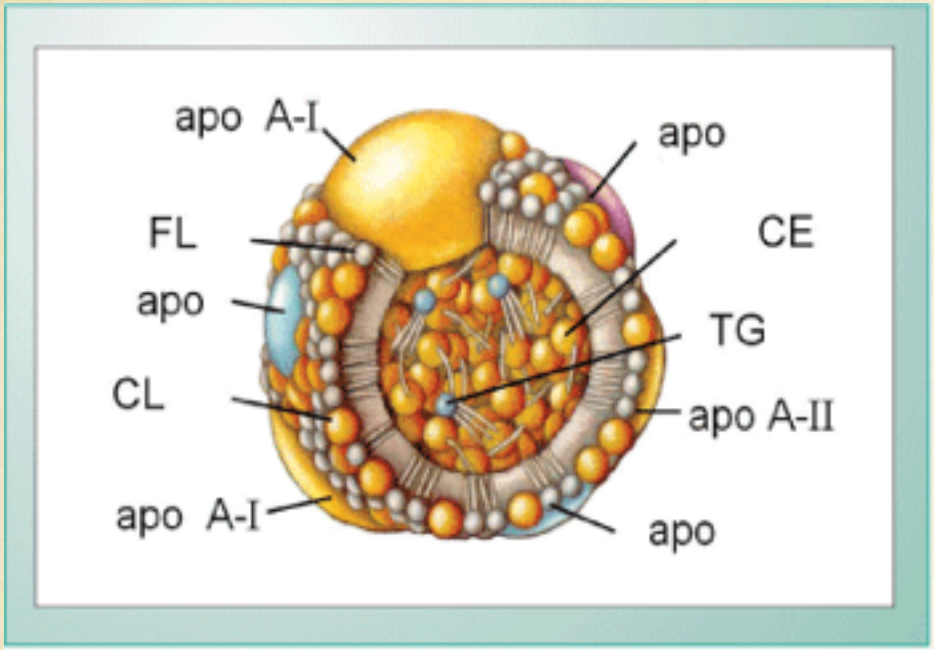
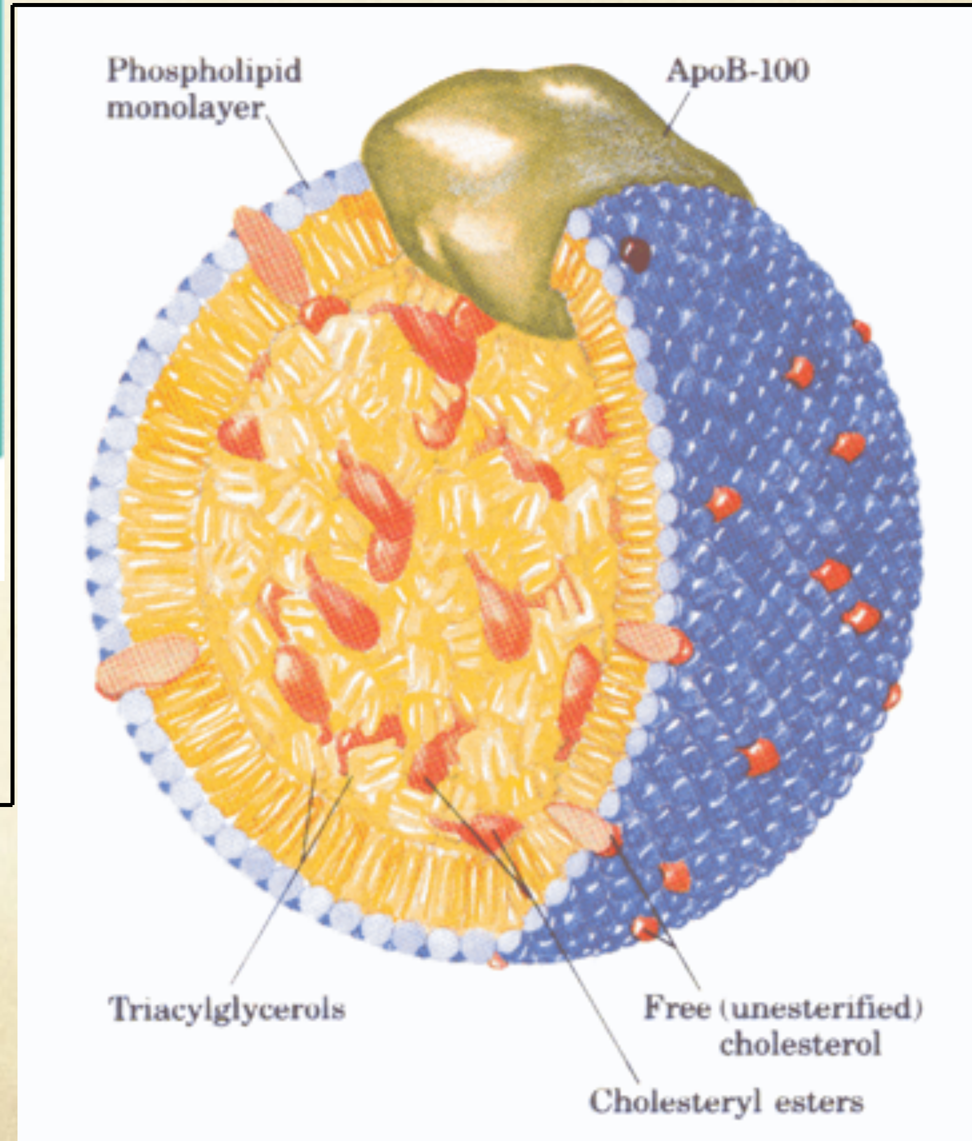
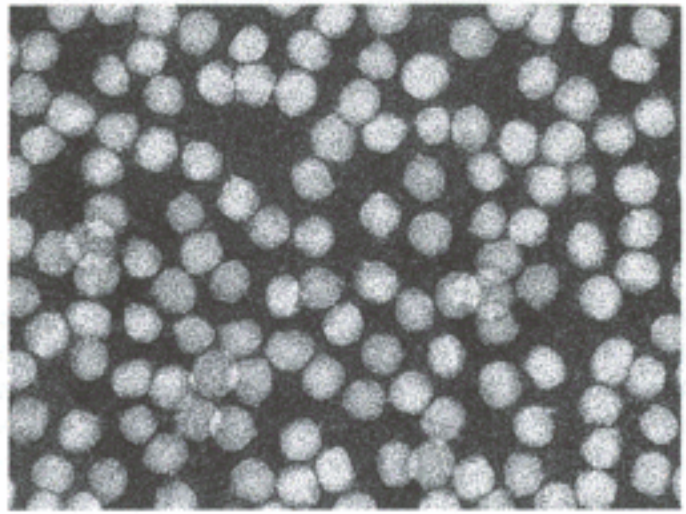


Fig. 1 - Constituição da lipoproteína de alta densidade (HDL).
FL= fosfolípides; apo = apoproteína; CL= colesterol; CE = colesterol esterificado; TG = triglicérides.

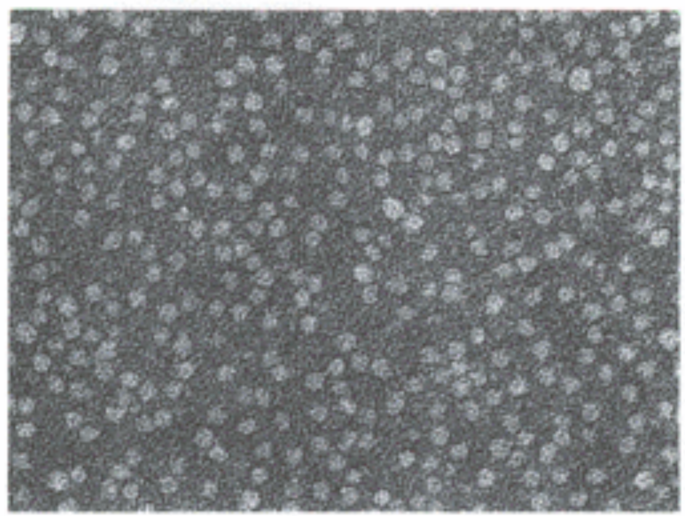
HDL



LDL



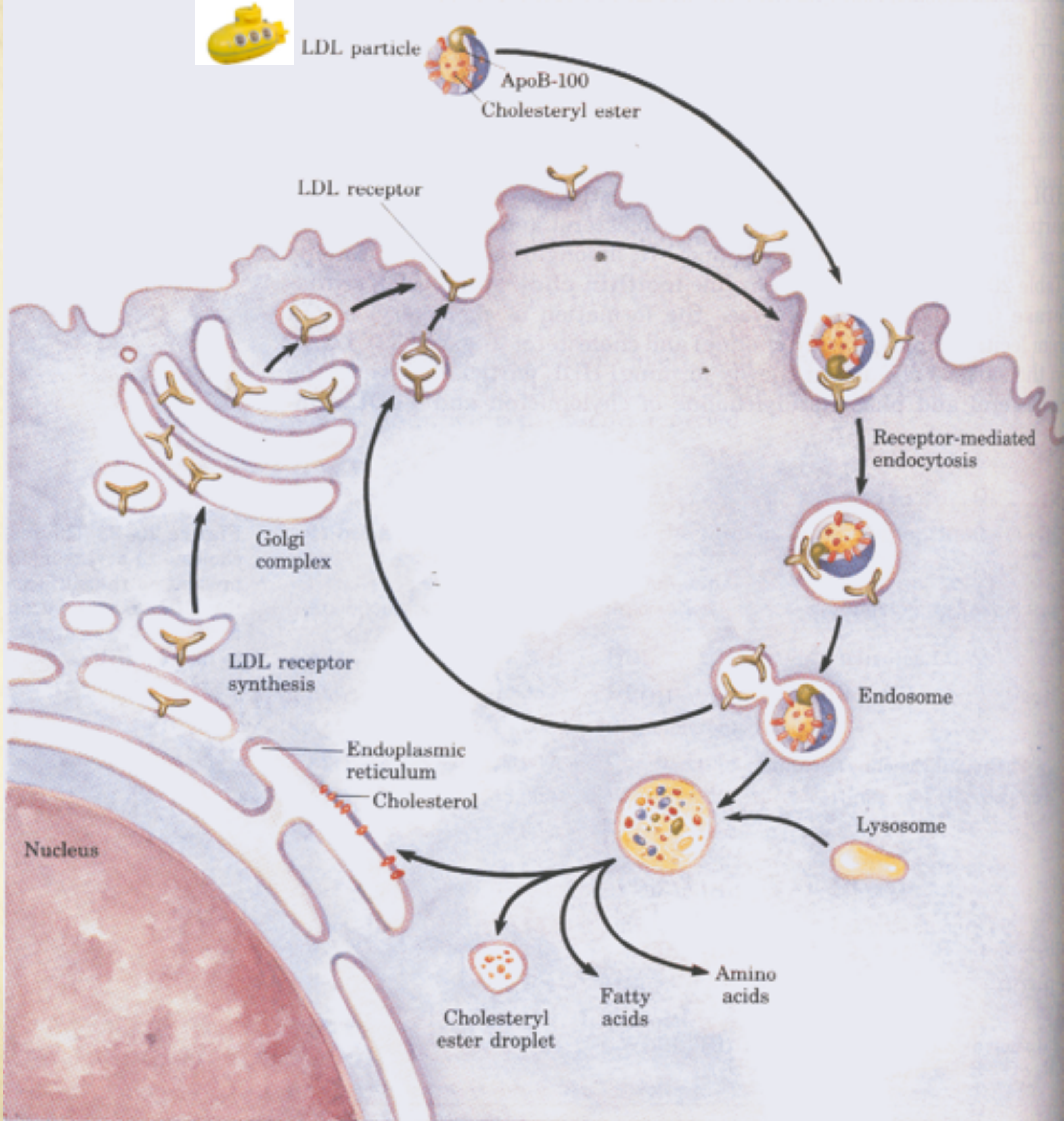
LDL (×180,000)



HDL (×180,000)

(b)

The LDL trip...



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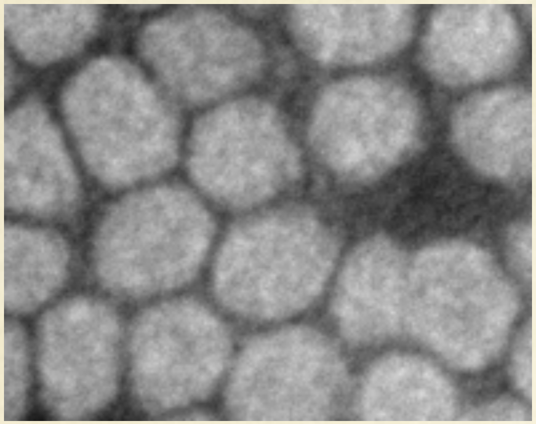
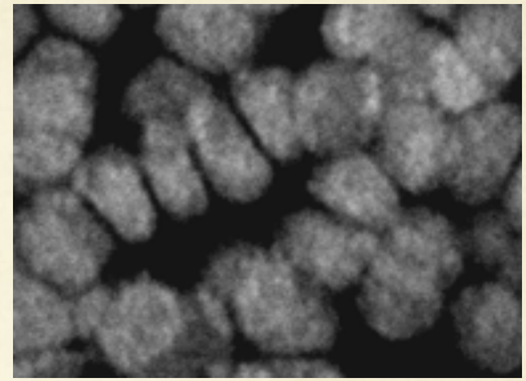
The oxidation of the LDL

"Normal" state



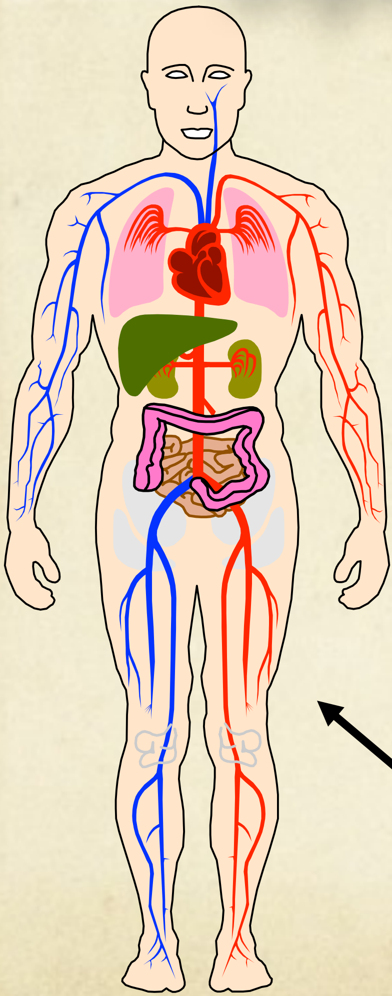
Disease state



oxidized LDL - moLDL

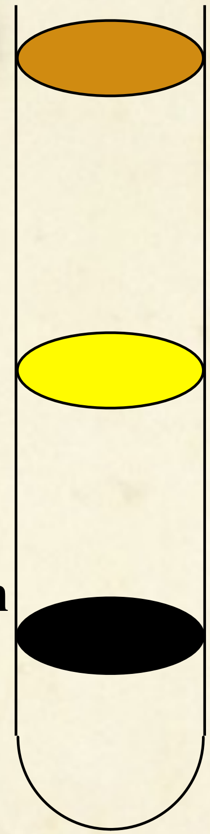
oxLDL induces the formation of aggregates: initial <u>nucleation units</u> through <u>linear</u> to fractals and <u>vesicles</u>

Sample preparation: Lipoproteins



plasma

Ultracentrifugation
10^3 g @ 4 ^oC



normolipidemic blood donor

(~~volunteer~~) (student!)

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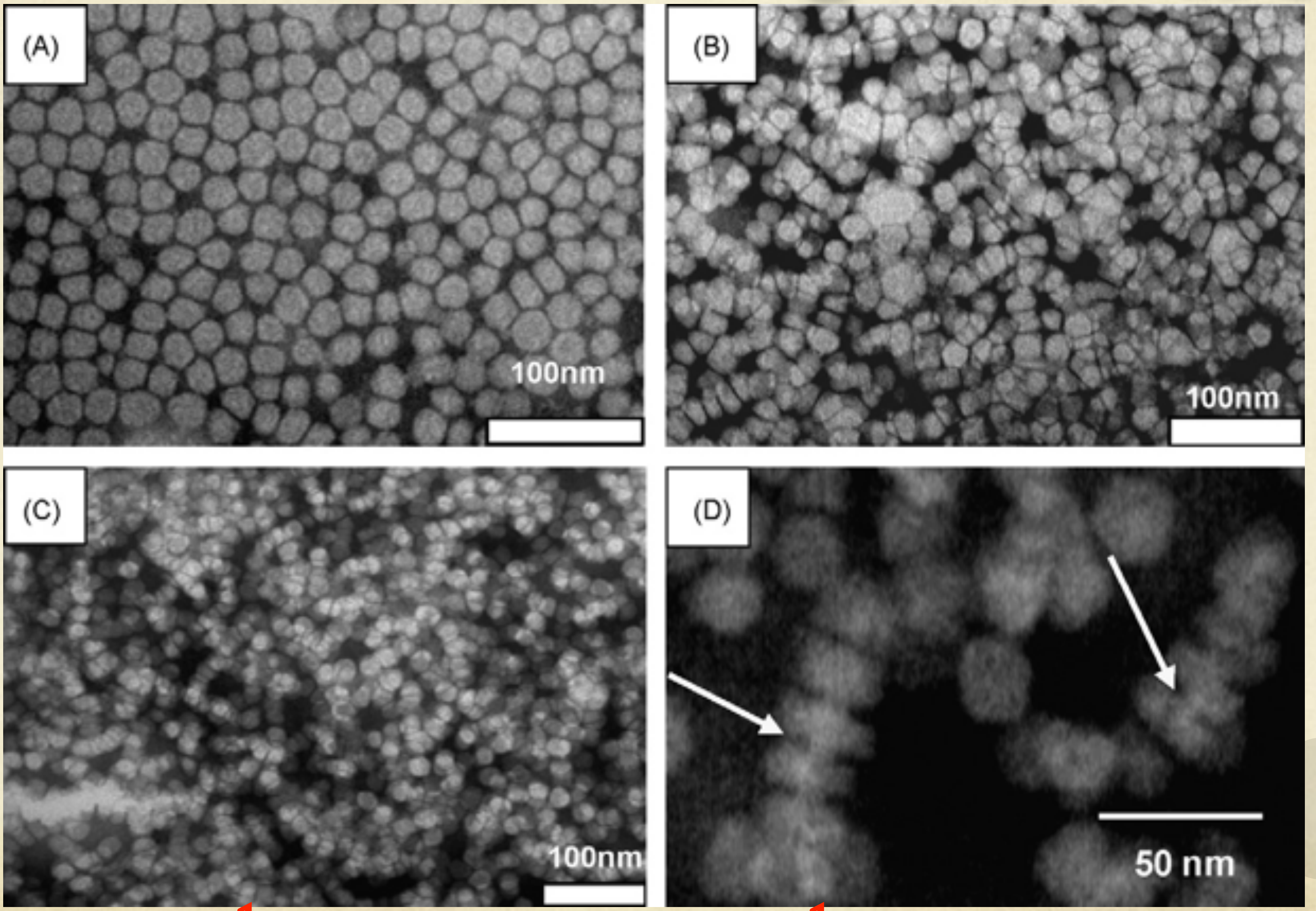
Oxidation of the LDL

CuLDL & FeLDL

TEM images

native

CuLDL



FeLDL

CuLDL

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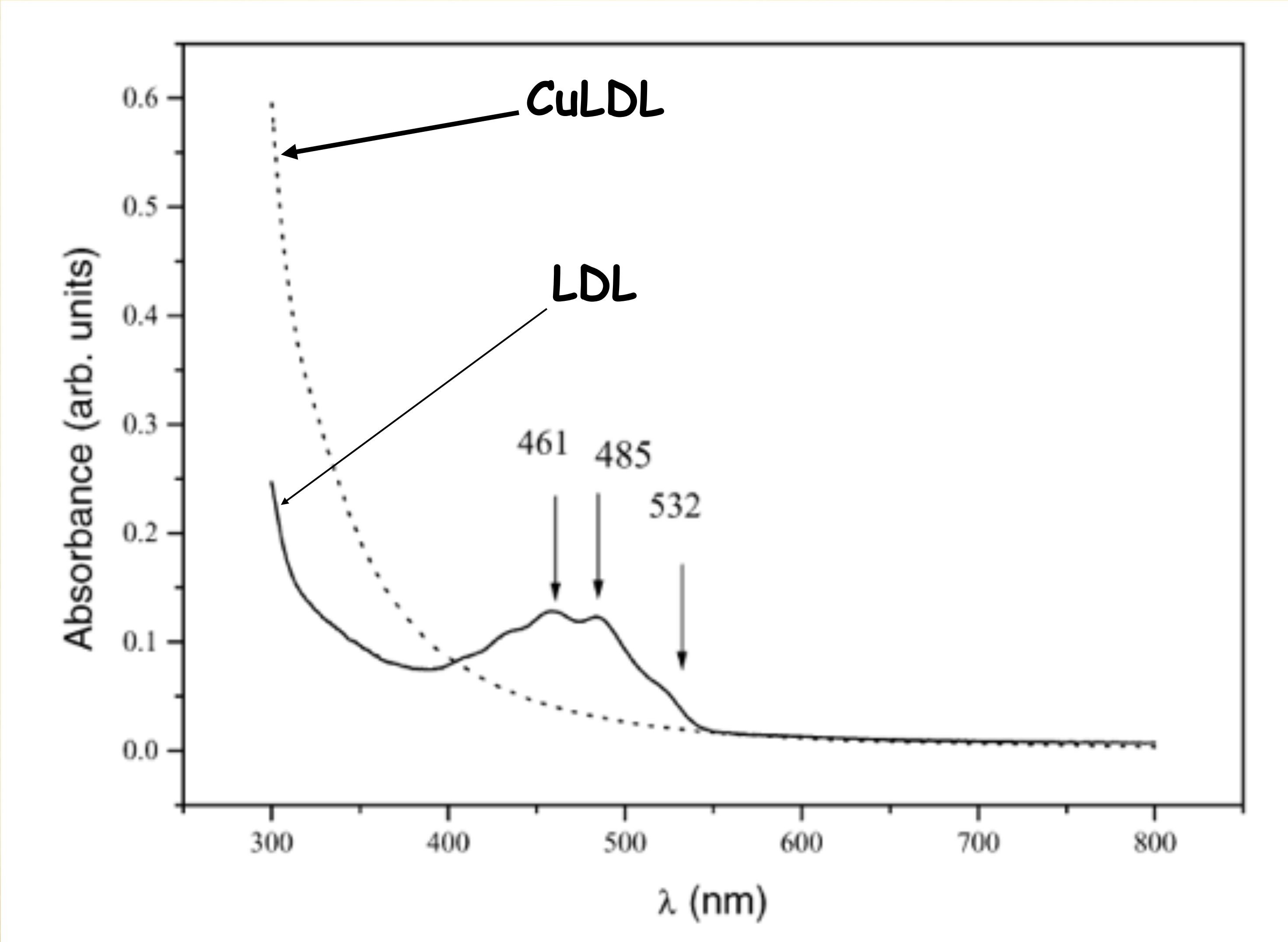
Optical absorbance



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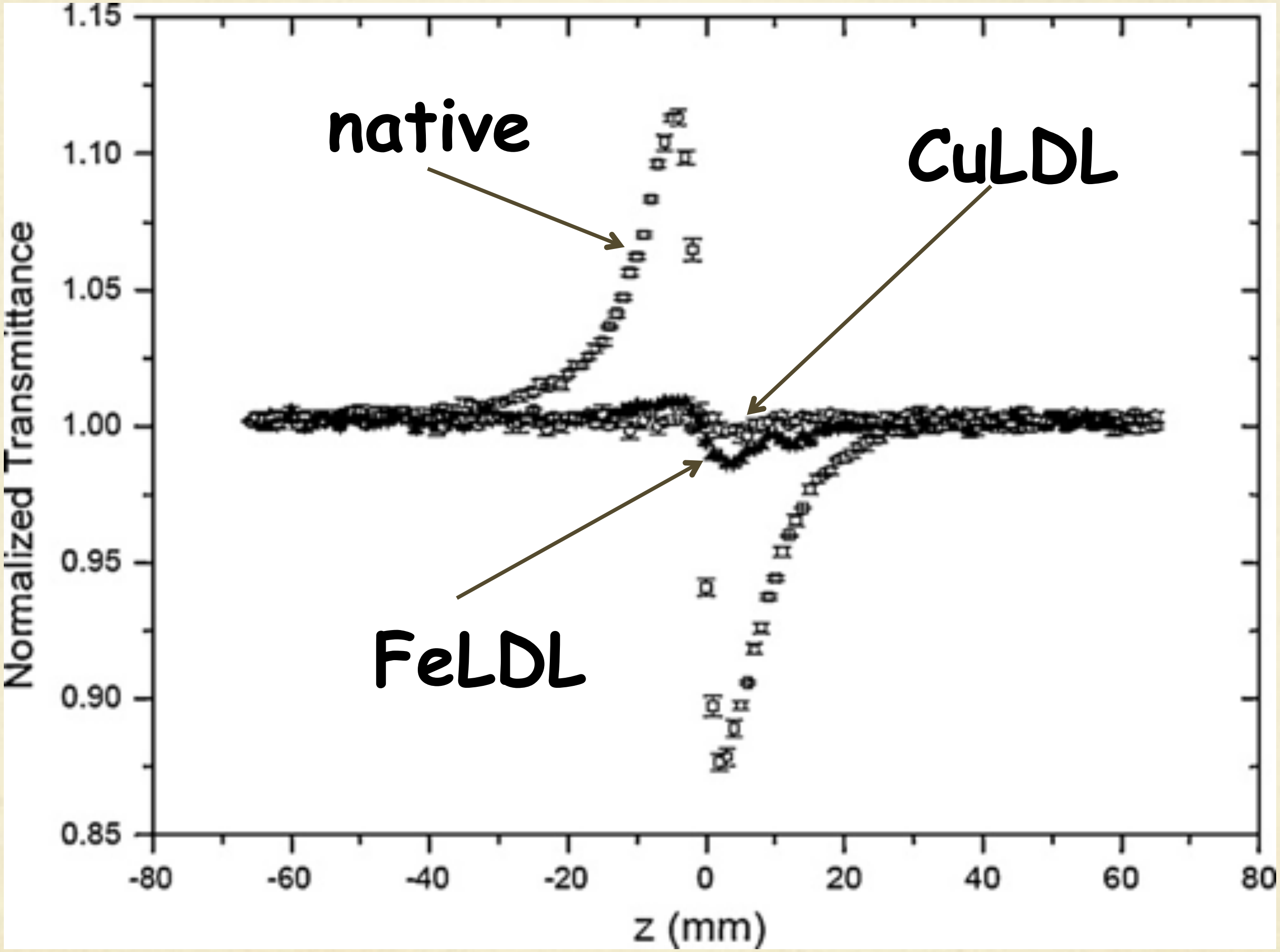
Typical Z-Scan results

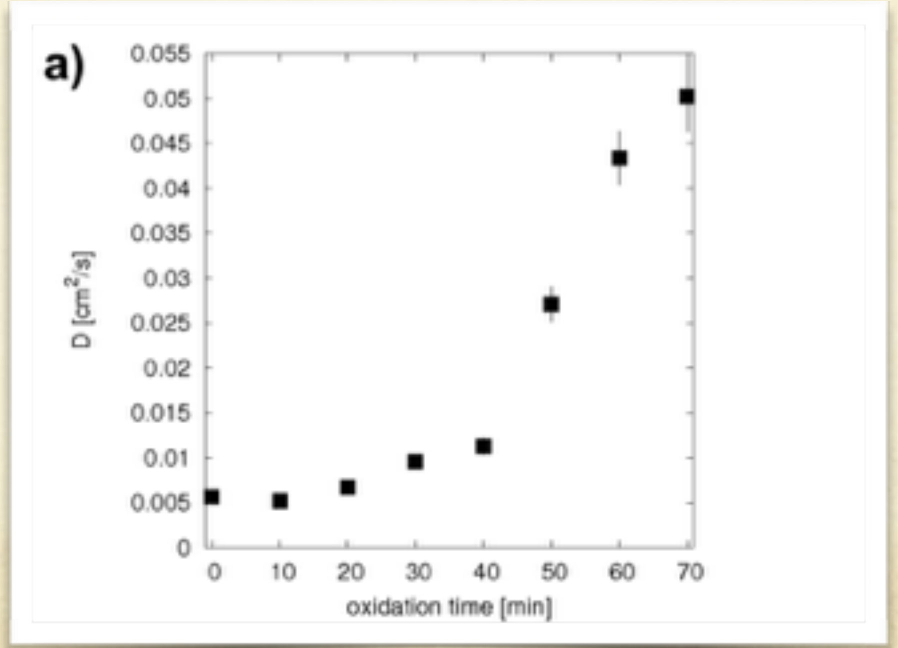


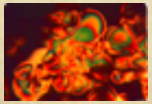
a) Modification of the structural properties of the membrane

b) Aggregation

c) Particle Disruption

Thermal diffusivity





Final remark

Nonlinear optics brings interesting informations about materials.

Interaction between optical fields and matter.

Fundamentals and applications.

Thanks!