Use and abuse of the effective-refractive-index concept in turbid colloidal systems

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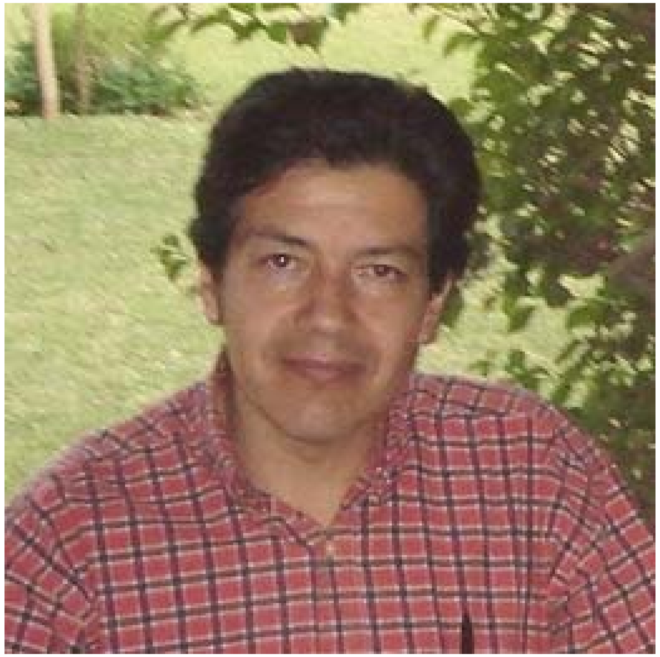
In collaboration with:

Alejandro Reyes **Augusto García**

and with

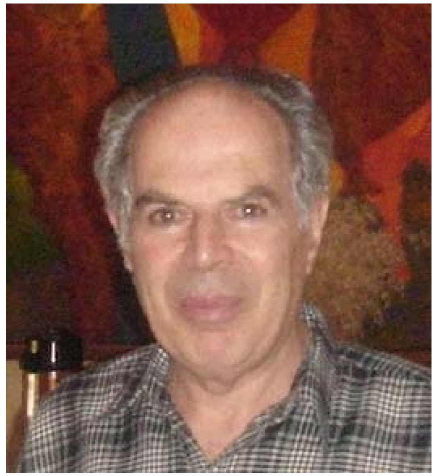


Felipe Pérez **Edahí Gutierrez**

Also,I acknowledge very interesting discussions with:

Eugenio Méndez

Luis Mochán



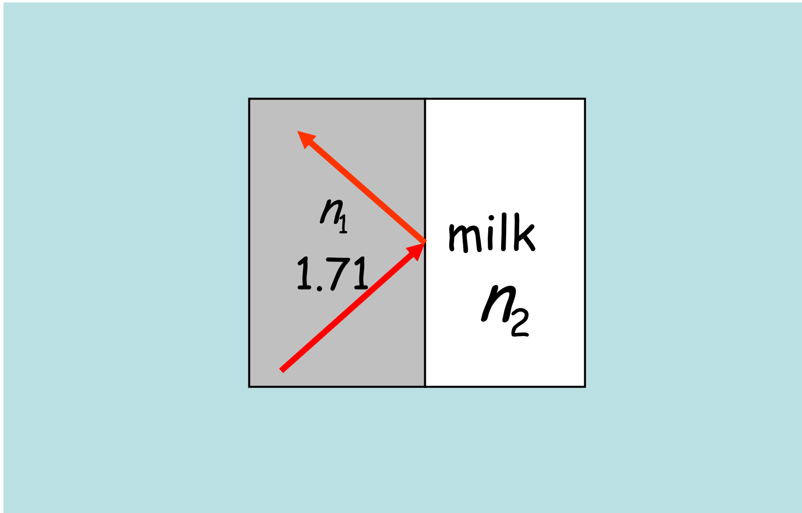
Peter Halevi

Motivation

internal-reflection configuration

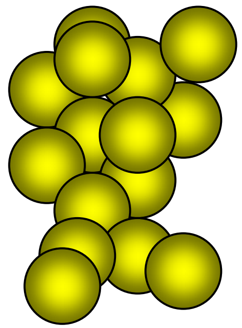
critical angle

$$\sin\theta_c = \frac{n_2}{n_1}$$

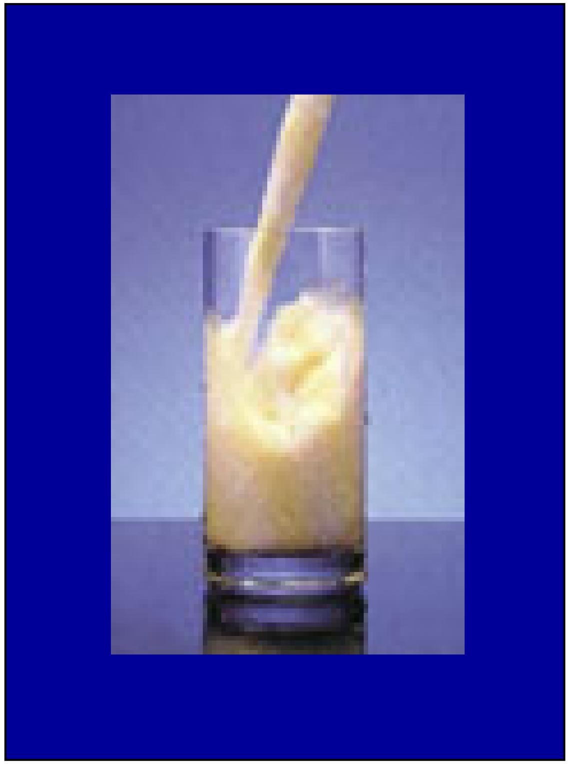


δn_2 → states of aggregation

Real time



Question

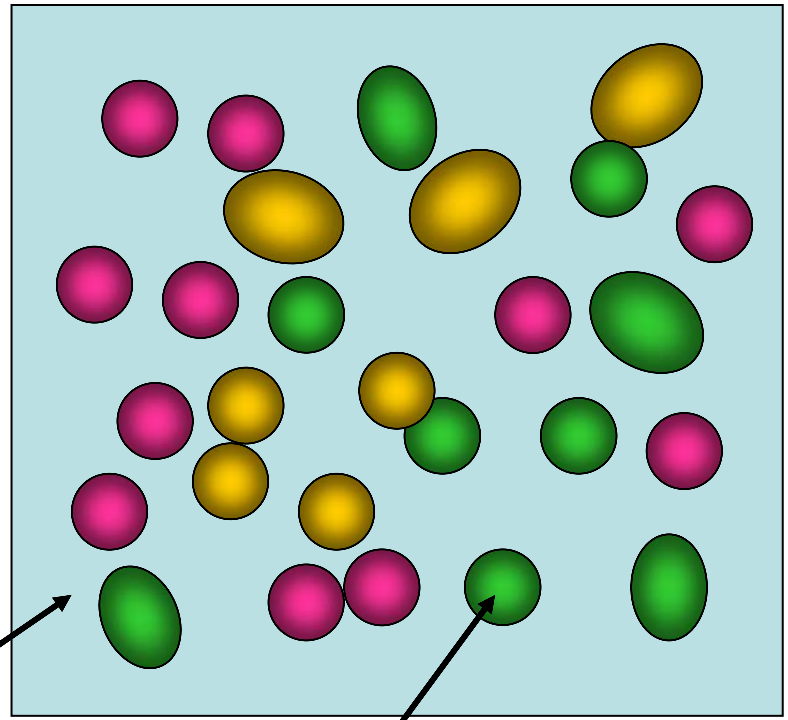


What is the index of refraction of milk?

…it is white…and turbid…

Colloid

Inhomogeneous phase dispersed within a homogeneous one



homogeneous phase

colloidal particles

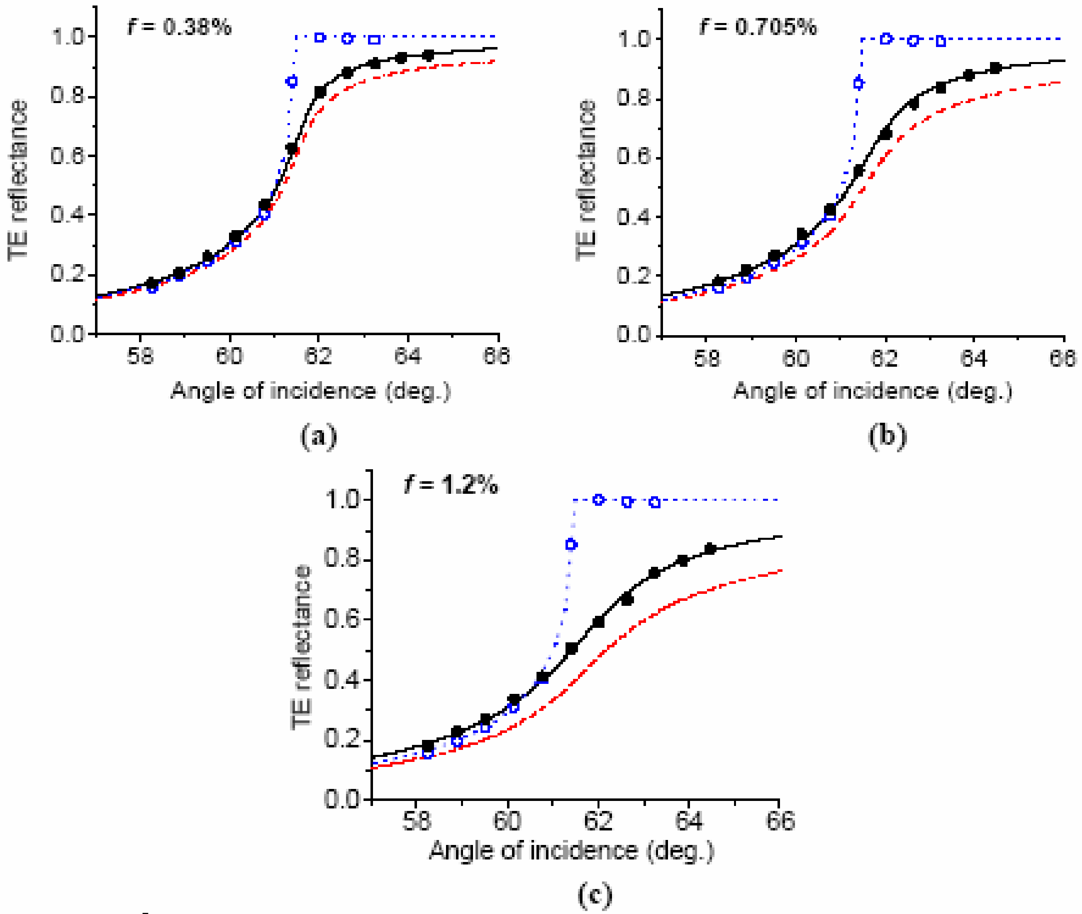
DISORDER

continuous phase	disperse phase	name	examples
liquid	solid	sol	milk, paints, blood, …
liquid	liquid	emulsion	oil/water, water/benzene
liquid	gas	foam	foam, whipped cream…
solid	solid	solid sol	composites, policrystals, rubys…
solid	liquid	solid emulsion	milky quartz, …
solid	gas	solid foam	porous media, opals
gas	solid	solid aereosol	smoke, powder
gas	liquid	liquid aereosol	fog

Photonic crystals and metamaterials: ordered colloids?

Measurements

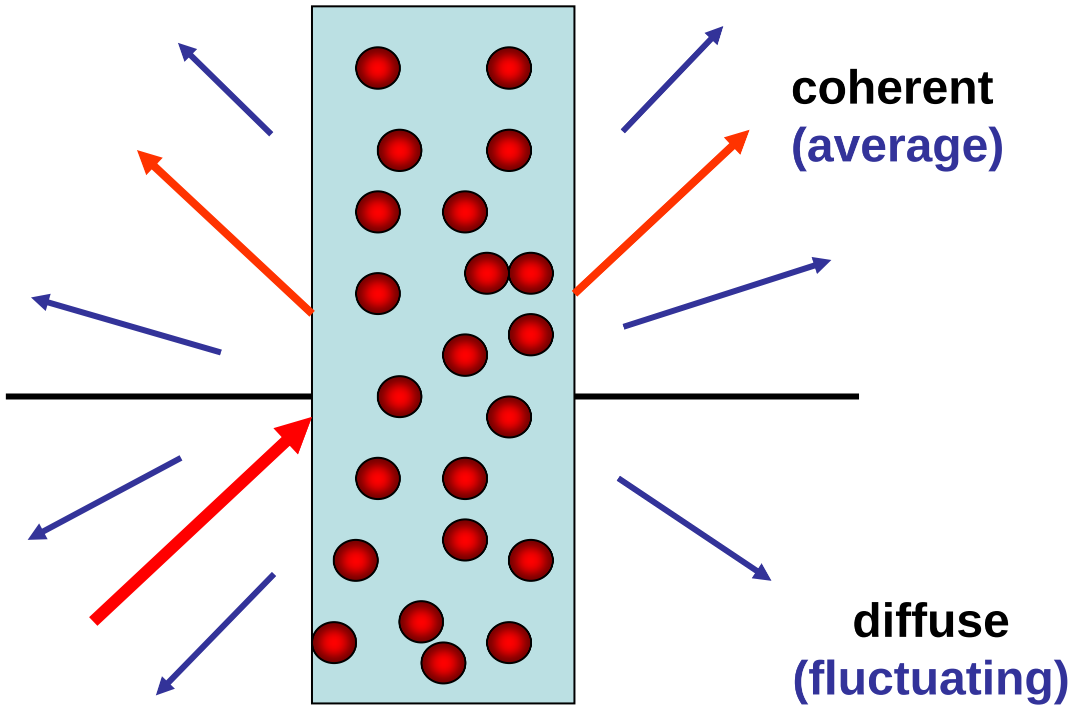
…reflectance around the critical angle…



….inconsistencies…

Turbidity

…light scattering…



OPTICAL SPECTRUM

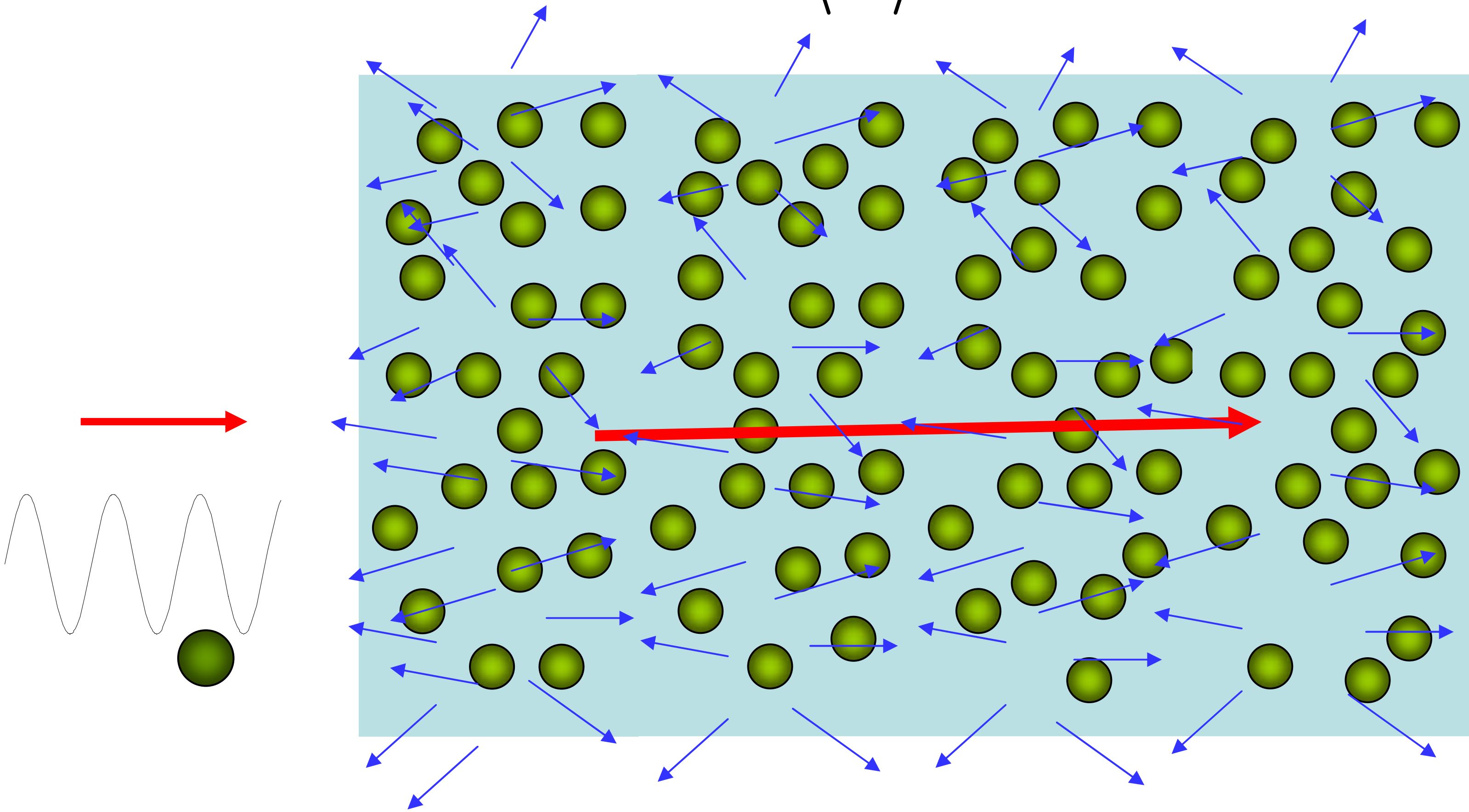
$400 \le \lambda \le 800$ nm

turbid

Total field

ensemble

$$\vec{E} = \langle \vec{E} \rangle + \delta \vec{E}$$



...probability...

$$\frac{d^3 r}{V_T}$$

"on the average"
homogeneous and isotropic

Small particles

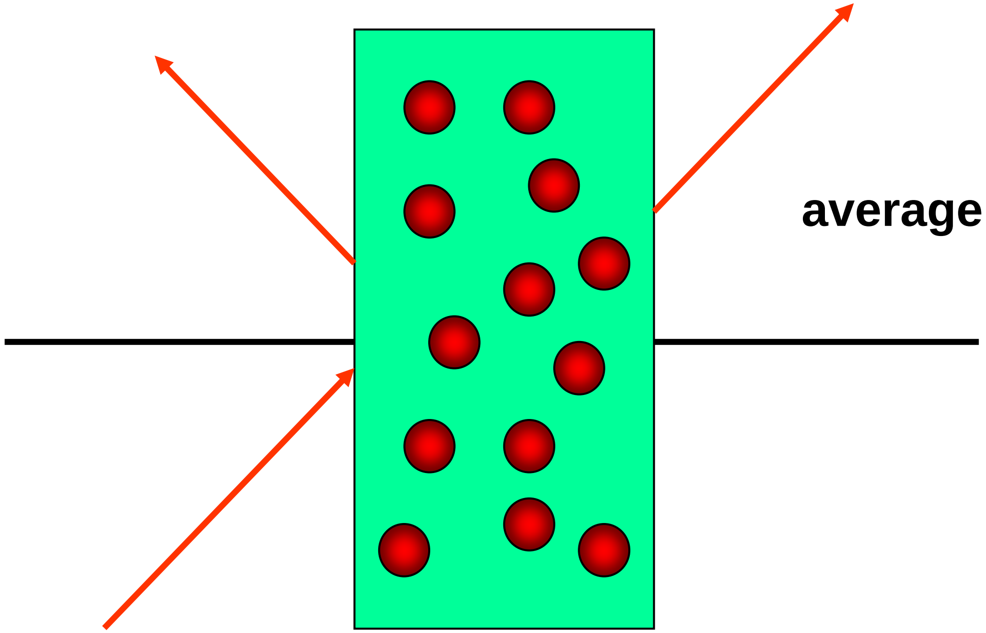
nano…

size parameter

$$ka = \frac{2\pi a}{\lambda} \ll 1$$

$$a \ll \frac{\lambda}{2\pi} \approx 0.1\,\mu m$$

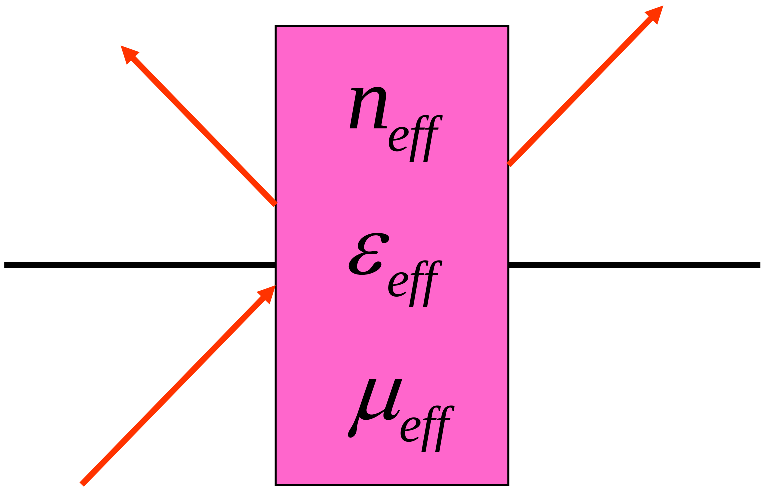
the diffuse field can be neglected



i.e. macroscopic electrodynamics

Effective medium

effective medium



effective properties

Effective-medium theories

Homogenization theories

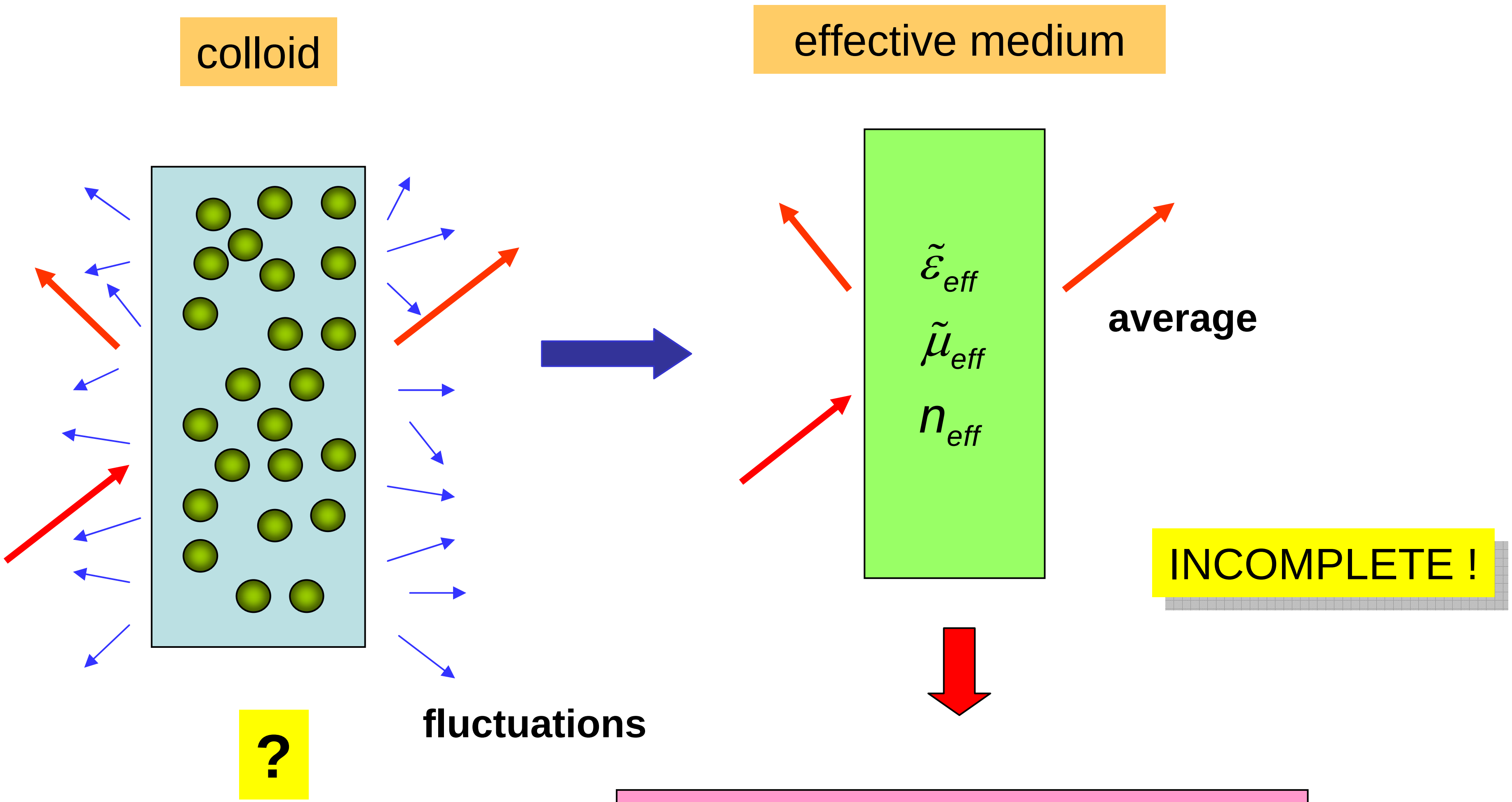
$$n_{eff}\left[\{optical\},\{structural\}\right]$$

"unrestricted"

Continuum Electrodynamics

Extended effective medium

BIG $a \approx \frac{\lambda}{2\pi} \approx 0.1\,\mu m$

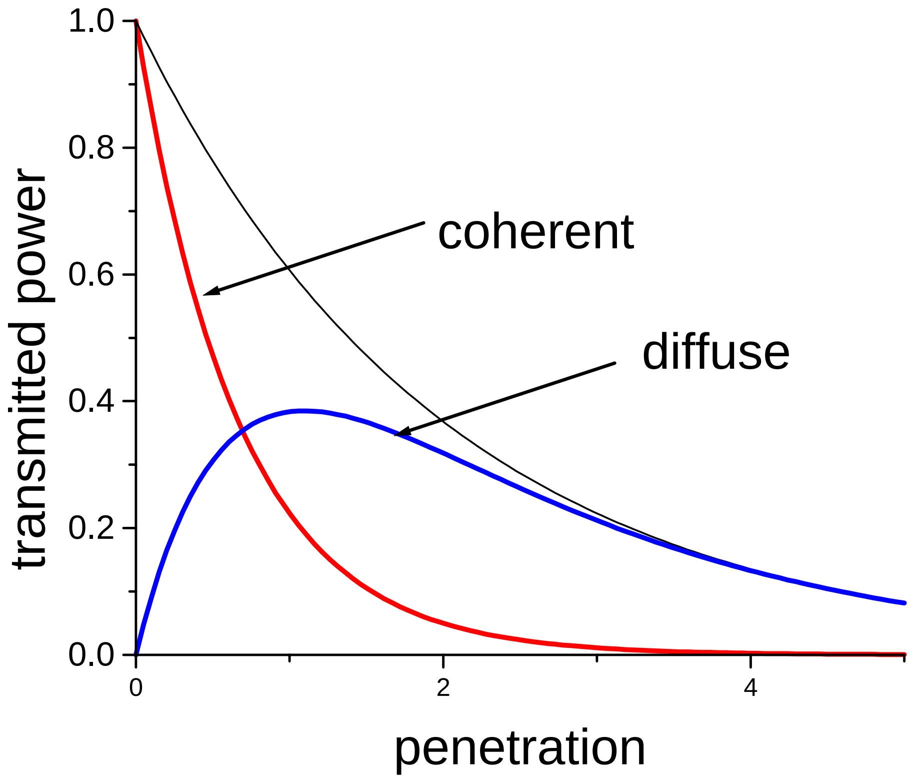


Continuum Electrodynamics

Energy conservation

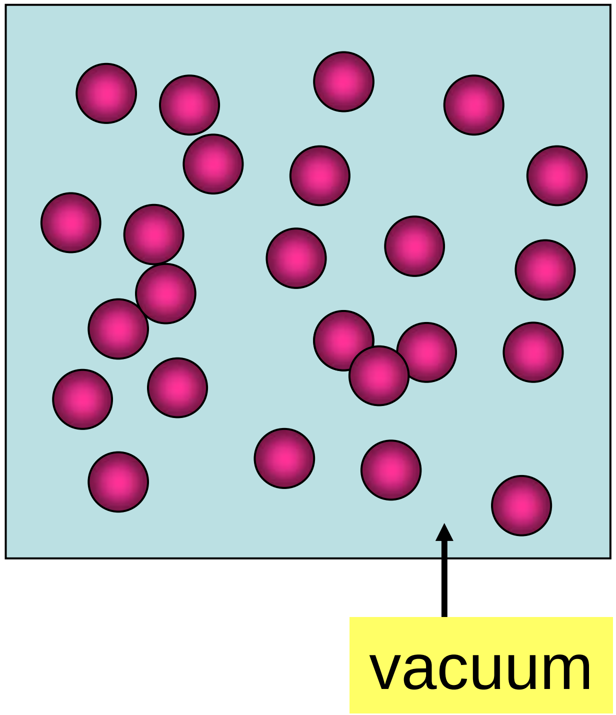
$$\left\langle Power \right\rangle \propto \left\langle E^2 \right\rangle = \left\langle E \right\rangle^2 + \left\langle \delta E^2 \right\rangle$$

$$ka \sim 1$$



Attempts

MODEL: Random system of identical spheres



$$a$$ identical

$$\mu = \mu_0$$ nonmagnetic

$$\left\{ \begin{array}{l} \varepsilon = \varepsilon_p(\omega) \\ n_p = \sqrt{\varepsilon_p(\omega)/\varepsilon_0} \\ \varepsilon_p(\omega) \equiv \varepsilon_0 + \frac{i}{\omega}\sigma_p(\omega) \end{array} \right.$$ local

$$k_0 = \frac{\omega}{c}$$

van de Hulst

Light scattering by small particles (1957)

$f \ll 1$ dilute

scattering matrix

$$\begin{pmatrix} E_{\parallel}^{s} \\ E_{\perp}^{s} \end{pmatrix} = \frac{e^{ikr}}{-ikr} \begin{pmatrix} S_2 & 0 \\ 0 & S_1 \end{pmatrix} \begin{pmatrix} E_{\parallel}^{inc} \\ E_{\perp}^{inc} \end{pmatrix}$$

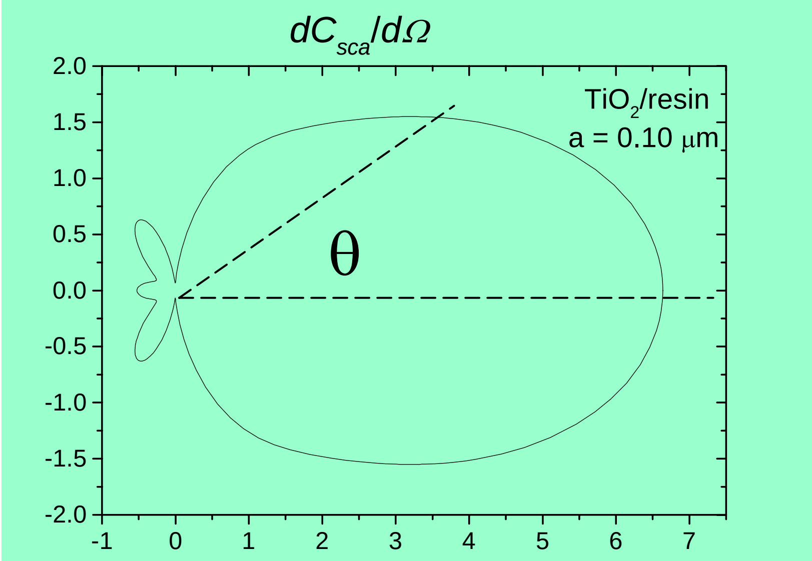
$$n_{eff} = 1 + i\gamma S(0)$$

δn_{eff} — complex

sphere $S_1(0) = S_2(0) = S(0)$

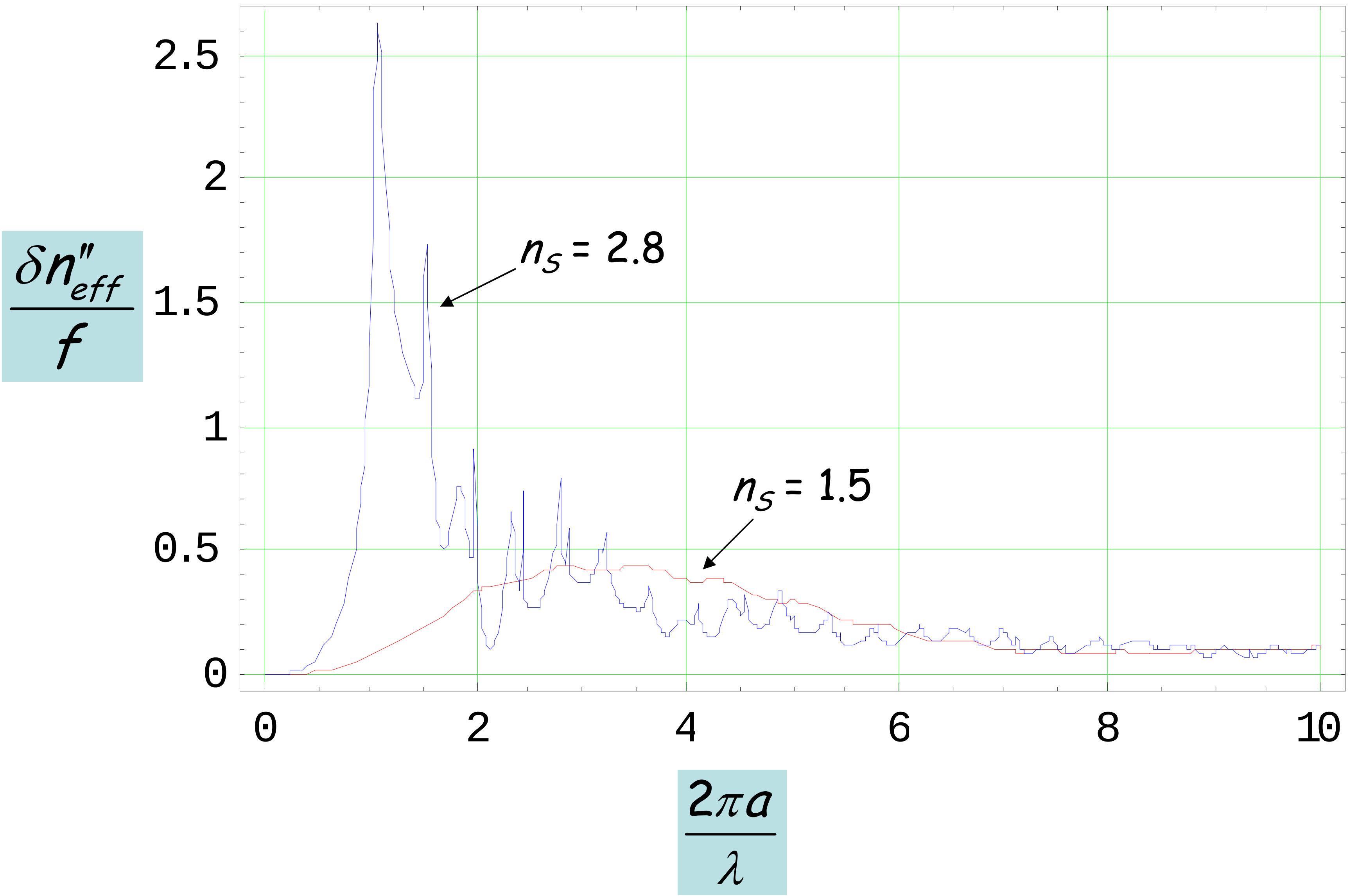
$$\gamma = \frac{3}{2}\frac{f}{(k_0 a)^3}$$

f: volume filling fraction



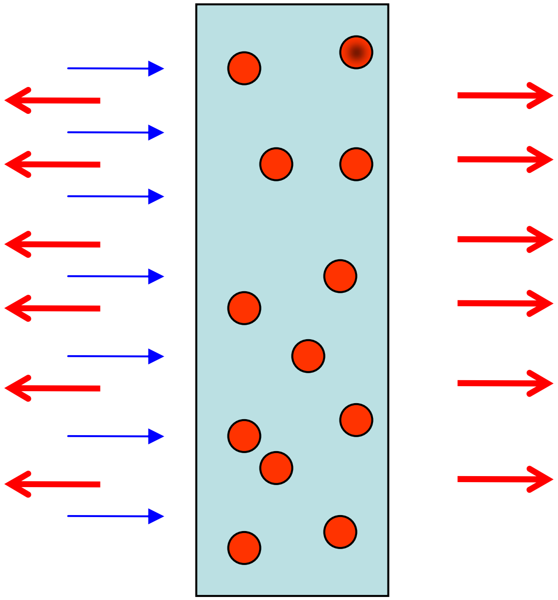
van de Hulst

scattering



Craig Bohren

J. Atmos Sci. 43, 468 (85)



transmission	$n_{eff} = 1 + i\gamma S(0)$
reflection	$n_{eff} = 1 + i\gamma S_1(\pi)$

$$r = \frac{\sqrt{\mu} - \sqrt{\varepsilon}}{\sqrt{\mu} + \sqrt{\varepsilon}}$$

Proposition

$$\varepsilon_{eff} = 1 + i\gamma\left[S(0) + S_1(\pi)\right]$$

$$\mu_{eff} = 1 + i\gamma\left[S(0) - S_1(\pi)\right]$$

MAGNETIC ?

RG Barrera & A García-Valenzuela

JOSA A **20**, 296 (2003)

COHERENT SCATTERING MODEL

$$\mu_{eff}^{TE}(\theta_i) = 1 + \frac{i\gamma S_-^{(1)}(\theta_i)}{\cos^2\theta_i}$$

MAGNETIC

$$\varepsilon_{eff}^{TE}(\theta_i) = 1 + i\gamma\left(2S_+^{(1)}(\theta_i) - S_-^{(1)}(\theta_i)\tan^2\theta_i\right)$$

$$S_+^{(1)}(\theta_i) = \frac{1}{2}\left[S(0) + S_1(\pi - 2\theta_i)\right]$$

$$S_-^{(1)}(\theta_i) = S(0) - S_1(\pi - 2\theta_i)$$

Small particles

$$S(0) = S_1(\pi - 2\theta_i)$$

$$\mu_{eff}^{TE} = 1$$

NON-MAGNETIC

Normal incidence

BOHREN

$$\varepsilon_{eff} = 1 + i\gamma\left[S(0) + S_1(\pi)\right]$$

$$\mu_{eff} = 1 + i\gamma\left[S(0) - S_1(\pi)\right]$$

Comment:
…a very unconfortable result…

Our new result

PRB **75**, 184202 (2007)

*IN TURBID COLLOIDAL SYSTEMS THE EFFECTIVE MEDIUM **EXISTS** BUT ITS ELECTROMAGNETIC RESPONSE IS **NONLOCAL***

Electromagnetic response

GENERALIZED EFFECTIVE CONDUCTIVITY

TOTAL →

$$\left\langle \vec{J}_{ind} \right\rangle = \hat{\sigma}_{eff} \left\langle \vec{E} \right\rangle$$

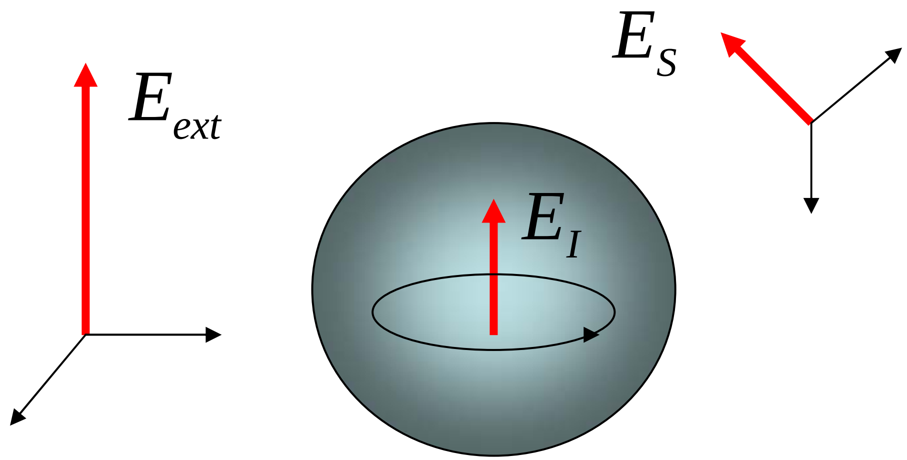
LINEAR OPERATOR

Nonlocal

$$\left\langle \vec{J}_{ind} \right\rangle (\vec{r};\omega) = \int \overleftrightarrow{\sigma}_{eff}(\vec{r},\vec{r}\,';\omega) \cdot \left\langle \vec{E} \right\rangle (\vec{r}\,';\omega)\, d^3 r'$$

local *vs* nonlocal

ISOLATED SPHERE



$$\sigma_S(\vec{r};\omega) = \begin{cases} \sigma_S(\omega) & \vec{r} \in V_S \\ 0 & \vec{r} \notin V_S \end{cases}$$

$$\vec{J}_{ind}(\vec{r};\omega) = \sigma_S(\vec{r};\omega)\vec{E}_I(\vec{r};\omega)$$

LOCAL

$$= \int \underbrace{\overleftrightarrow{\sigma}_S^{NL}(\vec{r},\vec{r}\,';\omega)}_{\text{NONLOCAL}} \cdot \vec{E}_{ext}(\vec{r}\,';\omega)\, d^3r'$$

NONLOCAL

Generalized NL conductivity

$$\overleftrightarrow{\sigma}_S^{NL}(\vec r,\vec r';\omega) =$$

$$U(\vec r;\omega)\left[\delta(\vec r-\vec r')\overleftrightarrow{I} + \int \overleftrightarrow{G}_0(\vec r,\vec r';\omega)\cdot\overleftrightarrow{\sigma}_S^{NL}(\vec r'',\vec r';\omega)d^3r''\right]$$

$$i\omega\mu_0\sigma_S(\vec r;\omega)$$

T matrix

$$i\omega\mu_0\overleftrightarrow{\sigma}_S^{NL}(\vec r,\vec r';\omega) \longrightarrow \overleftrightarrow{T}(\vec r,\vec r';\omega)$$

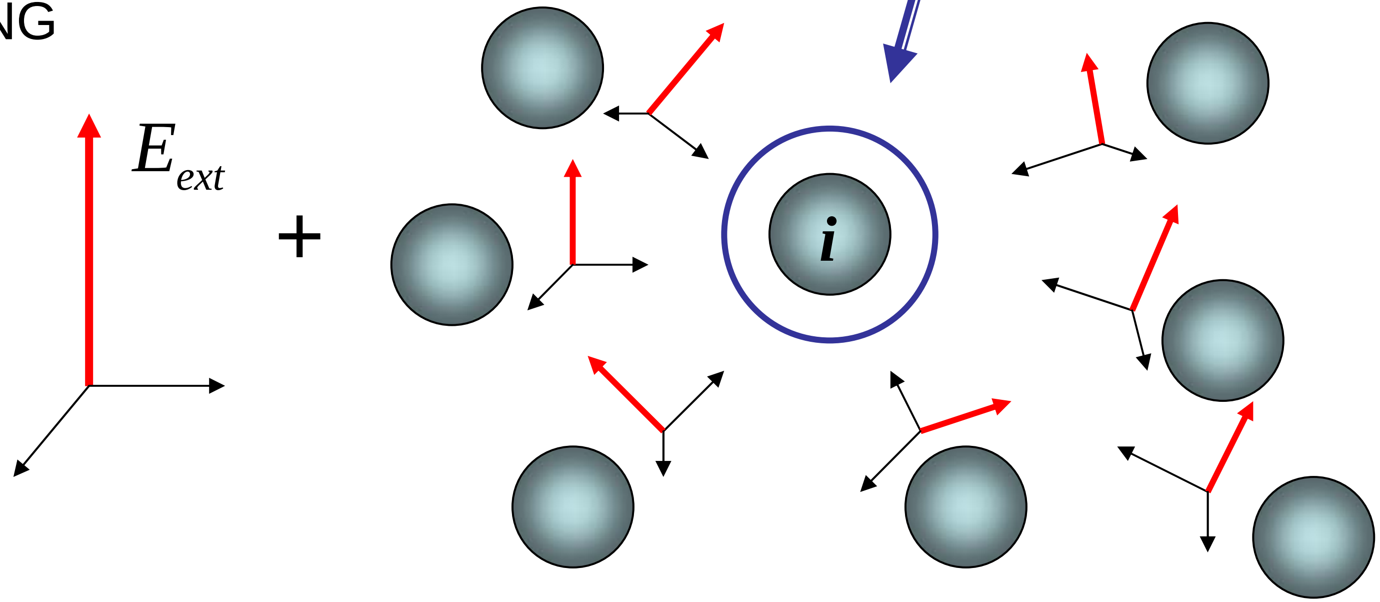
$$i\omega\mu_0\overleftrightarrow{\sigma}_S^{NL}(\vec p,\underline{\vec p'};\omega) \longrightarrow \overleftrightarrow{T}(\vec p,\vec p';\omega)$$

Total induced current

$$\vec{J}_{ind}(\vec{r};\omega) = \sum_i \vec{J}_{ind,i}(\vec{r};\omega)$$

$$= \sum_i \int \underbrace{\overleftrightarrow{\sigma}_S^{NL} \vec{r} - \vec{r}_i, \vec{r}\,' - \vec{r}_i; \omega)}_{\text{NONLOCAL}} \cdot \overbrace{\vec{E}_{exc,i}(\vec{r}\,'; \vec{r}_1, \vec{r}_2, \ldots \vec{r}_{i-1}, \vec{r}_{i+1}, \ldots \vec{r}_N; \omega)}^{\approx \left\langle \vec{E}(\vec{r}\,', \omega) \right\rangle} d^3 r'$$

EXCITING FIELD



Effective-Field Approximation

…valid in the dilute regime…

$$\vec{J}_{ind}(\vec{r};\omega) = \sum_i \int \overleftrightarrow{\sigma}_S^{NL}(\vec{r}-\vec{r}_i, \vec{r}\,'-\vec{r}_i;\omega) \cdot \left\langle \vec{E}(\vec{r}\,',\omega) \right\rangle d^3r'$$

$$\left\langle \vec{J}_{ind}(\vec{r};\omega) \right\rangle = \int \underbrace{\left\langle \sum_i \overleftrightarrow{\sigma}_S^{NL}(\vec{r}-\vec{r}_i, \vec{r}\,'-\vec{r}_i;\omega) \right\rangle}_{\overleftrightarrow{\sigma}_{eff}(|\vec{r}-\vec{r}\,'|;\omega)} \left\langle \vec{E}(\vec{r}\,',\omega) \right\rangle d^3r'$$

$\overleftrightarrow{\sigma}_{eff}(|\vec{r}-\vec{r}\,'|;\omega)$ ← GENERALIZED NONLOCAL CONDUCTIVITY

GENERALIZED NONLOCAL OHM'S LAW

Momentum representation

$$\langle \ldots \rangle \rightarrow \int \frac{d^3 r_i}{V_T}$$

NONLOCAL

$$\left\langle \vec{J} \right\rangle^{ind} (\vec{p},\omega) = \overleftrightarrow{\sigma}_{eff} (\vec{p},\omega) \cdot \left\langle \vec{E} \right\rangle (\vec{p},\omega)$$

$$\boxed{\overleftrightarrow{\sigma}_{eff} (\vec{p},\omega) = n_0 \overleftrightarrow{\sigma}_S^{NL} (\vec{p},\vec{p}' = \vec{p};\omega)}$$

$$n_0 = \frac{N}{V}$$

FT

$$\overleftrightarrow{\sigma}_S^{NL} (\vec{r},\vec{r}';\omega) \rightarrow \overleftrightarrow{\sigma}_S^{NL} (\vec{p},\vec{p}';\omega) \rightarrow \overleftrightarrow{\sigma}_S^{NL} (\vec{p},\underline{\vec{p}' = \vec{p}};\omega)$$

3 X 3 = 9

INTEGRAL EQUATION

LT scheme

homogeneous and isotropic “on the average”

$$\overleftrightarrow{\sigma}_{eff}(\vec{p};\omega) = \sigma^{L}_{eff}(p,\omega)\hat{p}\hat{p} + \sigma^{T}_{eff}(p,\omega)(\overline{\overline{1}} - \hat{p}\hat{p})$$

2

generalized effective nonlocal dielectric function

$$\overleftrightarrow{\varepsilon}_{eff}(\vec{p};\omega) = \overleftarrow{1}\varepsilon_0 + \frac{i}{\omega}\overleftrightarrow{\sigma}_{eff}(\vec{p};\omega)$$

“tradition”

$$\varepsilon^{L}_{eff}(p,\omega) \qquad \varepsilon^{T}_{eff}(p,\omega)$$

$pa \rightarrow 0$

Small pa

$$\tilde{\varepsilon}_{eff}^{L(T)}(p,\omega) = \tilde{\varepsilon}_{eff}^{[0]}(\omega) + \tilde{\varepsilon}_{eff}^{L(T)[2]}(\omega)\left(\underline{pa}\right)^2 + \ldots$$

$$\tilde{\varepsilon} \equiv \frac{\varepsilon}{\varepsilon_0}$$

$p \to 0$ "LOCAL LIMIT"

NONLOCAL DEPENDENCE

Calculation procedure

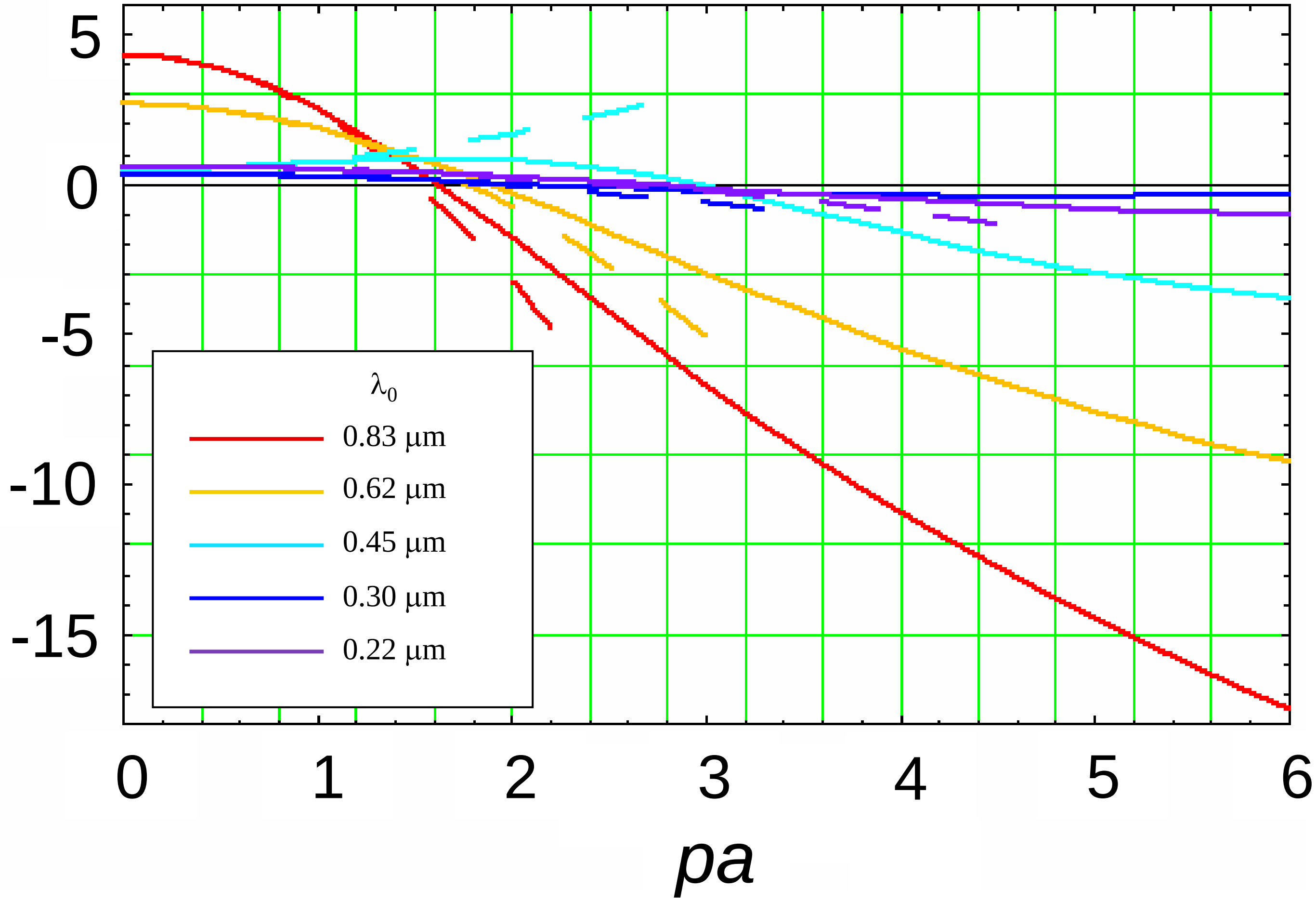
Phys. Rev. B, **75**, 184202 (2007)

Results

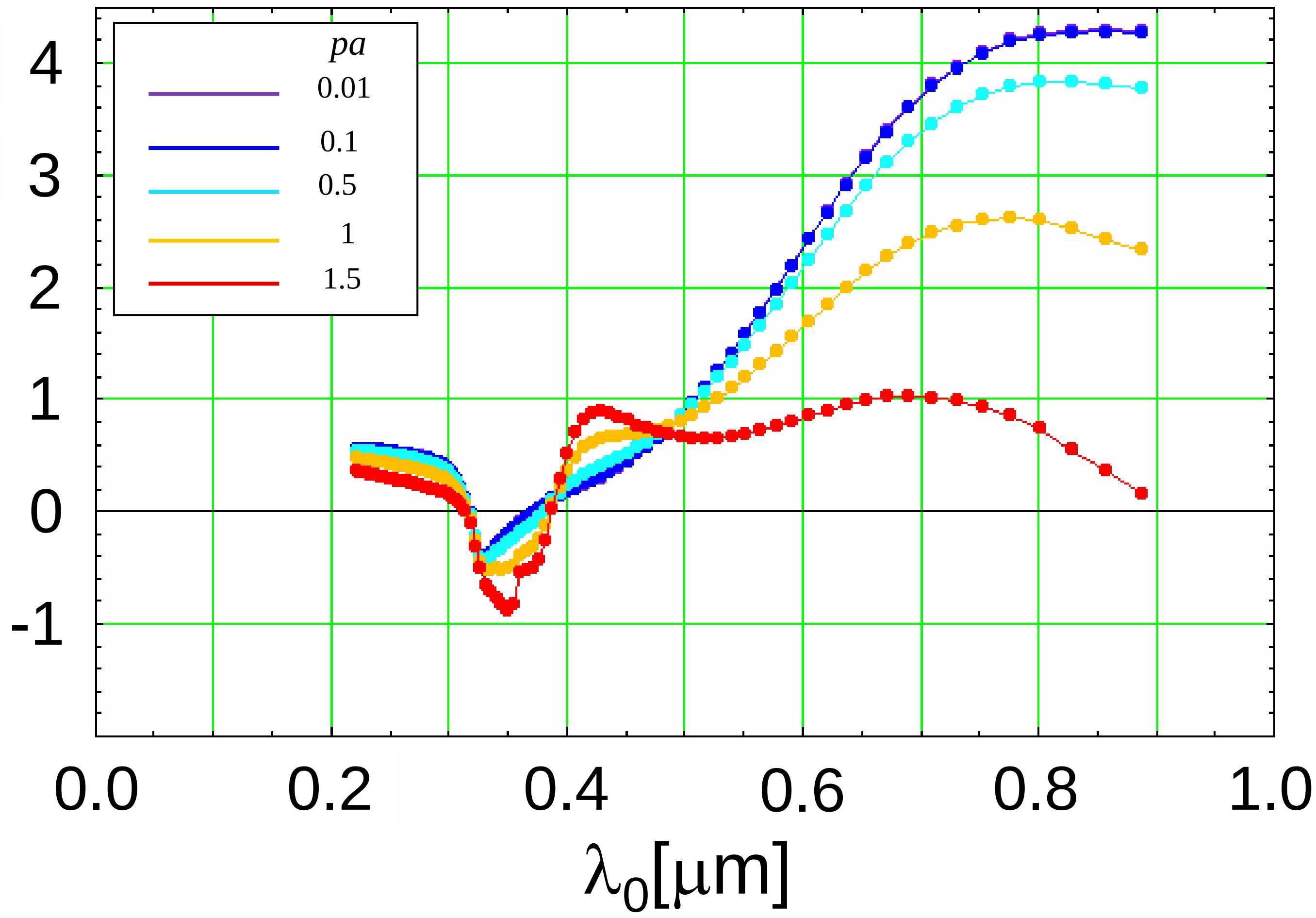
$$\varepsilon^T(p,\omega) = 1 + f \ \Delta$$

$$\frac{\varepsilon^T(p,\omega) - 1}{f} = \Delta$$

$$\frac{\mathrm{Re}[\tilde{\varepsilon}^{T}_{eff}(p,\omega)]-1}{f} \quad \textit{for Ag (radius} = 0.1\mu m)$$



$$\frac{\mathrm{Re}[\tilde{\varepsilon}_{eff}^{T}(p,\omega)]-1}{f} \quad for\ \ Ag\,(radius = 0.1\mu m)$$



Electromagnetic modes

$$p = p' + ip''$$

dispersion relation

longitudinal $\tilde{\varepsilon}^{L}_{eff}(p,\omega) = 0$

transverse $p = k_0 \sqrt{\tilde{\varepsilon}^{T}_{eff}(p,\omega)}$

$\Rightarrow$

$p^L(\omega)$

$p^T(\omega)$

effective index of refraction

$$p^T(\omega) = k_0 n_{eff}(\omega)$$

GENEALOGY $\equiv$

$p = k_0 \sqrt{\tilde{\varepsilon}^{T}_{eff}(p,\omega)}$ nonlocal

$p = k_0 \sqrt{\tilde{\varepsilon}^{T}_{eff}(p \to 0;\, \omega)}$ local

Comparisons

Exact

$$p = k_0 \sqrt{\tilde{\varepsilon}^{T}_{eff}(p,\omega)}$$

$$n_{eff}(\omega) = \frac{p^{T}(\omega)}{k_0}$$

Long wavelength approximation

local

$$p = k_0 \sqrt{\tilde{\varepsilon}^{[0]}_{eff}(\omega)} \Rightarrow n_{eff} = \sqrt{\tilde{\varepsilon}^{[0]}(\omega)}$$

Comparisons

Quadratic approximation

$$p = k_0 \sqrt{\tilde{\varepsilon}^{[0]}(\omega) + \tilde{\varepsilon}^{T[2]}(\omega)(pa)^2 + \ldots} \quad \Rightarrow \quad n_{eff} = \sqrt{\frac{\varepsilon^{[0]}(\omega)}{1-(k_0 a)^2\, \tilde{\varepsilon}^{T[2]}(\omega)}}$$

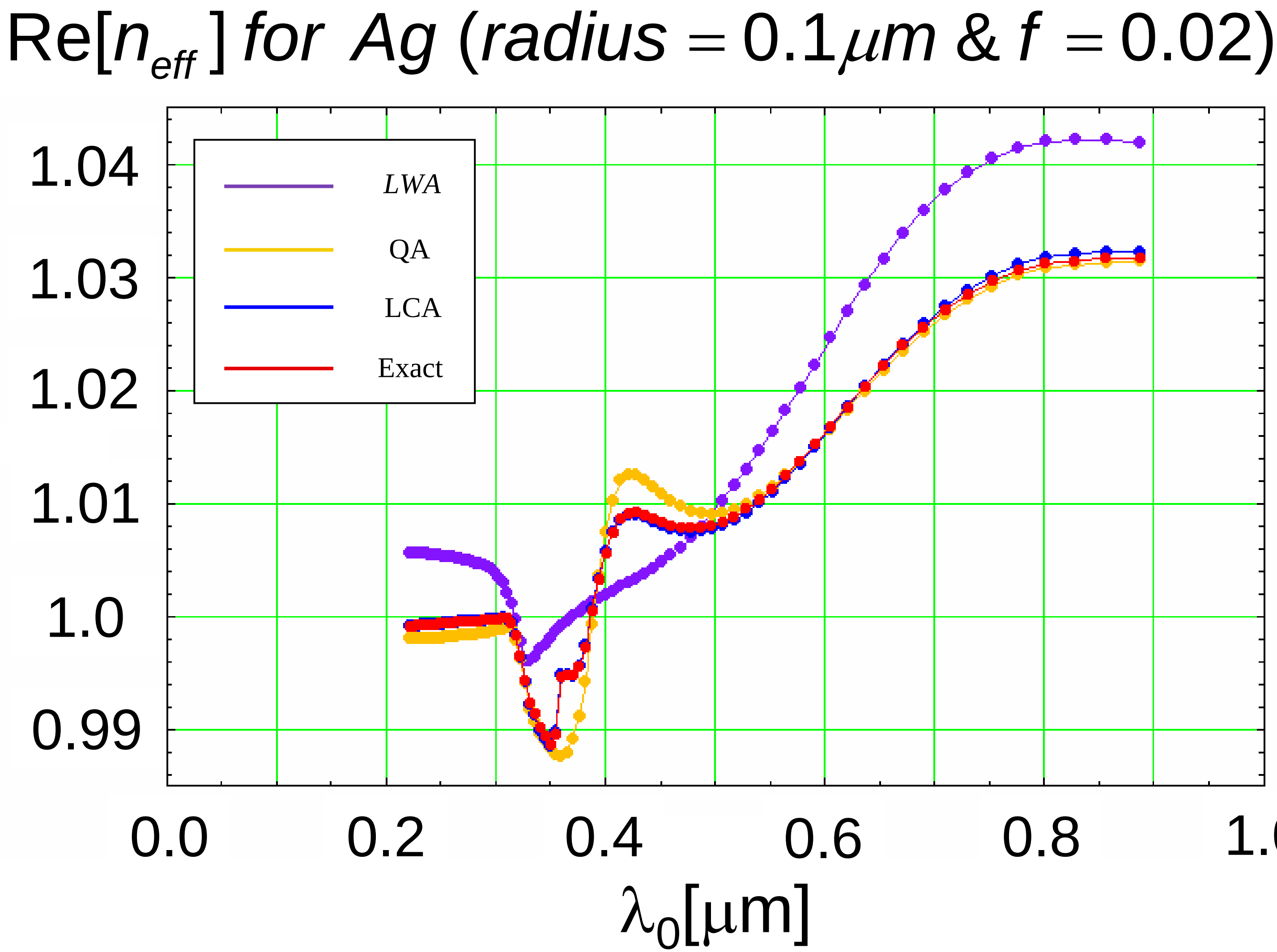
nonlocal

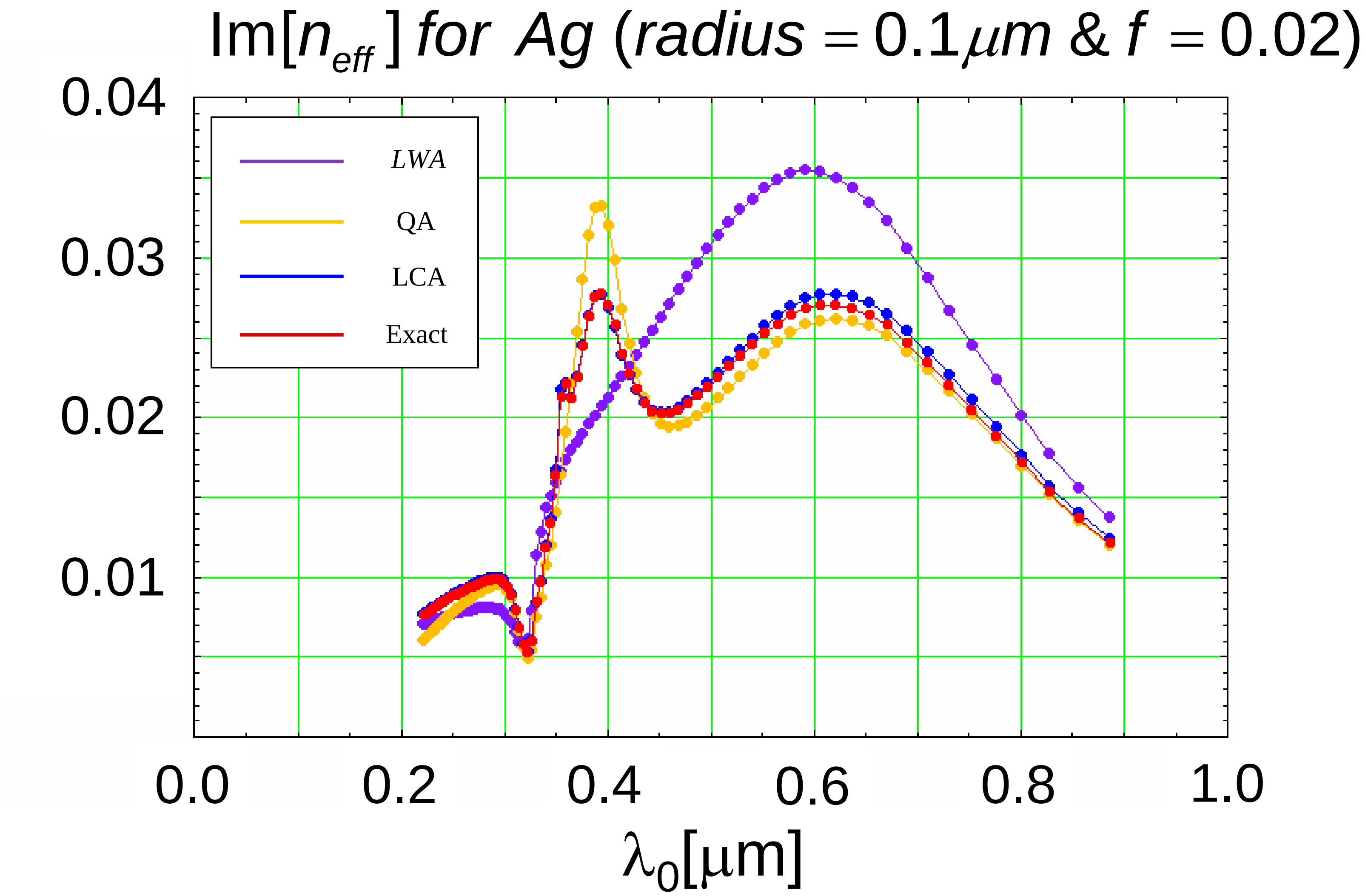
Light-cone approximation

$$p^2 = k_0^2\, \tilde{\varepsilon}^T(p = k_0, \omega) \quad \Rightarrow \quad n_{eff} = 1 + i\gamma S(0)$$

nonlocal

van de Hulst


Re[n_{eff}] for Ag (radius = 0.1μm & f = 0.02)
LWA
QA
LCA
Exact
1.04
1.03
1.02
1.01
1.0
0.99
0.0
0.2
0.4
0.6
0.8
1.0
λ_0[μm]



Im[n_{eff}] for Ag (radius = 0.1μm & f = 0.02)
0.04
0.03
0.02
0.01
LWA
QA
LCA
Exact
0.0
0.2
0.4
0.6
0.8
1.0
λ_0[μm]

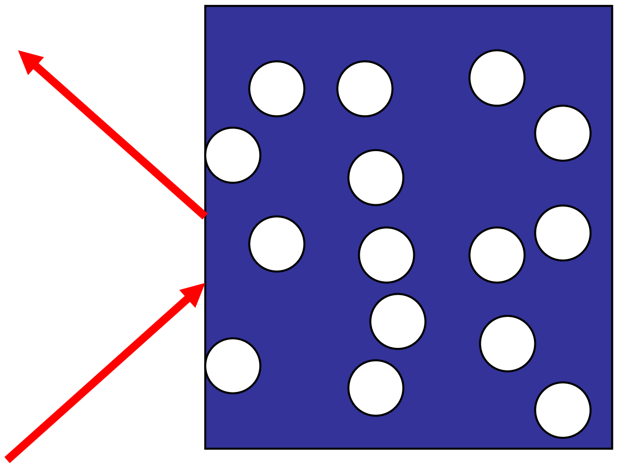
Reflection problem

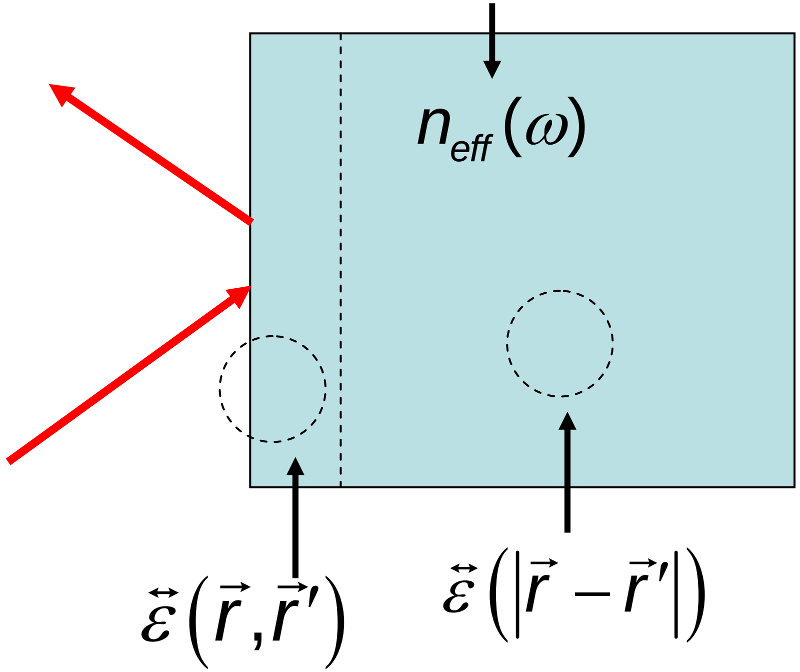
translational invariance

nonlocal nature

$\varepsilon^{T}_{eff}(p,\omega)$

$\varepsilon^{L}_{eff}(p,\omega)$

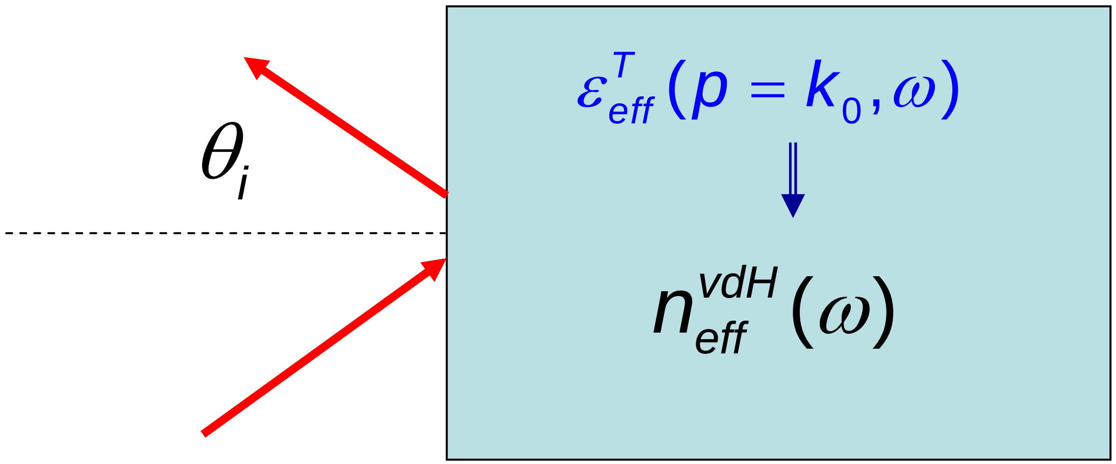




$n_{eff}(\omega)$ cannot be used in local CE (Fresnel's relations)

Abuse

nonlocal nature



LCA

$$R^{Fresnel}(\theta_i; n^{vdH}_{eff})$$

IEMM Isotropic effective-medium model

Internal Reflection configuration

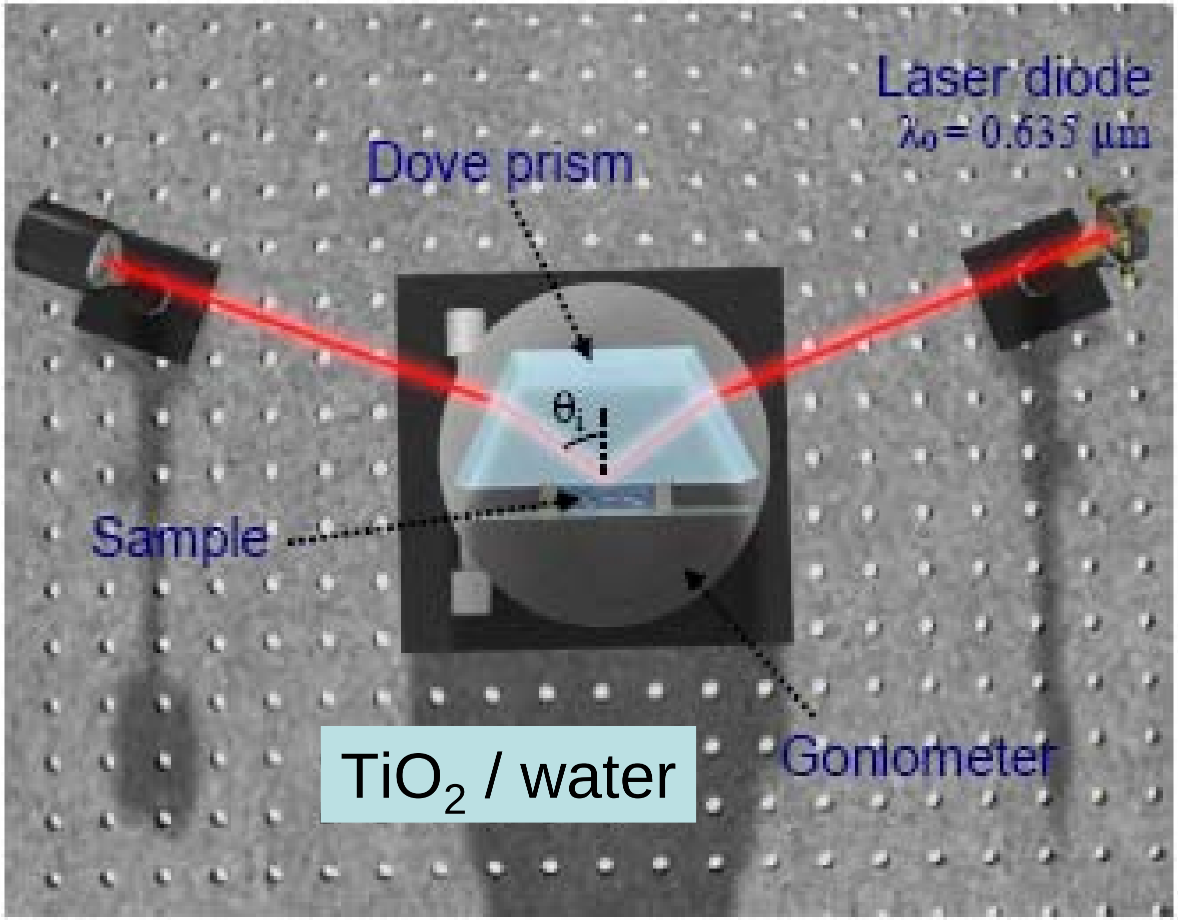
milk?

Internal reflection configuration

great sensitivity

IEMM

$$R^{Fresnel}(\theta_i; n_{eff}^{vdH})$$

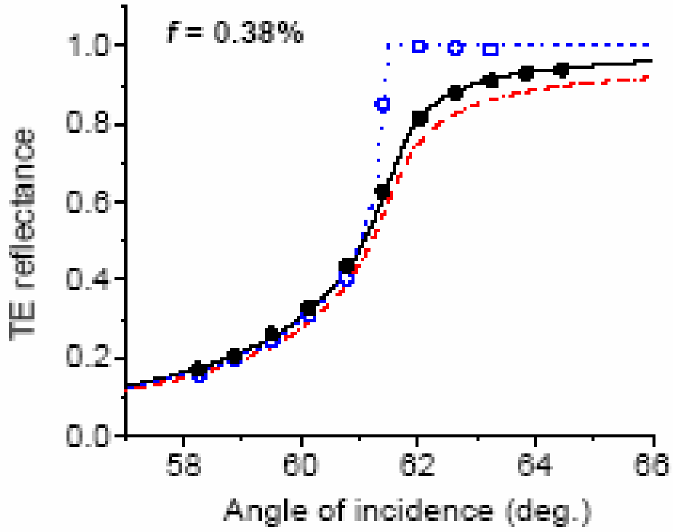


A García-Valenzuela, RG Barrera,
C. Sánchez-Pérez, A. Reyes-Coronado,
E Méndez, Optics Express, **13**, 6723 (2005)

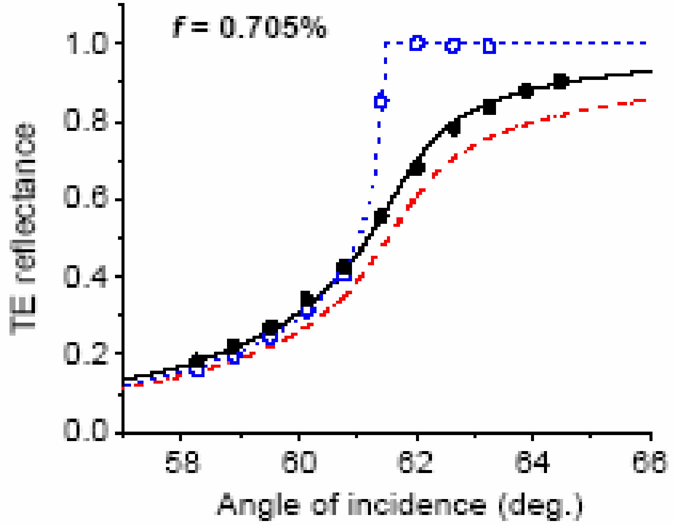
$$R(\theta_i)$$

Comparison

TiO_2 / water



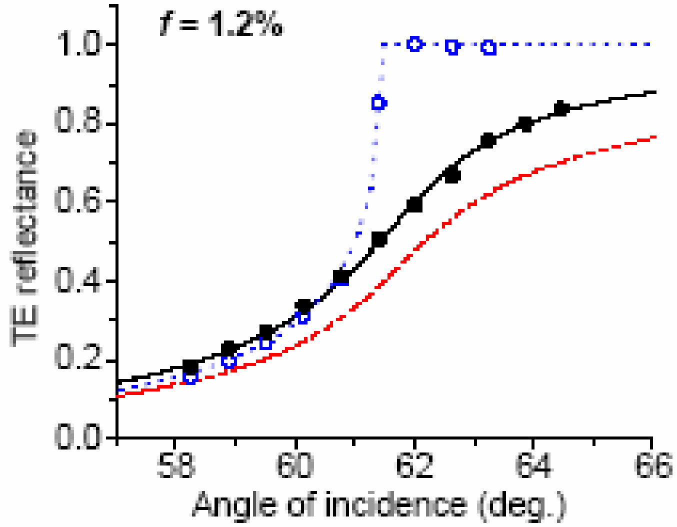
(a)



(b)

$$a_0 = 112 \text{ nm}$$

$$\sigma = 1.33$$



(c)

Pure water

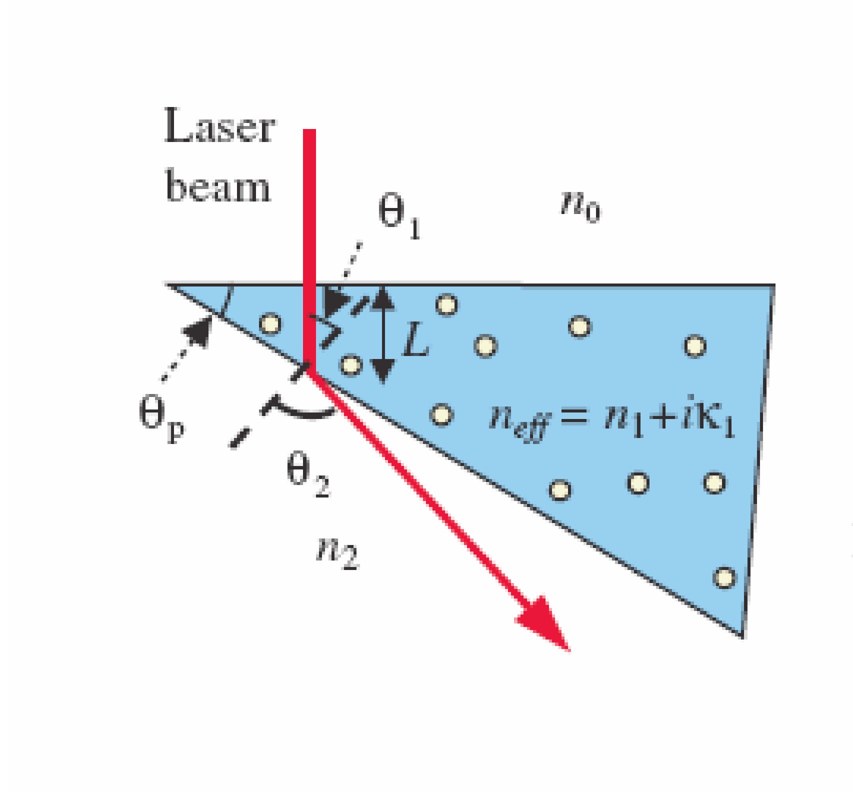
IEMM

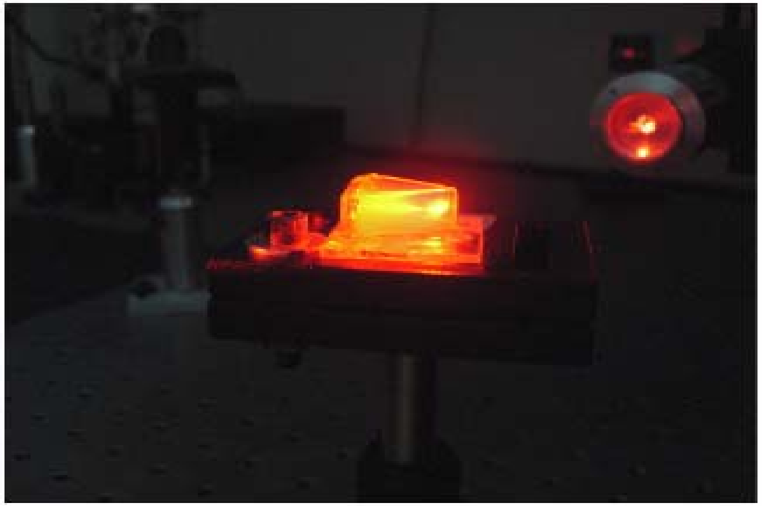
CSM

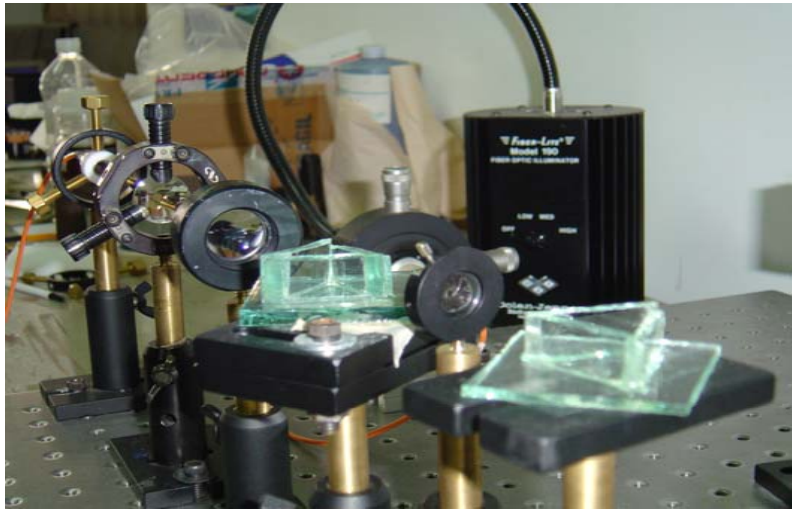
How to measure n_{eff}?

Latex spheres / water

Use refraction (propagation)







A. Reyes-Coronado, A García-Valenzuela,
C. Sánchez-Pérez, RG Barrera
New Journal of Physics **7** (2005) 89 [1-22]

Comparison

Fit with $n_{eff}^{van\ de\ Hulst}$

Table 1. Retrieved and nominal values of experimental parameters.

Particle size	Retrieved values	Nominal values
Small spheres	$a = 0.1076\ \mu m$	$a = 0.111 \pm 0.005\ \mu m$
	$n_{sphere} = 1.566$	$n_{sphere} = 1.588$
	$\theta_1 = 47.955°$	$\theta_1 = 48.1 \pm 0.22°$
	$L = 2.039$ mm	$L = 1.9 \pm 0.25$ mm
Medium spheres	$a = 0.155\ \mu m$	$a = 0.155 \pm 0.007\ \mu m$
	$n_{sphere} = 1.588$	$n_{sphere} = 1.588$
	$\theta_1 = 48.175°$	$\theta_1 = 48.1 \pm 0.22°$
	$L = 2.05$ mm	$L = 2 \pm 0.25$ mm
Large spheres	$a = 0.247\ \mu m$	$a = 0.24 \pm 0.01\ \mu m$
	$n_{sphere} = 1.55$	$n_{sphere} = 1.588$
	$\theta_1 = 48.337°$	$\theta_1 = 48.1 \pm 0.22°$
	$L = 1.65$ mm	$L = 1.9 \pm 0.25$ mm

NEXT STEP → CBS

$\epsilon\ \mu$ scheme

$$\left\langle \vec{J}_{ind} \right\rangle = \vec{J}_P + \vec{J}_M$$

$$\tilde{\varepsilon}_{eff}(p,\omega) = \varepsilon^L(p,\omega)$$

$$\tilde{\mu}_{eff}(p,\omega) = \frac{1}{1 - \frac{k_0^2}{p^2}\left(\varepsilon_{eff}^T(p,\omega) - \varepsilon_{eff}^L(p,\omega)\right)}$$

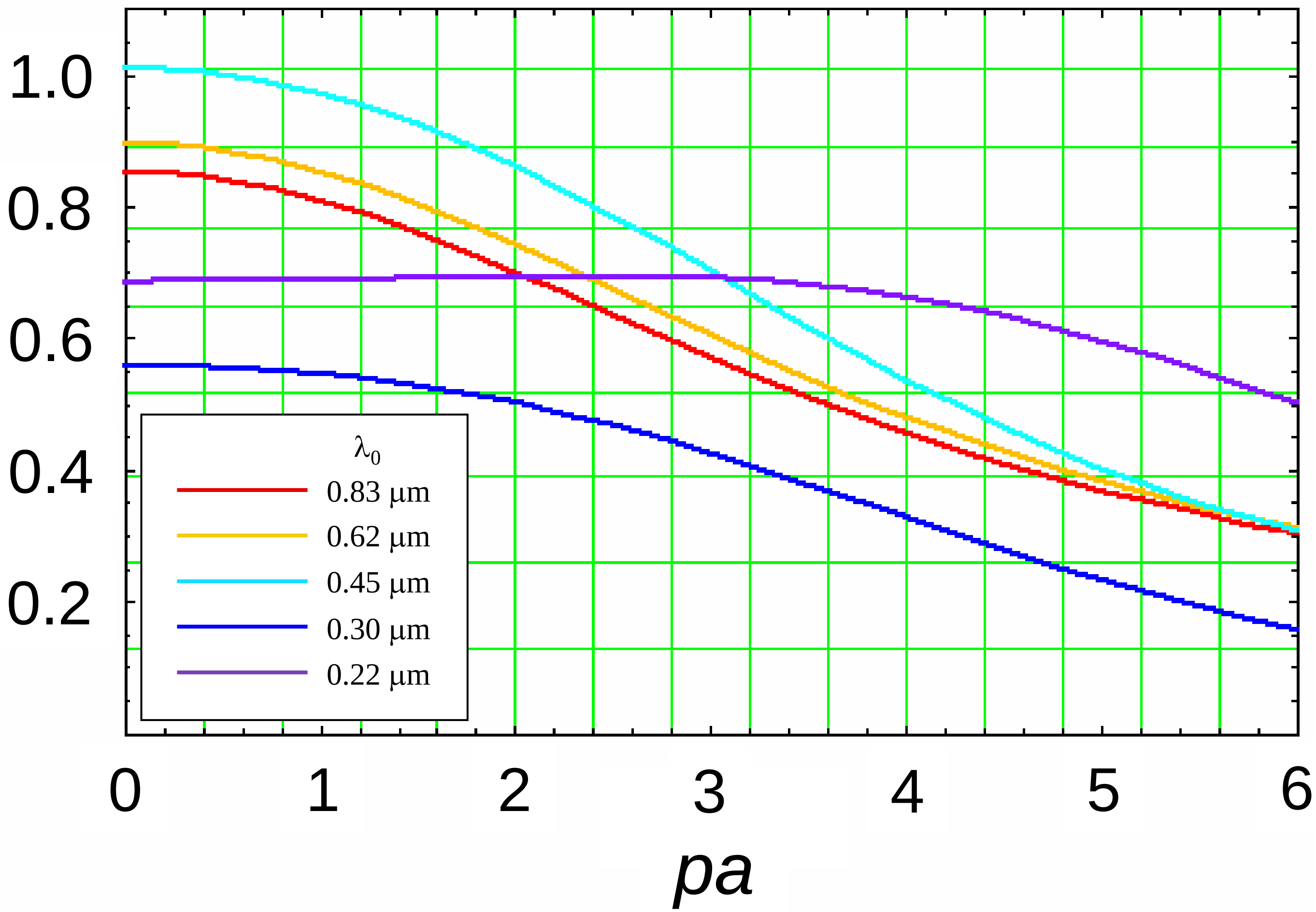
magnetic response !

Results

$$\tilde{\mu}_{eff}(p,\omega) = \frac{1}{1 - \frac{k_0^2}{p^2}\left(\underline{\varepsilon_{eff}^T(p,\omega) - \varepsilon_{eff}^L(p,\omega)}\right)}$$

$$\frac{1}{\tilde{\mu}_{eff}(p,\omega)} - 1 = -\frac{k_0^2}{p^2}\left(\underline{\varepsilon_{eff}^T(p,\omega) - \varepsilon_{eff}^L(p,\omega)}\right)$$

$$\frac{1}{f}\mathrm{Re}\left[\frac{1}{\tilde{\mu}_{eff}(p,\omega)}\right]-1 \quad for\ Ag\ (radius = 0.1\mu m)$$



OPTICAL MAGNETISM

Conclusions

We have developed an effective-medium approach to describe the optical properties of turbid colloids in the bulk, that is useful and complimentary to the multiple-scattering approach

In turbid colloidal systems the effective index of refraction, due to its nonlocal character, is able to describe the *propagation* of light, but it cannot describe its *reflection*

This is important because the naïve use of the effective index of refraction in the calculation of reflection amplitudes has been done many times without too much (intellectual) reflection

There is a nonlocal magnetic response in turbid colloidal systems even when its components are non magnetic (optical magnetism)

Perspectives

BULK

LONGITUDINAL MODES

$$\varepsilon^{L}(\vec{p},\omega) = 0$$

PROPAGATING MODES

DO THEY EXIST ?

ENERGY TRANSFER

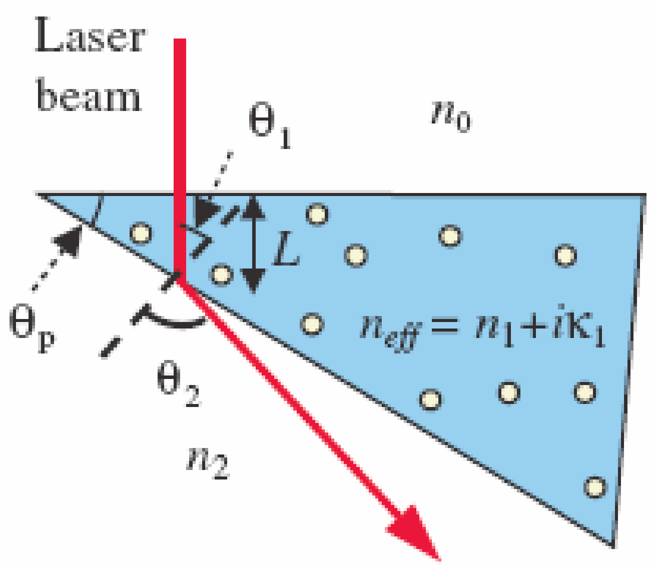
$$\vec{S} = \vec{E} \times \vec{H} = \vec{E} \times \hat{\mu}^{-1}\vec{B}$$

$$\vec{p}(\omega) \times \vec{E} = k_0 n_{eff}(\omega)\hat{p} \times \vec{B}$$

$$\vec{S} \cdot \hat{p} = ?$$

LEFTHANDED ?

Coherent-beam specroscopy



$n_{eff}(\lambda_0)$ → nonlocal effective-medium approach →
- particle-size distribution
- optical properties of the colloidal particles

Reflection

Coherent beam spectroscopy