Recent Advances on the Effective Optical Properties of Turbid Colloids

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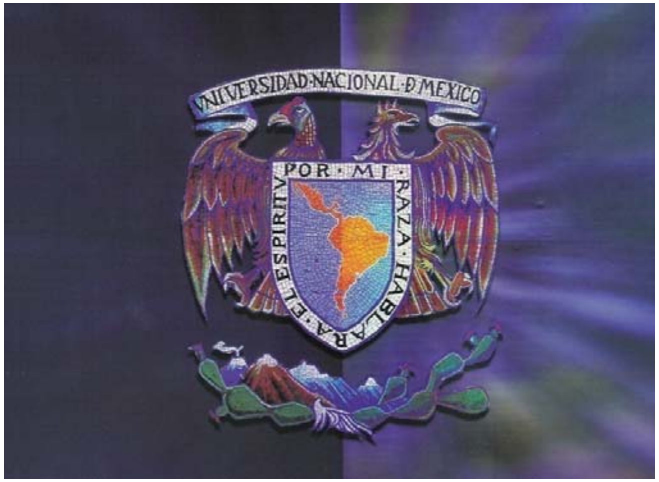

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Felipe Pérez

Luis Mochán

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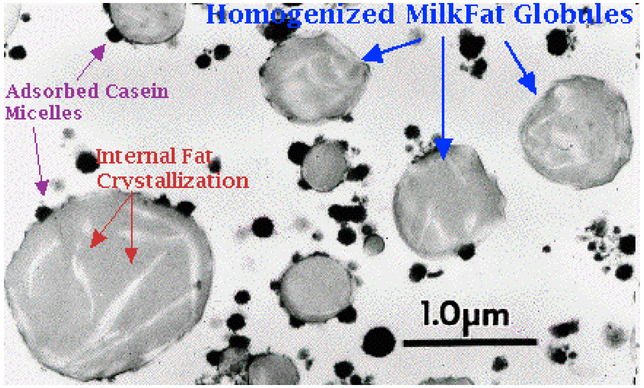
The problem

index of refraction of complex fluids

milk

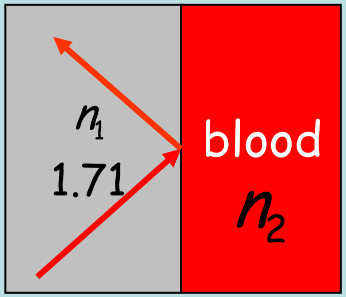


blood

optical properties

Refractive index

refractometer



Abbe-type

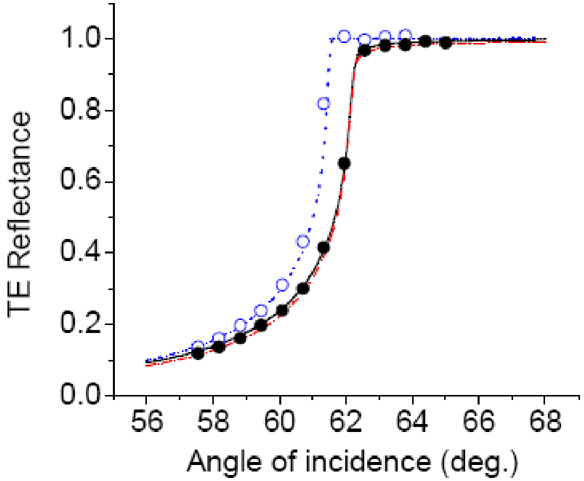
refraction

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

actually $\quad n_2 = n_2' + i n_2''$

reflectance

critical-angle refractometry



non-magnetic $\quad \mu_2 = \mu_0$

$$n_2 = \sqrt{\varepsilon_2 / \varepsilon_0} = n_2' + i n_2''$$

FIT

Fresnel´s relations

$$|r|^2 (n_2', n_2''; \theta_i)$$

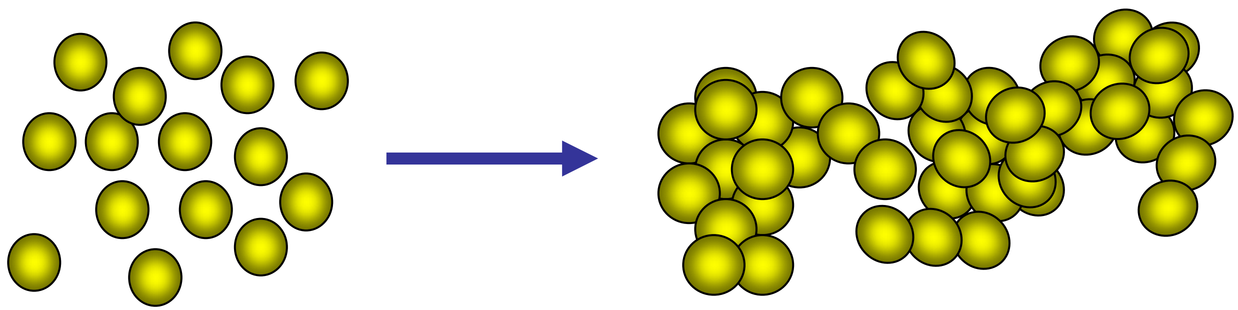
Applications

changes in structure $n_2 \to n_2 + \delta n_2$

δn_2 → states of aggregation

real time

MODEL

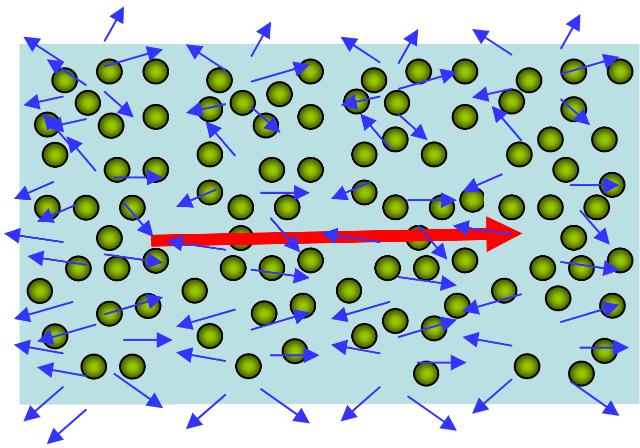


1.3333 → 1.3462 → 1.3489... $10^{-3} - 10^{-4}$

n_m n_2 δn_2

Index of refraction in continuum electrodynamics

Electrodynamics of continuous media

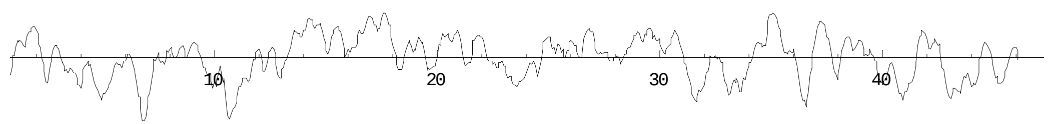


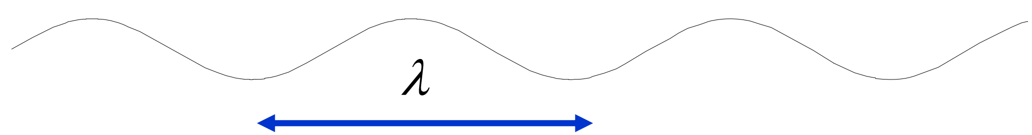
average fluctuations

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

spatial average

Average





$$\langle \vec{E} \rangle$$

macroscopic
coherent

Average power

Plane waves

$$\vec{S}=\frac{1}{2}\mathrm{Re}\left(\vec{E}\times\vec{H}^{*}\right)=\frac{1}{2}\mathrm{Re}\left[\left(\langle\vec{E}\rangle+\delta\vec{E}\right)\times\left(\langle\vec{H}\rangle+\delta\vec{H}\right)^{*}\right]=\langle\vec{S}\rangle+\cancel{\delta\vec{S}}$$

not enough

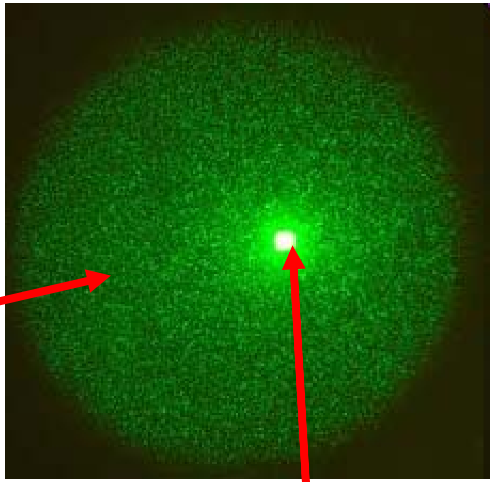
$$\langle\vec{S}\rangle=\underbrace{\langle\vec{E}\rangle\times\langle\vec{H}\rangle}_{\langle\vec{S}\rangle_{coh}}+\underbrace{\langle\delta\vec{E}\times\delta\vec{H}\rangle}_{\langle\vec{S}\rangle_{diffuse}}$$

$$\langle\vec{S}\rangle_{coh}\gg\langle\vec{S}\rangle_{diffuse}$$

one neglects the power carried by the diffuse field

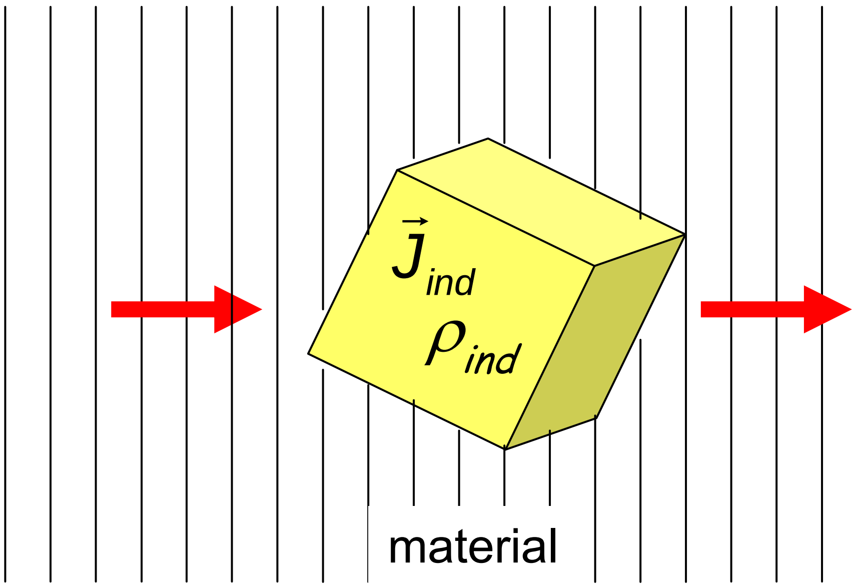
$\langle\vec{S}\rangle$

$\langle\vec{S}\rangle_{diffuse}$



$\langle\vec{S}\rangle_{coh}$

Average induced current



AVERAGE

$$\rho_{ind} \rightarrow \left\langle \rho_{ind} \right\rangle$$

$$\vec{J}_{ind} \rightarrow \left\langle \vec{J}_{ind} \right\rangle$$

$$\nabla \cdot \left\langle \vec{J}_{ind} \right\rangle + \frac{\partial \left\langle \rho_{ind} \right\rangle}{\partial t} = 0$$

Traditional approach $(\vec{P}, \vec{M})$

$$\left\langle \vec{J}_{ind} \right\rangle = \underbrace{\frac{\partial \vec{P}}{\partial t}}_{\vec{J}_P} + \underbrace{\nabla \times \vec{M}}_{\vec{J}_M}$$

MATERIAL FIELDS

polarization $\vec{P}$

magnetization $\vec{M}$

Tradition

Displacement field $\vec{D} = \varepsilon_0 \left\langle \vec{E} \right\rangle + \vec{P}$

H field $\vec{H} = \dfrac{\left\langle \vec{B} \right\rangle}{\mu_0} - \vec{M}$

Linear materials

Isotropic and homogeneous “*on the average*”

$$\vec{D} = \hat{\varepsilon} \left\langle \vec{E} \right\rangle \qquad \vec{H} = \hat{\mu}^{-1} \left\langle \vec{B} \right\rangle$$

Frequency domain

a_{NL}

time dispersion

$$\vec{D}(\vec{r},\omega) = \int \varepsilon(|\vec{r} - \vec{r}'|;\omega) \left\langle \vec{E} \right\rangle (\vec{r}',\omega) d^3 r' \qquad \vec{H}(\vec{r},\omega) = \int d^3 r' \mu^{-1}(|\vec{r} - \vec{r}'|;\omega) \left\langle \vec{B} \right\rangle (\vec{r}',\omega)$$

non-local

$\varepsilon(\vec{k},\omega)$ spatial dispersion $\dfrac{1}{\mu(\vec{k},\omega)}$

electric permittivity

magnetic permeability

Local optics

$$a_{NL} \ll \lambda$$

long-wavelength limit $(k \to 0)$

$$\varepsilon(k \to 0, \omega) = \underline{\varepsilon(\omega)}$$

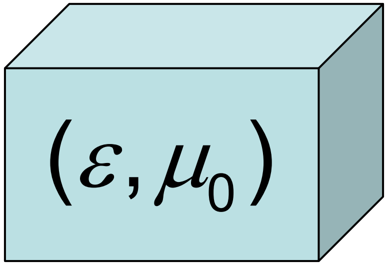
$$\mu(k \to 0, \omega) = \underline{\mu(\omega)}$$

$$\varepsilon(\omega) = \varepsilon'(\omega) + \underline{i\,\varepsilon''(\omega)}$$

$$\mu(\omega) \approx \mu_0$$

dissipation

Index of refraction



$$n(\omega) = \sqrt{\varepsilon(\omega) / \varepsilon_0}$$

$$= n'(\omega) + i\,n''(\omega)$$

"continuum"

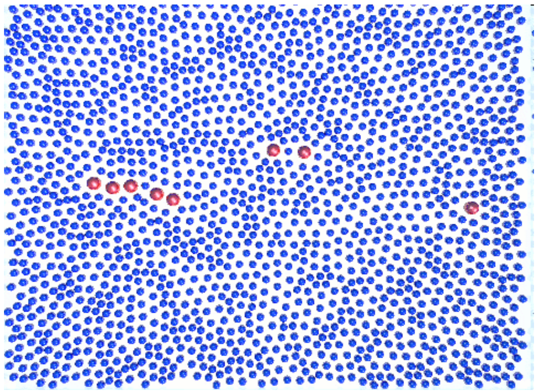
How about inhomogeneous materials?

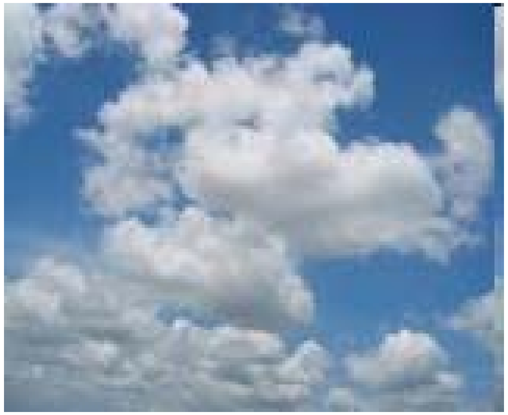
Can one extend the continuum approach?

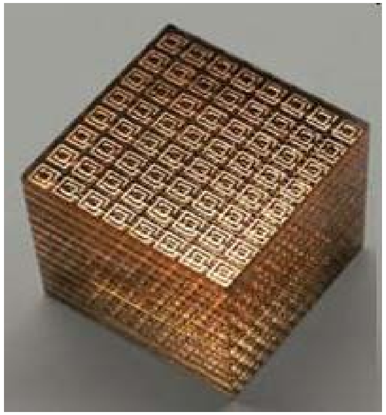
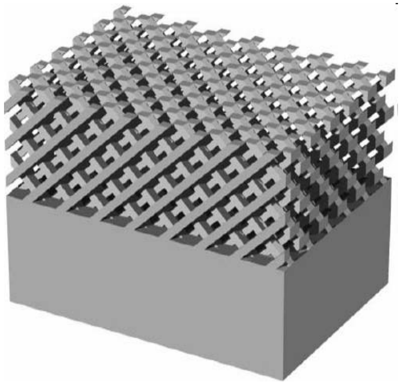
colloids

dispersed phase / homogeneous phase

EXAMPLES



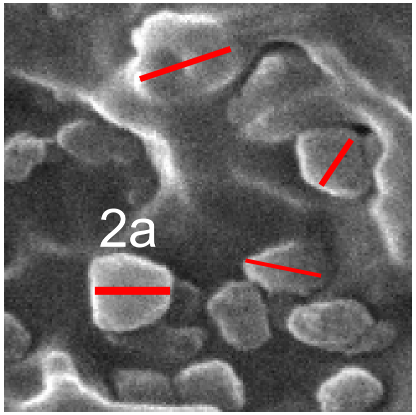



colloidal particles / matrix

“ordered” colloids

Optical properties

SIZE



gold colloids

transparency

turbidity

size parameter

$$ka = \frac{2\pi a n}{\lambda_0}$$

$$ka \ll 1$$

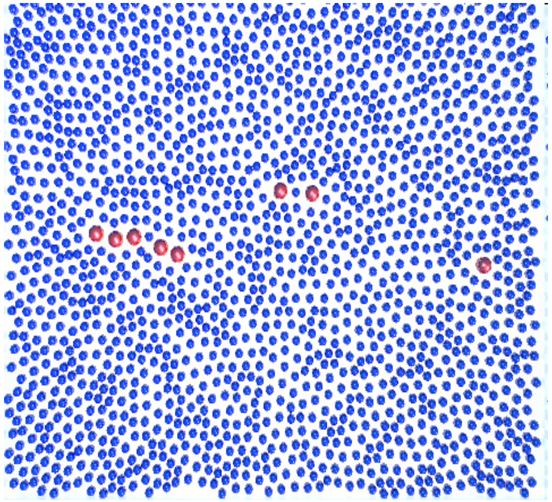
$$ka \sim 1$$

$$\langle \vec{S} \rangle_{diffuse} \ll \langle \vec{S} \rangle_{coh}$$

$$\langle \vec{S} \rangle_{diffuse} \sim \langle \vec{S} \rangle_{coh}$$

Effective-medium approach

homogenization



$$(\tilde{\varepsilon}_{eff}, \mu_{eff})$$

$$n_{eff} = \sqrt{\tilde{\varepsilon}_{eff}\,\mu_{eff}}$$

continuum

small particles $ka \ll 1$

always possible…
although it may be difficult

UNRESTRICTED

advantage

electrodynamics
of
continuous media

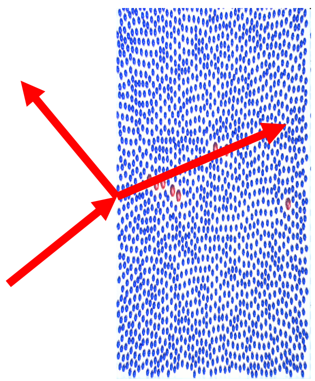
optical properties

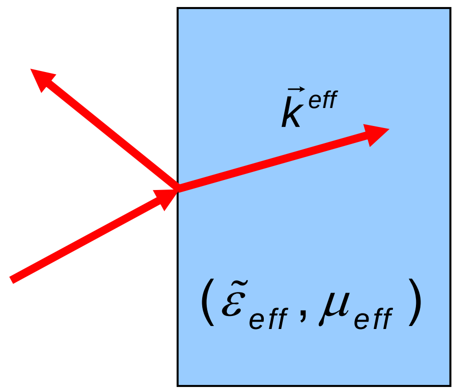
Reflection & refraction

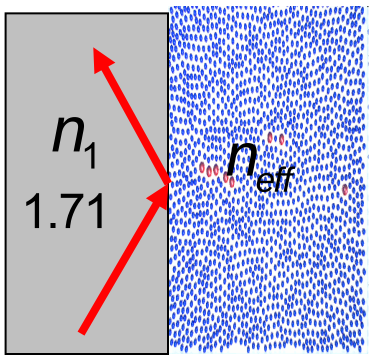
unrestricted

measurement

critical-angle
refractometry



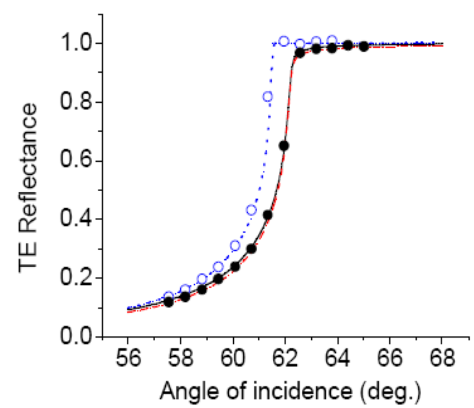




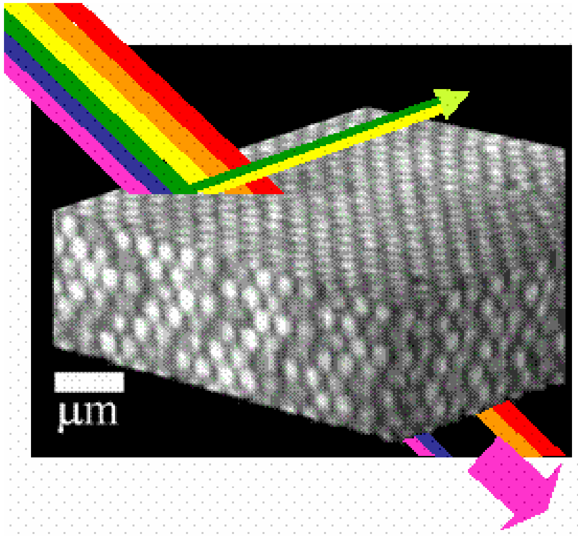
$$k^{eff} = k_0 n_{eff} \approx k_0 \sqrt{\varepsilon_{eff}}$$

Fresnel´s relation

$$r_p = \frac{\varepsilon_{eff} k_z^i - \varepsilon_0 k_z^{eff}}{\varepsilon_{eff} k_z^i + \varepsilon_0 k_z^{eff}}$$



$$ka \sim 1$$

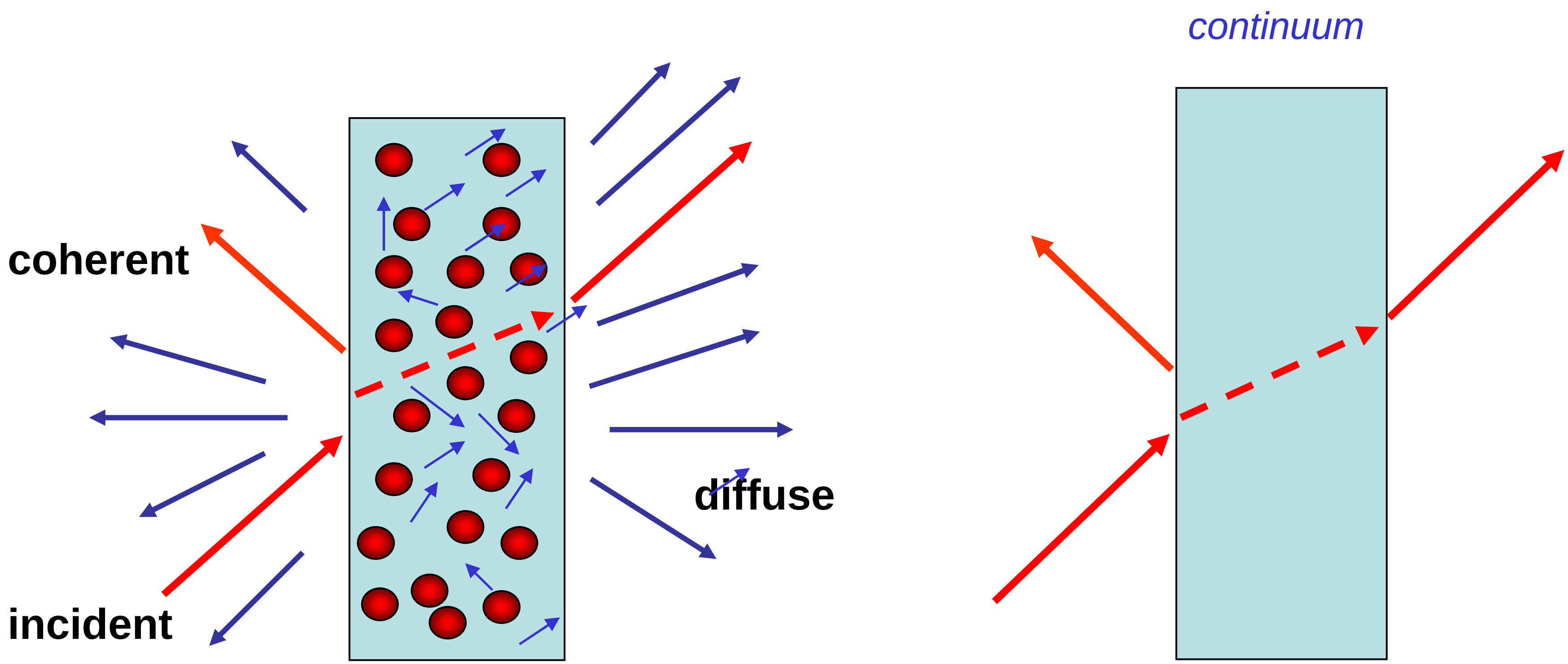


turbidity

diffraction

$$\left\langle \vec{S} \right\rangle_{diffuse} \sim \left\langle \vec{S} \right\rangle_{coh}$$

Is there an effective medium?

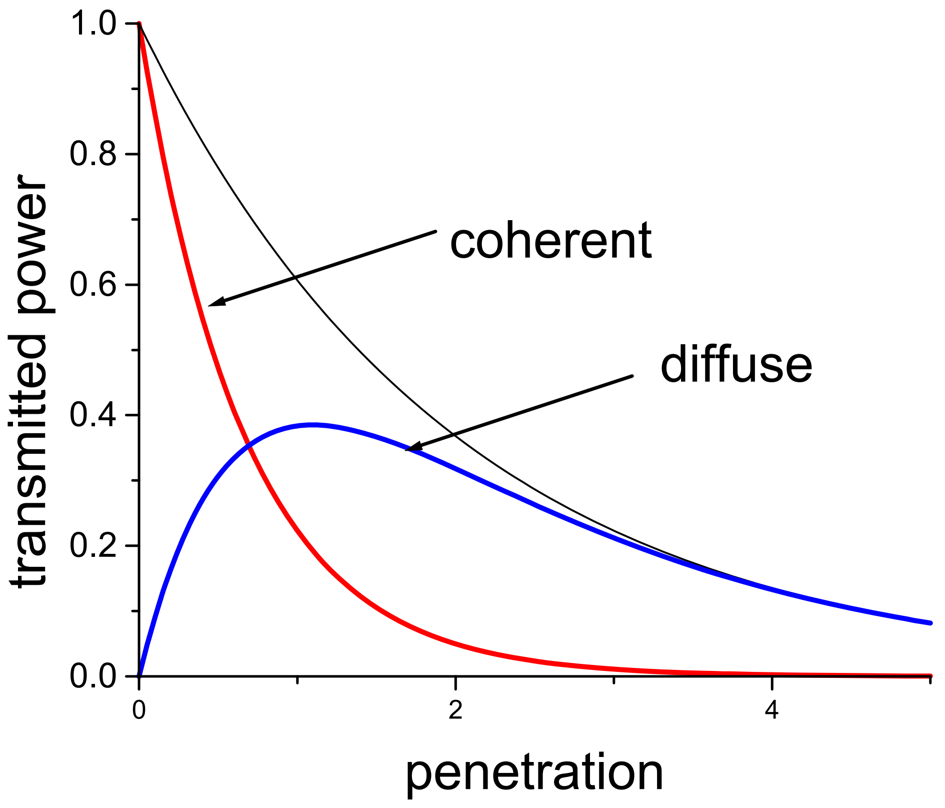


If there is one, it should be …. **for the coherent beam**

If there is one, the theory should be… **incomplete**

Energy conservation

$$Power \propto |E|^2 = |E_{AV}|^2 + |E_{fluc}|^2$$



effective properties… coherent beam… scattering… as... dissipation

Effective index of refraction

first attempts

van de Hulst

dilute limit

Light scattering by small particles (1957)

complex

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

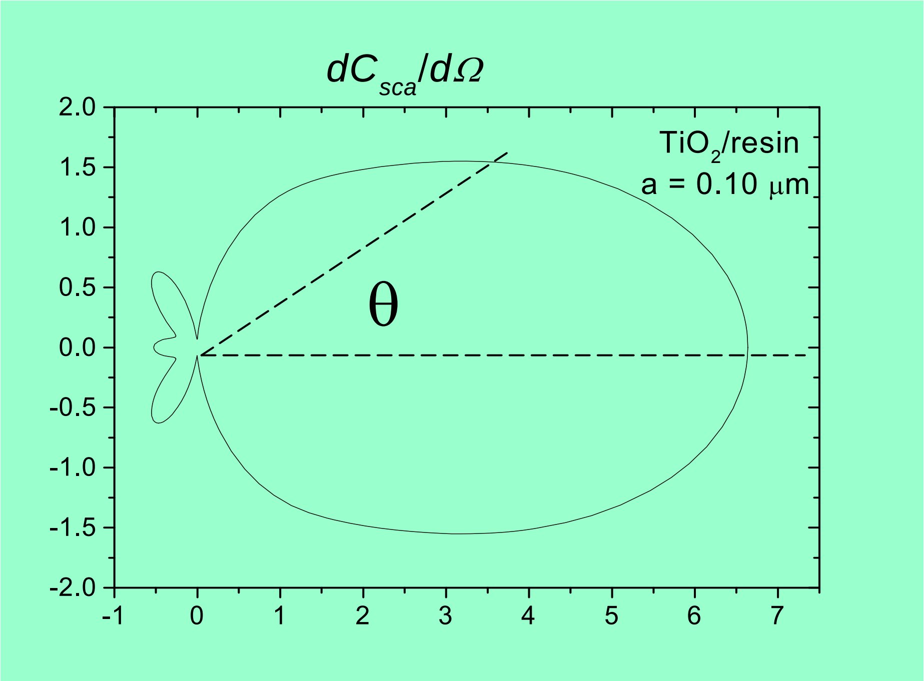
$$\gamma = \frac{3}{2}\frac{f}{(k_0 a)^3} \qquad \gamma \ll 1$$

sphere

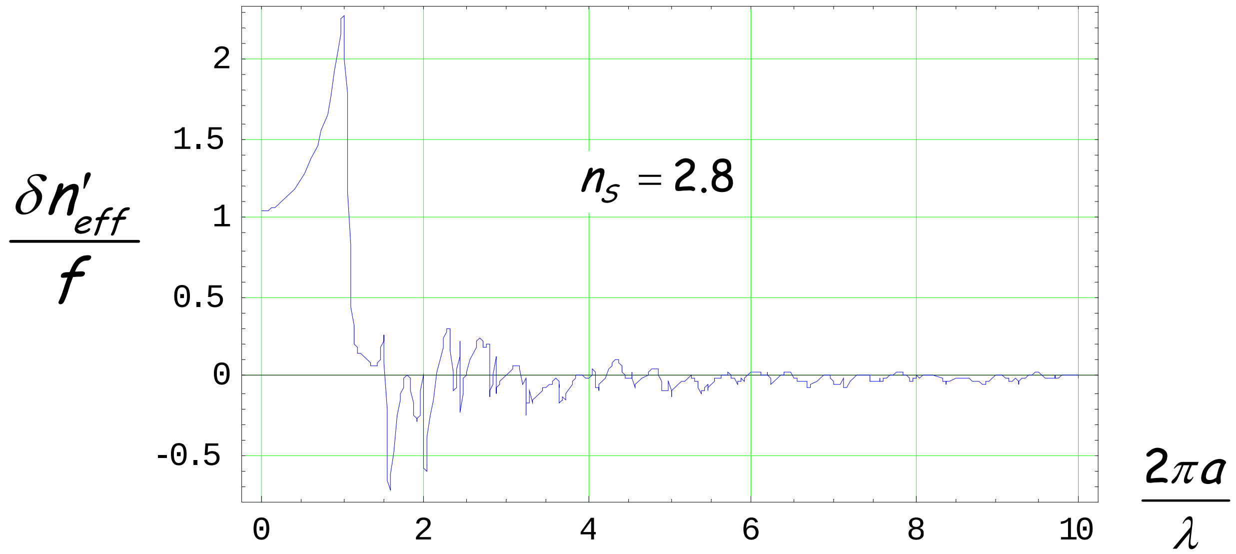
$$\begin{pmatrix} E_{\parallel}^{s} \\ E_{\perp}^{s} \end{pmatrix} = \frac{e^{ikr}}{-ikr} \begin{pmatrix} S_2(\theta) & 0 \\ 0 & S_1(\theta) \end{pmatrix} \begin{pmatrix} E_{\parallel}^{inc} \\ E_{\perp}^{inc} \end{pmatrix}$$

MIE

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

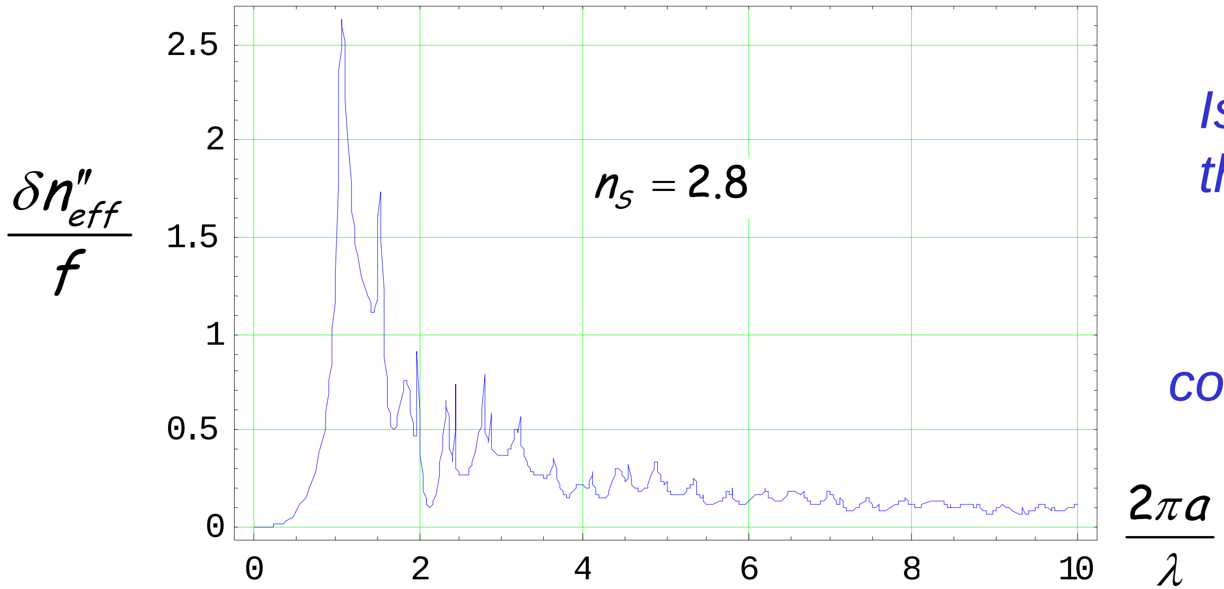


Effective index of refraction



Van de Hulst

$$\delta n_{eff} = i \frac{3}{2} \frac{S(0)}{(k_0 a)^3} f$$

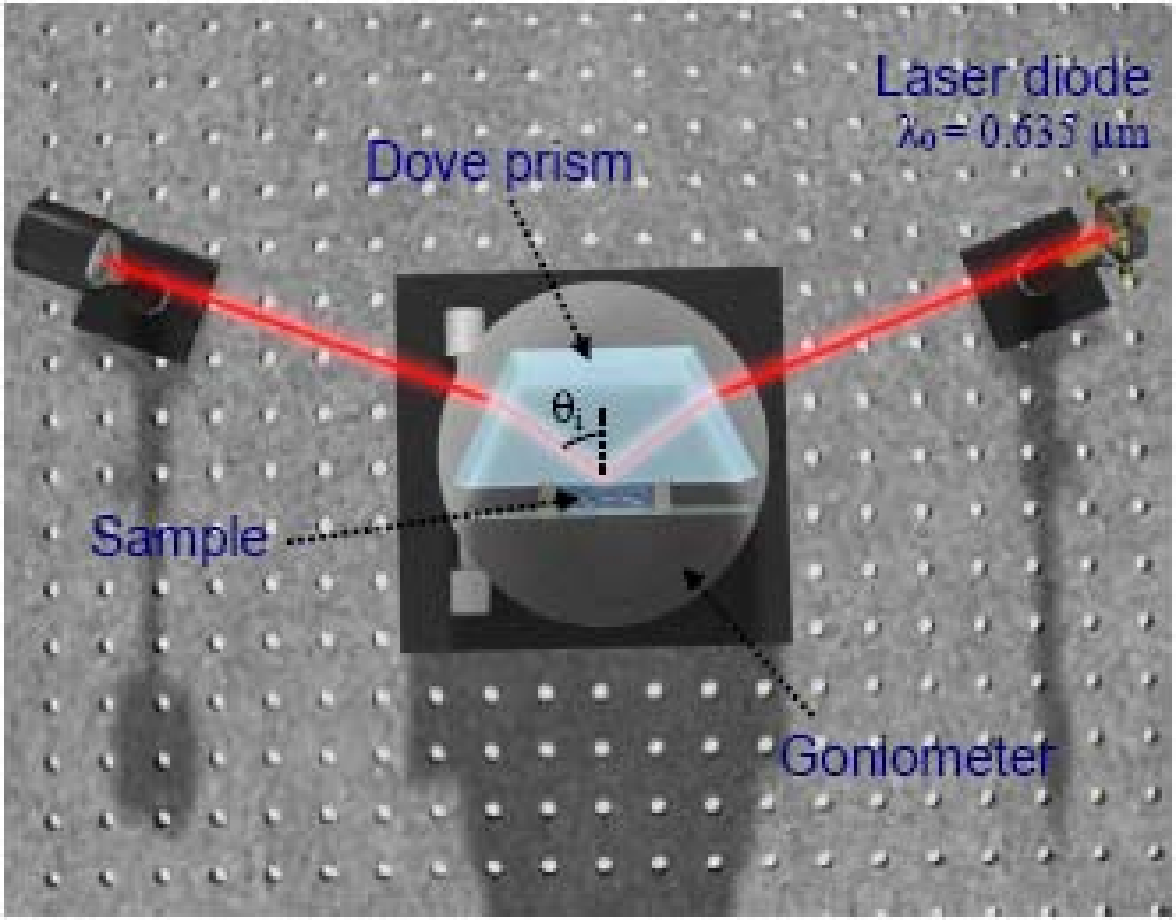


Is this effective-medium theory ***unrestricted****?*

compare with experiment

Comparison with experiment

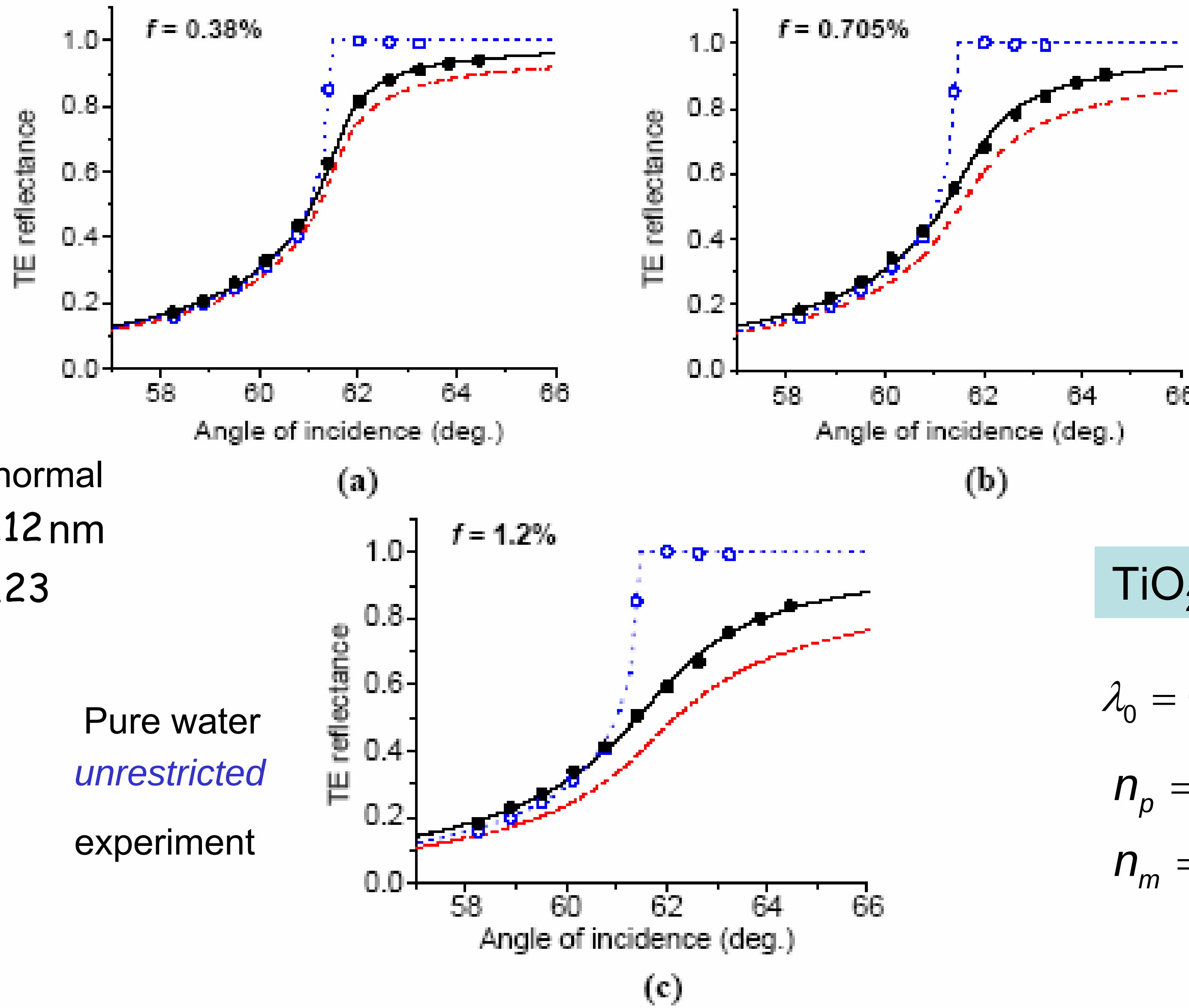
critical-angle refractometer



$R(\theta_i)$

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

Results



Log-normal

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

$\sigma = 1.23$

Pure water

unrestricted

experiment

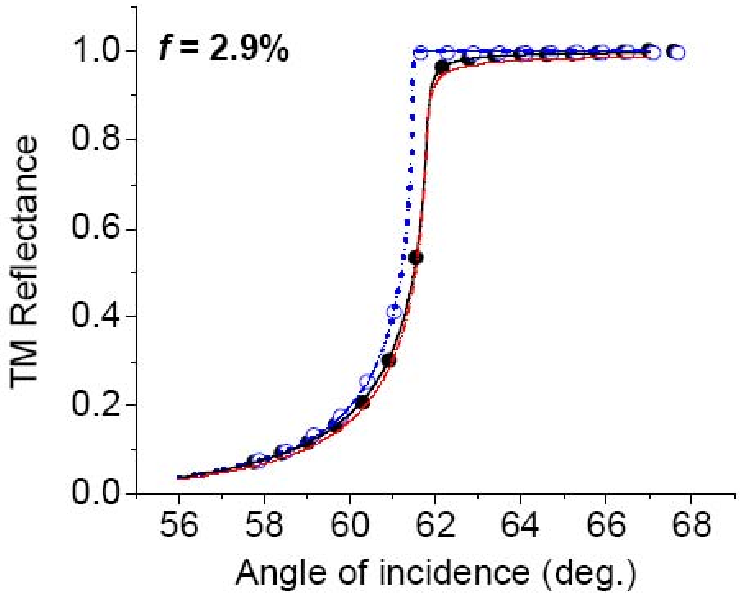
TiO_2 / water

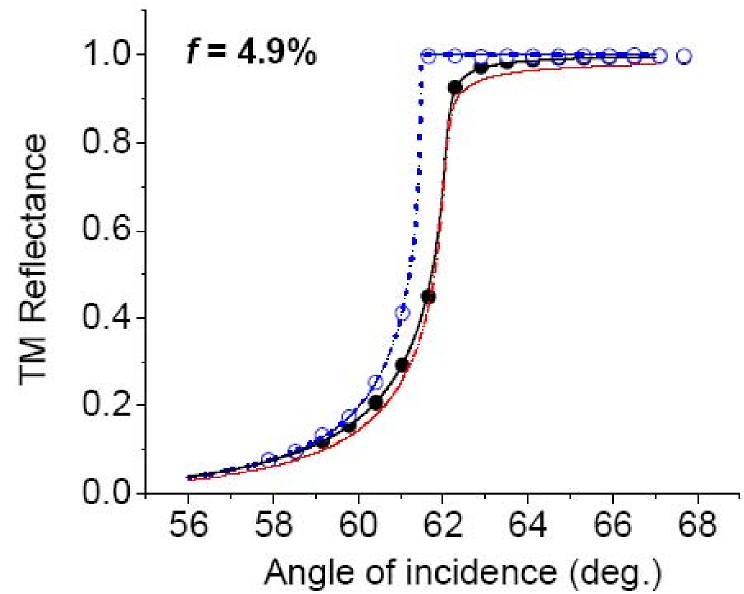
$\lambda_0 = 6350$ nm

$n_p = 2.73$

$n_m = 1.3313$

Results





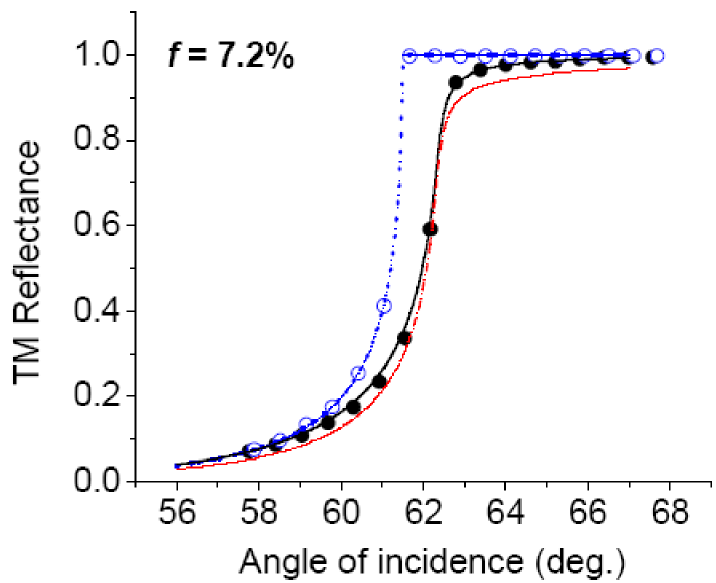
$n_p = 1.47$

$a_0 = 186.5$ nm

Pure water

unrestricted

experiment



latex / water

$\lambda_0 = 6350$ nm

$n_p = 2.73$

$n_m = 1.3313$

Meas. Sci. Technol. **8** (1997) 728–733. Printed in the UK PII: S0957-0233(97)80769-2

Refractive index errors in the critical-angle and the Brewster-angle methods applied to absorbing and heterogeneous materials

G H Meeten†

Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge CB3 0EL, UK

Received 9 January 1997, in final form 26 February 1997, accepted for publication 12 March 1997

5. Conclusion

We have studied the reflection of light at the interface between a transparent medium, and a sample material which may be optically absorbing or scattering, where the light is incident upon the sample from within the transparent medium. This is the configuration of most critical-angle refractometers, where the transparent medium is an optical prism of accurately known refractive index. The interpretation of the critical angle and the Brewster angle is shown to be complicated by the presence of absorption or heterogeneity in the sample, when the refractometer will generally read an apparent refractive index which is erroneous.

For a non-absorbing but heterogeneous sample a theoretical prediction of the measurement error in critical-angle or Brewster-angle refractometry is presently unavailable. Critical-angle results for suspensions show the effect of heterogeneity length scale through the effect of particle size. Good critical-angle measurements are possible even at high concentrations (50% vol.) if the particle diameter is less than about half the optical wavelength, and also at any concentration for particles much larger than the wavelength if the refractive index increment is negliglble. For intermediate particle diameters the angle dependence of reflectance may deviate grossly from that predicted by Fresnel's equations, with features which make definition of the critical angle and refractive index measurements impossible. Sufficient study has not been given to the effects of heterogeneity length scale and concentration to enable measurement criteria to be established for Brewster-angle refractometry.

Why?

Our result

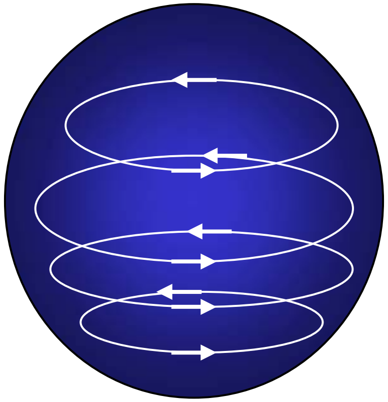
IN TURBID COLLOIDAL SYSTEMS AN EFFECTIVE MEDIUM **EXISTS,** BUT IT IS **NONLOCAL**

$$\varepsilon_{eff}(k,\omega)$$

$$\mu_{eff}(k,\omega)$$

magnetic response

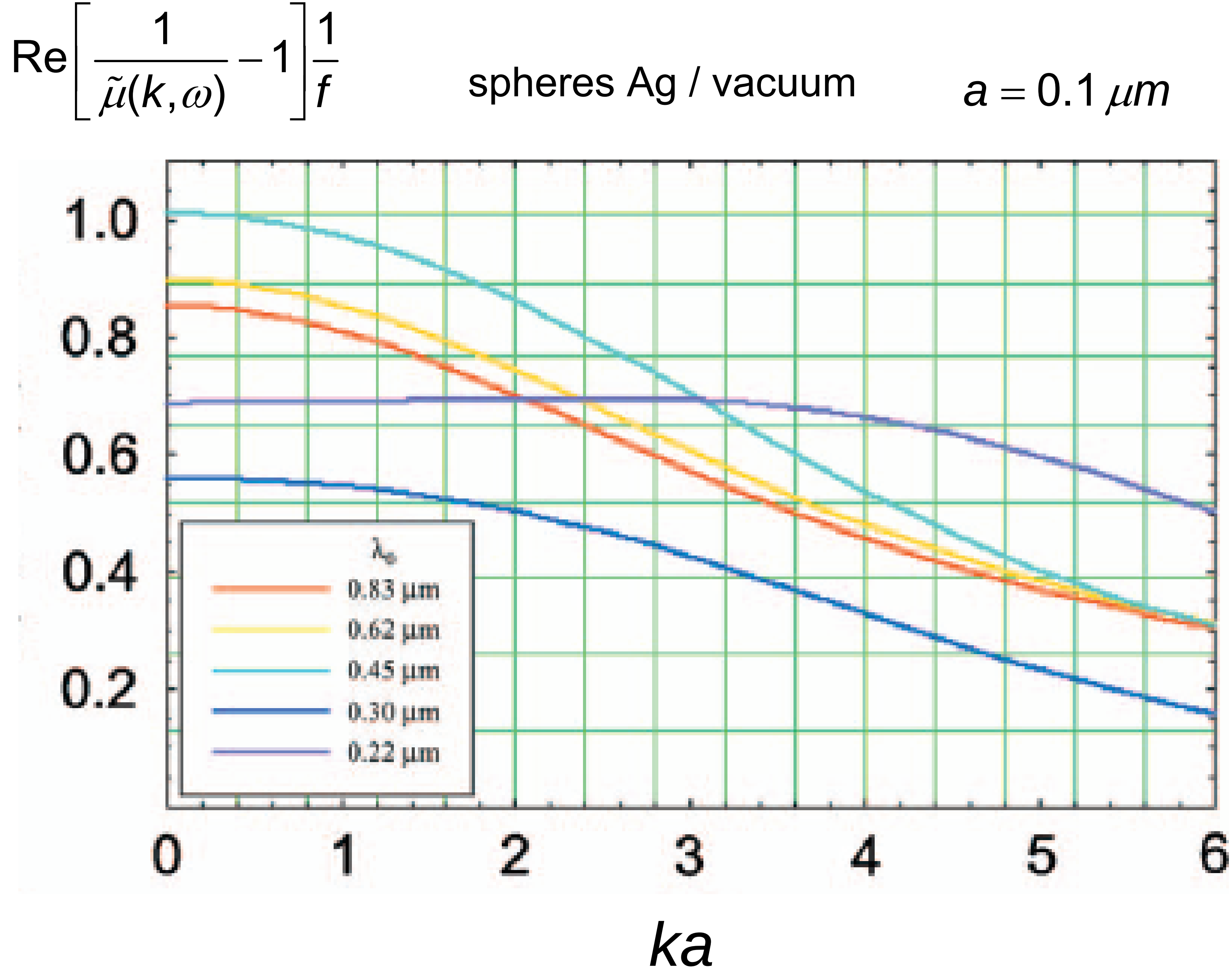
Fresnel´s equations are not valid



Nonlocal nature of the electrodynamic response of colloidal systems

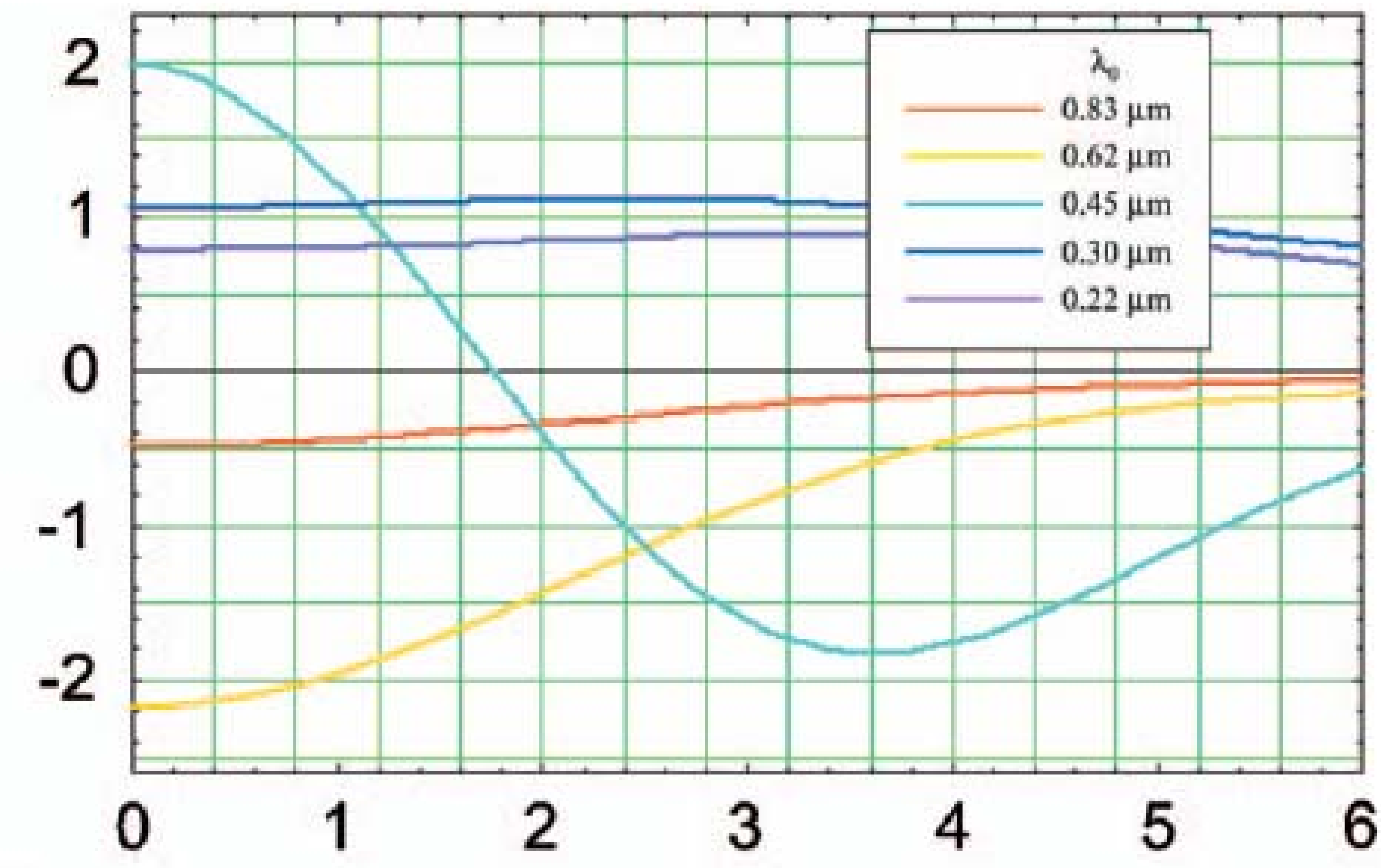
Rubén G. Barrera, Alejandro Reyes-Coronado & Augusto García-Valenzuela

Physical Review B **75**, 184202 (2007)



$\mathrm{Re}\left[\frac{1}{\tilde{\mu}(k,\omega)}-1\right]\frac{1}{f}$
spheres Ag / vacuum
$a = 0.1\,\mu m$
1.0
0.8
0.6
0.4
0.2
0
1
2
3
4
5
6
ka
λ₀
0.83 μm
0.62 μm
0.45 μm
0.30 μm
0.22 μm

$\mathrm{Re}\left[\frac{1}{\tilde{\mu}(k,\omega)}-1\right]\frac{1}{f}$ spheres TiO_2 / vacuum $a = 0.1\,\mu m$



ka

Electromagnetic modes

$$\varepsilon_{eff}(k,\omega) \quad \mu_{eff}(k,\omega) \quad \longleftrightarrow \quad \varepsilon_{eff}^{L}(k,\omega) \quad \varepsilon_{eff}^{T}(k,\omega)$$

"generalized"

dispersion relation NON-LOCAL $\vec{k} = \vec{k}' + i\vec{k}''$

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

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

effective index of refraction $k^{T}(\omega) = k_0 n_{eff}(\omega)$

Approximations

Local (long wavelength)

$$k = k_0 \sqrt{\tilde{\varepsilon}^T_{eff}(k \to 0, \omega)} = k_0 \sqrt{\tilde{\varepsilon}_{eff}(\omega)}$$

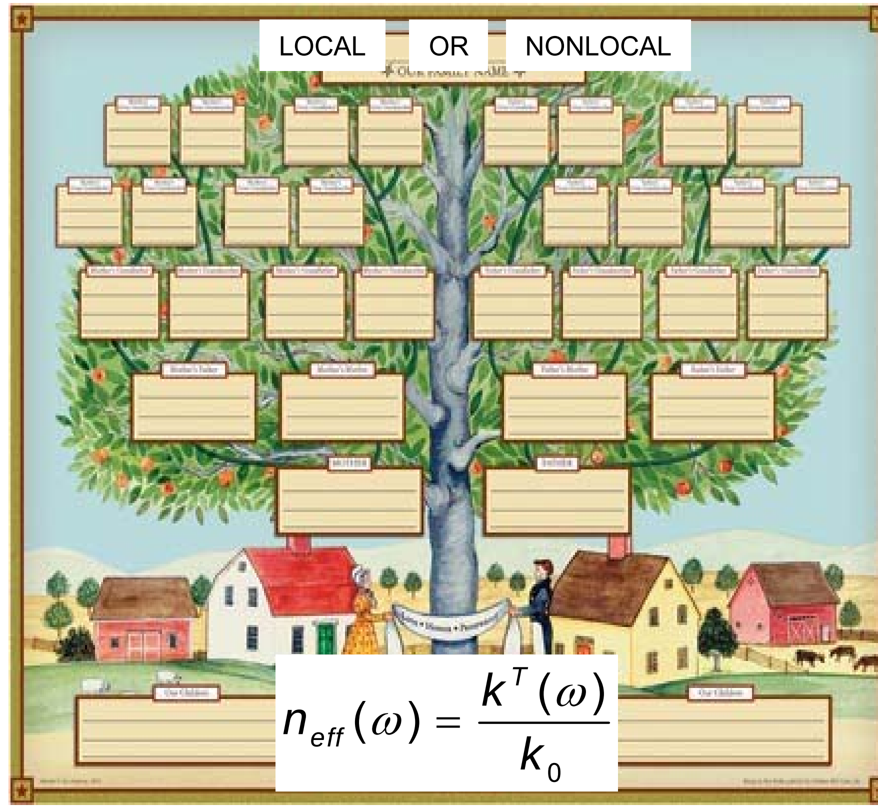
$$n_{eff}(\omega) = \sqrt{\varepsilon(\omega)}$$

Light-cone approximation (LCA)

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

$$n_{eff}(\omega) = \sqrt{\varepsilon^T(k_0, \omega)} \to 1 + i\gamma S(0)$$

LCA is close to the exact…



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

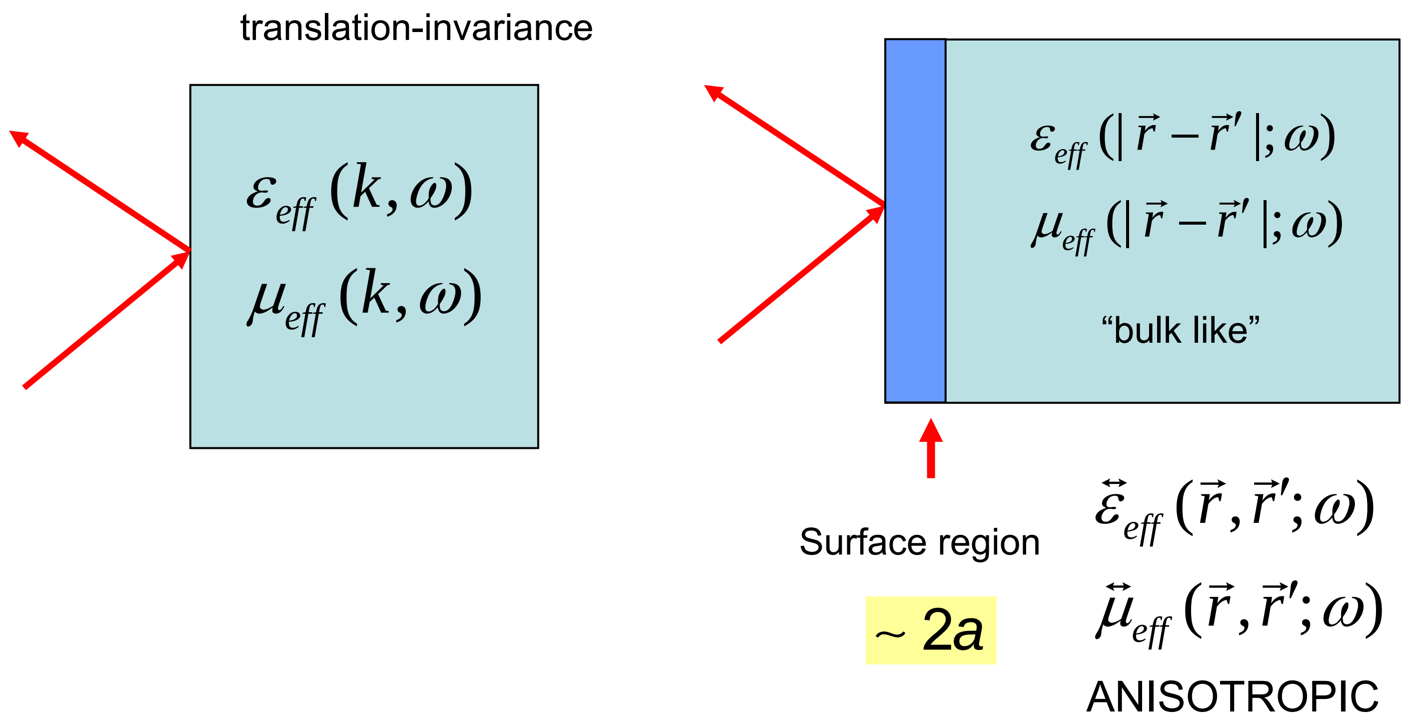
van de Hulst has a non-local ancestry
Thus it is restricted

How to measure the effective refractive index?

Critical-angle refractometry

- Reflectance from a medium with a non-local response

Reflectance of a half-space with an effective non-local response



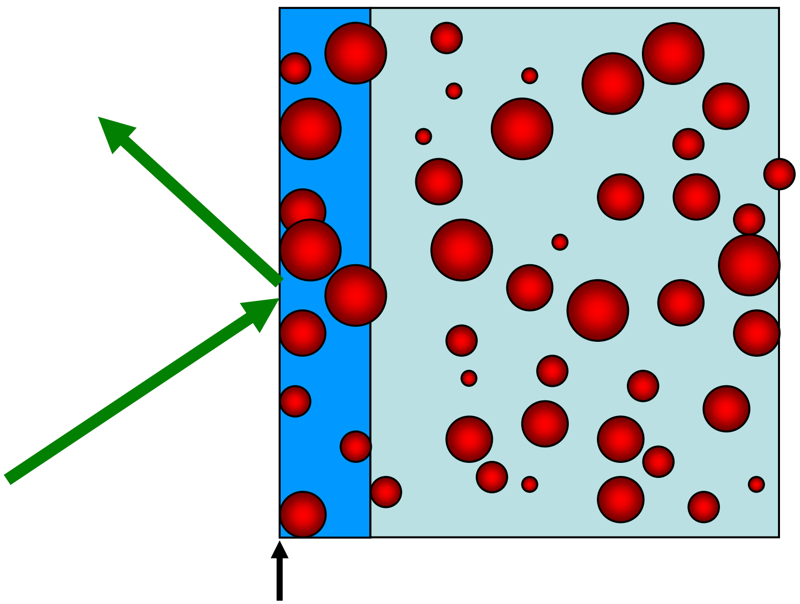
Although there are attempts…there is still not a reliable solution to the reflectance problem…

…but there will be one soon…

Practical problems

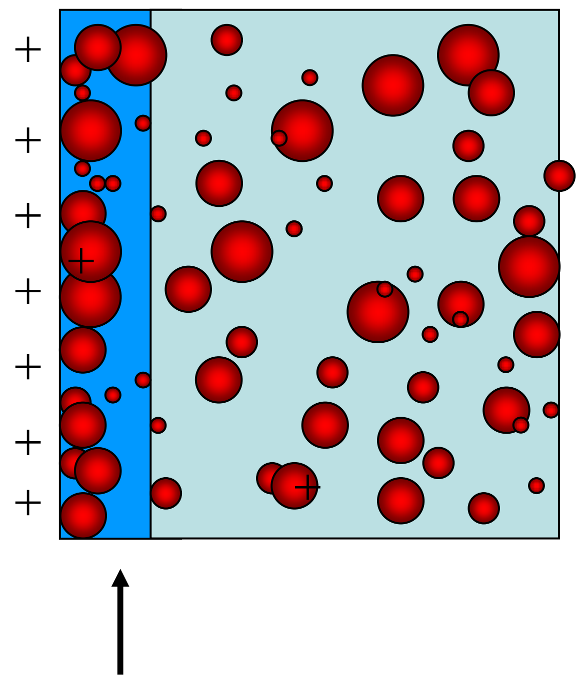
Surface sensitive

Probability interface



$z = 0$

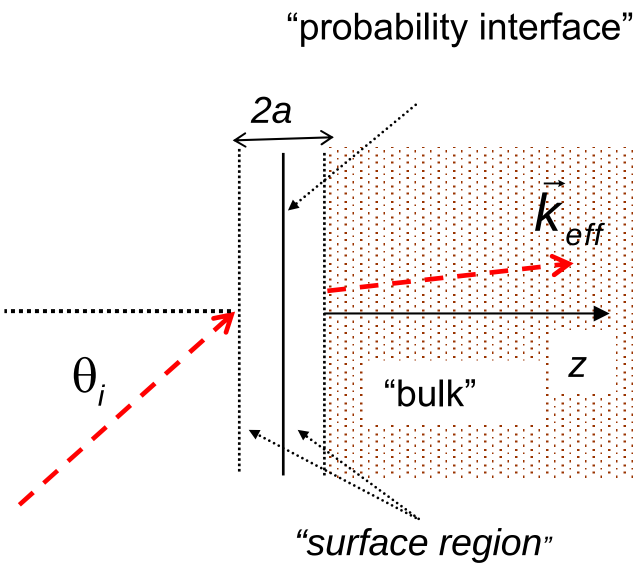
$$p(\vec{r}_j) = \begin{cases} \dfrac{d^3 r_j}{V} & \text{if} \quad z_j > 0 \\ 0 & \text{if} \quad z_j < 0. \end{cases}$$

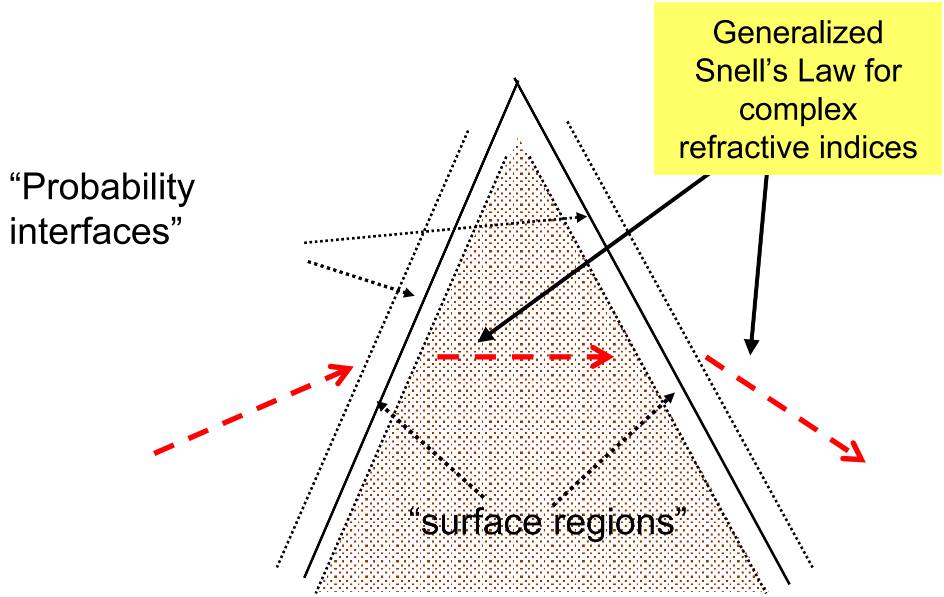


surface region

An alternative experimental set up to measure the effective refractive index

Non-local refraction





$$\vec{k}_{||}^{\,i} = k_{||}^{eff}$$

$$\sin\theta_i = n_{eff}(\omega)\sin\theta_t$$

local or non-local ancestry

absorption

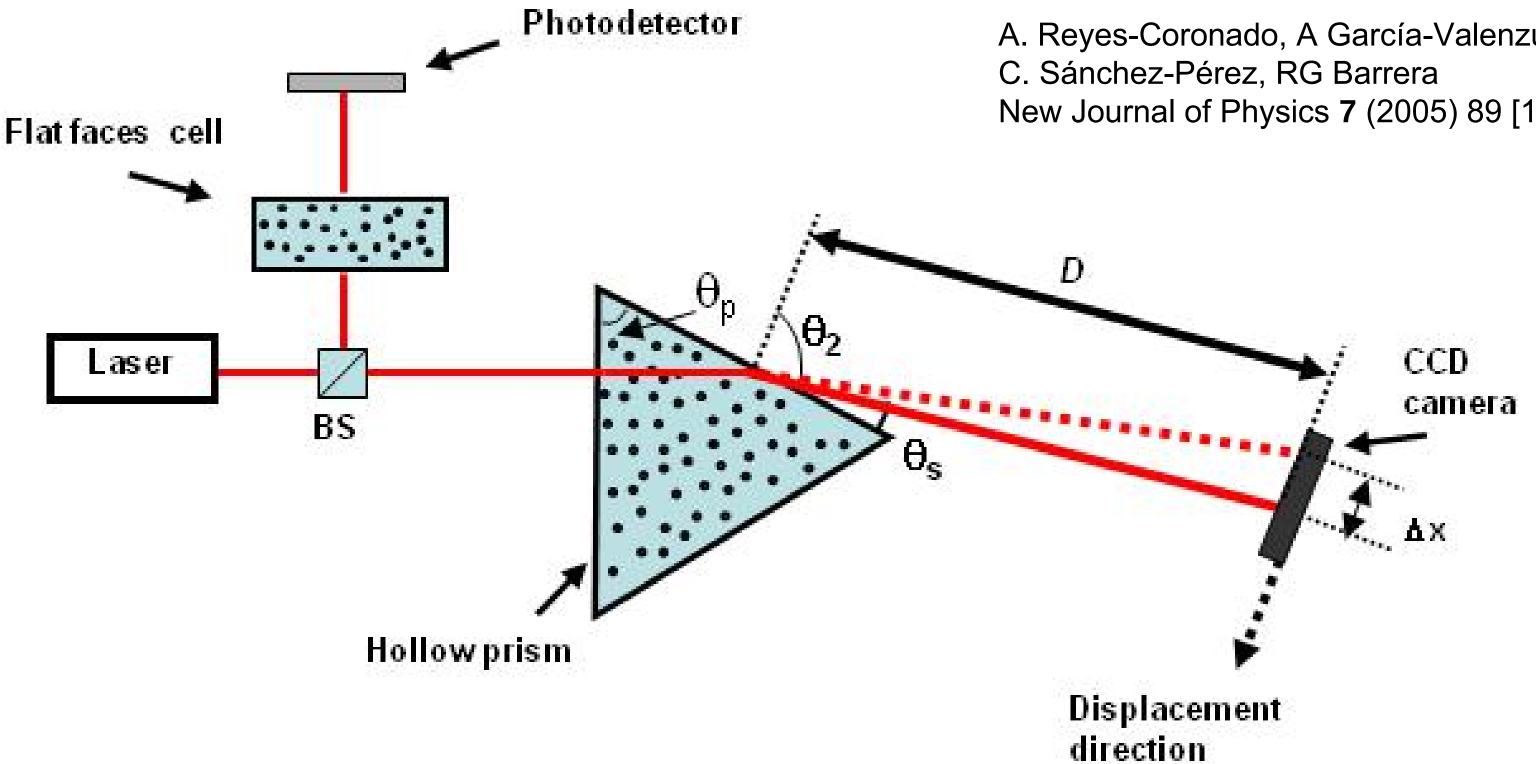
“generalized” Snell’s Law

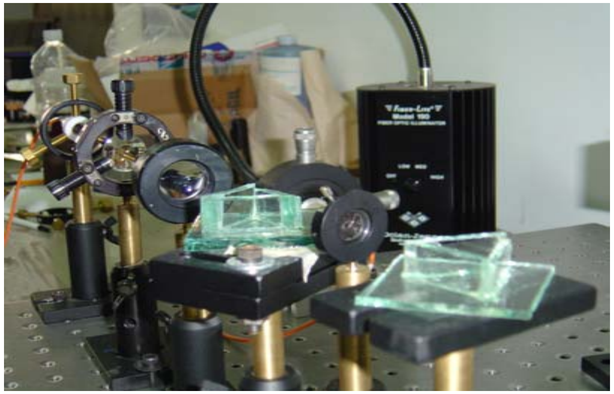
$$n_{eff} \rightarrow N_{eff}(\theta_i, n', n'')$$

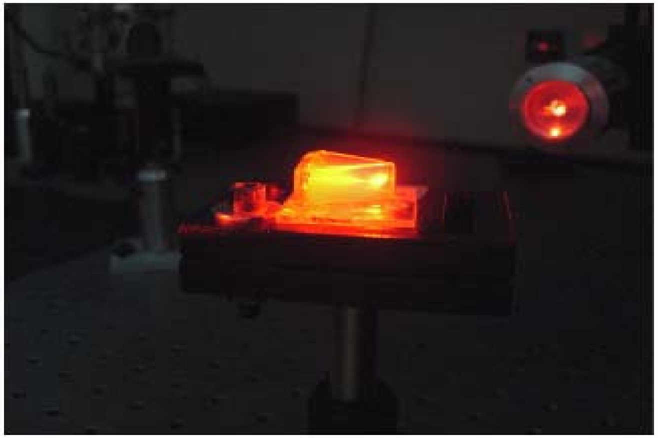
weak dependence

Experimental setup for refraction and extinction measurements

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





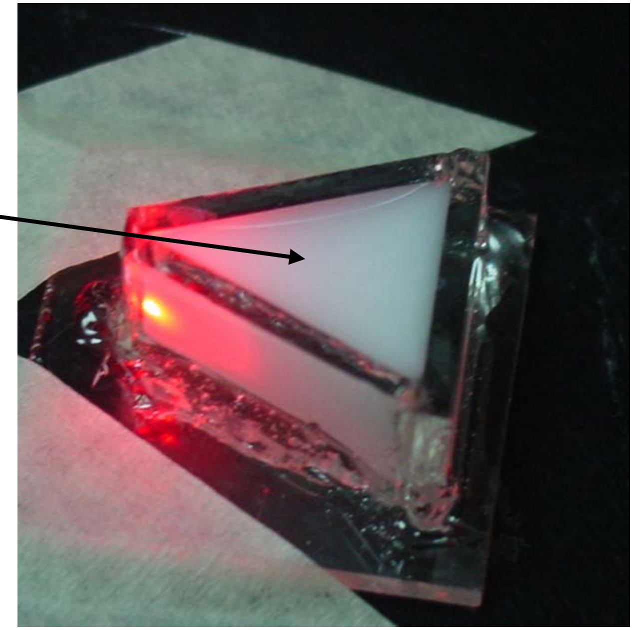


1.2 ml H_2O incial

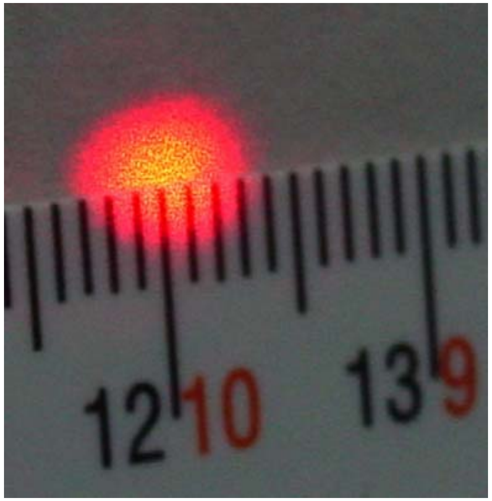
Latex particles in solution

$f = 1.2\%$

Diameter: 0.31 μm

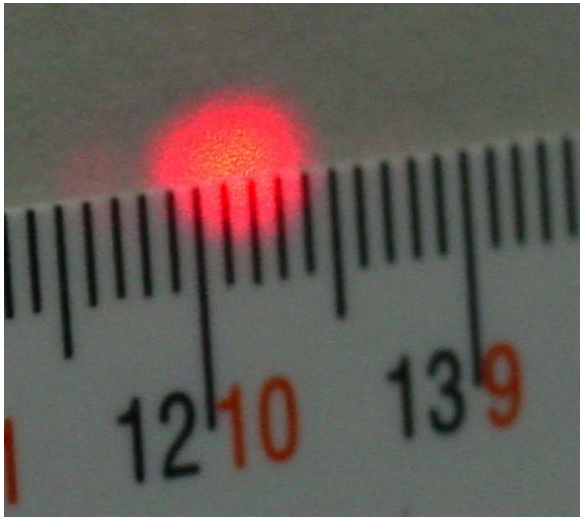


1.2 ml of water

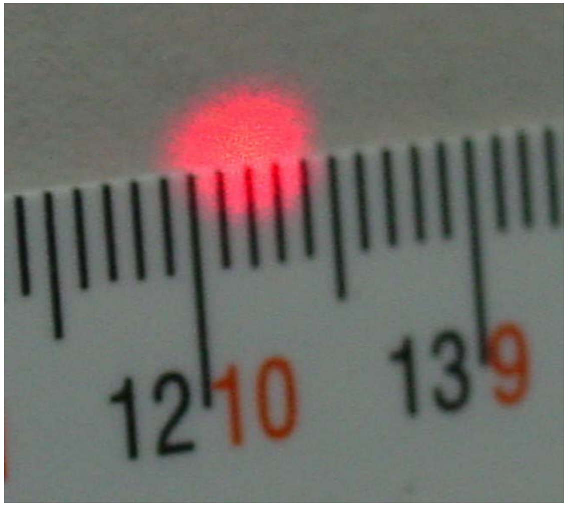


+ 0.15 ml in solution

+ 0.25 ml in solution

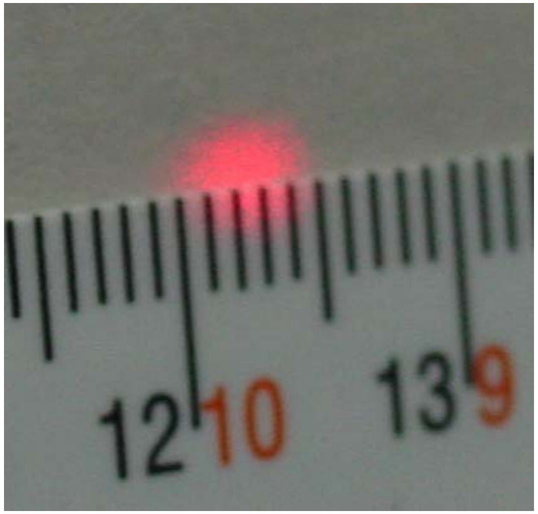


+ 0.35 ml in solution



+ 0.45 ml in solution

+ 0.55 ml in solution



Rigorous theoretical framework for particle sizing in turbid colloids using light refraction

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On the retrieval of particle size from the effective optical properties of colloids

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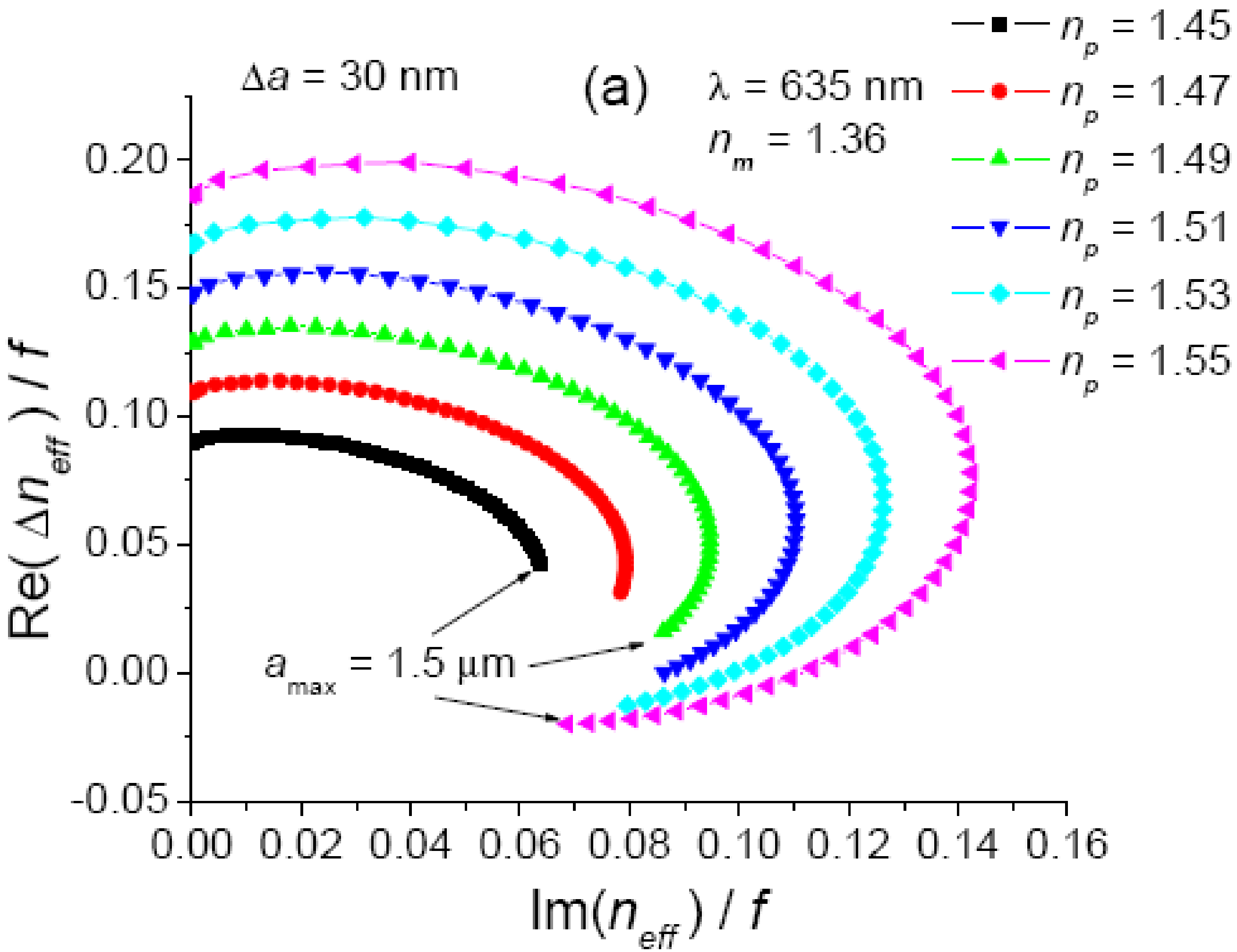
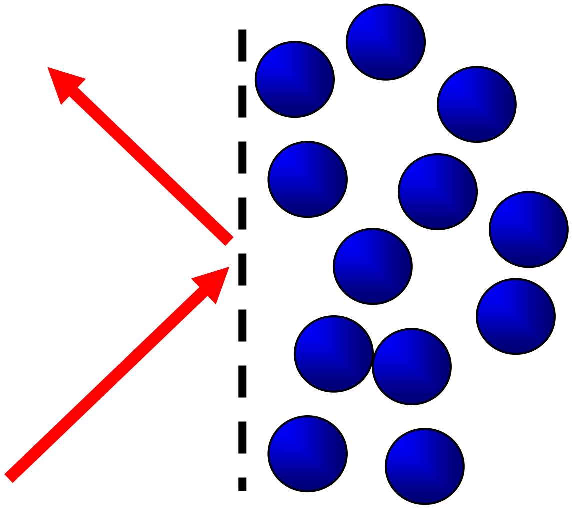


Fig. 3. Graphs of $\mathrm{Im}(n_{eff})\ /f$ versus $\mathrm{Re}(n_{eff})\ /f$ for a colloid with a matrix of refractive index $n_m = 1.36$ and particles of refractive index $n_p = 1.45, 1.47, \ldots 1.55$. The symbols in each plot in (a) are for a particles of radius $a = 0$, 30nm, 60nm, …1500 nm. In (b) are for $a = 0$, 5nm, 10nm, 15nm, …50nm.

Effective-medium & multiple-scattering



effective medium   scattering theory

$$i\omega\mu_0 \overleftrightarrow{\sigma}_{eff}(\vec{k},\vec{k}') \rightarrow \overleftrightarrow{T}(\vec{k},\vec{k}')$$

coherent-scattering model

dilute regime

$$r = \frac{\gamma k^2 S_m(\pi - 2\theta_i)}{i(k_z^i + k_z^{eff})k_z^i - \gamma k^2 S(0)}$$

$$pol.\,s \quad m = 1$$
$$pol.\,p \quad m = 2$$

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

"generalized" conductivity

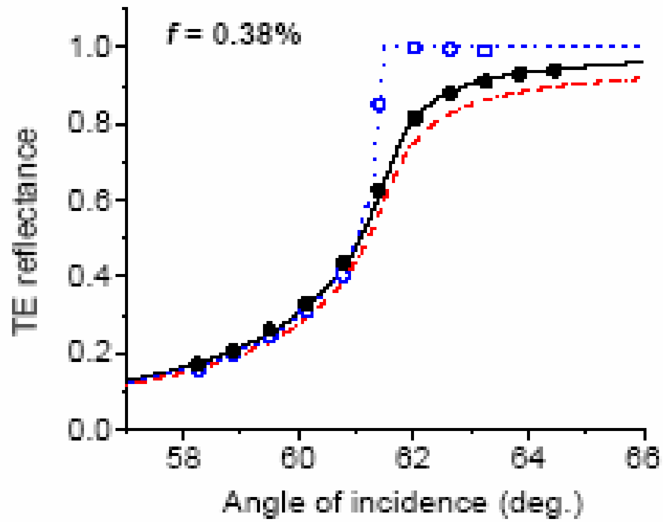
$$\vec{J}_{ind}(\vec{k},\omega) = \int \overleftrightarrow{\sigma}_{eff}(\vec{k},\vec{k}';\omega)\cdot\left\langle \vec{E}\right\rangle(\vec{k}',\omega)\,d^3k'$$

TOTAL

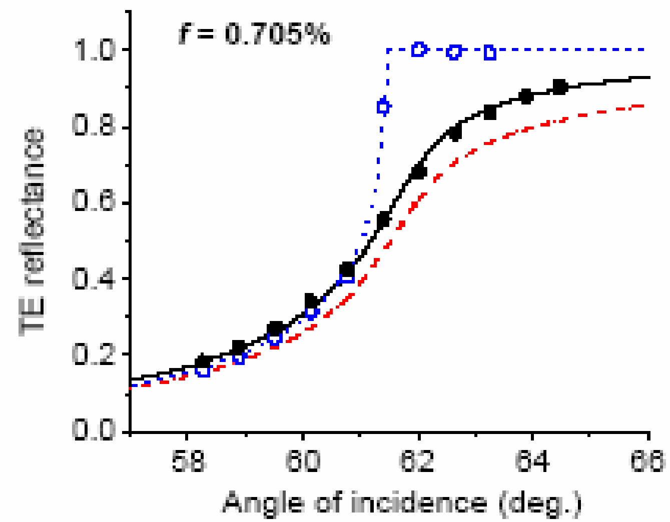
BULK → $\overleftrightarrow{\sigma}_{eff}(\vec{k},\vec{k};\omega)$

J. Opt. Soc. Am. A/Vol. 20, No. 2/February 2003
Journal of Quantitative Spectroscopy & Radiative Transfer 79–80 (2003) 627– 647

Results



(a)

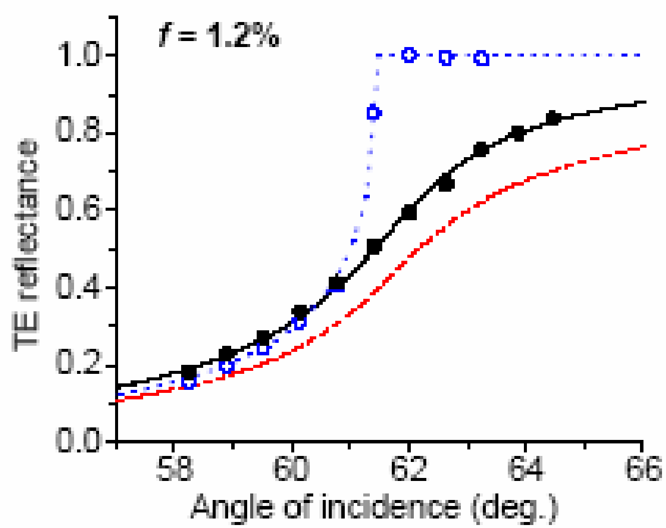


(b)

Log-normal

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

$\sigma = 1.23$



(c)

Pure water

unrestricted

experiment

CSM

TiO_2 / water

$\lambda_0 = 6350$ nm

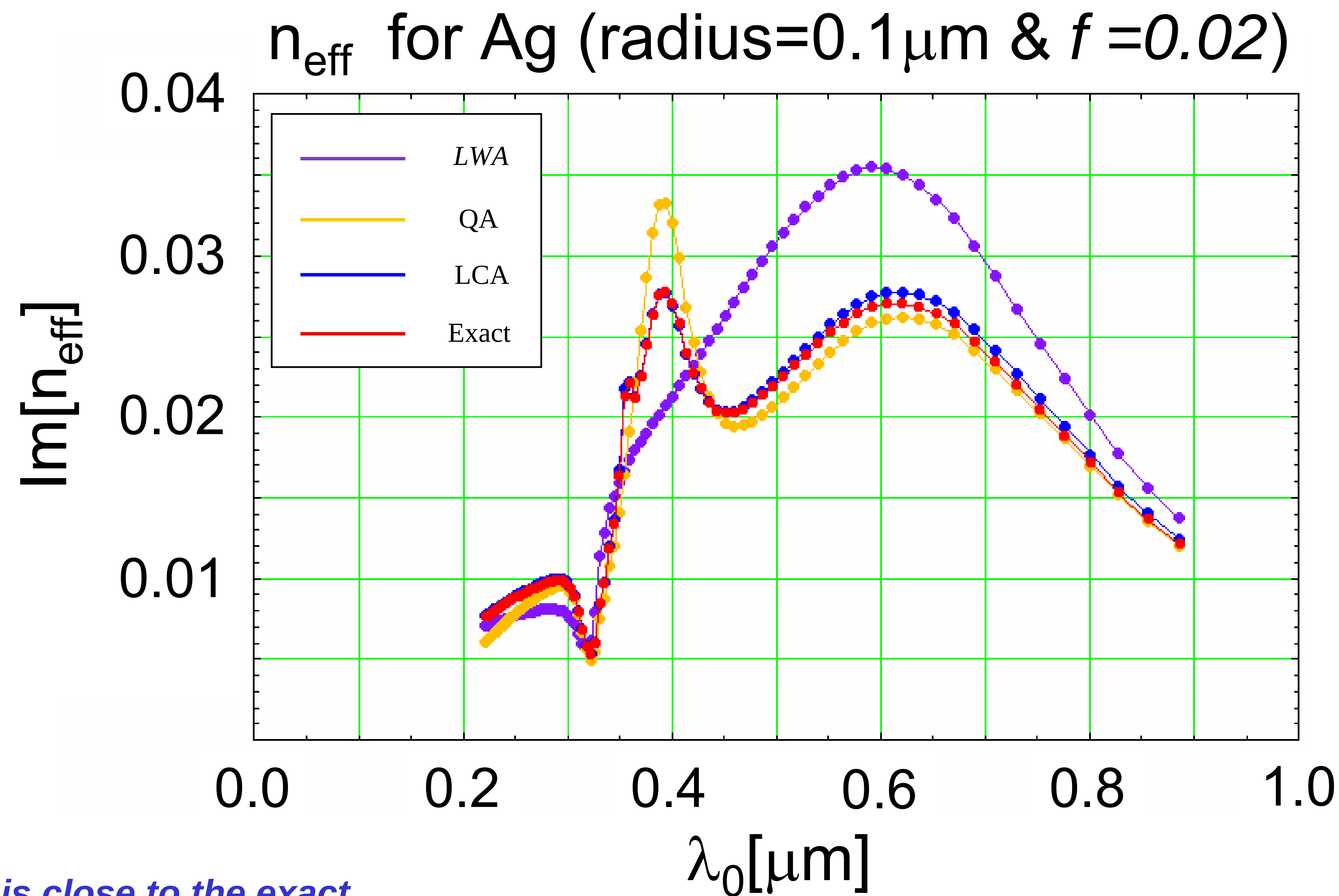
$n_p = 2.73$

$n_m = 1.3313$

CONCLUSIONS

We have provided arguments for the use of refraction as a secure way for the experimental determination of the effective index of refraction in turbid colloids.

Danke schön



LCA is close to the exact…

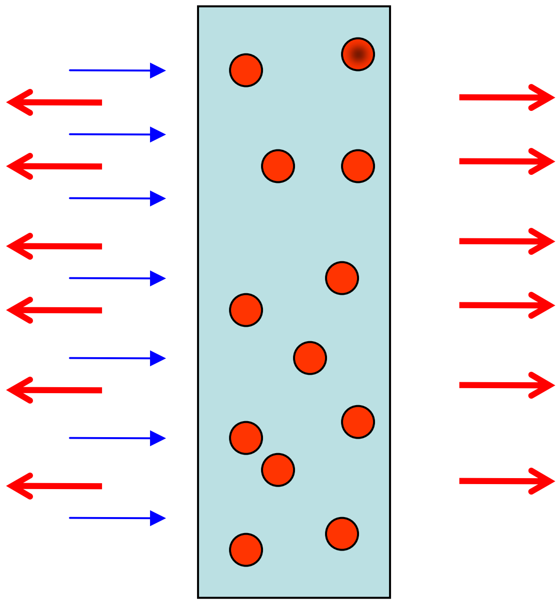
van de Hulst has a non-local ancestry
Thus it is restricted

Craig Bohren

J. Atmos Sci. 43, 468 (85)

multiple-scattering theory

Effective-medium approach



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

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

Proposition

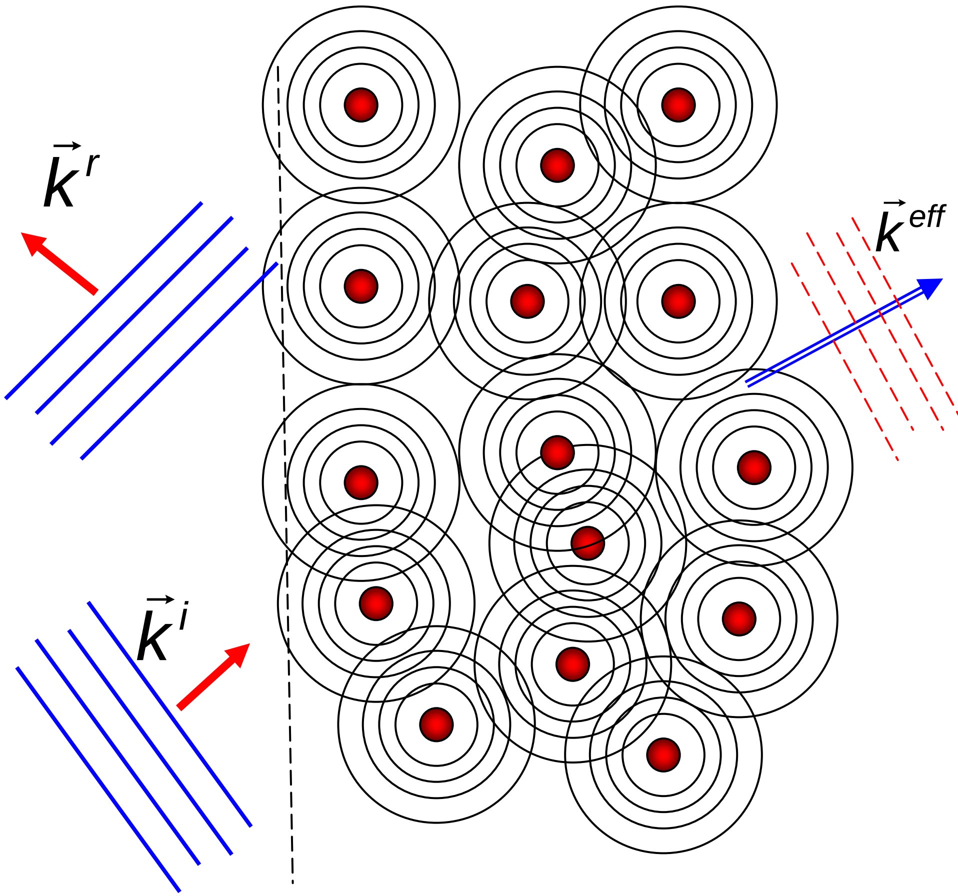
$$\varepsilon_{eff} = 1 + i\gamma\left[S(0) + S_1(\pi)\right]$$
$$\mu_{eff} = 1 + i\gamma\left[S(0) - S_1(\pi)\right]$$

MAGNETIC ?

$$r = \frac{\sqrt{\mu_{eff}} - \sqrt{\varepsilon_{eff}}}{\sqrt{\mu_{eff}} + \sqrt{\varepsilon_{eff}}}$$

multiple-scattering theory

dilute



$Z = 0$

EFA $\quad \vec{E}_p^{exc} \approx \langle \vec{E} \rangle$

coherent-scattering model

$$r = \frac{\gamma k^2 S_m(\pi - 2\theta_i)}{i(k_z^i + k_z^{eff})k_z^i - \gamma k^2 S(0)}$$

$pol.\,s \quad m = 1$

$pol.\,p \quad m = 2$

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

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Effective medium

assume to be unrestricted

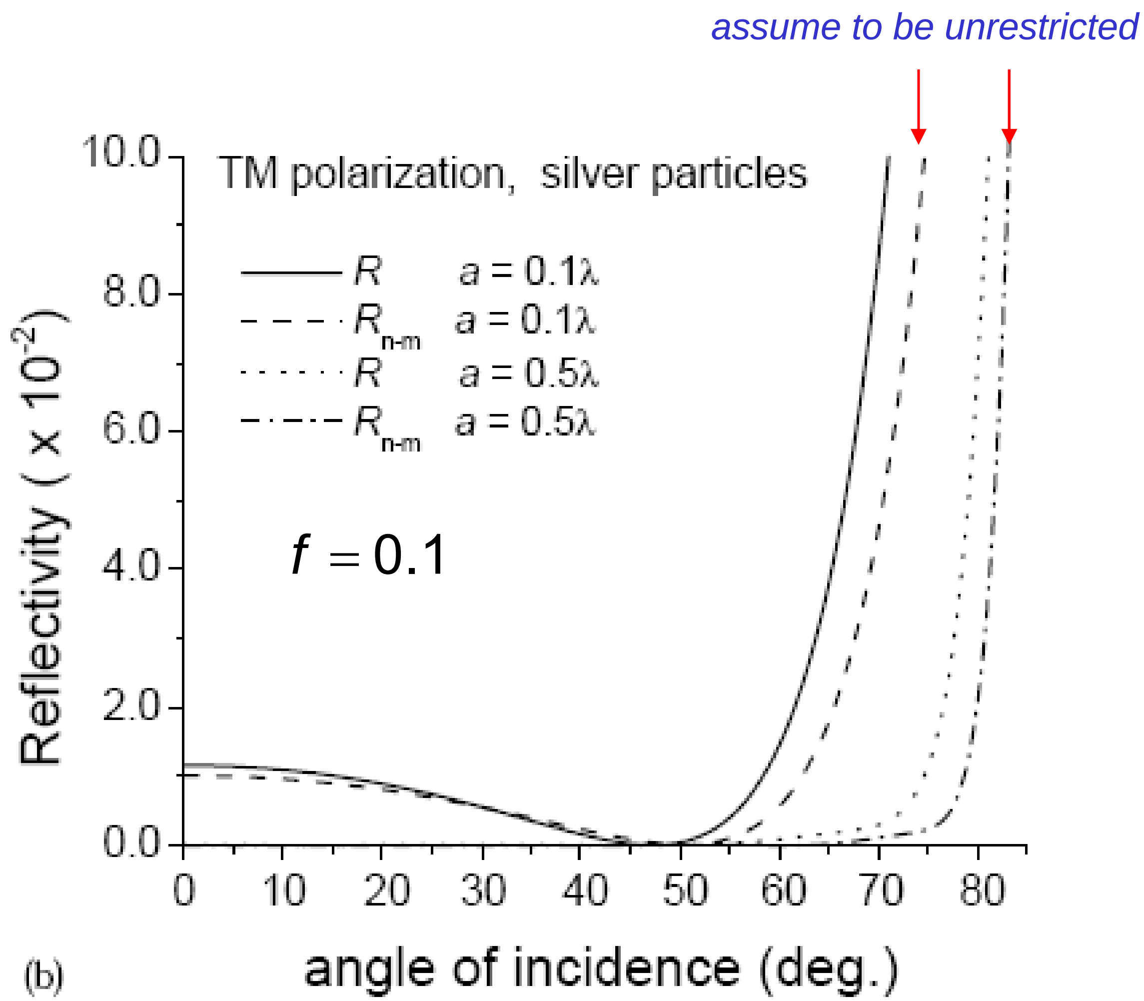
$$n_{eff} = 1 + i\,\underbrace{\gamma\, S(0)}$$

$$\tilde{\mu}_{eff} = 1$$

$$\tilde{\varepsilon}_{eff} = \sqrt{n_{eff}}$$

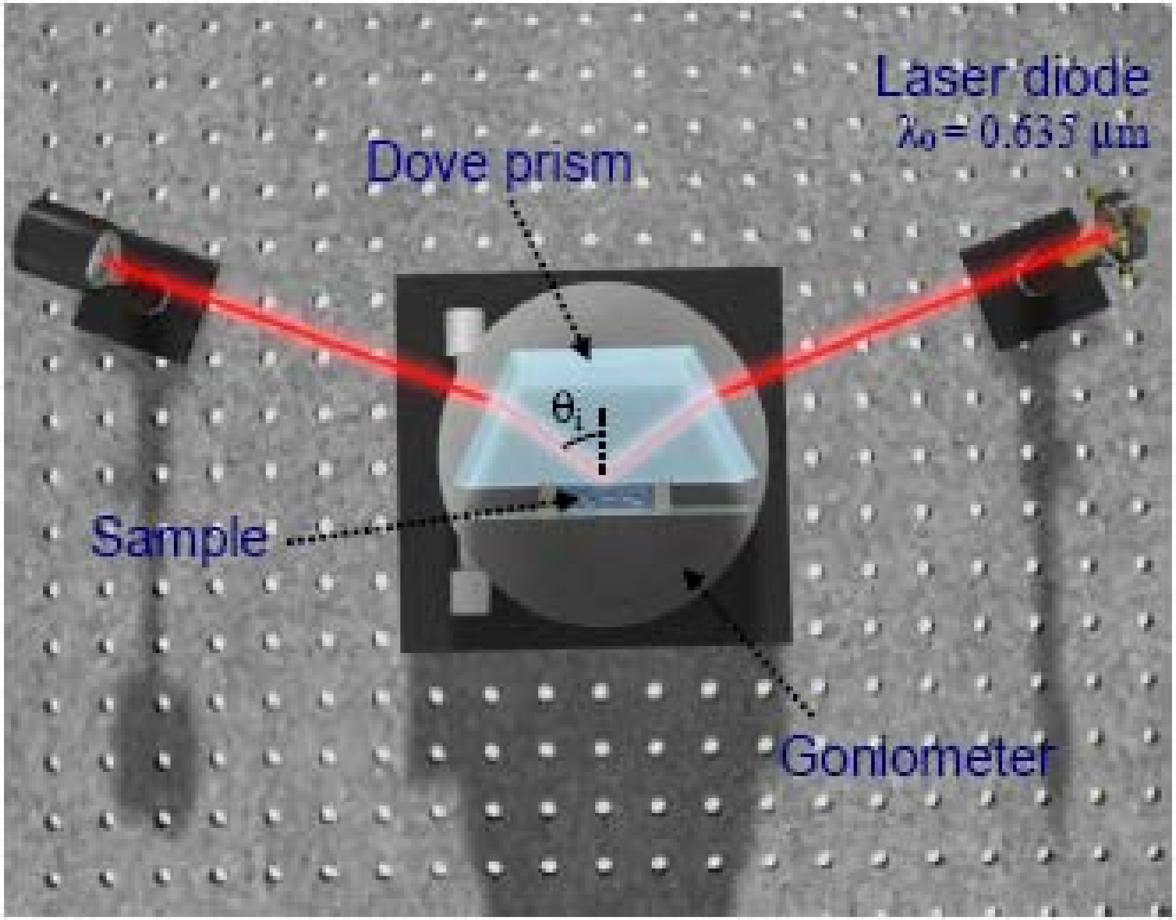
↓

Fresnel's relations



Comparison with experiment

critical-angle refractometer



$R(\theta_i)$

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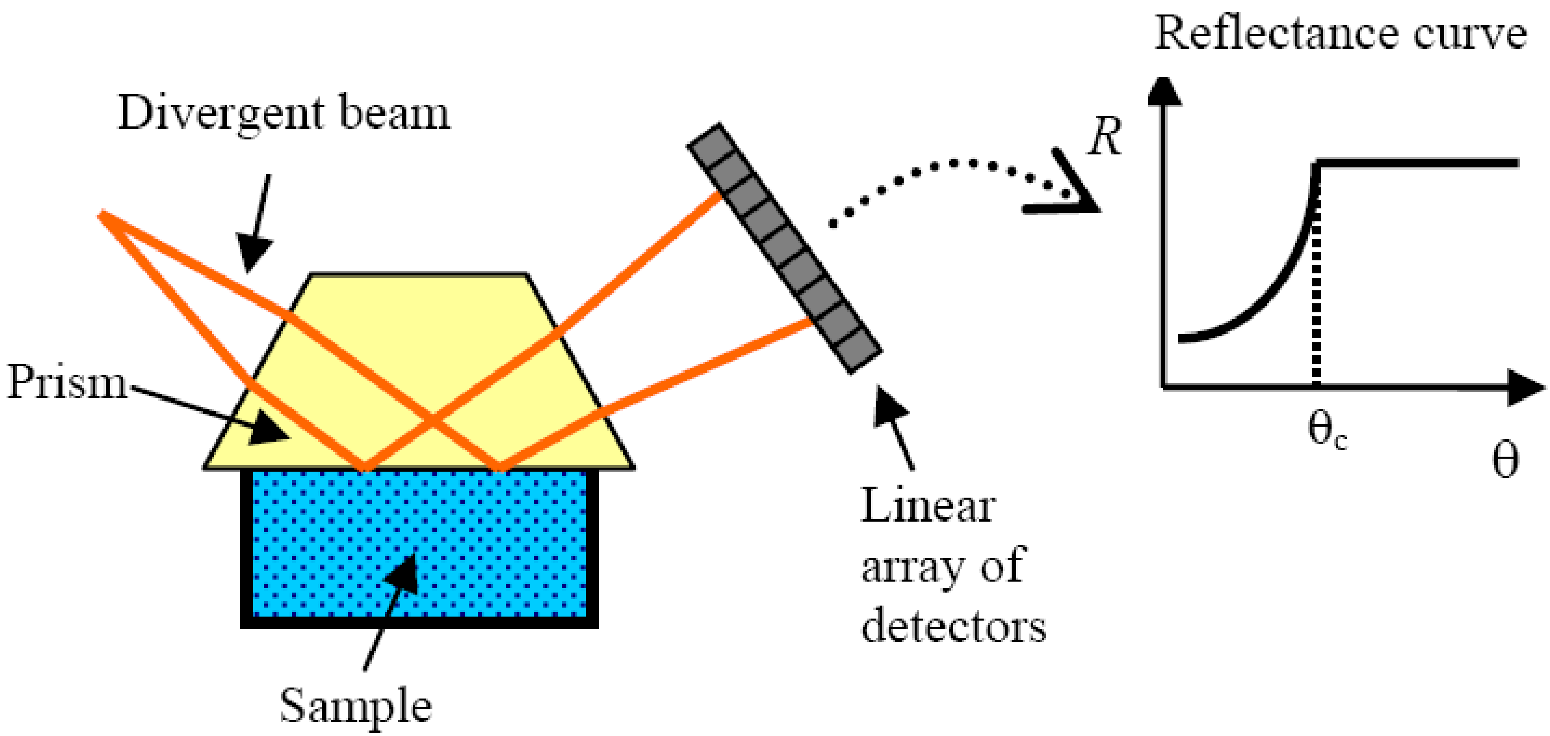
E Méndez, *Optics Express*, **13**, 6723 (2005)

Comparison with experiment

critical-angle refractometer



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E Méndez, *Optics Express*, **13**, 6723 (2005)

Internal reflection configuration

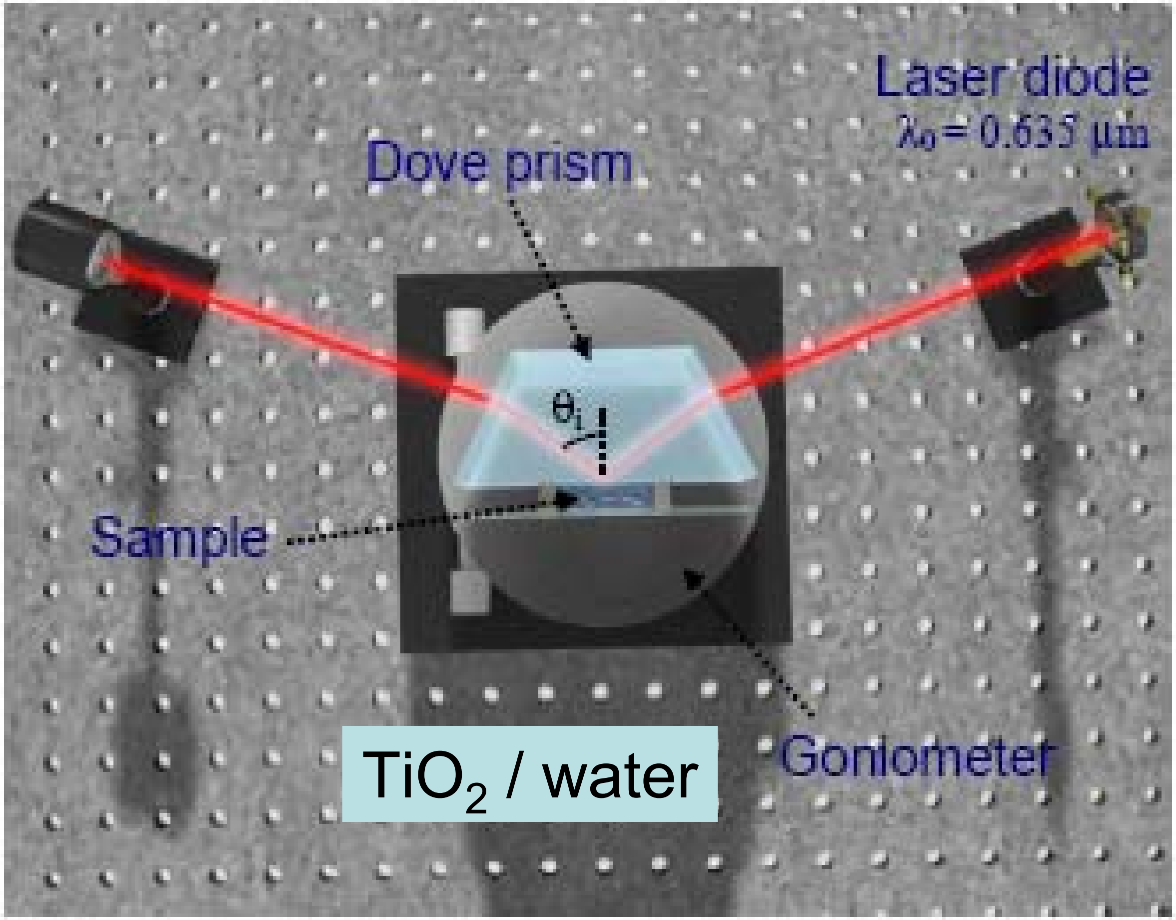
great sensitivity

assume to beunrestricted

$$R^{Fresnel}(\theta_i; n_{eff}^{vdH}, \mu_{eff} = 1)$$

Coherent scattering model

$$R = \left| \frac{\gamma k^2 S_m(\pi - 2\theta_i)}{i(k_z^i + k_z^{eff})k_z^i - \gamma k^2 S(0)} \right|^2$$



TiO_2 / water

$R(\theta_i)$

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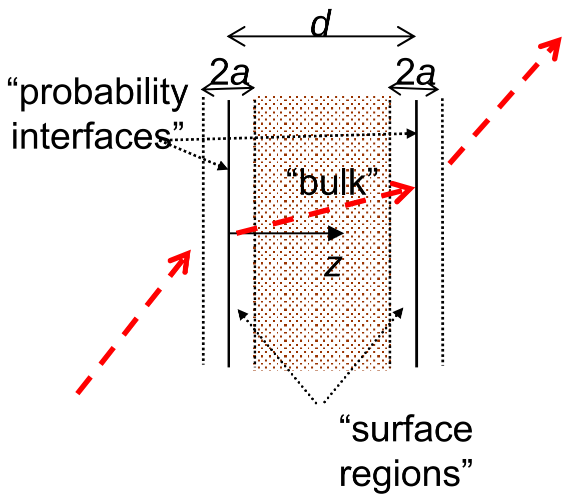
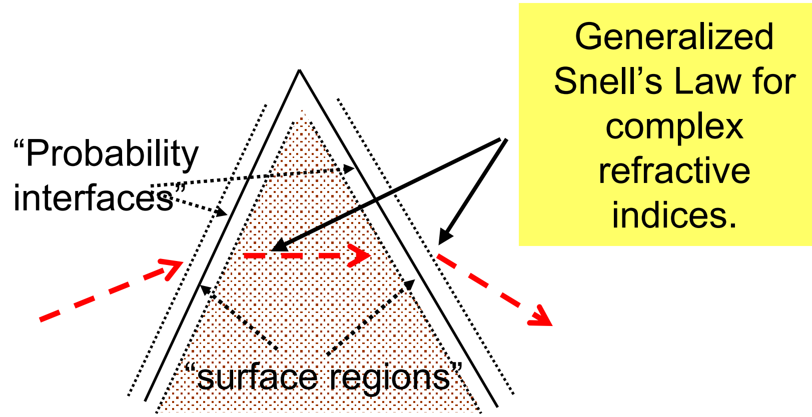
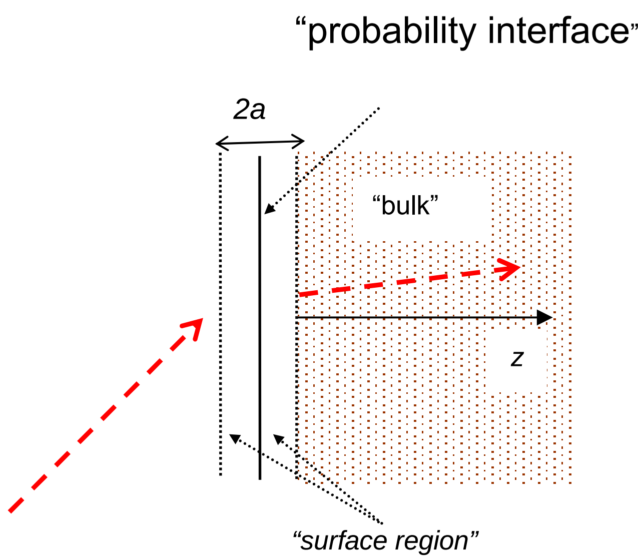
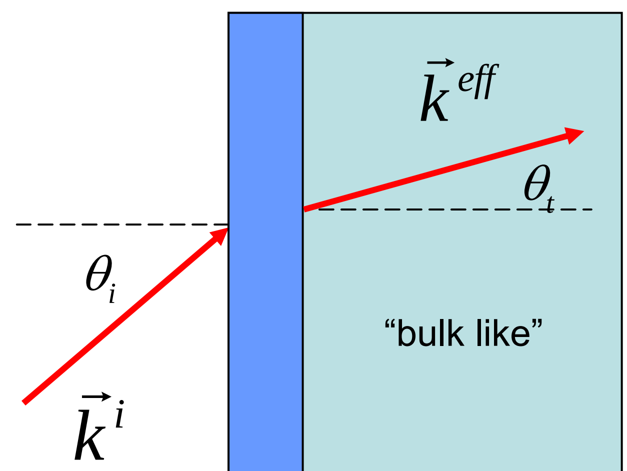

d
2a
2a
“probability interfaces”
“bulk”
z
“surface regions”


“Probability interfaces”
“surface regions”
Generalized Snell’s Law for complex refractive indices.


“probability interface”
2a
“bulk”
z
“surface region”


$\vec{k}^{eff}$
θ_t
θ_i
$\vec{k}^{i}$
“bulk like”