Experiment vs. modelling: what's the problem?

Bill Barnes

University of Exeter, UK

Much of the material discussed here will soon be published as an article by the *Journal of Optics A: Pure and Applied Optics*.

The good

outline

The good

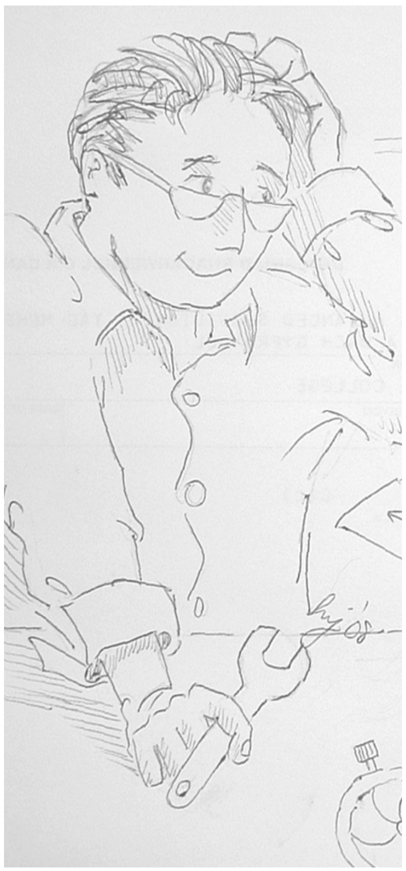
The bad

The good

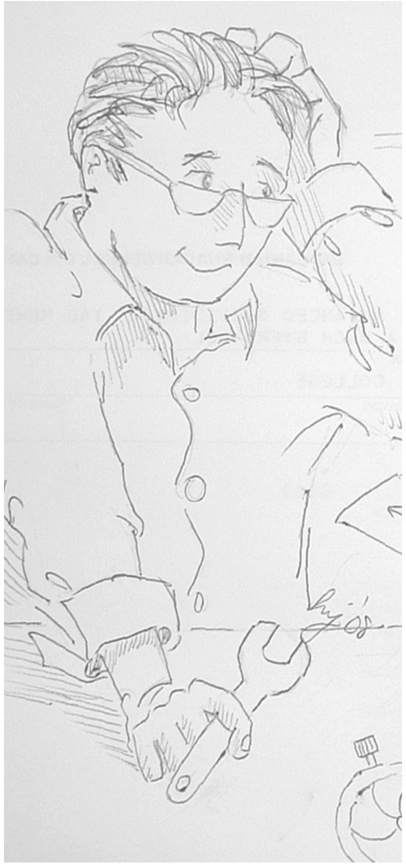
The bad

The ugly

outline



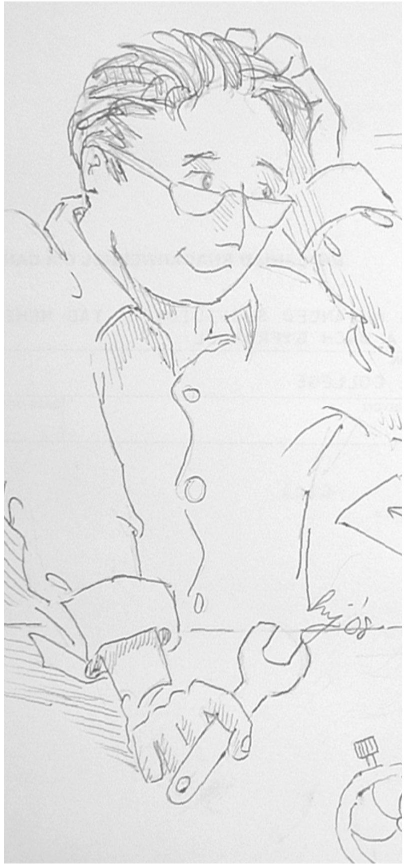
experimentalist's perspective



experimentalist's perspective

The good: experiments (they are real!)

outline

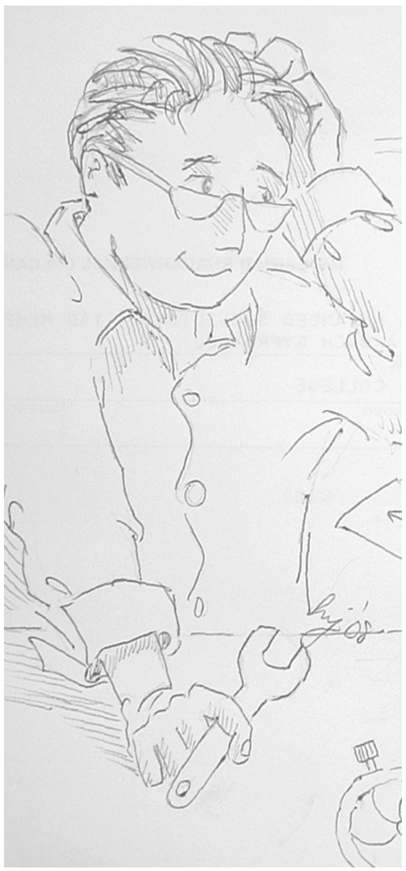


experimentalist’s perspective

The good: experiments (they are real!)

The bad: models (never match data)

outline



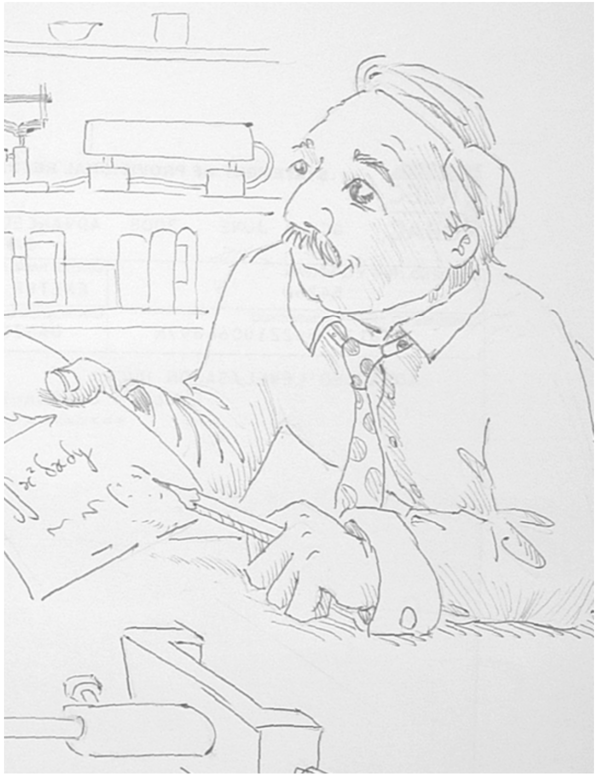
experimentalist's perspective

The good: experiments (they are real!)

The bad: models (never match data)

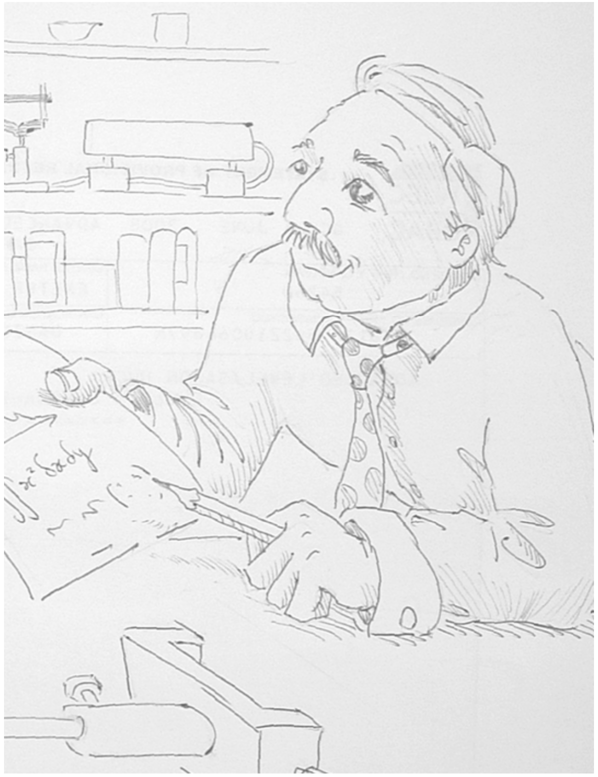
The ugly: theory (incomprehensible)

outline



theorist's perspective

The good: theory (its pure!)



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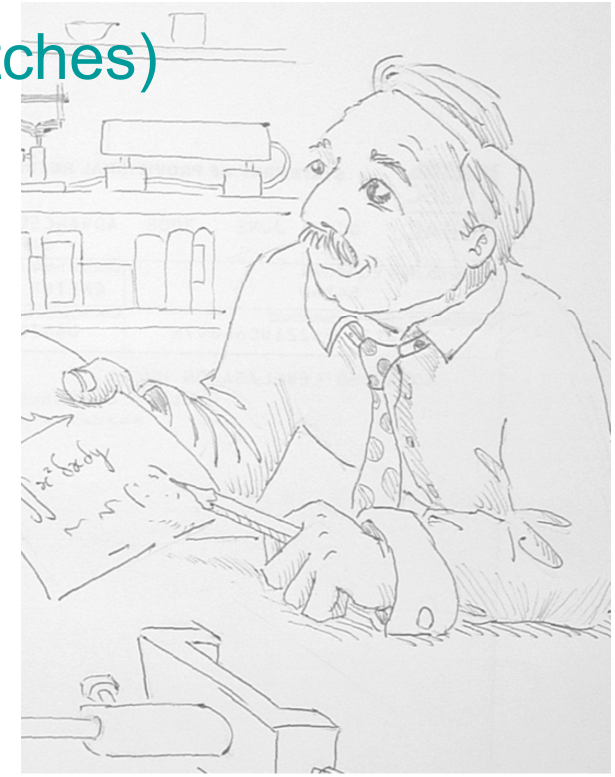

theorist's perspective

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The good: theory (its pure!)

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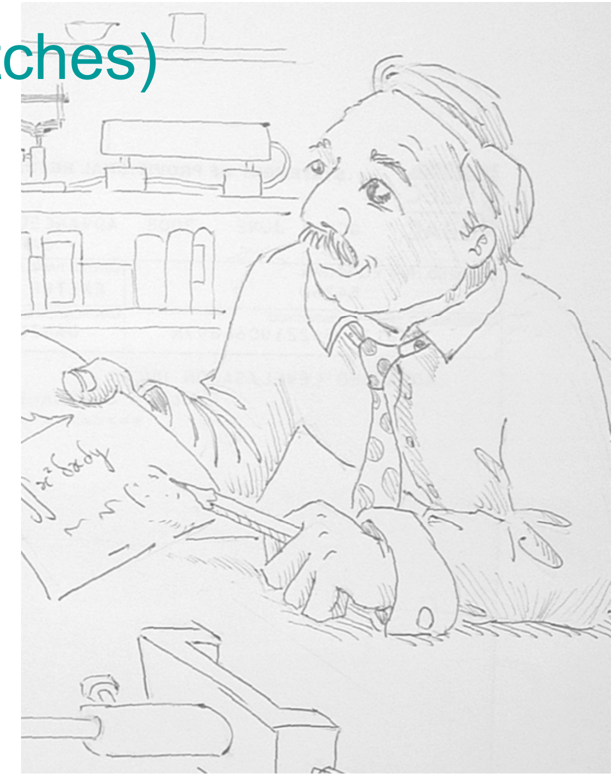
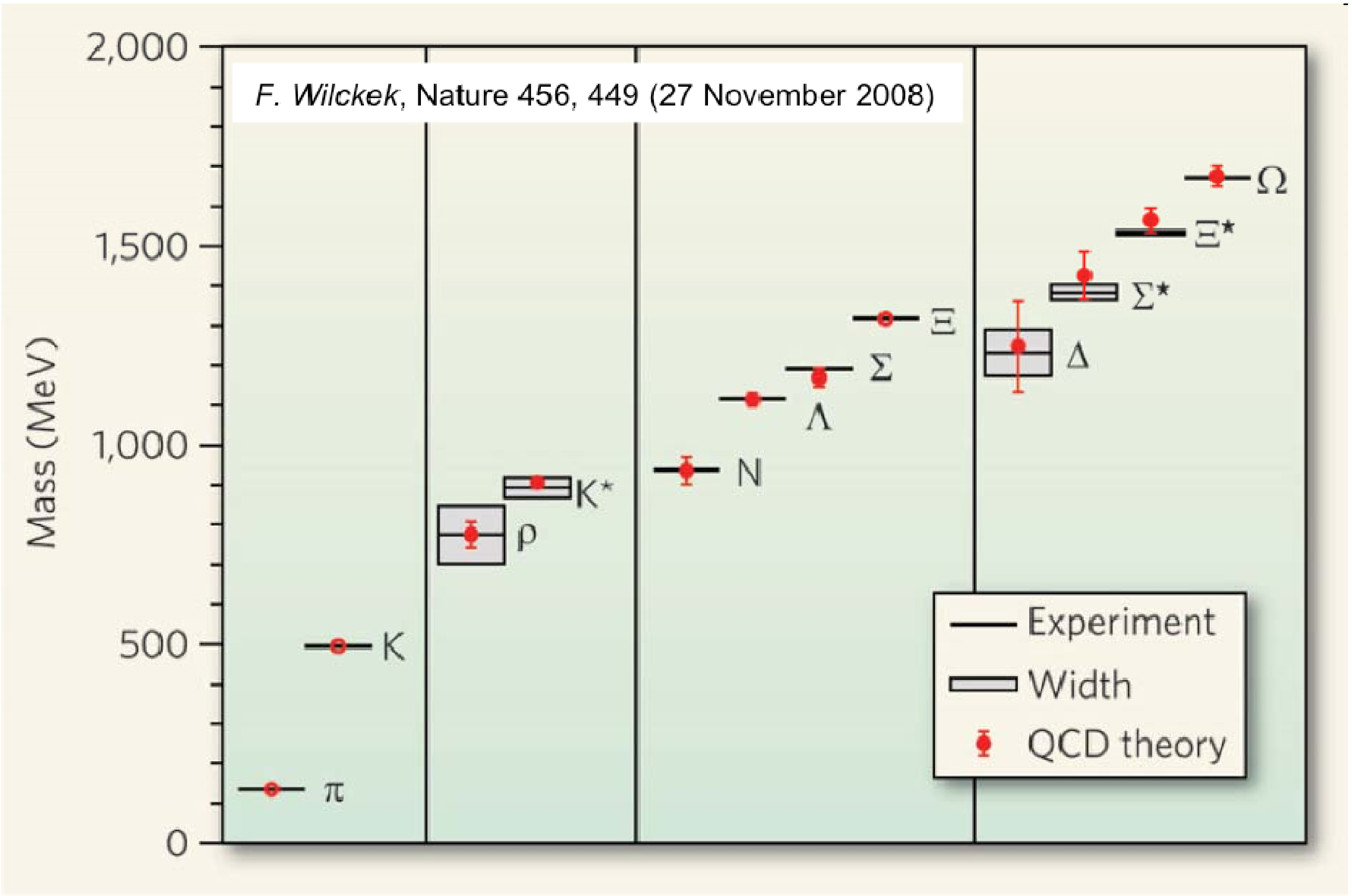
The ugly: fabrication details..



experiment *vs.* theory

Dürr et al. Science **322** 1224 (Nov 21st 2008)



Science is a mixture of experiment and theory – that's the real beauty

plasmonics

plasmon modes – confinement and control of light in (deep) sub-wavelength regime

Plasmonics

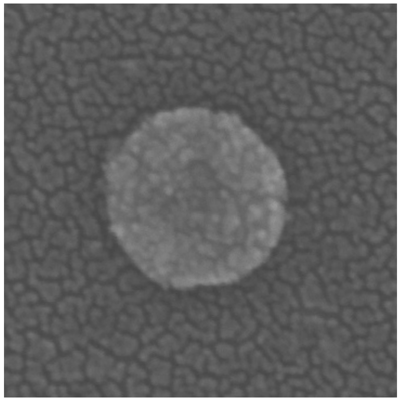
- Biosensing/Immunoassay
- Sub-wavelength photonics
- SP circuits
- Quantum cascade lasers
- Spaser
- Thermal cancer therapy (targeted absorption)
- High harmonic generation
- SP based metamaterials
- Controlling optical molecular processes (emission, absorption..)
- Photo-stable labels/probes in biomedicine

only possible through combination of nanofabrication and computation

a simple problem

Chris Burrows

Scattering of light by a metallic disc. “I’ll even get rid of the substrate!”



gold disc made by electron-beam lithography
immersed in index matching oil
120 nm dia, 30 nm thick

Burrows and Barnes
unpublished

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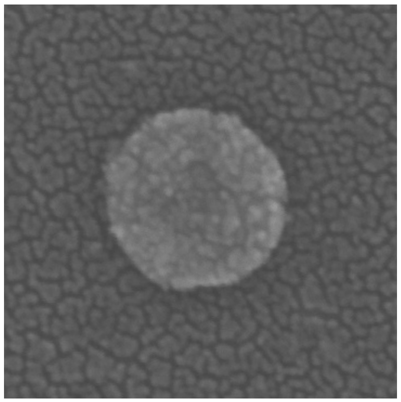
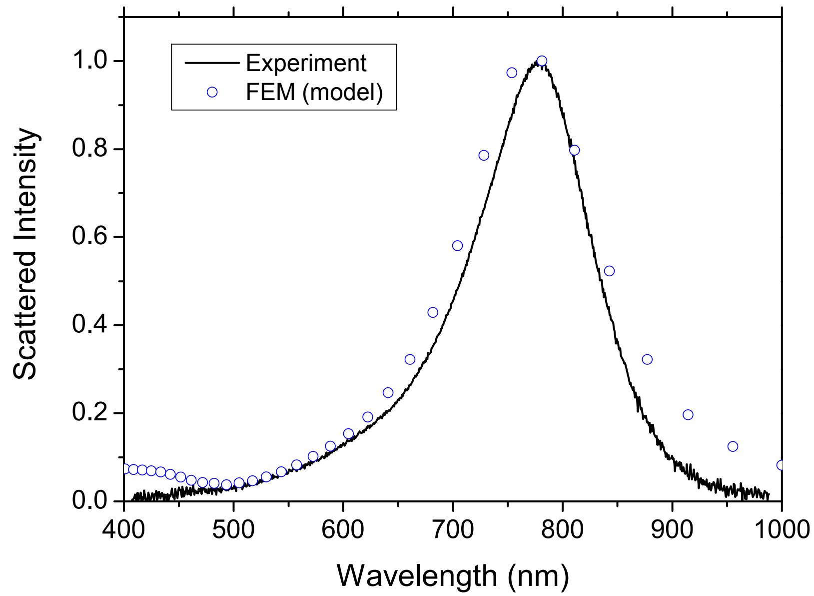


mesh scale ~ 3 nm



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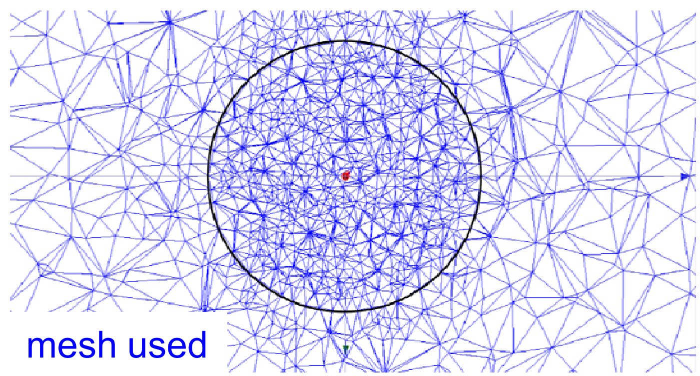
exact shape? grains? surface contamination?..



mesh used

….illumination and collection?

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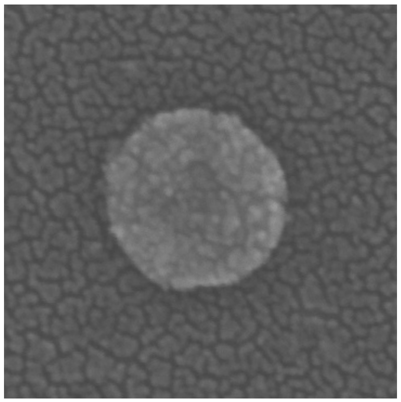

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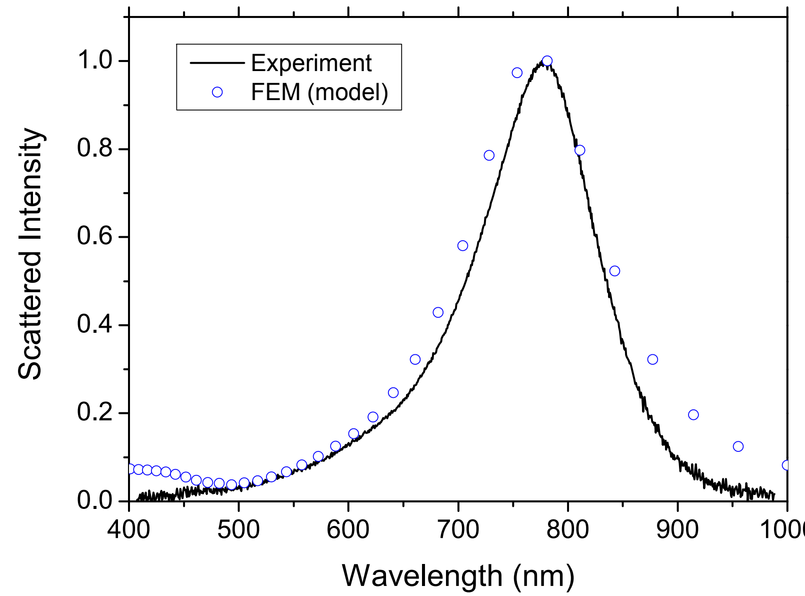

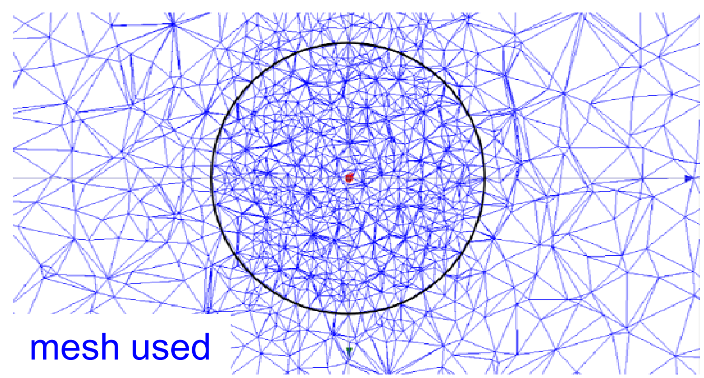

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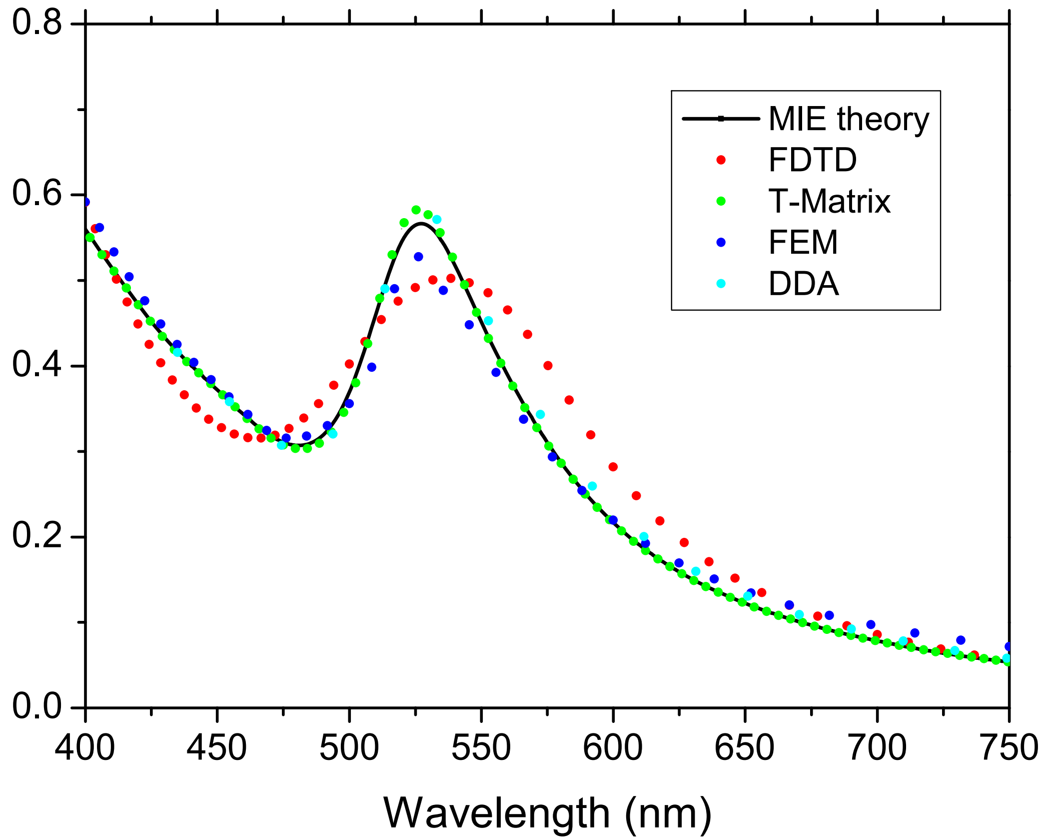
Scattering of light by a metallic sphere: comparison of techniques



approach:	comp time
Mie theory (ε:J&C):	1 s
T-matrix (ε:J&C):	100 s
DDA: (ε:J&C)	1000 s
FDTD (Drude):	10000 s
FEM: (ε:J&C)	10000 s

80 nm gold sphere in vacuum

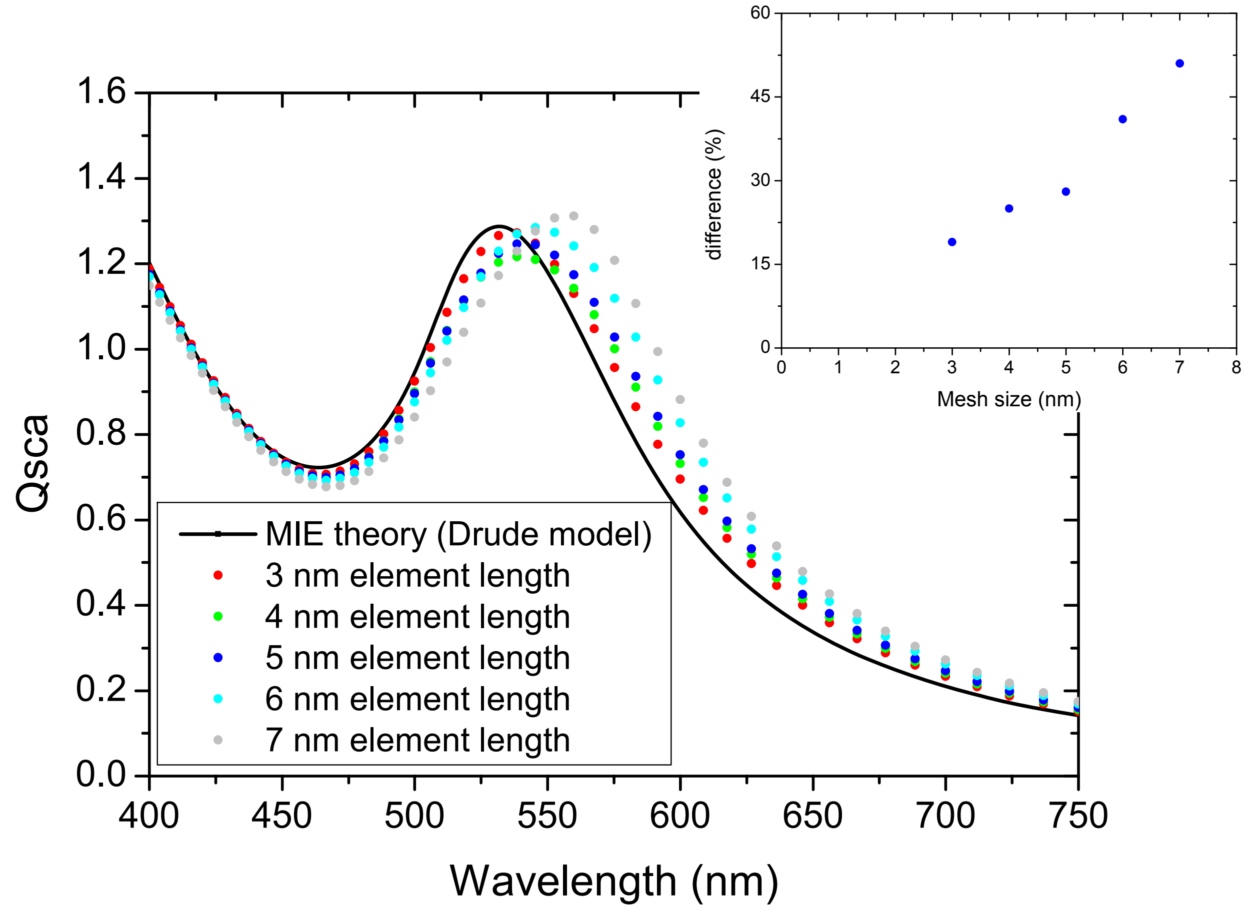
First shot at using different approaches

a simple problem

James Parsons

Scattering of light by a metallic sphere in vacuum: comparison of techniques

FDTD approach – effect of mesh size



meshing needed at 1 nm level (<< wavelength)

a simple problem

Scattering of light by a metallic sphere: comparison of techniques

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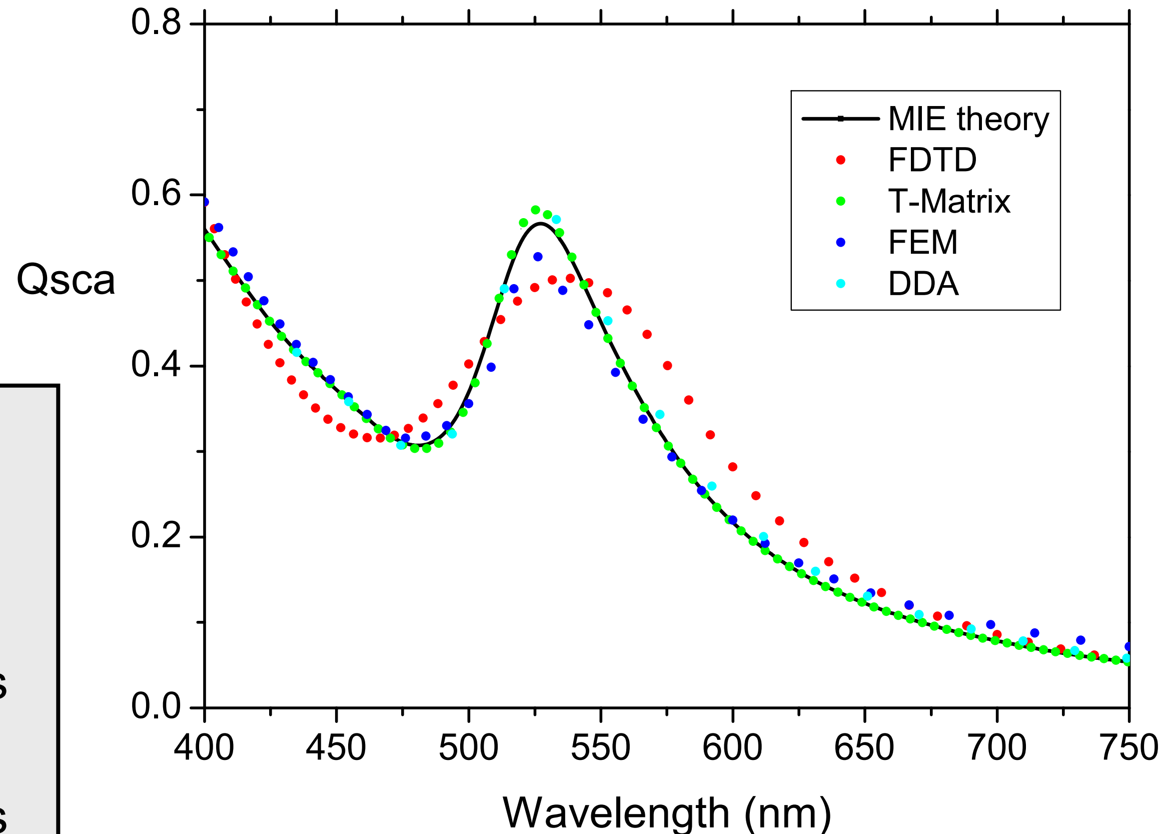

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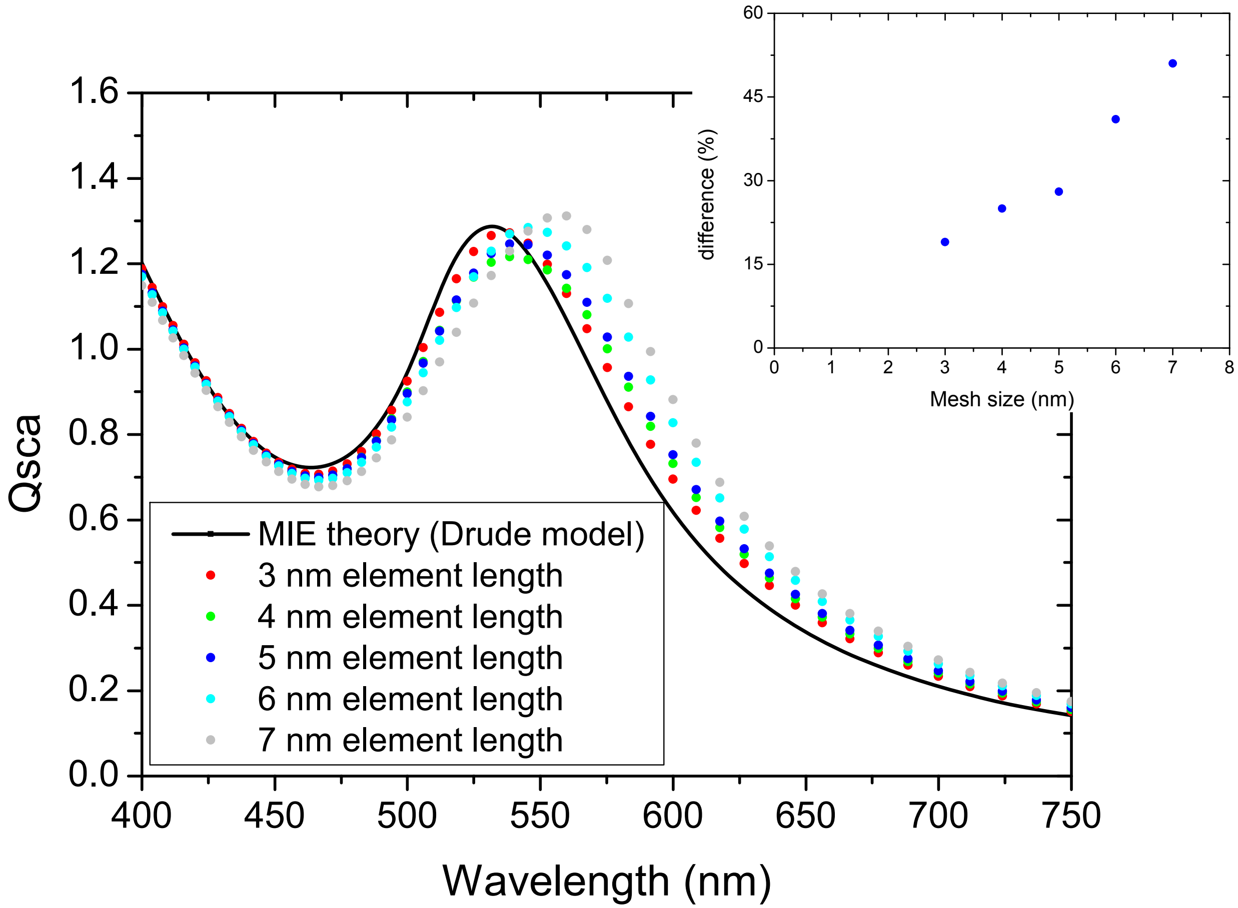

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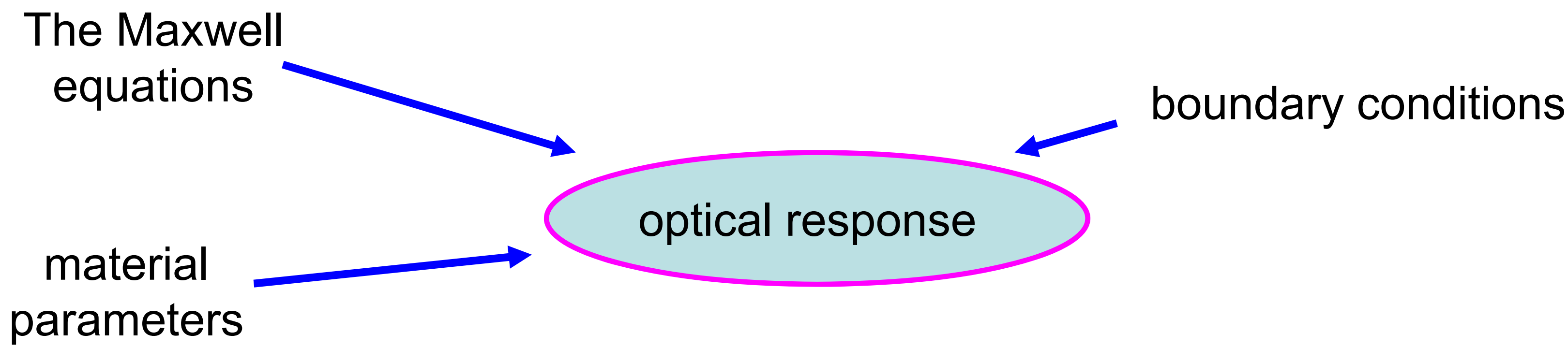
theory – EM & structured materials



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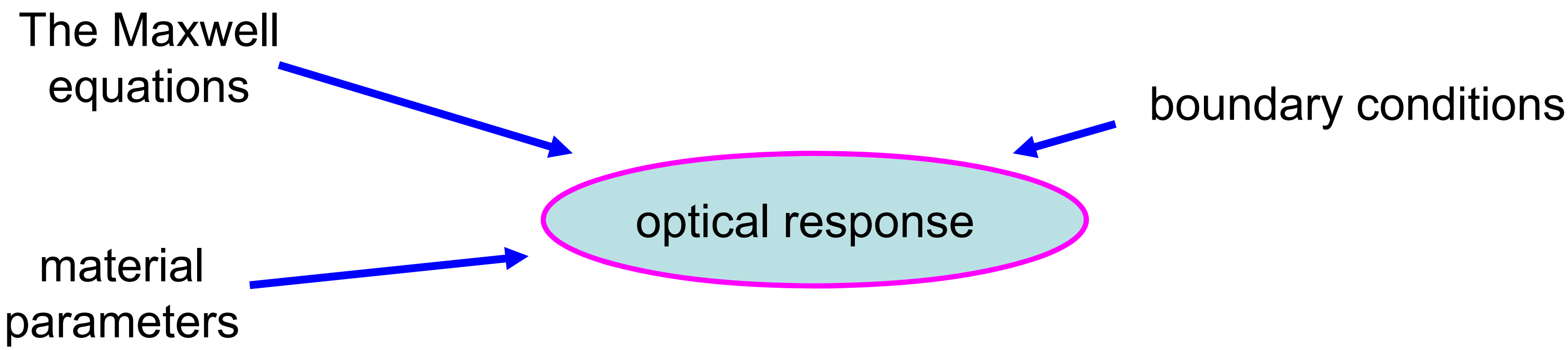

purpose of model

build understanding, explore physics…. design tools

what do we require?

modes, field profiles, field enhancement, LDOS, cross-sections, polarization behaviour…

so what's the problem?

informal survey – (1) relative permittivity, $\varepsilon(\omega)$, (2) meshing.

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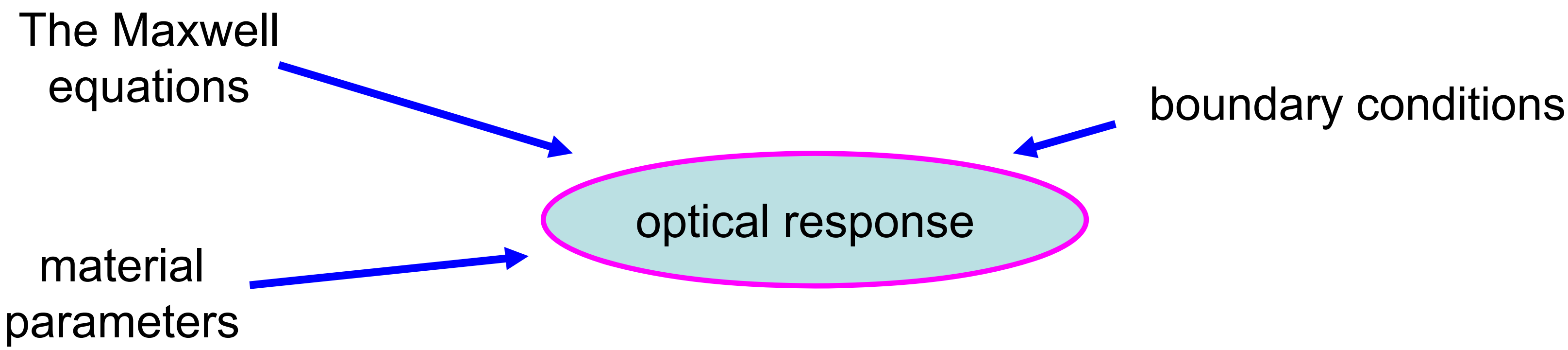

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experimental problems
not well enough controlled/specified, contamination, morphology, illumination, internal structure…

models
assumptions/and approximations too restrictive, perfectly periodic structures, bulk $\varepsilon(\omega)$

computational approaches

- Mie theory
- Finite difference time domain (FDTD)
- Finite element method (FEM)
- Green's dyadic method
- Boundary element method (BEM)
- Dipole-dipole approximation (DDA)
- Multiple multi-poles (MMP)
- Rigorous coupled wave/Fourier modal method
- Coordinate transformation (Chandezon)
- Effective media
- ….I wish I could remember!!………….

how well do they cope with,

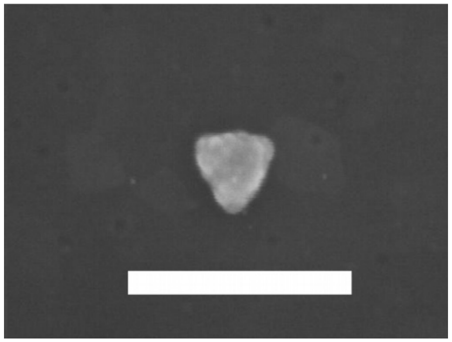
- anisotropy?
- nonlinearity?
- transient behaviour?
- random structures?

…….?

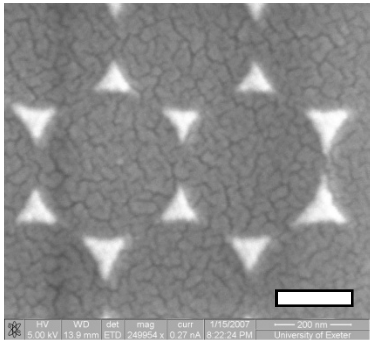
experimental details

fabrication !!!

electron-beam lithography vs. nanosphere lithography



scale bar 300 nm



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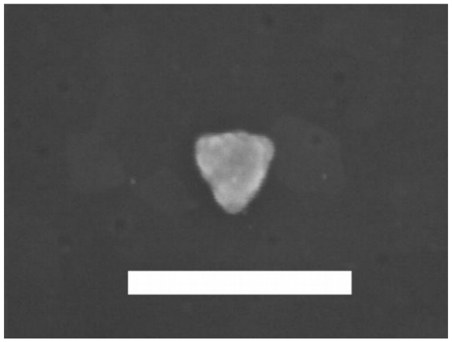

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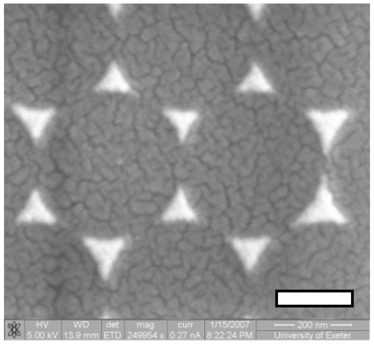
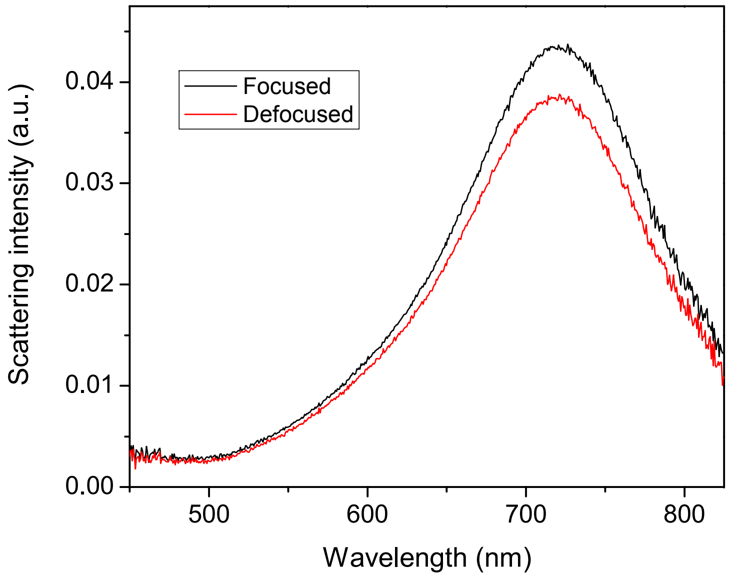


scale bar 200 nm

focussing!

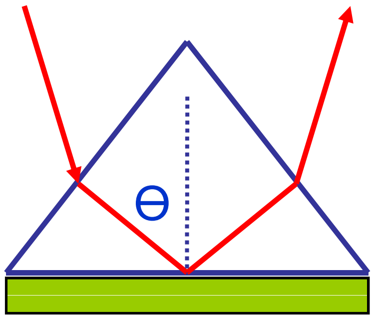


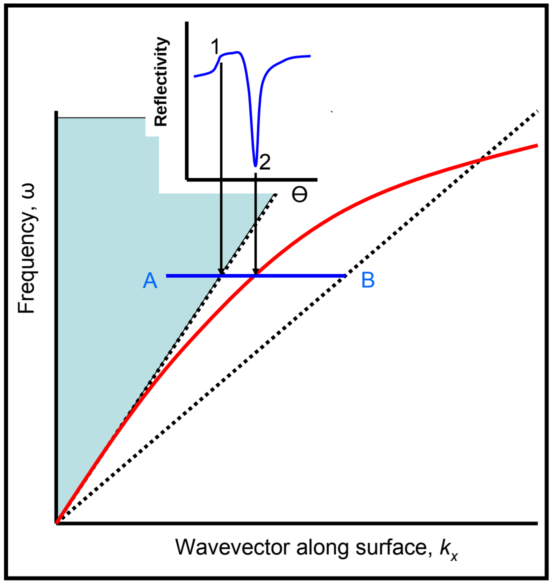
scattered light collected from single gold disc in dark-field

we would like to determine cross-section…

stepping back – planar metal film

surface plasmon-polariton on a planar gold film





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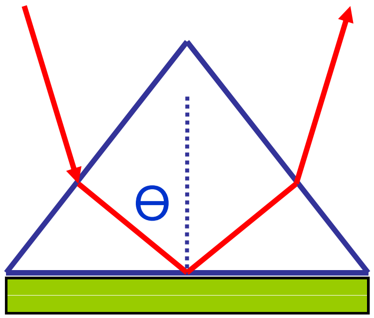

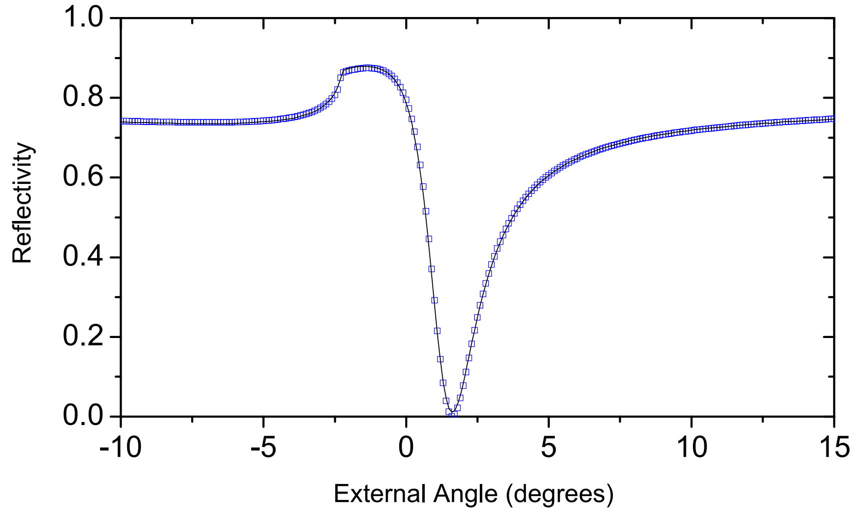

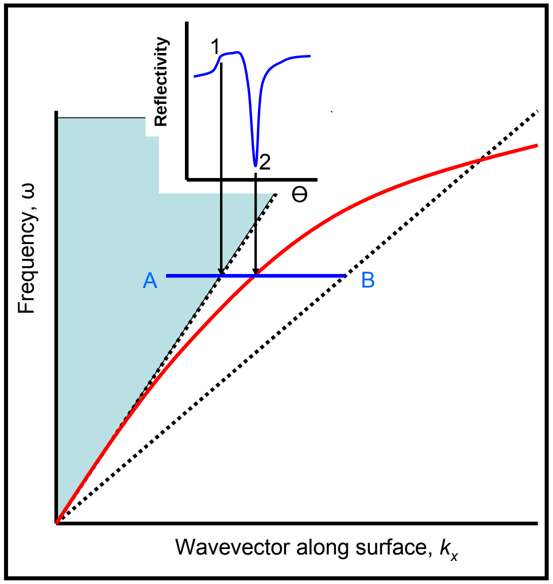

gold film parameters from fit of Fresnel's equations to data

permittivity, ε = -10.73 (± 0.02) + 1.279i (±0.005), d = 47.2 nm ± 0.1

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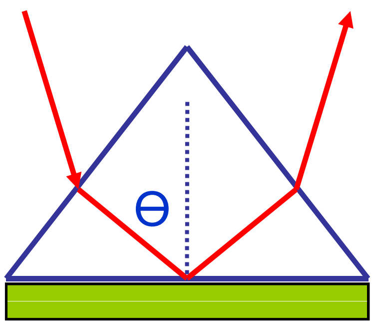

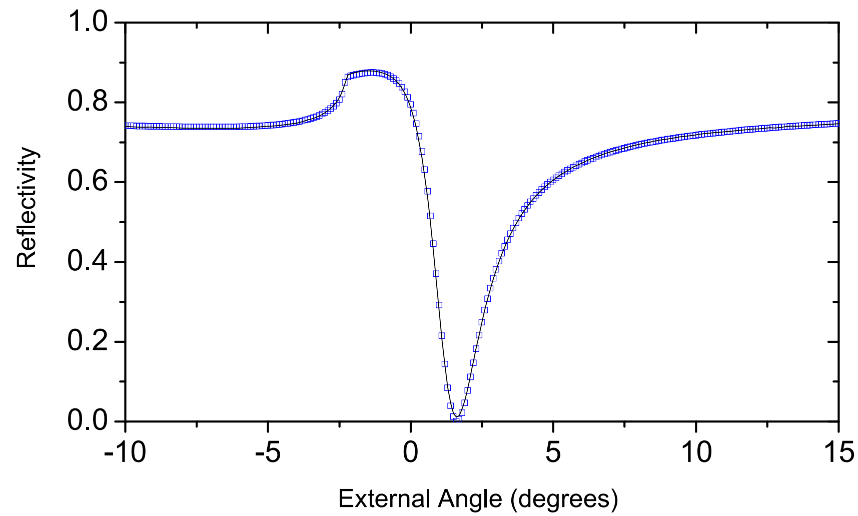

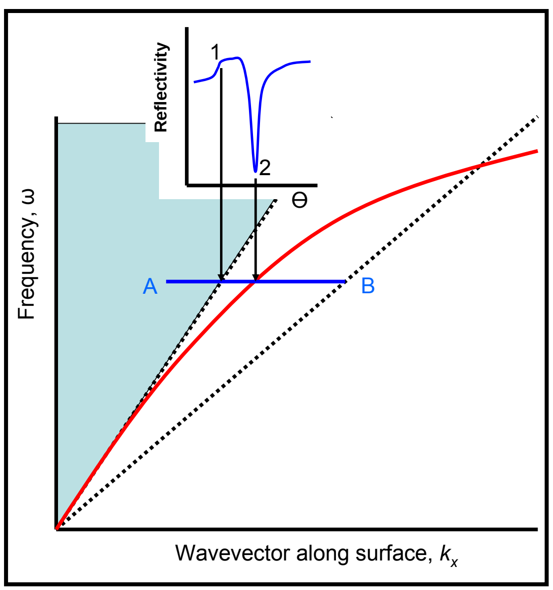

gold film parameters from fit of Fresnel's equations to data

permittivity, ε = -10.73 (± 0.02) + 1.279i (±0.005), d = 47.2 nm ± 0.1

but

Johnson and Christie (PRB **6** 4370 (1972))

ε = -12.3 + ~1.2i

and

Lynch and Huttner, "Handbook of Optical Constants of Solids", (1985), ed. Palik

ε= -10.4 + 1.4i

whilst

Innes and Sambles (J Phys F: Met **17** 277 (1987))

ε= -11.8 + 1.36i

stepping back – planar metal film

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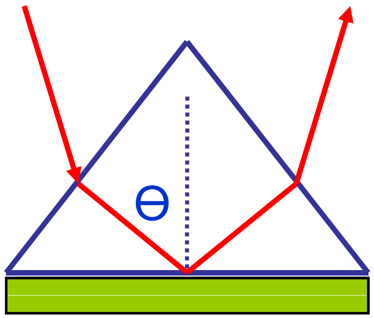

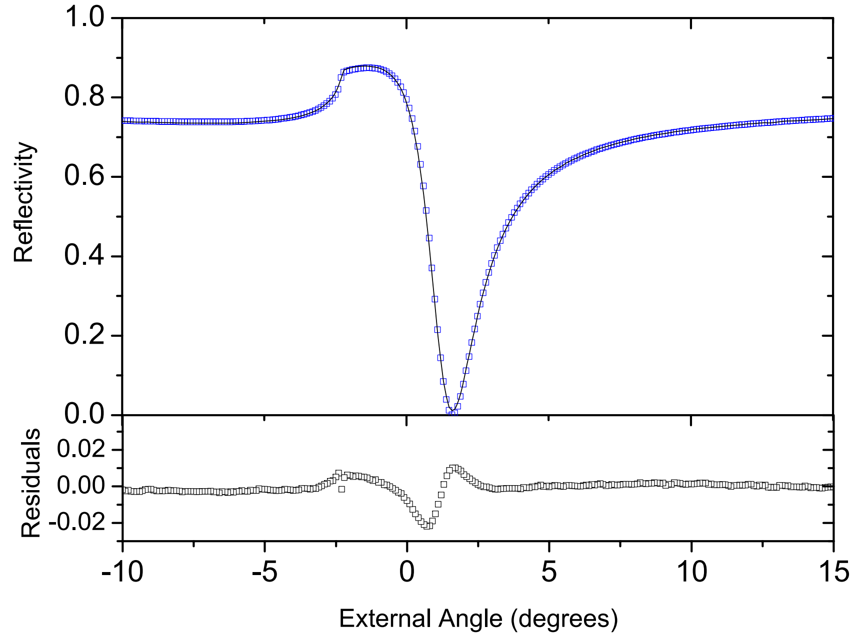

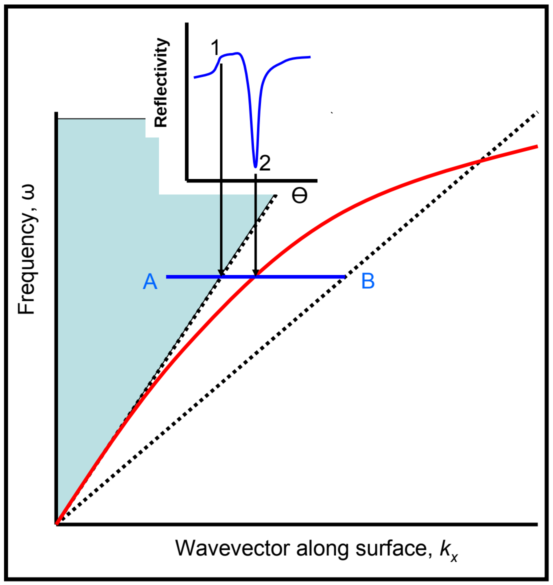

residuals show up a problem
surface roughness?
grain boundaries?

stepping back – planar metal film

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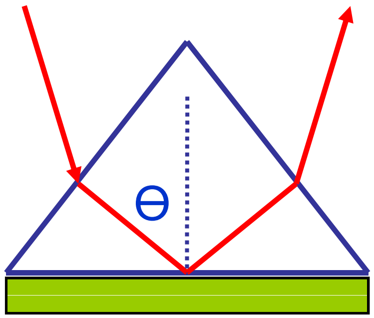

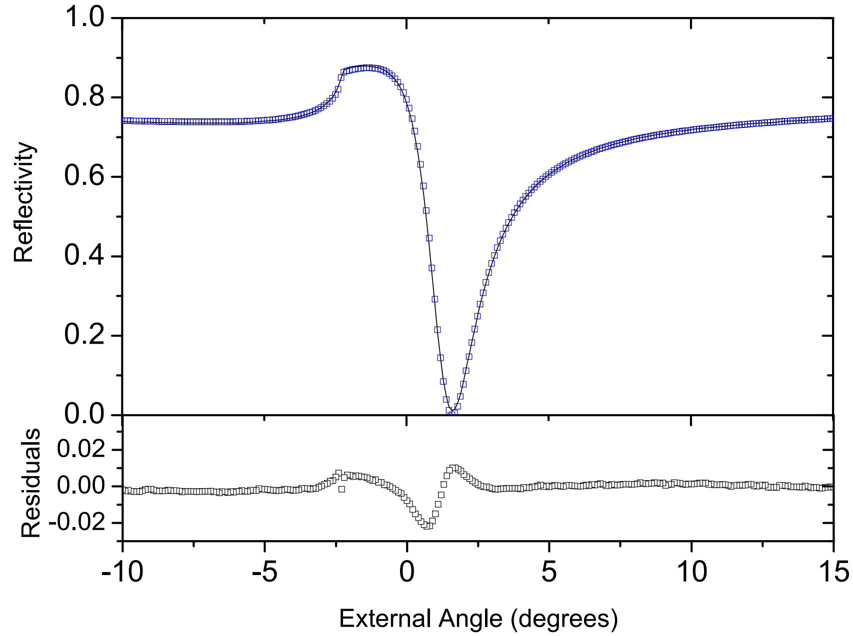

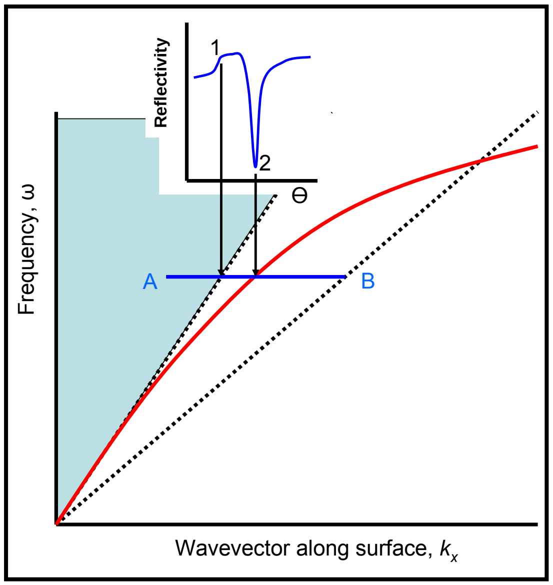

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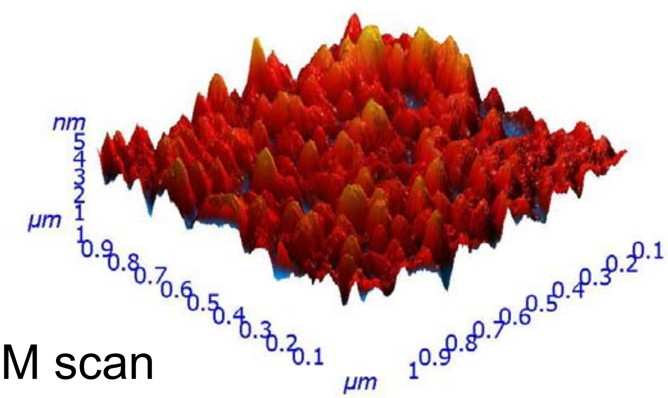
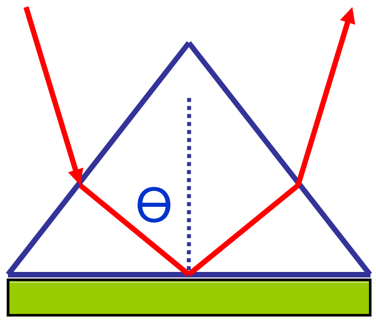


AFM scan

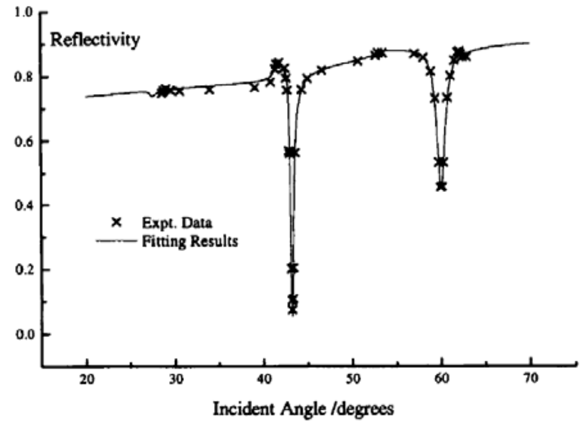
stepping back – planar metal film

…in fact there is an SPP supported by both metal surfaces…



Corrugated film used so as to allow grating coupling to prism-silver SPP

Nash and Sambles (J Mod Opt **46** 1793 (1999))



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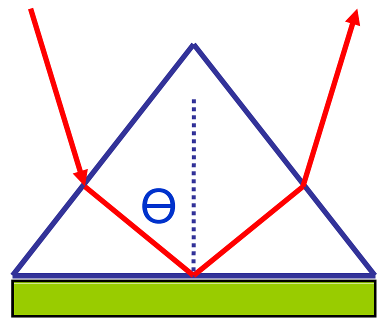

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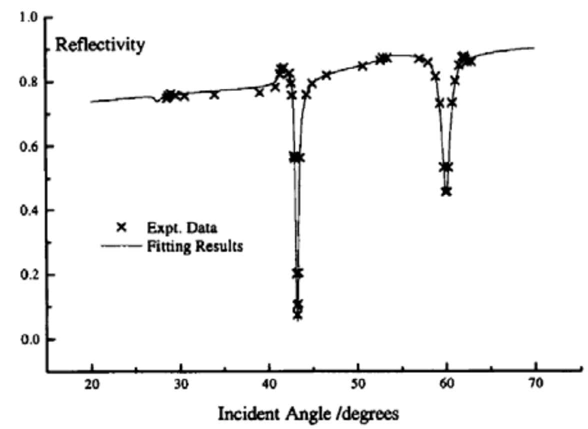
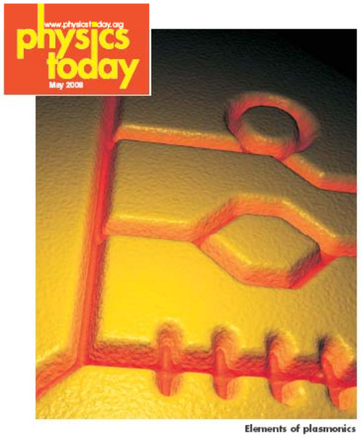


wavelength 633 nm

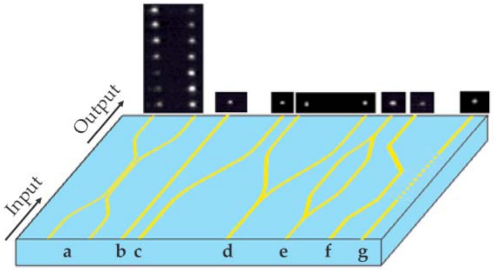
Silver film thickness/nm	Glass/Silver interface ε_r	Glass/Silver interface ε_i	Silver/Air interface ε_r	Silver/Air interface ε_i	Uncertainties $\Delta\varepsilon_{r,i}$	Uncertainties thickness
31.1	−20.41	0.92	−14.74	0.69	±0.1	±1
50.1	−21.06	0.94	−13.85	0.90	±0.1	±2
58.6	−20.99	0.79	−15.56	0.58	±0.1	±2
76.2	−21.36	0.78	−14.50	0.43	±0.1	±4
86.2	−21.01	0.82	−17.02	0.49	±0.1	±5
125.3	−20.86	0.79	−17. 92	0.49	±0.1	±5

even a simple planar film can not be described by just one $\varepsilon(\omega)$,

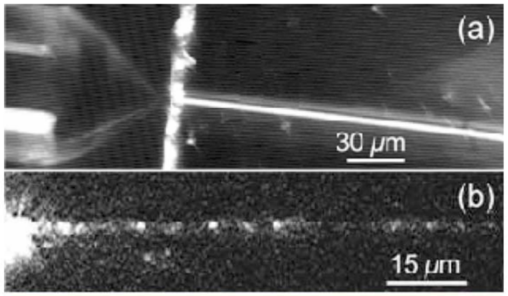
SPP waveguides and roughness



Ebbesen, Genet and Bozhevolnyi



Charbonneau et al. Opt Exp **13** 977 2008



Nielsen et al. Opt Lett **33** 2800 2008

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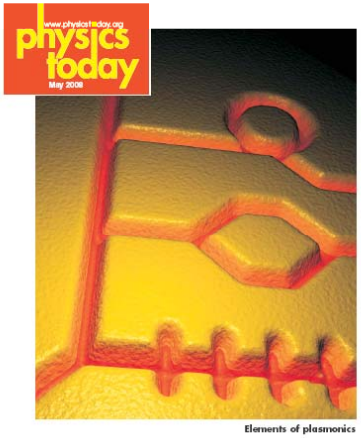

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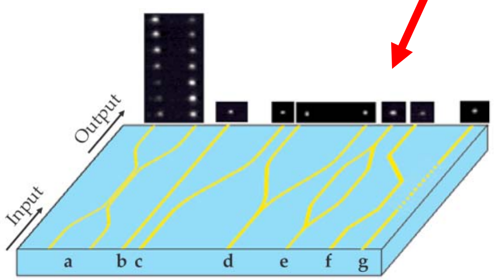

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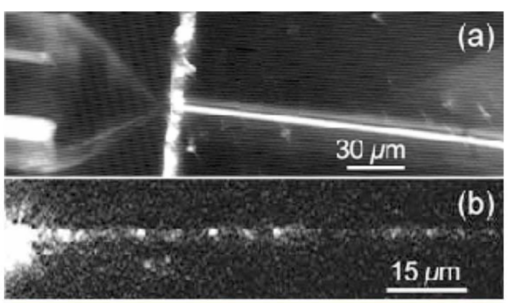
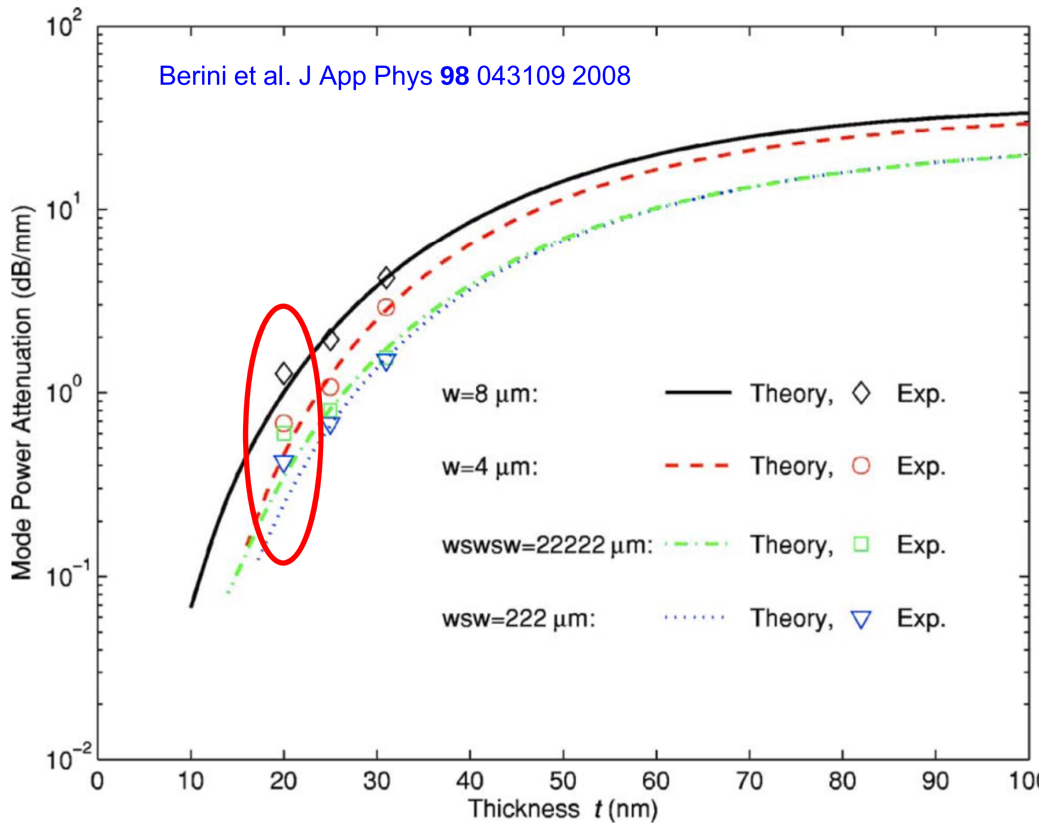


Nielsen et al. Opt Lett **33** 2800 2008

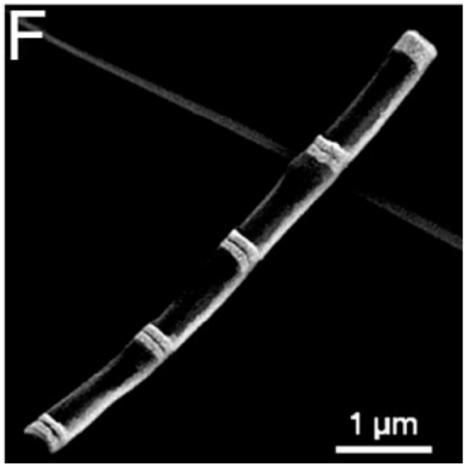
strip waveguides – coupled SPP mode (LRSPP)
loss should fall as thickness of metal reduced but…

roughness and grain boundaries influence attenuation
- not well understood



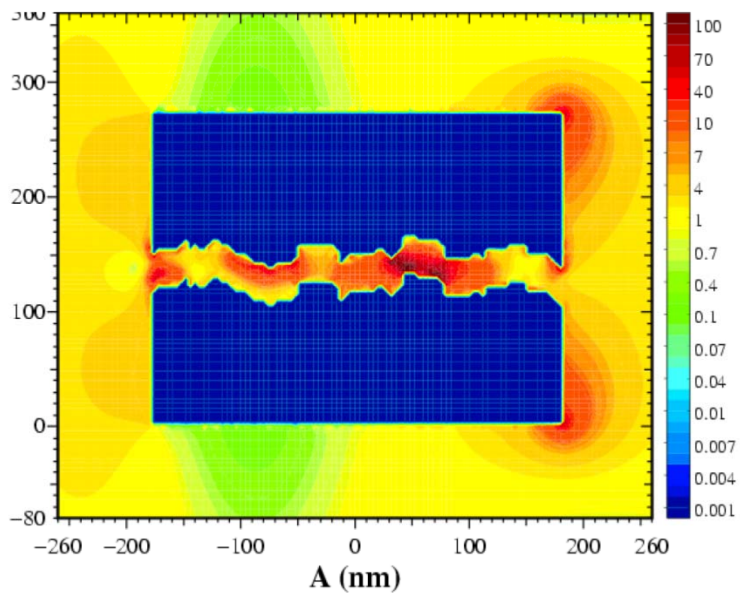
roughness and field enhancement

looking at Raman signal from double disc



Qin et al. (PNAS **103** 13300 (2006))

optimum disc-disc spacing 10 nm from DDA calculations
but 30 nm from experiment



IEI^2 for gold dimer – 32 nm separation

and Schatz (MRS Proceedings 2008)

including roughness
– hot spots

optimum separation is
now 32 nm from calculations

hot spots may dominate system behaviour!

roughness and field enhancement

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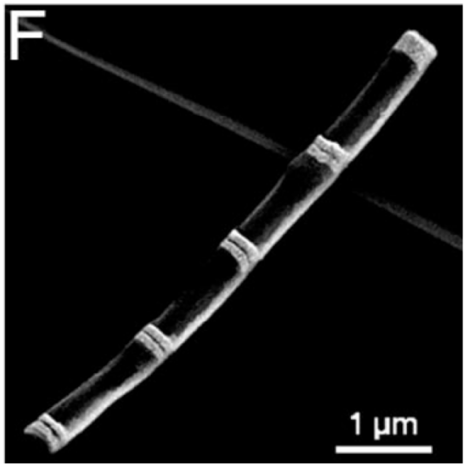

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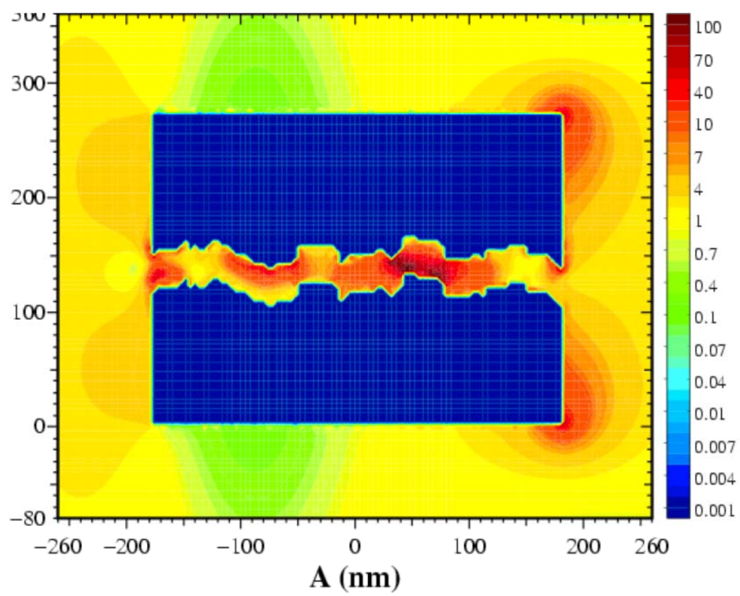


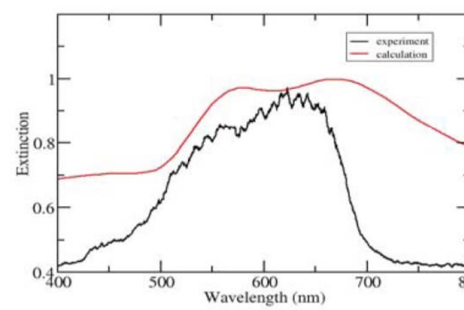
IEI² for gold dimer – 32 nm separation

and Schatz (MRS Proceedings 2008)

including roughness
– hot spots

optimum separation is
now 32 nm from calculations

but extinction spectrum!...



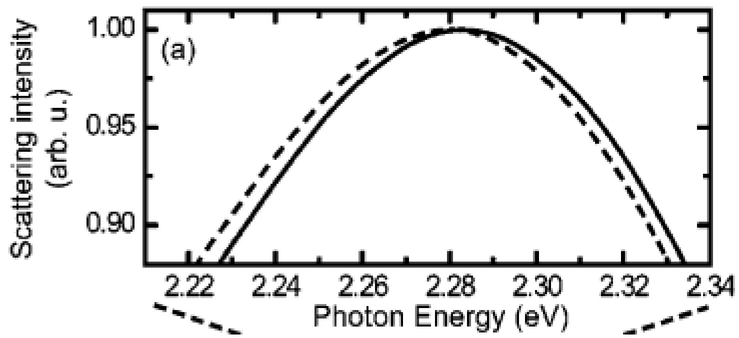
hot spots may dominate system behaviour!

contamination: basis of SPR sensing

Localised **S**urface **P**lasmon **R**esonance (LSPR)
of gold and copper nano-triangles

Gold

- sensing presence of bound target molecules



Raschke et al., Nano Lett. , **3**, 935 (2003)

- able to detect just a few hundred molecules

McFarland and van Duyne, Nano Lett. , **3**, 1057 (2003)

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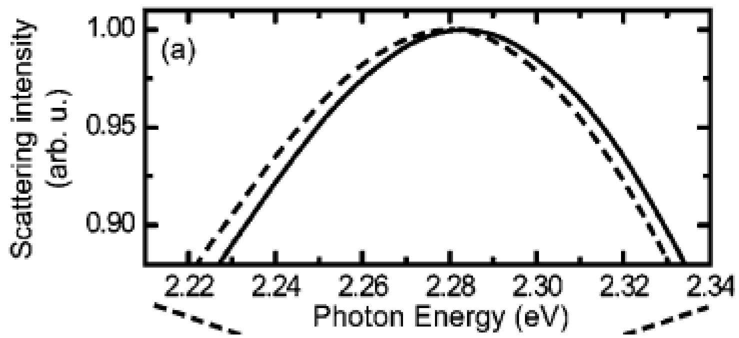

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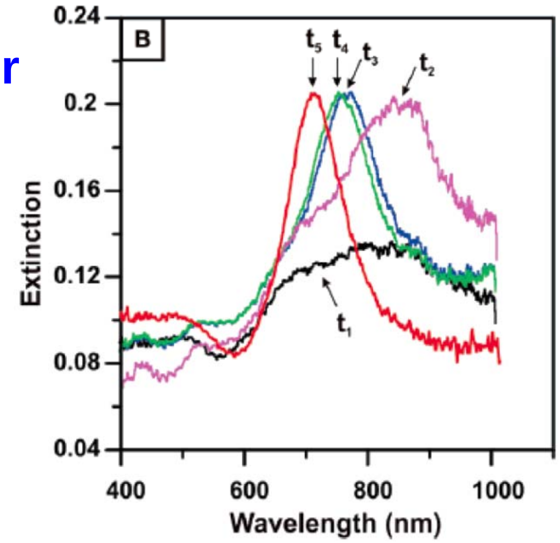
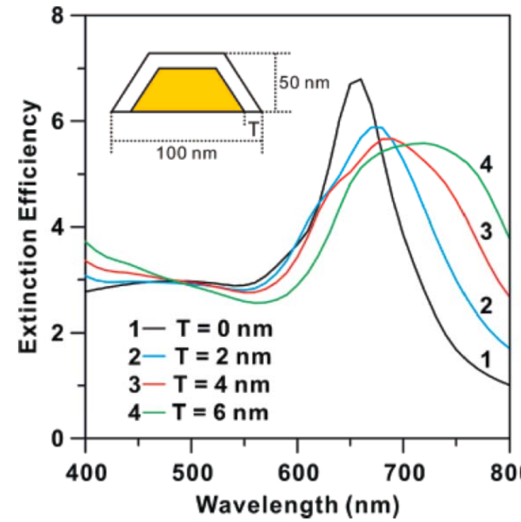
Copper



when surface oxide layer is removed, copper shows good plasmon resonance

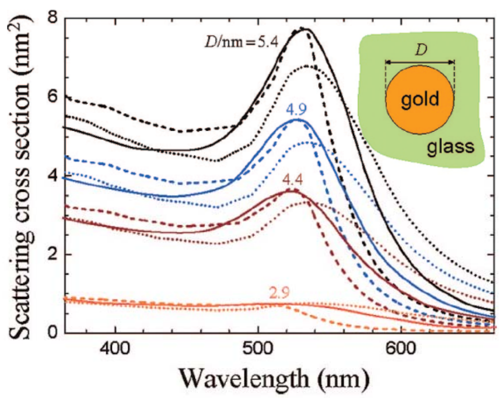


Chan et al. Nano Lett. , **7**, 1947 (2007)

chemical state of surface important

break down of bulk description

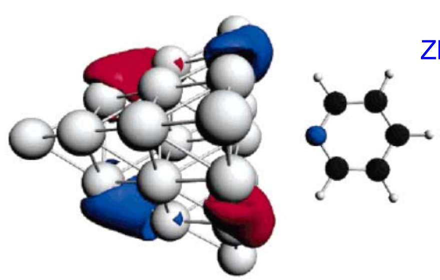
- roughness
- grain boundaries
- surface scattering
- non-local effects ..interface as a selvedge (J. Sipe, Phys Rev B **22**, 1589 (1980))
- down to what length scale can we ignore atomic nature of material?



Garciá de Abajo J Phys Chem C **112** 17983 2008

solid lines: —— experiment
analytical finite-size effect: ….. dotted
non-local theory: - - - dashed

- do we need to combine atomic (QM) description and bulk (EM) description?

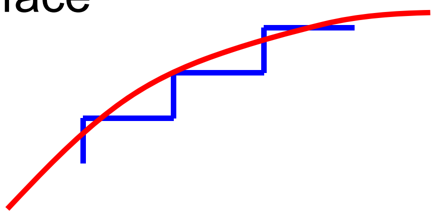


Zhao et al. J Am Chem Soc **128 2911** 2006

density-functional theory used to calculate
Raman intensities for pyridine-Ag_{20} cluster

problems with the mesh

- Optical regime – mesh is needed down to 1 nm scale
- Big mismatch between this mesh size and wavelength (>10^2)
- Fields at surface not well represented by staircase surface



….models might be flawed – but do we have experimental control at this level?

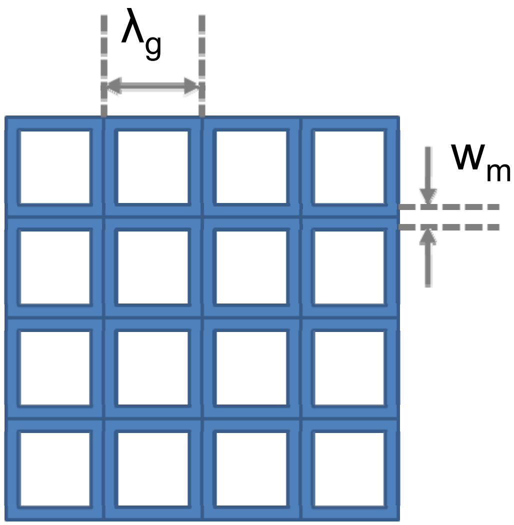
we don’t have to go to the optical - problems exist at microwave frequencies!

problems with the mesh

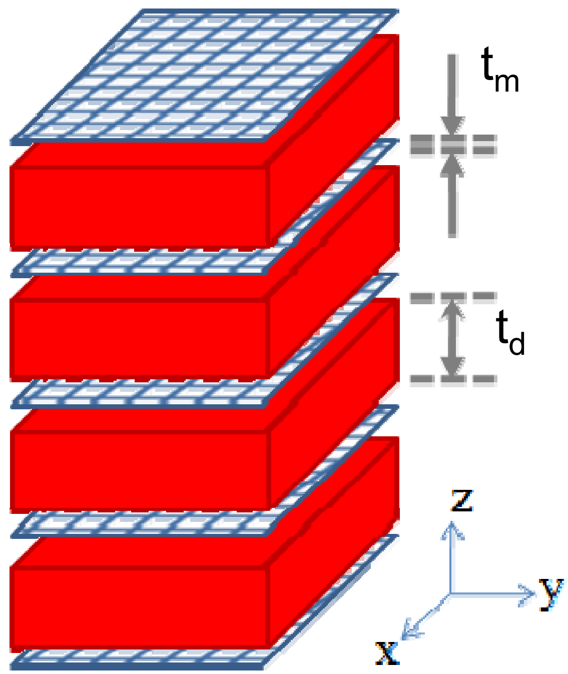
Celia Butler

A metal-dielectric stack – the metal being a grid (hole array)

(Butler et al., submitted to PRL May 2009)



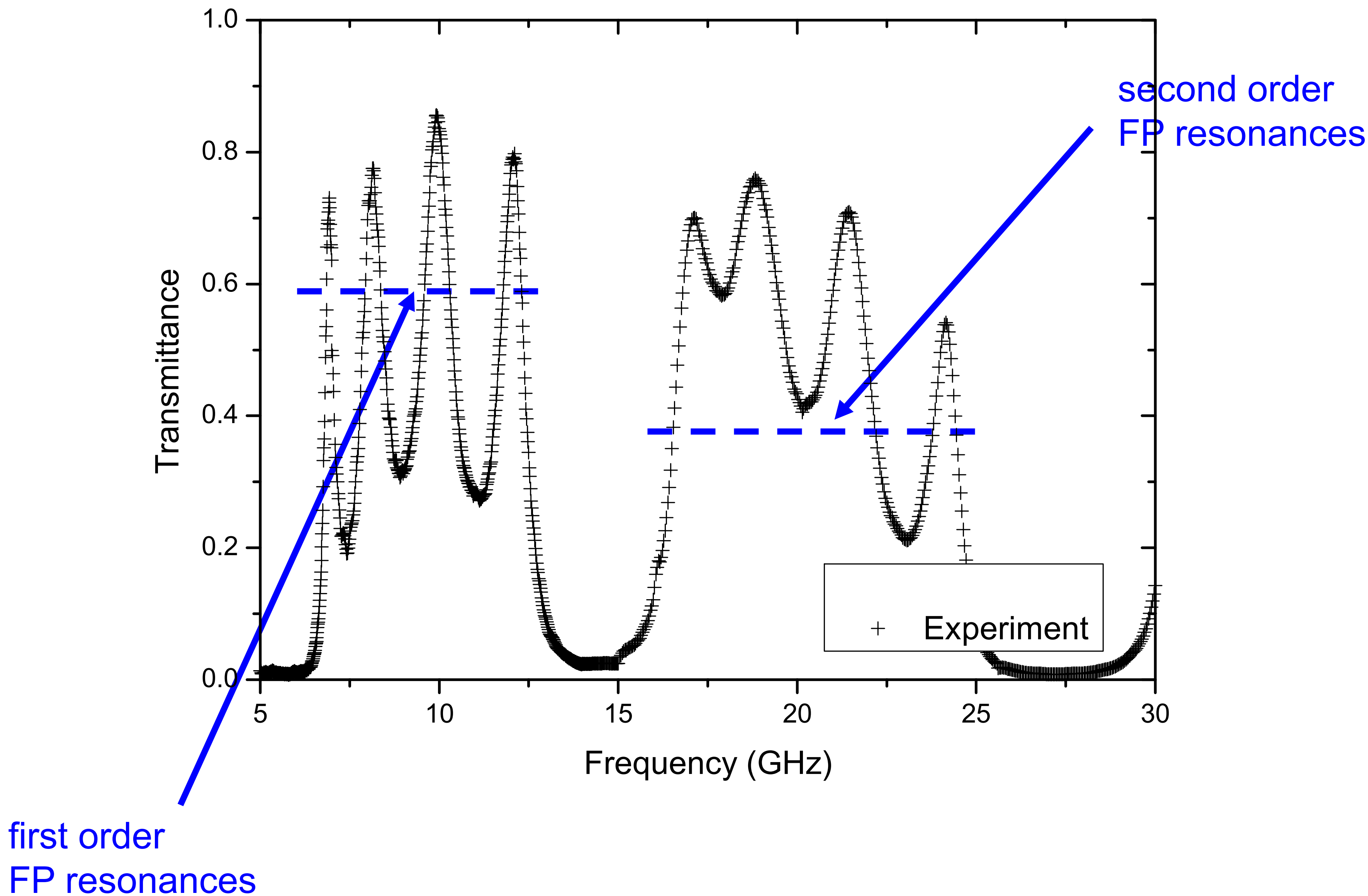
the air-filled hole array metamaterial, blue represents copper
t_m = 18μm,
λ_g = 5mm,
w_m = 0.2mm.



the metamaterial/dielectric stack, where red regions represent the dielectric
t_d = 6.35mm

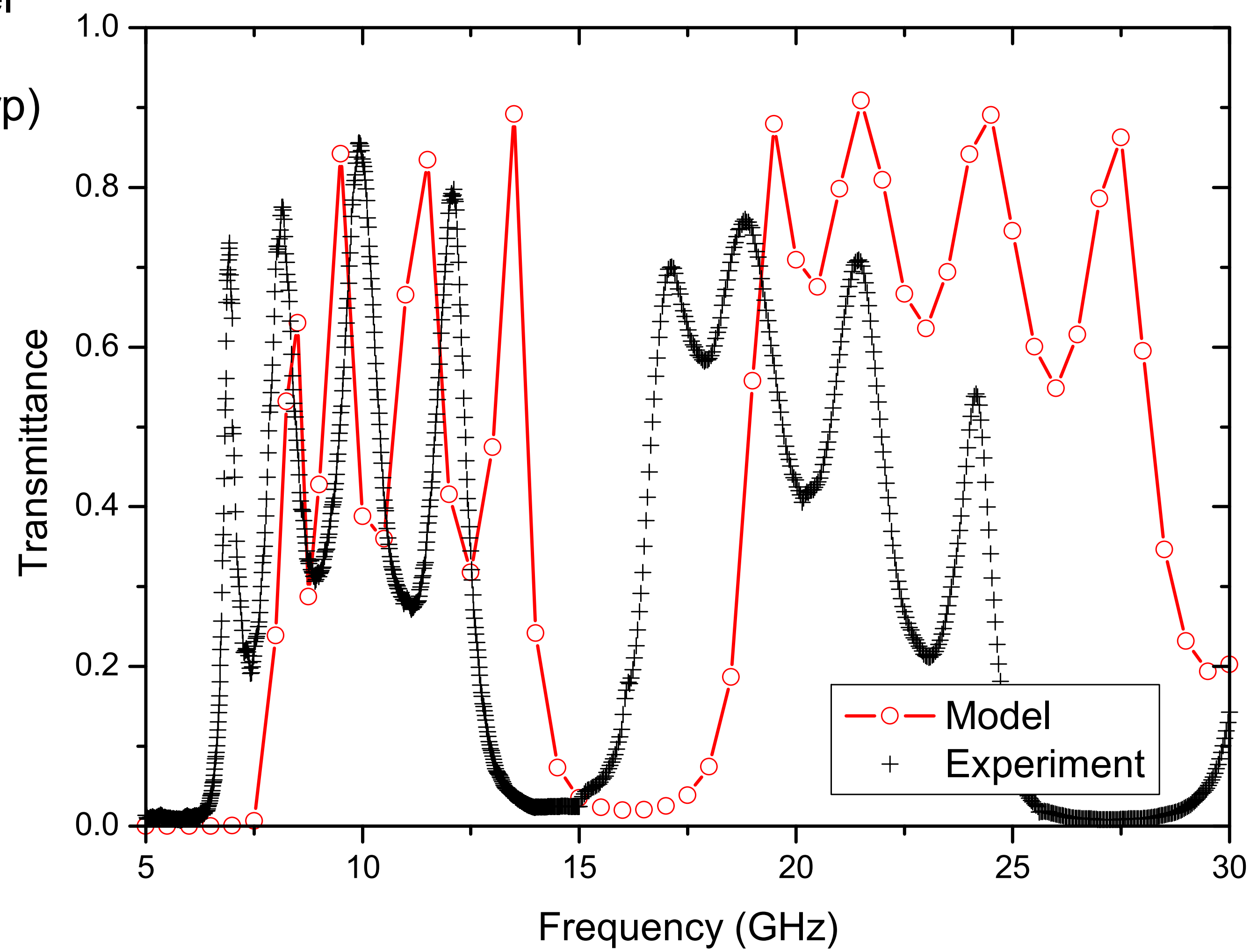
- frequency range of interest is 5 GHz – 40 GHz
- equivalent wavelength range is 7.5 mm – 6 cm

problems with the mesh



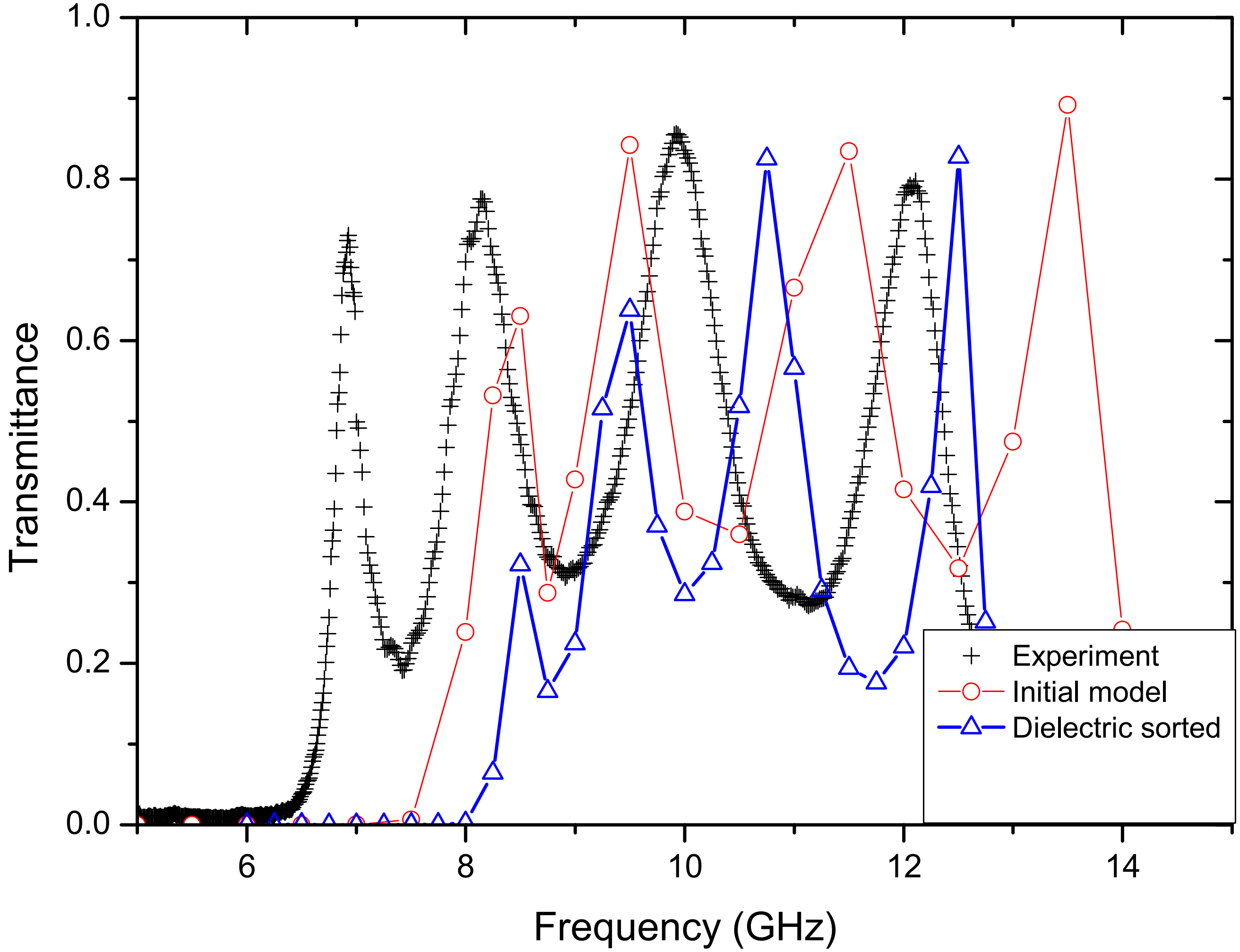
problems with the mesh

FEM model
HFSS
(Ansoft corp)



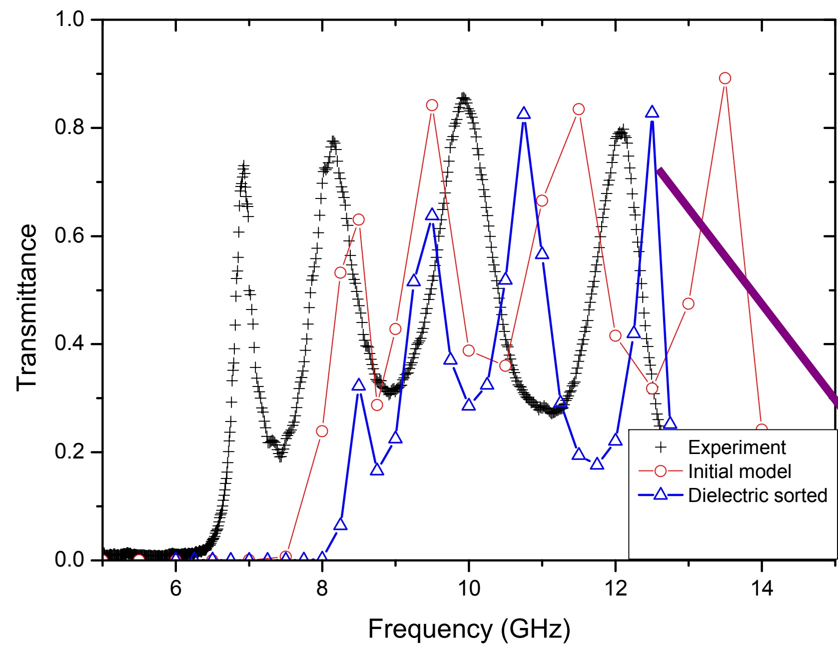
- 10% mismatch in frequency
- looks as though thickness and/or permittivity of spacer is wrong

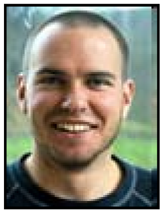
problems with the mesh



measure permittivity independently $\varepsilon = 2.55 + 0.0i$ ⟶ $\varepsilon = 3.00 + 0.004i$

problems with the mesh

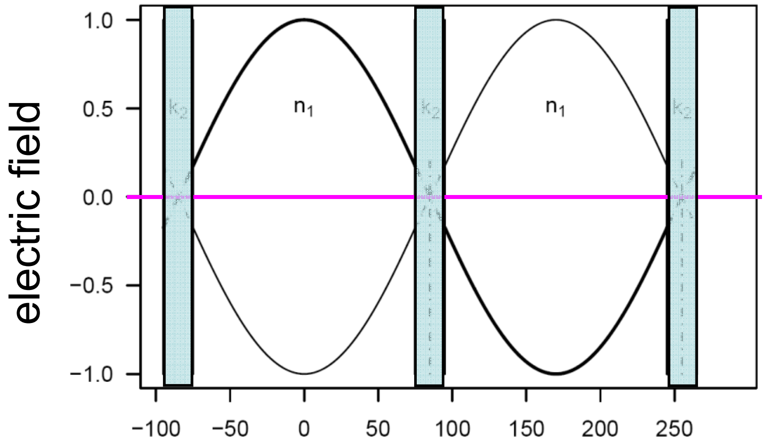




Martyn Gadsdon

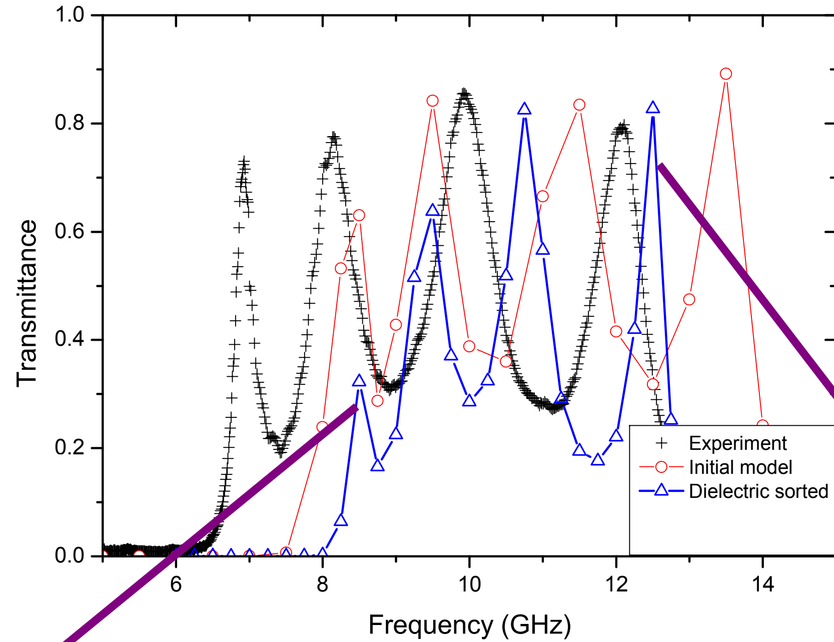
Gadsdon, Parsons and Sambles, sub to JOSAB (2008)

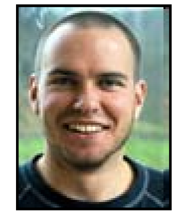
high-freq solution



cos distribution – little field in metal

problems with the mesh





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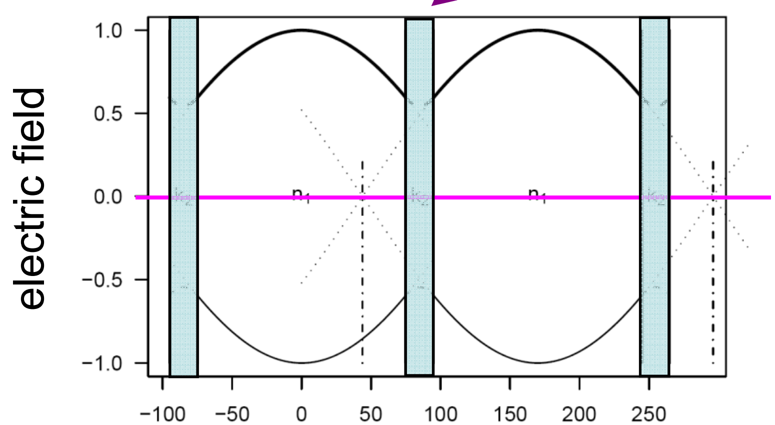
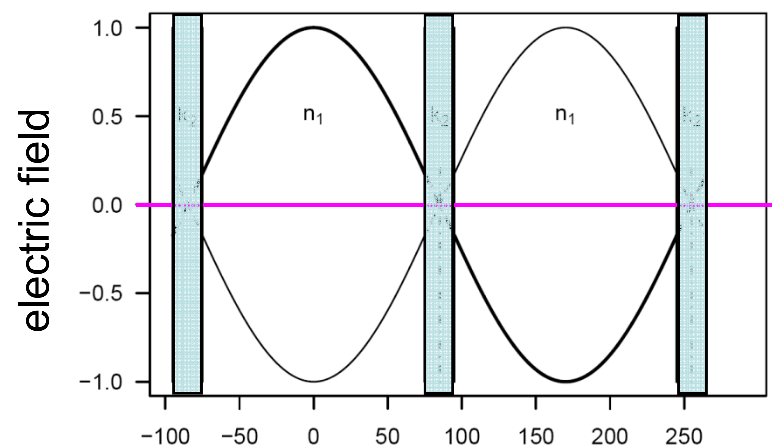
low-freq solution

high-freq solution

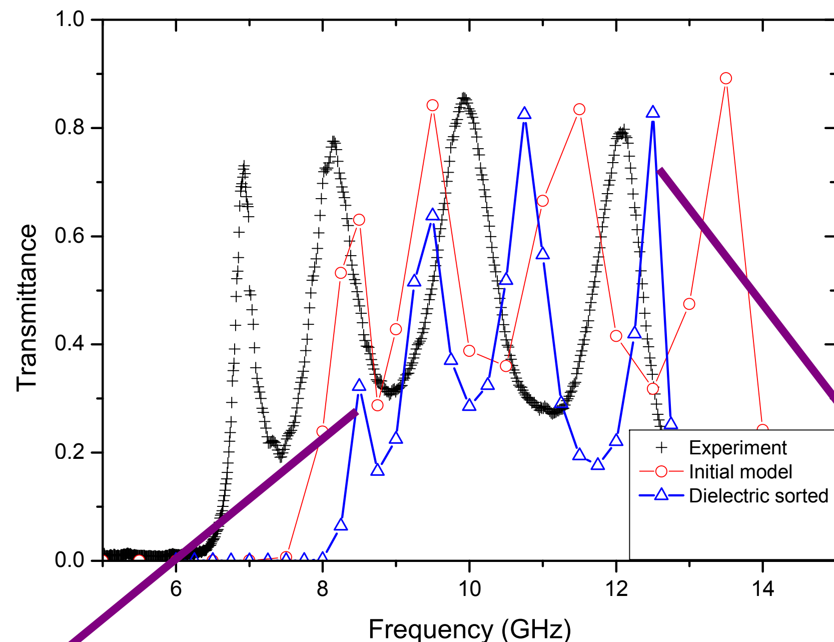


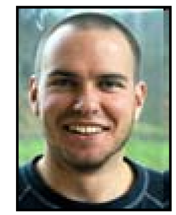


sinh distribution – considerable field in metal

cos distribution – little field in metal

problems with the mesh





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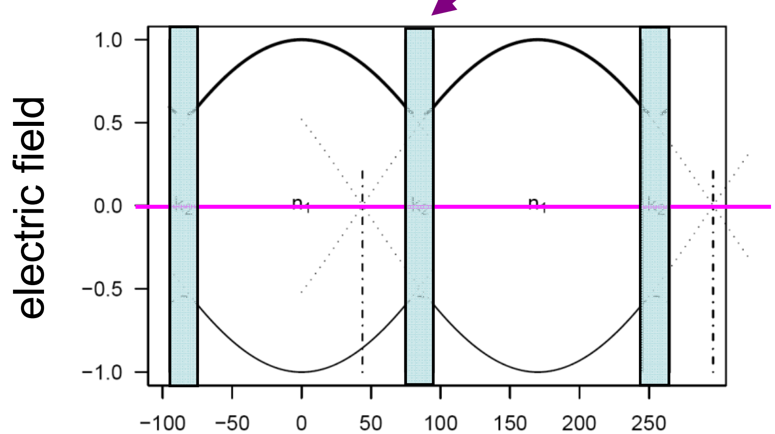
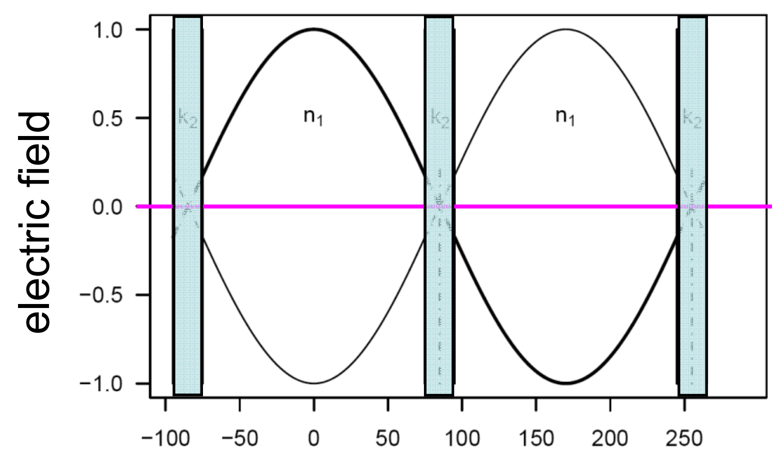
high-freq solution



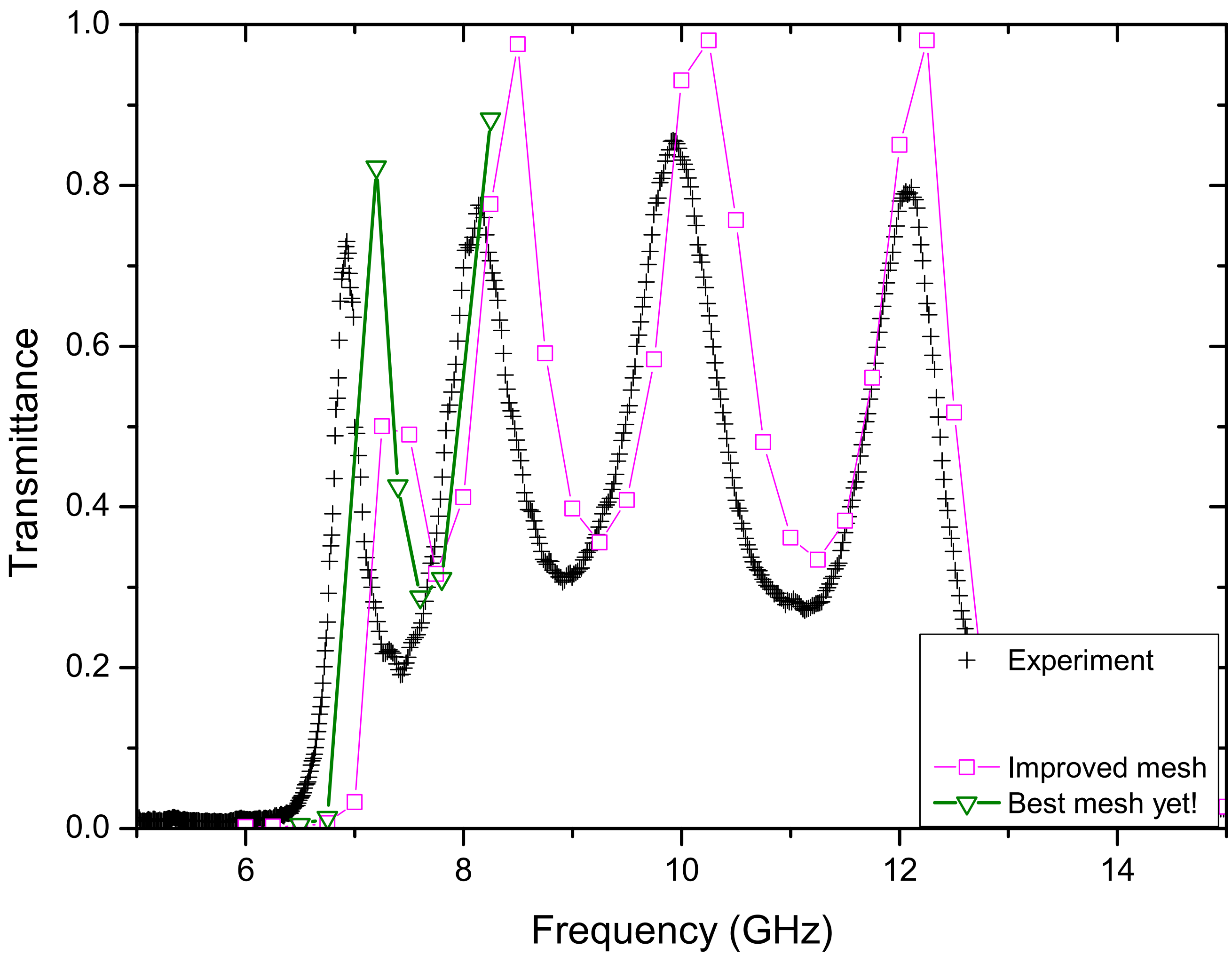


sinh distribution – considerable field in metal

cos distribution – little field in metal

meshing more important for low-freq modes

problems with the mesh



Skin depth in Copper at ~ GHz is 1 micron, $10^{-4} \times$ wavelength

where does this leave us?

summary

- **experimental**: situation far from being well defined or under control
- mixture of **analytic and computational** approaches is essential – lots of good theory and models already available but…..
- **provided bulk description of matter valid**, equations are well known and problems are computational intensity and boundary conditions (morphology etc. – hard to specify problem well enough (random structures?)
- **validation** – quantitative agreement still difficult e.g. cross sections, range of validity

New Physics?

- **non-linearity** (esp. of metal) – CARS, TPL…
- Atomic scale/**quantum effects** (break down of bulk description)
- inclusion of **gain media**

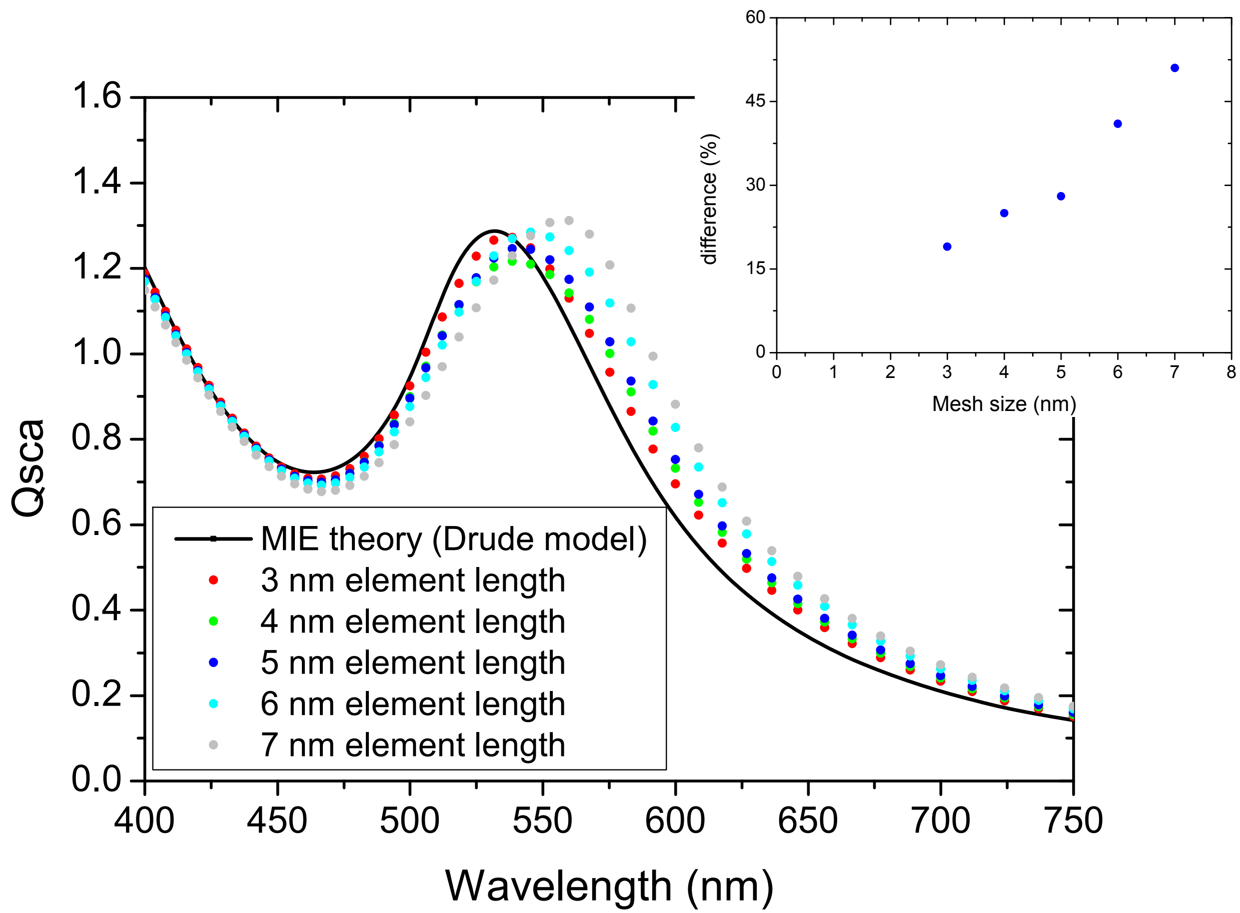
Questions & Answers

a simple problem

James Parsons

Scattering of light by a metallic sphere in vacuum: comparison of techniques

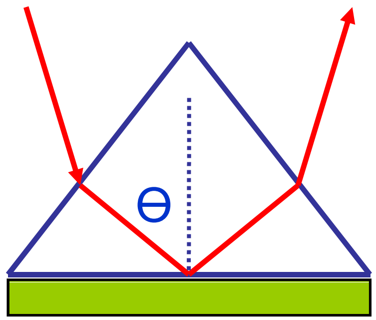
FDTD approach – effect of mesh size



meshing needed at 1 nm level (<< wavelength)

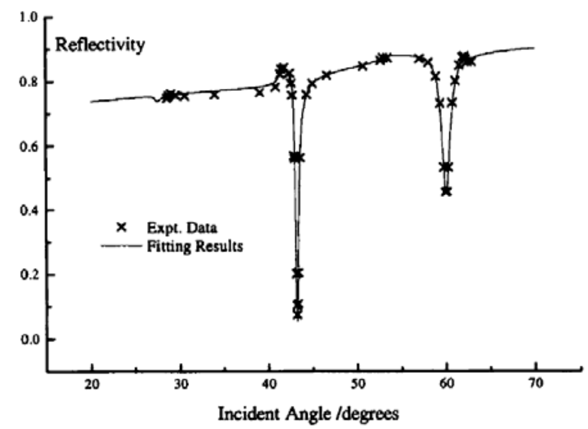
stepping back – planar metal film

…in fact there is an SPP supported by both metal surfaces…



Corrugated film used so as to allow grating coupling to prism-silver SPP

Nash and Sambles (J Mod Opt **46** 1793 (1999))



wavelength 633 nm

Silver film thickness/nm	Glass/Silver interface ε_r	Glass/Silver interface ε_i	Silver/Air interface ε_r	Silver/Air interface ε_i	Uncertainties $\Delta\varepsilon_{r,i}$	Uncertainties thickness
31.1	−20.41	0.92	−14.74	0.69	±0.1	±1
50.1	−21.06	0.94	−13.85	0.90	±0.1	±2
58.6	−20.99	0.79	−15.56	0.58	±0.1	±2
76.2	−21.36	0.78	−14.50	0.43	±0.1	±4
86.2	−21.01	0.82	−17.02	0.49	±0.1	±5
125.3	−20.86	0.79	−17. 92	0.49	±0.1	±5

even a simple planar film can not be described by just one $\varepsilon(\omega)$,