Università di Pisa
LM Materials and Nanotechnology - a.a. 2016/17

Spectroscopy of Nanomaterials II sem – part 10

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Optical near-fields and related techniques: seeing close, seeing small

OUTLOOK

We well know how diffraction can affect optical spectroscopy of nanomaterials, ruling the ultimate diffraction achievable in conventional (general purpose) configurations

Diffraction is strongly involved in near-fields, which can be considered as created by strongly diffracting apertures

Quite surprising is to discover that near-fields can be used to obtain sub-diffraction spatial resolution in virtually all (almost all) spectroscopy configurations

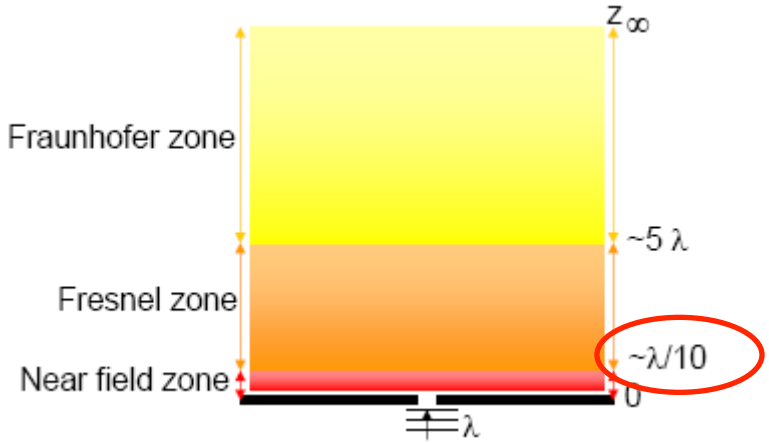
Furthermore, being near-fields relevant close to small-sized apertures, emitters, scatterers, they play a rather ubiquitous role in nano-optics and nanophotonics

Today's menu:
- Appetizers: near-field cooked à la Fourier, à la Heisenberg, à la Maxwell, and other variants
- Main course of tapered fibers, used in scanning probe microscopy, garnished with several examples of optical spectroscpy of different materials
- Dessert: tip enhanced spectroscopies, Raman flavoured

NEAR-FIELD I

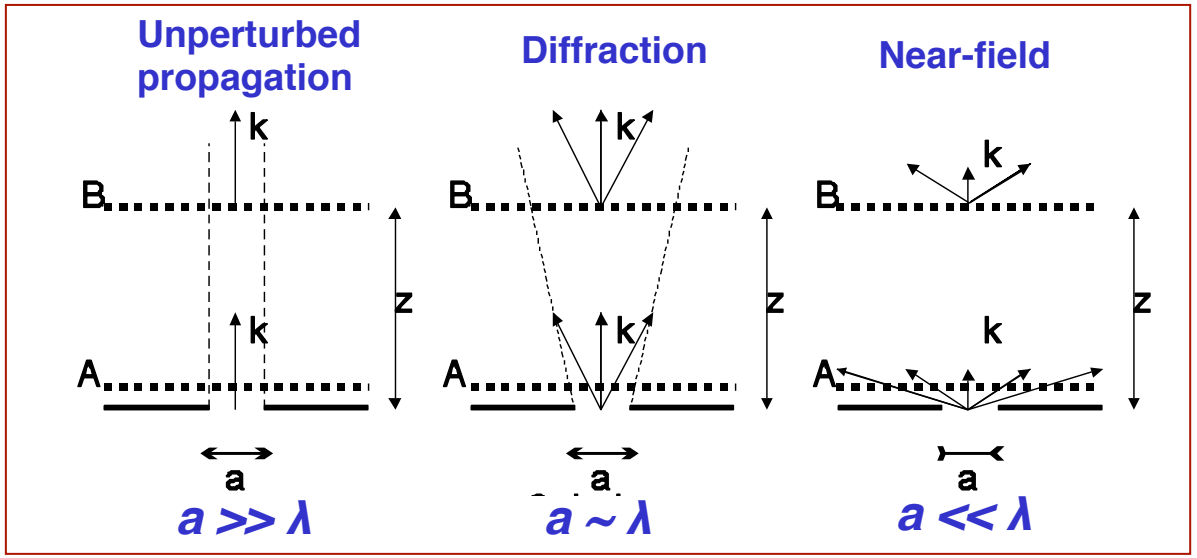
Basic idea of the near-field:
To stay **near** the emitter, where "near" means at a (small) fraction of the wavelength

Typically, for ordinary emitters near-field is indistinguishable from conventional (propagating) radiation…



…but…

If the emitter is, e.g., a small, sub-wavelength sized, aperture, near-field "prevails"

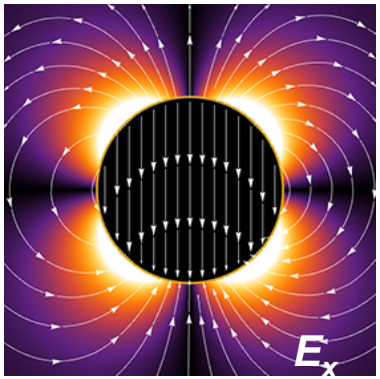


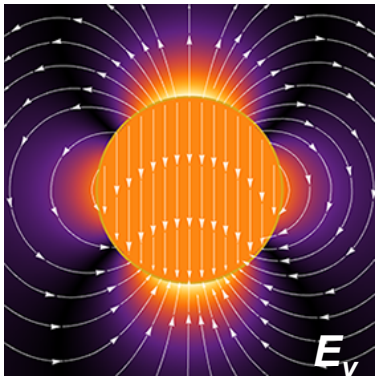
ALREADY SEEN

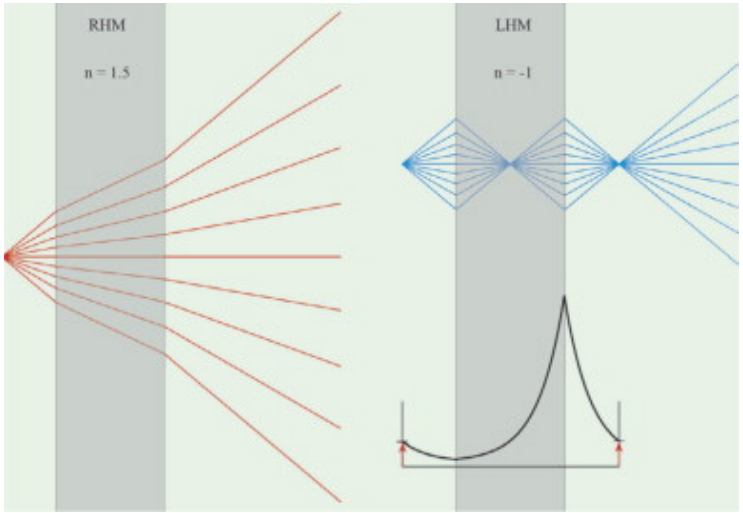
The concept of near-field and the related consequences are ubiquitous in the nanophotonics world

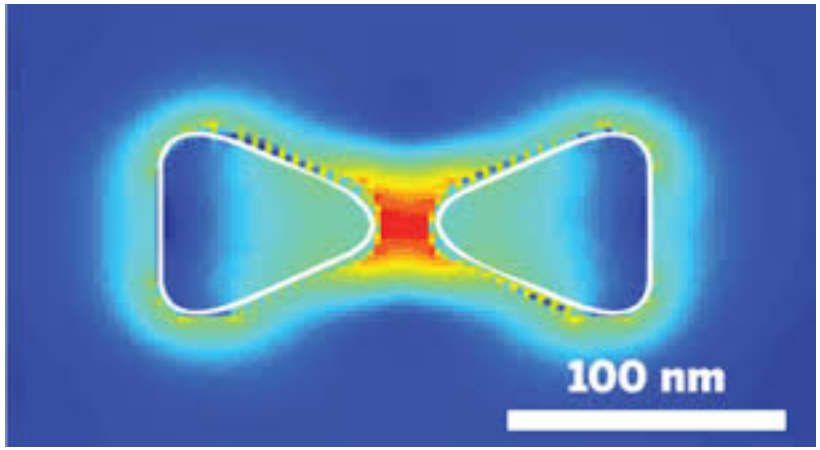
For instance:
Field enhancement in localized plasmon resonances occurs in the near-field

Refraction in a LHM produces "amplification" in the near-field (actually non discussed)









NEAR-FIELD II

According to Fourier *optics*:

$$g_{out}(x,y,z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} T(k_x,k_y) G_{in}(k_x,k_y,z) e^{i2\pi(k_x x + k_y y)}\, dk_x\, dk_y$$

$$G_{in}(k_x,k_y,z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g_{in}(x,y) e^{-i2\pi(k_x x + k_y y)} e^{i2\pi k_z z}\, dx\, dy$$

Due to the small aperture size, the transfer function *T* mimics the transfer function of a **low-pass filter** with very high cut-off frequency (spatial frequency):

$$T(k_x,k_y) \simeq 1 \quad \text{for} \quad -u < k_{x,y} < u$$

$$\text{with } u \sim 1/a$$

Reconstruction of sub-wavelength details in the image is possible according to Fourier

On the other hand

$$G_{in}(k_x,k_y,z) = \int_{-a/2}^{+a/2} \int_{-a/2}^{+a/2} g_{in}(x,y) e^{-i2\pi(k_x x + k_y y)} e^{i2\pi k_z z}\, dx\, dy \approx$$

$$\approx f(k_x,k_y) e^{-i2\pi(k_x a + k_y a)} e^{i2\pi k_z z}$$

The near-field gets an evanescent, non-propagating character

$$k = \frac{2\pi}{\lambda} = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

$$\rightarrow k_z = \sqrt{\left(\frac{2\pi}{\lambda}\right)^2 - \left(k_x^2 + k_y^2\right)}$$

$$\text{for } k_x, k_y \rightarrow u \text{ , } k_z \in \text{Im}$$

NEAR-FIELD III

Hole (or object) size *a* > λ

- low spatial frequencies
- root > 0
- k_z real
- progressive wave along *z*

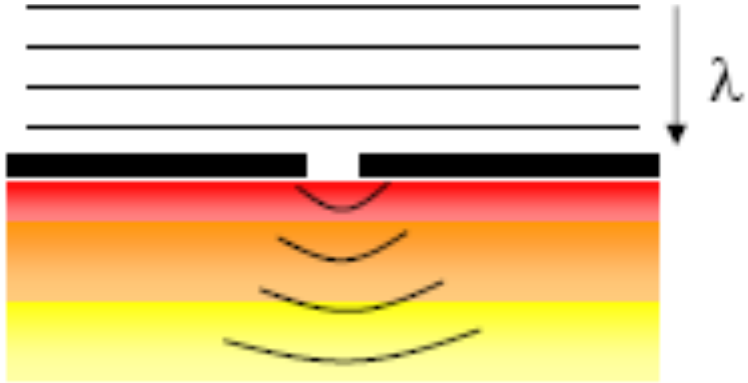
$$g_{out}(x,y,z) \sim f(k_x,k_y)e^{i(k_x x+k_y y)}e^{ik_z z}$$

Hole (or object) size *a* < λ

- high spatial frequencies
- root < 0
- k_z imaginary
- evanescent wave along *z*

$$g_{out}(x,y,z) \sim f(k_x,k_y)e^{-\alpha z}$$

Note:
in the far-field there is still a propagating wave, strongly diffracted and attenuated because of the small aperture size *(Fraunhofer diffraction)*



HEISENBERG, DIFFRACTION AND NEAR-FIELD

Diffraction can be seen as a sort of consequence of Heisenberg's (uncertainty) principle: this is the content of a conceptual experiment (Heisenberg's microscope)

Propagating waves:
k_i are real and $|k_x| \le k = 2\pi/\lambda$

$\Downarrow$

Heisenberg's principle: $k_x \ge 2\pi / \Delta x$

$\Delta x \ge \lambda$
(actual parameters give the Abbe's limit)

… but …

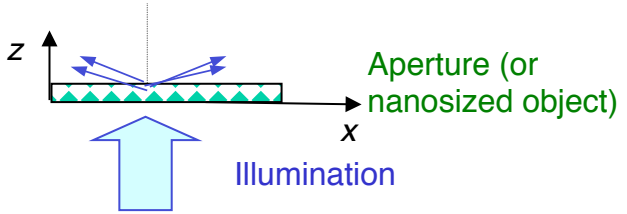
In **non-propagating (e.g., evanescent)** waves:
k_i can be imaginary, and, e.g.: $|k_x| \ge k = 2\pi/\lambda$

$\Downarrow$

The Heisenberg's principle is no longer ruling the ultimate resolution!

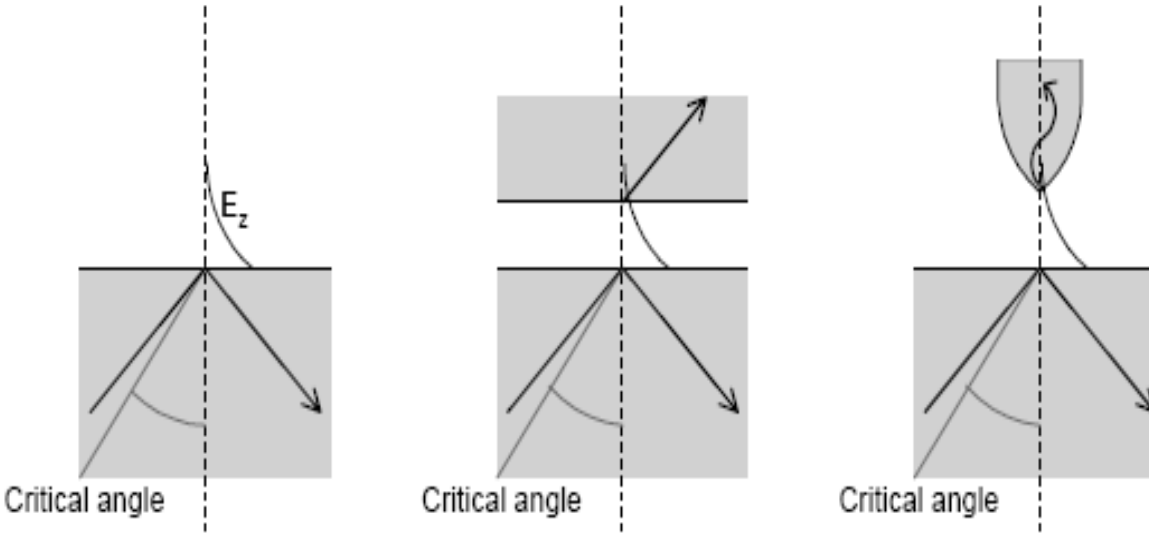
Extreme diffraction means wavevectors for the field leaving the aperture (or a nanosized object) gets a large in-plane component

→ ***Propagation is somehow frustrated***



In some sense, near-field enables using ultra-diffractive fields for beating the diffraction limit

CONVERTING AN EVANESCENT FIELD



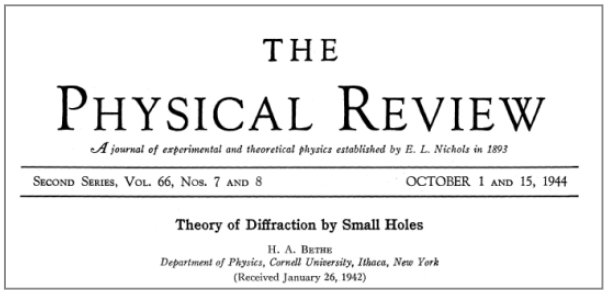
The evanescent field at a surface can be “converted” into an ordinary (propagating) e.m. wave through a sort of **photon tunneling** process across a vacuum gap

→ ***near-field at a surface can be “captured” by a suitable probe***
→ ***near-field can couple to a surface and gets a propagating character***

Or, if you have a fluorescent object, **the fluorescence can be excited by the near-field** (it is the time-dependence, i.e., the frequency that must be “resonant”) and collected in the far-field

Or, if you have a scatterer (a nanosized object) **near-field can be scattered in the far-field**

NEAR-FIELD AND MAXWELL EQS

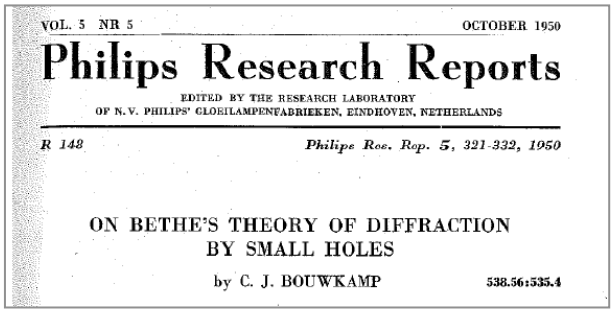


THE
PHYSICAL REVIEW
A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 66, NOS. 7 AND 8 — OCTOBER 1 AND 15, 1944

Theory of Diffraction by Small Holes

H. A. BETHE
Department of Physics, Cornell University, Ithaca, New York
(Received January 26, 1942)



VOL. 5 NR 5 — OCTOBER 1950

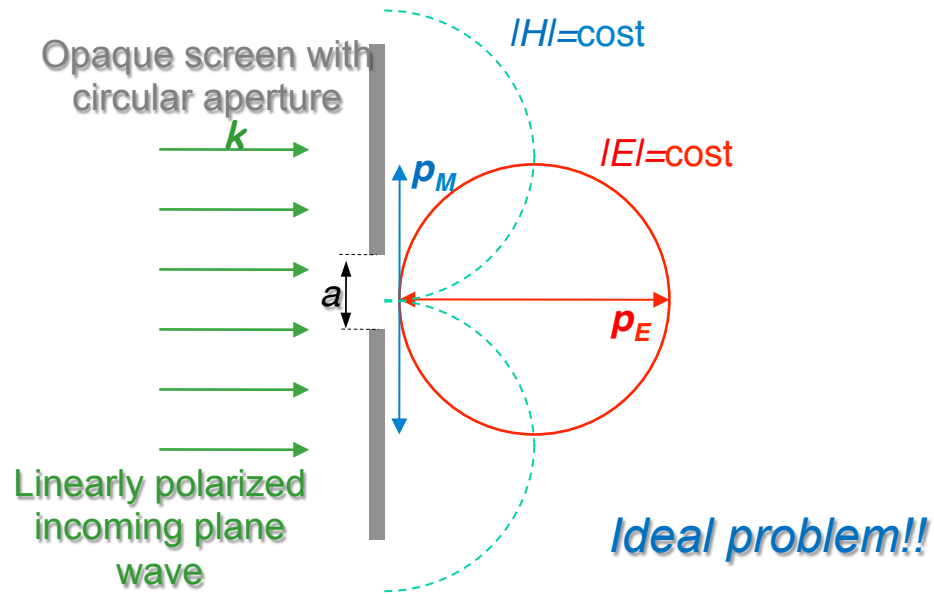
Philips Research Reports

EDITED BY THE RESEARCH LABORATORY OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN, EINDHOVEN, NETHERLANDS

R 148 — *Philips Res. Rep. 5, 321-332, 1950*

ON BETHE'S THEORY OF DIFFRACTION BY SMALL HOLES

by C. J. BOUWKAMP — 538.56:535.4



Ideal problem!!

$$\mathbf{E} = \frac{1}{4\pi\varepsilon_0} k^2 (\mathbf{n}\times\mathbf{p})\times\mathbf{n}\frac{e^{ikr}}{r} + [3\mathbf{n}(\mathbf{n}\cdot\mathbf{p}) - \mathbf{p}]\left(\frac{1}{r^3} - \frac{ik}{r^2}\right)e^{ikr}$$

$$\mathbf{H} = \frac{ck^2}{4\pi}(\mathbf{n}\times\mathbf{p})\frac{e^{ikr}}{r}\left(1 - \frac{1}{ikr}\right)$$

In the near-field *(r→0, kr<<1)*

$$\mathbf{E} = \frac{1}{4\pi\varepsilon_0}[3\mathbf{n}(\mathbf{n}\cdot\mathbf{p}) - \mathbf{p}]\frac{1}{r^3}$$

"Static" dipole behavior
→ *no propagation*

$$\mathbf{H} = \frac{i\omega}{4\pi}(\mathbf{n}\times\mathbf{p})\frac{1}{r^2}$$

NUMERICAL CALCULATIONS

The actual field distribution is perturbed by the presence of the imaged object

⇓

Numerical simulations (e.g., multiple multipole, FDTD, etc) needed

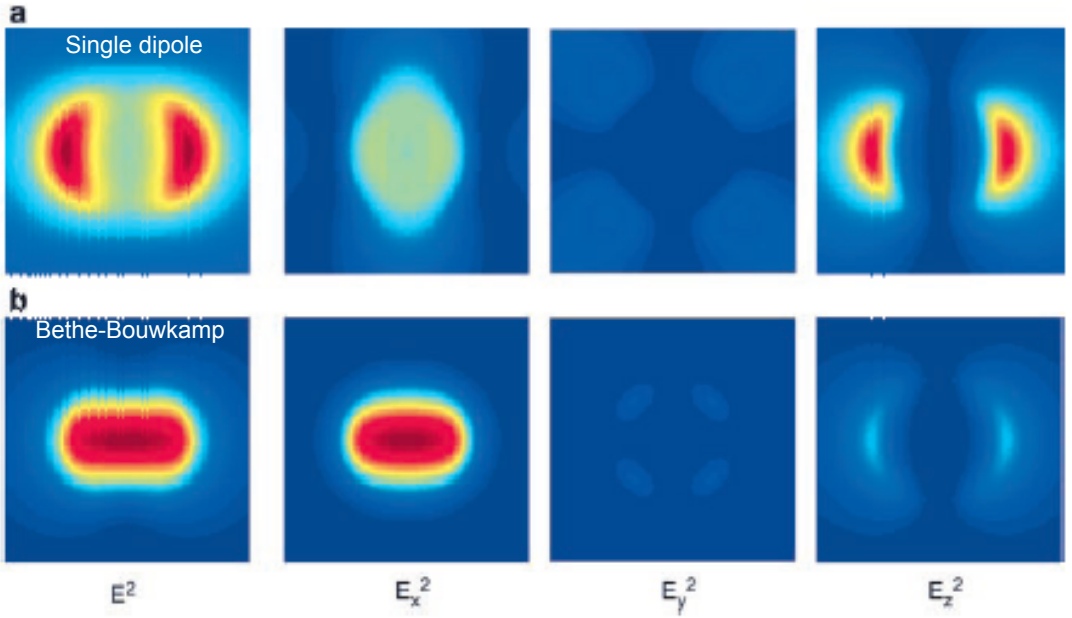


Fig. 3 – Intensity maps for the electric field (E^2 and components E_x^2, E_y^2, and E_z^2) at a distance of $z = 0.3a$ from the tip aperture of radius a created by (a) a surface charge distribution as illustrated in fig. 2, and (b) a planar Bethe aperture (Bethe-Bouwkamp solution). All images show an area of $4a$ by $4a$, and the images in each row share the same color bar. The two images on the left correspond to those that would be obtained using a pointlike, scalar detector for the electric field (*e.g.* an idealized, infinitely small fluorescent nanosphere). The images of the last three columns correspond to fluorescence images predicted for pointlike vector detectors for the electric field (*e.g.* single, fluorescent molecules) oriented along the x, y, and z direction, respectively.

Actual space distribution of the near-field can differ from the ideal case because of interaction with objects and of border effects

EUROPHYSICS LETTERS 1 April 2004
Europhys. Lett., **66** (1), pp. 41–47 (2004)
DOI: 10.1209/epl/i2003-10138-7

The optical near-field of an aperture tip

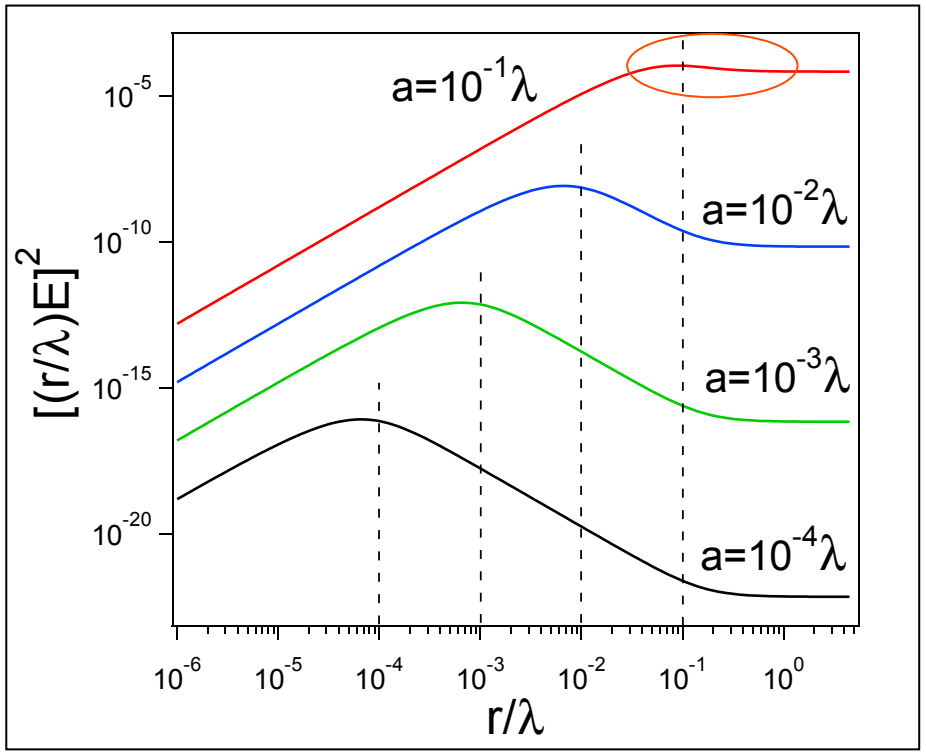
A. DREZET, M. J. NASSE, S. HUANT and J. C. WOEHL(*)

LOCALIZATION OF THE E.M. FIELD

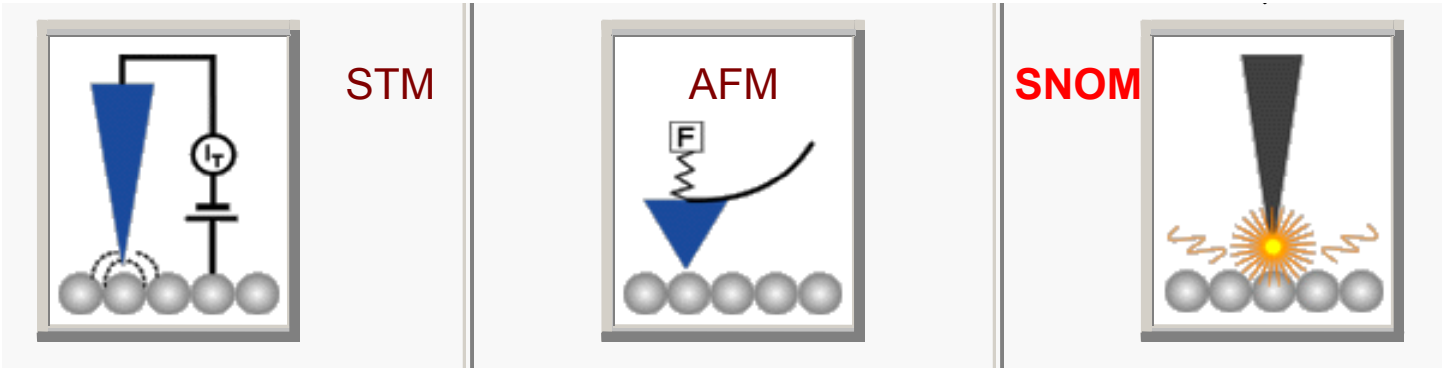
In practical terms near-field enables a spatial localization of the e.m. field in a size **ruled by the aperture**

Typically, localization is on a λ/5-λ/10 scale

→ ***Ideal resolving power ~ λ/5-λ/10***
→ ***Resolving power no longer ruled by diffraction!!***



The Scanning Near-field Optical Microscope (SNOM, aka NSOM) is based on such concept



BRIEF HISTORY

1928/1932

E.H. Synge proposes the idea of using a small aperture to image a surface with sub-wavelength resolution using optical light. For the small opening, he suggests using either a pinhole in a metal plate or a quartz cone that is coated with a metal except for at the tip. He discusses his theories with A. Einstein, who helps him develop his ideas. [E.H. Synge, "A suggested method for extending the microscopic resolution into the ultramicroscopic region" Phil. Mag. 6, 356 (1928); E.H. Synge, "An application of piezoelectricity to microscopy", Phil. Mag., 13, 297 (1932)].

1956

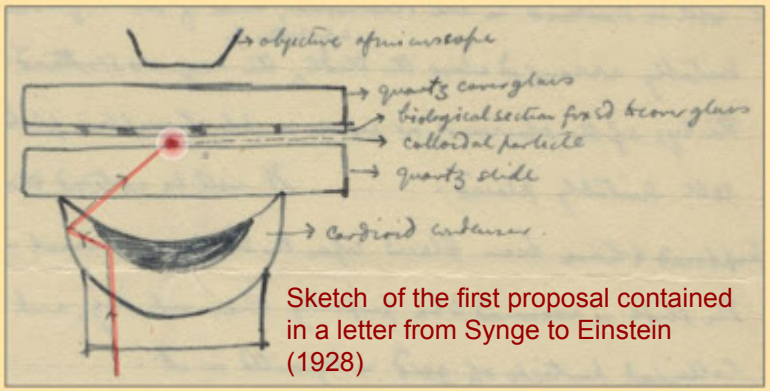
J.A. O'Keefe, a mathematician, proposes the concept of Near-Field Microscopy without knowing about Synge's earlier papers. However, he recognizes the practical difficulties of near field microscopy and writes the following about his proposal: "The realization of this proposal is rather remote, because of the difficulty providing for relative motion between the pinhole and the object, when the object must be brought so close to the pinhole." [J.A. O'Keefe, "Resolving power of visible light", J. of the Opt. Soc. of America, 46, 359 (1956)].
In the same year, Baez performs an experiment that acoustically demonstrates the principle of near field imaging. At a frequency of 2.4 kHz (ë = 14 cm), he shows that an object (his finger) smaller than the wavelength of the sound can be resolved.

1972

E.A. Ash and G. Nichols demonstrate ë / 60 resolution in a scanning near field microwave microscope using 3 cm radiation. [E.A. Ash and G. Nichols, "Super-resolution aperture scanning microscope", Nature 237, 510 (1972)].

1984

The first papers on the application of NSOM appear. These papers are the first to show that NSOM is a practical possibiltity, spurring the growth of this new scientific field. [A. Lewis, M. Isaacson, A. Harootunian and A. Murray, Ultramicroscopy 13, 227 (1984); D.W. Pohl, W. Denk and M. Lanz, APL 44, 651 (1984)].



Sketch of the first proposal contained in a letter from Synge to Einstein (1928)

The Nobel Prize in Chemistry 2014

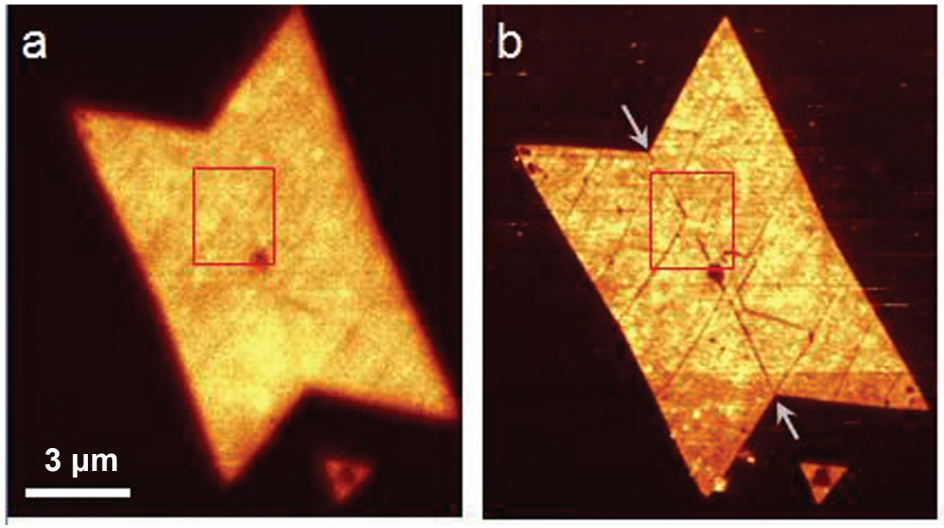
Photo: A. Mahmoud
Eric Betzig
Prize share: 1/3

Photo: A. Mahmoud
Stefan W. Hell
Prize share: 1/3

Photo: A. Mahmoud
William E. Moerner
Prize share: 1/3

Eric Betzig was among the discoverers of SNOM (not very satisfied, though)

ENHANCED RESOLUTION



SNOM and confocal PL images of butterfly-shaped monolayered MoS_2 prepared on an ITO-coated glass substrate

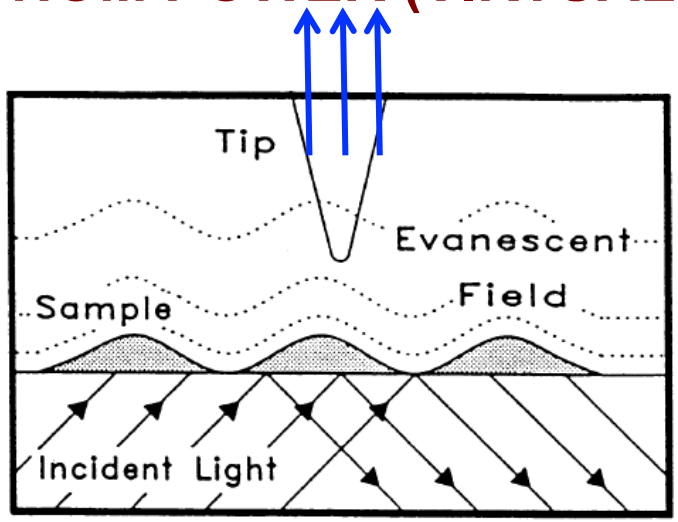
Spatial resolution is actually enhanced compared to confocal microscopy

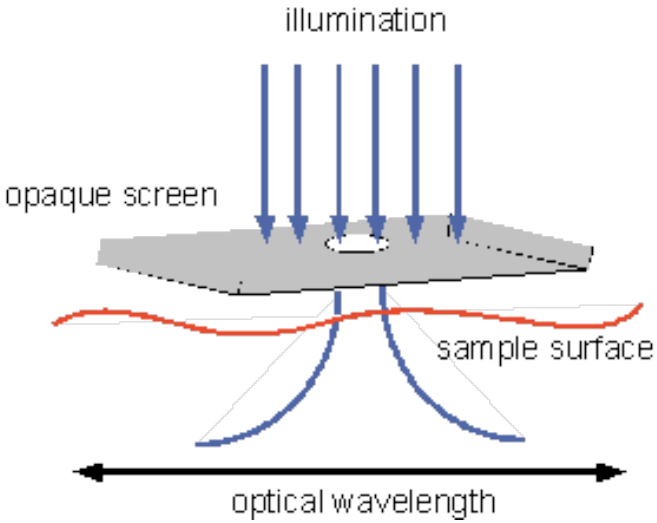
In actual operating conditions, the resolving power can reach to few tens of nm range

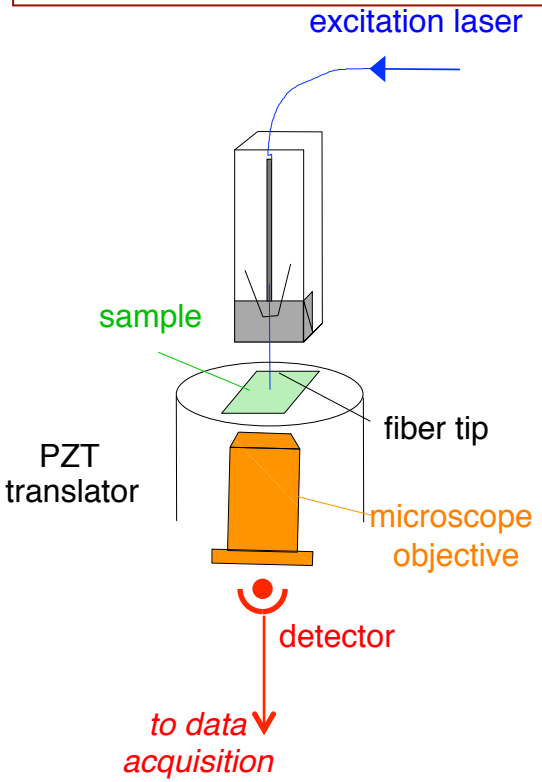
Lee, et al., Nanoscale (2015)

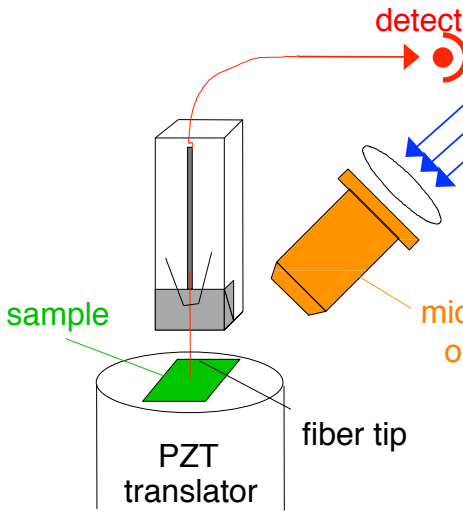
SNOM POWER (VIRTUALLY)

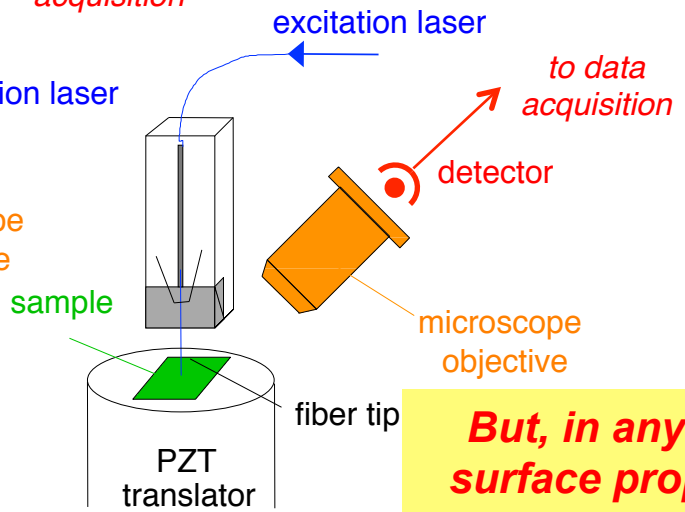
Virtually, all configurations of conventional microscopy can be translated into a near-field version, e.g., **collection**, **illumination**, scattering, fluorescence, optical activity, etc.







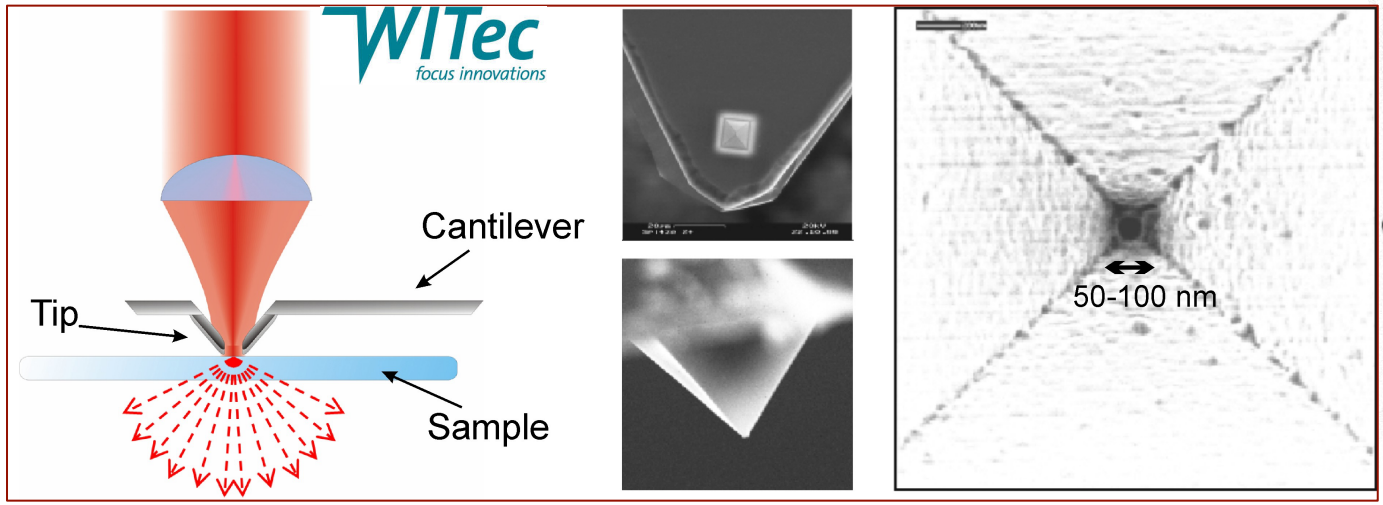


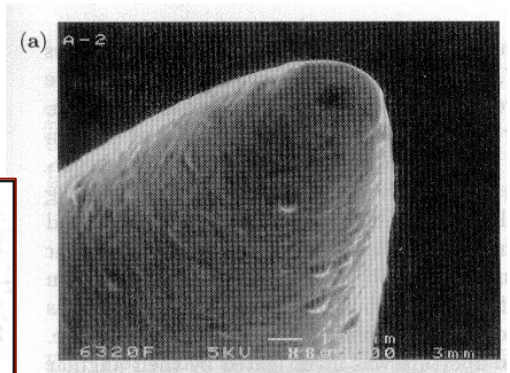


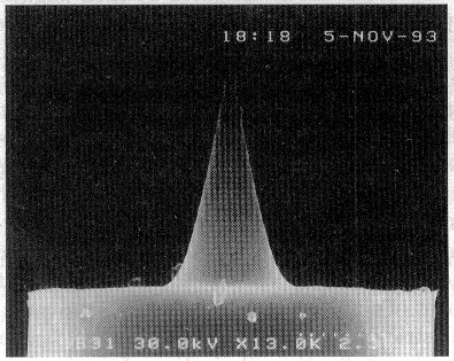
But, in any case, surface properties are probed

SNOM PROBES (APERTURE)

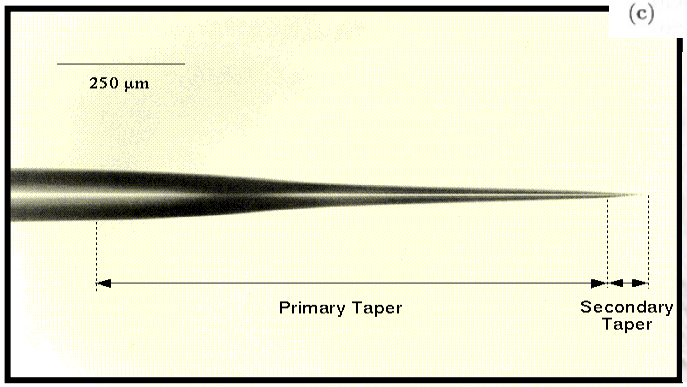
Hollow pyramids (cantilevered) or tapered optical fibers are used as SNOM probes

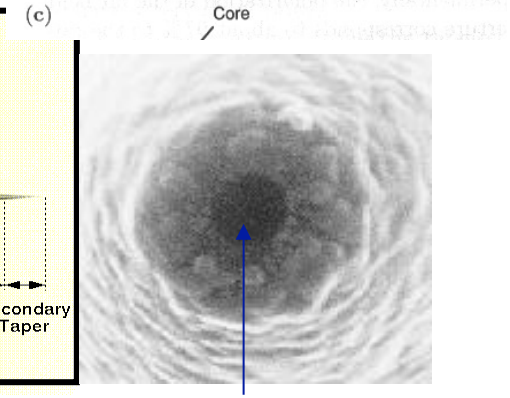






We will restrict here to tapered optical fibers probes

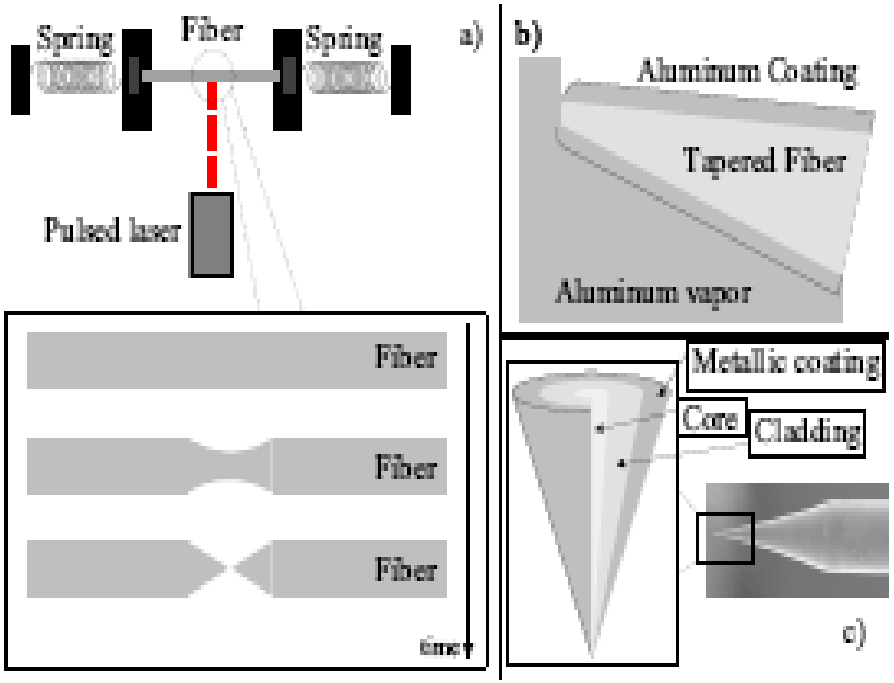




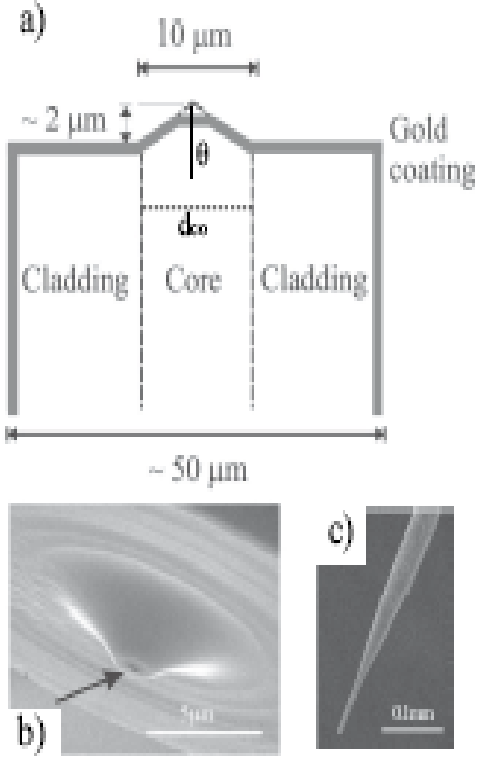
Typical aperture diameter
50-100 nm

TAPERED OPTICAL FIBERS

Conventional probe fabrication (*heat and pull)*



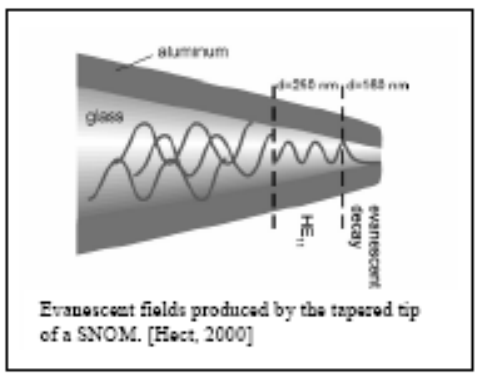
Chemical etching



The final result is a conical (tapered) optical fiber, with the taper metal-coated in order to prevent losses, and an apical (uncoated) hole playing the role of the aperture

TAPER BEHAVIOR

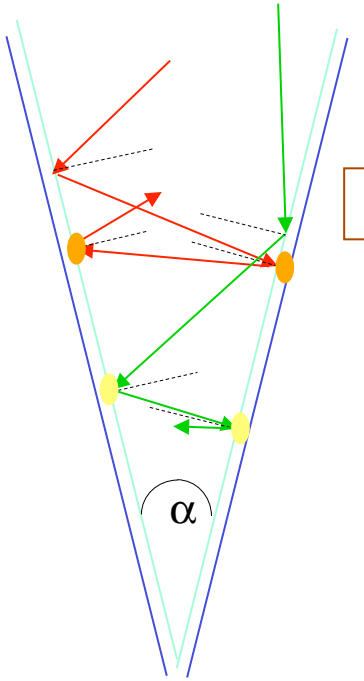
A whole slew of scanning near field optical microscopes (SNOMs) have been developed by researchers over the past 15 years. These microscopes smash the diffraction limit of far field microscopes, potentially achieving resolution an order of magnitude better than a standard confocal microscope [Hect 2000]. One such SNOM is the scanning tunneling optical microscope. This microscope uses a sharp glass tip to locally frustrate total internal reflection below a surface, indirectly imaging features on that surface at high spatial resolution. Aperture based SNOMs are more common and more practical. [Hect 2000] They produce an evanescent field by forcing light through a small aperture (see figure). The evanescent field locally illuminates the sample. Once free of the aperture, the field is no longer evanescent, and it expands in the far field to be picked up by a detector. To achieve high resolution, the aperture must be small, and close to the sample surface so the field is tightly confined when it interacts with the sample. Full analysis of the field-sample interaction of a SNOM is a difficult or impossible undertaking, but the data produced can yield important and detailed information about a sample surface.



Evanescent fields produced by the tapered tip of a SNOM. [Hect, 2000]

Suggested reading: Hecht et al., J. Chem Phys. 112, 7761 (2000).

A simplified ray optics picture in the tapered region.
Light can both:
- be back reflected
- (partially) absorbed by the metal layer

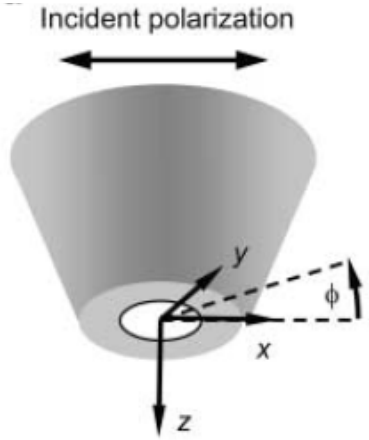


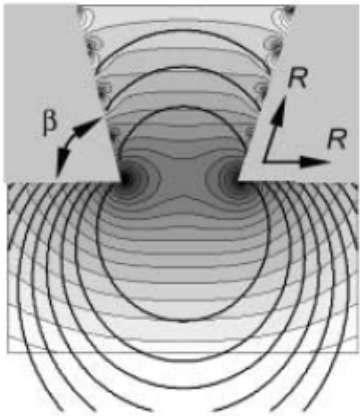
$$\theta_{i,n} = \theta_{i,n-1} - \alpha$$

Note: metal layer (typ Cr, Ni) can absorb radiation → power entering the fiber cannot exceed the mW range!

Note: probe "throughput" (i.e., ratio between output/input power) is quite low for fiber probes, ~ 10^{-5} – 10^{-8}, but near field **intensity** can be large enough for sensitive anlyses

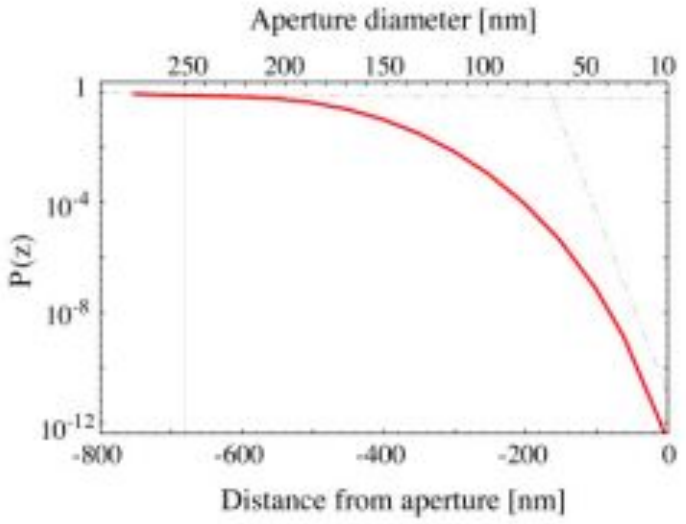
LIMITATIONS (A FEW)



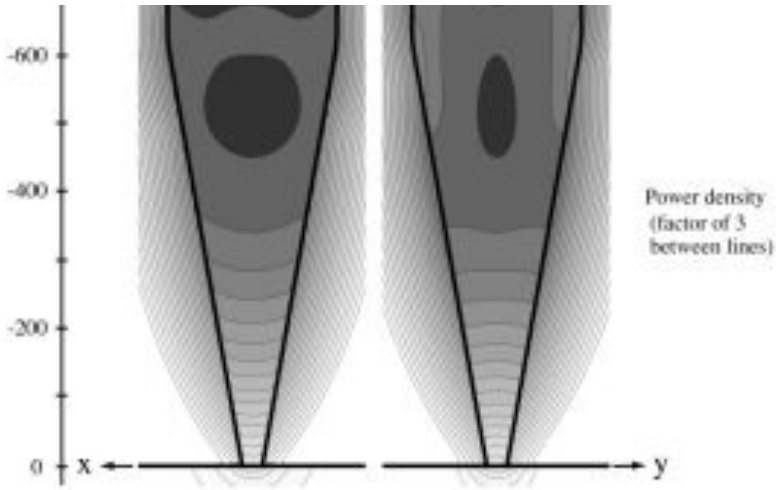


In a real, tapered fiber probe, understanding the actual field distribution inside and right outside the probe is difficult, since:

- It is not an aperture in a thin opaque screen
- The taper angle and all (polarization-depending) processes occuring in the taper affect the field
- Details of the aperture shape can be relevant



L. Novotny and D. W. Pohl, in *Photons and Local Probes*, NATO ASI Series E, p.21-33, Kluwer Academic, 1995.



L. Novotny and D. W. Pohl, in *Photons and Local Probes*, NATO ASI Series E, p.21-33, Kluwer Academic, 1995.

TIP-TO-SURFACE DISTANCE

A distinctive feature of near-field is that its amplitude rapidly drops to zero within a range ~*a*

⇩

During the scan, the probe tip must be kept "close" to the surface (typ at a distance < 10 nm)

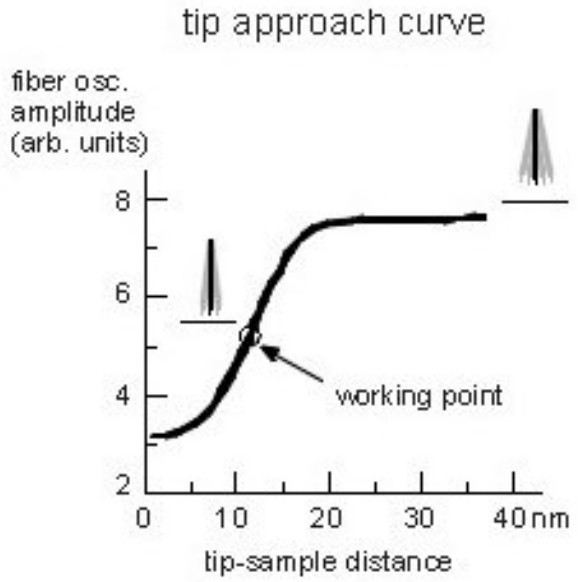
"Constant gap" operation is strictly required for the SNOM images to be reliable

⇩

A method to continuously monitor tip/sample distance is needed
A feedback acting on the vertical piezo displacement is used (as, e.g., in any SPM)

⇩

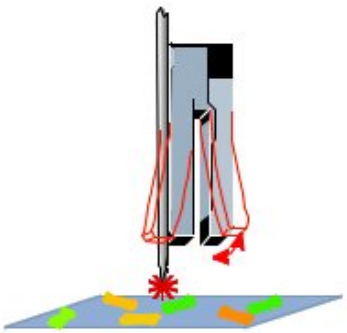
A topography image is simultaneously acquired during each scan, with a lateral resolution depending on the probe size, typ in the 100 nm range

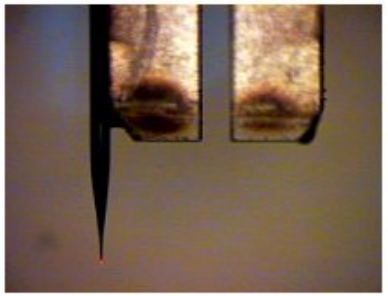


If the tip is kept in **longitudinal** oscillation, the oscillation amplitude depends on the distance due to shear-forces (mostly associated with friction of the air layers between tip and surface)

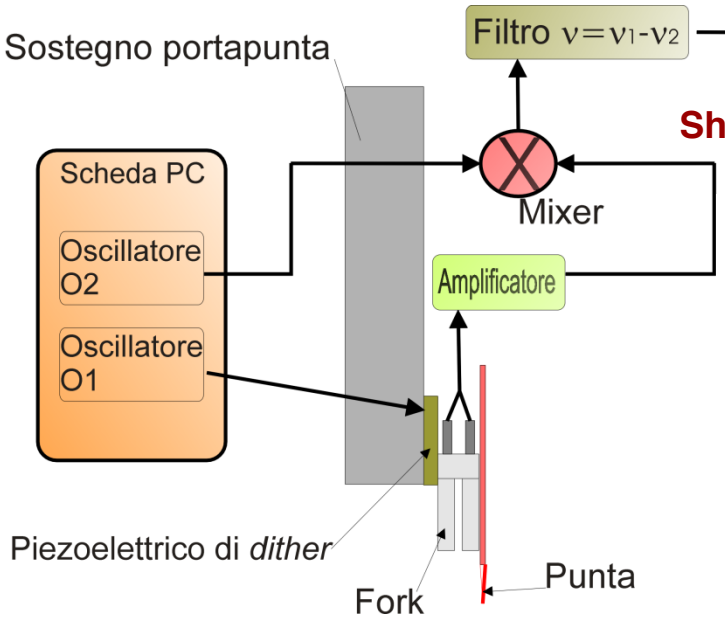
Notes:
Oscillation amplitude must be small (typ ~ 1 nm) to prevent resolution loss
Oscillation at resonance frequency is required to get maximum sensitivity

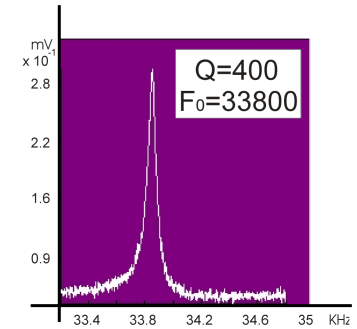
SHEAR-FORCES AND TOPOGRAPHY





Fiber tip is glued onto a *tuning fork* (a quartz diapason acting as a mechanical oscillator and showing capabilities to measure the oscillation amplitude)



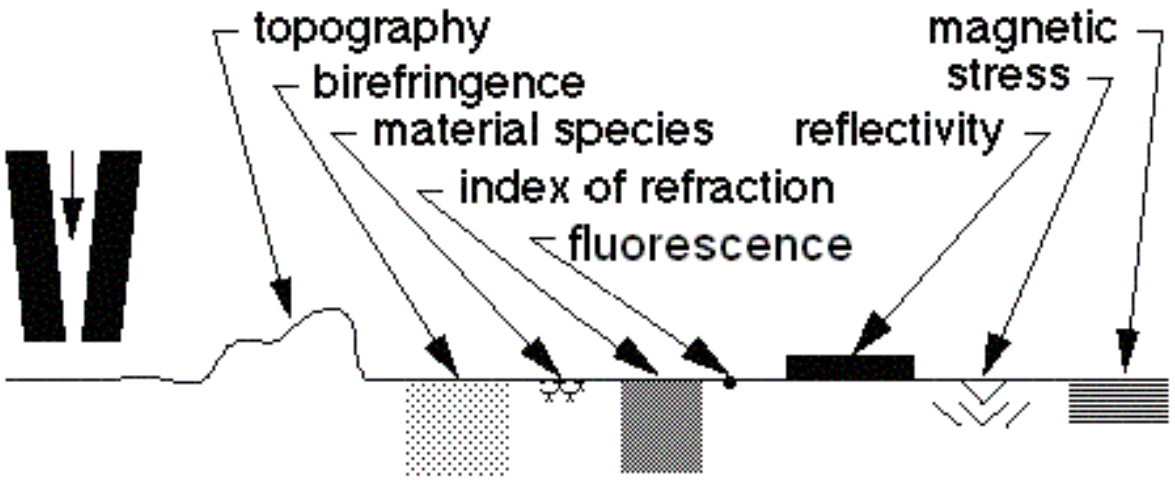


Mech resonance spectrum (undamped oscillation)

- A dithering piezoelectric transducer keeps the probe tip in oscillation along a direction **parallel** to the surface
- Oscillation amplitude is monitored by a *tuning fork*
- When the distance gets smaller (typ., below 10 nm), the oscillation is **damped** (and phase is changed) due to **shear-forces** involving many effects (e.g., viscous interaction of the air layer between tip and sample)
- Similar to AFM in tapping mode, but for the oscillation direction, the relevant distance and the involved mechanisms

A topography map is acquired simulatneously and in the same region of the optical maps

ACCESSIBLE CONTRAST MECHANISMS



Virtually, there are no limitations to the range of optical features that can be measured at the local scale, i.e., to the optical spectroscopies that can be realized in the near-field

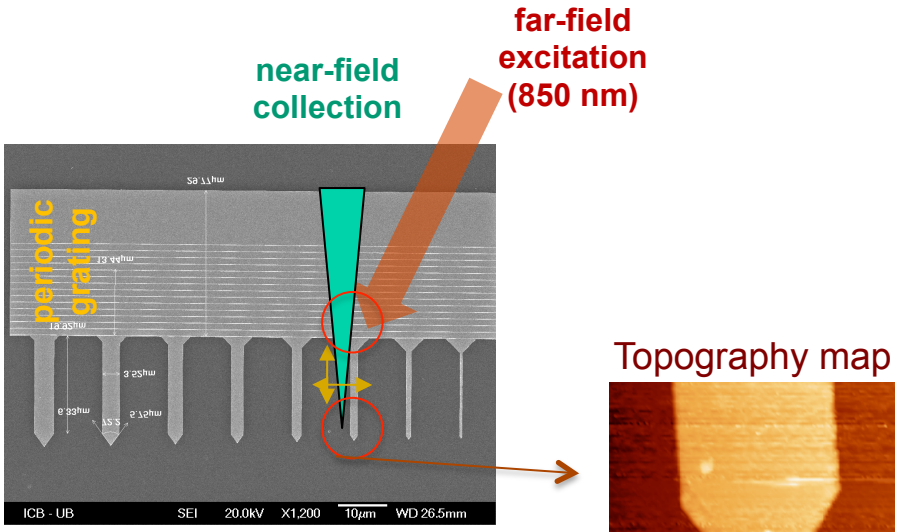
Note, however, that only surface phenomena can be analyzed (unless complicated models for data interpretation are deployed)

A range of possible configurations is feasible in order to operate different nanoscale spectroscopies

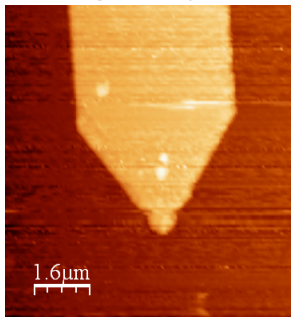
A selection of examples is given here in the following

EXAMPLES IN PLASMONICS

Sample:
pattern of lithographed gold film on glass, with a grating connected to a waveguide/concentrator featuring a tapered end

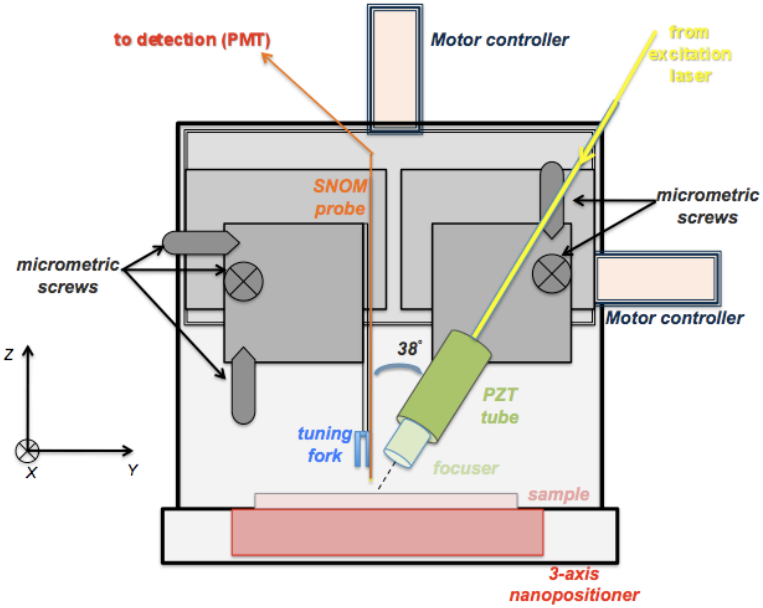


Topography map



Goal:
to investigate the propagation of **surface plasmon** modes along plasmonic waveguides/ concentrators

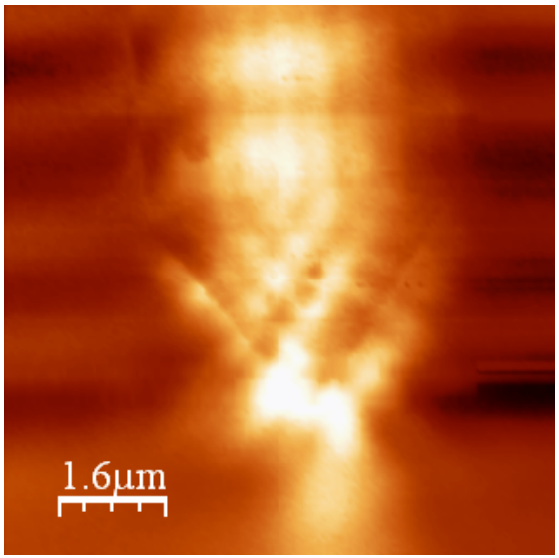
Method:
collection mode SNOM



Far-field excitation and near-field collection are accomplished at different positions
→ *propagation can be investigated at the local scale*

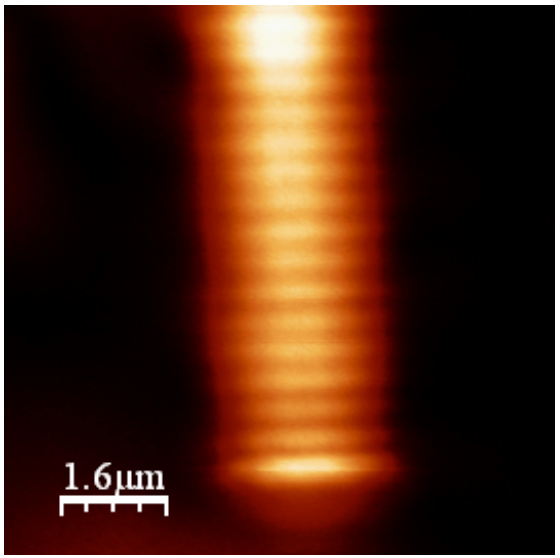
SPP PROPAGATION

SNOM map

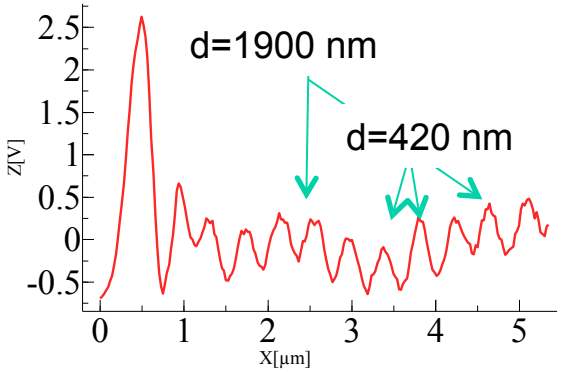


- Surface plasmon modes collected in the near-field down to the tapered end
- Concentrator effect at the tapered end is evident

SNOM map



- Interference between propagating and counterporpagating plasmon modes well seen in flat-end waveguides



✓Confirmation of plasmonic waveguide behavior

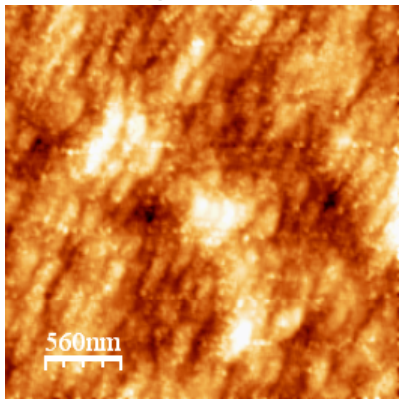
✓Complete characterization accomplished

[J. Berthelot, et al., JOSA B (2012)]

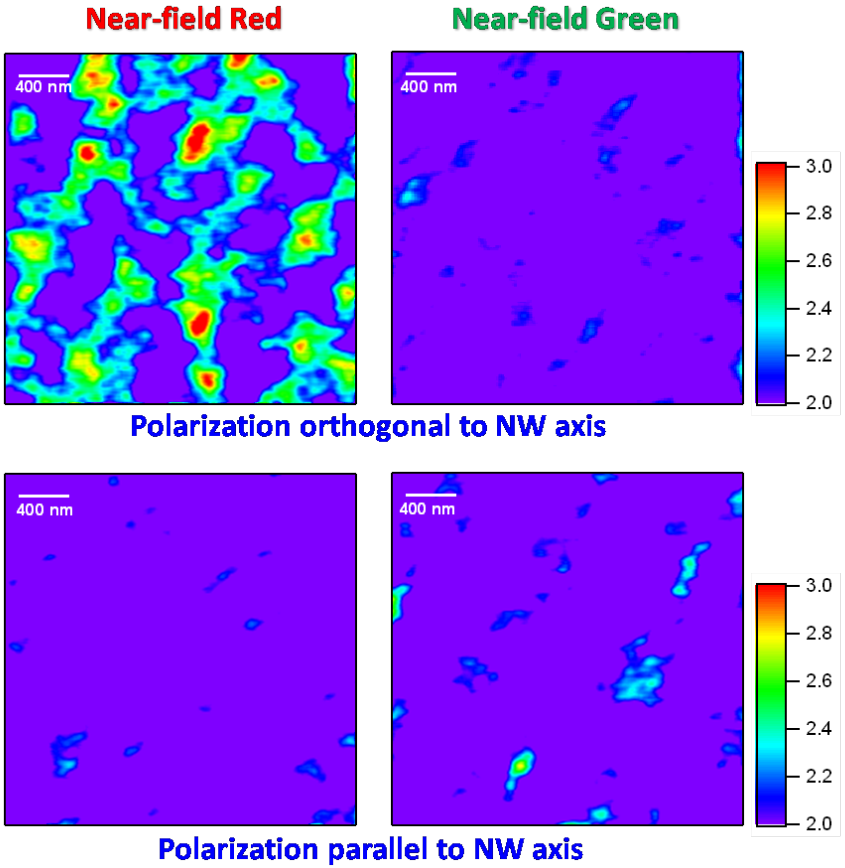
LSP HOT-SPOTS

Sample:
gold nanowire arrays made by ion beam sputtering at grazing incidence (*produced at Univ. Genova by F. Buatier de Mongeot)*

Topography map



Goals:
- to determine the spatial distribution of e.m. field at the local scale
- to identify the **hot-spots** due to the collective plasmonic resonances in the inhomogeneous gold nanoparticle arrangement



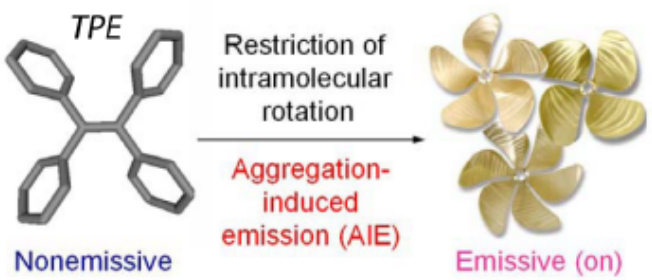
Hot-spots clearly detected and spatially mapped
(only with proper wavelength and polarization of the far-field excitation)

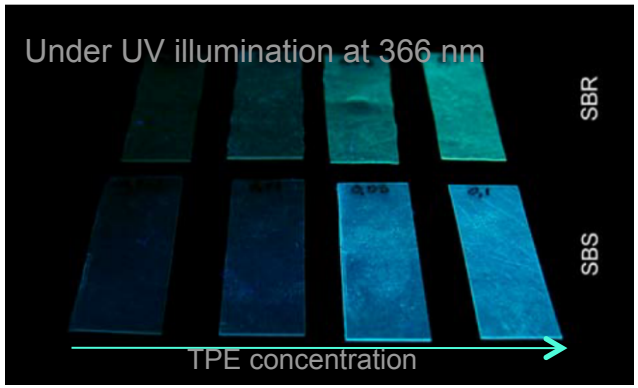
[C. D'Andrea, et al., J. Phys. Chem. C (2014);
M. D'Acunto, et al., Beilstein J (2017)]

SMART POLYMERS I

Samples:
host-guest systems consisting of dye molecules dispersed in a polymer matrix (*produced by A. Pucci, G. Ruggeri at DCCI)*

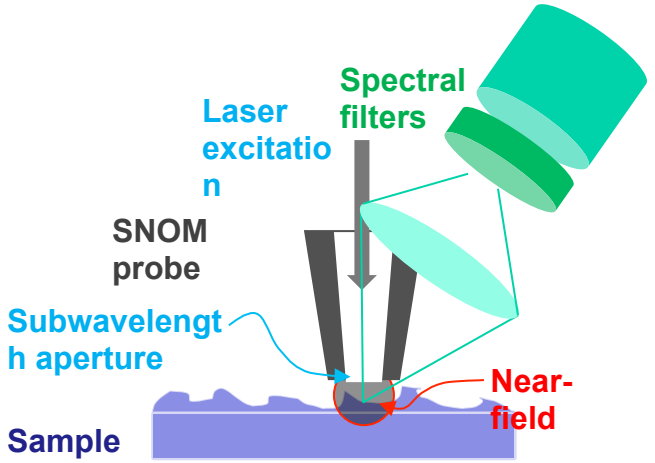
TPE in styrene/butadiene





Goal:
to identify emission domains at the local scale and to relate them with the matrix conditions

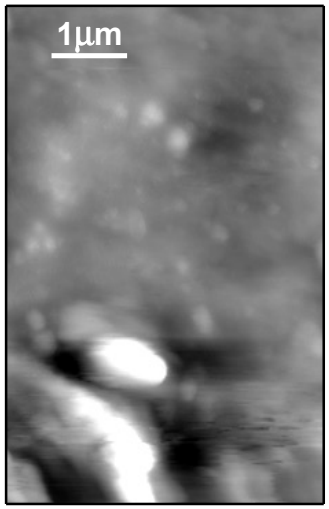
Method:
Local excitation of the sample by the near-field, photoluminescence collected in the far-field

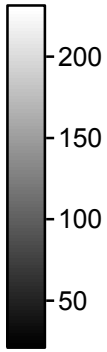


The degree of molecular aggregation, depending on concentration, matrix structure and/on the application of mechanical stress, affects the photoluminescence properties

SMART POLYMERS II

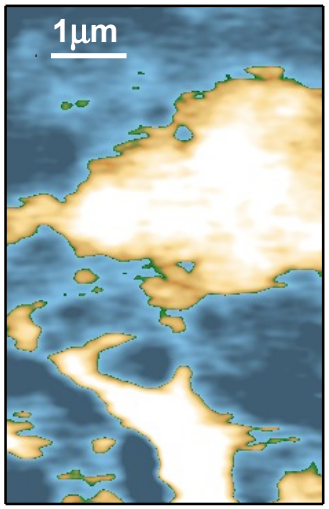
Topography map

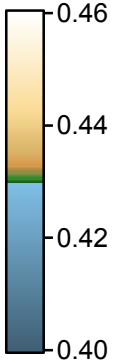




Random polymer matrix

Photoluminescence maps



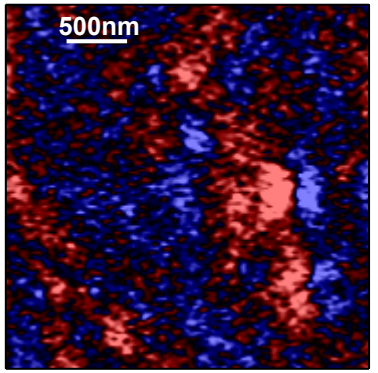


Near-field excitation at 405 nm
Photoluminescence integrated above 450 nm

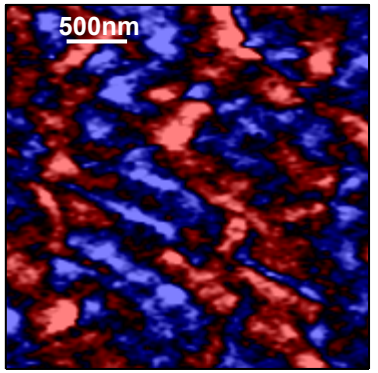
Strongly inhomogeneous spatial distribution of photoluminescence featuring:

- **Large scale "islands"**
- **Small size domains, depending on the structure of the guest matrix**

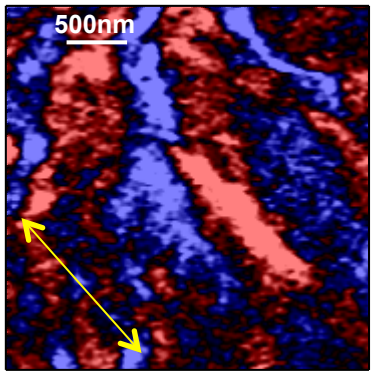
[G. Iasilli, et al., Macromol. Chem. Phys. (2014)]



Random polymer matrix (SBR)



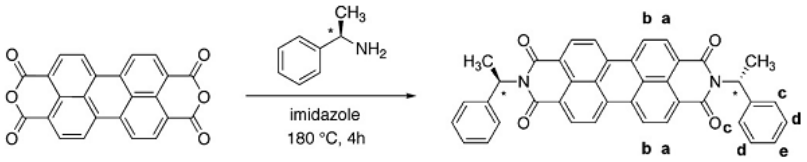
Block copolymer matrix (SBS)



Block copolymer matrix (SBS), *mechanically drawn*

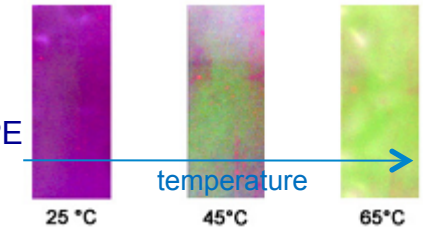
SMART POLYMERS III

R-pery in Low Lin Dens PE (LLDPE)

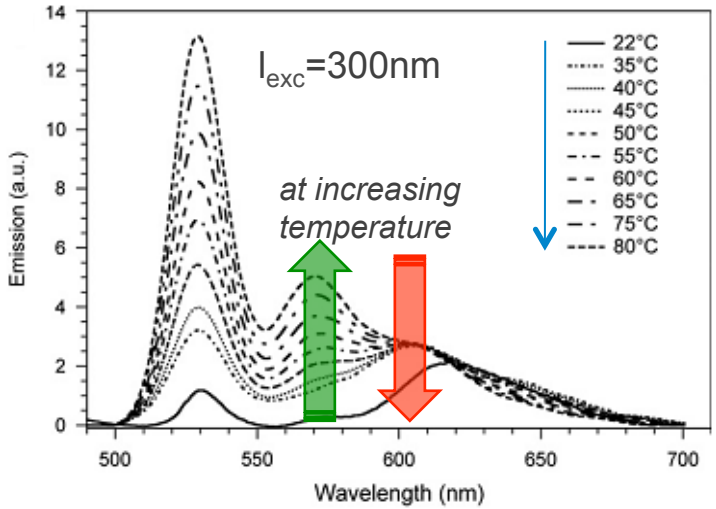


Thermochromic effect
(at the macro-scale)

Under UV illumination
R-Pery 0.1% wt. in LLDPE

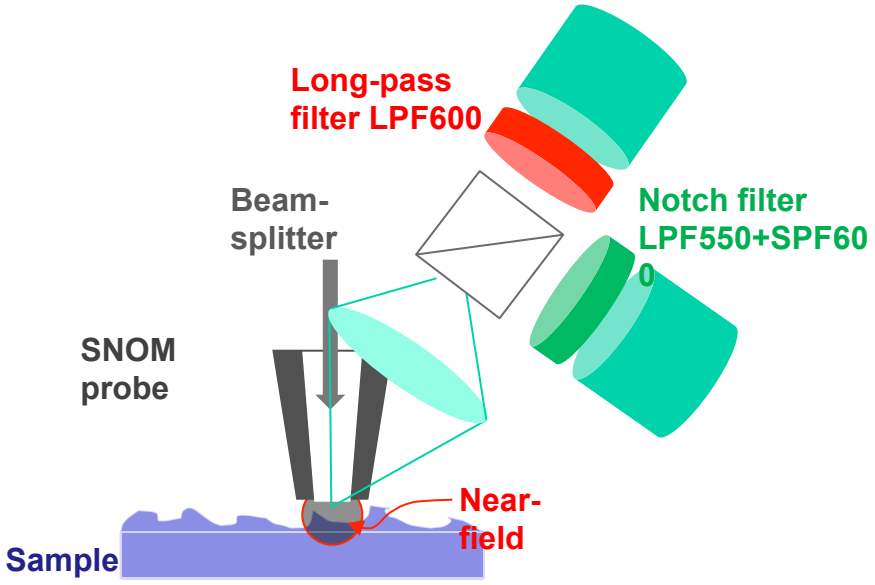


Macroscopic emission spectrum

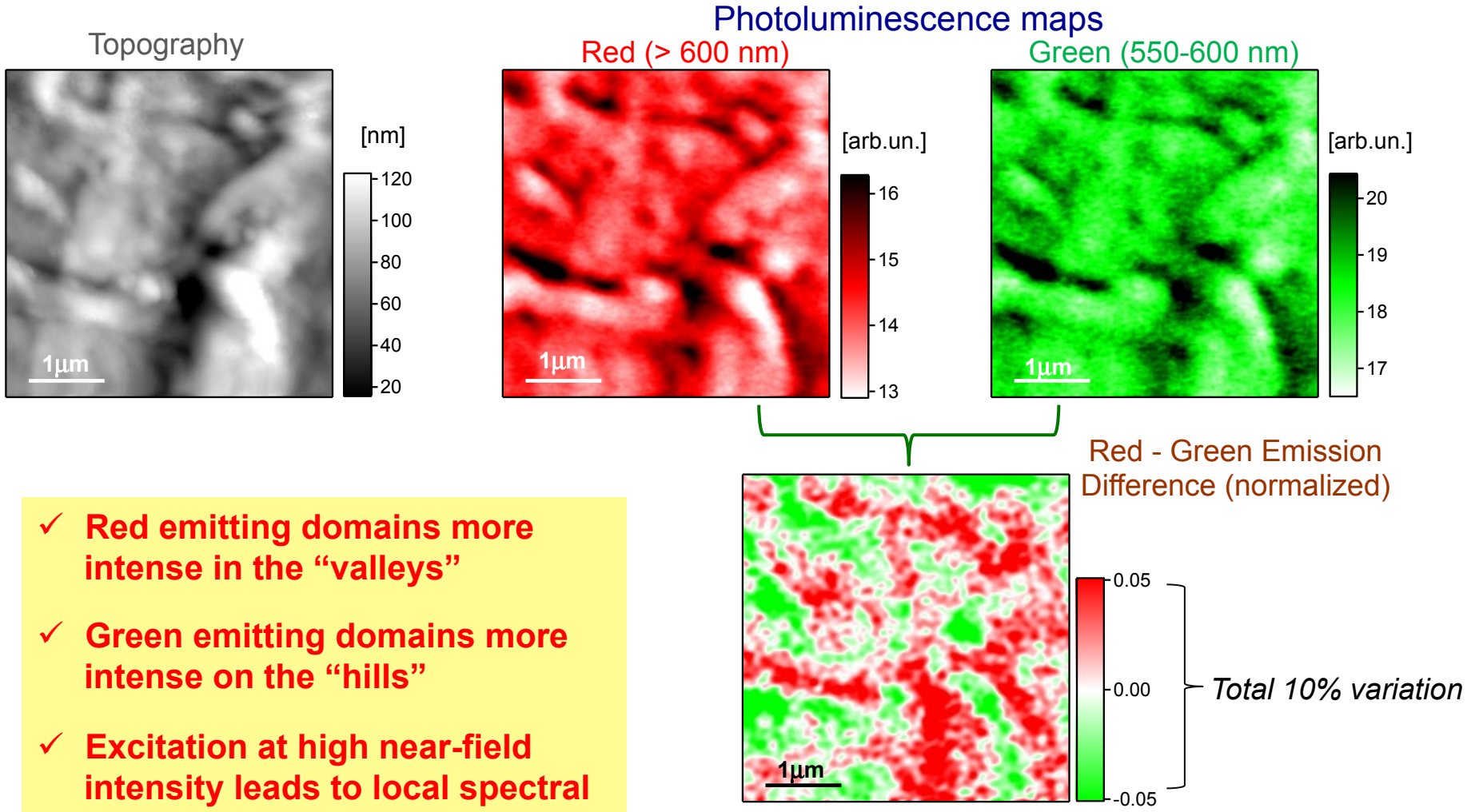


Goal:
to identify emission domains at the local scale and to investigate their properties as a function of temperature

Method:
Local excitation of the sample in the near-field, photoluminescence collected in the far-field with simultaneous two color detection

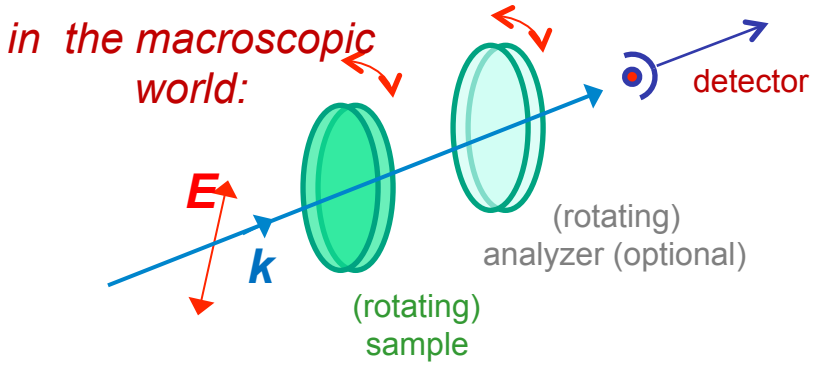


SMART POLYMERS IV



- ✓ **Red emitting domains more intense in the "valleys"**
- ✓ **Green emitting domains more intense on the "hills"**
- ✓ **Excitation at high near-field intensity leads to local spectral modifications (*not shown here*)**

OPTICAL ACTIVITY



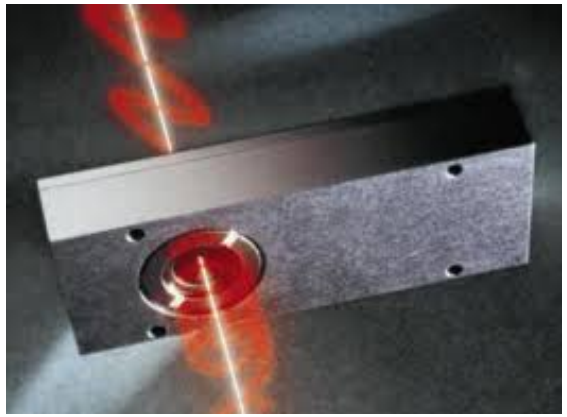
Optical activity, i.e., the response of a material to **polarized radiation**, is a key point in many applications and fundamental issues

Its **analysis and measurement** at the local scale is a challenging task

✓ **Basic idea**:
*to excite the sample in the near-field with a **polarization modulated** radiation*
to apply demodulation techniques in order to extract the physical quantities of interest

The method has been applied to a variety of properties such as, birefringence, linear and circular dichroism

POLARIZATION MODULATION



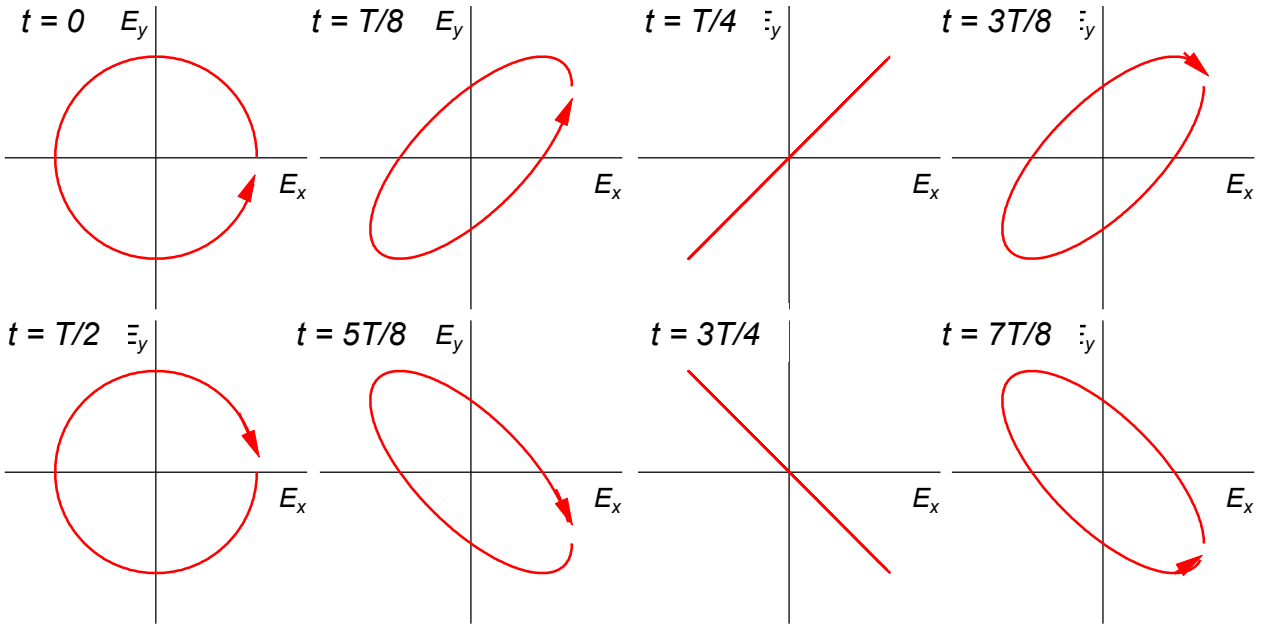
Core of the setup:
photoelastic modulator (Hinds Instrument PEM-100)

$$\vec{E}_{PEM} = \frac{E_0}{\sqrt{2}}\left(\hat{e}_x + \exp(i\varphi(t))\hat{e}_y\right) \qquad \varphi(t) = A\cos(2\pi f t)$$

At the SNOM probe input, laser polarization is periodically manipulated (circular-elliptical-linear)

Circular polarization achieved twice in a modulation period *T* (left- and right-handed)

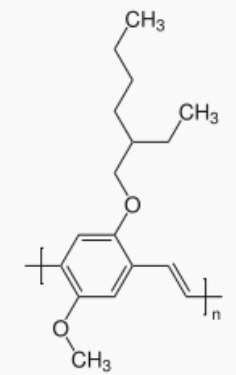
Produced polarization states (at different times)

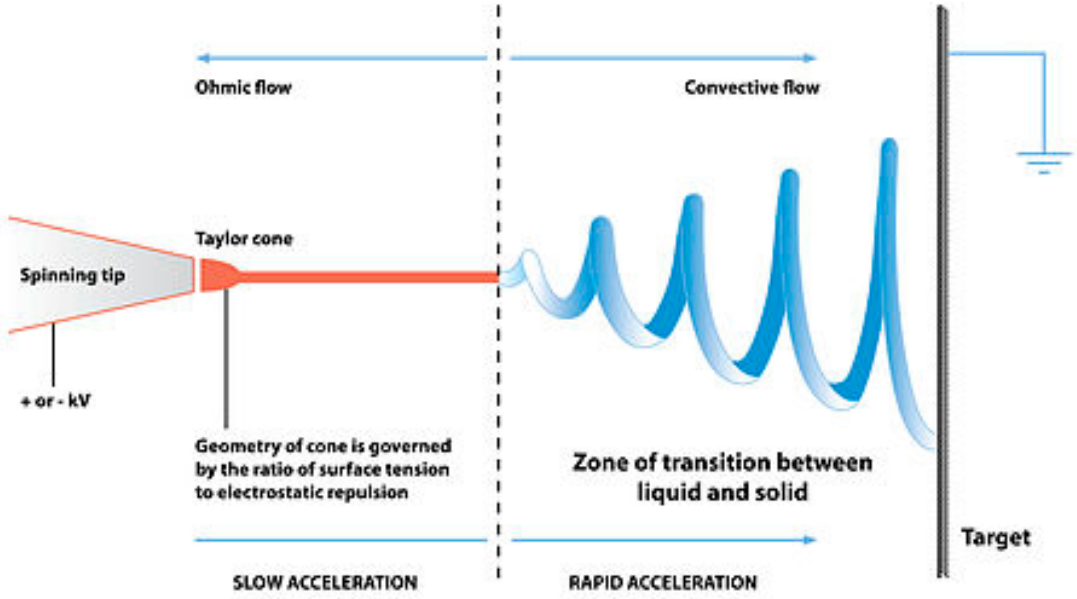


Assuming as input a linearly polarized radiation at 45 degrees, A = π/2, T = 2π/f with *f* = 50 kHz

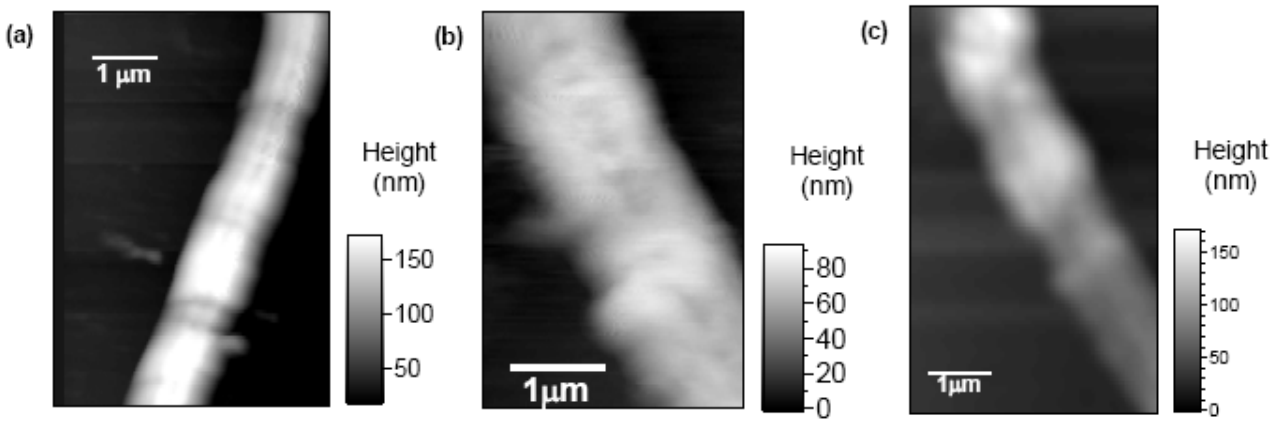
EXAMPLE I : ELECTROSPUN FIBERS

Sample:
MEH-PPV polymer prepared in micro- and nano-fibers through electro-spinning

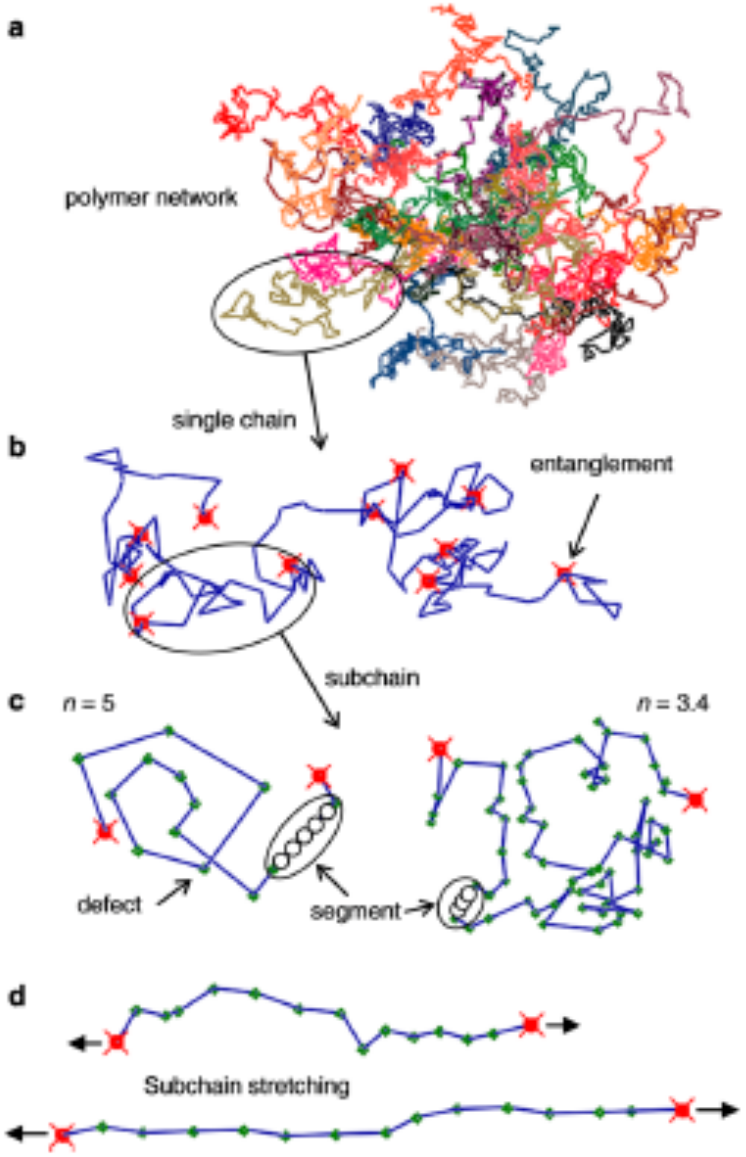




Example of topography maps



MOTIVATIONS



hypothesis (model)

fabrication parameters

⇩

structure

⇩

local physical properties

⇩

linear dichroism

Model:

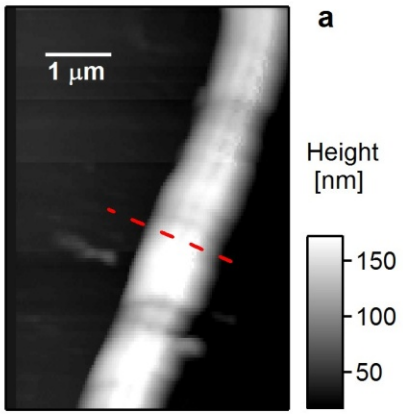
- inhomogeneous structure across the fiber width due to spontaneous stretching processes
- fiber core made of strongly aligned polymer molecules

expected linear dichroism in the core

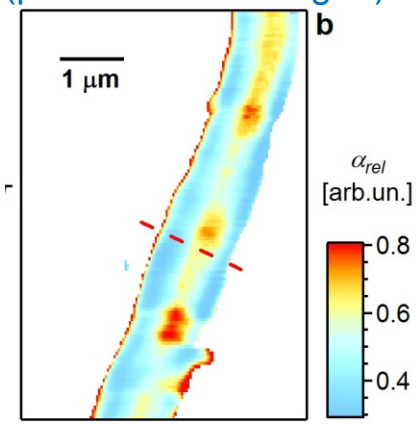
Polarization analysis with sufficient spatial resolution needed to assess the model

RESULTS

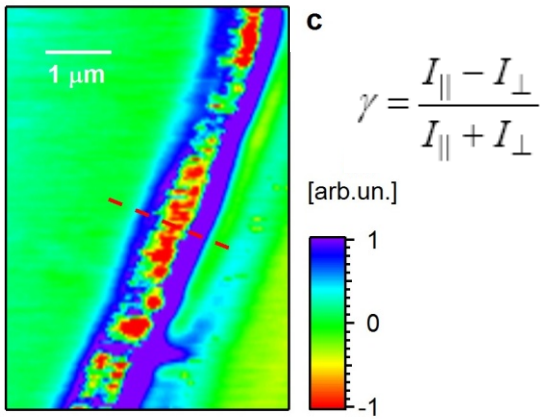
Topography map



Absorption coeff.
(polarization averaged)



Linear dichroic ratio

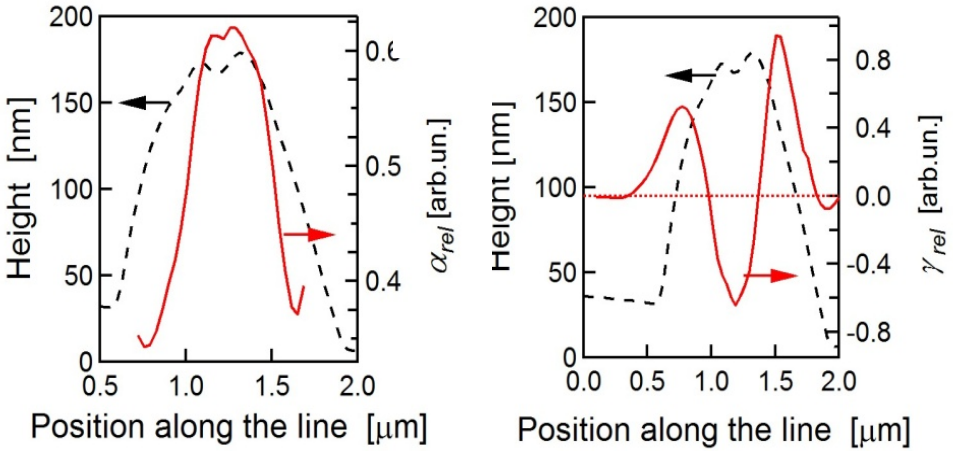


$$\gamma = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

The model is substantially confirmed

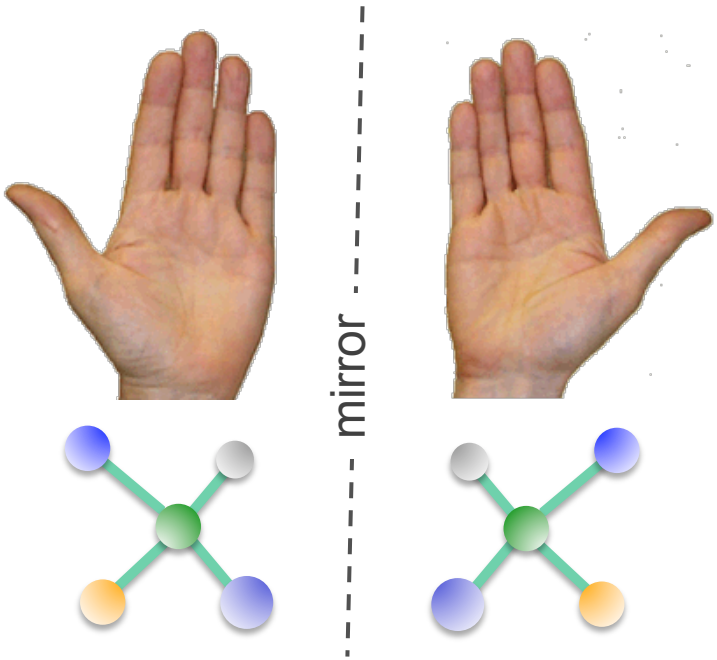
Engineering the optical properties of the fiber is feasible

Line profiles of topography, absorption, dichroic ratio



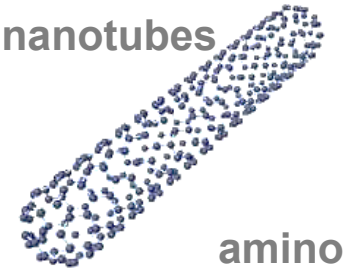
[A.Camposeo, et al., Nano Lett. (2013);
A.Camposeo, et al., Macromol. (2014)]

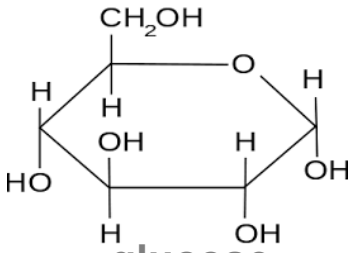
CHIRALITY AND CIRCULAR DICHROISM I



Molecular chirality:
describes a molecular structure whose mirror image cannot be superimposed

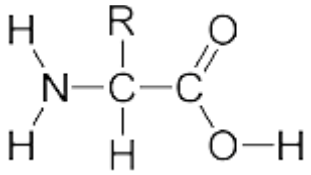
carbon nanotubes





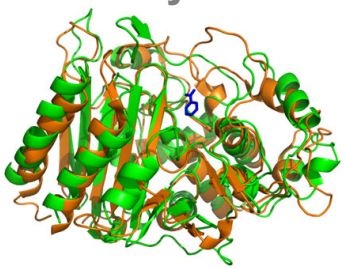
glucose

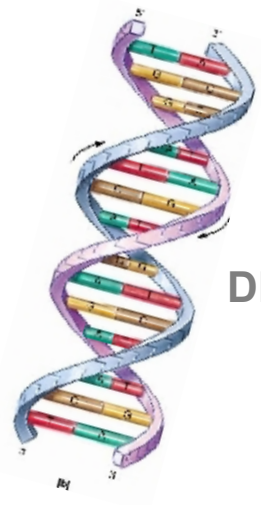
amino acids



Chirality is extremely frequent in biomolecular building blocks (homochirality in nature is an intriguing issue)

enzymes

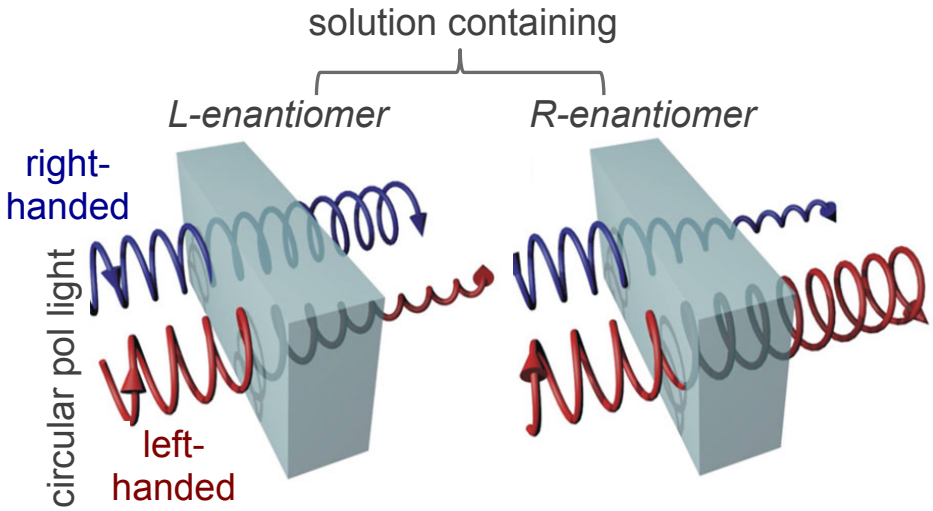




DNA

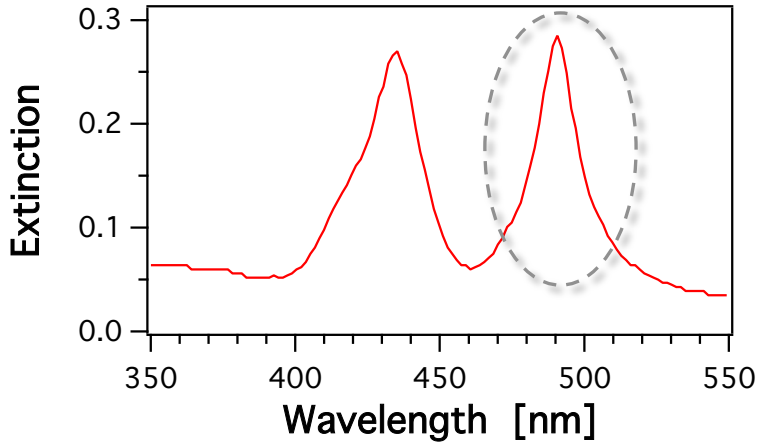
CHIRALITY AND CIRCULAR DICHROISM II

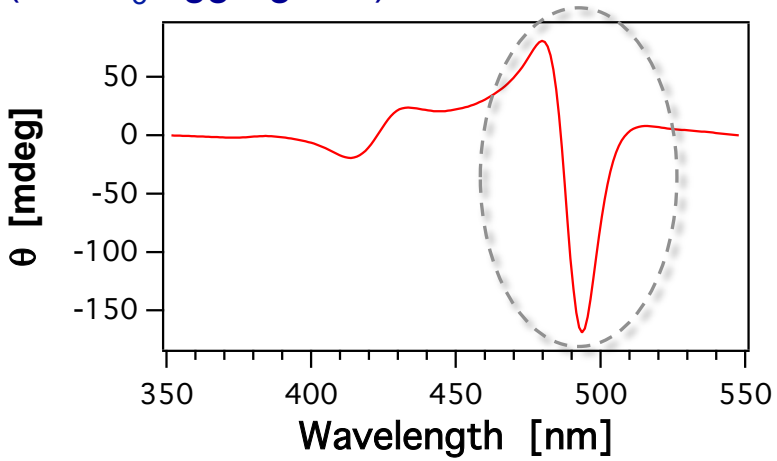
Chirality is inherently associated with circular dichroism (CD)



CD spectroscopy is a powerful tool to investigate chirality in the liquid phase

For the sample of our interest ($TPPS_3$ aggregates) in solution:

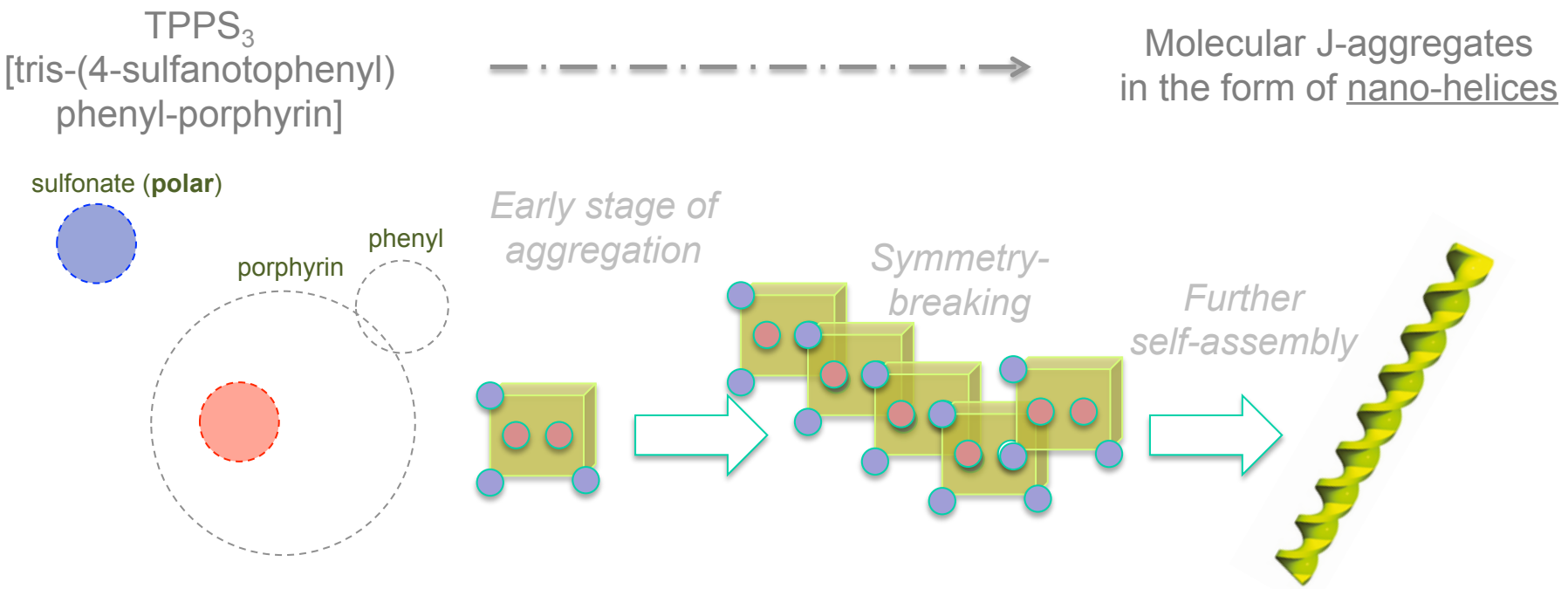




CD very hard to be observed in the solid state

EXAMPLE II : PORPHYRIN NANOSTRUCTURES

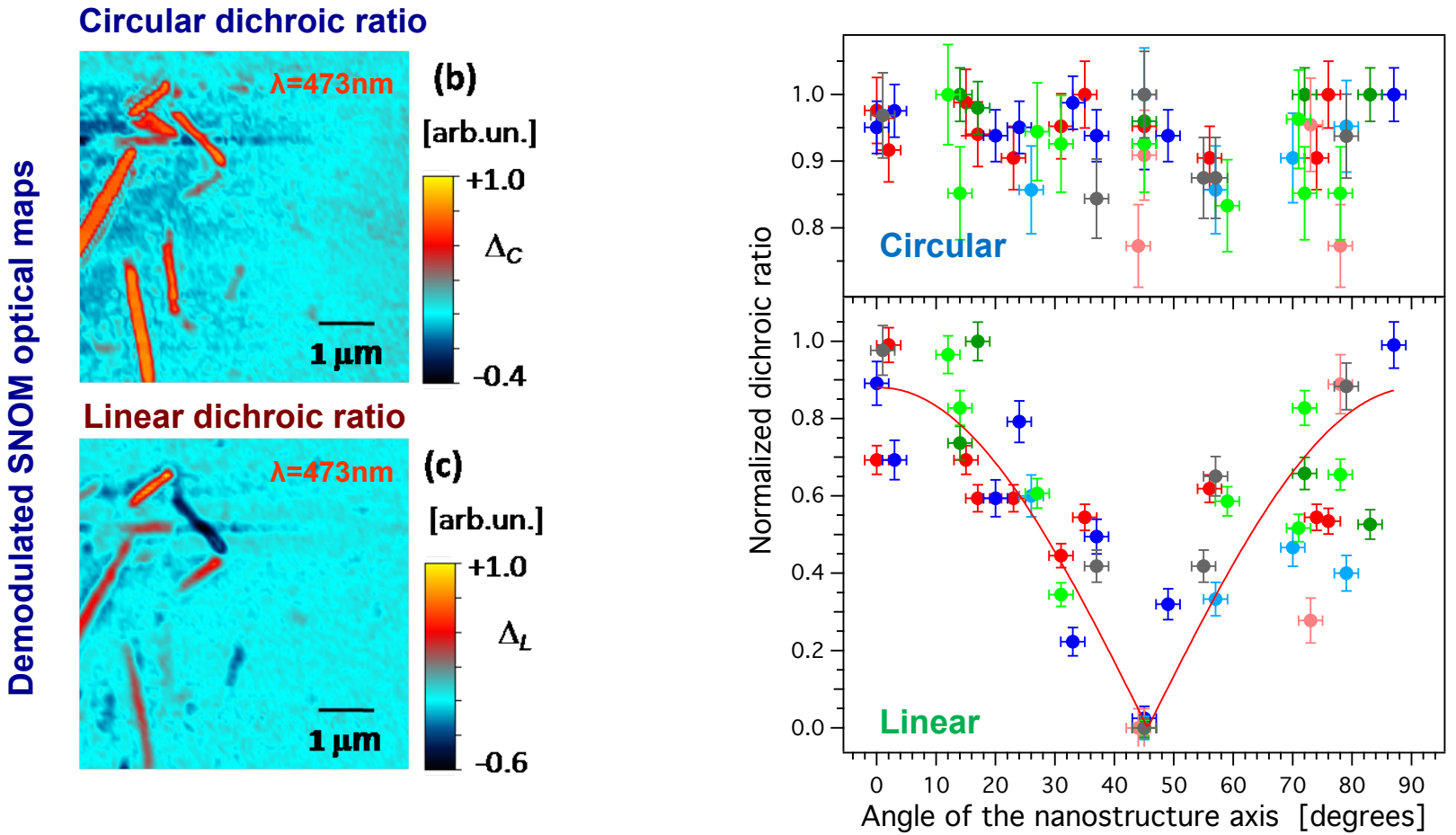
- ✓ Chirality can clearly stem from mutual arrangement of different achiral molecules
- ✓ In the case of the $TPPS_3$ porphyrin system, a self-assembly molecular aggregation process in the liquid phase can occur



Hypothesis: chirality originates from molecules self-assembled in nano-helices

Need for high resolution optical methods able to probe individual, deposited, nanostructures

CIRCULAR DICHROISM AT THE SOLID STATE



Linear dichroism related to the elongated (anisotropic) structure

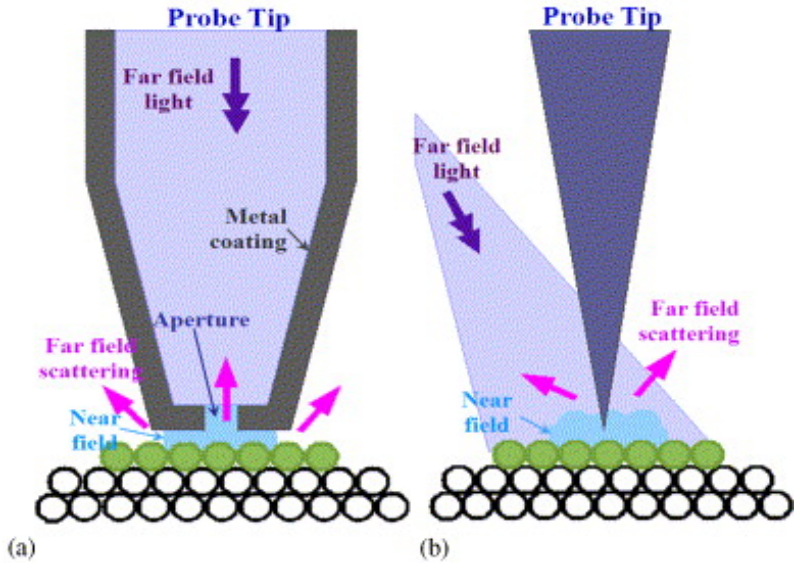
Circular dichroism intrinsic to the material nanostructure

[F.Tantussi, et al., Nanoscale (2014);
G.Lazzini, et al., SPIE Proc., (2016)]

APERTURELESS AND TIP-ENHANCED

A variant of SNOM is based on aperture-less probes

Such probes are available, semiconducting or, more frequently, metal-made, with nanometer apical size (the same technology of STM or AFM probes)



A metal tip (similar to STM probes) is illuminated by a far-field

→ Scattering produces a near-field localized at the tip

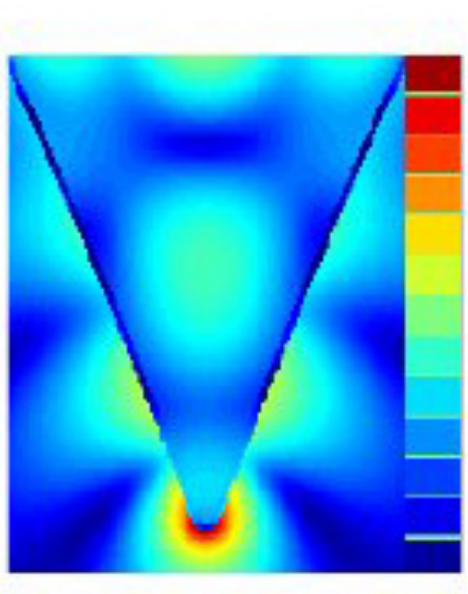
→ Assuming prevalent interaction with the (higher intensity) near-field, spatial resolution is obtained

(unfortunately, discrimination between near-field excited and far-field excited features is not always simple)

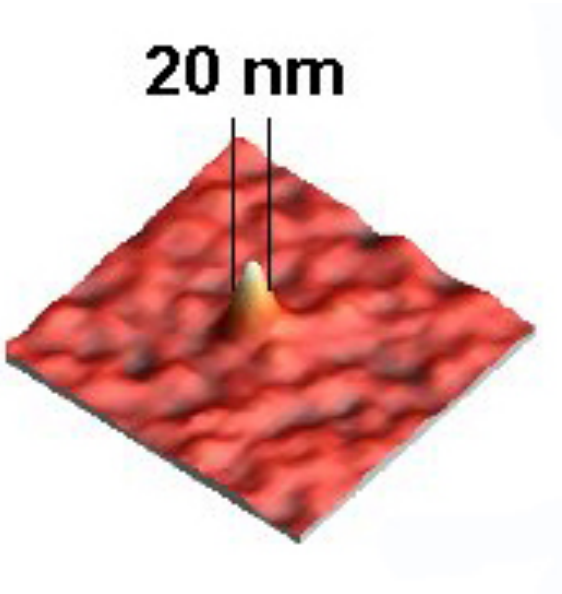
APERTURELESS RESOLUTION

Apertureless-SNOM is mostly used with fluorescent samples, thanks to the straightforward (bandpass filter based) discrimination of illumination and fluorescence signals

The extremely small size of the tip ensures excellent spatial resolution



Spatial distribution of electric field close to the tip



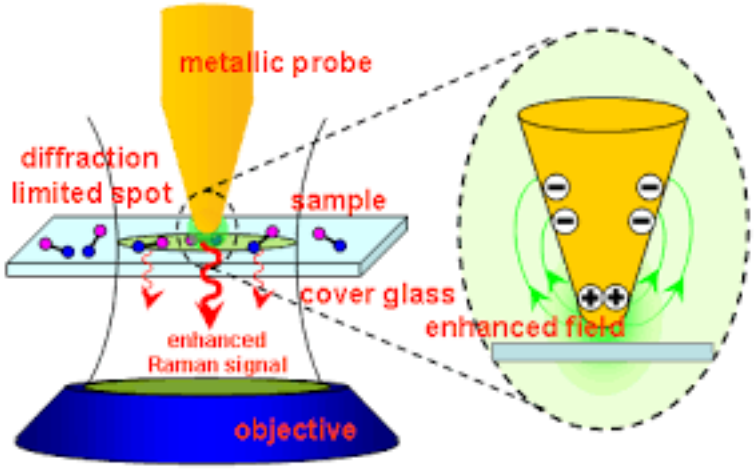
SNOM image of a single dye molecule anchored on a substrate

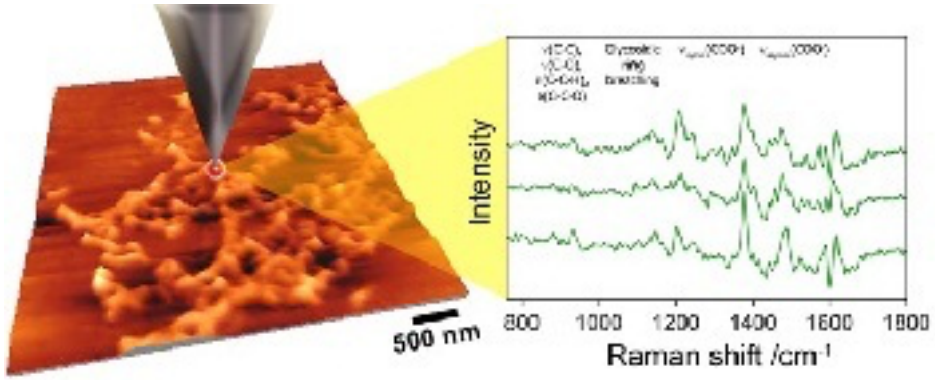
Anselmetti, Bielefeld Universitaet

TIP-ENHANCED RAMAN SPECTROSCOPY

Further variant of the SNOM is the so-called TERS: the local enhancement of the electric field close to a (noble) metal, e.g., gold tip is used to excite Raman lines

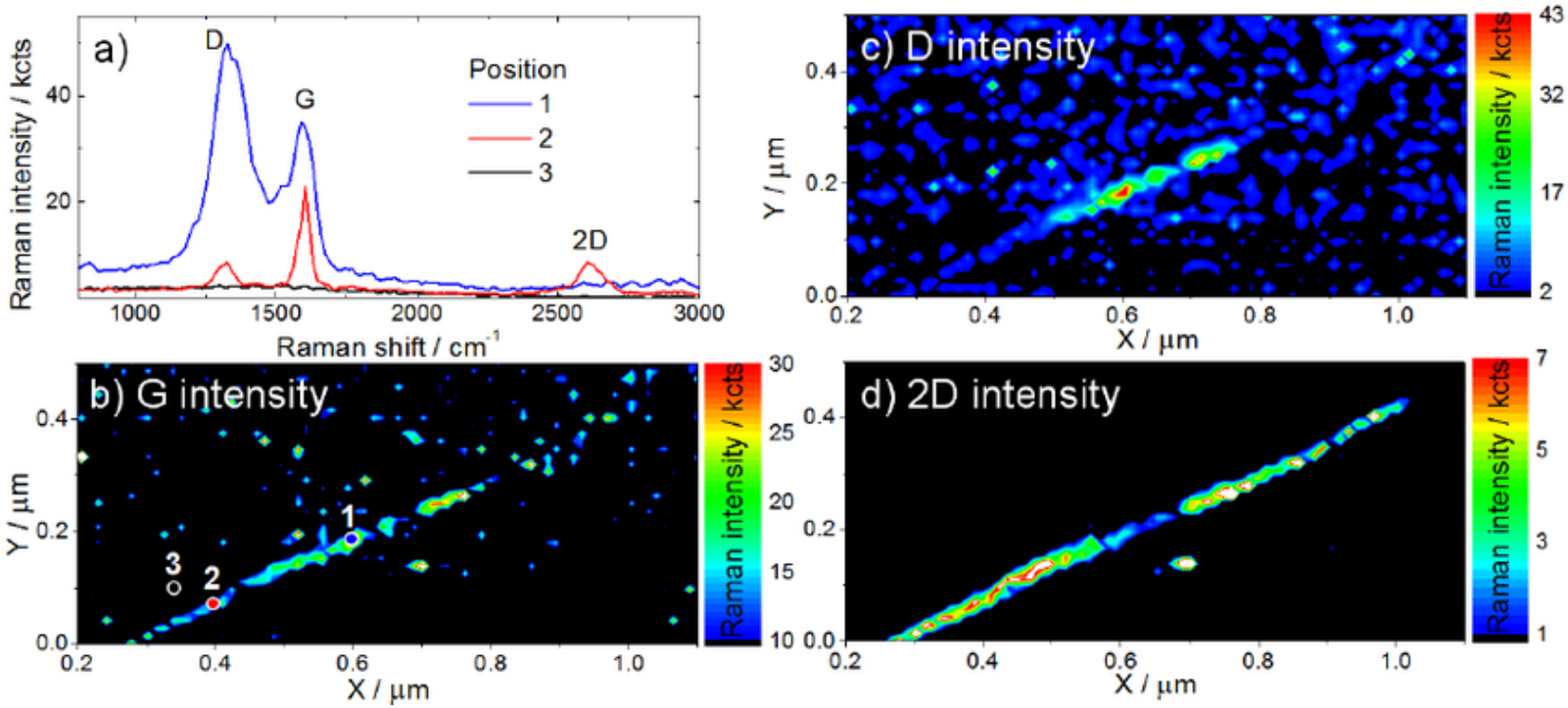
In some sense, the TERS approach is a reverse of SERS: the enhancement provided by the substrate in SERS is here enabled by the scanning tip





The excellent species selectivity of Raman can be effectively coupled with the very good resolving power of SNOM leading to highly-sensitive spectroscopy of nanomaterials

TERS EXAMPLES

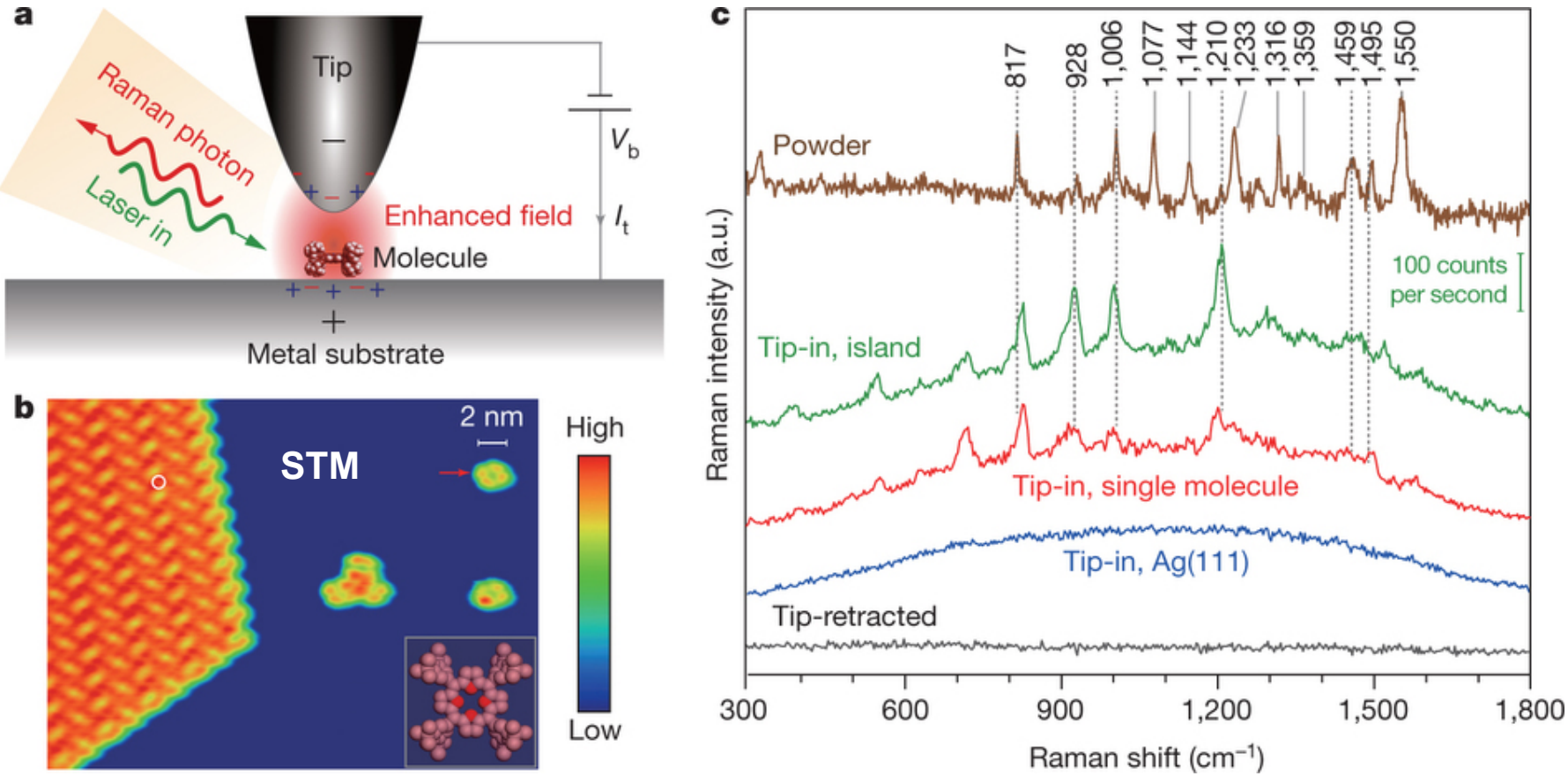


A typical example of TERS is with Carbon Nanotubes, showing particularly intense Raman bands related to their structure

Note that typical size of single walls CNT is on the nanometer range

Sheremet. et al., Chemnitz (2014)

TERS+STM



Molecular islands of H_2TBPP deposited on Ag

Zhang, et al. Nature (2013)

CONCLUSIONS

- ✓ Near-field entails the e.m. field in proximity to small structures, and therefore plays a crucial role in the optical interaction between closely spaced, nanosized objects

- ✓ Near-field can be produced by a sort of extreme diffraction from nanosized apertures and its properties in imaging can be understood by looking at the problem from different standpoints:
  - (i) Fourier optics
  - (ii) Heisenberg principle
  - (iii) Maxwell equations

- ✓ A (virtually) extremely powerful spectroscopy of nanomaterials can be built based on near-fields

- ✓ However, technical and practical limitations exist to run such spectroscopies, and results, while being useful, are often controversial and non completely satisfying

In any case, the meaning of making optical spectroscopy of nanomaterials should be finally clarified!!!

FURTHER READING

For a comprehensive reference on near-field and nano-optics

A. Zayats and D. Richards, Nano-optics and near-field optical microscopy, Artech House, Boston (2009).

A paper on SNOM from the NT-MDT company:

http://www.azonano.com/article.aspx?ArticleID=2250

A comprehensive list of references on SNOM can be found at

http://zeiss-campus.magnet.fsu.edu/referencelibrary/superresolution/nsom.html

A review on SNOM, authored by Novotny and Stranick, can be found at

http://www.optics.rochester.edu/workgroups/novotny/muri03/publications/stranick06a.pdf

A (rather old) review on SNOM applications to materials, authored by Dunn, is

http://pubs.acs.org/doi/abs/10.1021/cr980130e