X-Ray Diffraction as a key to the Structure of Materials
Interpretation of scattering patterns in real and reciprocal space

ESRF | The European Synchrotron

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X-ray nanoprobe group
ESRF

OUTLINE

1 “Internal” structure of materials – macroscopic characteristics: importance of experimental physics to understand fundamental properties

The dilemma of x-ray optics

2 X-rays in structural analysis: diffraction as a sensing parameter for inter-atomic distances

3 Introduction to diffraction and reciprocal space

4 Limits of reciprocal space

5 Getting the most out of real and reciprocal space,
<u>How can we get the holy grail ?</u>

STRUCTURE AND PROPERTIES:
HOW CAN WE KNOW AND WHAT DO WE KNOW?

We know..

Glass is brittle,

(->experiment)

Shape cannot be changed easily

Glass is transparent

electrically insulating and a poor heat conductor

Metals are much less brittle can be formed/ deformed,

Metals are opaque

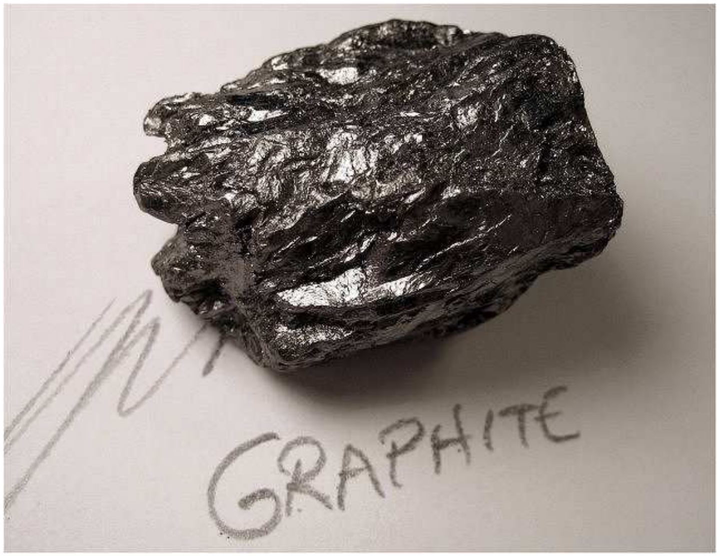
Metals conduct well electricity and heat

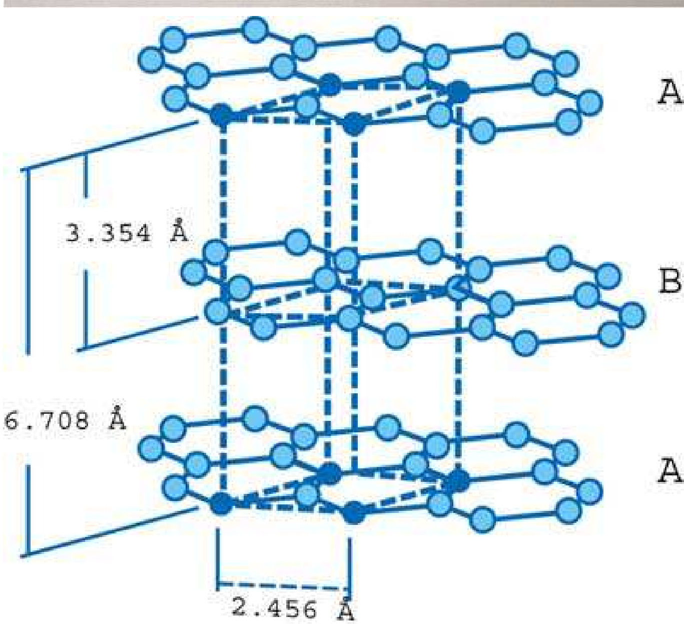
Mechanical properties

Optical properties

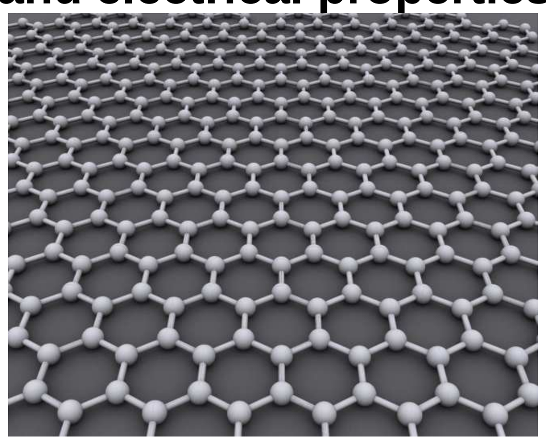
Electrical properties

STRUCUTRE FUNCTION RELATIONSHIP





Novoselov & Geim Nobel Price 2010:
Using scotch tape to lift of one atomic layer of *Graphene,*
With outstanding mechanical and electrical properties



2010: single layers of MoS_2 turn out to have outstanding electronic properties.

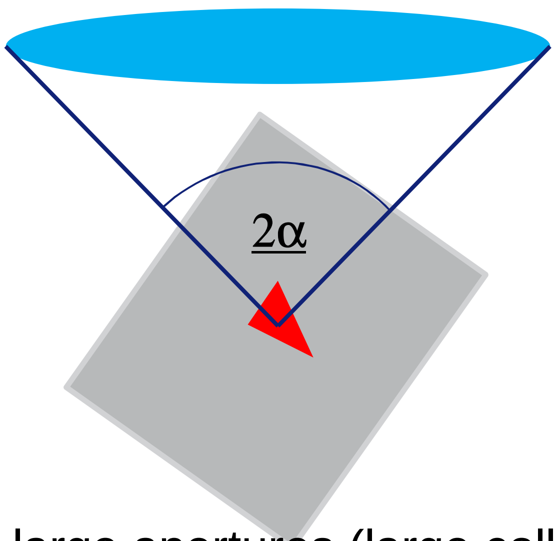
ATOMIC STRUCTURE STUDIED WITH X-RAYS

Atomic distances typically 0.1 nm (1 Å)

X-ray wavelength (typical)
λ=0.01…0.1 nm

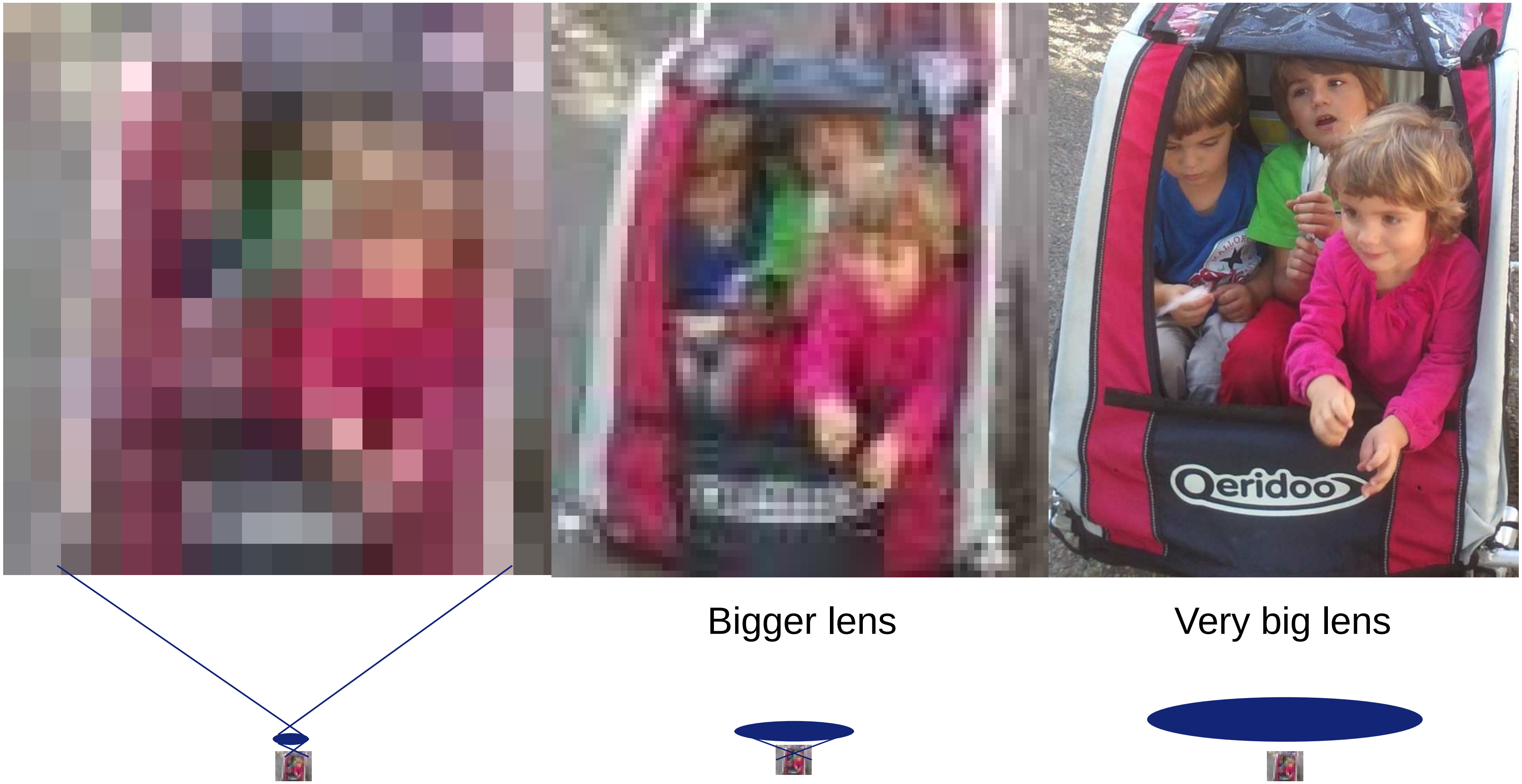
Light λ~500nm

Resolution Δ**x** of a light microscope:
Δ**x** = 1.22*λ/2NA~0.6*λ/(**n*sin**α)



High resolution means small wavelengths and large apertures (large collection angles)

Be careful with “1000-times magnification” Microscopes



Magnification: geometrical optics (no reasonable limits, everything is allowed)
Resolution (=Δx): real information: limited (at least) by quantum mechanics

X-RAY OPTICS: THE DILEMMA OF REFRACTION

interaction of electromagnetic waves (light!) and matter (~electron clouds)

The refractive index is expressed as n=1- δ+iβ= $\sqrt{\varepsilon\mu} \approx \sqrt{\varepsilon} = \sqrt{\varepsilon_0(1+\chi)}$

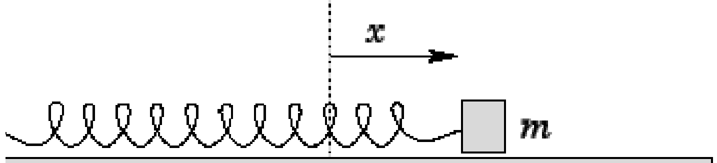
n $\approx \sqrt{1+\chi}$ χ=polarizability

The polarizability χ describes the polarization P as a function of a field E: P~χE; in the mechanical equivalent, 1/χ is similar to a spring constant

$$\rho_m \ddot{s}(t) + Bs(t) = \rho_e E(t)$$

Inertia Spring constant driving force

Driven oscillator equivalent to simple mechanical model



We replace s(t) by the Polarization P(t)=ρ_es

Damping factor (friction): ϕ (we ignore the origin)

$$\ddot{P}(t) + \omega_0^2 P(t) + \phi \dot{P}(t) = \frac{\rho_e^2}{\rho_m} E(t)$$

SOLUTION OF "EQUATION OF MOTION"

$n \approx \sqrt{1+\chi}$ With P~χ $\ddot{P}(t) + \omega_0^2 P(t) + \phi \dot{P}(t) = \frac{\rho_e^2}{\rho_m} E(t)$

What else can we interpret from the mechanical equivalent ?

Amplitude

$$X_0 \cong P \propto \frac{\omega_0^2}{\sqrt{(\omega_0^2 - \omega^2)^2 + \phi^2 \omega^2}}$$

es

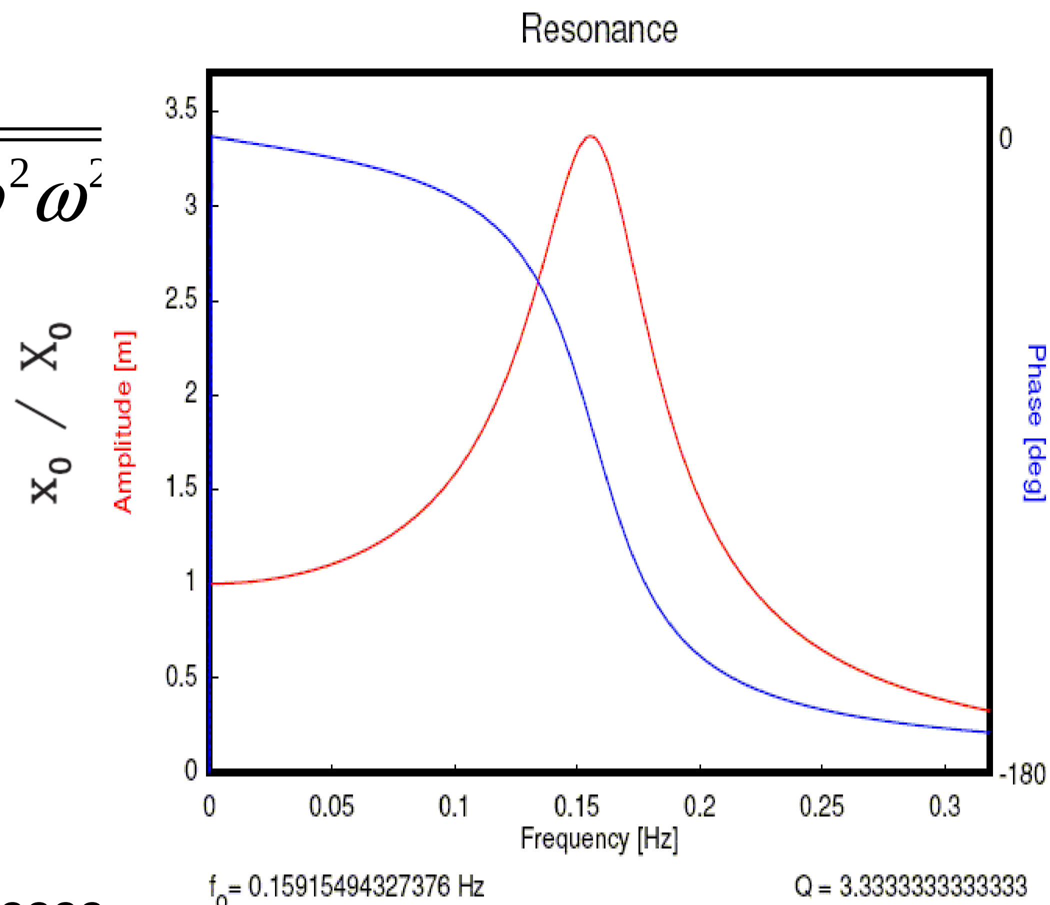
n is

P-> 0

egime is

romatic!!,

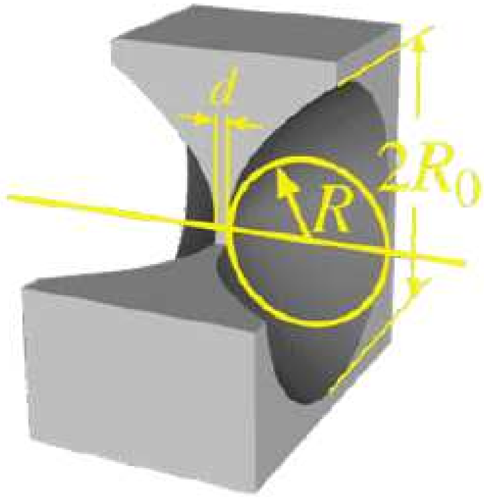
n≈0.99999..



REFRACTIVE X-RAY OPTICS

Lens surfaces must be paraboloids of rotation

single lens



parameters for Be lenses:

R = 50 to 1500µm

$2R_0$ = 0.45 to 2.5mm

d below 30µm

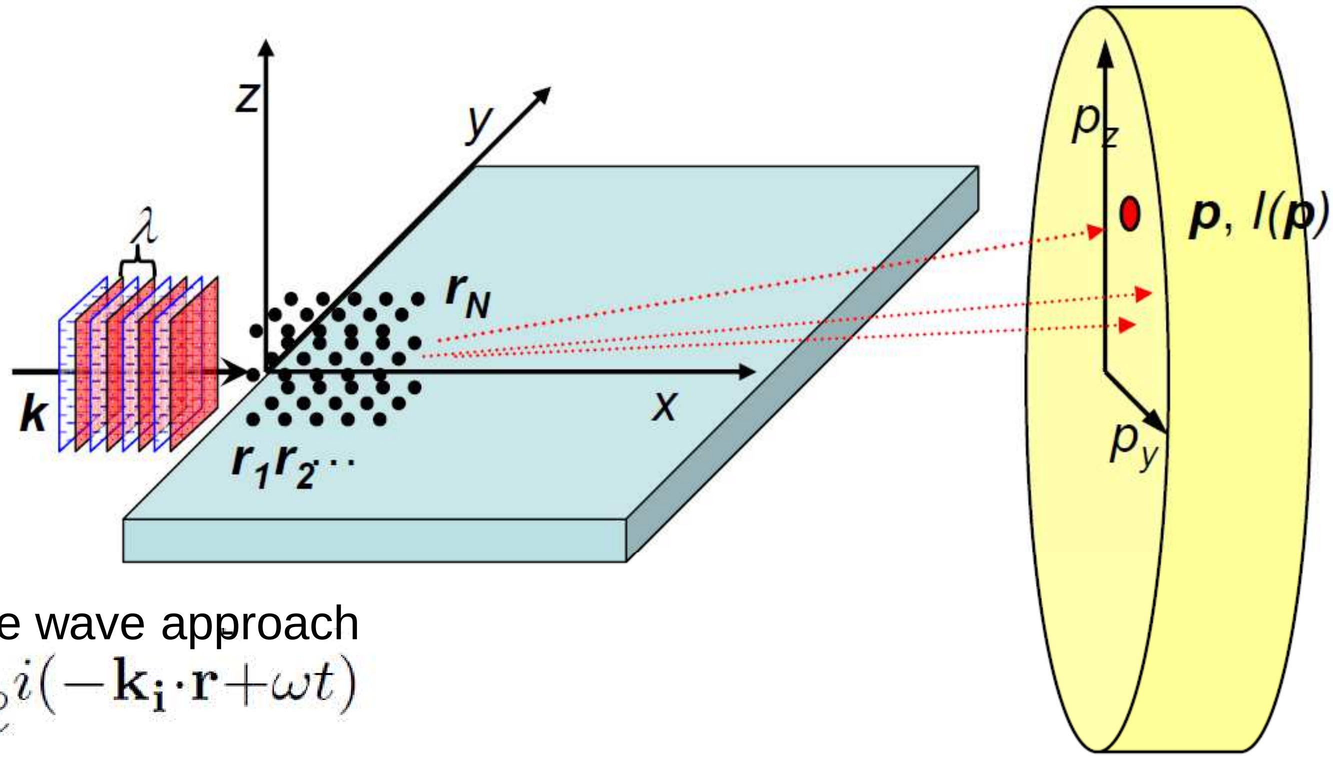
Resolution $\Delta\mathbf{x}$ = 1.22*λ/2NA~0.6*λ/(**n*sin**α)

parabolic profile: no spherical aberration

focusing in full plane

=> excellent imaging optics

DIFFRACTION AND RECIPROCAL SPACE



Plane wave approach

$$\hat{A} e^{i(-\mathbf{k_i}\cdot\mathbf{r}+\omega t)}$$

At the observation point we record

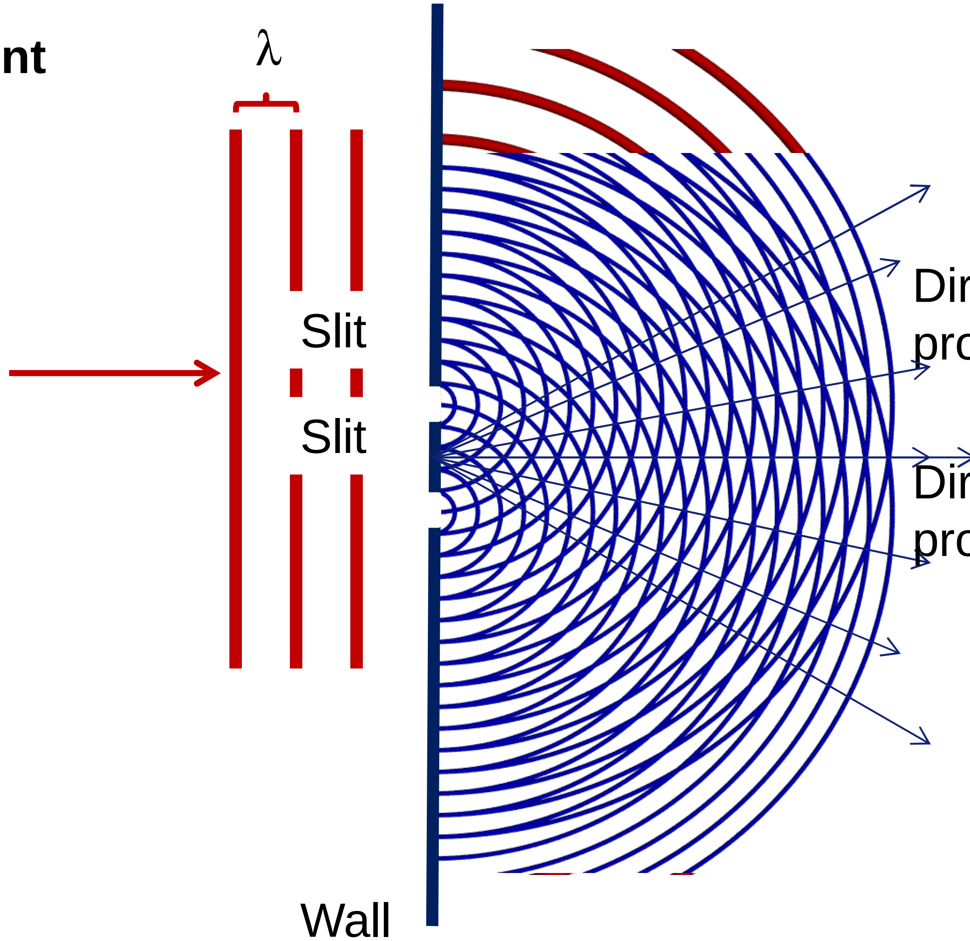
Fourier Transform
r->Q

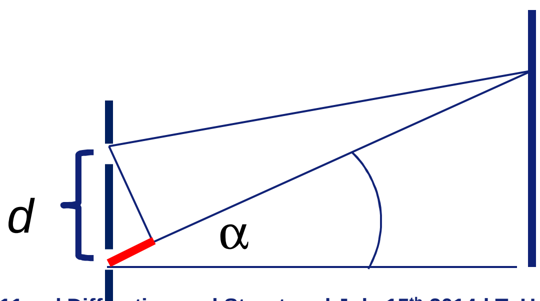
$$I =< \left| \sum_{j=1}^{N} \hat{A}_j e^{i(\mathbf{k_f}-\mathbf{k_i})\cdot\mathbf{r_j}} e^{i\omega t} \right|^2 >_t = \left| \int \rho(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}} \cdot \mathbf{dr} \right|^2$$

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as $\rho(\mathbf{r}) = \sum_{j=1}^{N} \hat{A}_j \delta(\mathbf{r_j})$

DIFFRACTION AND RECIPROCAL SPACE

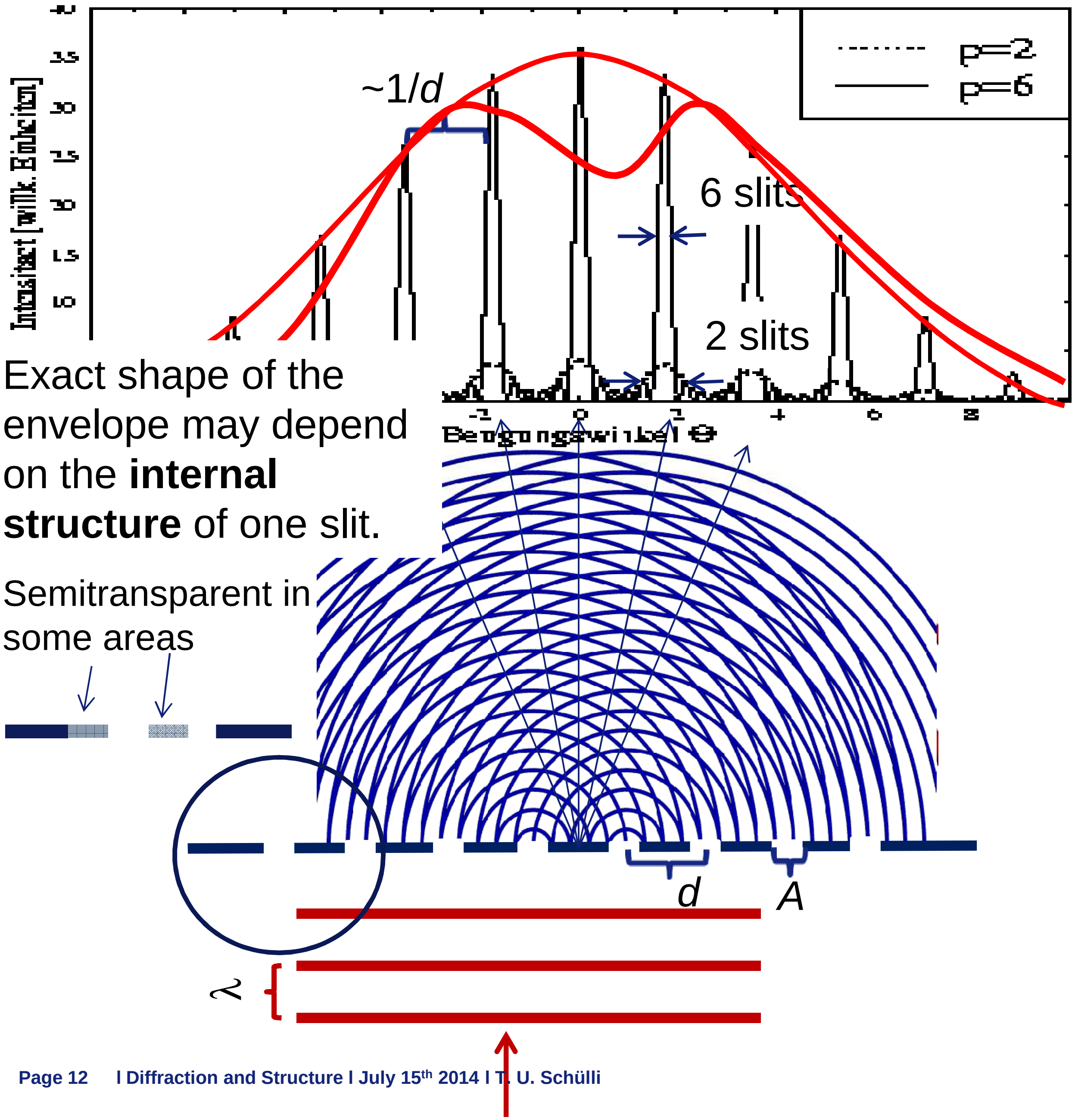
Young's experiment





=Path difference $\stackrel{!}{=}$ $n*\lambda = d*\sin\alpha$

DIFFRACTION FROM A PERIODIC GRATING



Angular distance of the peaks<->determines distances of the slits (grating parameter)

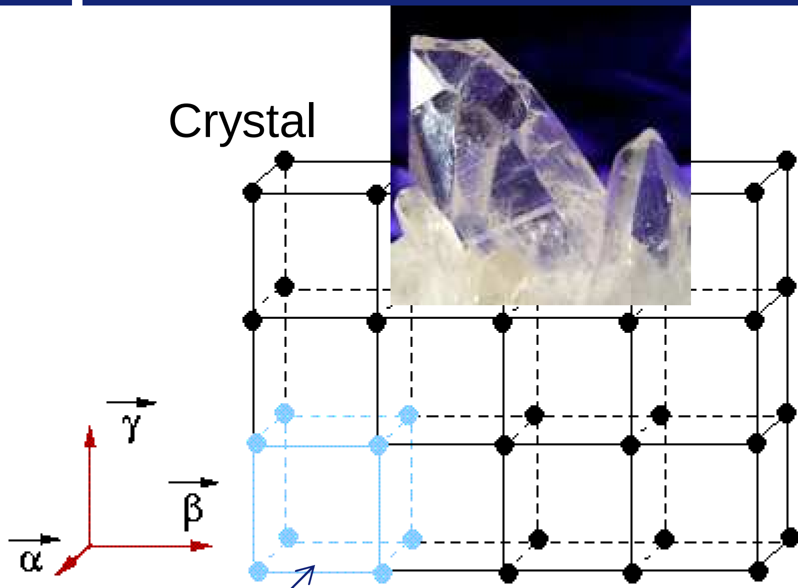
The width of the peaks (FWHM) depends on the number *p* of illuminated slits
FWHM~*1/p*

Exact shape of the envelope may depend on the **internal structure** of one slit.

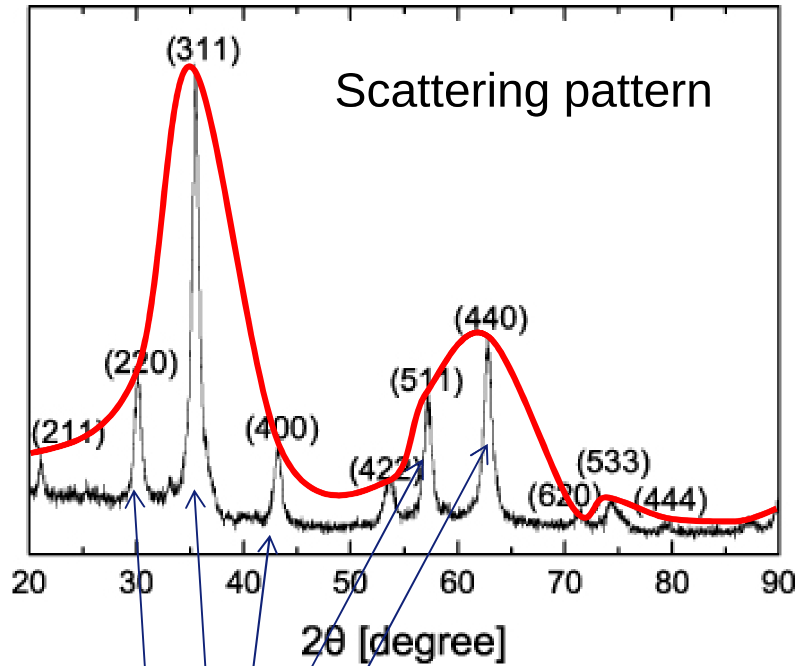
Semitransparent in some areas

The **envelope** of the peaks determines the **width *A*** of one slit.
FWHM~*1/A*

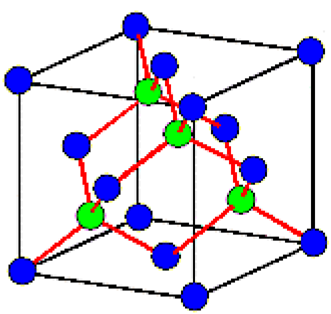
STRUCTURE RESOLUTION IN RECIPROCAL SPACE



"Unit cell" (smallest repetitive building block)



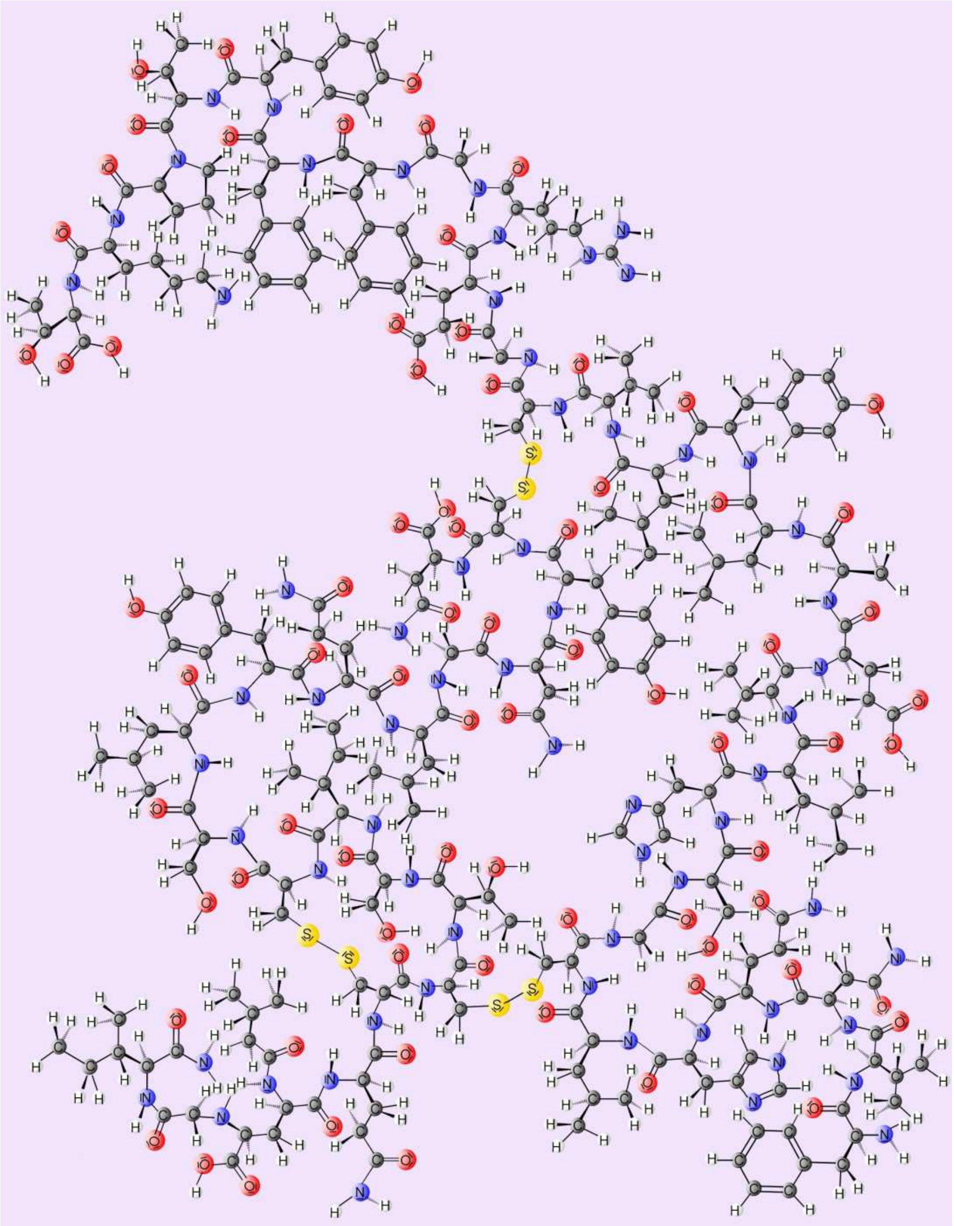
"Bragg-peaks" corresponding to different net planes)



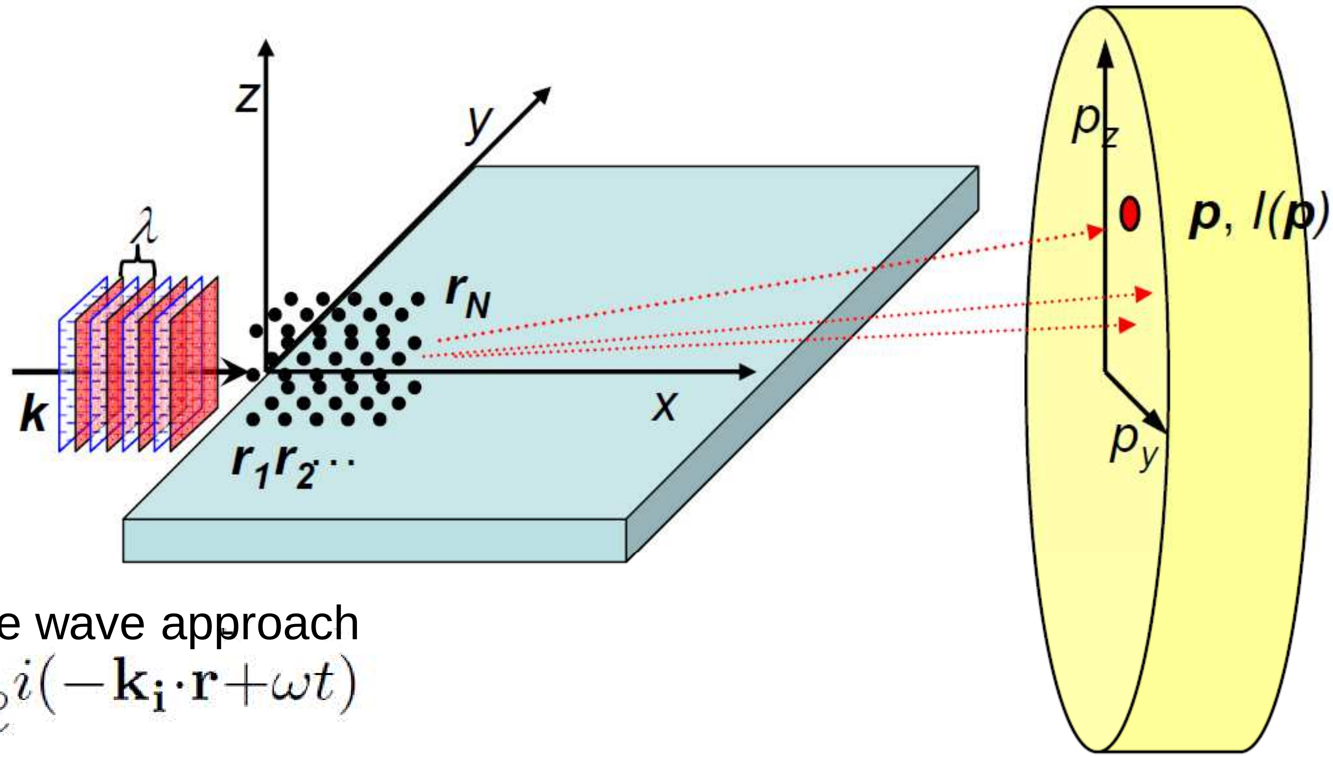
Envelope->

Information about the atomic arrangement inside the unit cell.

COMPLEX MOLECULE: INSULIN



DIFFRACTION AND RECIPROCAL SPACE



Plane wave approach

$$\hat{A}e^{i(-\mathbf{k_i}\cdot\mathbf{r}+\omega t)}$$

At the observation point we record

Fourier Transform
r->Q

$$I = <|\sum_{j=1}^{N}\hat{A}_j e^{i(\mathbf{k_f}-\mathbf{k_i})\cdot\mathbf{r_j}} e^{i\omega t}|^2>_t = |\int \rho(\mathbf{r})\, e^{i\mathbf{Q}\cdot\mathbf{r}}\cdot\mathbf{dr}|^2$$

We admit that only the time averaged Intensity can be measured and that the point scatterers can be described as $\rho(\mathbf{r}) = \sum_{j=1}^{N}\hat{A}_j\delta(\mathbf{r_j})$

FOURIER TRANSFORM: USEFUL RELATIONS

Fourier Transform
r->Q

$$I = <| \sum_{j=1}^{N} \hat{A}_j e^{i(\mathbf{k_f}-\mathbf{k_i})\cdot\mathbf{r_j}} e^{i\omega t} |^2>_t = | \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} \cdot \mathbf{dr} |^2$$

1. Linearity: The FT of $\rho(\vec{r}) = f(\vec{r}) + g(\vec{r})$ is

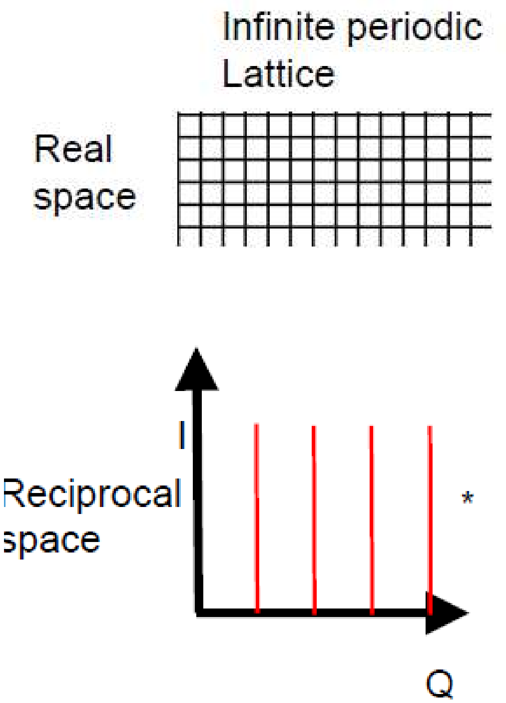
$$FT[f(\vec{r}) + g(\vec{r})] = FT[f(\vec{r})] + FT[g(\vec{r})]$$

2. Convolution: $\rho(\vec{r}) = \int f(\vec{\xi})\, g(\vec{r} - \vec{\xi})\, d\vec{\xi}$

$$FT[f(\vec{r}) * g(\vec{r})] = FT[f(\vec{r})] \bullet FT[g(\vec{r})]$$

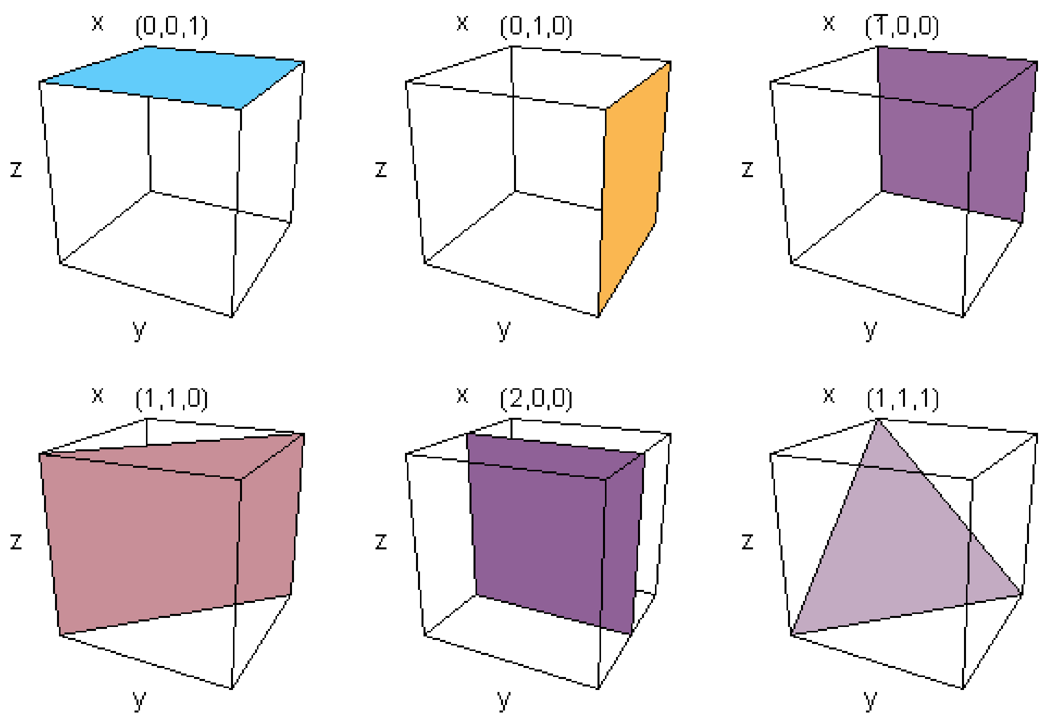
FT “ converts” a convolution in a product and vice versa

WE CAN BUILT A SMALL CRYSTAL



Big Crystals-sharp peaks, small crystals broad peaks. Peak intensities depend on the structure factor.

Miller indices “naming of Bragg peaks”: “*(hkl)-peak*” means that the considered netplanes intercept the unit cell axes at positions a/h, b/k, c/l or x/h, y/k, z/l.

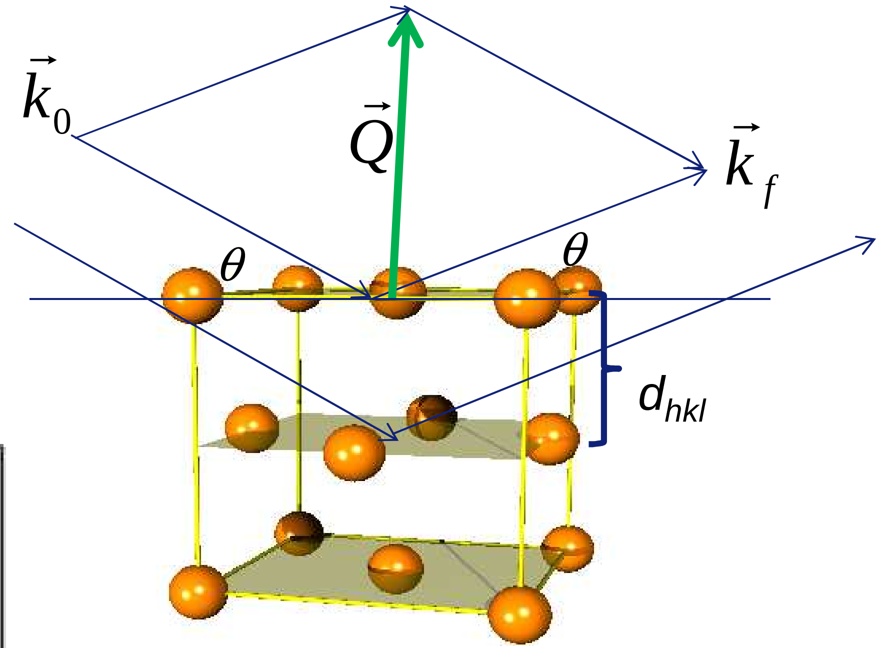


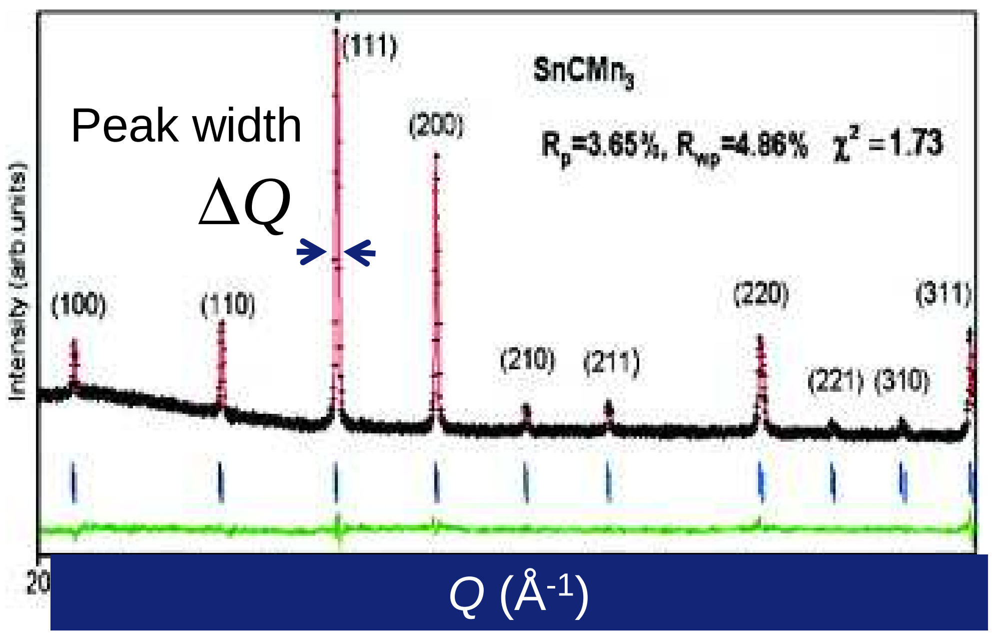
Higher indices ->closer net-plane spacings -> higher Q-values.

USEFUL RELATIONS IN (RECIPROCAL) Q-SPACE:

Braggs law: sinθ=λ/2d

$$Q = \frac{4\pi \sin\theta}{\lambda} \qquad \text{with} \qquad k = \frac{2\pi}{\lambda}$$





Useful relations:

1)Lattice spacing: $$d_{hkl} = \frac{2\pi}{Q_{hkl}}$$

2)Particle size: $$D = \frac{2\pi}{\Delta Q}$$

SIZE BROADENING AND STRAIN BROADENING

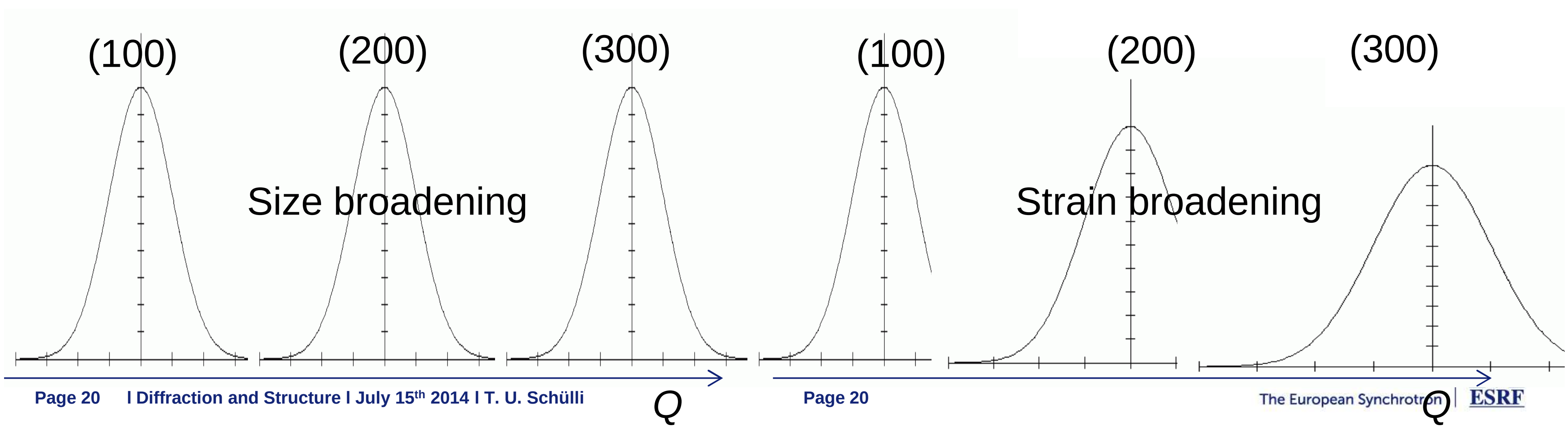
Strain may lead to lattice parameter changes or gradients within one crystal.

Assuming a *d*-spacing change Δd:

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d} \qquad \frac{\Delta Q}{\Delta d} = -\frac{2\pi}{d^2}$$

Strain broadening $$\Delta Q(\Delta d) = -\frac{\Delta d}{d}\frac{2\pi}{d} = -\frac{\Delta d}{d} Q$$ Depends on *Q* itself

Particle size (D) broadening: $$\Delta Q(D) = \frac{2\pi}{D}$$ No *Q* - dependence



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DETERMINATION OF LATTICE PARAMETERS

$$Q = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d}$$

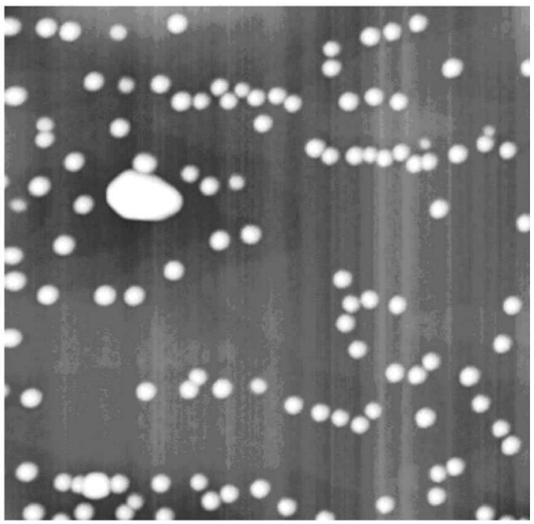
Resolution only limited by well-definition of the wavelength λ and beam divergence.

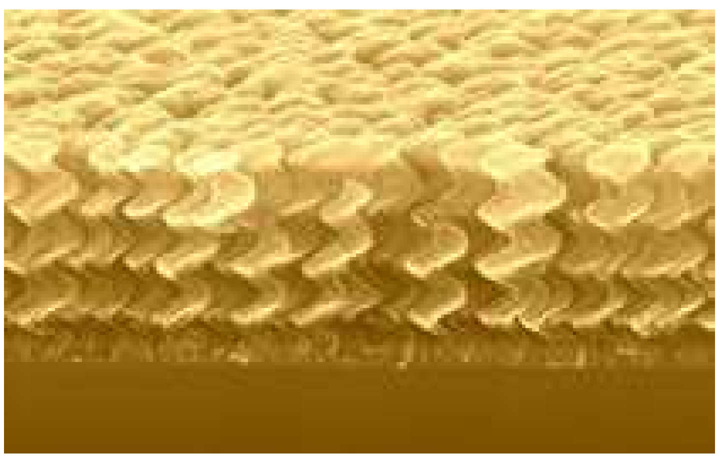
Typical absolute resolution of 10^{-4}-10^{-5} possible without too much effort

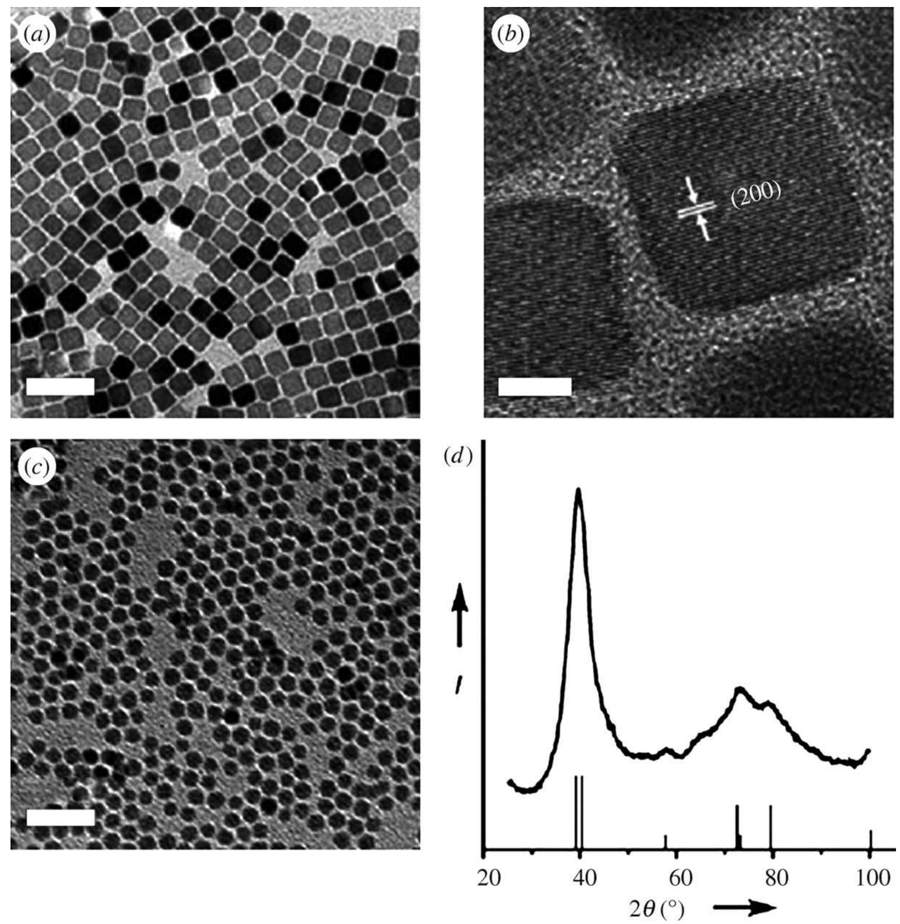
Simple structure resolution may not require that. But in order to separate different phases or in order to measure small perturbations in perfect crystals (strain) this is important

LIMITS OF RECIPROCAL SPACE

Most of diffraction experiments use “big and homogeneous” samples, like Homogeneous ensembles of nanostructures, chemical solutions or 2D “infinite” structures as surfaces, thin films, …

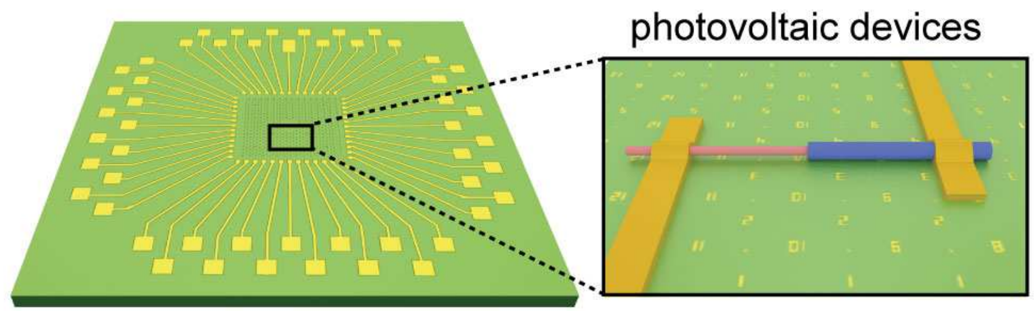


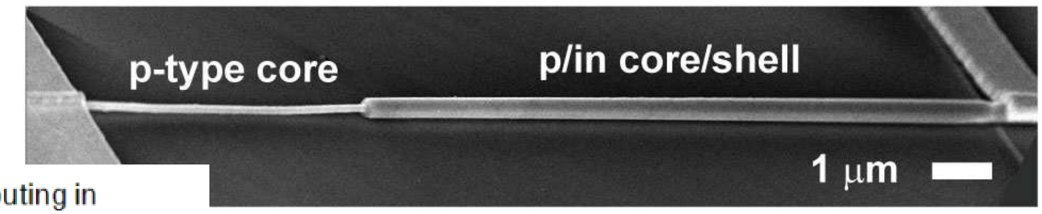


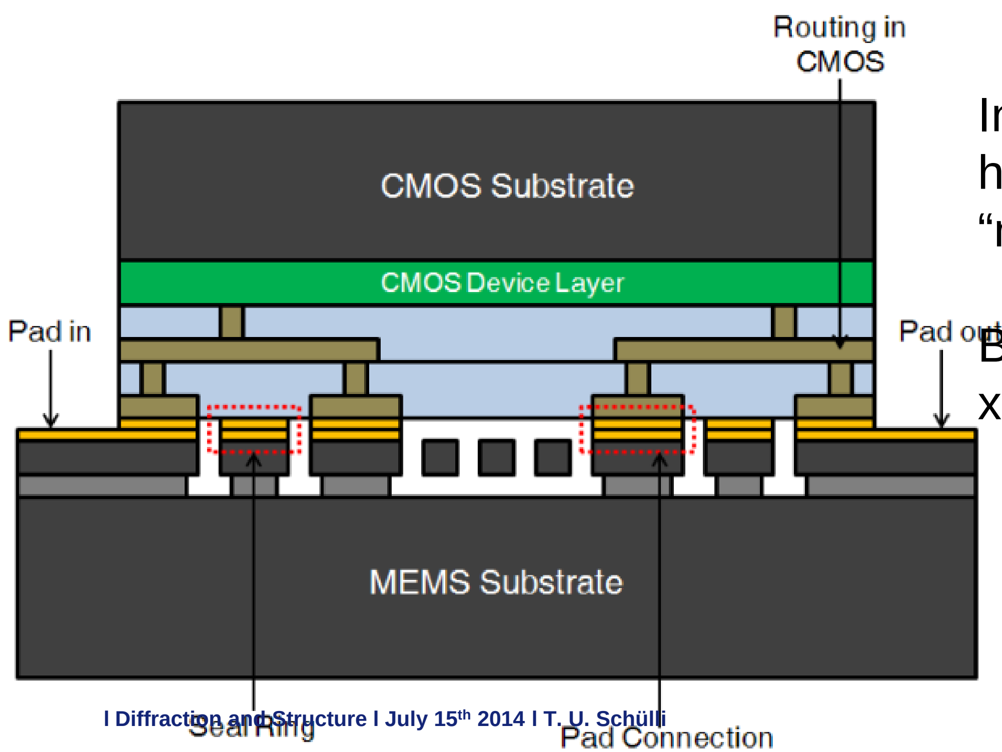


HETEROGENEOUS STRUCTURES (DEVICES)

Presence of multiple materials on different lengths scales: new strategy required.







In many intersting systems, heterogeneity happens to be on the “mesoscale” (not atomic scale).

Beams of 100 nm can be produced by x-ray optics

DIFFRACTION (AND) IMAGING TECHNIQUES

Radiography vs. Diffraction

Imaging: full field technique with spatial resolution ~sub mm (traditional sources)

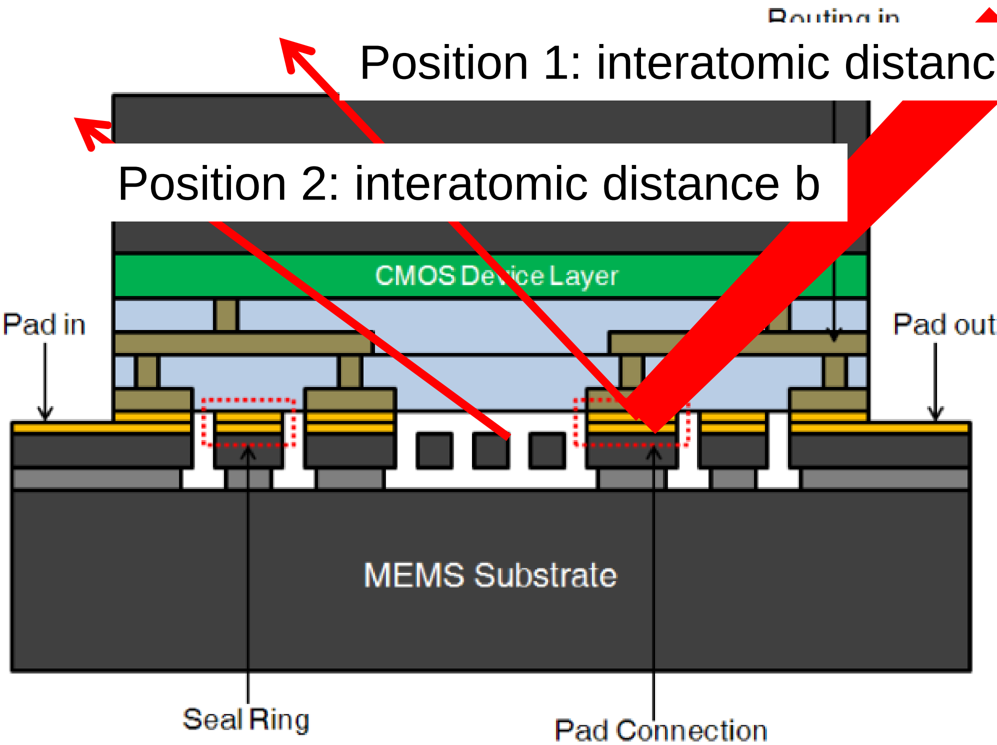
Diffraction : spatial **resolution** limited in any case and traded in for angular resolution

DIFFRACTION AND SCATTERING: ADVANTAGES

Objects can be far away (leaves a lot of space around the sample)

Angular resolution obtained by diffraction leads to spatial **information** below λ -> "interferometric" technique(~0.0001 nm for Bragg diffraction in crystals)

Limits: requires spatially homogeneous samples



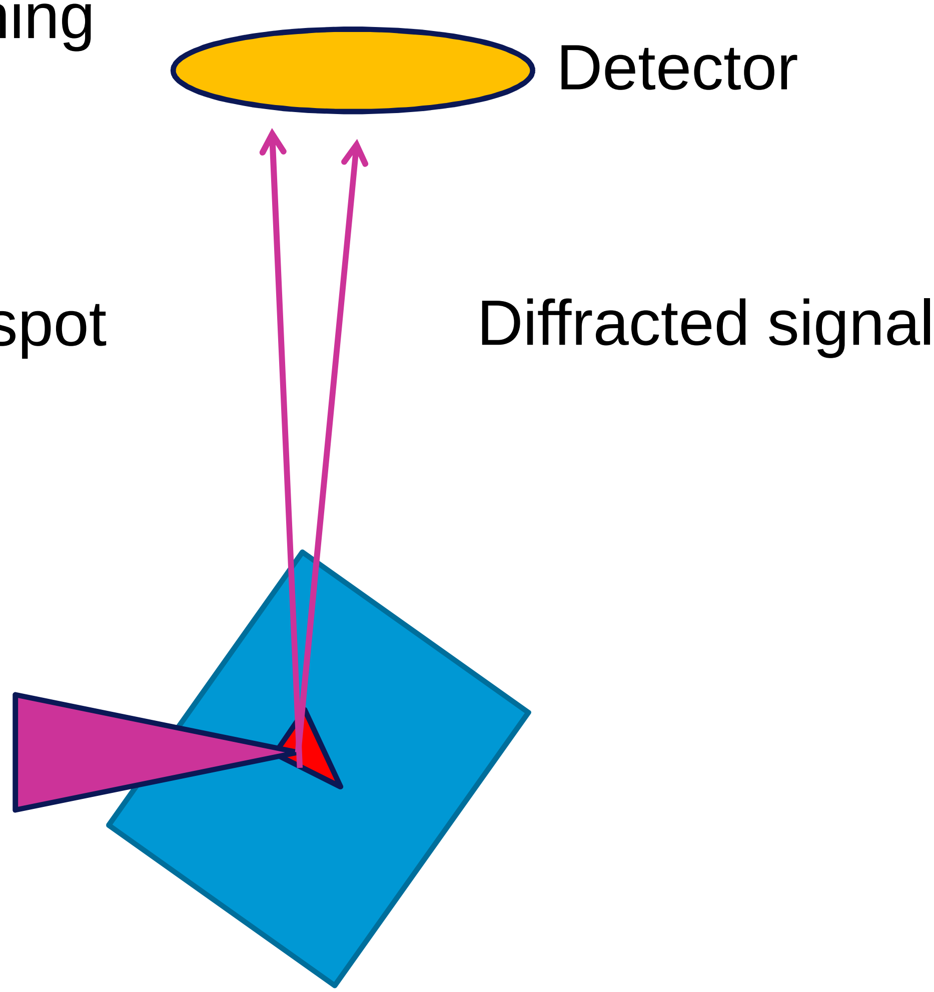
In many interesting systems, heterogeneity happens to be on the "mesoscale" (not atomic scale).

Combining small x-ray beams with diffraction

DIFFRACTION IMAGING: SCANNING PROBE

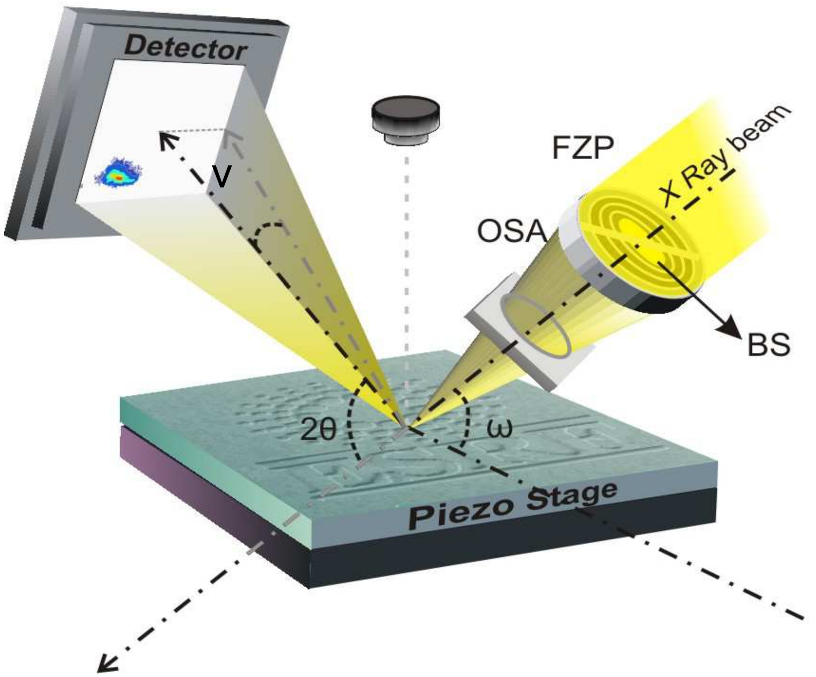
Use of focused beam/ scanning technique.

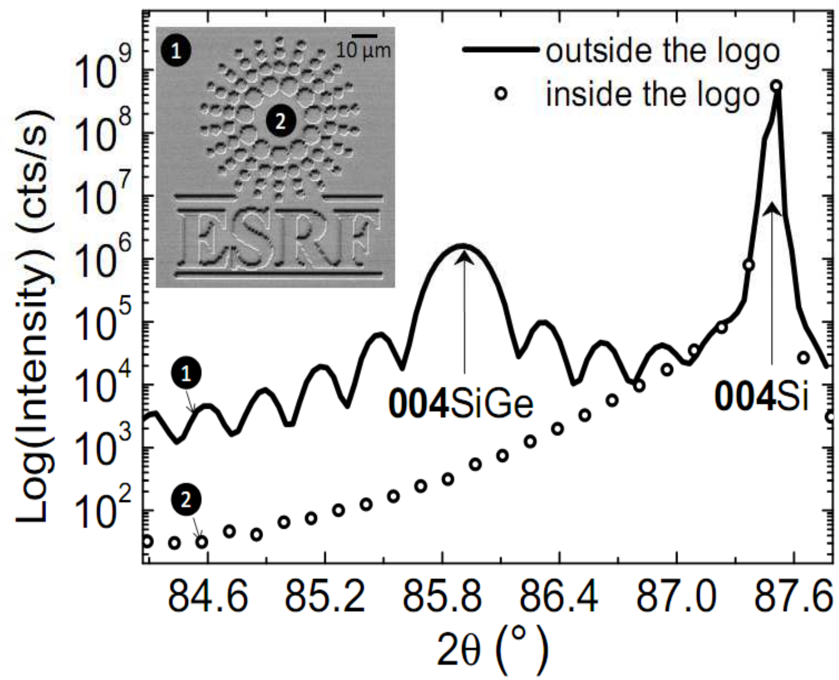
Resolution limited by beam spot
Sub 100 nm are possible



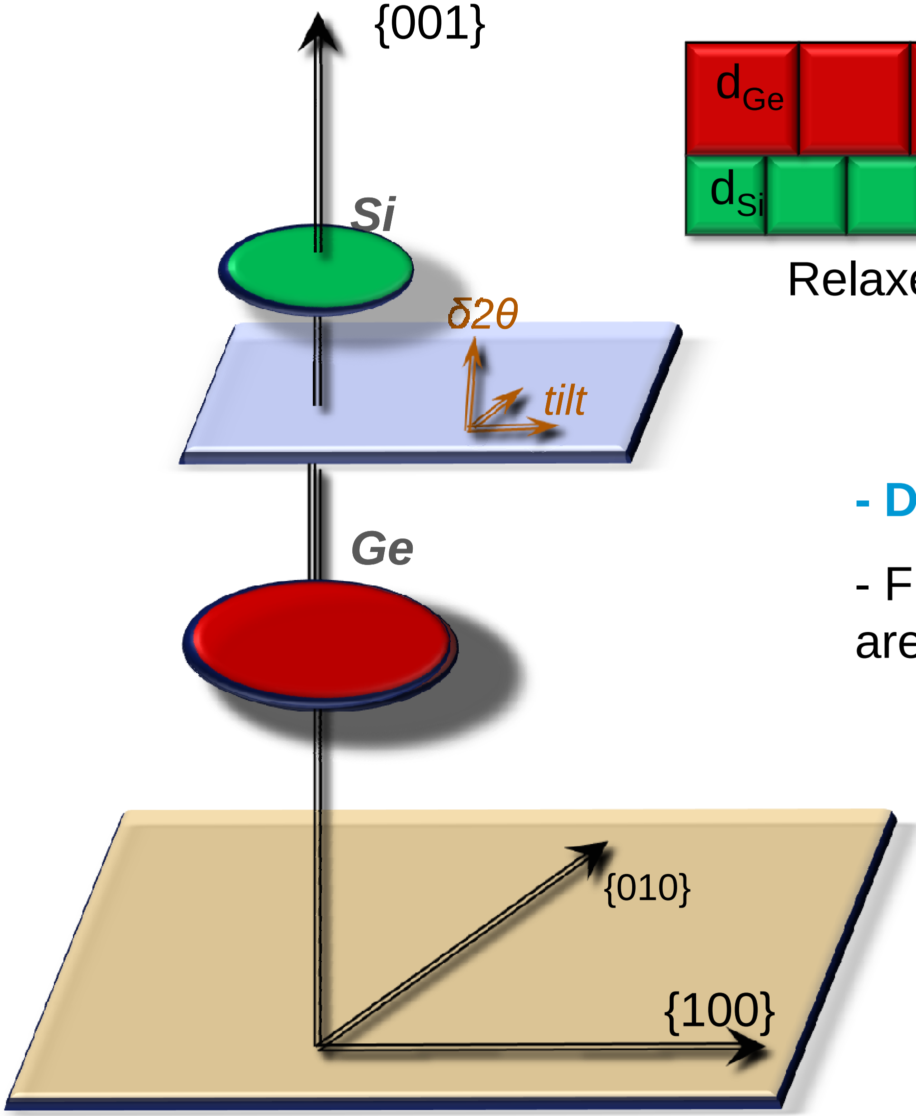
STRUCTURED THIN FILM: TYPICAL FOR A DEVICE

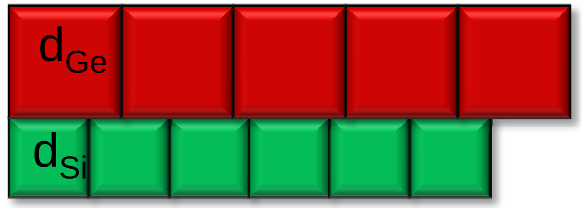
o $Si_{0.8}Ge_{0.2}$ layer grown on a Si (001) substrate patterned by focused ion beam (FIB) to draw the ESRF logo.



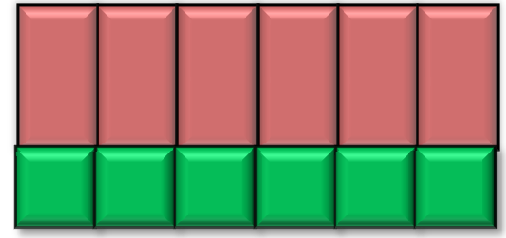


STRAIN AND ORIENTATION





Relaxed Film

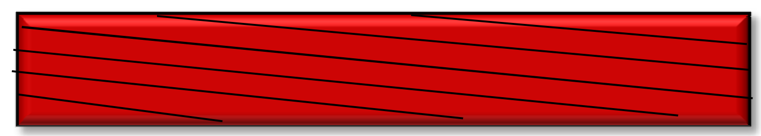


Strained Film

- Determine the degree of strain:

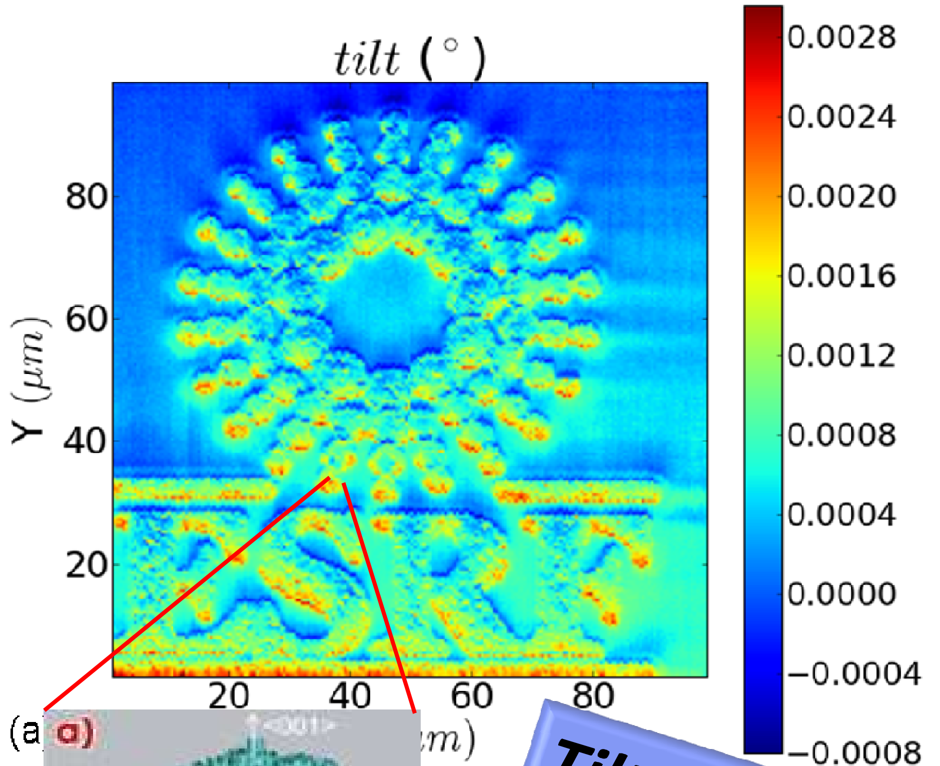
- Fully strained: the lattice parameters of the film are strained to fit to the substrate

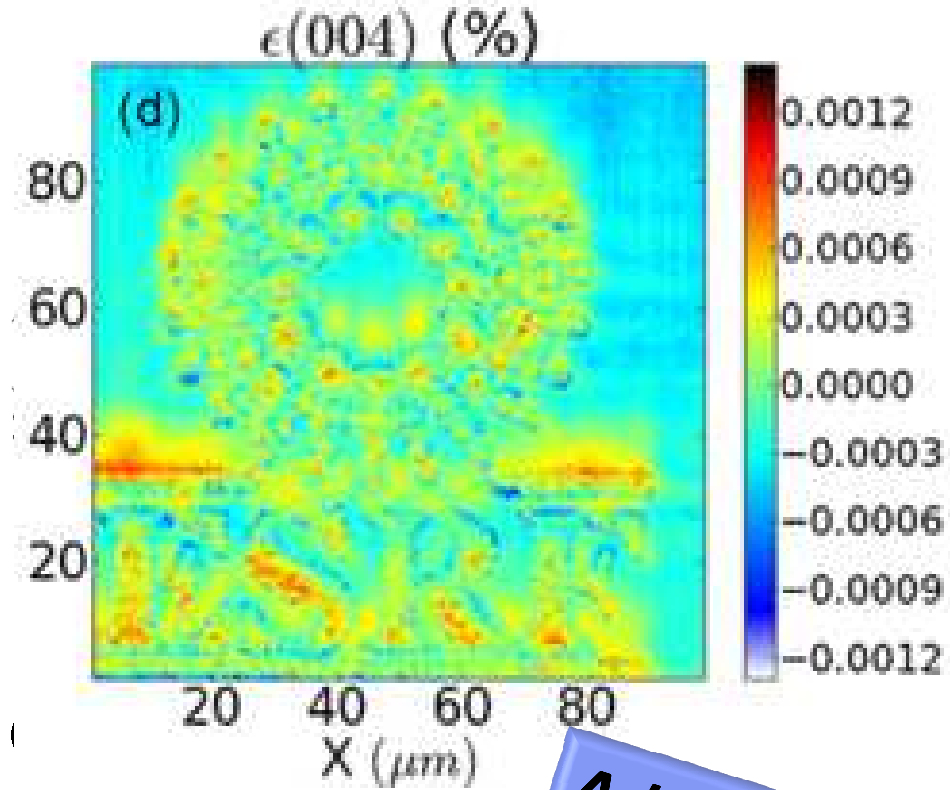
- Tilts appears as perpendicular shifts



o The Bragg peak position in reciprocal space is essential for retrieving all information related to strain and/or tilts in the structure.

Full treatment allows to image lattice tilts and strain





Tilt < 10^{-3} °

Δd/d < 10^{-5}

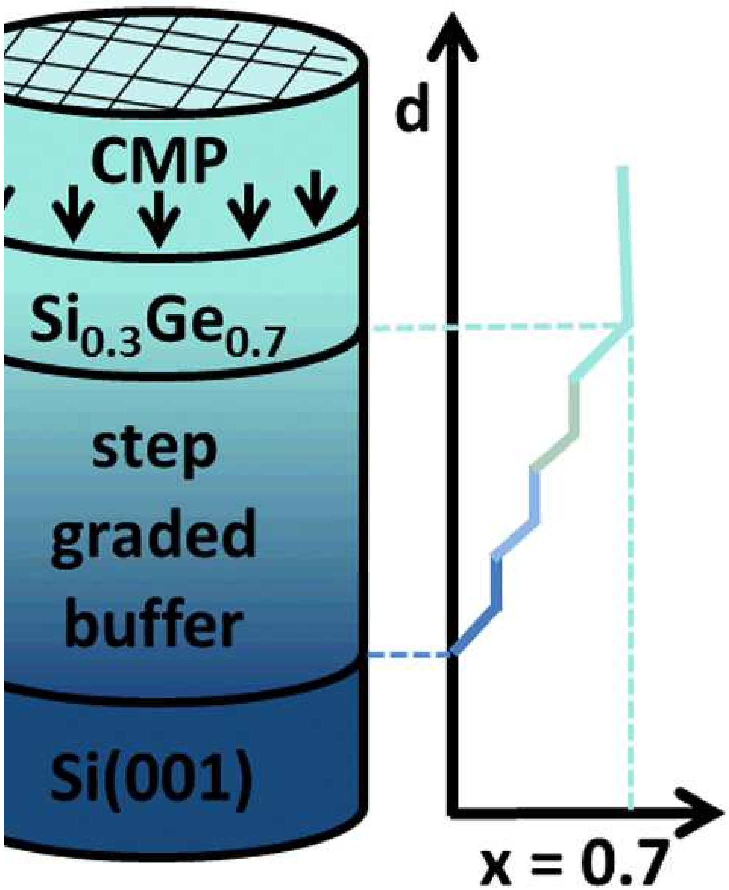
3D Reciprocal Map in each pixel

Relative strain levels of Δa/a 10^{-6} can trace a landscape (= we can "see" a ΔT of a few K potentially in buried systems working devices)

Spatial resolution:100 nm

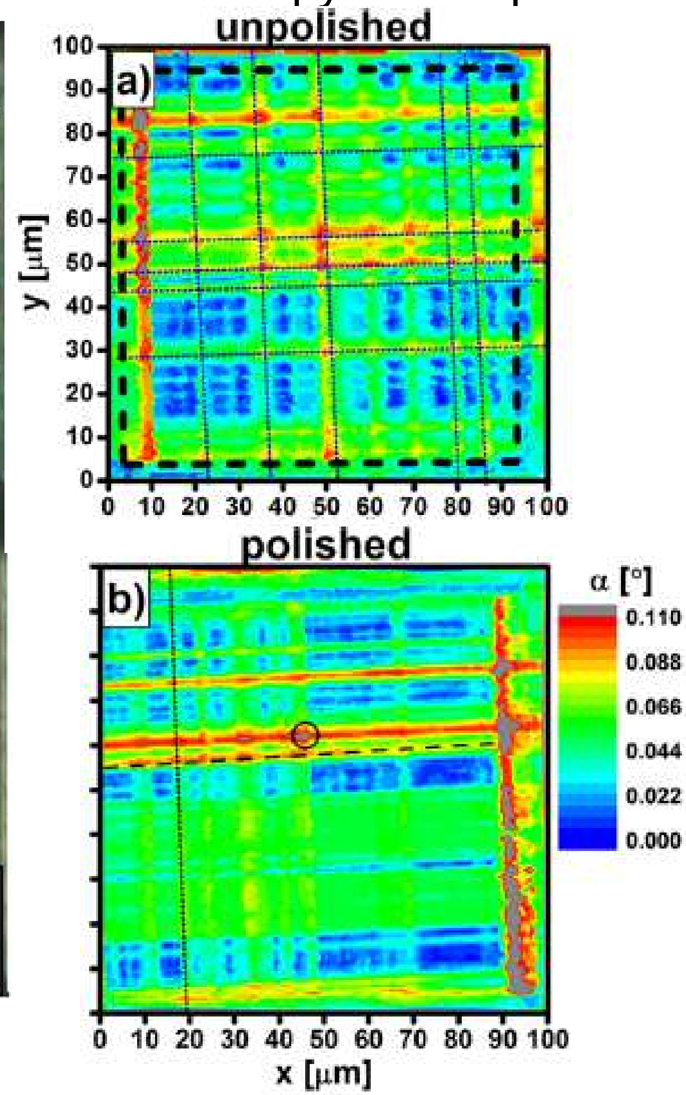
G. A. Chahine, M.-I. Richard, R. A. Homs-Regojo et al., *J. Appl. Cryst.* (2014)

DIFFRACTION IMAGING: CROSS HATCHES IN GRADED BUFFERS



Light interference microscopy

Scanning x-ray diffraction microscopy: Tilt maps



Zöllner, Richard, Chahine: Appl. Mat.&Interf. 2015

Surface roughness

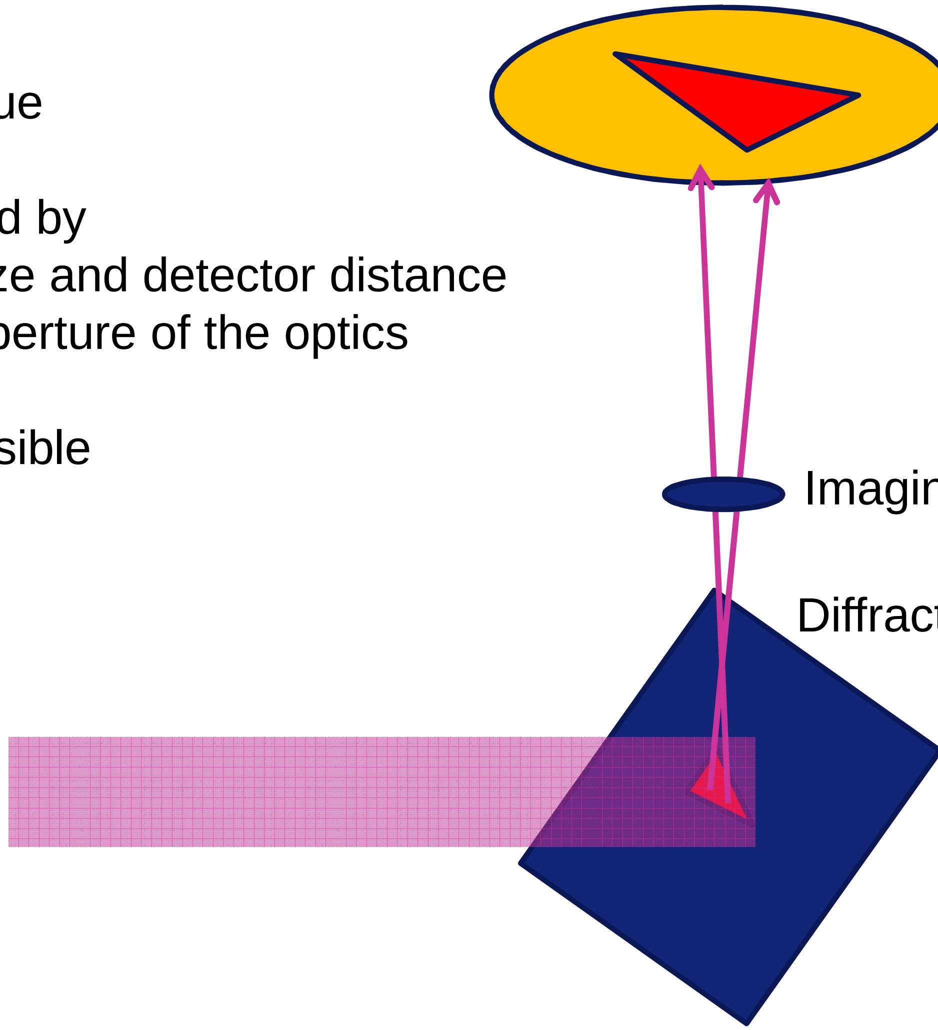
Lattice undulations

DIFFRACTION IMAGING: FULL FIELD

Full field technique

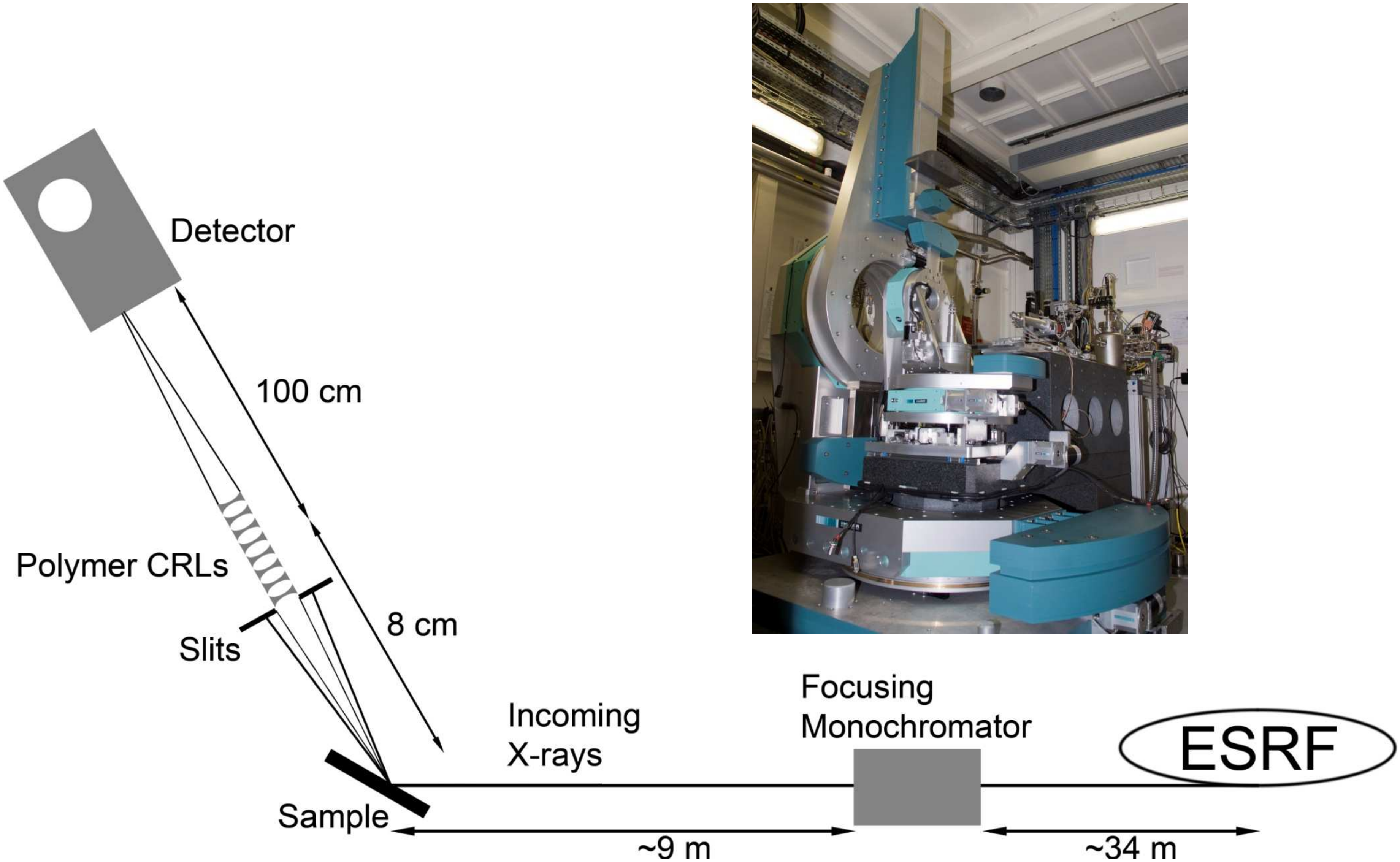
Resolution limited by
Detector pixel size and detector distance
and numerical aperture of the optics

Sub 100 nm possible

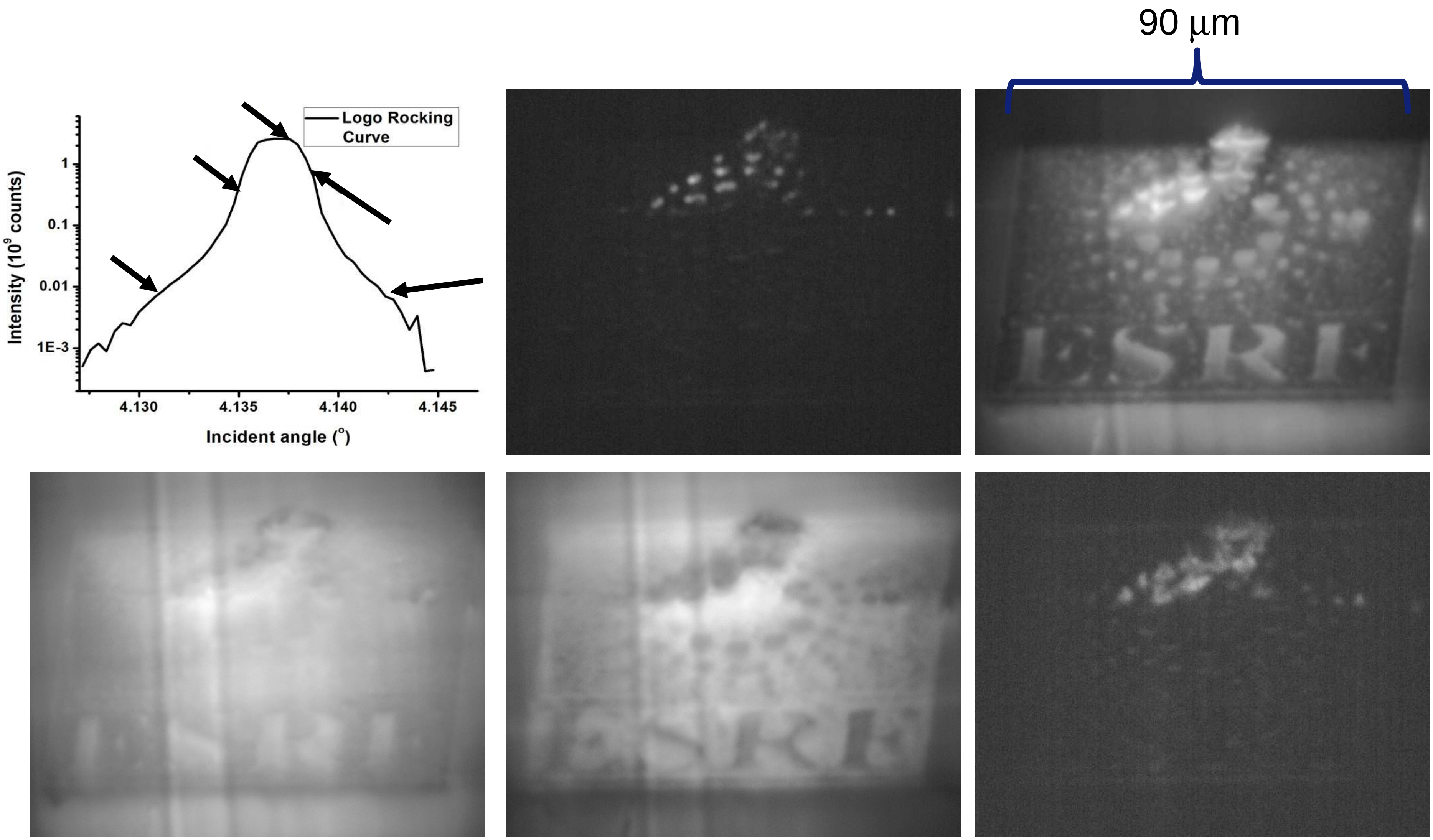


Real potential needs long detector arms

SETUP

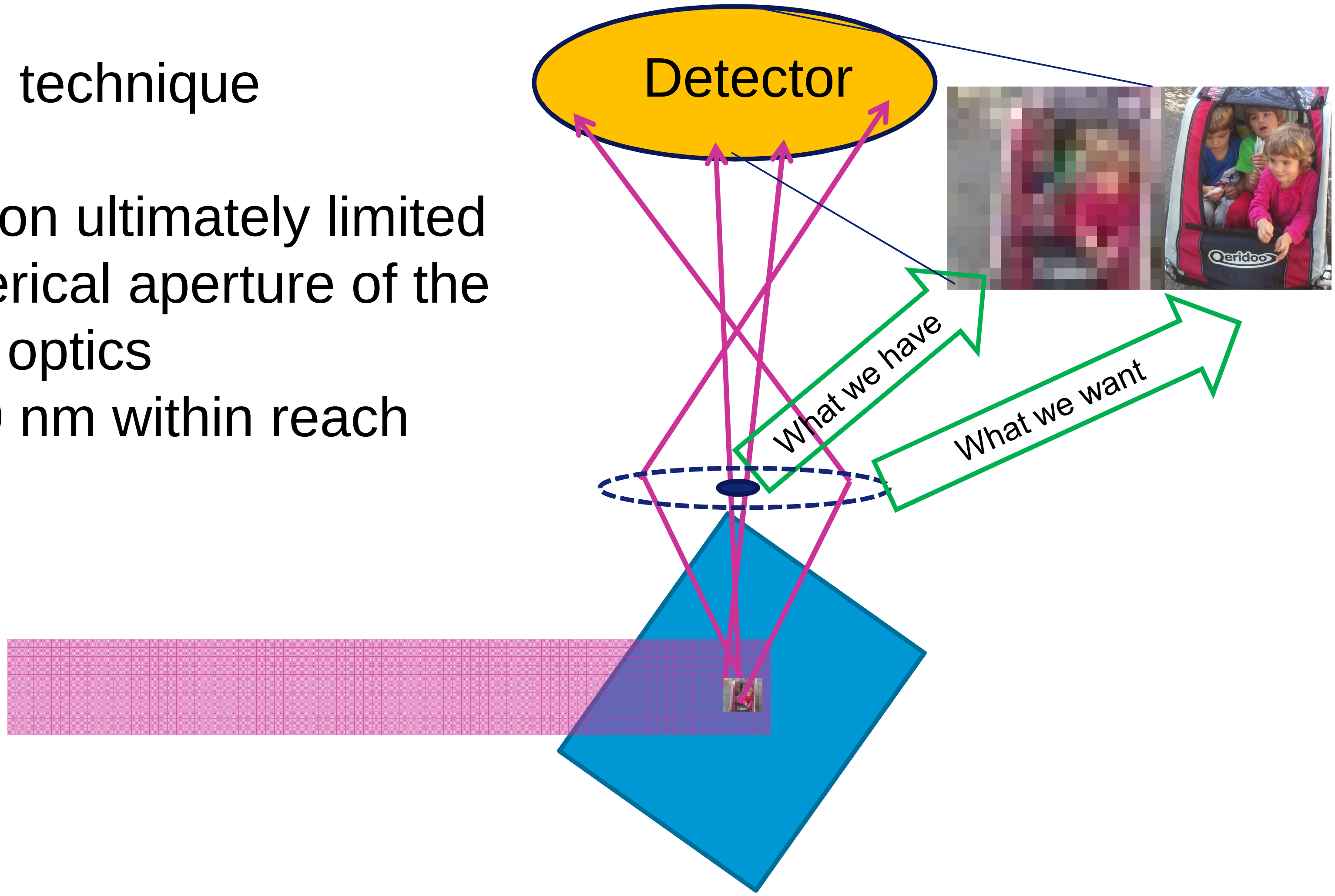

Detector
100 cm
Polymer CRLs
Slits
8 cm
Incoming
X-rays
Focusing
Monochromator
ESRF
Sample
~9 m
~34 m

DIFFRACTION IMAGING



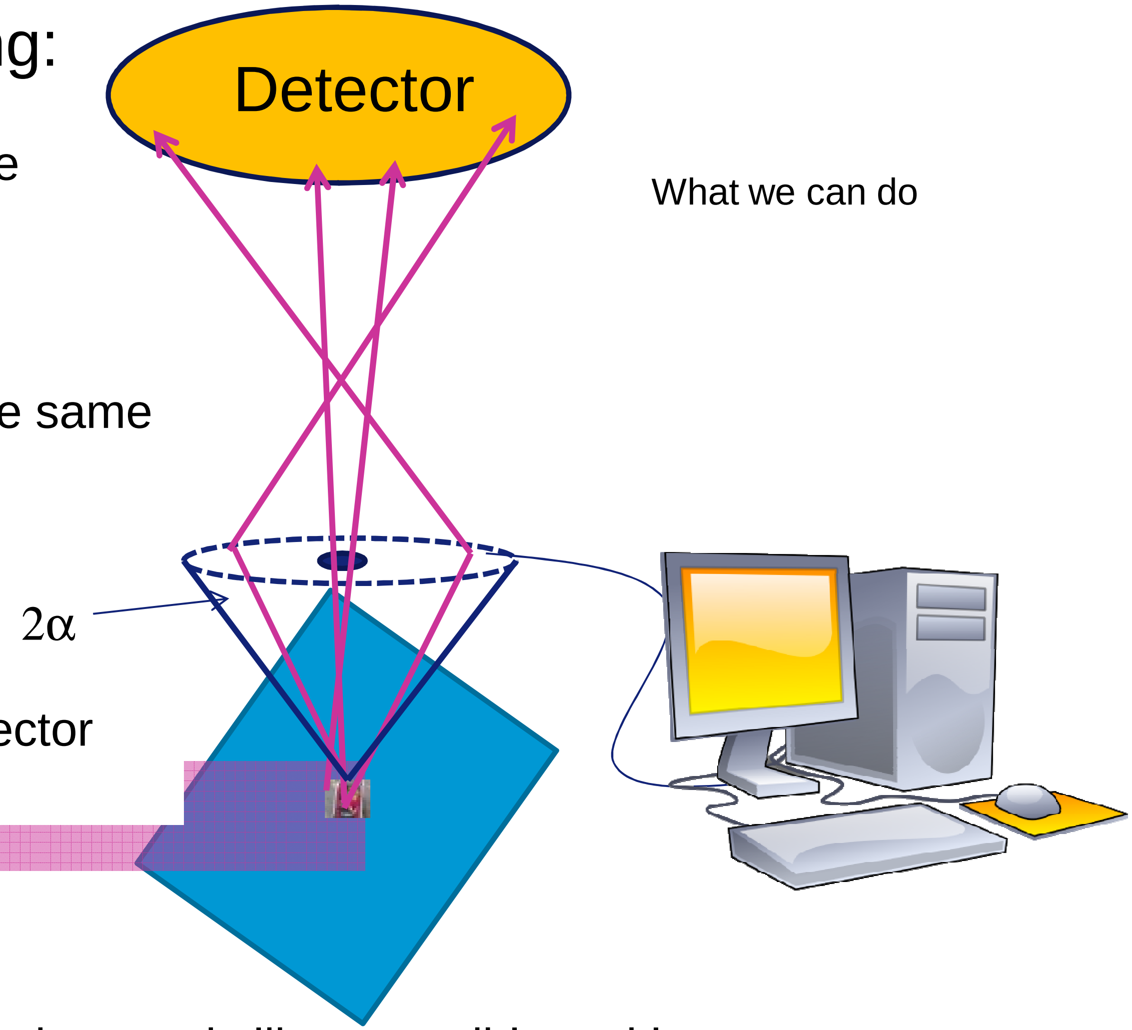
Full field technique

Resolution ultimately limited by numerical aperture of the imaging optics
Sub 100 nm within reach



Coherent Diffraction Imaging:

Theory of optics is very well known.
-> Measure all emitted rays from the sample and replace the lens by a computer to calculate the image



What we can do

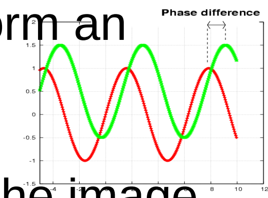
The physics of resolution remains the same

$$\Delta \mathbf{x} = \frac{1.22 * \lambda}{2 * n * \sin\alpha}$$

Instead of the lens we need a detector with a large opening angle.

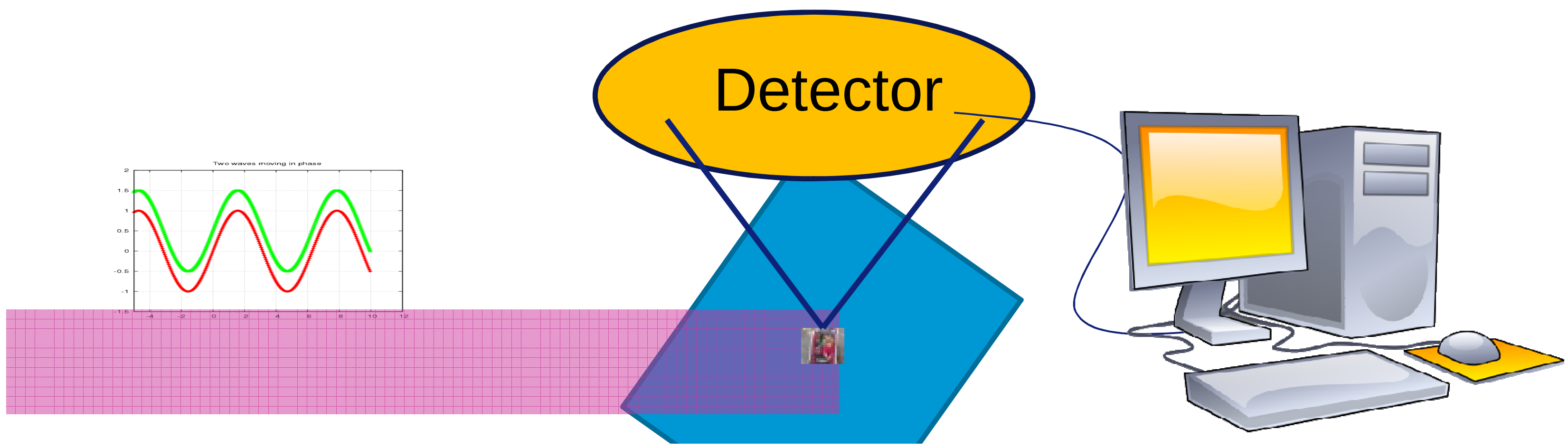
We need perfect detectors: A noisy detector is like a sandblasted lens.
And we need single photon detection at near 100% efficiency

Another Problem : Waves have amplitudes and phases: they interfere to form an image;



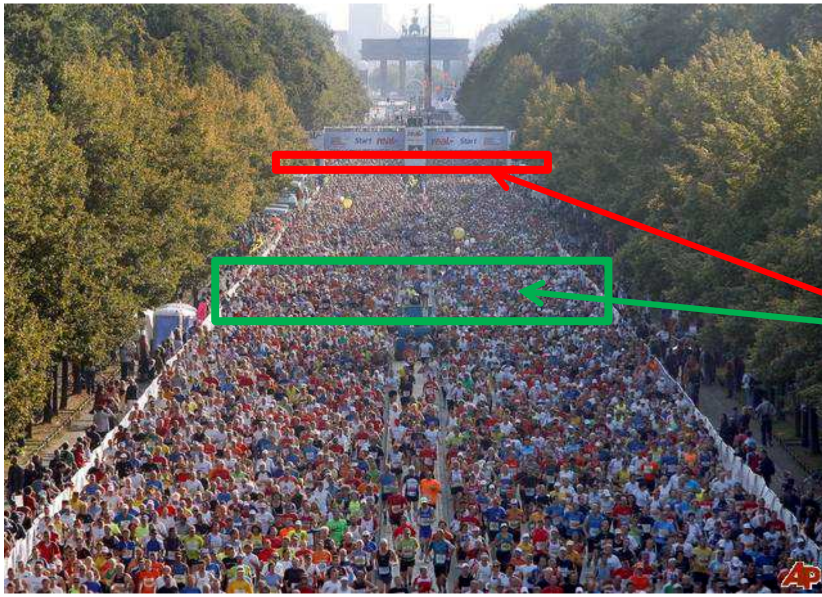
Refraction (as in a real lens) preserves the phase information, crucial for the image
Detection measures only the intensity (number of photons) and not their phase

From a quantum mechanical point of view, refraction (preserves Δp) by a lens cannot be replaced by detection (destroys Δp): Equivalence between Abbé and Heisenberg.

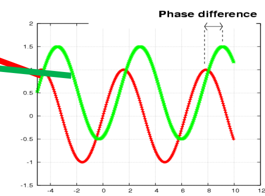


The loss of phase information cannot be recovered by a computer.
We have thus to know the phase beforehand.
The sample has to be illuminated with photons that are all in phase with each other
This is the definition of a coherent beam

PHASE OF PHOTONS AND COHERENT BEAMS



Marathon:
photons=runners
Phase depends on the exact departure time of the runners



We have to select one single phase. The rest of the runners cannot be used for the experiment.

We select the “coherent fraction” (Runners that all have roughly the same departure time).
ESRF coherent fraction: <1%

Flux available for “normal” light imaging and coherent diffraction x-ray imaging:
5 Watt LED: 10^{19} photons/second (incoherent but with optics we can use them all)

ESRF coherent flux: 10^{11} photons/second (@ 8keV) -> 10^{19} photons in 1 year

X-ray tube coh. flux: few photons/second,10^{19} photons in 10^{10} years (the age of this world)

COHERENT DIFFRACTION TECHNIQUES

Use of focused beam/ scanning technique.

Resolution below beam spot size possible by reconstruction of scattering pattern

limits imposed by coherent flux vs. stability of the sample and sample/ beam stability in general and detector surface (numerical aperture)

Resolution below 10 nm possible