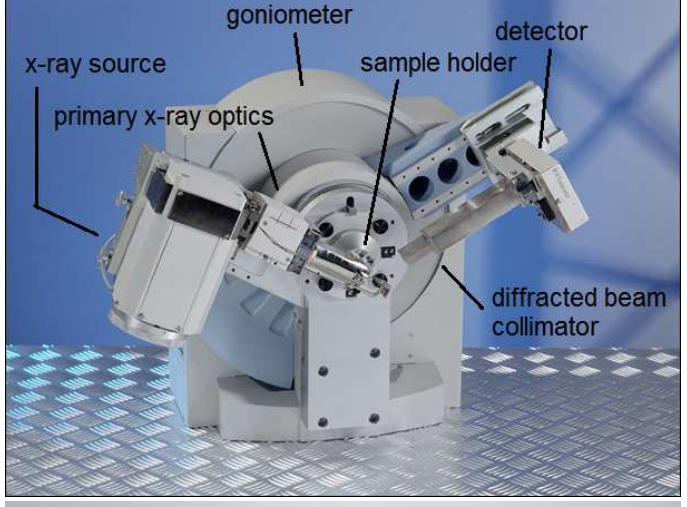
Small-angle scattering camera types

- Diffractometer
  - Point-by-point measurement in $q \rightarrow$ long measurement time
  - Well-defined angular resolution
- Line-focus (Kratky) camera
  - high intensity
  - instrumental smearing of the scattering curve
- Pinhole camera
  - low distortion
  - easily tunable
  - simple principle
- ...



Characteristic parameters

Final goal: measure weakly scattering samples in short times

X-ray beam

- High flux
- Highly parallel (divergence $\ll 1$ mrad)
- Monochromatic ($\Delta\lambda/\lambda$)

Angular resolution

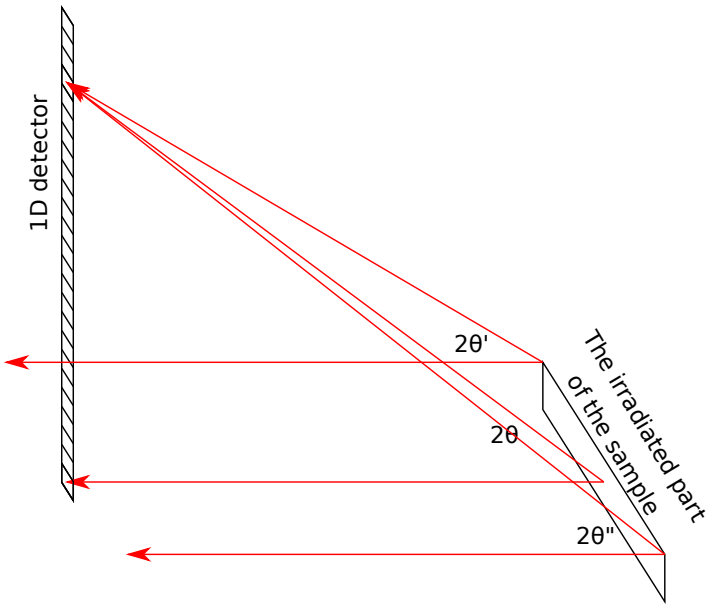
- Sample-to-detector distance
- Shape and size of the detector area
- Pixel size

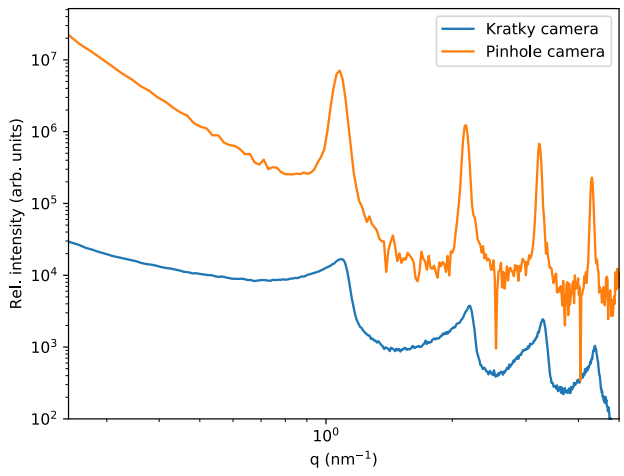
Noise

- Electronic noise from the detector
- Parasitic scattering (comes from the X-ray source, scattered, but not by the sample)
- External radiation

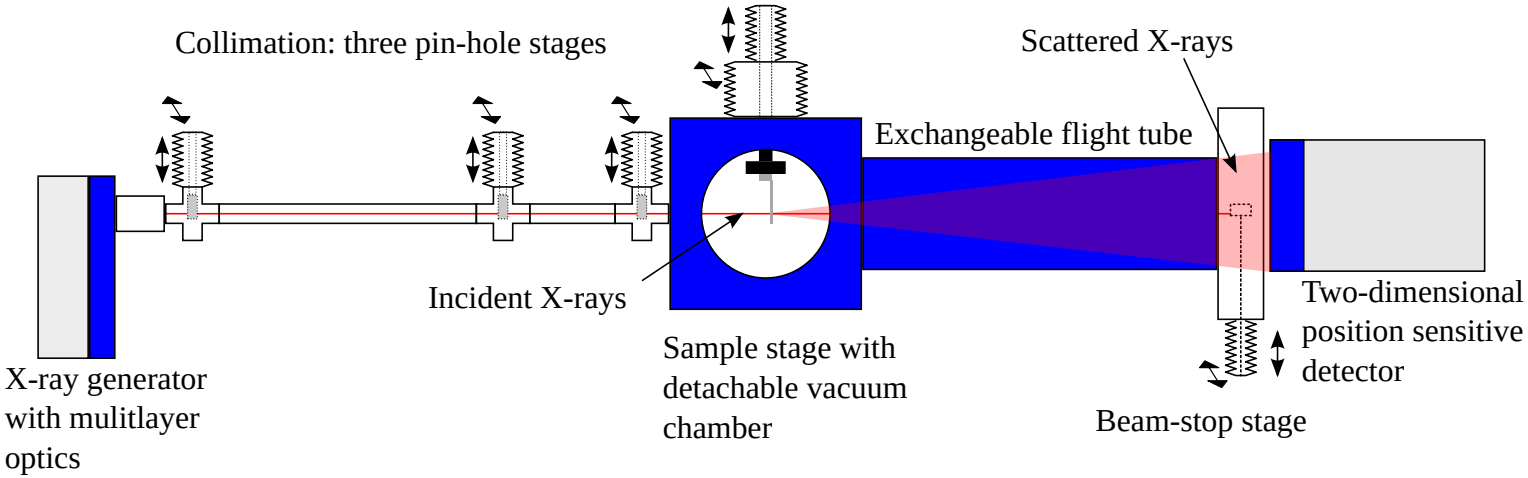
Line-focus Kratky camera

- Compact, small footprint
- 1D position sensitive detector
- Fixed sample-to-detector distance
- No moving parts
- Kratky-type collimation block
- Typical beam size: 2-3 cm $\times$ <1 mm
- High intensity on the sample but smearing on the scattering curve
- *Post hoc* numeric correction needed





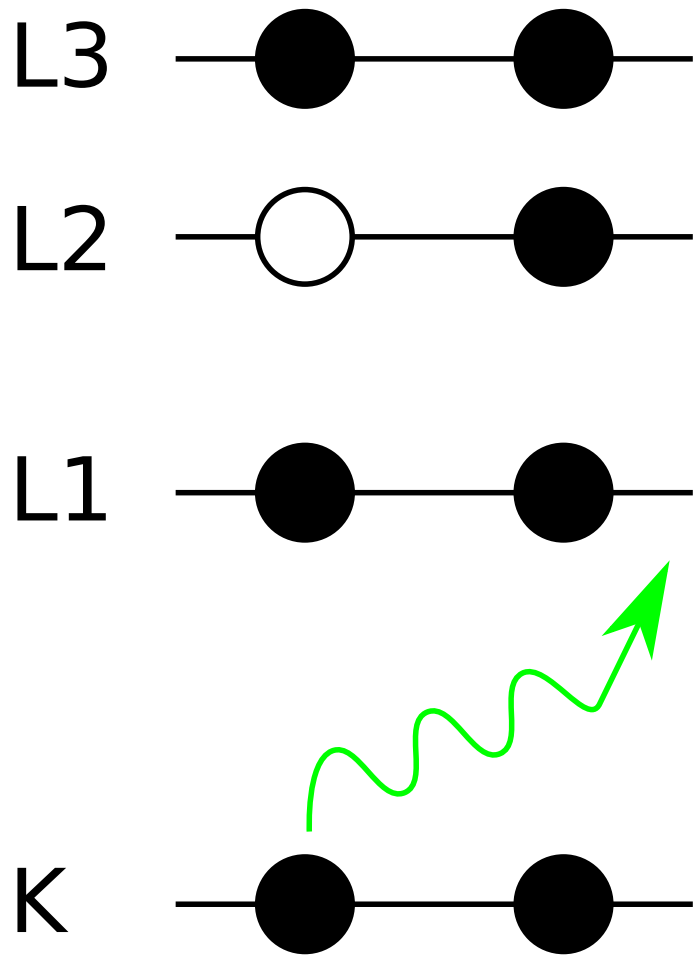
Point focus (pinhole) camera



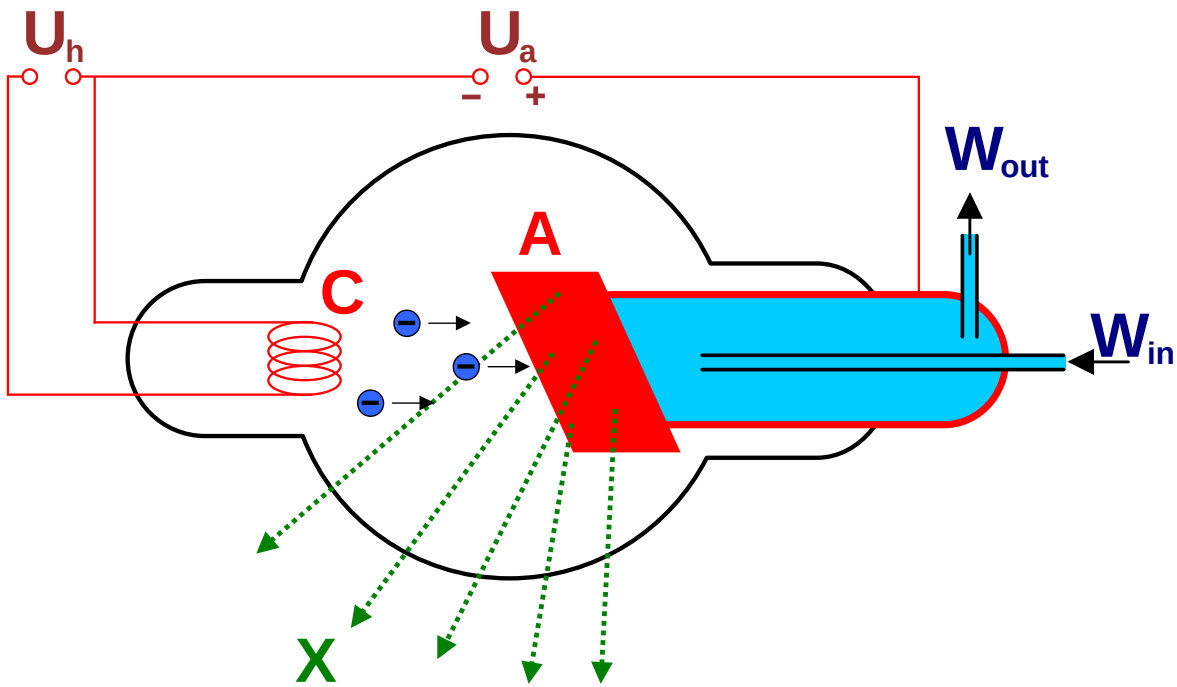
- Small beam size (<1 mm), low divergence
- Exchangeable sample-to-detector distance: tuning of the angular range
- Negligible smearing, typically no correction needed
- Easy to set up and align (compared to the Kratky block)
- Larger footprint but more possibilities
- Not (just) a “routine” instrument

Characteristic X-radiation

- Excitation of the electronic shell with high-energy particles
- An electron is freed and exits
- The remaining hole is filled by an electron from an outer shell
- The binding energy difference is ejected in the form of a photon
- Characteristic radiation: the energy of the photon ($h\nu = hc/\lambda$) is the binding energy difference
- The energy of the incoming particle (E_{in}) must be larger than the binding energy of the shell
- $\Rightarrow h\nu < E_{\text{in}}$

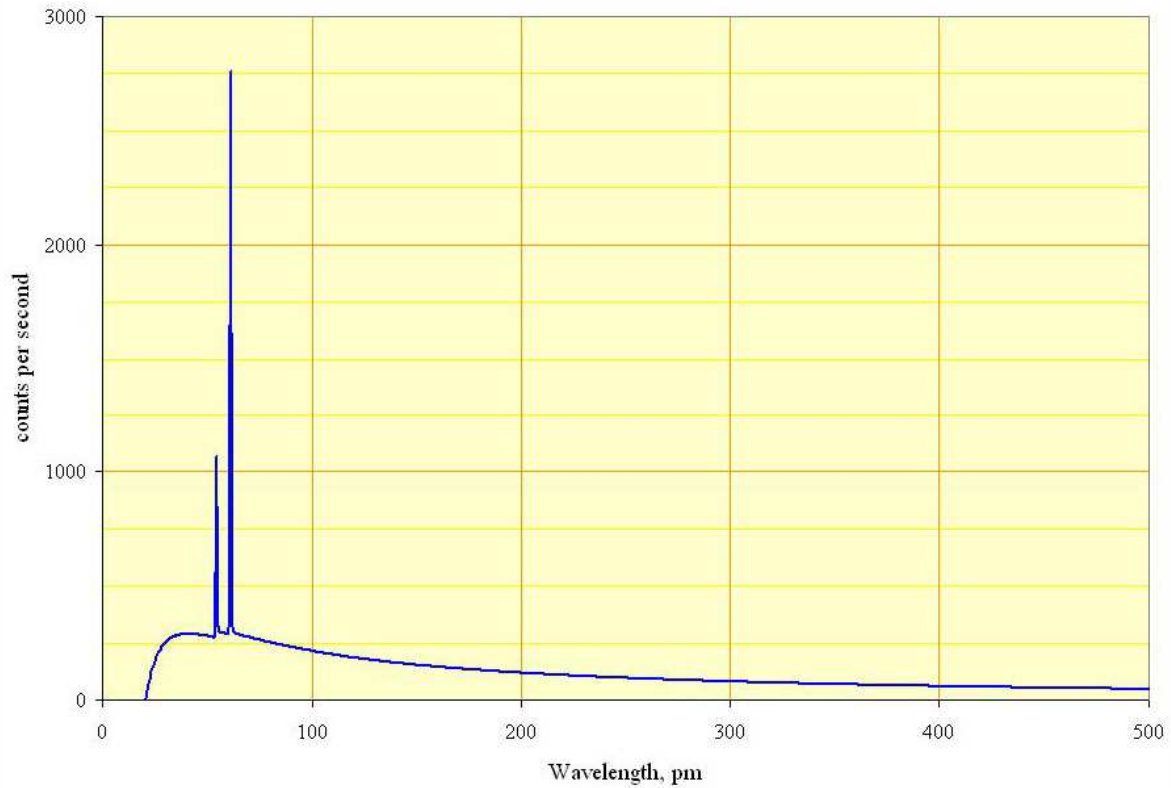


How an X-ray tube works?



- Cathode (C): heated filament, electrons exit due to the thermionic effect
- U_a: accelerating voltage (40-100 kV): electrons accelerate towards the anode
- Anode (A): the incident electrons produce characteristic radiation (X)
- High heat load on the anode: cooling is needed! (W_{in}, W_{out})

Wavelength spectrum of the X-ray tube



- Peaks: characteristic radiation
- Continuous baseline: “Bremsstrahlung”

Bremsstrahlung

- An accelerating charged particle produces electromagnetic radiation
- The total emitted power if the acceleration is parallel to the velocity:

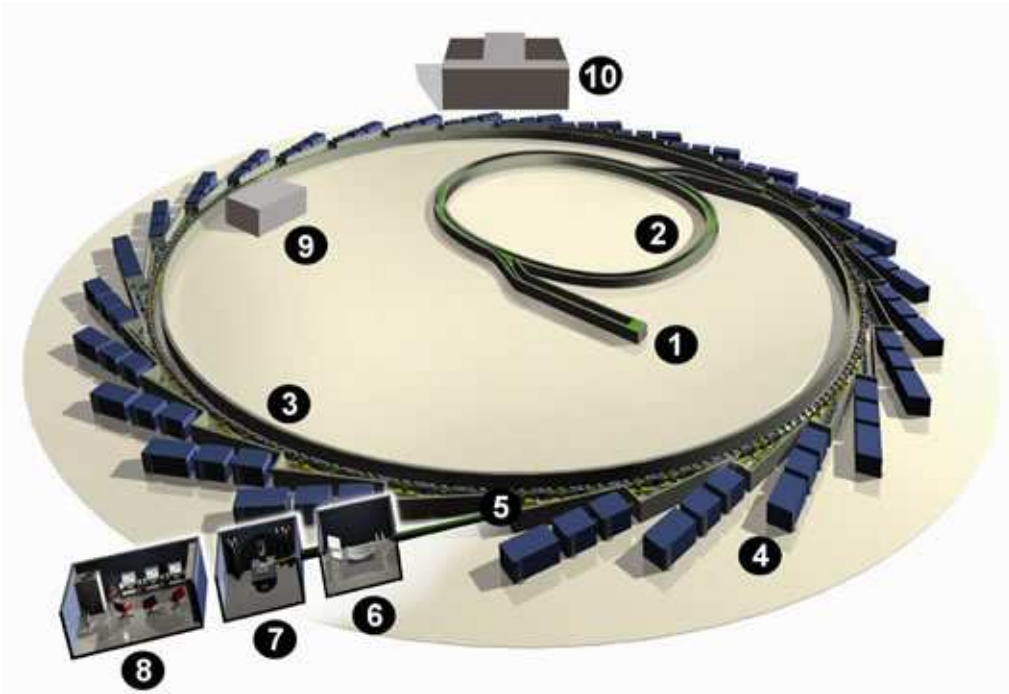
$$P_{a\parallel v} = \frac{q^2 a^2 \gamma^6}{6\pi\varepsilon_0 c^3}; \qquad \vec{\beta} = \vec{v}/c; \qquad \gamma = \frac{1}{\sqrt{1-\beta^2}}$$

- Electrons decelerate in the anode $\Rightarrow$ radiation!
- Charged particles on a circular orbit: the velocity (as a vector) changes $\Rightarrow$ centripetal acceleration
- $\Rightarrow$ orbiting charged particle emits electromagnetic radiation
- Where do we encounter orbiting charged particles?

Synchrotron radiation

Electromagnetic radiation detected in the tangential direction of charged particles orbiting on a circular path

1. Electron gun and linear accelerator (linac)
2. Pre-accelerator ring (booster)
3. Storage ring
4. Experiment hall
5. Beamline
6. Optics hutch: mirrors, monochromators etc.
7. Experiment hutch
8. Experiment control room
9. Machine control room
10. Main building



Storage ring

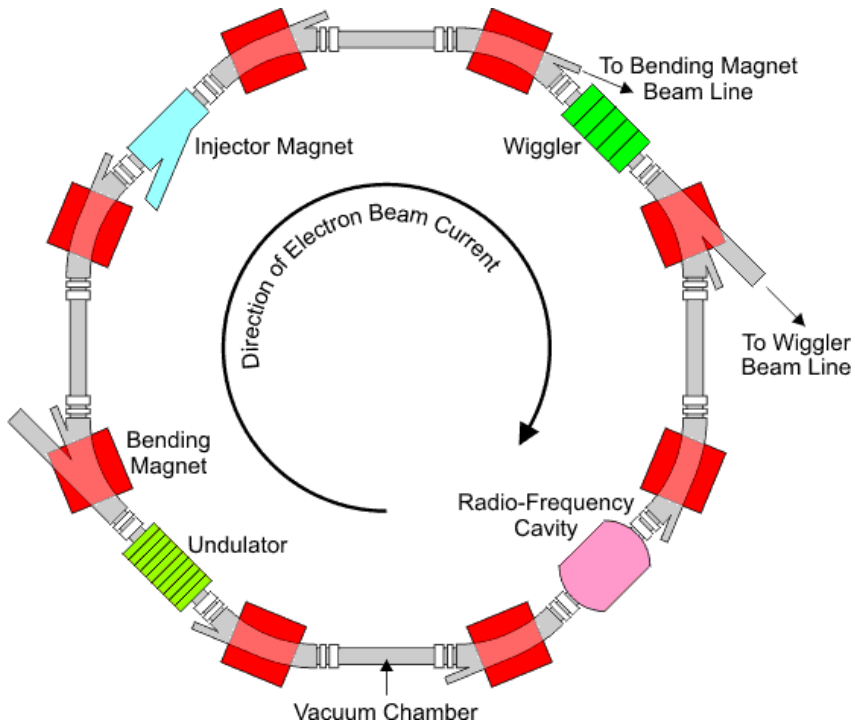
Vacuum chamber: $< 10^{-8}$ mbar

RF cavity: feeding back the emitted energy

Injector magnet: replacement of the absorbed electrons

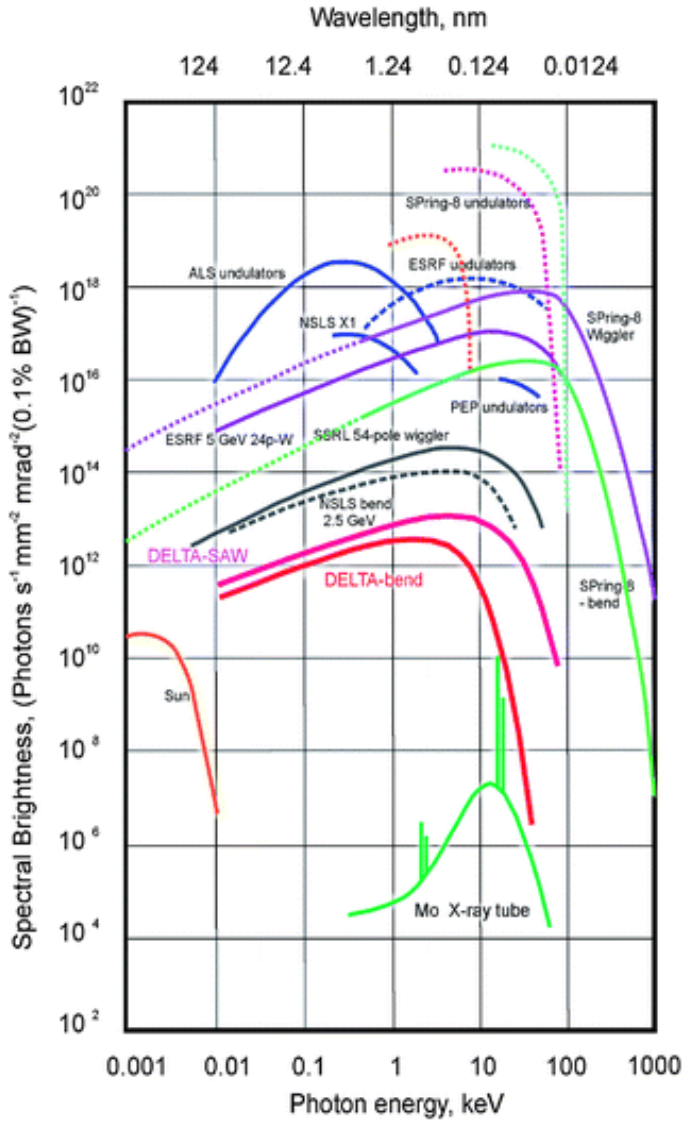
Bending magnets: Circular orbit, producing radiation

Wigglers and undulators: periodic magnets, producing high intensity radiation



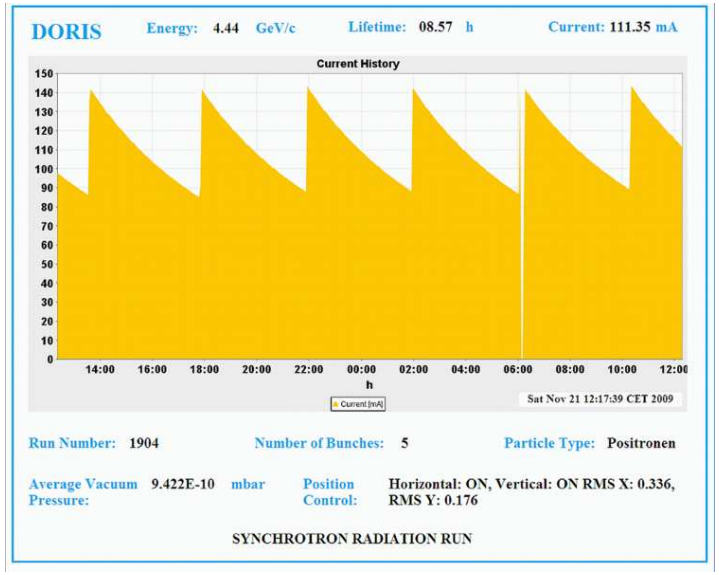
Radiation production in a synchrotron storage ring

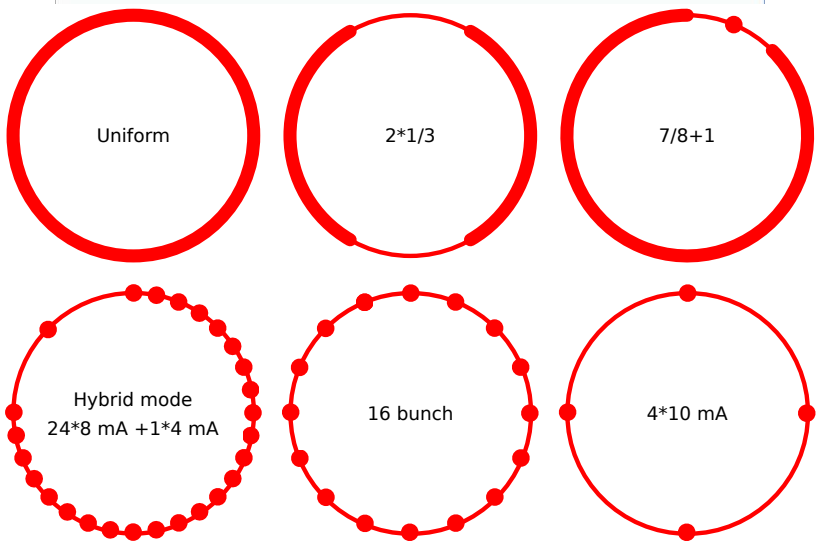
- Charged praticles (typically electrons) orbit in bunches: *synchrotrons are pulsed sources*
- Feeding back lost energy and compacting bunches: RF cavities/resonators
- Bending magnets: Lorentz-force
- Wiggler: many bending magnets after each other
- Undulator: constructive interference of radiation produced in subsequent bends



Time structure of synchrotron radiation

- Intensity is not constant in time
- Long time scale: replacing the absorbed particles
  - Occasionally (4-8 hours): “injection”
  - Continuously: “top-up mode”
- Short time scale: dispersion of the bunches around the orbit
  - Time-resolved experiments
  - Pump-probe techniques





Advantages of synchrotron radiation

High intensity: Short measurement times, SAXS imaging
Pulsed radiation: time-resolved experiments
Tunable wavelength: ASAXS

Beamtime proposal system

1. Submit a beamtime proposal: scientific topic, relevance, why do you need a synchrotron...
2. Proposal gets refereed
3. Successful proposal: beamtime is scheduled
4. The experiments (1-5 days on-site)
5. Back home, evaluate the data (several GBytes)
6. "da capo al fine"

Advantages of a laboratory SAXS instrument

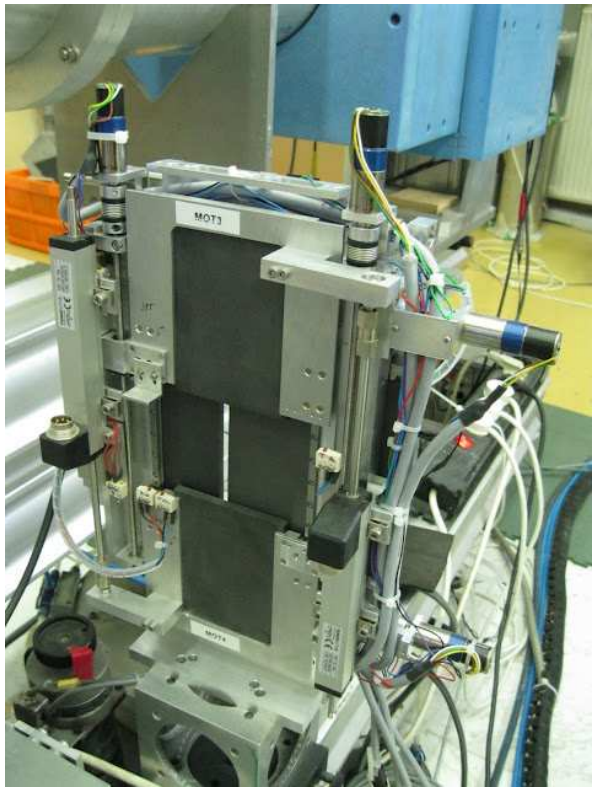
- High availability (it is always there)
- Can be tuned or event rebuilt
- The same camera, just the source is different
- Chemistry lab, sample preparation is near
- Slow measurements, but "infinite" beamtime
- Preparation for synchrotron measurements
  - Better beamtime proposal
  - Preliminary characterization/screening

Collimation: why do we need that?

- The scattering cross-section of X-rays is really small
  - the un-scattered intensity is more than $\times 1000$ as strong!
- The direct (not scatterd) radiation:
  - may damage the detector
  - a global read-out detector cannot detect the weaker scattered radiation
- Differentiation between scattered and non-scattered radiation:
  - Beam stop before the detector
  - Parallel beam with a small cross-section
- Beam shaping:
  - Optical elements: mirrors, capillaries, X-ray lenses
  - "Cutting" with slits

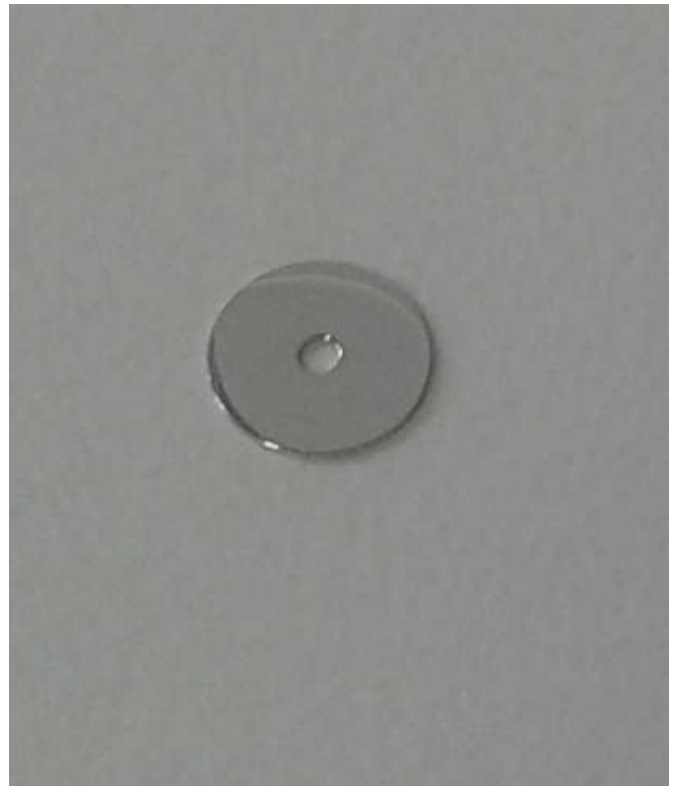
Slits / pinholes

Adjustable slit system



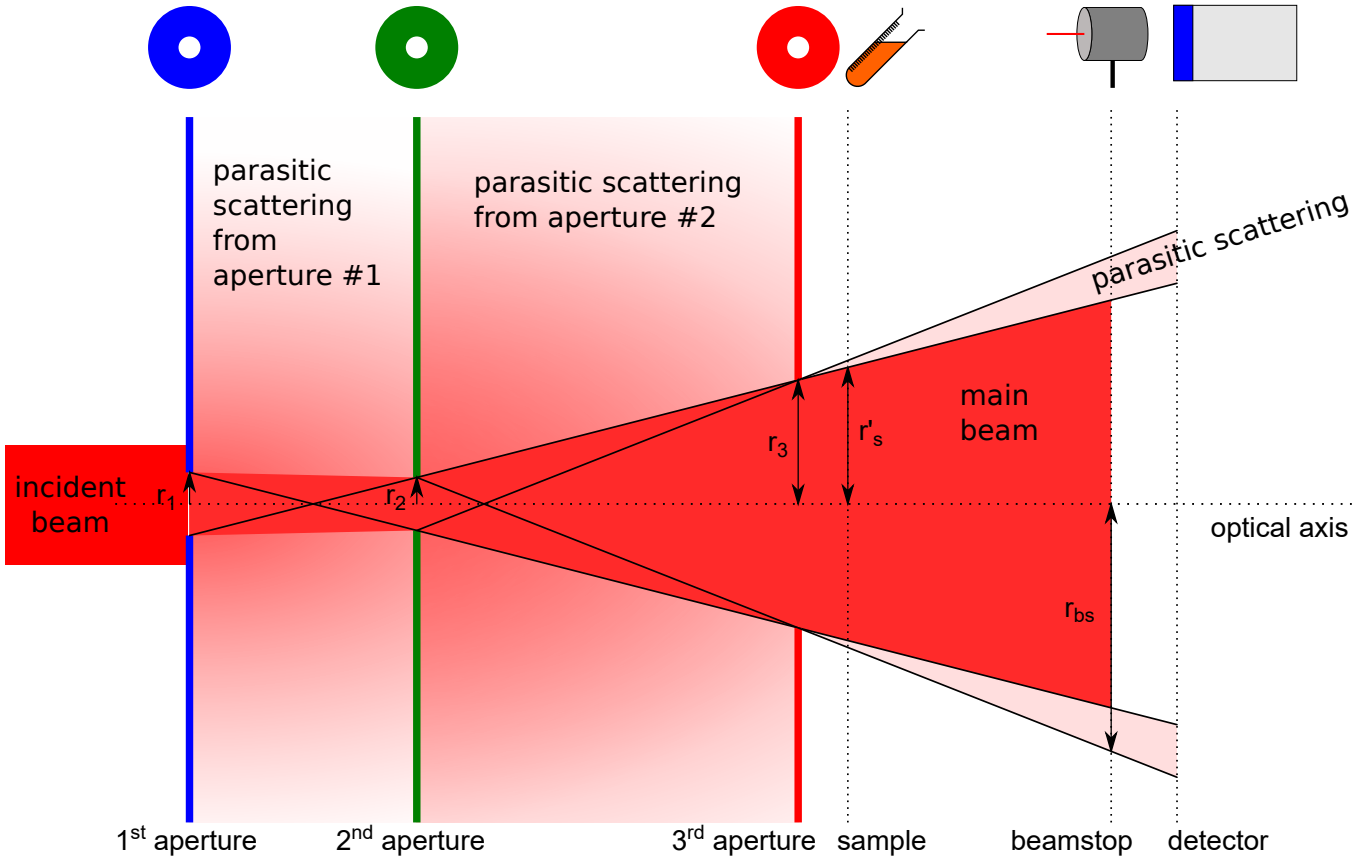
- Aperture changeable in two directions
- Rectangular beam shape

Pinholes



- Simple / cheap
- Round beam shape

Three aperture collimation scheme



Roles of the apertures

1. Limiting the size of the incoming beam
2. Limiting the divergence
3. Covering the parasitic scattering

Sample environment

Sample environment

- Air has small-angle scattering
  - In vacuum
  - Helium, hydrogen ($\Delta\rho$ small)
  - Minimizing the in-air beam path
- *In situ* measurements
  - Temperature
  - Shear
  - Magnetic field
  - Mixing

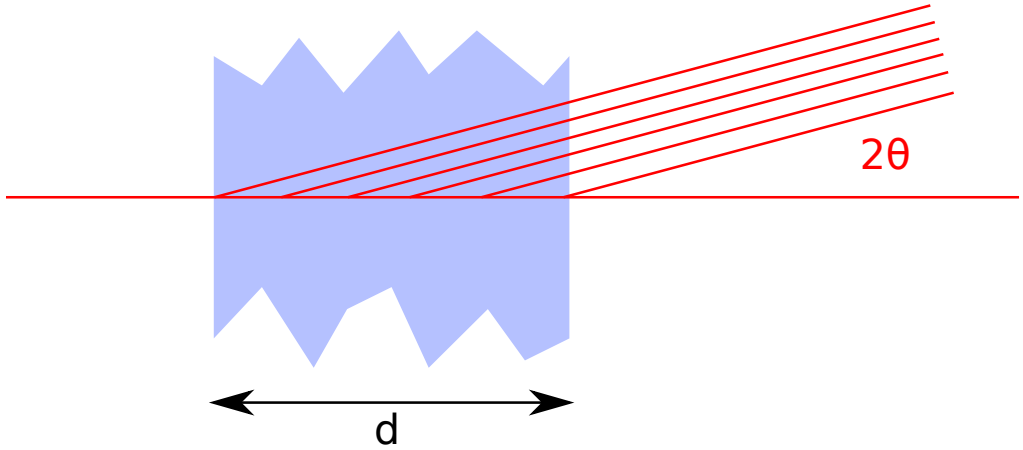
Typical sample requirements

Self-carrying solids: homogeneous platelets, cross-section larger than the beam

Liquids: vacuum-safe sample holders (glass/quartz capillaries) >20 μl

Powders: to be avoided (strong power-law scattering from the surfaces of powder particles)

Ideal sample thickness



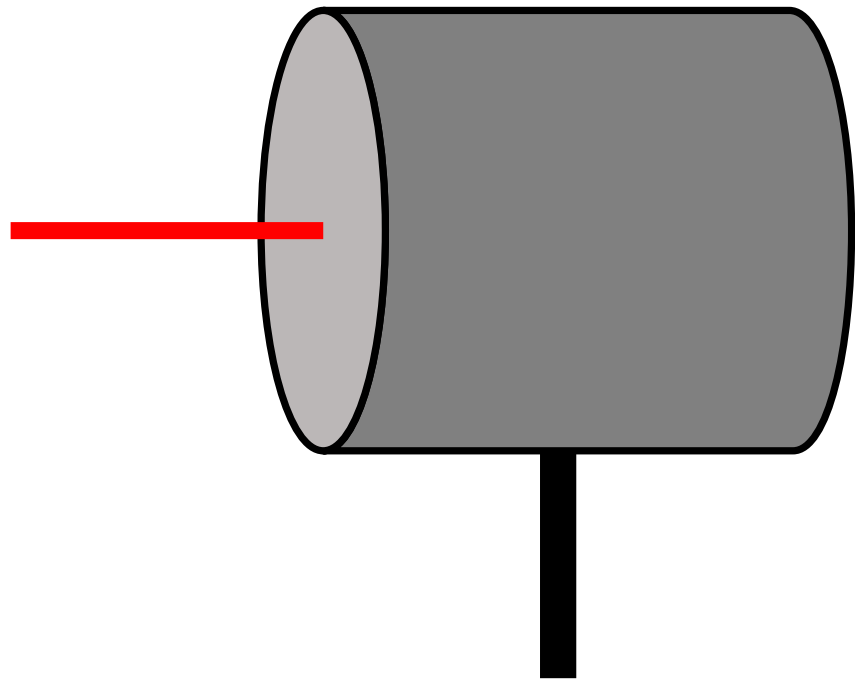
- Scattered and non-scattered rays are partially absorbed by matter
- Lambert-Beer law: $I(d) = I_0 e^{-\mu d} = I_0 T$
- Scattered intensity: $I(q, d) \propto I_0 e^{-\mu d} d$
- Maximizing the scattered intensity: $\frac{\partial I(q,d)}{\partial d} = 0$

$$\begin{aligned} \frac{\partial e^{-\mu d} d}{\partial d} = -e^{-\mu d}\mu d + e^{-\mu d} &= 0 \\ 1 &= \mu d \\ d &= \boxed{1/\mu} \end{aligned}$$

- Water: $1/\mu \approx 1$ mm with Cu Kα radiation (8048 keV, 0.15418 nm)

Beam stop

- Absorbing X-rays not scattered by the sample
- Intensity: non-scattered $\gg$ scattered
- Reasons
  1. Spare the detector from high intensities
  2. Avoid the scattering of matter in the beam after the sample
- Opaque: absorbs all photons
- Semitransparent: beam spot on the detector: easy determination of the center



Detector

- Measuring the angle-dependence of the intensity
- Energy resolution $\leftrightarrow$ **position resolution**
- Requirements:
  - Good position resolution (small pixel size, minimal pixel cross-talk)
  - Linearity (the detected signal is proportional to the incoming intensity)
  - High counting speed (frequency)
  - Low noise
  - No distortions
  - Large sensor shape
- Typical types

  Gas-filled counters: linearity, low noise, energy selectivity, slow, global readout, large pixels, aging

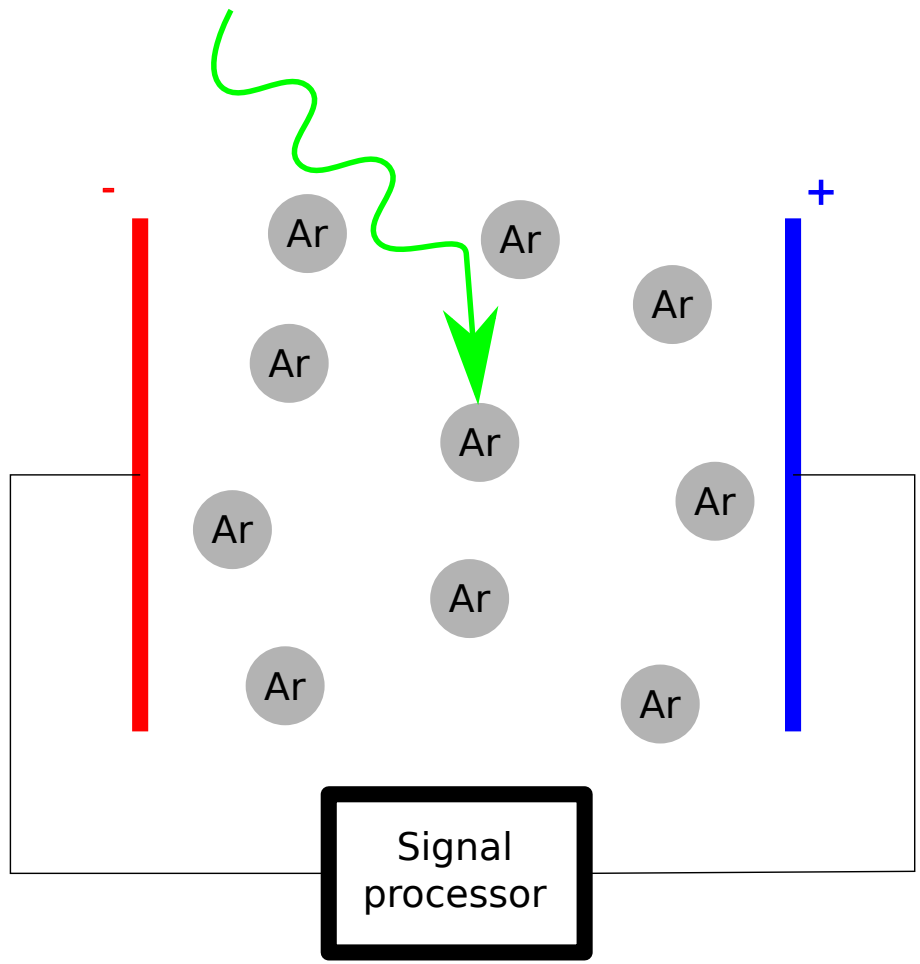
  CCD detectors: fast readout, small pixel size, large electronic noise

  CMOS detectors: fast readout, pratically no electronic noise, expensive

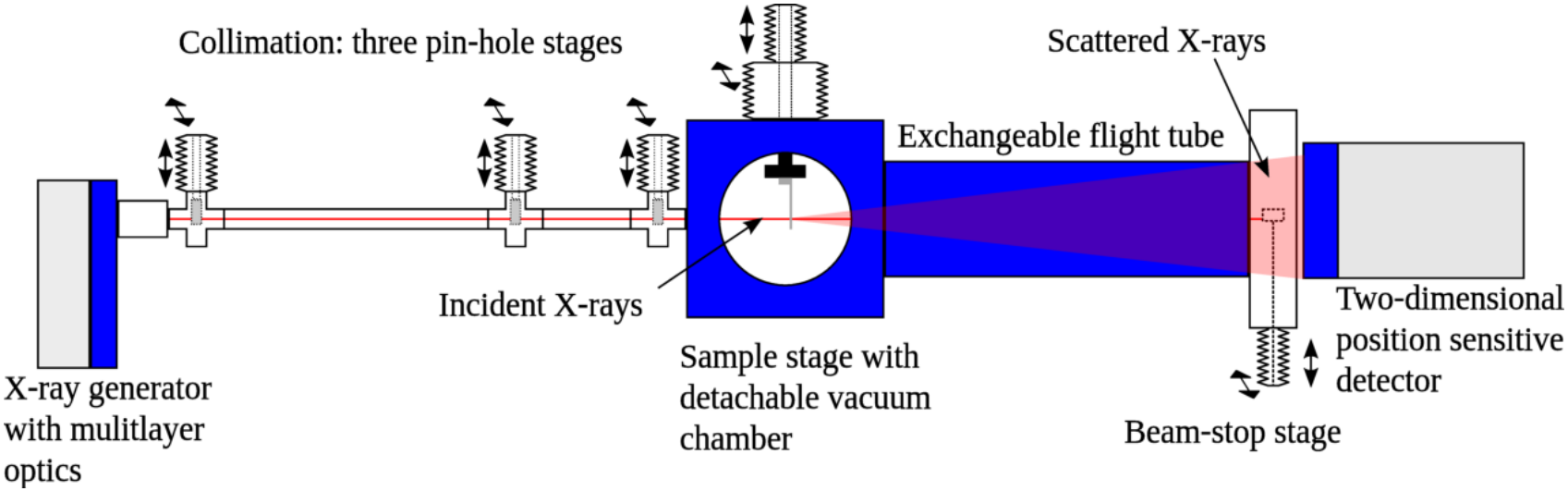
  Image plate: linearity, slow readout, cumbersome handling, aging

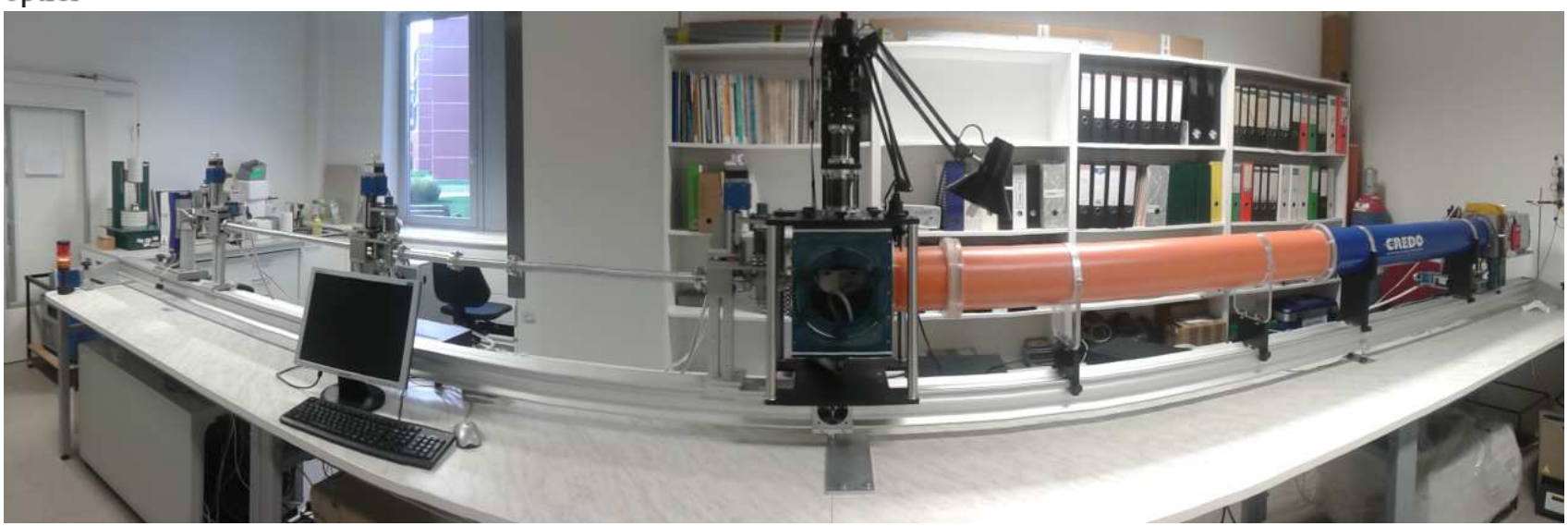
Operation principle of the proportional counter

1. Gas-filled counting chamber
2. Primary ionization by the incoming X-ray photon
3. Ions and electrons accelerate towards the electrodes
4. Secondary ionizations
5. Charge multiplication
6. Ion- and electron avalanches hit the electrodes
7. Recombination, pulse signals
8. Integral pulse height $\propto h\nu$
9. Detection of the pulses by the electronics



CREDO


Collimation: three pin-hole stages
Scattered X-rays
Exchangeable flight tube
Incident X-rays
Two-dimensional position sensitive detector
X-ray generator with mulitlayer optics
Sample stage with detachable vacuum chamber
Beam-stop stage


CREDO

CREDO

- GeniX^{3D} Cu ULD X-ray generator (30 W, $\lambda = 0.154$ nm, divergence <0.4 mrad HW20%M)
- Pilatus-300k hybrid pixel CMOS detector (619 $\times$ 478 pixel, 172 μm, noiseless, independent 20 bit counters for each pixel)
- 3-pinhole collimation
- Motorized sample stage, pinholes, beam stop
- Self-developed, automated data acquisition software
  - Instrument control
  - Carrying out the needed corrections and calibrations automatically

`https://credo.ttk.mta.hu`

B1 („JUSIFA")

- **J**ülich's **U**ser-dedicated **S**catter**i**ng **Fa**cility
- Deutsches Elektronensynchrotron (DESY), Hamburg
- DORIS III storage ring
- dedicated instrument for ASAXS (anomalous SAXS)
- Gabriel MWPC, Pilatus-300k, Pilatus-1M detectors
- *1989 - †2012

Procedure of a "typical" SAXS experiment

1. Turn on the instrument, warm up the X-ray tube (45 minutes)
2. Optimize the geometry (30-45 mins)
   - Sample-to-detector size, beam stop size $\Rightarrow$ smallest attainable q
   - Select pinhole sizes and spacings: no parasitic scattering, highest intensity at the sample
3. Sample preparation, capillary filling (1/2-2 hours)
   - $\approx$ 1 mm borosilicate glass capillaries
   - Sealing: 2-component epoxy resin / melting
4. Preparation measurements: search for sample motor positions, measure transmissions (30-45 mins)
5. Automatic measurement sequence (several hours / overnight)
   - 5.1 Blank measurements (dark current, empty beam)
   - 5.2 Reference samples (q, $d\sigma/d\Omega$)
   - 5.3 Samples
   - 5.4 Repeat...

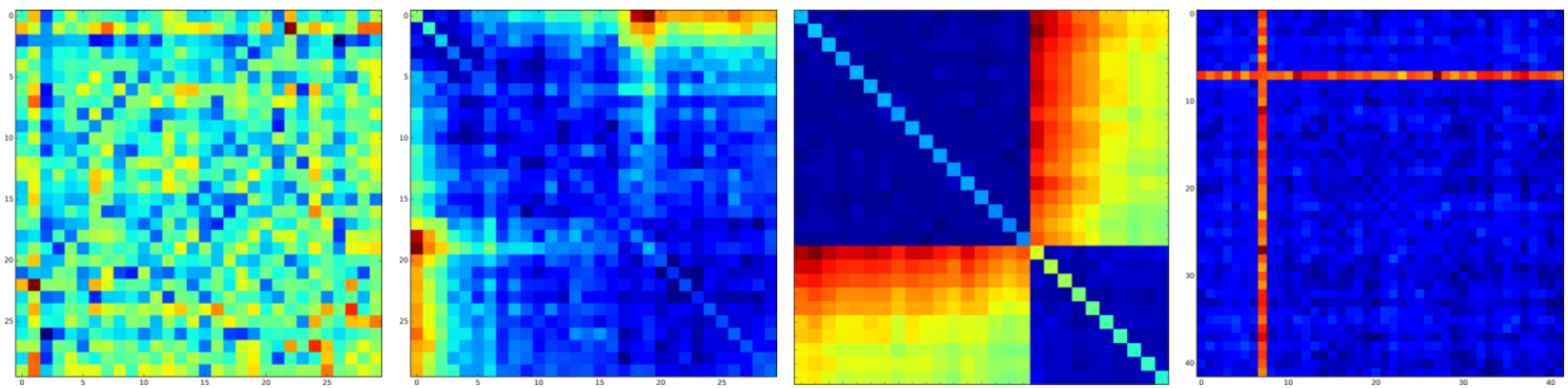
Distribution of the measurement time

It is useful to measure many short exposures instead of one long

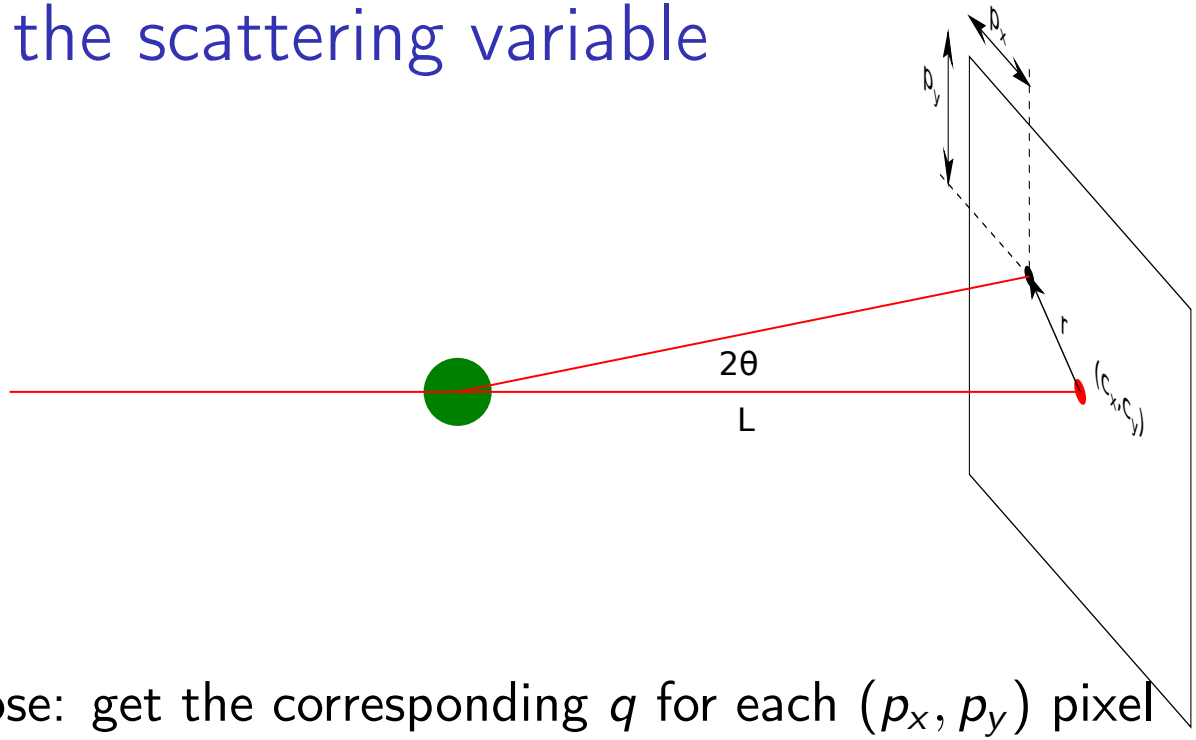
- Time resolution (TRSAXS)
- Frequent re-measuring of references
- Assessment of the stability of the samples and the instrument
- Excluding affected exposures with statistical tests:
  - Difference of the j-th and j'-th scattering curve:

$$\Delta_{jj'} = \begin{cases} \sum_k \left(I_j(q_k) - I_{j'}(q_k)\right)^2 & \text{if} \quad j \neq j' \\ \langle \Delta_{jl} \rangle_{l \neq j} & \text{if} \quad j = j' \end{cases}$$

  - Replacing the diagonal items with row averages: $\Delta_{jj} \rightarrow$ how much does the j-th curve differ from all the others



Calibrating the scattering variable



- Purpose: get the corresponding q for each (p_x, p_y) pixel
- If the direct beam would hit the detector at (c_x, c_y), the pixel size is h and L is the sample-to-detector distance:

$$2\theta = \tan^{-1}\frac{r}{L}; \quad r = h\sqrt{(p_x - c_x)^2 + (p_y - c_y)^2}$$

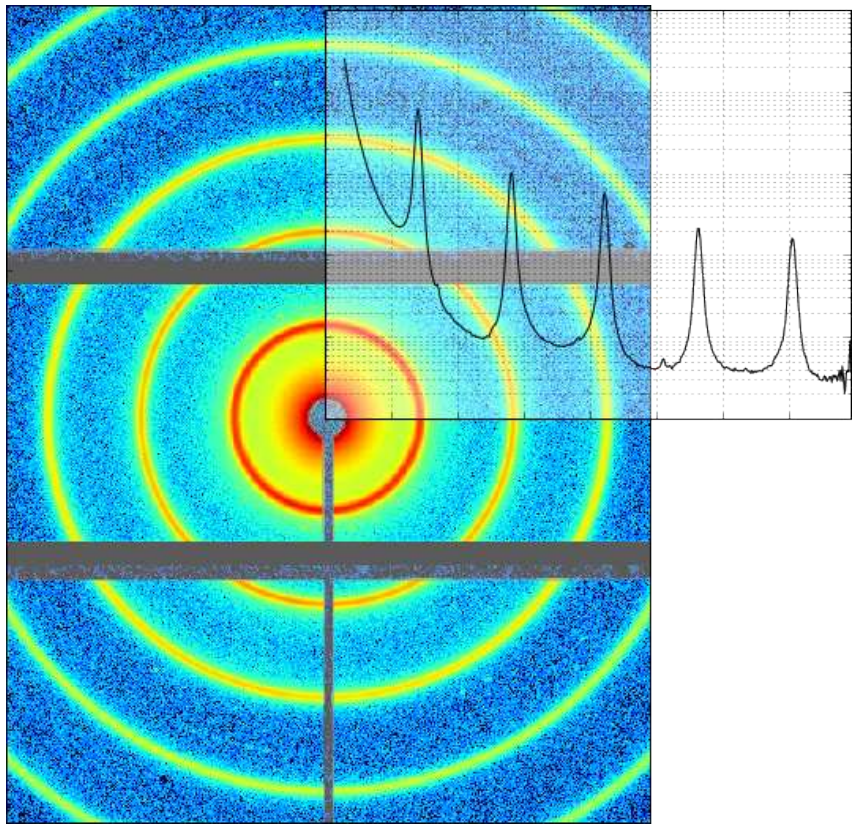
$$\boxed{q = \frac{4\pi}{\lambda}\sin\left(\frac{1}{2}\tan^{-1}\left(\frac{h\sqrt{(p_x - c_x)^2 + (p_y - c_y)^2}}{L}\right)\right)}$$

Calibrating of the scattering variable

- The sample-to-detector distance is tricky to measure directly
- Calibration samples: silver-stearate, silver-behenate, SBA15, LaB_6, tripalmitine...
  - high intensity, sharp peaks in the scattering
  - stable: vs. time and vs. temperature
  - *peak positions are known*
- Principle of finding the sample-to-detector distance:
  - Peak positions are known (q_i)
  - Measured peak positions in *pixel* units (p_i)
  - Fitting of the function

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{1}{2}\underbrace{\tan^{-1}(ph/L)}_{2\theta}\right) \rightarrow$$

determine L

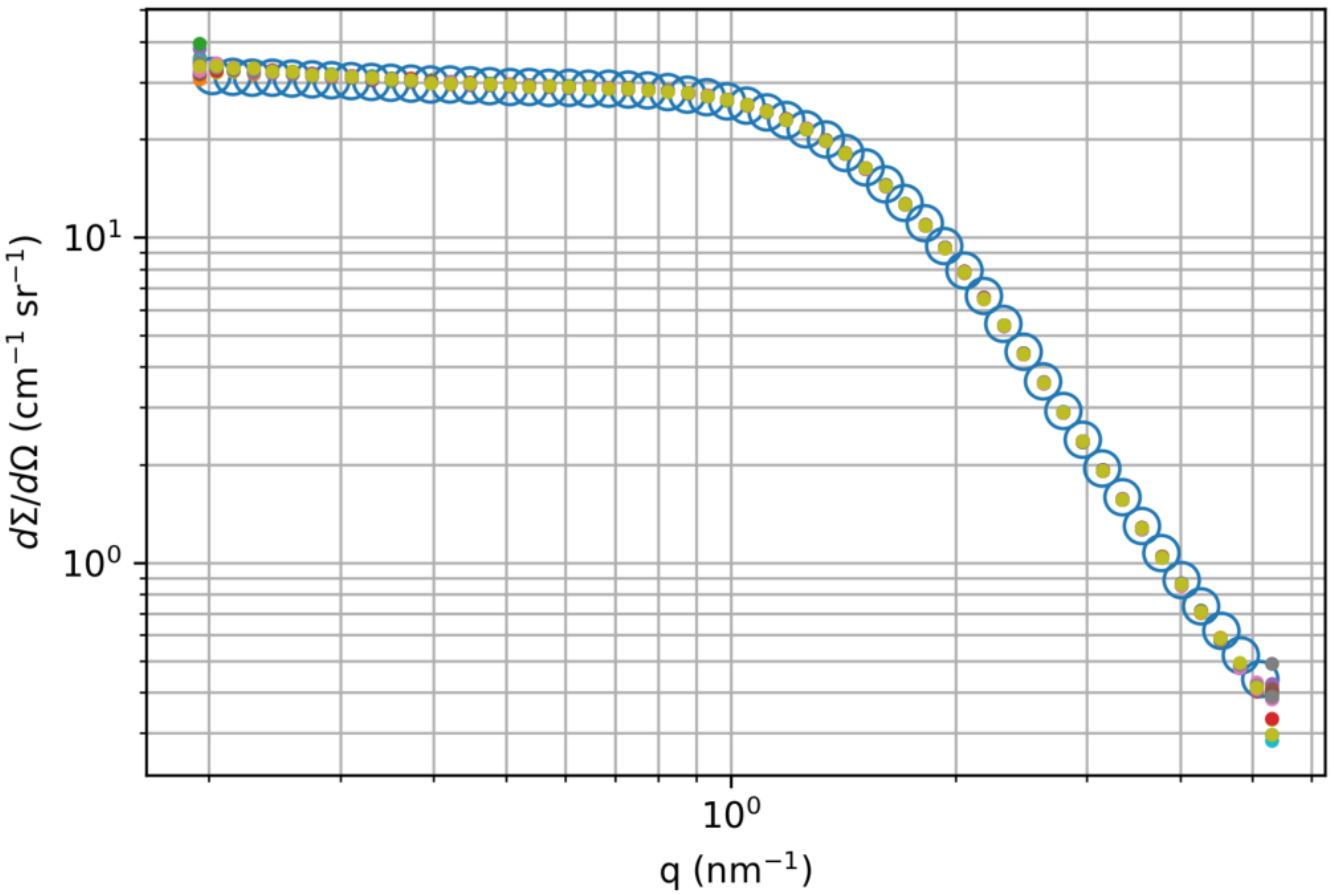


Calibration of the scattering intensity

- Purpose: scale the count rates to differential scattering cross-section (cm^{-1} sr^{-1})
- Independent from instrumental parameters:
  - Sample thickness
  - Beam shape and intensity
  - Quantum efficiency[1] of the detector
  - Measurement geometry
- Many parameters cannot be measured
- Reference sample:
  - Strong scattering
  - "Flat" scattering curve (not sensitive to miscalibrations in q)
  - Intensity is known in absolute units
    - Measured with other methods (e.g. glassy carbon, lupolen)
    - Known from theory (e.g. water, nanoparticle suspension)
- Measure the reference sample and your samples under the same conditions $\rightarrow$ the same intensity scaling factor applies

[1] The probability of the detection of an incoming photon

Intensity calibration with glassy carbon



If the curves are appropriately corrected, the scaling factor is the inverse of the beam flux!