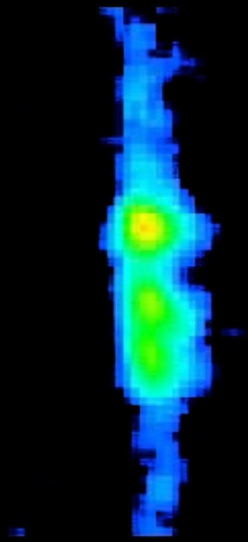
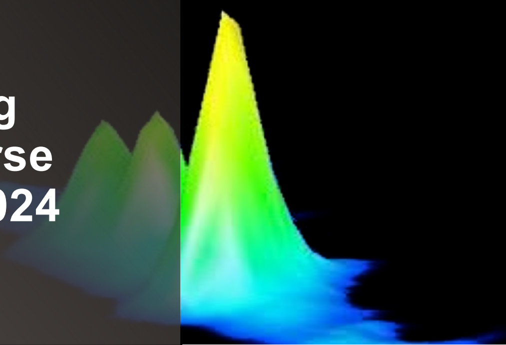


2.2 Small-angle scattering and x-ray reflectometry

Scattering
Block Course
12.-13.02.2024



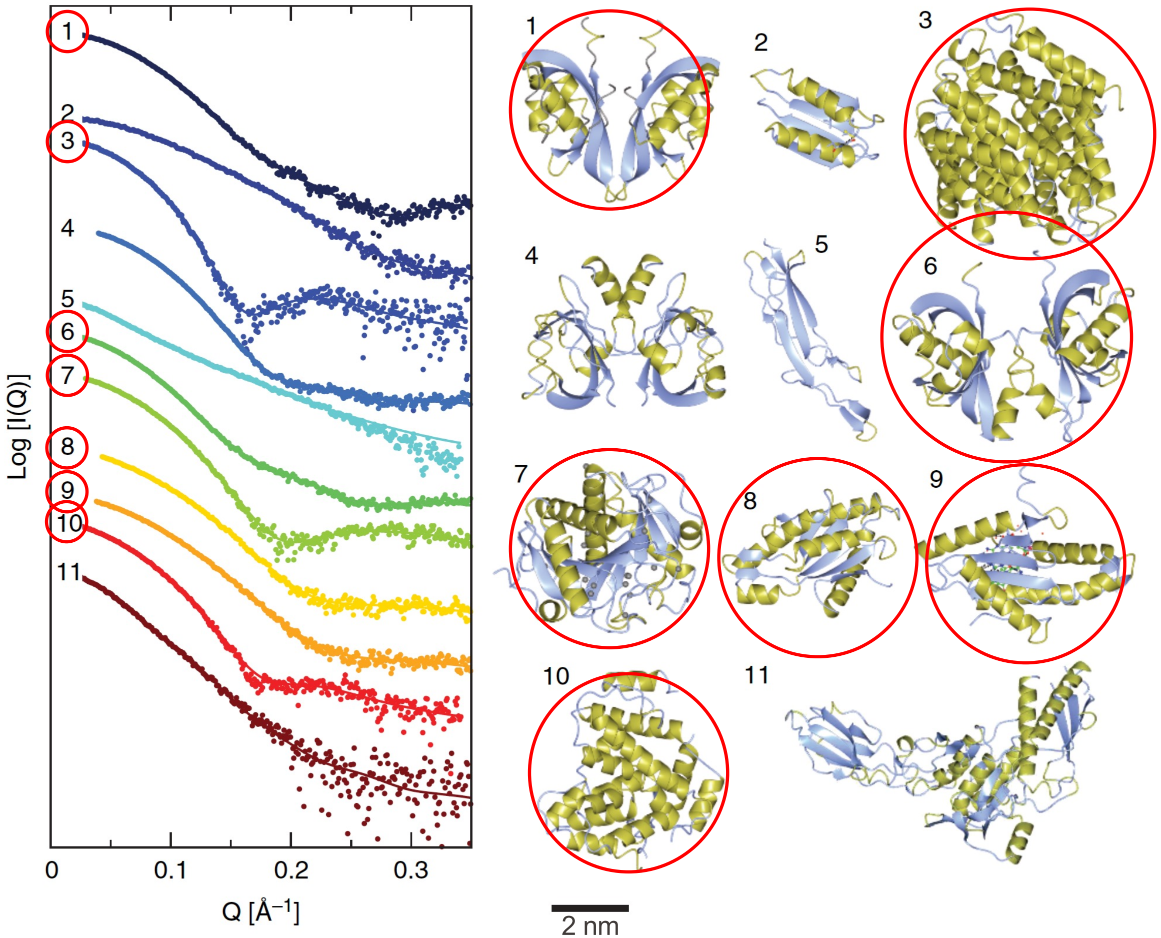
Prof. Philip Willmott

PSI

University of Zurich[UZH]

Small-angle x-ray scattering

SAXS – Introduction



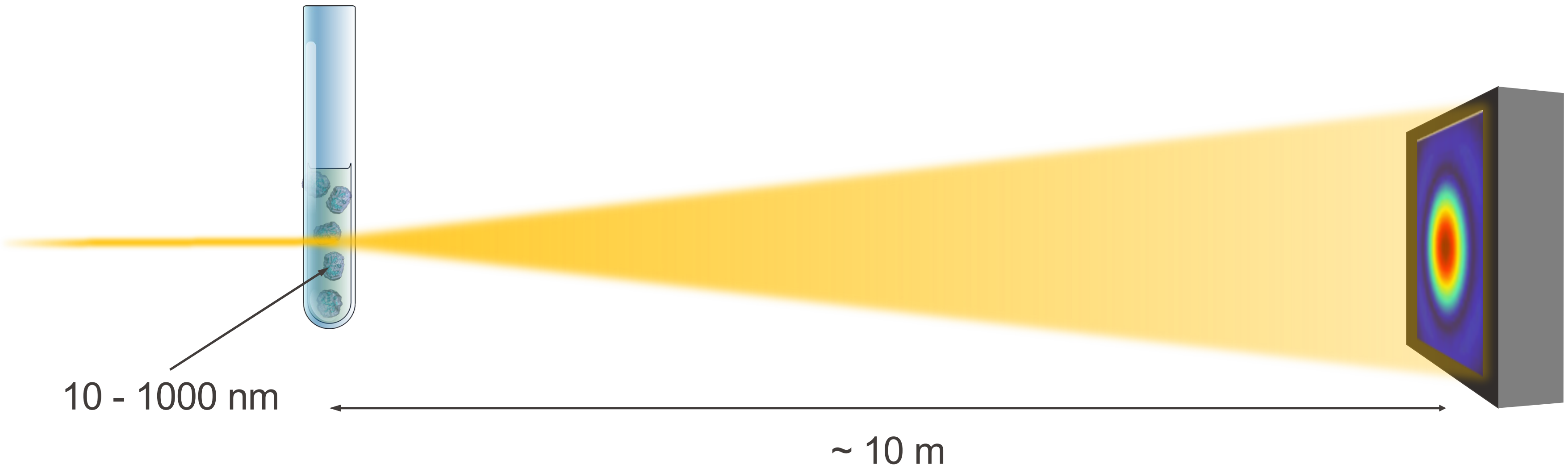
- Technique to investigate the structure of mesoscopic objects
  - Crystallinity not required
- From Bragg's law for low θ ($\sin\theta \simeq \theta$)
- Object, characteristic size d
  $\lambda = 2d\theta \Rightarrow \theta = \lambda/2d \ll 1$
  - $Q = 2\pi/d$
  - $d \sim 10 - 1000$ nm

  $\left.\begin{array}{l} Q = 2\pi/d \\ d \sim 10 - 1000 \text{ nm} \end{array}\right\} Q \sim 0.05 – 0.0005 \text{ Å}^{-1}$
- Applications
  - Colloidal science
  - Polymer science
  - Cell biology
  - Surface film structures
  - Systems without long-range structure – complementary to XRD

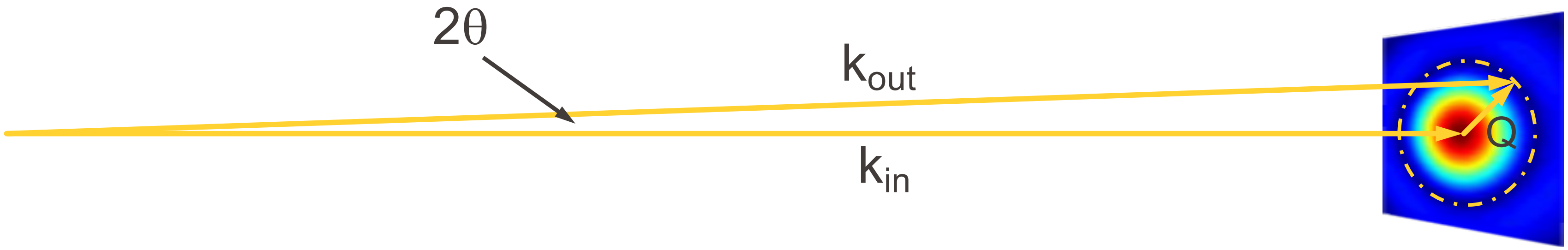
See T.D. Grant *et al.*, Biopolymers DOI:10.1038/s41598-018-26182-1

SAXS – Introduction

- Measures $\Delta\rho$, difference in electron density between object and its surroundings
  - If $\Delta\rho = 0$, object appears to be transparent
  - All SAXS arises from surfaces or interfaces
- e.g., protein $\rho = 0.44\ e/Å^3$, pure water $\rho = 0.33\ e/Å^3$
- Intensity proportional to
  - $(\Delta\rho)^2$
  - N_p, number of scatterers



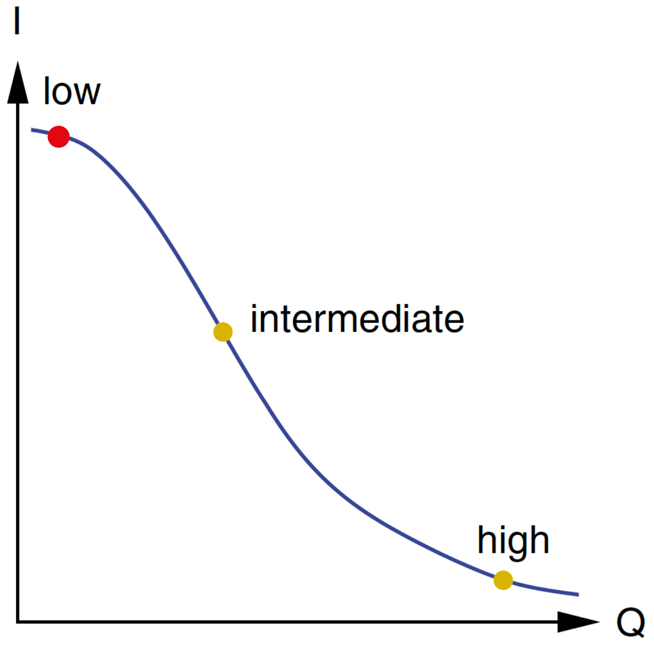
SAXS scattering vector magnitudes

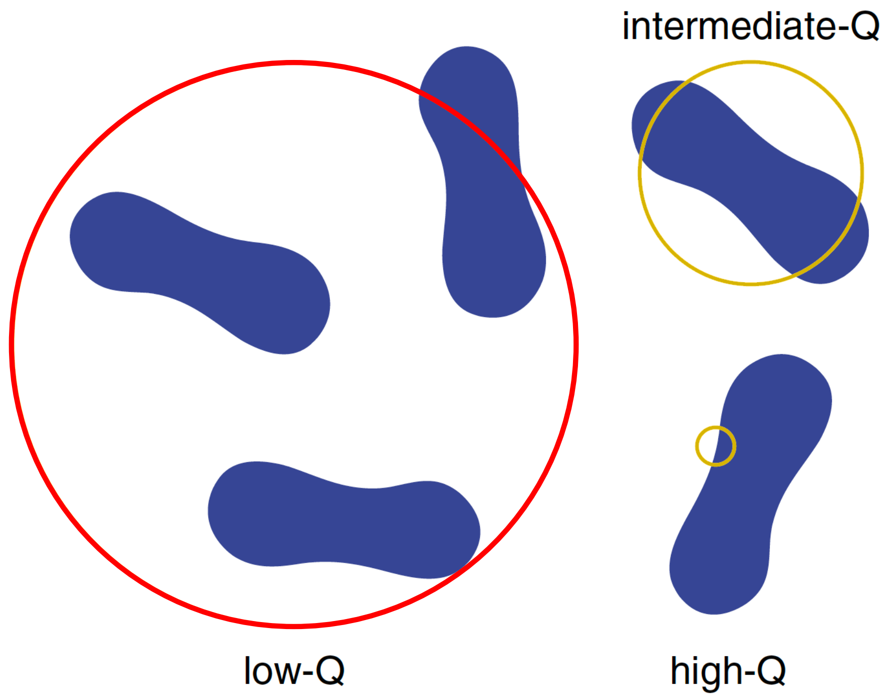


$$Q = 2|k|\theta = 4\pi\theta/\lambda = 2\pi/d$$

Q-regimes and what they're good for

- For a given Q, resolution = $2\pi/Q$
- Low Q
  - General size, no information on shape
  - "Guinier" regime

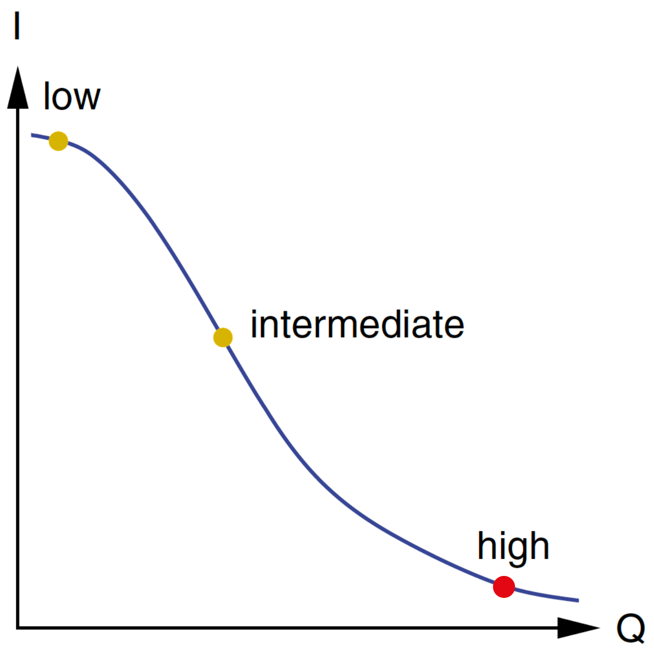


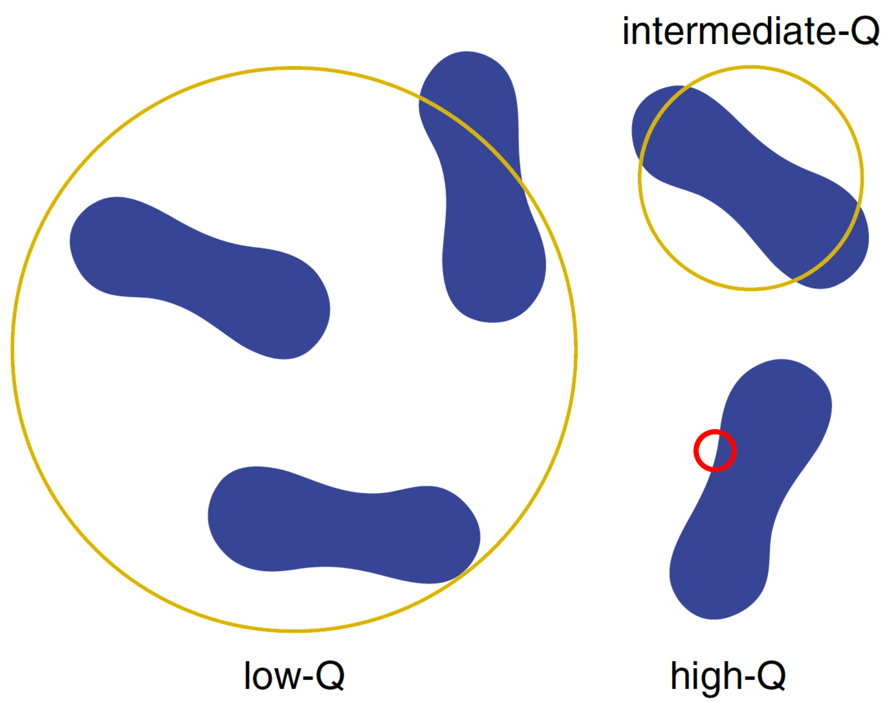


Q-regimes and what they're good for

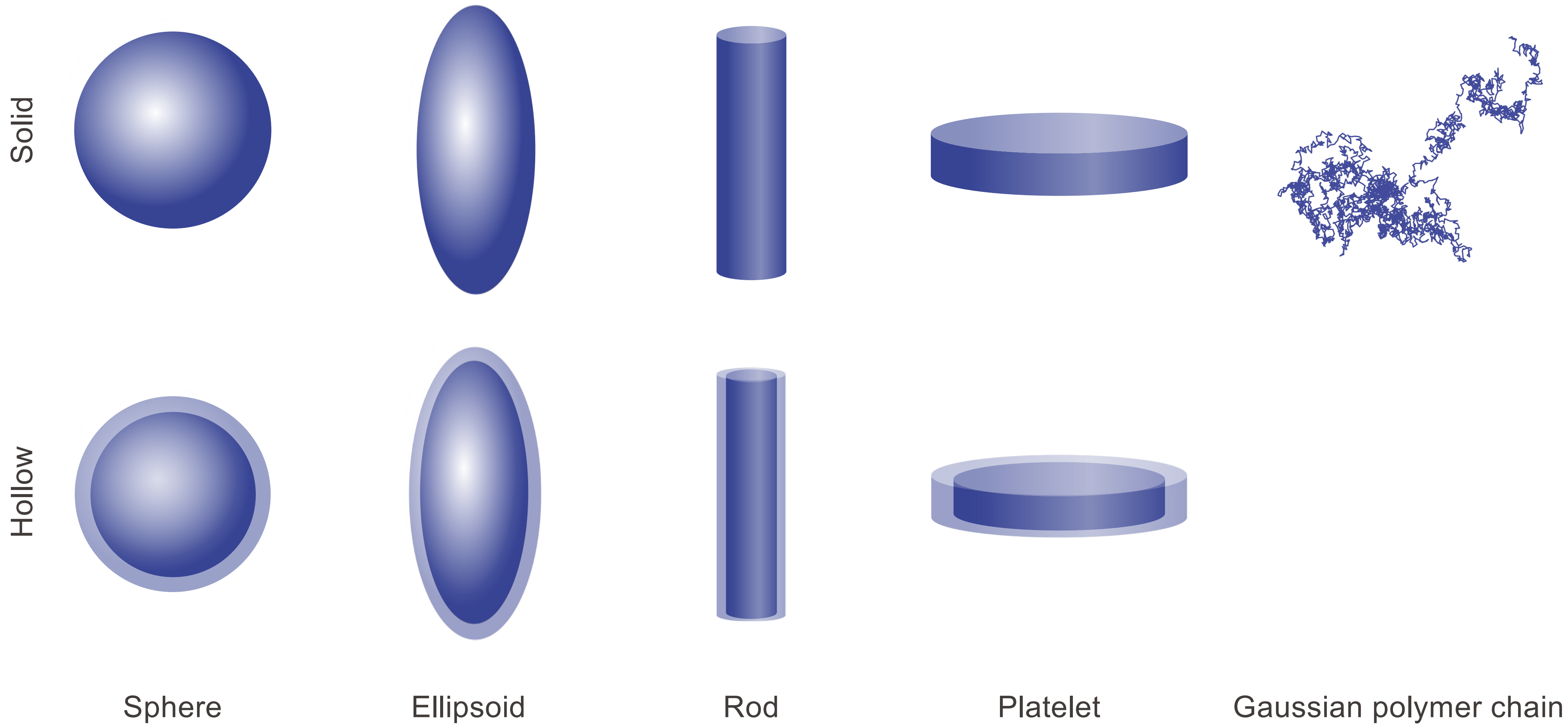
- For a given Q, resolution = $2\pi/Q$

- High Q
  - Probes surface/interface where there are changes in electron density
  - "Porod" regime

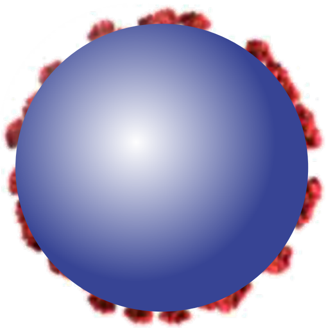




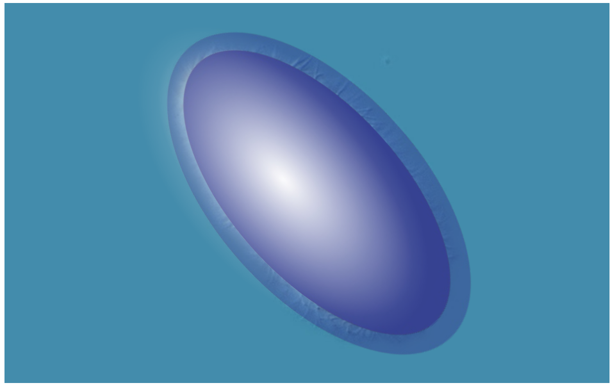
Idealized shapes of particular interest



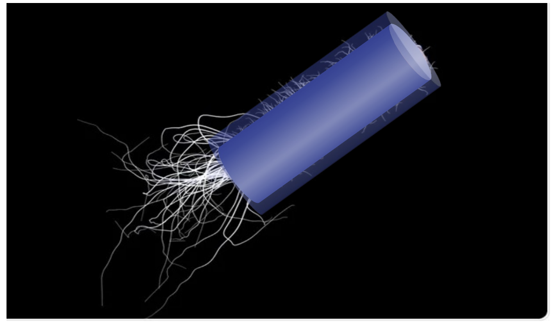
Idealized shapes of particular interest



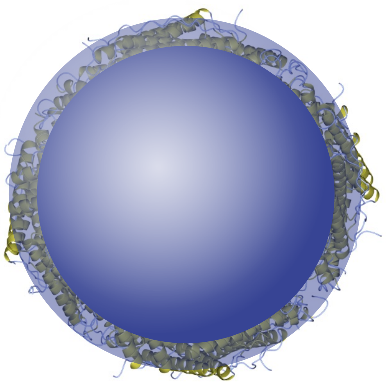
COVID-19 virus



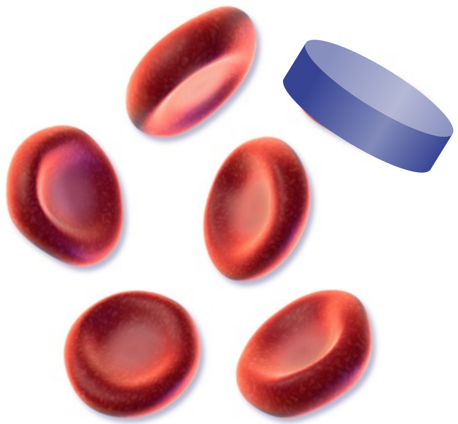
Paramecium



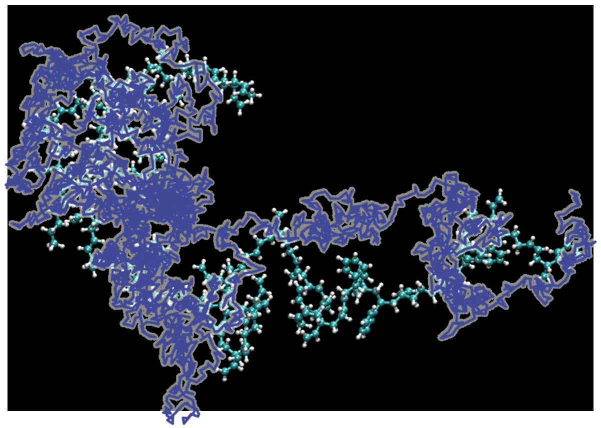
Bacillus bacterium



Apoferritin protein



Red blood cells



Styrene-butadiene copolymer chain

Scattering curves – general comments

$$I(Q) = NV^2(\Delta\rho)^2\,[\mathcal{F}(Q)\overset{\simeq 1}{\cancel{\mathcal{S}(Q)}}]^2 + \cancel{B}$$

Number density of particles

Volume of particle

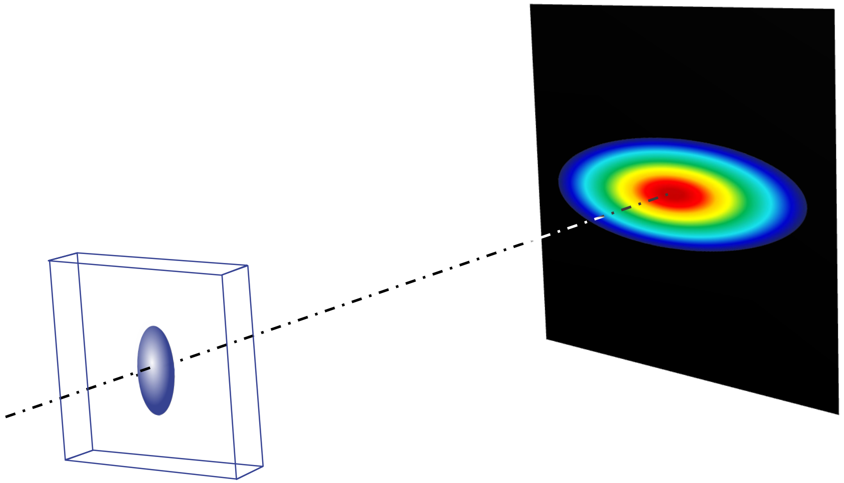
Electron-density contrast of particle

Form factor of particle

Coherence factor

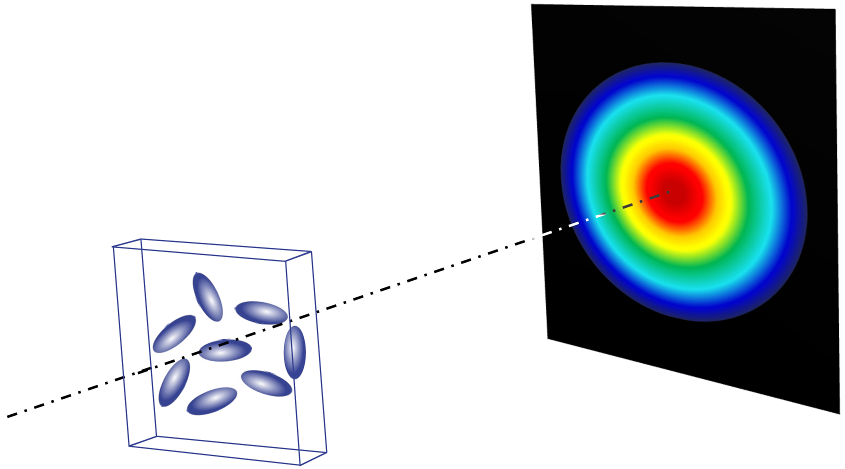
Background signal

Scattering curves – single particle v random ensemble



Fixed orientation

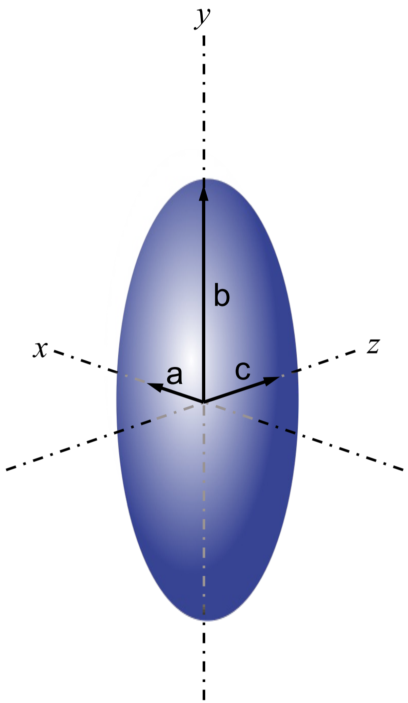
$$I(\mathbf{Q})$$



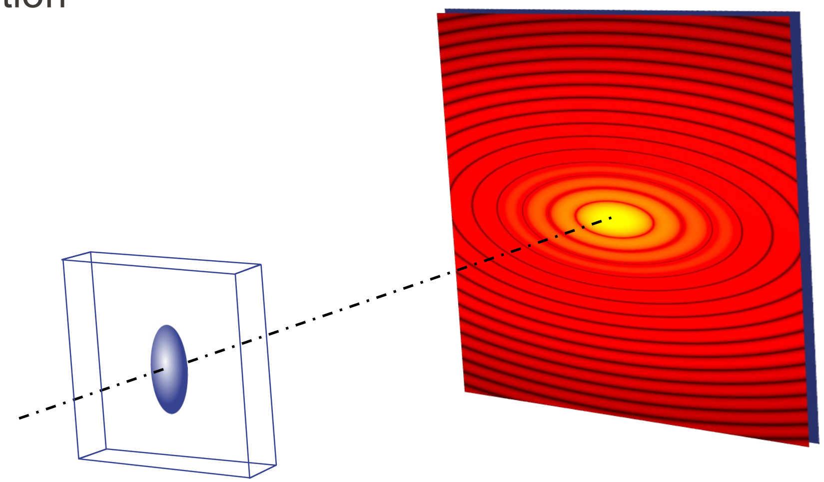
Randomly oriented ensemble

$$I^{\mathrm{ro}}(Q) = \frac{n}{4\pi}\int_0^{2\pi} d\alpha \int_0^{\pi} \sin\beta \, d\beta \, I(\mathbf{Q})$$

Scattering curves – ellipsoid, fixed orientation



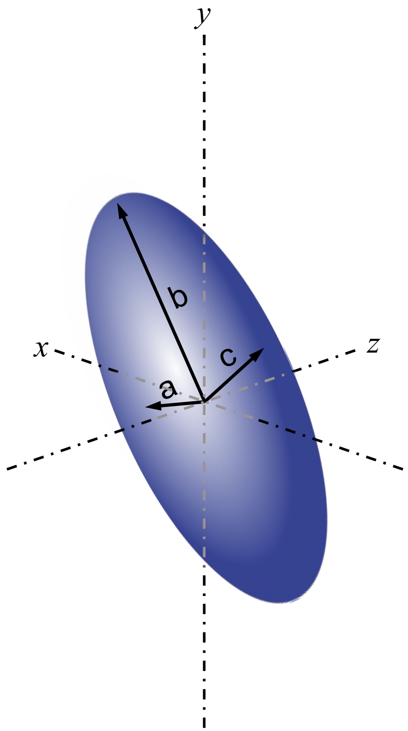
Fixed orientation



$$I_{\mathrm{ell}}(\mathbf{Q}) = I_{\mathrm{ell}}(Q_x, Q_y) = (r_0 \Delta\rho)^2 \left(\frac{4}{3}\pi abc\right)^2 \left(3\,\frac{\sin\phi - \phi\cos\phi}{\phi^3}\right)^2$$

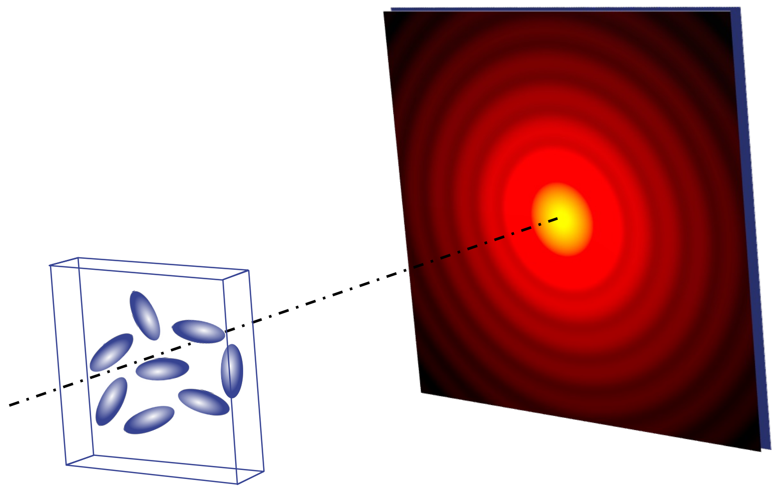
$$\phi = \sqrt{a^2 Q_x^2 + b^2 Q_y^2}$$

Scattering curves – ellipsoid, randomly oriented ensemble



Average (integrate) over both polar angles α and β between 0 and $\pi/2$

Randomly oriented ensemble

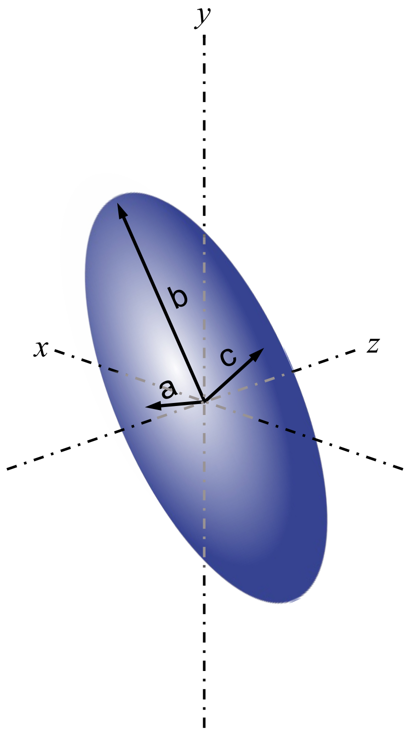


$$I_{\mathrm{ell}}^{\mathrm{ro}}(Q) = (r_0 \Delta\rho)^2 \left(\frac{4}{3}\pi abc\right)^2$$

$$\times \frac{2}{\pi} \int_0^{\pi/2} d\alpha \int_0^{\pi/2} \sin\beta \, d\beta \left(3 \frac{\sin\phi - \phi\cos\phi}{\phi^3}\right)^2$$

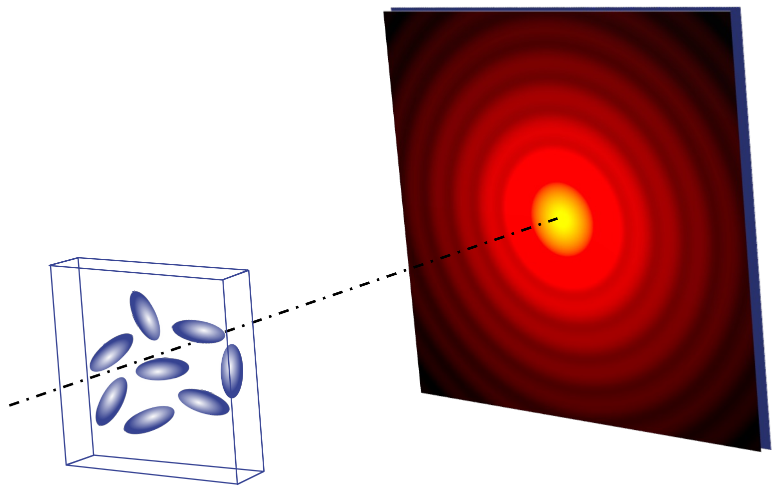
$$\phi = Q\sqrt{(a^2 \sin^2\alpha + b^2 \cos^2\alpha)\sin^2\beta + c^2 \cos^2\beta}$$

Scattering curves – ellipsoid to sphere



Average (integrate) over both polar angles α and β between 0 and $\pi/2$

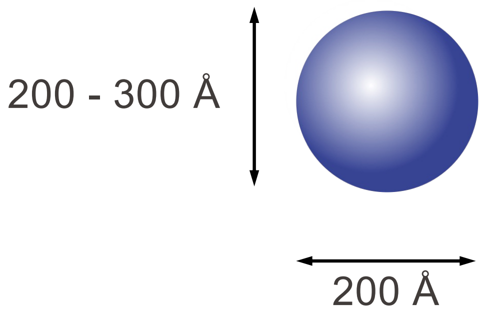
Randomly oriented ensemble

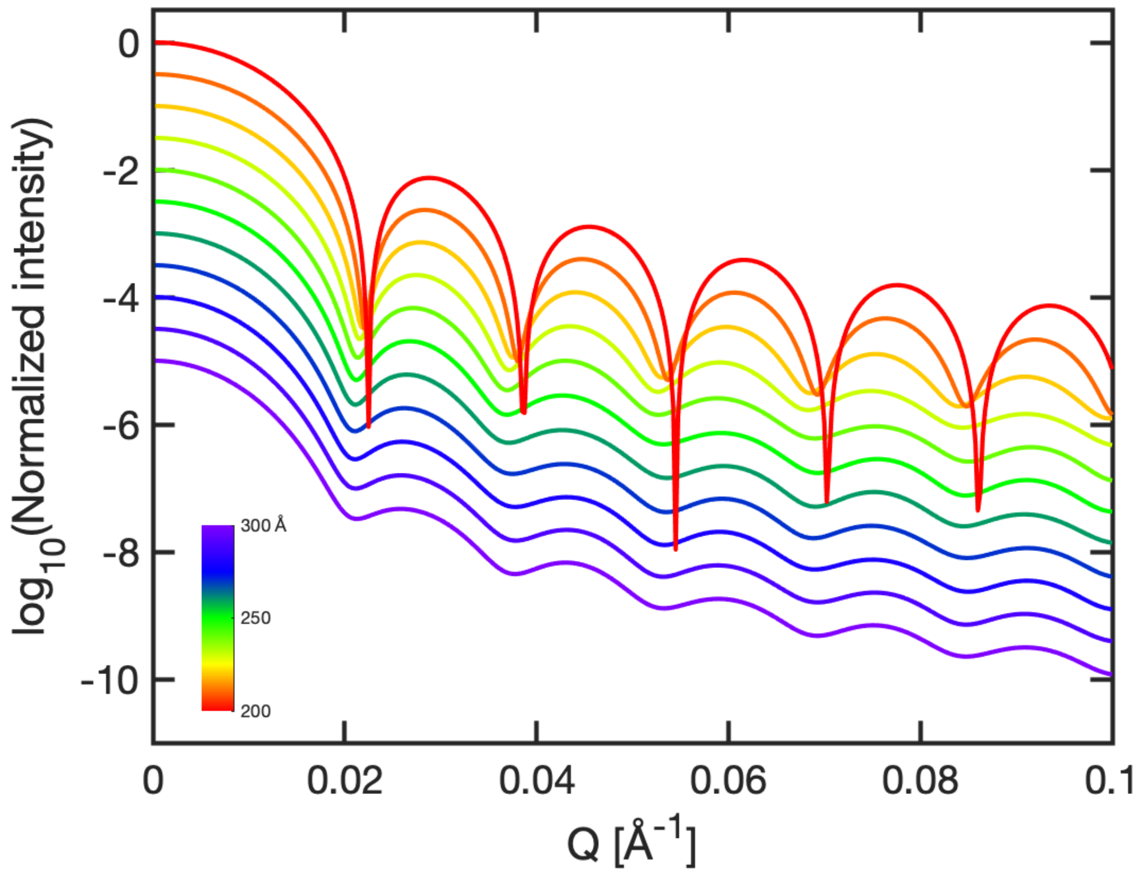


If $a = b = c\,?\;\Rightarrow\;\phi = Qa$

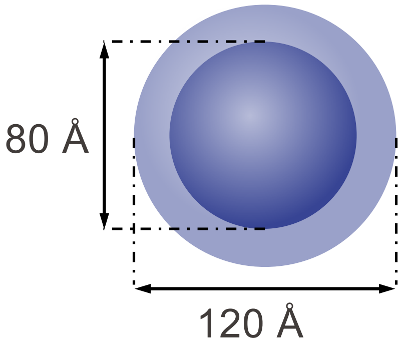
$$I_{\mathrm{ell}}^{\mathrm{ro}} = I_{\mathrm{sph}} = (r_0\Delta\rho)^2\left(\frac{4}{3}\pi a^3\right)^2\left(3\,\frac{\sin(Qa) - Qa\cos(Qa)}{(Qa)^3}\right)^2$$

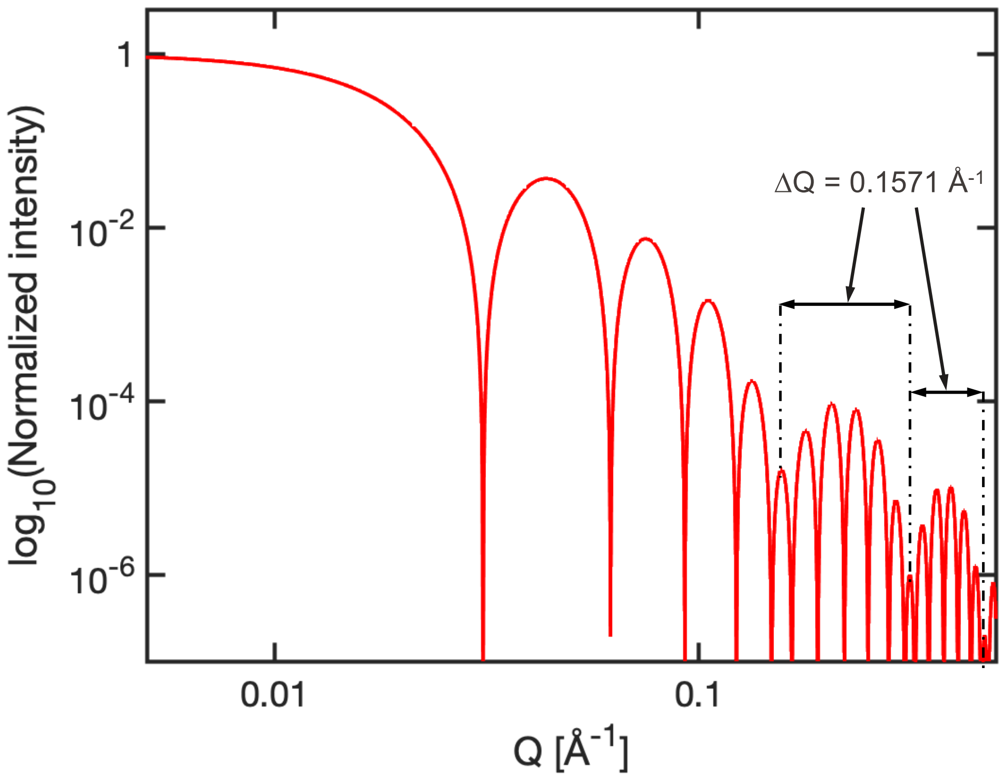
Scattering curves – solid spheres





Scattering curves – hollow spheres

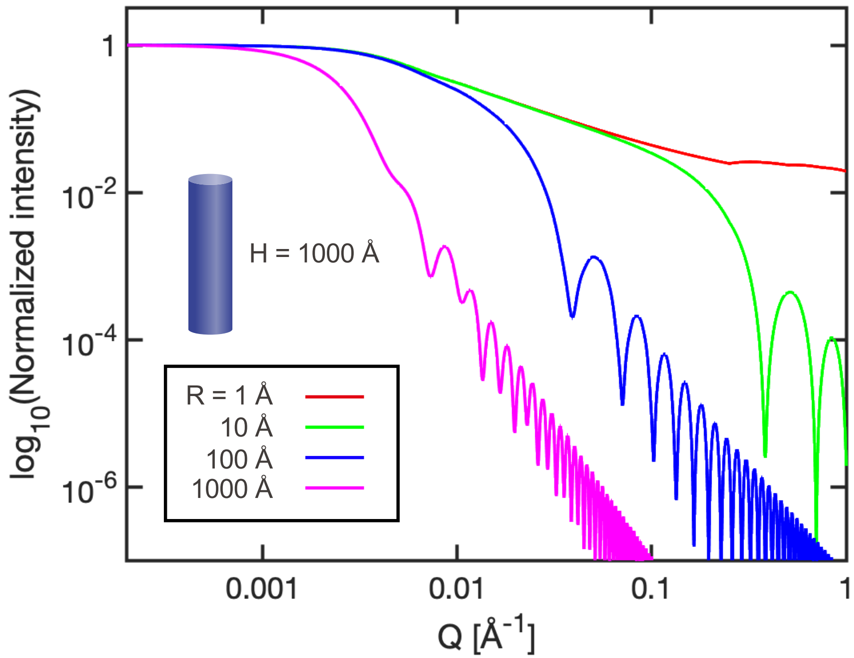


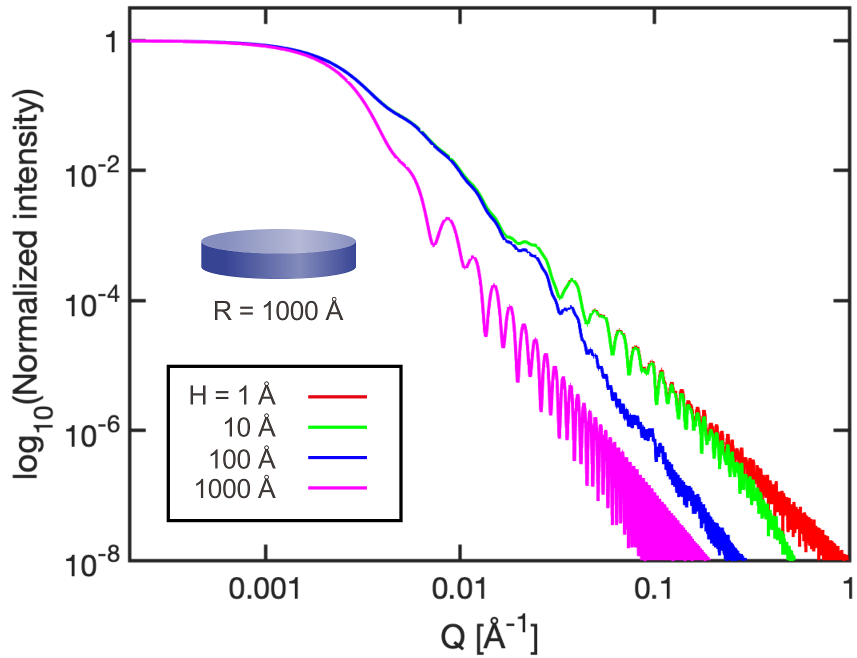


$$\Delta Q = 2\pi/(R_2 - R_1)$$

$$I(Q) = I_0 \left\{ \frac{3}{R_2^3 - R_1^3} \left[\left(\frac{\sin(QR_2) - QR_2\cos(QR_2)}{Q^3} \right) - \left(\frac{\sin(QR_1) - QR_1\cos(QR_1)}{Q^3} \right) \right] \right\}^2$$

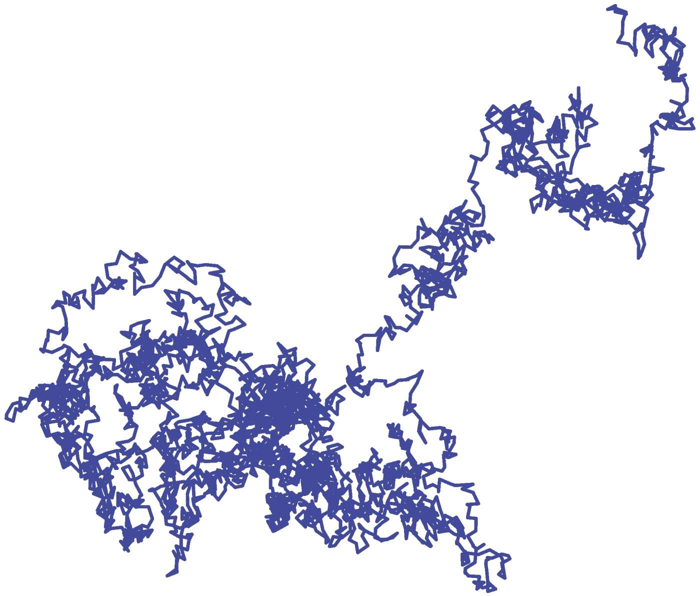
Scattering curves – rods and platelets



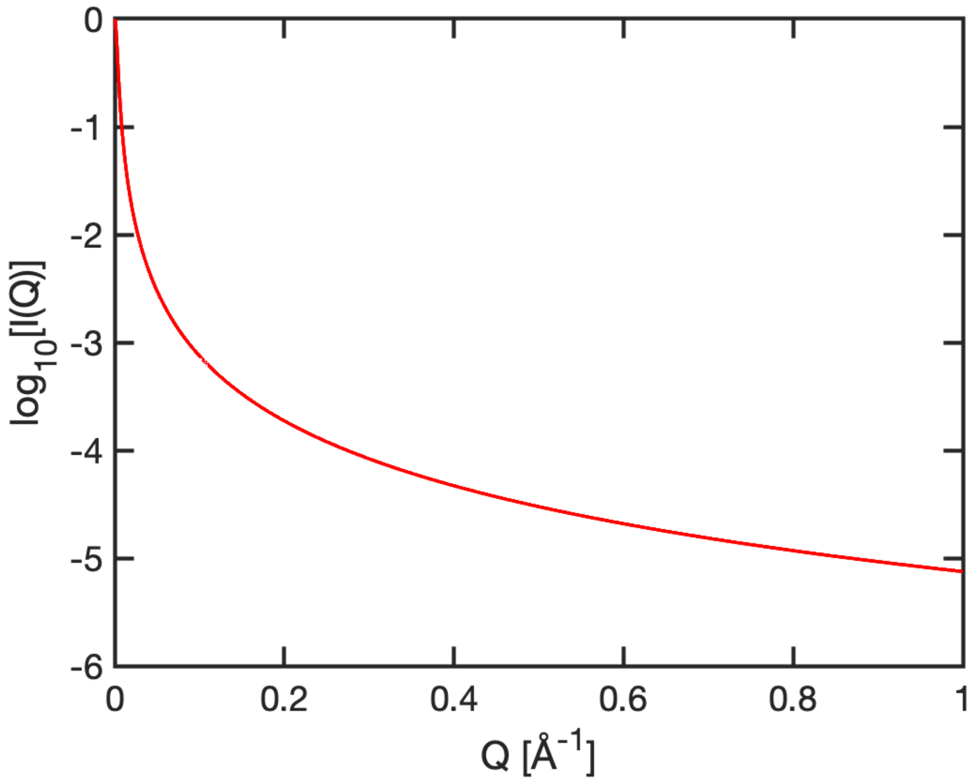


$$I(Q) = 4\int_0^1 \frac{J_1^2[QR(1-x^2)^{1/2}]}{[QR(1-x^2)^{1/2}]^2}\cdot\frac{\sin^2(QHx/2)}{(QHx/2)^2}\,dx$$

Scattering curves – Gaussian chains

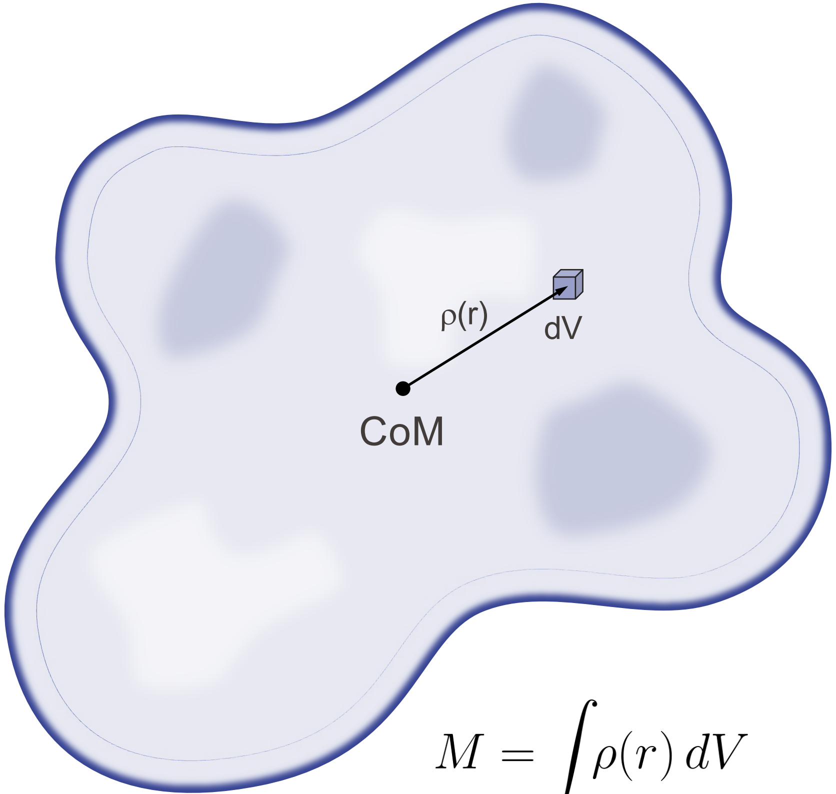


n links, each length a, random orientation
"Gaussian chain"



$$I(Q) = \frac{2I_0}{\phi^2}\left[\exp(-\phi) + \phi - 1\right] \qquad \text{whereby} \quad \phi = Q^2 a^2 n/6$$

Radius of gyration



$$M = \int \rho(r)\, dV$$

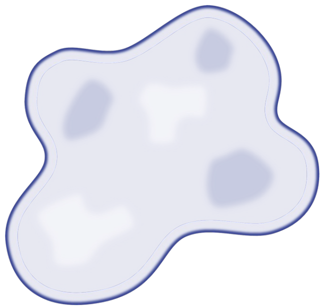
- Moment of inertia

$$I = \int \rho(r) r^2\, dV$$

- Radius of gyration

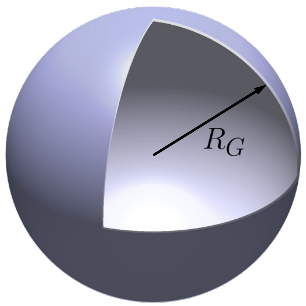
$$I = M R_G^2$$

$$\Rightarrow R_G = \left[\left(\int \rho(r) r^2\, dV \right) / \left(\int \rho(r)\, dV \right) \right]^{1/2}$$



Object, mass M

$\equiv$

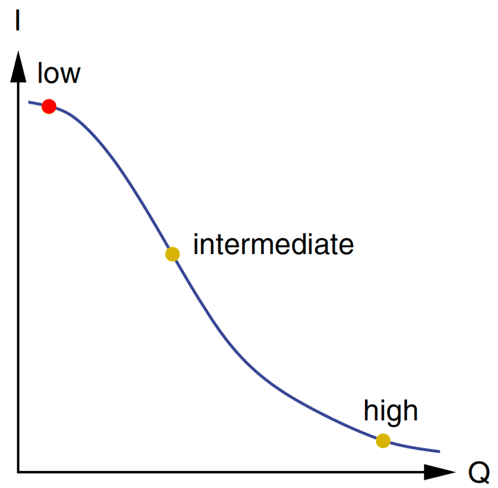


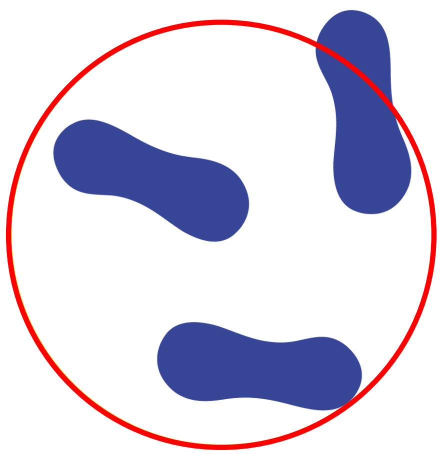
Hollow shell,
mass M, radius R_G

Radius of gyration

Object	R_G^2
Solid sphere radius r	$\frac{3}{5}r^2$
Hollow sphere radii r_1 and $r_2 > r_1$	$\frac{3}{5}\frac{r_2^5 - r_1^5}{r_2^3 - r_1^3}$
Solid cylindrical rod radius r, height L	$\frac{r^2}{2} + \frac{L^2}{12}$
Solid rectangular beam width W, height H, length L	$\frac{W^2 + H^2 + L^2}{12}$
Hollow tube radii r_1, r_2, height L	$\frac{r_1^2 + r_2^2}{2} + \frac{L^2}{12}$
Solid ellipsoid semi-axes a, b, c	$\frac{a^2 + b^2 + c^2}{5}$
Hollow ellipsoid outer semi-axes a, b, c, inner semi-axes αa, βb, γc	$\frac{(1 - \alpha^3\beta\gamma)a^2 + (1 - \alpha\beta^3\gamma)b^2 + (1 - \alpha\beta\gamma^3)c^2}{5(1 - \alpha\beta\gamma)}$
Solid elliptical cylinder semi-axes a, b, height L	$\frac{a^2 + b^2}{4} + \frac{L^2}{12}$
Hollow elliptical cylinder outer semi-axes a, b, outer height L, inner semi-axes αa, βb, inner height γL	$\frac{3(1 - \alpha^3\beta\gamma)a^2 + 3(1 - \alpha\beta^3\gamma)b^2 + (1 - \alpha\beta\gamma^3)L^2}{12(1 - \alpha\beta\gamma)}$
Randomly folded polymer chain, n monomers of length a	$\frac{a^2 n}{6}$

Guinier regime





- Q ≪ 2π/a
  - a = characteristic length of scattering object
  - Details of object shape excluded
  - Only information on overall size
    - i.e., radius of gyration
- Goal: simple expression for I(Q) for Q ≪ 2π/a
  - Choose particle type with I(Q) that lends itself to simplification
    - Sphere!

$$I_{\text{sph}} = I_0 \left(\frac{3\left[\sin(Qa) - Qa\cos(Qa)\right]}{(Qa)^3} \right)^2$$

    - Use

$$\sin(x) \approx x - x^3/6 + x^5/120 - \cdots$$
$$\cos(x) \approx 1 - x^2/2 + x^4/24 - \cdots$$

Guinier regime

$$I_{\mathrm{sph}}(x \equiv Qr \ll 1) \approx I_0 \left(\frac{3\left[\cancel{x} - x^3/6 + x^5/120 \cdots - \cancel{x} + x^3/2 - x^5/24 + \cdots\right]}{x^3} \right)^2$$

$$= I_0 \left(\frac{3\left[x^3/3 - x^5/30\right]}{x^3} \right)^2$$

$$= I_0 \left(1 - x^2/10\right)^2 \approx I_0 \left(1 - x^2/5\right)$$

But for a sphere of radius r,

$$R_G^2 = \frac{3}{5} r^2$$

$$\Rightarrow I_{\mathrm{sph}}(Qr \ll 1) = I_0 \left(1 - Q^2 R_G^2/3\right)$$

$$\boxed{\approx I_0 \exp(-Q^2 R_G^2/3)}$$

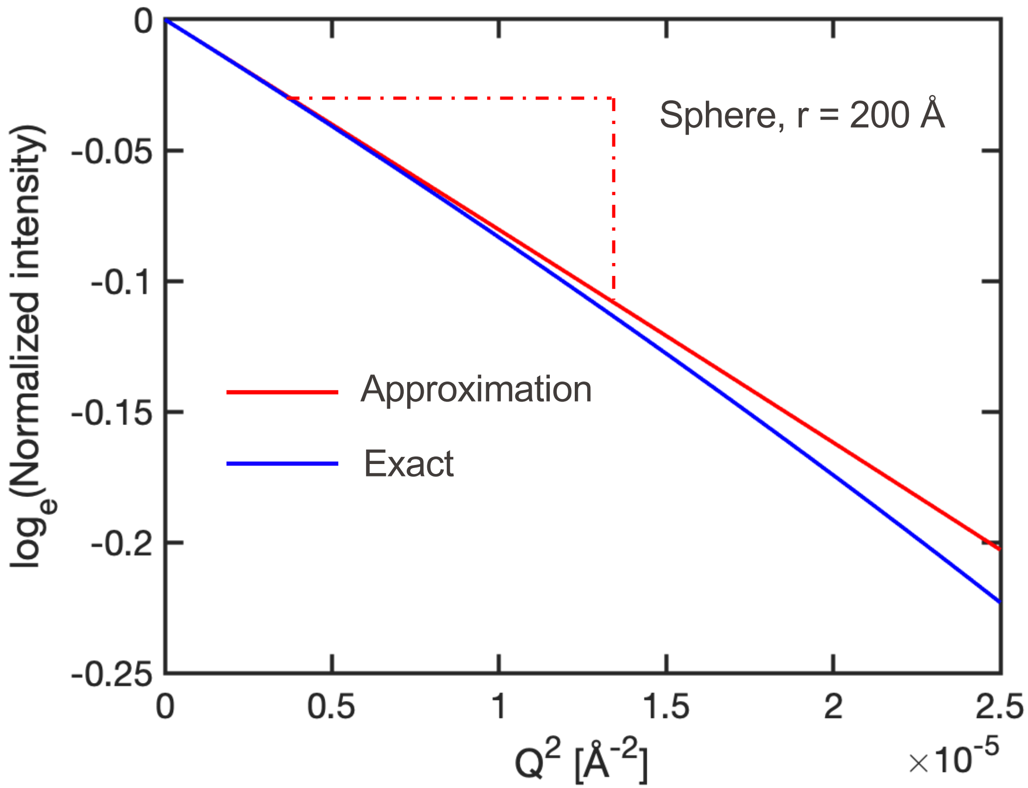
- Plot ln[I(Q)] v Q^2
  - Gradient = $-R_G^2/3$
- N.B. Valid for ALL objects, not only spheres!!

Guinier regime

- Plot ln[I(Q)] v Q^2
  - Valid for
    - $Q \ll 1/200$ Å^{-1}
    - $Q^2 \ll 2.5 \times 10^{-5}$ Å^{-2}
  - Gradient = $-R_G^2/3$

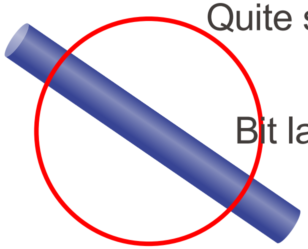
  - $R_G^2/3 = (0.20115/2.5 \times 10^{-5})$ Å^2
    $= 8.0459 \times 10^3$ Å^2

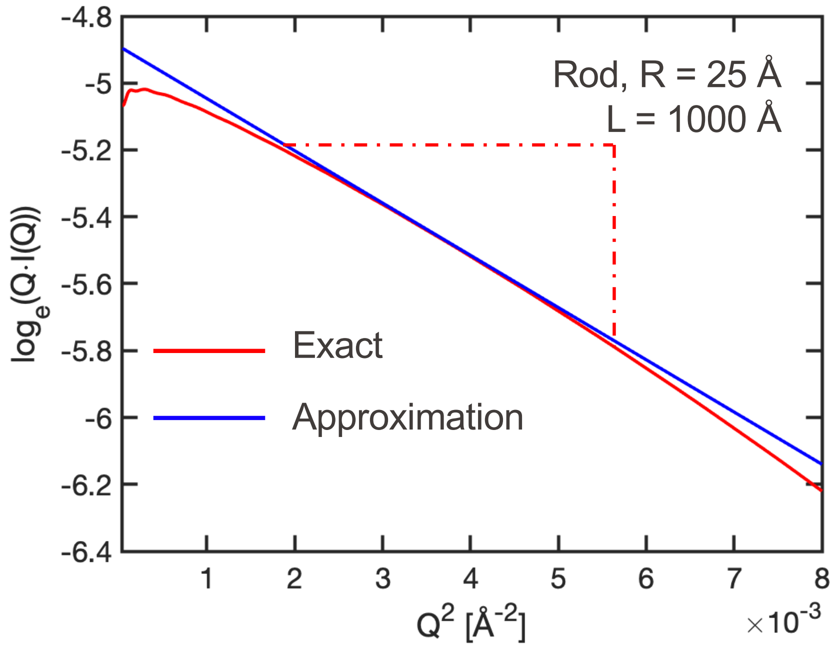
    $R_G^2/3 = r^2/5 \Rightarrow r =$ **200.6 Å**



Extended Guinier regime for rods

- Objects with widely differing characteristic lengths
  - Thin rods L ≫ R
  - Flat platelets R ≫ H





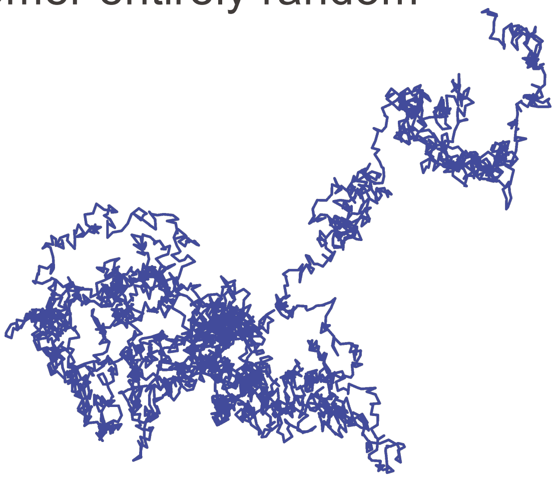
$$I(Q) = \frac{AI_0}{Q} \exp\left(-\frac{R_G^2 Q^2}{2}\right); \quad QL > 2\pi;\ QR \ll 2\pi$$

$$R_G = R/\sqrt{2}$$

Gradient = -160
R = 25.3 Å

Gaussian chains – Guinier regime

- Polymers consisting of a single chain of monomers with the orientation of each monomer entirely random



n links, each length a, random orientation
"Gaussian chain"

$$I(Q) = \frac{2I_0}{\phi^2}\left[\exp(-\phi) + \phi - 1\right],$$

whereby $\phi = Q^2a^2n/6$

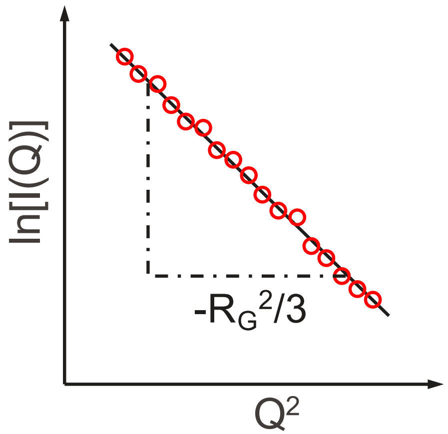
- Small Q:

$$I(Q) \approx \frac{2I_0}{\phi^2}\left(\underbrace{1 - \phi + \phi^2/2 - \phi^3/6 + \cdots}_{\approx\exp(-\phi)} + \phi - 1\right)$$

$$= I_0\,(1 - \phi/3) \approx \exp(-\phi/3) = \exp(-a^2nQ^2/18)$$

$$\Rightarrow R_G^2 = a^2n/6$$

- Plot I(Q) v Q^2 to determine R_G



Gaussian chains – Kratky plots

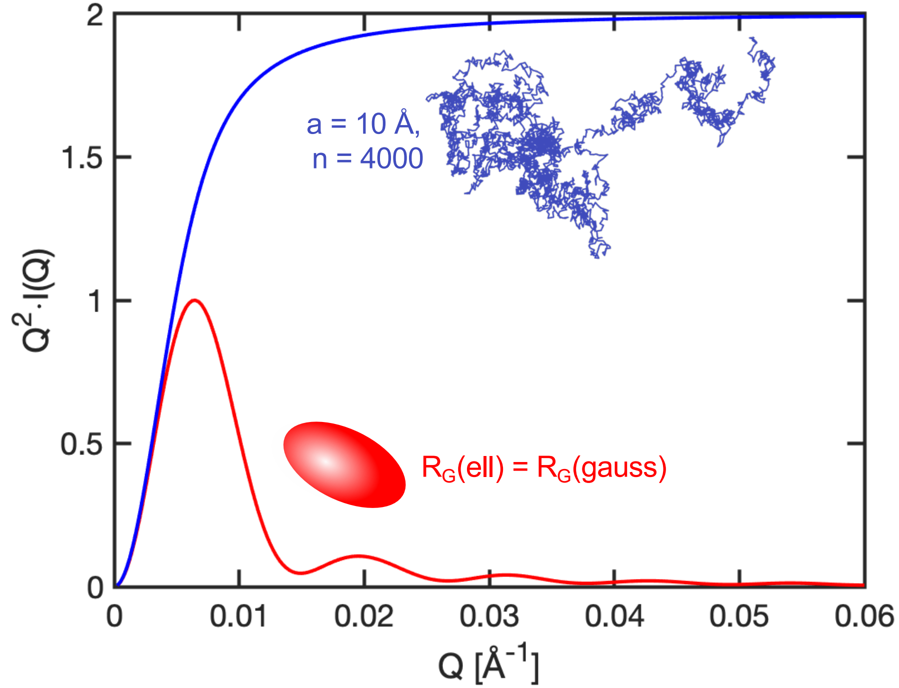
- Plot of $Q^2 I(Q)$ v Q
  - Provides information on compactness of polymer chains
  - Open "Gaussian" chain?
  - Closed ellipsoidal structure?
- Gaussian chain (e.g.,unfolded protein)

$$I(Q) = \frac{2I_0}{\phi^2}\left[\exp(-\phi) + \phi - 1\right]$$

$$\Rightarrow \phi I(Q) = 2I_0 \frac{\left[\exp(-\phi) + \phi - 1\right]}{\phi}$$

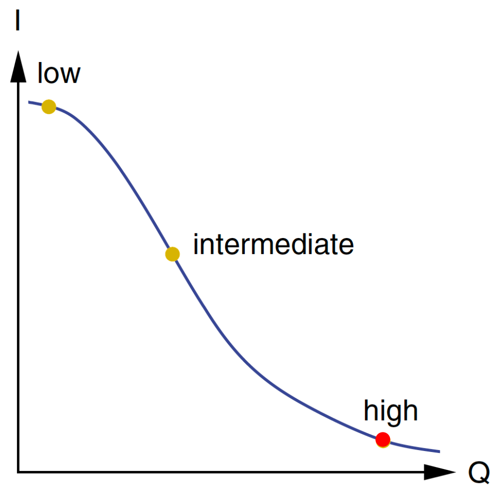
  - Larger Q: $\phi I(Q) \approx 2I_0$

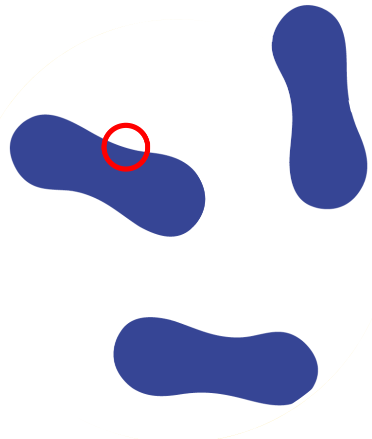
- Compact ellipsoid (e.g., globular protein)
  - Large Q: $\phi I(Q) \approx 0$



PROVIDES IMPORTANT INFORMATION ABOUT DEGREE OF PROTEIN FOLDING!!

Porod regime, Porod's law, and the Porod plot





low-Q

- $Q \gg 2\pi/a$
  - a = characteristic length of scattering object
  - Probes local features at surface
    - i.e., interfaces with $\Delta\rho$ across boundary
    - If Q large enough, surface is smooth at that scale (Fresnel equations for reflectivity, see following video on x-ray reflectivity)
- Remember:

$$I(Q) = NV^2(\Delta\rho)^2[\mathcal{F}(Q)]^2$$

  - For spheres and high Q:

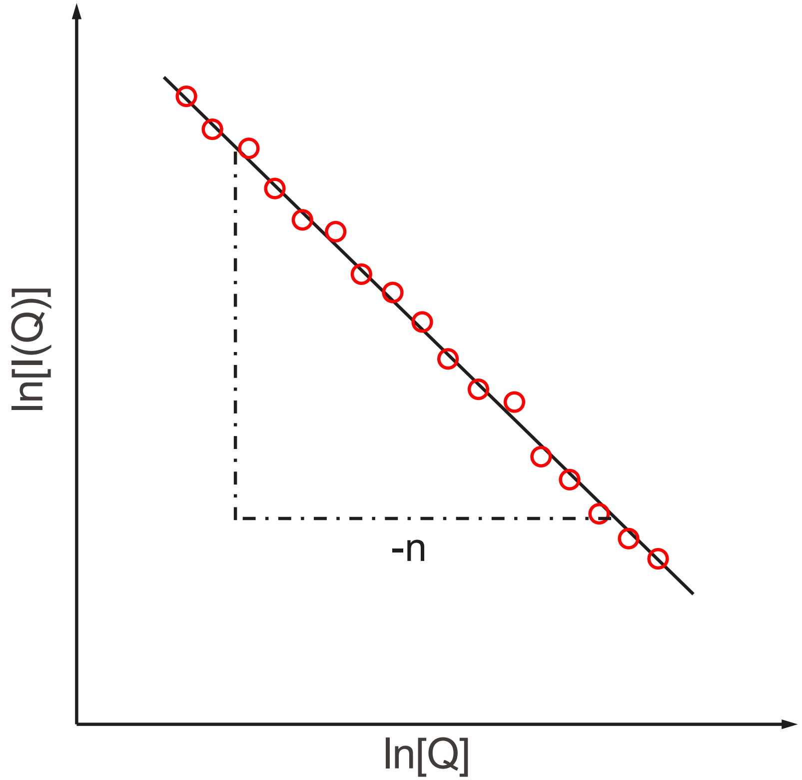
$$\boxed{[\mathcal{F}(Q)]^2 = \frac{3}{2R^3}\left(\frac{S}{V}\right)\frac{1}{Q^4}}$$

Porod's law

$$\left(S = 4\pi r^2 \qquad V = \frac{4}{3}\pi r^3\right)$$

$$\boxed{\Rightarrow I(Q) = 2\pi N(\Delta\rho)^2\frac{S}{Q^4}}$$

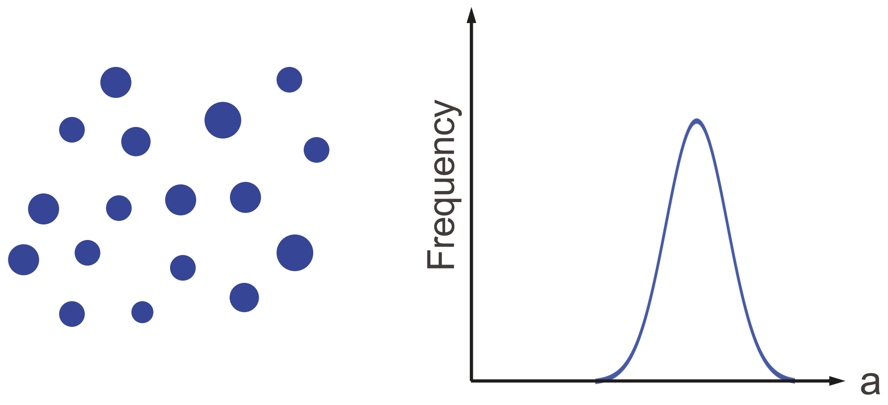
Porod regime, Porod's law, and the Porod plot

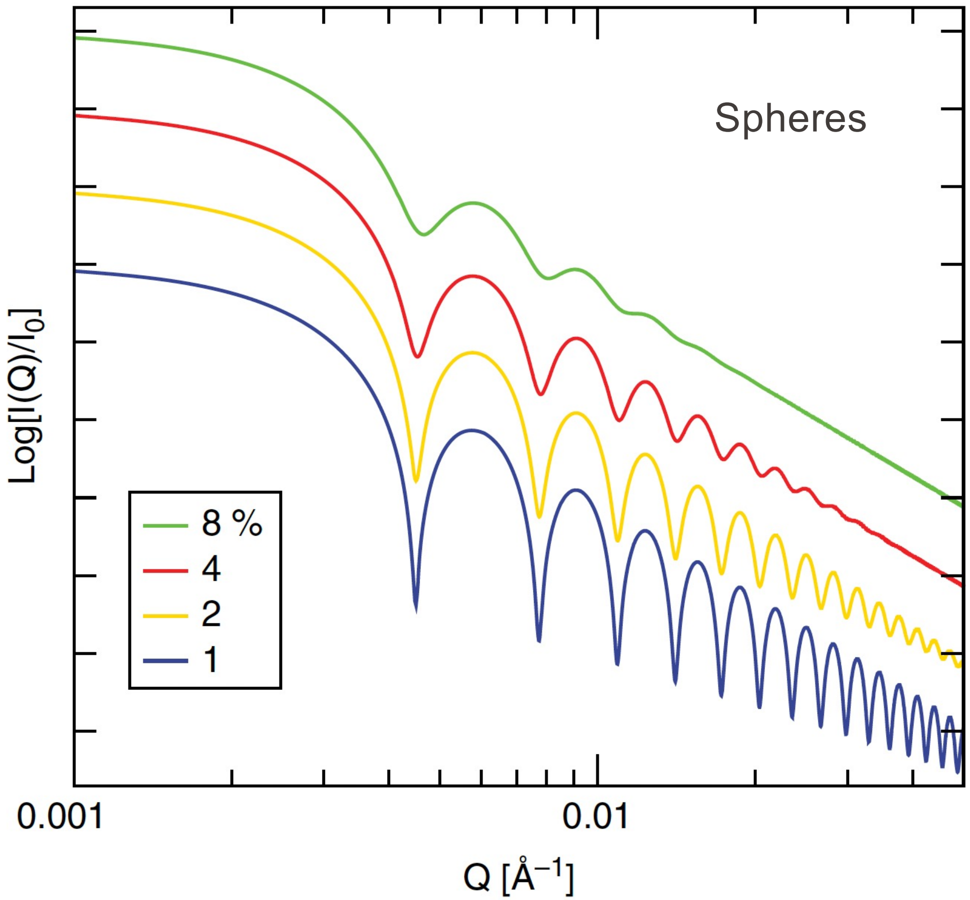


- Porod plot: high Q
- Gradient -n
- n = …
  - 1: rigid thin rods (1D)
  - 2: Gaussian chain
  - 3 – 4: rough interfaces
  - 4: smooth surface (c.f. x-ray reflectivity)

Polydispersity

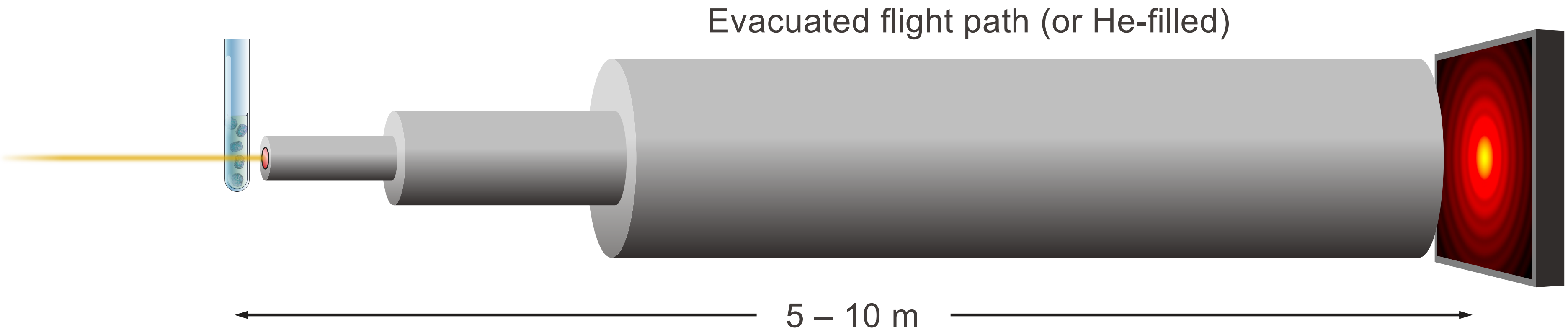
- Ensemble of objects with same shape but range of sizes



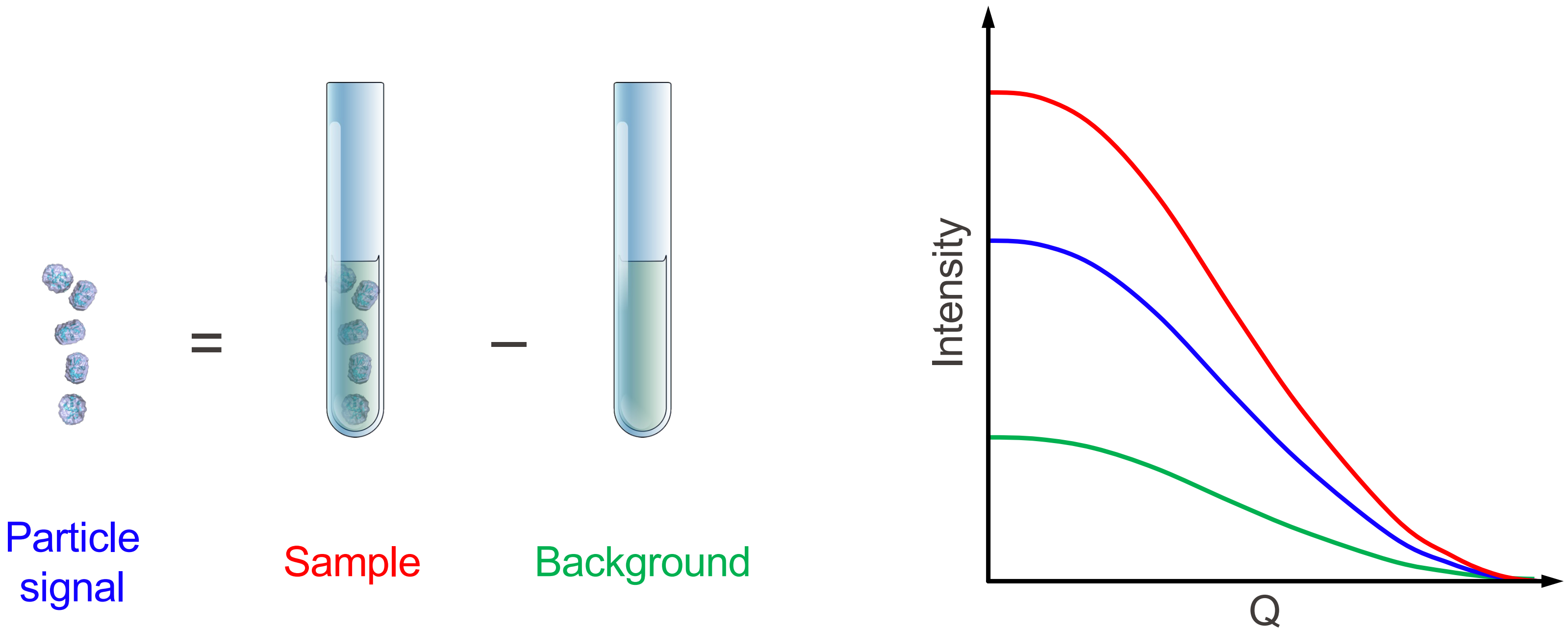


$$\mathrm{FWHM} = (8\ln 2)^{1/2}\sigma \approx 2.355\,\sigma$$

Experimental details



Background subtraction



X-ray reflectometry

Introductory comments

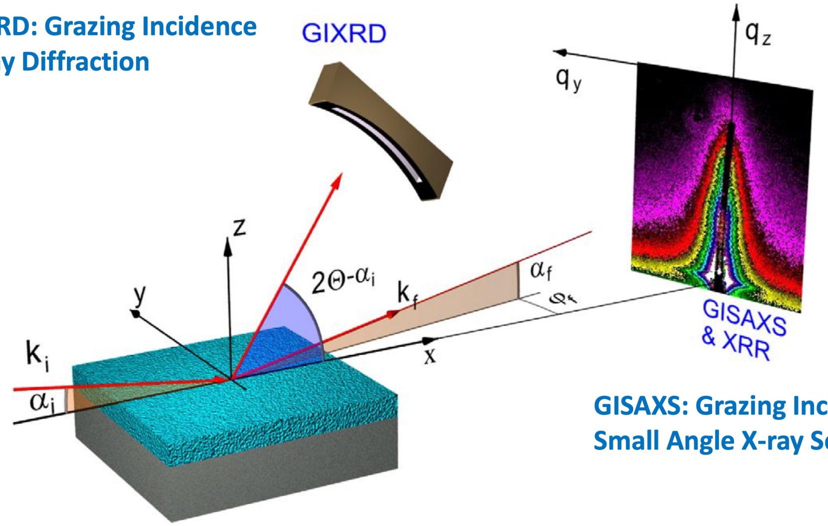
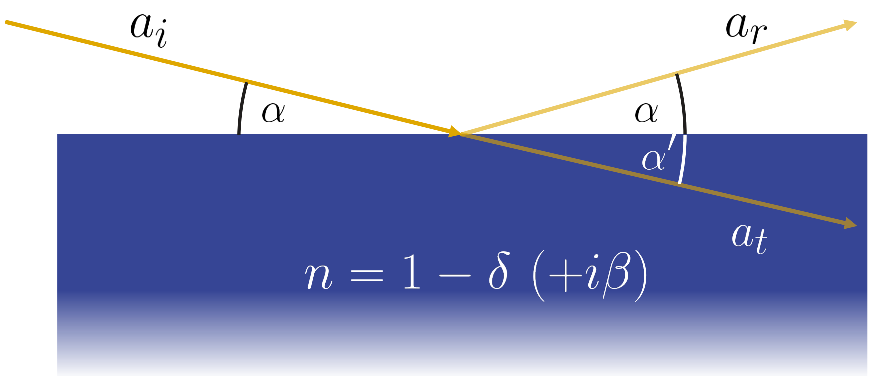


Image taken from:
https://psec.uchicago.edu/blogs/photocathode_development/wp-content/uploads/2013/03/Introduction-of-X-ray-Reflectivity11.pdf

- Determination of properties of surfaces, interfaces, thin films, multilayers
  - Thickness
  - Roughness
  - Density profiles
- XRR measures specularly reflected x-ray intensity as a function of α, the grazing incidence angle, typically up to approximately 2^o
  - Intensity drops $\propto \alpha^{-4} \Rightarrow$ need for SR
  - Start measurement a little below α_c

The Fresnel equations for reflectivity



$$a_i = a_r + a_t$$

- Snell's law

$$\frac{\cos\alpha}{\cos\alpha'} = 1 - \delta$$

$$\cos x \approx 1 - x^2/2 \;\; (\text{for } x \ll 1)$$

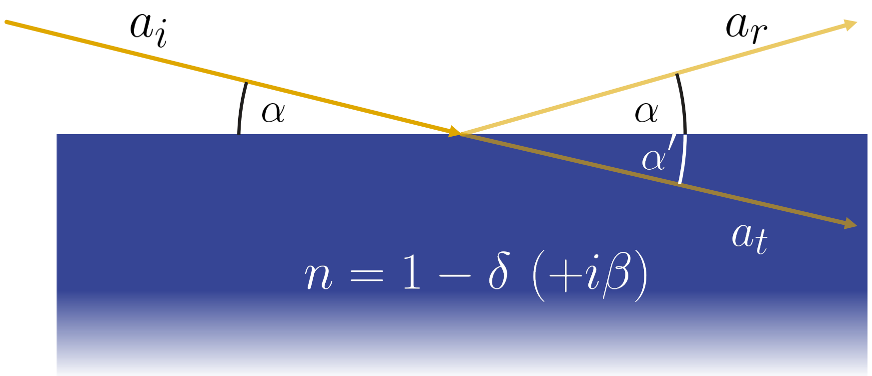
$$\Rightarrow \frac{1 - \alpha^2/2}{1 - \alpha'^2/2} = 1 - \delta$$

$$\Rightarrow 1 - \alpha^2/2 = 1 - \alpha'^2/2 - \delta + \cancel{\delta\alpha'^2/2}$$

$$\boxed{\Rightarrow \alpha^2 \approx \alpha'^2 + 2\delta}$$

The Fresnel equations for reflectivity

$$r = a_r / a_i$$



$$a_i = a_r + a_t$$

- Reflection amplitude

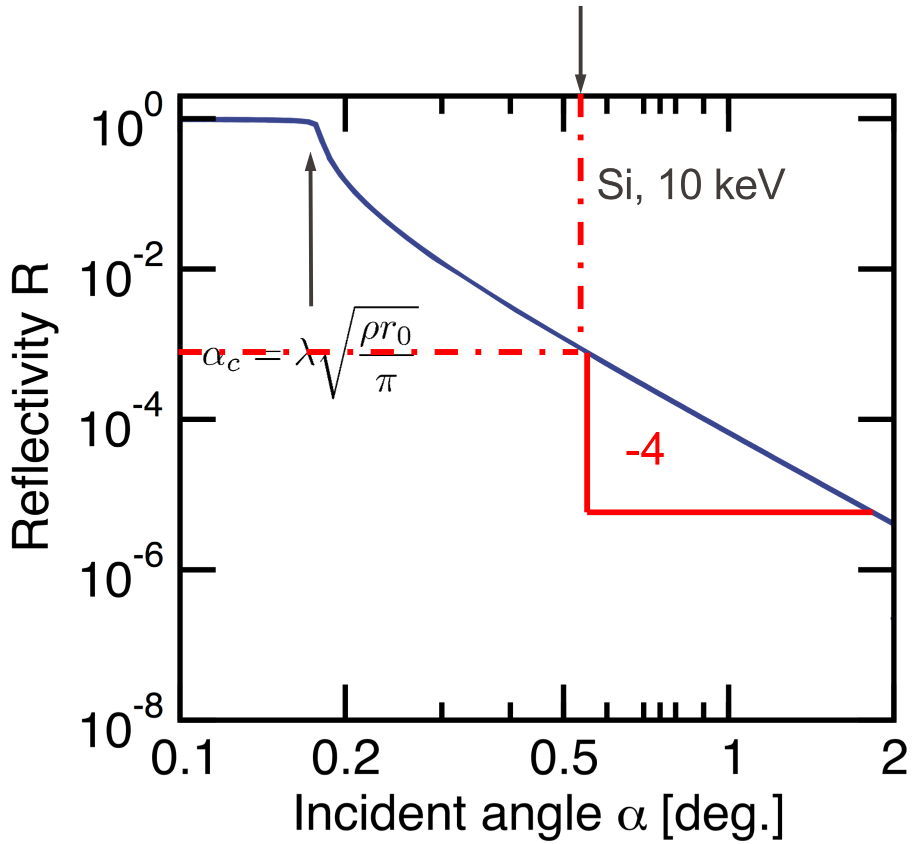
$$\begin{aligned} r &= \frac{\alpha - \alpha'}{\alpha + \alpha'} \\ &= \frac{\alpha - \sqrt{\alpha^2 - 2\delta}}{\alpha + \sqrt{\alpha^2 - 2\delta}} \\ &= \frac{1 - \sqrt{1 - 2\delta/\alpha^2}}{1 + \sqrt{1 - 2\delta/\alpha^2}} \end{aligned}$$

$$(1-x)^n \approx 1 - nx$$

$$\begin{aligned} \Rightarrow r &= \frac{1 - (1 - \delta/\alpha^2)}{1 + (1 - \cancel{\delta/\alpha^2})} \\ &= \frac{\delta}{2\alpha^2} \end{aligned}$$

$$\boxed{R = r^2 = \frac{\delta^2}{4\alpha^4}}$$

The Fresnel equations for reflectivity



- Reflectivity (perfectly smooth surface)

$$\boxed{R = r^2 = \frac{\delta^2}{4\alpha^4}}$$

- But

$$\alpha_c = \sqrt{2\delta}$$

$$\Rightarrow R = \left(\frac{\alpha_c}{2\alpha}\right)^4 ; \ \alpha \gg \alpha_c$$

- $\alpha_c \Rightarrow$ electron density, material type

$$\alpha_c = \lambda\sqrt{\frac{\rho r_0}{\pi}}$$

- Rule of thumb:

$$\alpha_c \ [\mathrm{deg.}] = \left(\frac{Z^{1/2}}{30}\right) \lambda \ [\text{Å}]$$

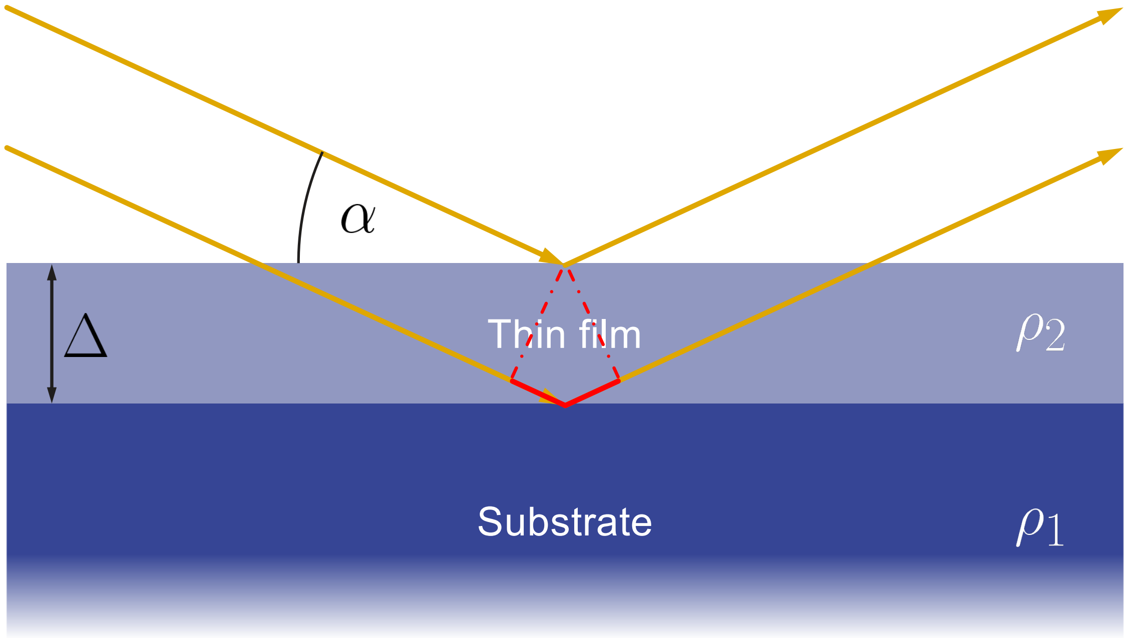
Surface and interface roughness

- Roughness $\gtrsim \lambda$?
  - Reflectivity impacted

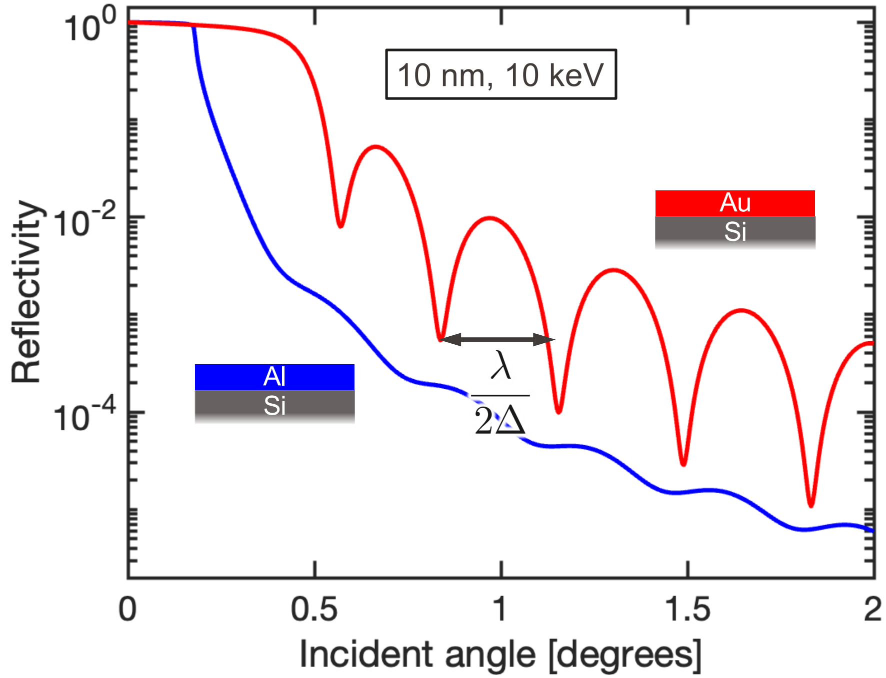
R.M.S. roughness σ

$$f_R(z) = e^{(-z^2/2\sigma^2)}$$

Thin films and Kiessig fringes

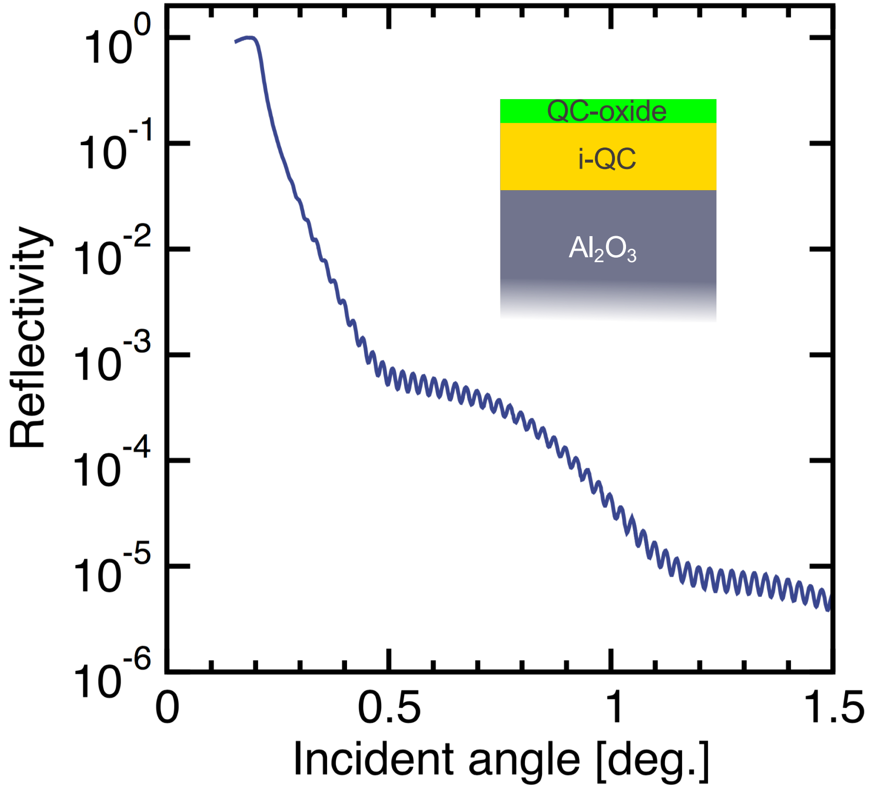


$$\mathrm{OPD} = m\lambda \approx 2\Delta\alpha$$



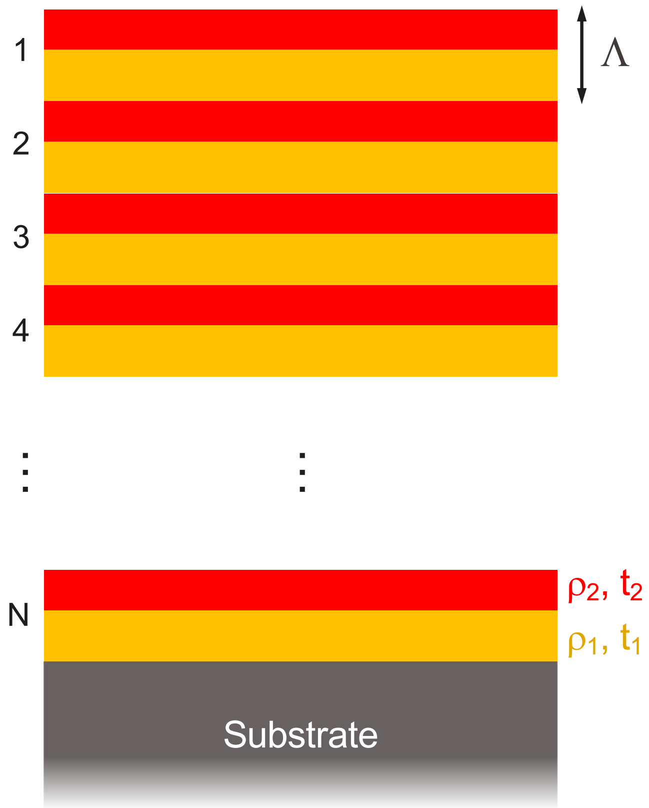
$$\rho_{\mathrm{Si}} = 0.699\ \mathrm{e}/\mathrm{\AA}^3$$
$$\rho_{\mathrm{Al}} = 0.783\ \mathrm{e}/\mathrm{\AA}^3$$
$$\rho_{\mathrm{Au}} = 4.666\ \mathrm{e}/\mathrm{\AA}^3$$

Thin film example – quasicrystal TiNiZr on Al_2O_3



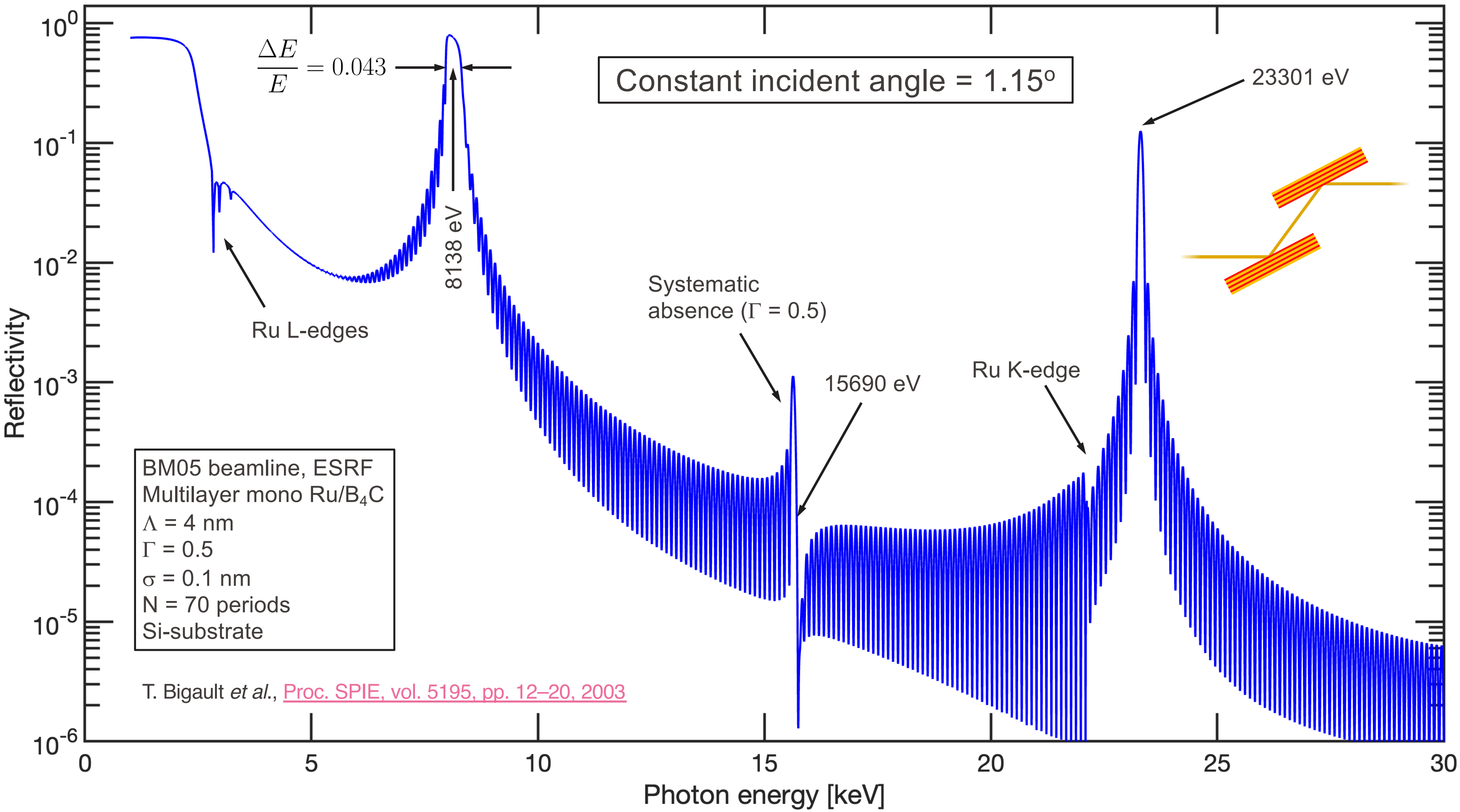
- TiNiZr alloy icosahedral quasicrystal thin film deposited on sapphire(0001)
  - 120 nm thick
  - 1-Å radiation
    - Slow oscillation: $\Delta\theta = 0.72^o$
    - $\Delta = \lambda/(2\Delta\theta) = 3.98$ nm
  - Oxidized in air $\Rightarrow$ 4 nm QC-oxide

Multilayers



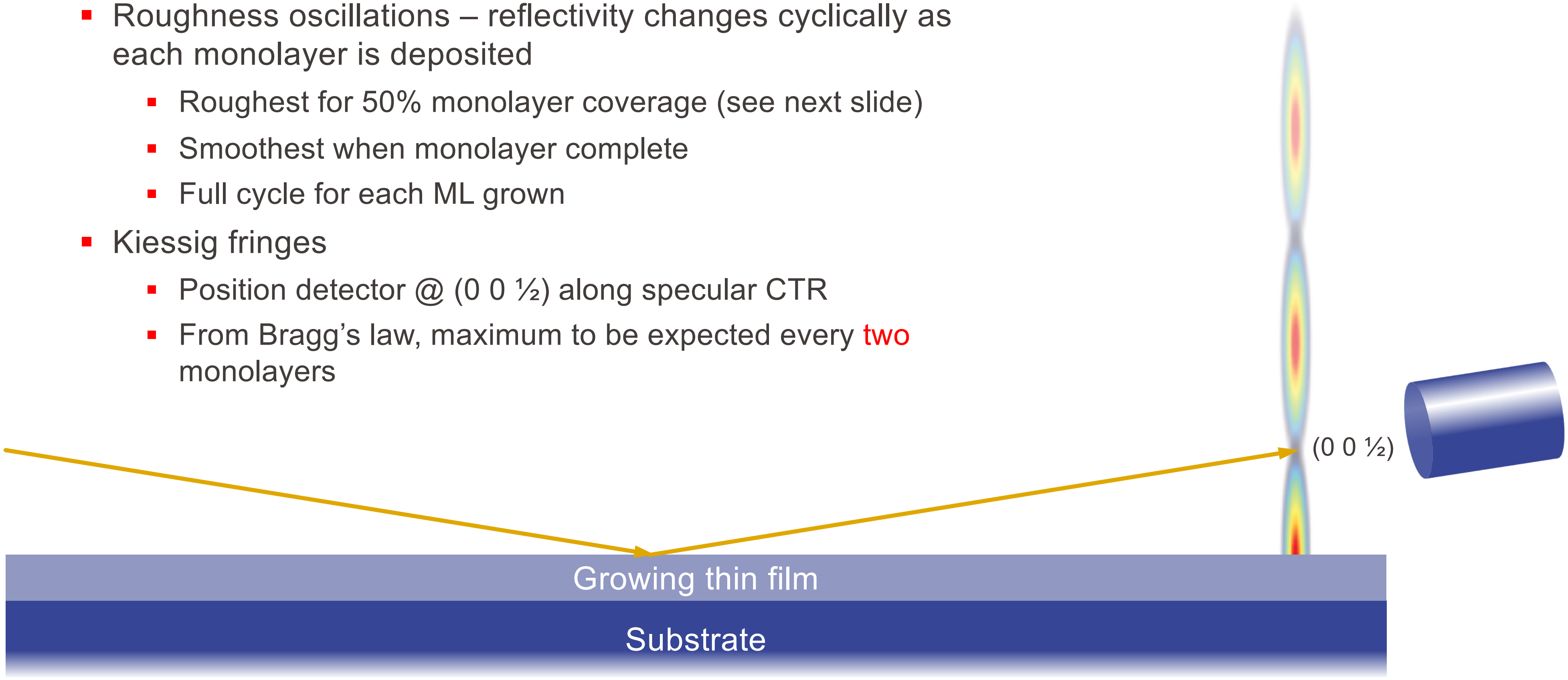
- ML defined by:
  - Two sublayers of differing electron density
    - One low density ρ_1, thickness t_1
    - One high density ρ_2, thickness t_2
  - Periodicity $\Lambda = t_1 + t_2$
  - Ratio of t_1 sublayer thickness to $\Lambda = \Gamma$
  - Number of periods N
  - Substrate type
  - Interfacial interdiffusivity/roughness

Multilayers

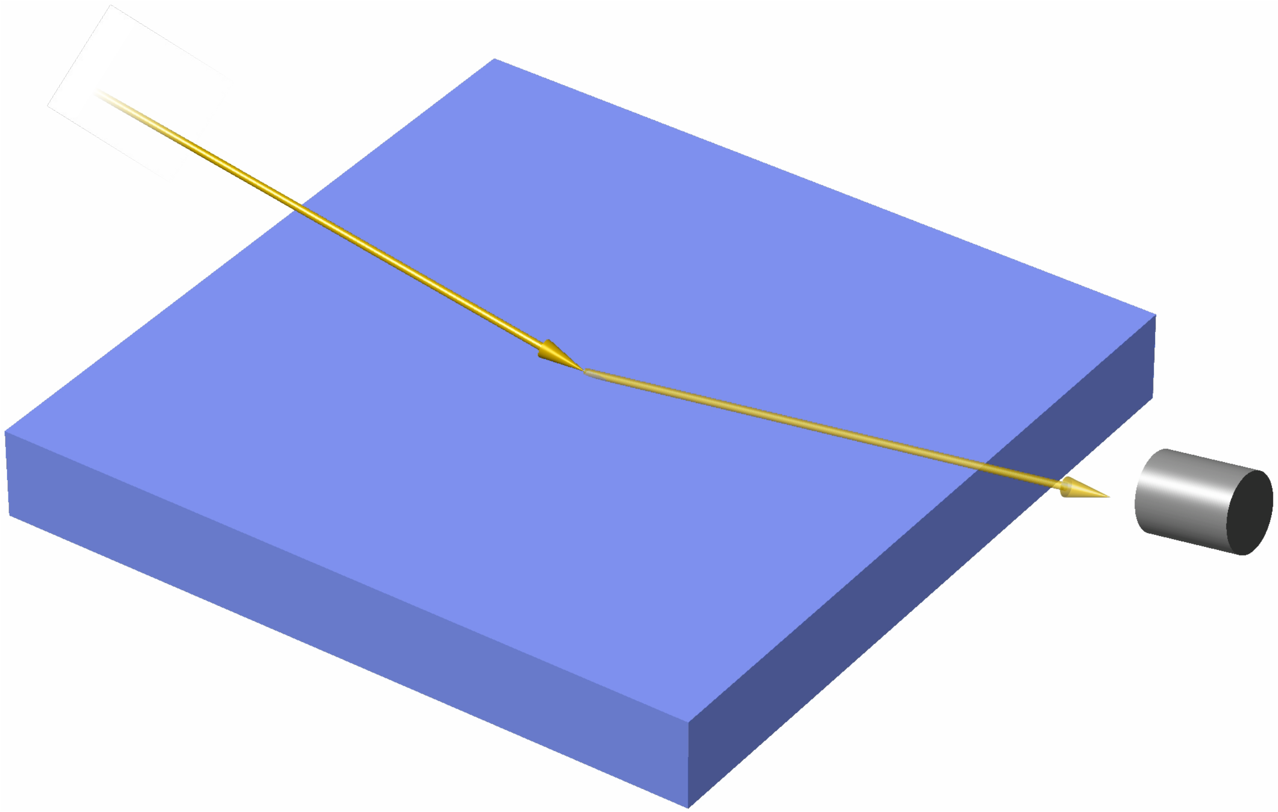


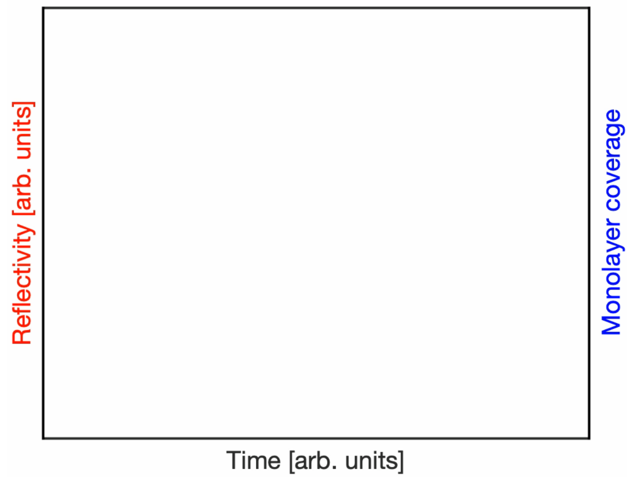
Monitoring thin film growth with XRR

- Two effects
  - Roughness oscillations – reflectivity changes cyclically as each monolayer is deposited
    - Roughest for 50% monolayer coverage (see next slide)
    - Smoothest when monolayer complete
    - Full cycle for each ML grown
  - Kiessig fringes
    - Position detector @ (0 0 ½) along specular CTR
    - From Bragg's law, maximum to be expected every two monolayers

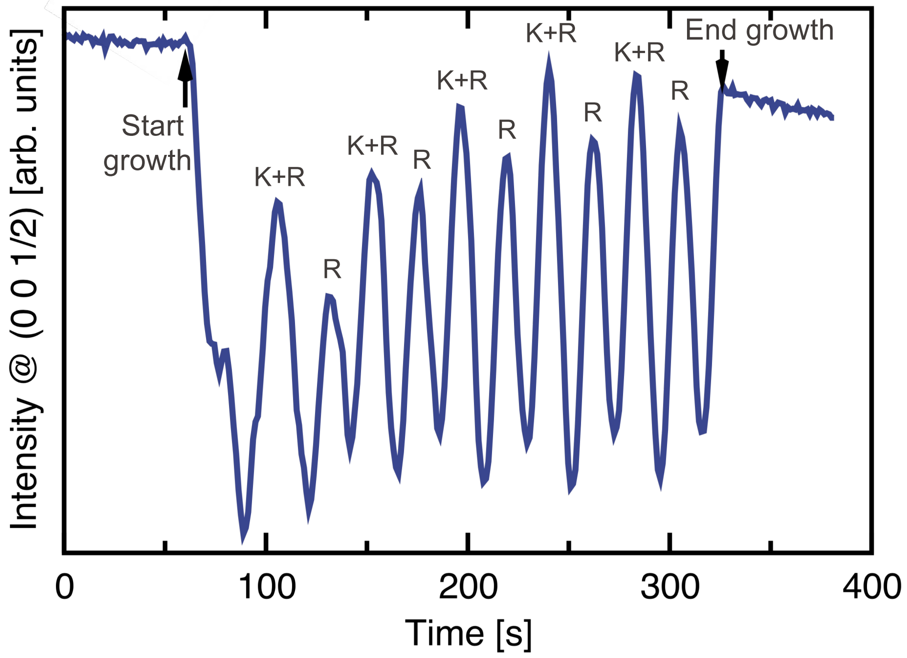


Monitoring thin film growth with XRR

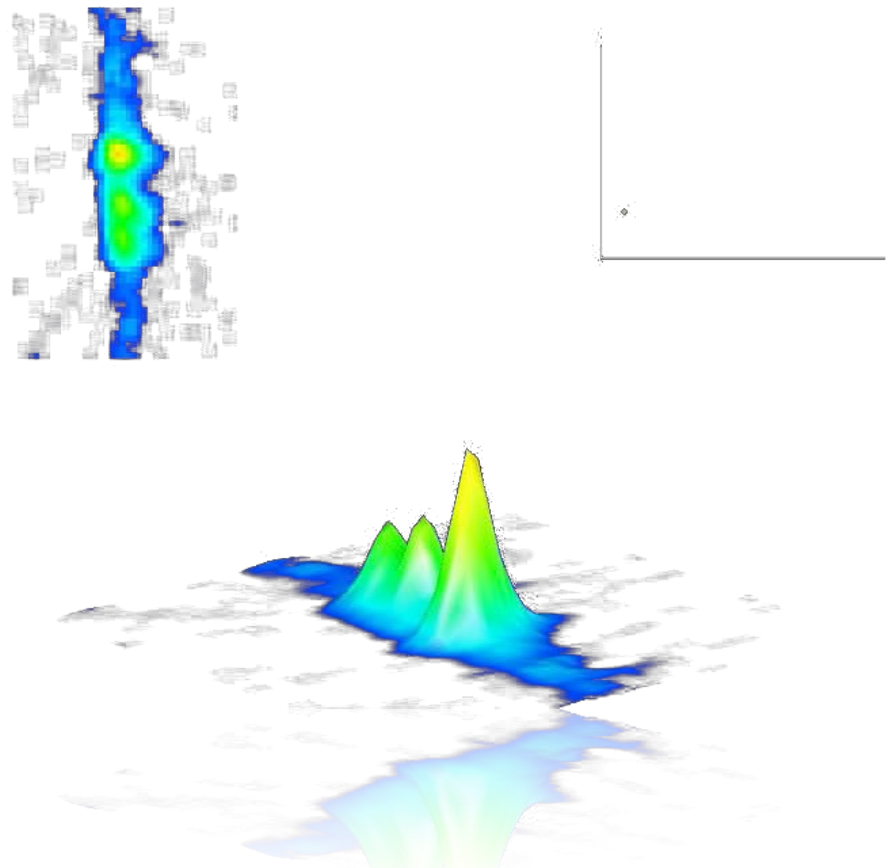




Monitoring thin film growth with XRR



12 ML growth of $La_{1-x}Sr_xMnO_3$



Movie of YBCO HTSC growth in-situ