Small Angle X-Ray Scattering (SAXS)
from Bulks and Surfaces

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Columbia University, October 28, 2015

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Center for Functional Nanomaterials, one of the 5 Department of Energy premier Nano-centers.
Broad range of methods/instruments are open for use (free of charge, via proposal) including the use beamlines

National Synchrotron Light Source II- the world brightest synchrotron (became operational in 2015)

Outline

- ✓ **Why Scattering and its Basics**

- ✓ **Small Angle X-ray Scattering (SAXS)**

  - ✓ **Scattering from Individual Objects**

  - ✓ **Scattering from Lattices and Complex Organizations**

- ✓ **Surface Scattering**

  - ✓ **Grazing Incidence Small Angle X-ray Scattering (GISAXS)**

  - ✓ **X-ray Reflectivity (XRR)**

- ✓ **Instrumentation and data processing**

- ✓ **Examples of Applications for Material Studies (through the talk)**

Probing Different Length-Scales

Crystallography   *Microstructure*   *Structure*

Virus

Proteins

Bacteria

Atomic Structure
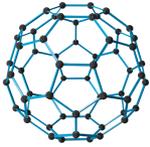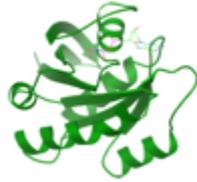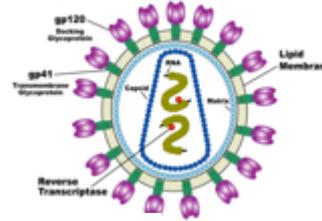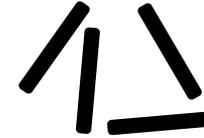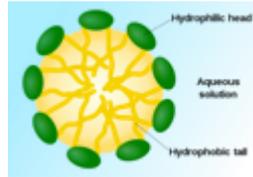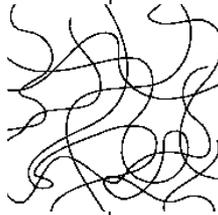
Micelles   Polymers   Grain Structure
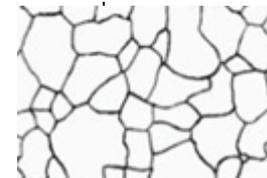
Porosity   Precipitates

Optical Microscopy

Electron Microscopy

Electron Diffr.

X-ray Diffraction   X-ray Small Angle Scattering   X-ray Ultra Small
                                                                   Angle Scattering
Neutron diffraction   Neutron Small Angle Scattering

Various Spectroscopy Methods (Inelastic scattering)

10^{-9} 10^{-7} 10^{-5}

Nanoscale objects:
same elements - new properties

Macro gold

Nano gold

Why scattering?

- **Advantages:**
  - **Fast**
  - **Meaningful global average instead of just local (spurious?) information**
  - **Can probe buried, 3D structures (instead of surfaces or projections)**
  - **In-situ and non-destructive:**
    - **Can probe in liquid state, *during* transformations, inside functioning devices, …**
- **Main disadvantage:**
  - **Hard to interpret data**
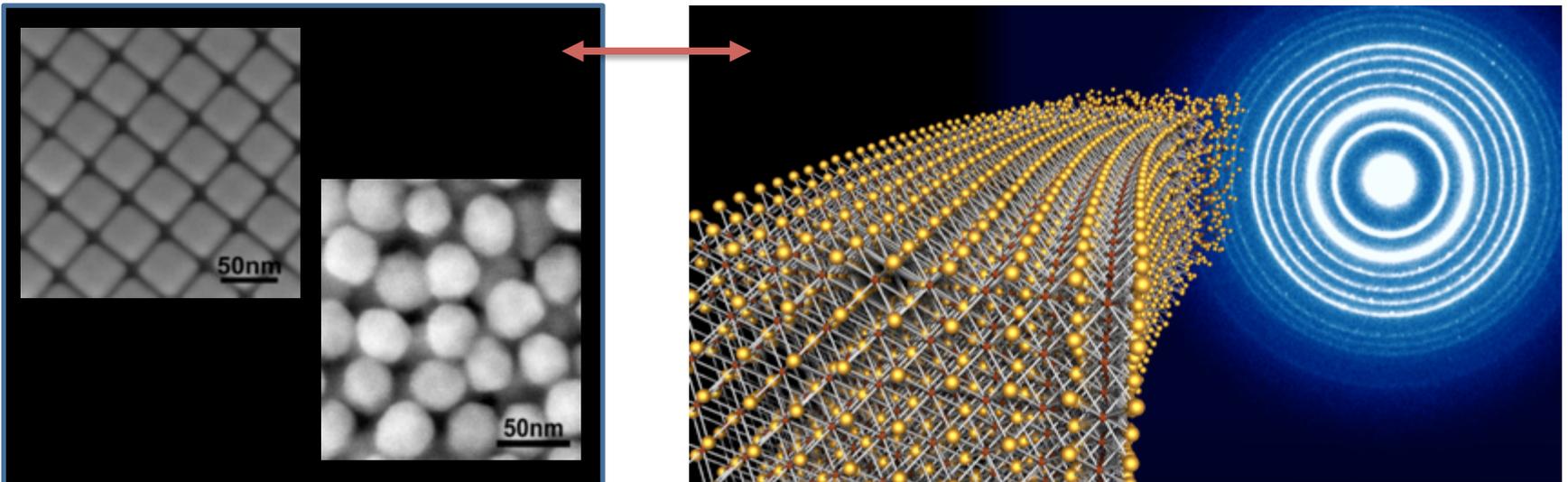
Different "kinds" of Scattering

Organization of constituents
("Structure Factor")

		Random	Periodic
Constituents ("Form Factor")	Simple	Gases, liquids, glasses, …	Crystals, …
	Arbitrary	Colloids, proteins in solution, …	Lithography, nano-particle lattices, …
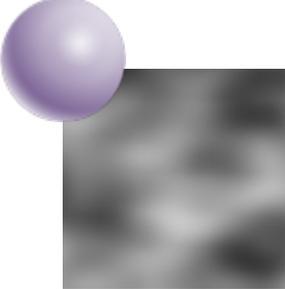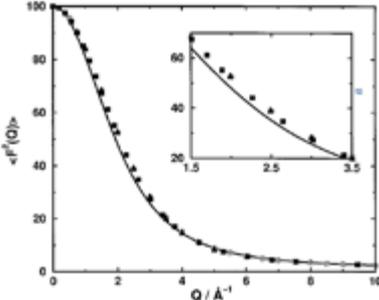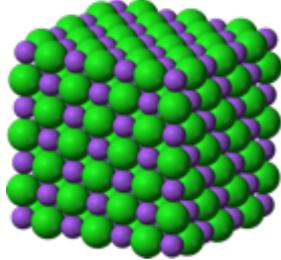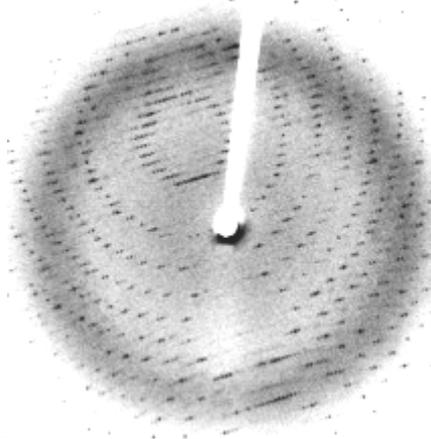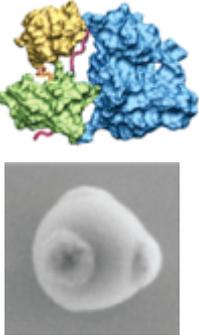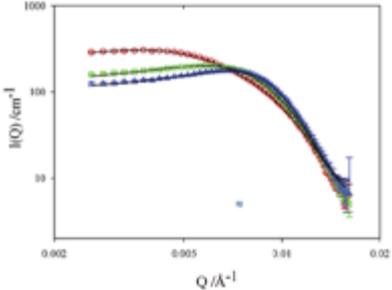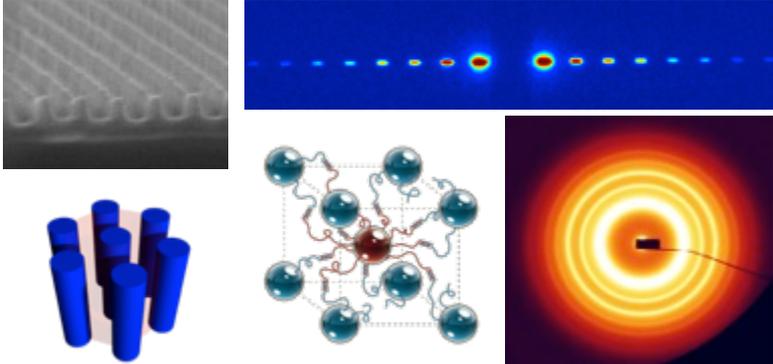
A Brief History of Small Angle Scattering

- SAS methods were introduced in the 1930s, by André Guinier

- Throughout the 1938 – 1950s, Guinier and others developed SAS fundamentals (inc. Peter Debye, Otto Kratky, Günther Porod)

- First experiments with proteins occurred in the 1950s

- The use of SAS increased with the 'user friendly' beamlines that adopted the method.

- Since the mid-1990's, the number of SAS publications has increased.
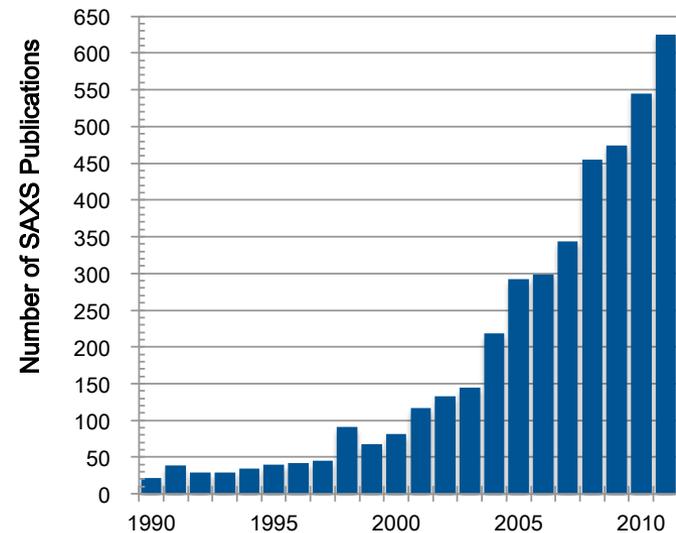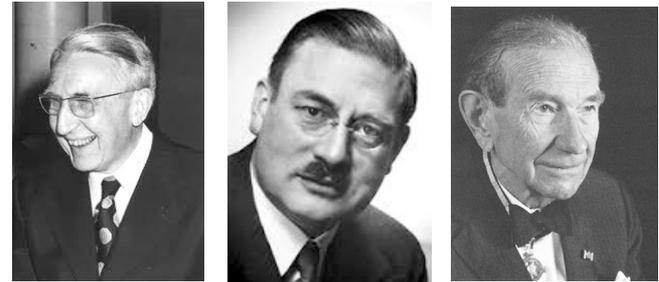
What can We Measure?

- Size of scatterer
- Amount of scatterers
- Polydispersity
- Distribution of scatterers
- Shape of scatterers
- Morphology of scatterers
- Composition of scatterers
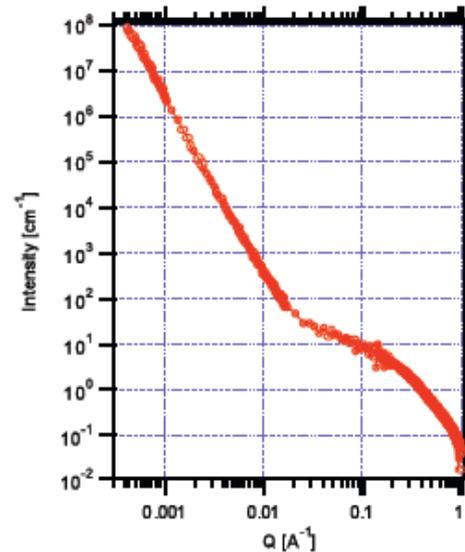
- There is *strong* dependence between some of these terms.
- SAS experiments, *complemented by other measurements*, can yield rich information about the microstructure.

Scattering vs Imaging: Reveal the Difference

Hydrogels formed from block copolymer of Lysine and Valine

Darrin Pochan, U. Delaware
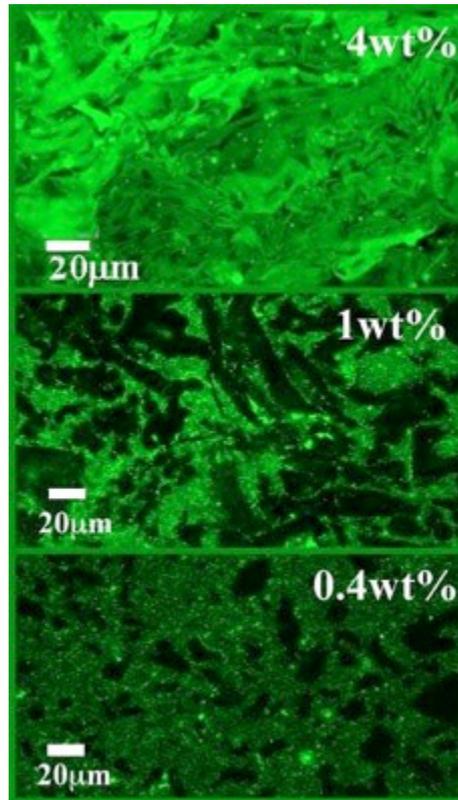
Confocal Microscopy
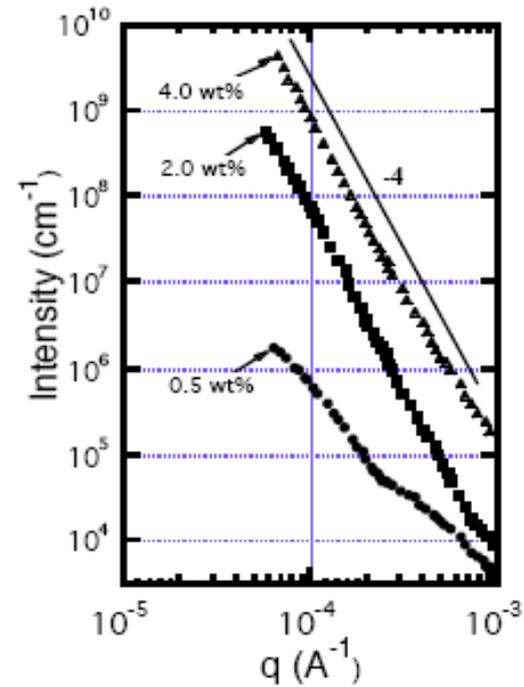
USANS

Images miss differences

Scattering vs Imaging: Discover the Similarity

Isotactic polystyrene foams

Jim Aubert, SNL

$Rg = 0.50\ \mu m$

$Rg = 0.35\ \mu m$

$\sim q^{-2.8}$

Intensity $(cm)^{-1}$

- Ball
- Strut

$q\ (A^{-1})$
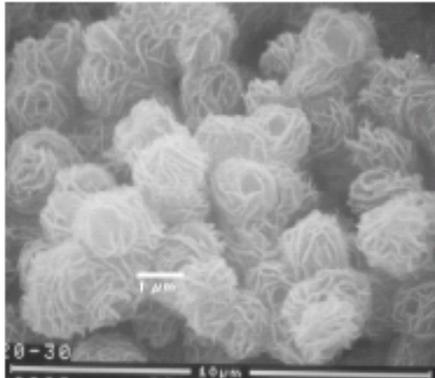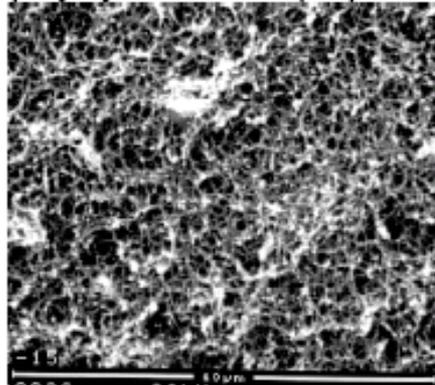
10 µm
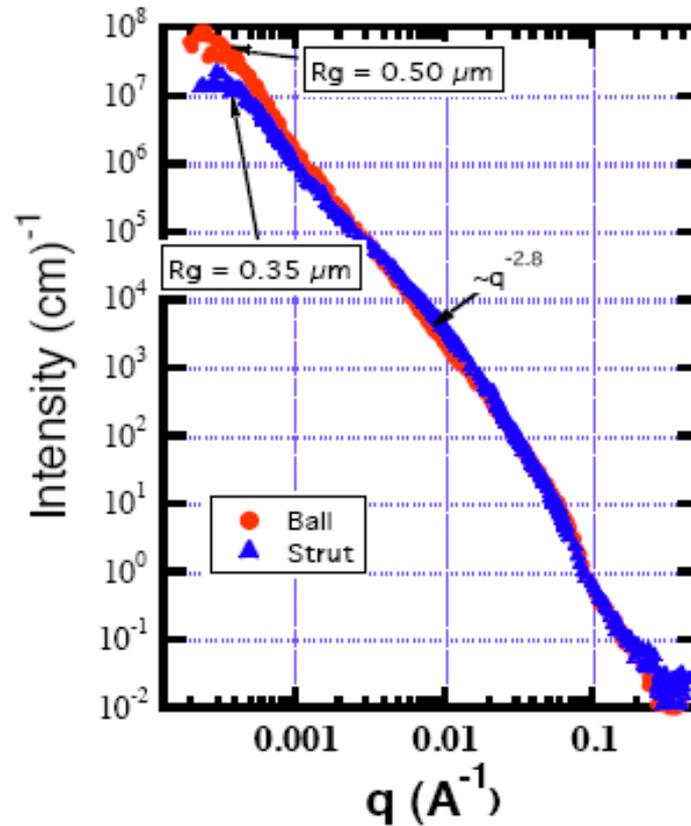
Images miss similarity

Scattering methods

- Neutron Scattering - scatter from nucleus, element sensitive
- X-rays scatter off of all the atoms/particles in the sample (sensitive to electron density difference)
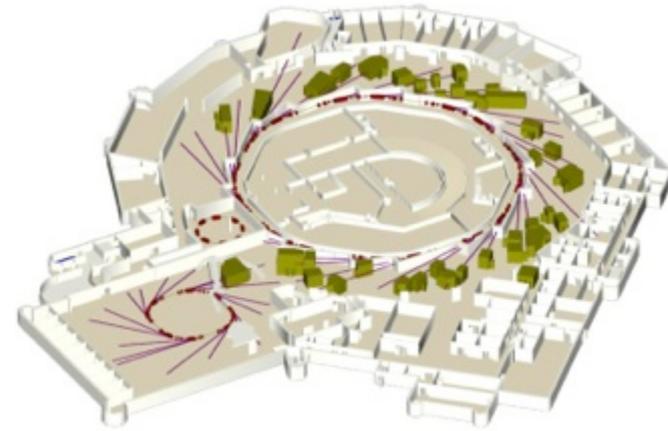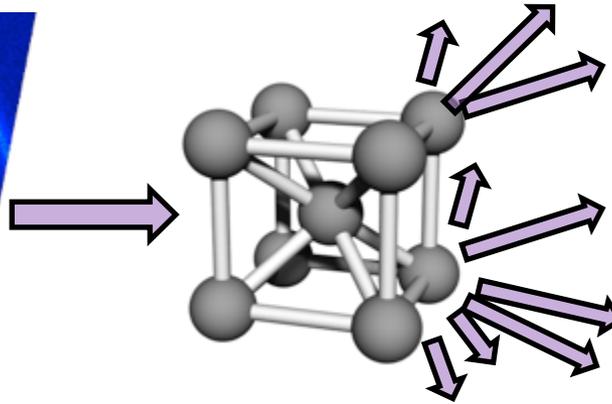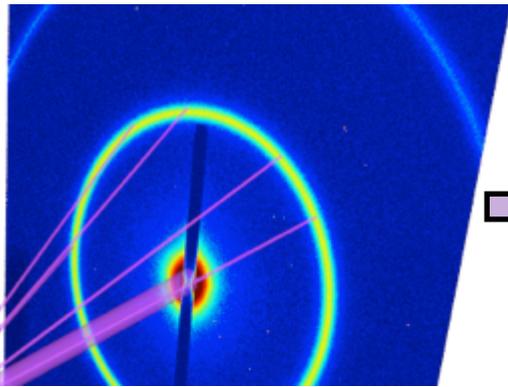
- The scattered waves interfere, which produces distinct spots or rings at specific angles…

$$n\lambda = 2d\sin\theta$$
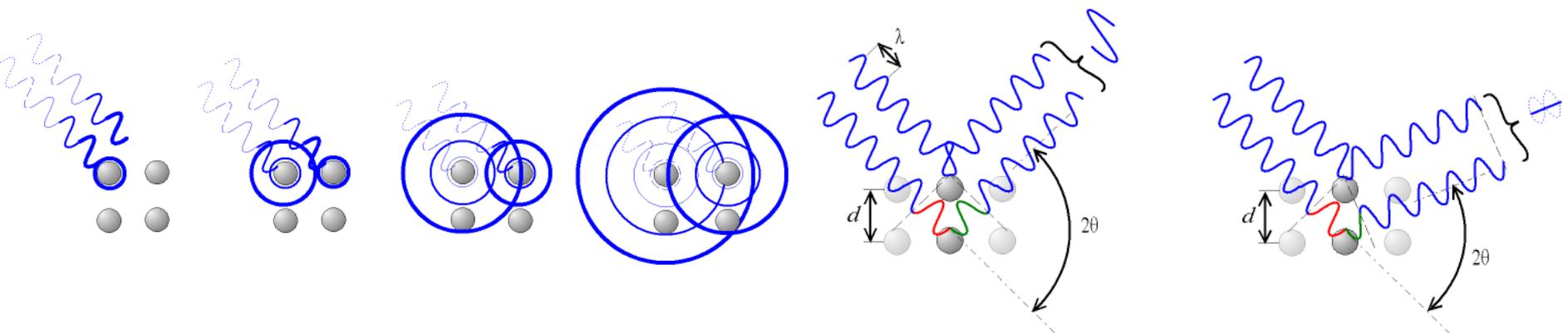
Small Angle Scattering

Sizes measured

X-ray source   X-ray detector

Bragg angle = θ

2θ = diffraction angle

Sample
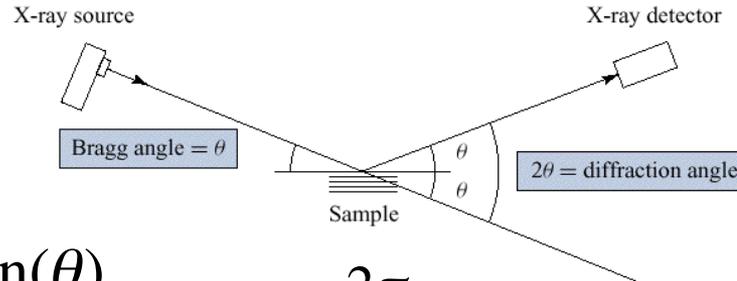
$$q = 4\pi \frac{\sin(\theta)}{\lambda} \qquad d = \frac{2\pi}{q}$$

Q [A^{-1}]	D [nm]	2Q [deg] 12keV
1	0.6	10
0.1	6	1
0.01	60	0.1
0.001	600	0.01
0.0002	3000 (3 um)	0.001

Detector dynamic range is important – Intensity ~ q^4

Q or q is wavevector transfer
D or d is characteristic length

Crystallography vs. SAXS
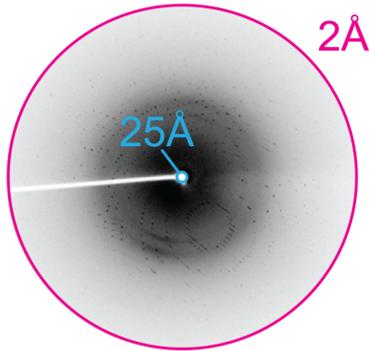
hkl	I	σ(I)
002	14800	450
003	31	28
004	16450	532
005	97	54
006	12950	385
008	17780	620

Advantage	Limitation
Atomic structure information	Requires a crystal
Readily available software	Flexible portions may not be seen

Integrated profile

Log(I) vs q [Å^{-1}]
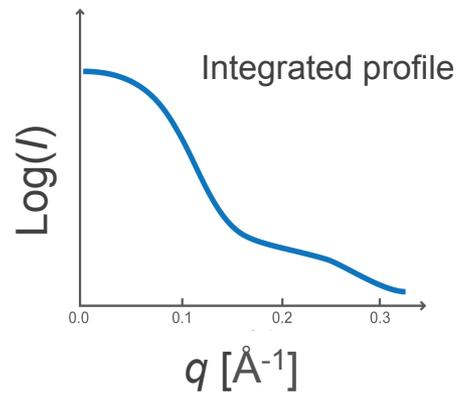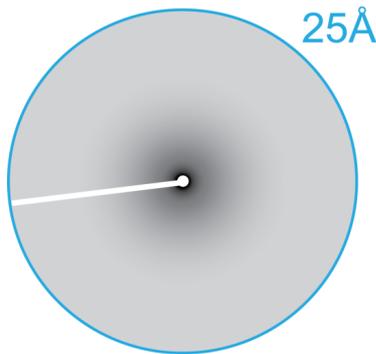
Advantage	Limitation
Analysis in native conditions	Low resolution (10-20 Å)
May see 'floppy' domains not apparent in crystal structures	Modeling ambiguity

Images from Q Rev Biophys. 40, 2007, 191

Atomic Form Factor

Atomic form factors are fundamental parameters in X-ray techniques.

Electron cloud in atoms has radial density distribution $\rho(r)$

$$f(q) = 4\pi \int \rho(r) r^2 \frac{\sin(qr)}{qr} dr$$

$\rho(r)$ were obtained from quantum chemical calculations. Atomic form factors for all elements and important ions were tabulated in International Tables for Crystallography and other handbooks.

- $f(0)=Z$

- Atoms with higher Z will scatter stronger.

- $f(q)$ decreases slowly along q in region (SAXS) of q close to 0

- In low-resolution model reconstruction from SAXS data using $f(q)$=**const**
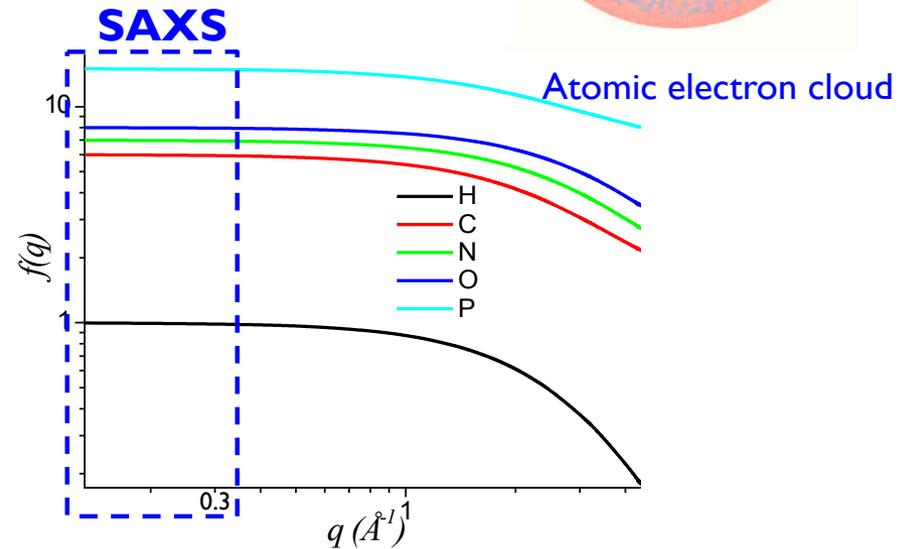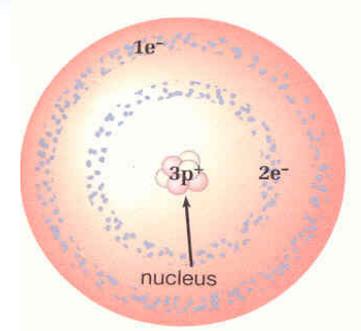
Data taken from International Tables for Crystallography, Vol. C, Table 6.1.1.1

Examples of scattering

Diffuse scattering
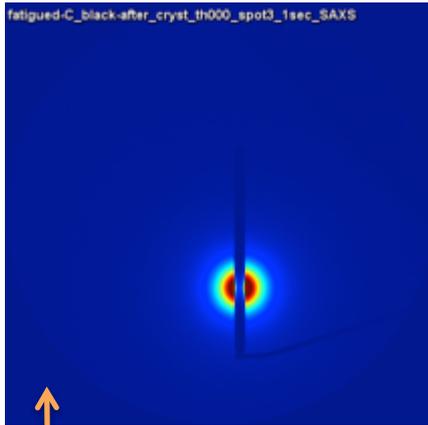
Multiple length scales. Complimentary methods are helpful

- Large dynamical range of scattering
- Not necessarily a specific features are present
- Integration and background corrections needed

Weak ordering
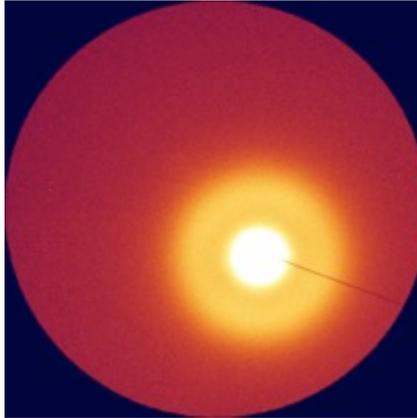
Prevailing length scale in the system

Oriented sample
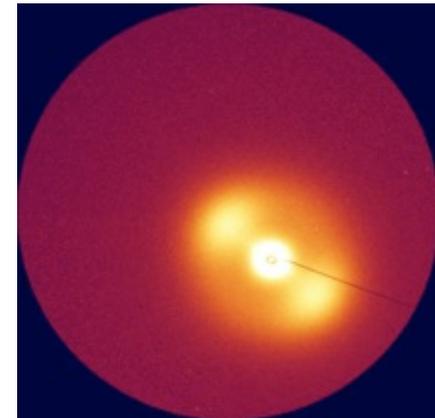
Oriented sample. Can find orientation direction and degree of orientation
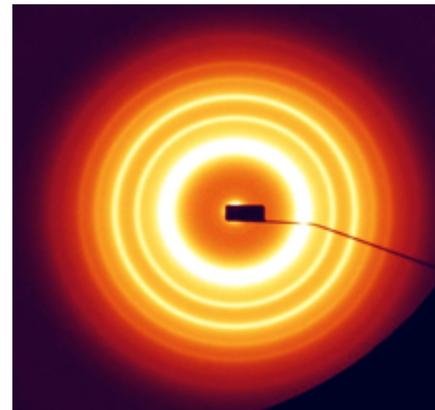
Small Angle Diffraction Well defined periodic nanostructures

What can we see?

Scattering length density

Measure of interaction difference of radiation with atoms/molecules in object and surroundings

ρ_2

ρ_1

LIGHT: refractive index (electronic structure)
X-RAYS: scattering length (electronic structure)
NEUTRONS: scattering length (nuclear structure)

Mass density

Scattering length
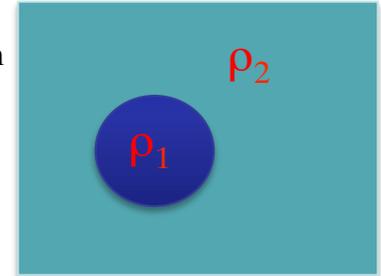
$$\rho = \frac{\rho_m N_A}{M} \sum_i n_i b_i$$

$$b_i = \frac{e^2}{4\pi\varepsilon_0 m_e c^2} f_1$$
$$= r_e f_1$$

[units Å^{-2}]

Molecular weight

real part of atomic scattering factor

Contrast = (ρ_1 - ρ_2)^2

natural (e.g. porous silica and air) or deliberately changed

valid for n and X-rays (ASAXS)
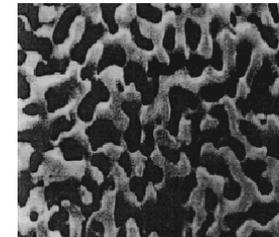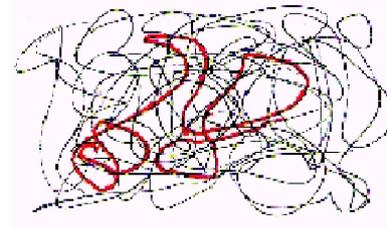
When the monster came, Lola, like the peppered moth and the arctic hare, remained motionless and undetected. Harold. of course. was immediately devoured.

© 1988 Universal Press Syndicate

When the monster came, Lola, like the peppered moth and the arctic hare, remained motionless and undetected. Harold, of course, was immediately devoured.

Contrast in scattering

Babinet principle
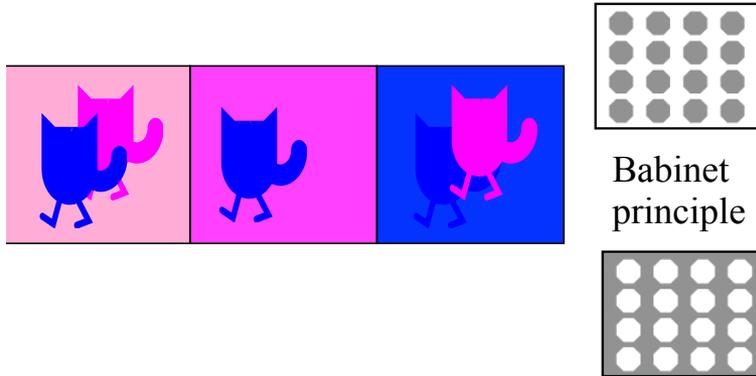
Element	Neutrons (10^{-12} cm)	X-rays (10^{-12} cm)	Electrons	
^{1}H	-0.374	0.28	1	○
^{2}H (D)	0.667	0.28	1	○
C	0.665	1.67	6	
N	0.940	1.97	7	
O	0.580	2.25	8	
P	0.520	4.23	15	

Anomalous Small-Angle X-ray Scattering

- Why anomalous SAXS?
  - Element-specific contrast variation
  - Use to separate population distributions of scatterers
- Will ASAXS solve every problem?
  - Not even close
  - The easy problems are already taken

Anomalous dispersion terms of Yb in SN-88 near the Yb L_{III} edge (8.939 keV)
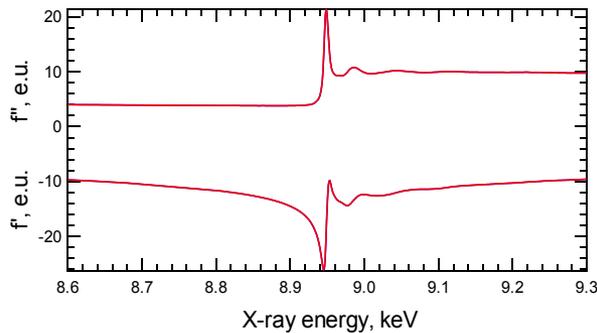
Neutrons

Contrast matching
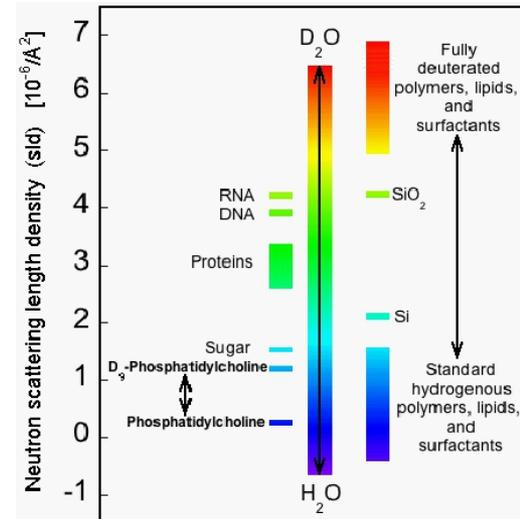
SAXS is a broad range of methods
what type of information it can provide?

Small angle scattering,
form factor, ~F(q), (dilute limit)
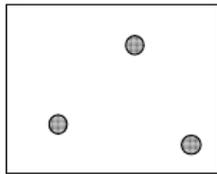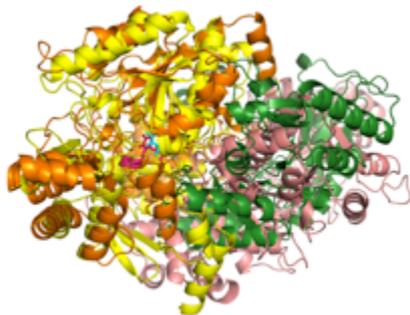
Small angle diffraction,
form factor, ~S(q), (particles "interact")

Same particle size and shape
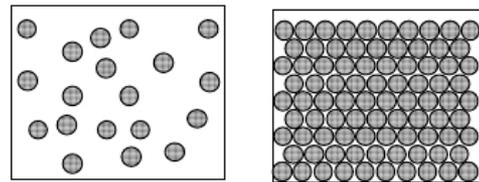
Particle size and shape variations

Same particle size and shape

Multiple particle types
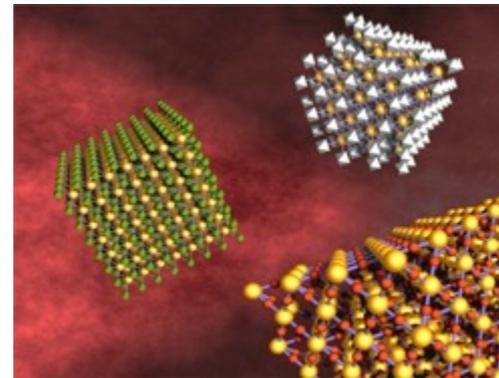
Outline

SAXS Experiment

sample

beam stop

X-ray source

Angles are are below few deg.

2θ

Wavevector transfer, or momentum transfer

$$q = \frac{4\pi \sin\theta}{\lambda}$$

X

momentum transfer

degrees

q [Å^{-1}]

1D avg

Intensity

Azimuthal integration

q [Å^{-1}]

$\mathbf{q} = \mathbf{k} - \mathbf{k_0}$

scattered X-rays

k

2θ

k_0

incoming X-rays
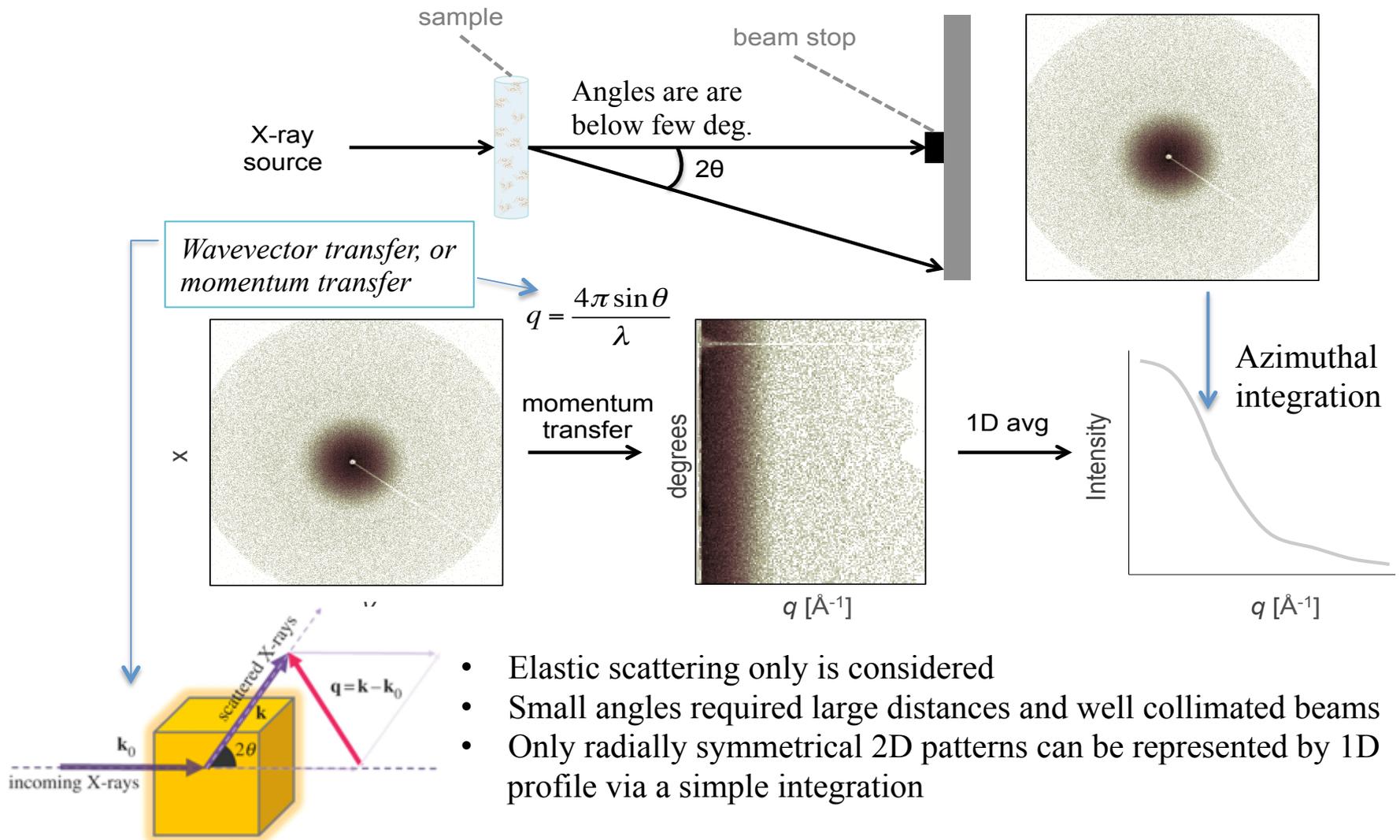
- Elastic scattering only is considered
- Small angles required large distances and well collimated beams
- Only radially symmetrical 2D patterns can be represented by 1D profile via a simple integration

SAXS from Molecular Solutions

Atomic apparent form factor / contrast :

$$A_j(q) = f_j(q) - g_j(q)$$

atomic form factor in vacuum

form factor of excluded solvent

X-ray scattering total amplitude:

$$\sum_j A_j \exp(i\vec{q} \bullet \vec{r}_j)$$

In solution, X-ray beam sees all orientations of molecules :

$$I(q) = \langle I(\vec{q}) \rangle_\Omega = \left\{ \left\langle \sum_j A_j \exp(i\vec{q} \bullet \vec{r}_j) \right\rangle_\Omega \right\}^2$$

loss of phase information

loss of angular direction

$$= \sum_j \sum_k A_j A_k \frac{\sin(qr_{jk})}{qr_{jk}} = \sum_j A_j^2 + 2\sum_j \sum_{k>j} A_j A_k \frac{\sin(qr_{jk})}{qr_{jk}}$$

Atom pair distance / Structural information

Individual contribution

interference

Solution x-ray scattering is a 1D profile which encodes molecular structural information.

form factors of particles j and k can be used in a similar way

Real space 3D Molecule

fixed orientation

Reciprocal space; 2D anisotropic image/data

averaged orientation

Reciprocal space; 2D isotropic image/data

Radial averaging

1D profile Reciprocal space

1D scattering profile is the Fourier transform of 3d structure.
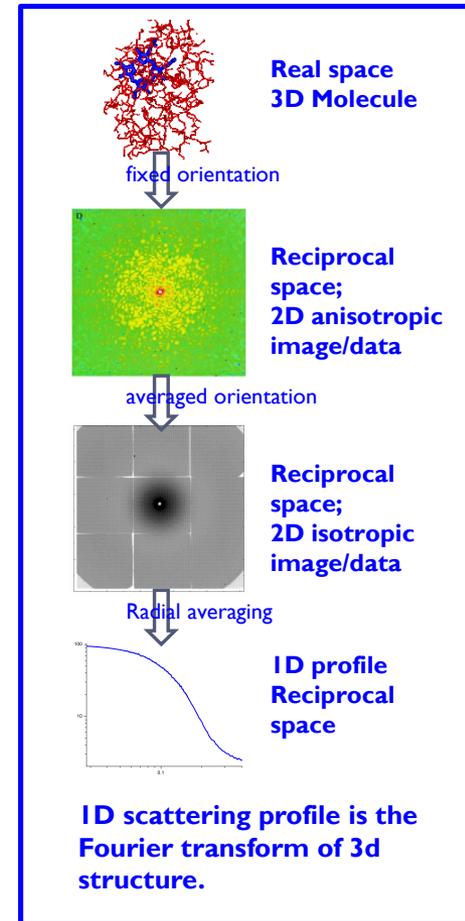
Depends on structure/ interactions

What do we measure in SAXS?

Measured quantity

$$\boxed{I(q) \propto \frac{d\Sigma(q)}{d\Omega} = \frac{N}{V} V^2_{particle} (\rho_1 - \rho_2)^2 P(q) S(q)}$$

Dilute = independent scatterers = NO interparticle effects

Total intensity = sum of individual particle scattering

$$I(q) \propto \frac{N}{V} V^2_{particle} (\rho_1 - \rho_2)^2 P(q) \cancel{S(q)}$$

P(q) = Form factor - SHAPE and SIZE information

P(q) is dimensionless and P(0) = 1

In the literature, as in this presentation, both P(q) and F(q) are commonly used symbols for form factors

Form Factor for Sphere

The form factors of some objects with simple shapes have analytical formula expression, for example, sphere. Sphere is a widely used model in characterizing the size or size distribution of globular particles in structural biology and nanoscale material science.

Sphere with homogenous electron density and radius R:

$$F(q) = \frac{3(\sin(qR) - qR\cos(qR))}{(qR)^3}$$

$$I(q) = F^2(q) = \left(\frac{3(\sin(qR) - qR\cos(qR))}{(qR)^3} \right)^2$$

From the scattering curve, we can estimate the radius of the sphere:

$$R \approx \frac{4.493}{q_{01}}$$

For centro-symmetric object:

$$A(\vec{q}) = \int \rho(\vec{r})\exp(-i\vec{q}\cdot\vec{r})\,dr$$

$$A(q) = 4\pi \int_0^\infty \rho(r)\frac{\sin(qr)}{qr}r^2 dr = 4\pi \int_0^R \frac{\sin(qr)}{qr}r^2 dr$$

$$= \frac{4\pi}{q} \int_0^R \sin(qr)\,r\,dr = \dots \quad \text{(partial integration)}\dots$$

$$= \frac{4}{3}\pi \, R^3 \, \frac{3[\sin(qR) - qR\cos(qR)]}{(qR)^3}$$
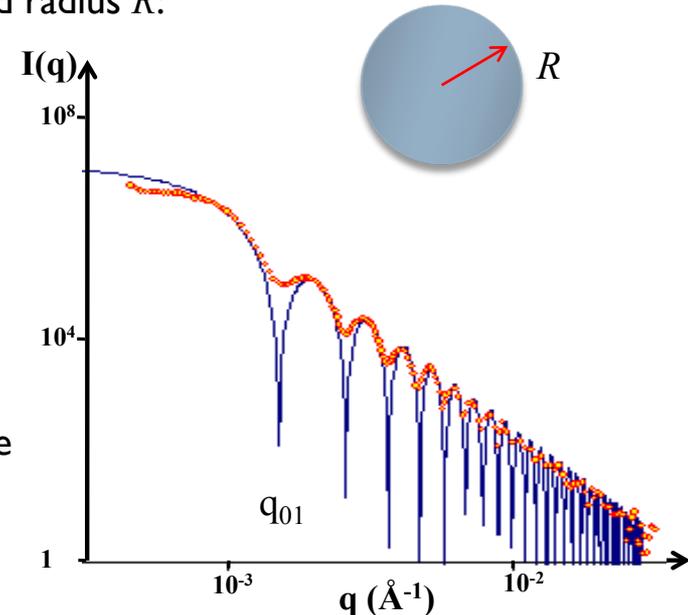
> Scattering profile of silica spheres (red) and simulation based on perfect sphere (blue)
> Discrepancy of silica scattering from sphere model due to size polydispersity, imperfect spherical shape, etc.

Figure modified from: Lambard, Lessieur and Zemb, J. Phys. I France, 1992, (2) 1191

Effect of Particle Size and Polydispersity

(volume fraction = 1%, contrast = 10^{-6} Å^{-2}, bkgd = 0.01)

Polydispersity

100 Å
$q_{firstmin}=4.493/R=0.044$ Å^{-1}

400 Å
$q_{firstmin}=4.493/R =0.011$ Å^{-1}
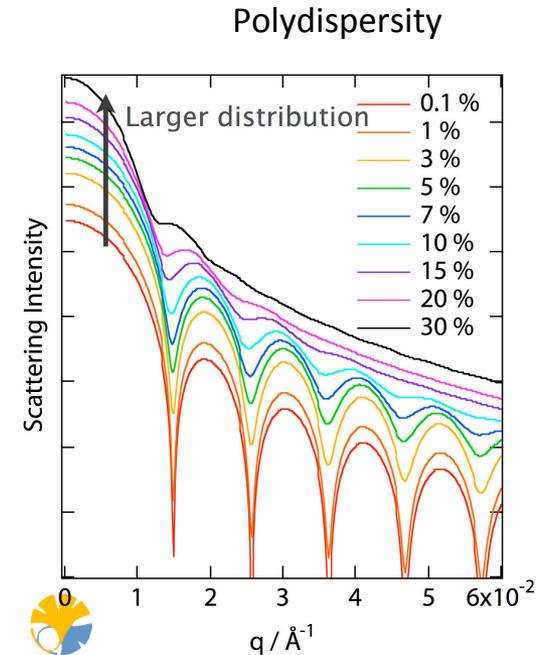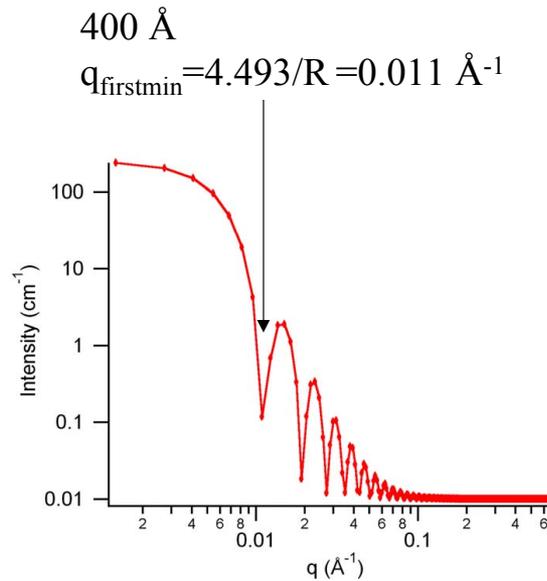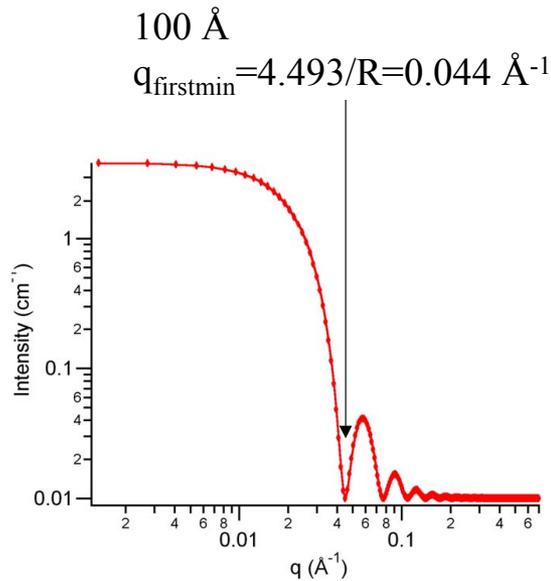
- Instrument resolution can significantly affect the data, masking "true" size distribution, the sample might be not so bad (polidisperse) as it might look
- Resolution should be accounted to separate effect of polydispersity

Scattering from Individual Shaped Objects

Common Form Factors of Shaped Objects (many more were computed numerically)

SAXS Scattering

Morphologies	$P(q)$ or $P^2(q)$ – depends on source	Morphologies
Spheres (radius :R)	$\dfrac{9}{(qR)^6}[\sin(qR) - qR\cdot\cos(qR)]^2 = A_{sph}^2(qR)$	
Spherical shells (outer radius: R_1 inner radius: R_2)	$\dfrac{[R_1^3\cdot A_{sph}(qR_1) - R_2^3\cdot A_{sph}(qR_2)]^2}{(R_1^3 - R_2^3)^2}$	
Triaxial ellipsoids (semiaxes: a,b,c)	$\int_0^1\int_0^1 A_{sph}^2[q\sqrt{a^2\cos^2(\pi x/2) + b^2\sin^2(\pi x/2)(1-y^2)_1 + c^2 y^2}\,]\,dx\,dy$	
Cylinders (radius: R length: L)	$4\int_0^1 \dfrac{J_1^2[qR\sqrt{1-x^2}\,]}{[qR\sqrt{1-x^2}\,]^2}\dfrac{\sin^2(qLx/2)}{(qLx/2)^2}\,dx$ $J_1(x)$ is the first kind Bessel function of order 1	
Thin disk (radius: R)	By setting L = 0 $\qquad\dfrac{2 - J_1(2qR)/qR}{q^2R^2}$	
Long rod (length: L)	By setting R = 0 $\qquad \dfrac{2}{qL}\int_0^{qL}\dfrac{\sin(t)}{t}\,dt - \dfrac{\sin^2(qL/2)}{(qL/2)^2}$	
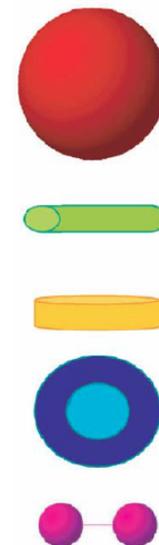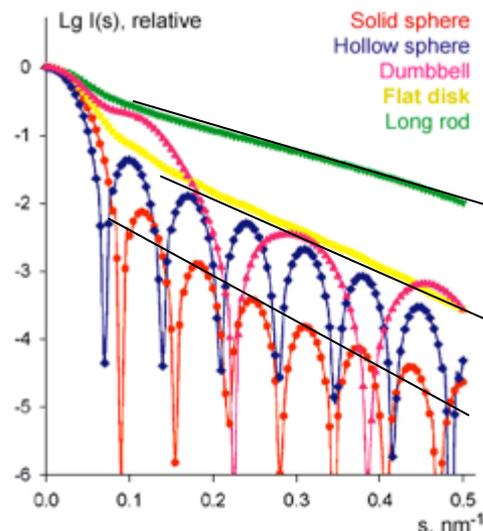
"Structure Analysis by Small Angle X-Ray and Neutron Scattering" L. A. Feigen and D. I. Svergun

$$I(q)\sim q^{-\alpha}$$

$$\alpha = \begin{cases} 3 & \text{Sphere} \\ 2 & \text{Disk} \\ 1 & \text{Rod} \end{cases}$$

Radius of Gyration and Guinier Law

$$R_g^2 = \frac{\iiint |\mathbf{r} - \mathbf{r}_c|^2 \rho(\mathbf{r})d^3\mathbf{r}}{\iiint \rho(\mathbf{r})d^3\mathbf{r}}$$
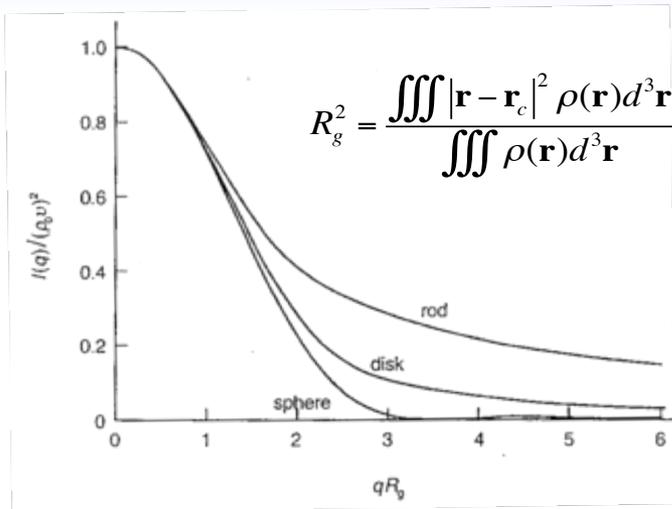
The characteristics of objects are encoded in the low-q scattering via **radius of gyration (R_g)-** calculated as the root mean square distance of the object's parts from its center of gravity

Sphere   Thin rod   Thin disc   Cylinder

$$R_g^2 = \frac{3}{5}R^2 \qquad R_g{}^2 = \frac{L^2}{12} \qquad R_g{}^2 = \frac{R^2}{2} \qquad R_g{}^2 = \frac{d^2}{8} + \frac{L^2}{12}$$

$$I(q) \sim \langle |F(\mathbf{q})|^2 \rangle$$
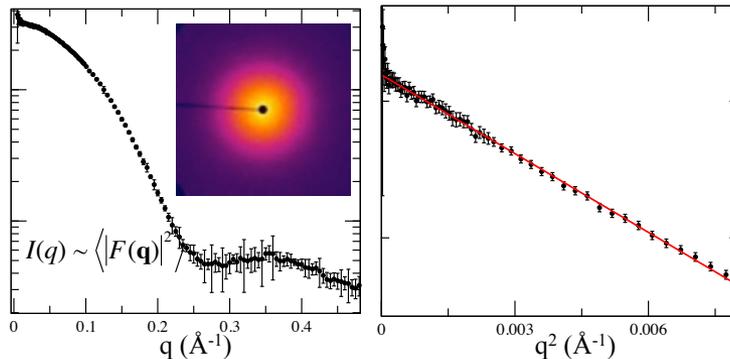
Guinier Law (valid when qR_g<1.3)

$$I(q \to 0) \sim I_0 \exp(-q^2 R_g{}^2 / 3)$$

$$\ln I(q) \sim \ln I_0 - \frac{R_g{}^2}{3}q^2$$

• Guiner Law allows finding R_g without any model assumption
• The Guinier region of the scattering data would not be linear if sample contains aggregation

Determining R_g from Guinier Plots

- Guinier Law

$$\ln[I(q)] \cong -\frac{q^2 R_G^2}{3} + \ln[I(0)]$$

  R_g – radius of gyration
  $I(0)$ – forward scattering

- Plot ln I vs. q^2
  - q-min $< q < 1.3 R_G^{-1}$
  - Slope α R_g
  - Check for linearity
- I(0) gives an independent estimation of the molar mass of the protein. Requires accurate protein concentration determination

Points 9 to 18 fidel = 0.35
sRg limits: 0.700 to 1.28
Rg = 47.4 ± 0.614
I_0 = 6.047 ± 5.63 e^{-2}

q_{min}

q_{max}

q^2 [Å^{-1}]
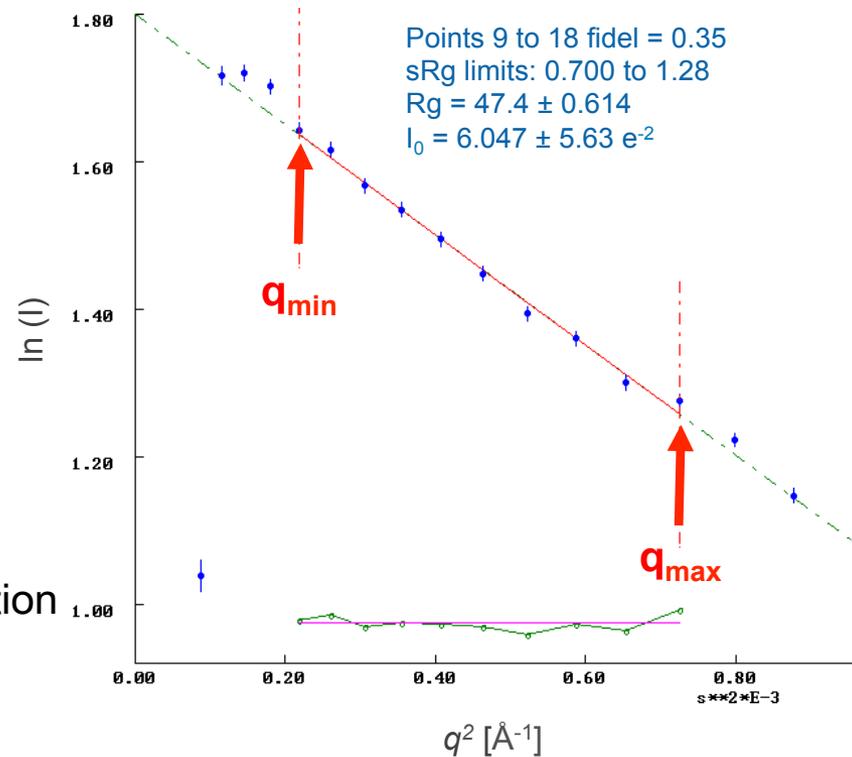
Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences 1938, 206:1374-1376
Petoukhov, et. al., *J. Appl. Cryst.* 40, s223 (2007)

Guinier Law Examples

- Deviant Guinier Plots aren't necessarily 'bad' as they tell you something about the state of the macromolecule in solution
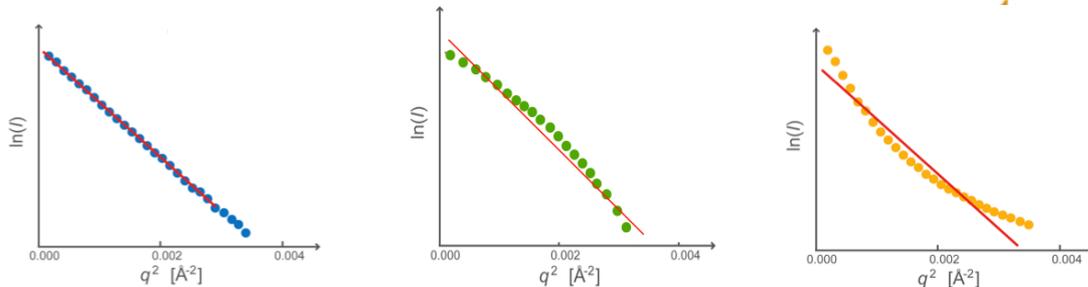
- BSA Example
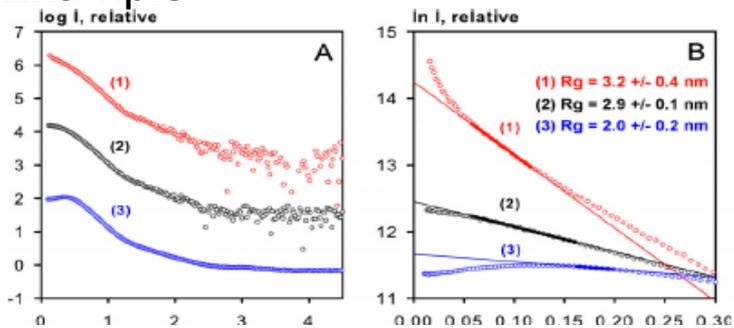
BSA
1) aggregated
2) 'good' data
3) inter-particle repulsion

Journal of Structural Biology 172 (2010) 128

Basics for Interpreting Guinier plots

- What is the q_{min} in your experimental data?
    - For very large particles, you will need a lower q_{min} to use the Guinier region for R_g determination.
    - This will also be determined by the number of data points in your 1D profile.
- The qmax will depend on the shape of your molecule.
    - For spherical particles, $q_{max} < 1.3*R_g$
    - For elongated particles, $q_{max} < 0.8*R_g$
- The Guinier also provides I(0), which is proportional to the # of electrons in the scattering particle (MW).

Scattering from Polymers
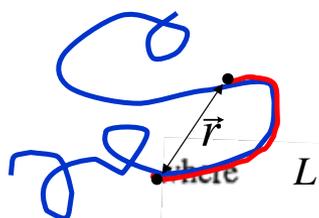
Polymer chain is not compact object, r described by Gaussian

$I(q) \sim D(x)$

Debye function

$$D(x) = \frac{2(e^{-x} + x - 1)}{x^2}, \quad x = \frac{q^2 N l^2}{6} = q^2 \langle R_g^2 \rangle$$

for q-> 0

$$D(x) = 1 - \frac{q^2 \langle R_g^2 \rangle}{3} + \cdots$$

rod

random coil

disk

qR_a
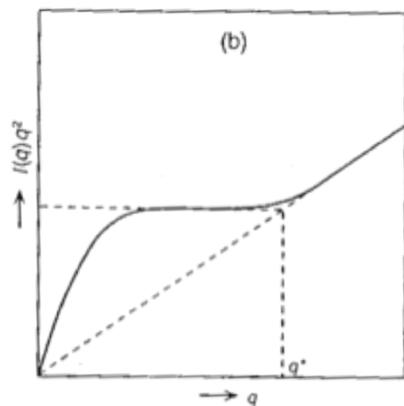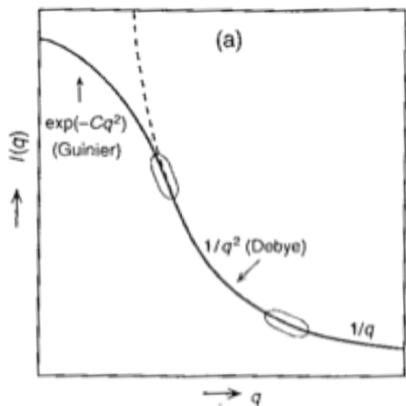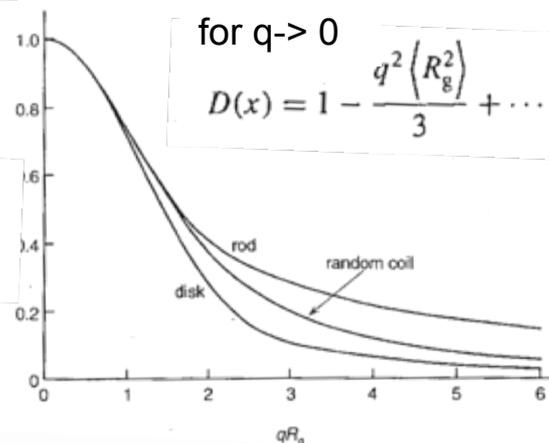
Figure 5.5 (a, b) Schematic presentation of the expected characteristics of the single chain scattering function in different q regions. (After Kratky and Porod.[11,13])

exp($-Cq^2$) (Guinier)

$1/q^2$ (Debye)

$1/q$

q^*

worm chain model:

Kratky-Porod chain

gaussian chain

thin rod

$q^2 I(q)/(\rho_0 v)^2$ (10^{-4}Å^{-2})

q (Å^{-1})

- Zooming into different q ranges reveal polymer structure on different scales

q^{-1}

$qD \ll 1$ $qD \cong 1$ $qD \geq 2$ $qL_P \geq 2$

„Magnification" increases

From Ryong-Joon Roe, "Methods of X-ray and Neutron Scattering in Polymer Science"
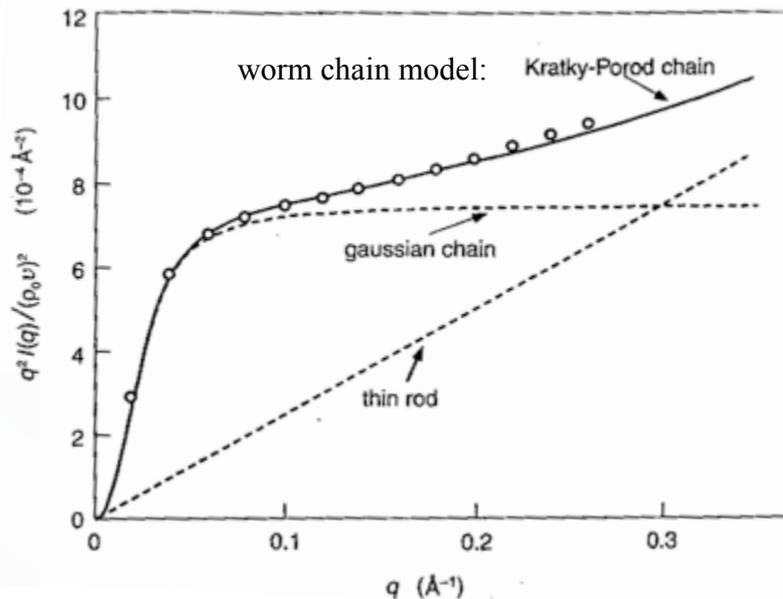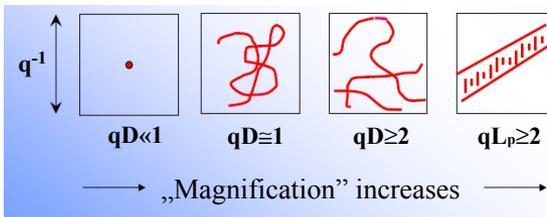
Kratky Plot (Iq^2 vs q):
reveling polymer/macromolecule structure (compactness)

- Plot Iq^2 vs. q.

- Differentiation between folded and unfolded protein

Folded

Partially unfolded

Unfolded

$q^2 I$

$q [Å^{-1}]$

0.0   0.1   0.2   0.3

$q^2 I$

$q [Å^{-1}]$

0.0   0.1   0.2   0.3

$q^2 I$

$q [Å^{-1}]$

0.0   0.1   0.2   0.3
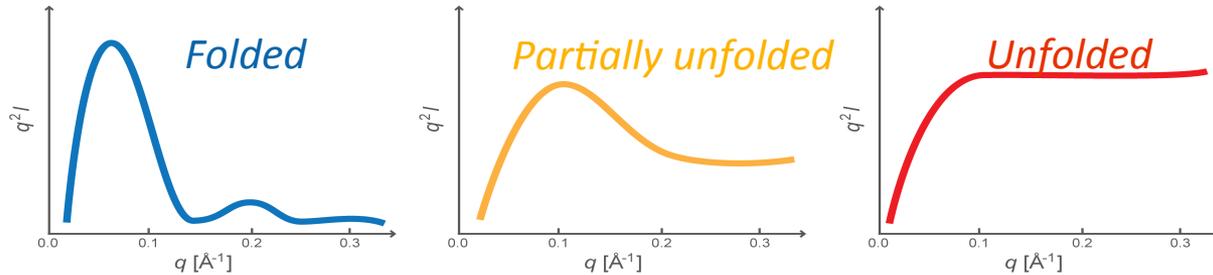
- Compact (i.e. folded) macromolecules exhibit a bell-shaped curve in a Kratky Plot
  - $I(q)$ vs. q^2, $I(q)$ vs. q^4
- Extended (i.e. unfolded) macromolecules have plateau at higher q

- Kratky Plot examples

log I, relative

C

(1)
(2)
(3)
(4)

s, nm^{-1}

I*s^2

D

(1)
(2)
(3)
(4)

s, nm^{-1}
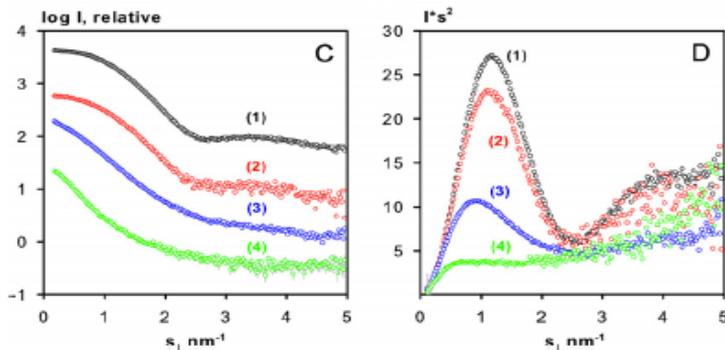
Lysozyme
1) folded
2) Partially folded (8 M urea)
3) Partially folded (90° C)
4) Unfolded (8 M urea at 90° C)

Journal of Structural Biology 172 (2010) 128–141.

Porod Invariant

- Porod invariant, Q, is the integral of the area of the Kratky curve

$$Q = \int_0^\infty I(q)q^2 dq$$

$q^2 I(q)$

$q2$

0.05   0.1   0.15   0.2
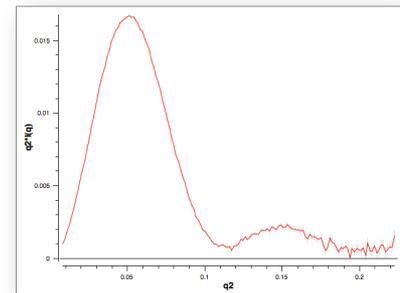
- Q is a concentration independent value and is proportional to molecular mass.

Distance distribution function

P(r): distance distribution function is related to the frequencies of distances within particle

$$P(r) = r^2 \int_0^\infty I(q) \frac{\sin(qr)}{qr} 4\pi q^2 dq$$
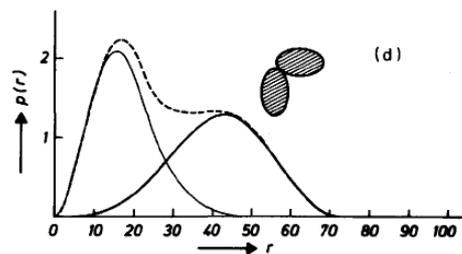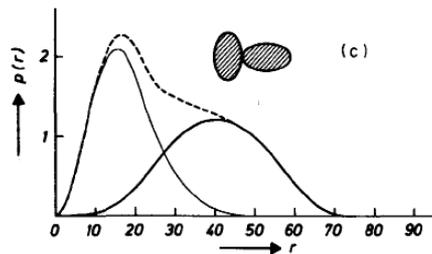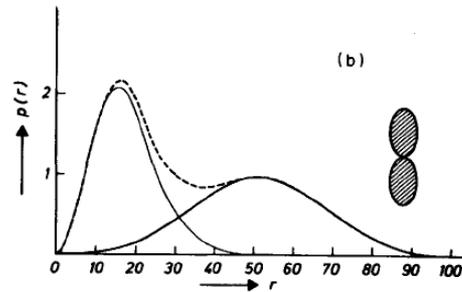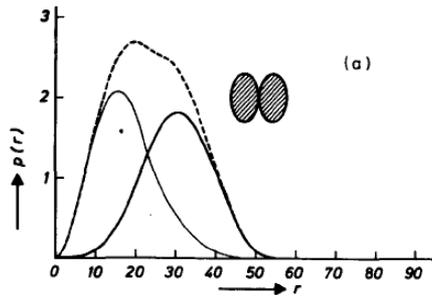
• Calculation of *P(r)* from data in limited q-range requires specialized algorithm

Glatter and Kratky
Small Angle X-ray Scattering

Deriving Information from SAXS Data

SAXS pattern

Guinier plot

Kratky plot

Pair distribution function
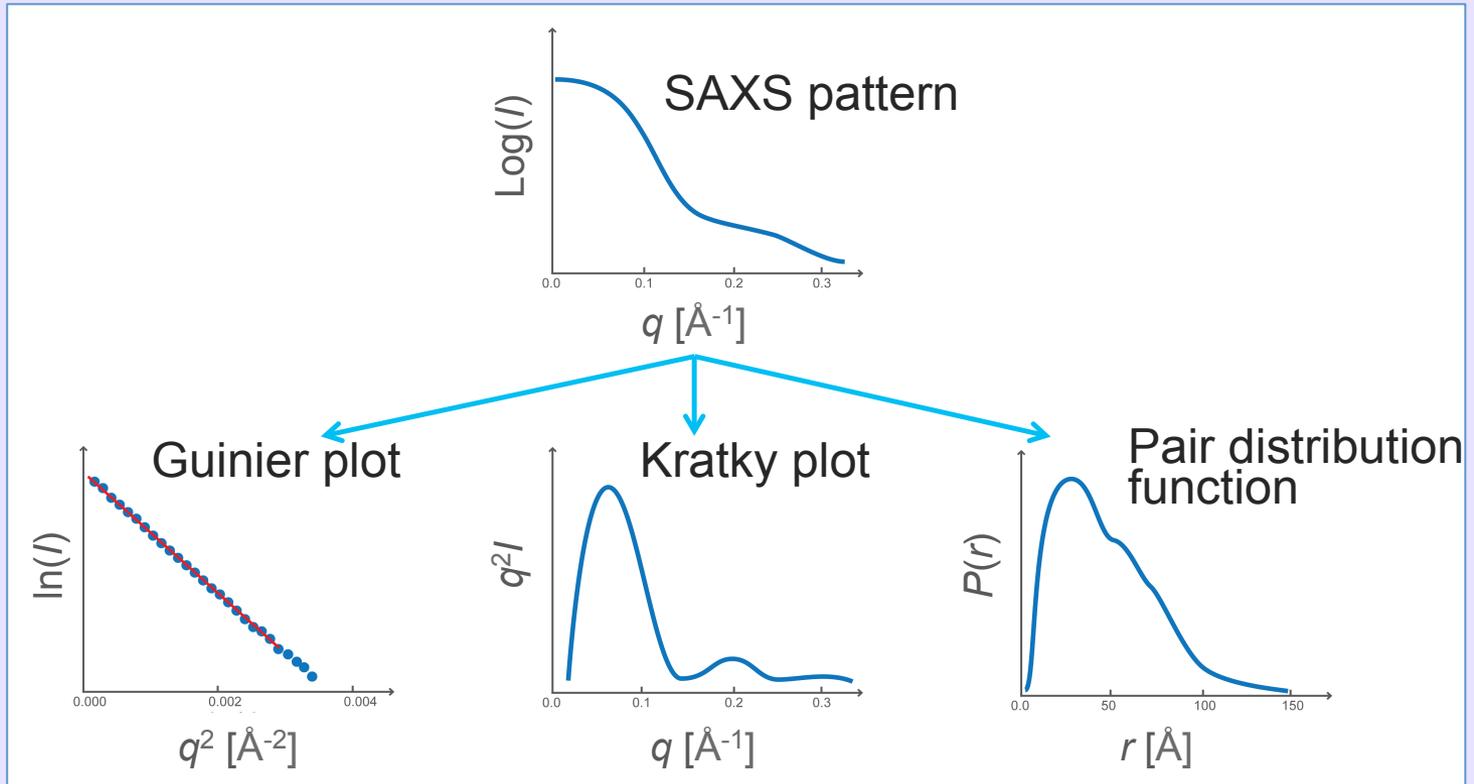
R_g Compactness   Shape

Applications of SAXS:
Complex Protein Structures can be Revealed in situ
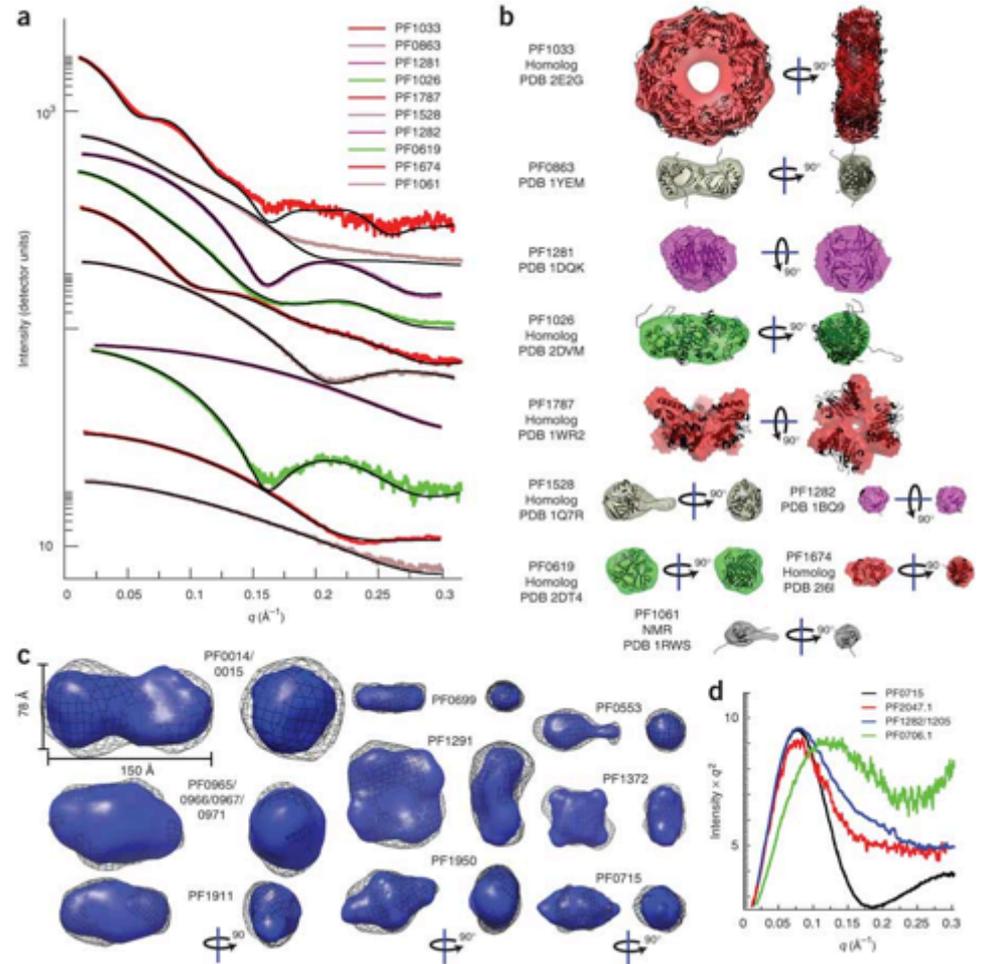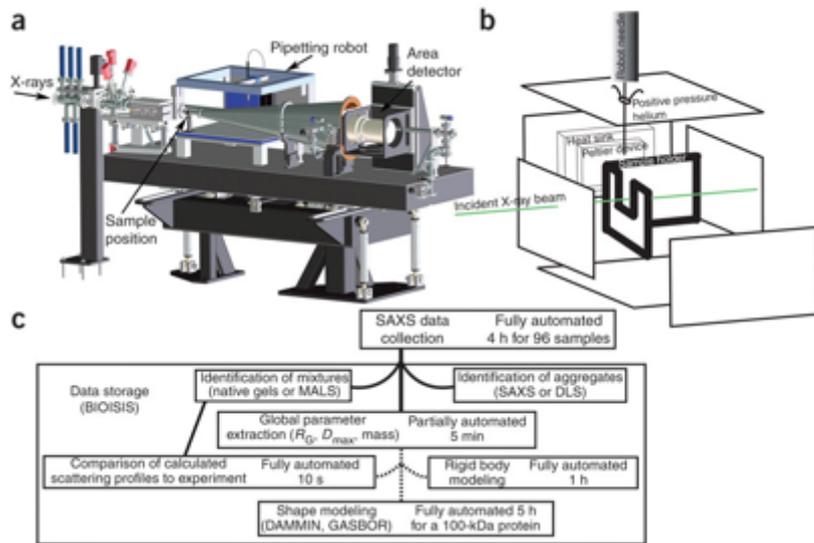
Hura et al, Nature Methods 6, 606 (2009)

Molecular flexibility

Conformation of Hck tyrosine kinase in solution
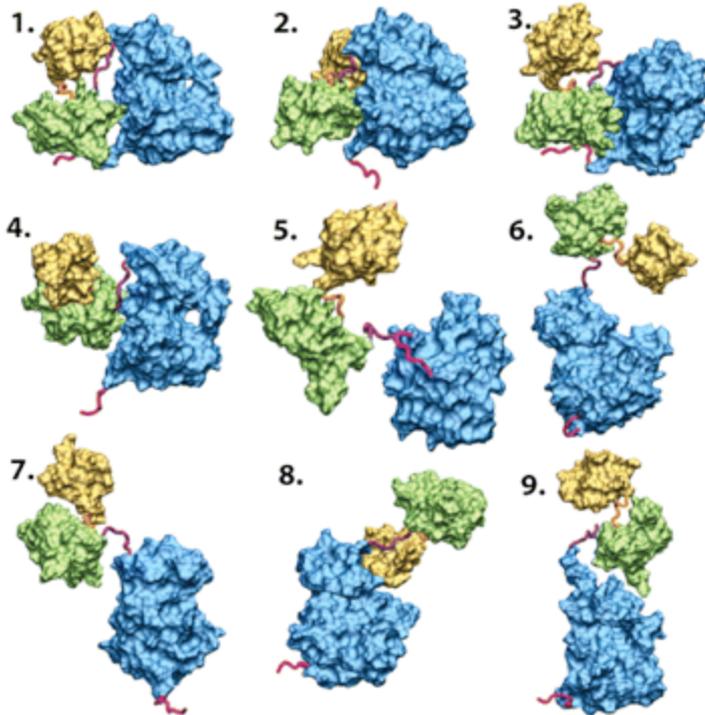
• Flexible structures can/should be modeled as an ensemble of multiple conformations

S. Yang et.al., PNAS, 2010

Scattering Regions

Guinier region

Porod region

1D object   2D object   3D object
$I(Q) \sim Q^{-1}$ Q^{-2} Q^{-4}

$Q^{-5/3}$ Q^{-2} Q^{-3} Q^{-3} Q^{-4}
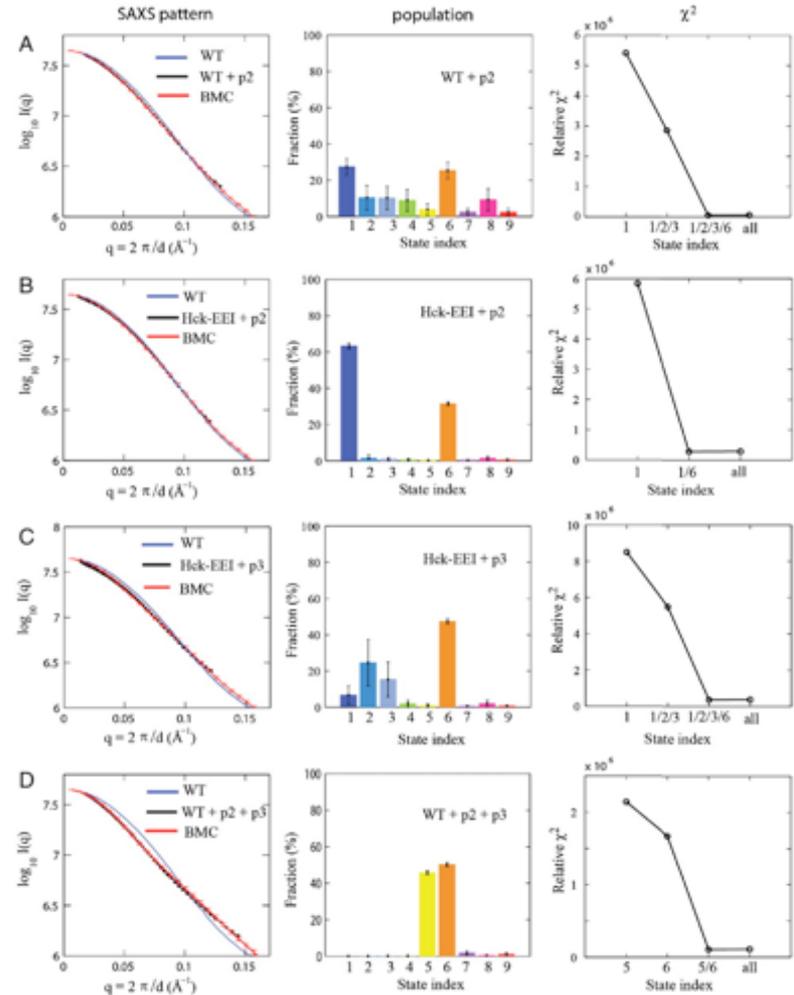
MASS FRACTALS   SURFACE FRACTALS
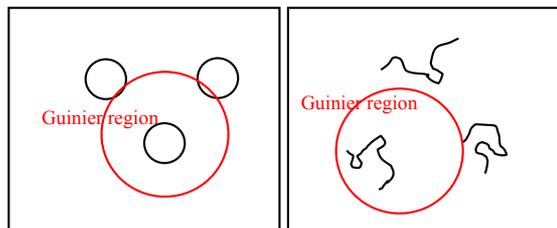
1. region   **2. region**   **3. region**

interparticle interferences   intraparticle interferences   interface

$e^{-Rg^2 q^2/3}$ (Guinier law)

q^{-1} (cylindrical particles)

q^{-2} (lamellar)

q^{-4} (spheres)

Lg I(s), relative
Solid sphere
Hollow sphere
Dumbbell
Flat disk
Long rod

s, nm^{-1}
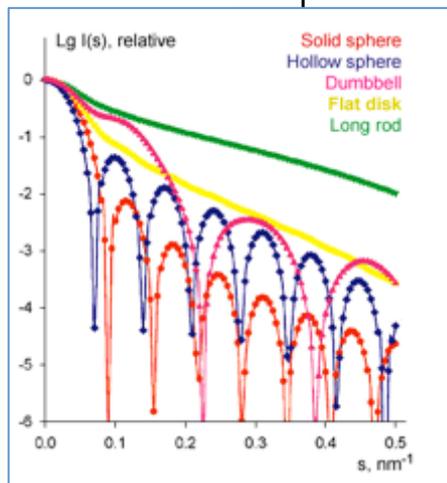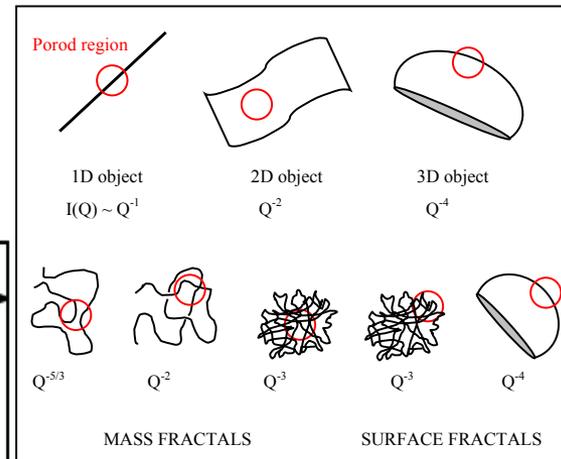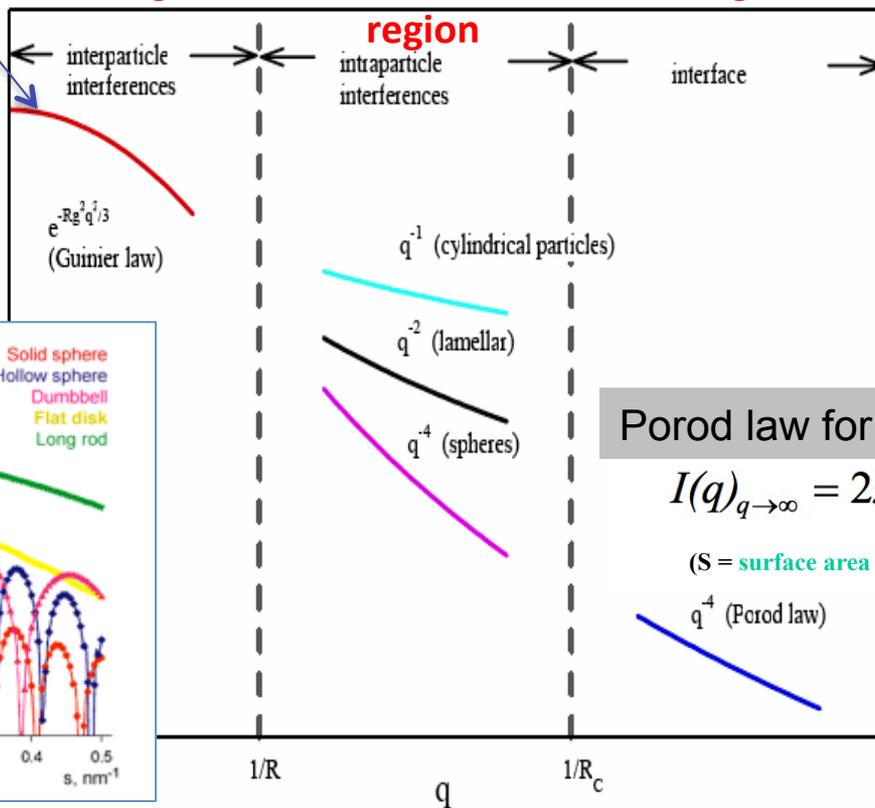
Porod law for smooth particle

$$I(q)_{q \to \infty} = 2\pi S \left(\rho_1 - \rho_2 \right)^2 q^{-4}$$

(S = **surface area** per unit volume)

q^{-4} (Porod law)

$1/R$ $1/R_c$

q

Mass Fractal

Real Space

$$M \sim R^{dm}$$

$$M \sim v \sim R^3$$

$$M \sim v \sim R^2$$

$$M \sim v \sim R^1$$

$$M \sim v \sim R^{1.66}$$

$d_m = 3$

Dispersion

$d_m = 2$
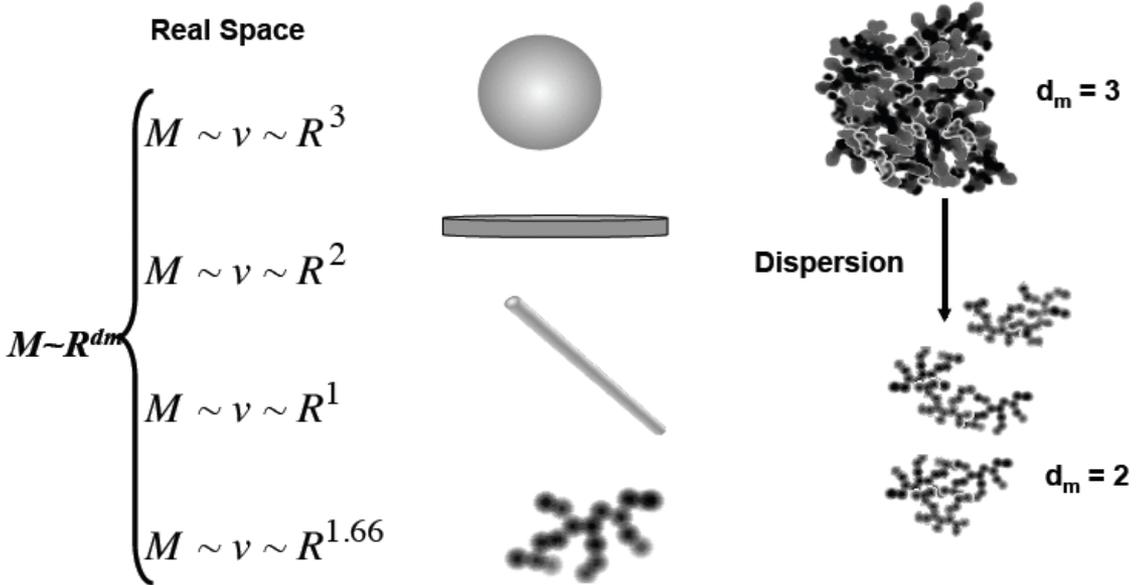
Mass fractal dimension d_m

Scattering Behavior

$$I(q) \sim q^{d_s - 2d_m}$$

qR = 1

€

~ S/q^{-x}
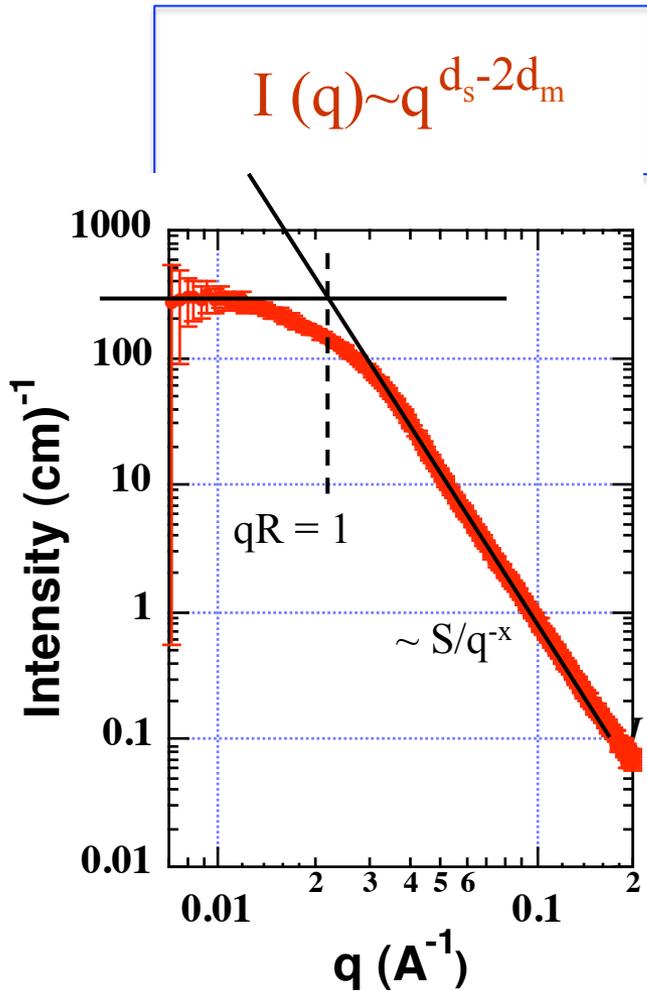
Structure		Scaling realtion	Porod Slope $d_s - 2d_m$ $qR \gg 1$
Smooth Surface		$d_m = 3$ $d_s = 2$	-4
Rough Surface		$d_m = 3$ $2 < d_s =< 3$	$-3 <= \text{Slope} <= -4$
Mass Fractal		$1 <= d_m = d_s <= 3$	$-1 <= \text{Slope} <= -3$
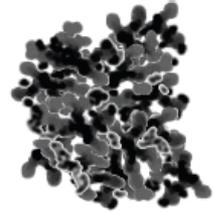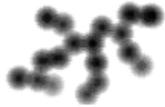
Nanoparticles — 50-200 nm

Polymeric micelles — 20 nm

Liposomes — 40-400 nm

Dendrimers — 1-10 nm

Polymer-drug conjugates — 6-15 nm
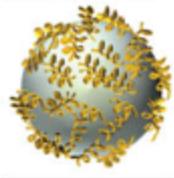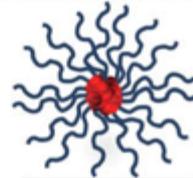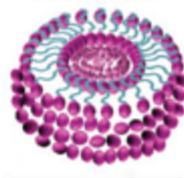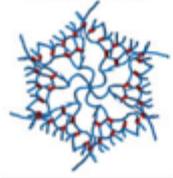
Hierarchical structure – analysis
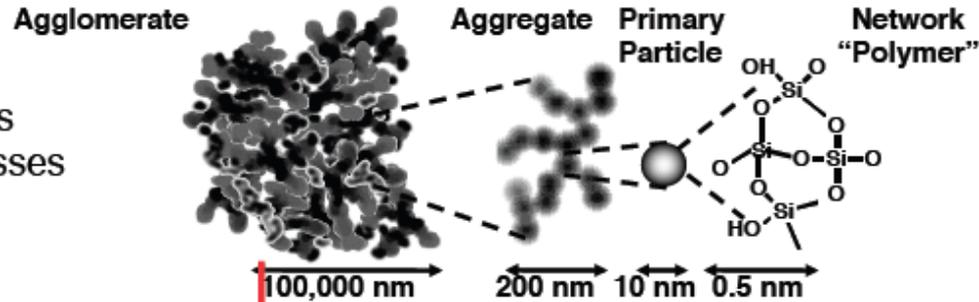
Outline

✓ **Why Scattering and its Basics**

✓ **Small Angle X-ray Scattering (SAXS)**

   ✓ **Scattering from Individual Objects**

   ✓ **Scattering from Lattices and Complex Organizations**

✓ **Surface Scattering**

   ✓ **Grazing Incidence Small Angle X-ray Scattering (GISAXS)**

   ✓ **X-ray Reflectivity (XRR)**

✓ **Instrumentation and data processing**
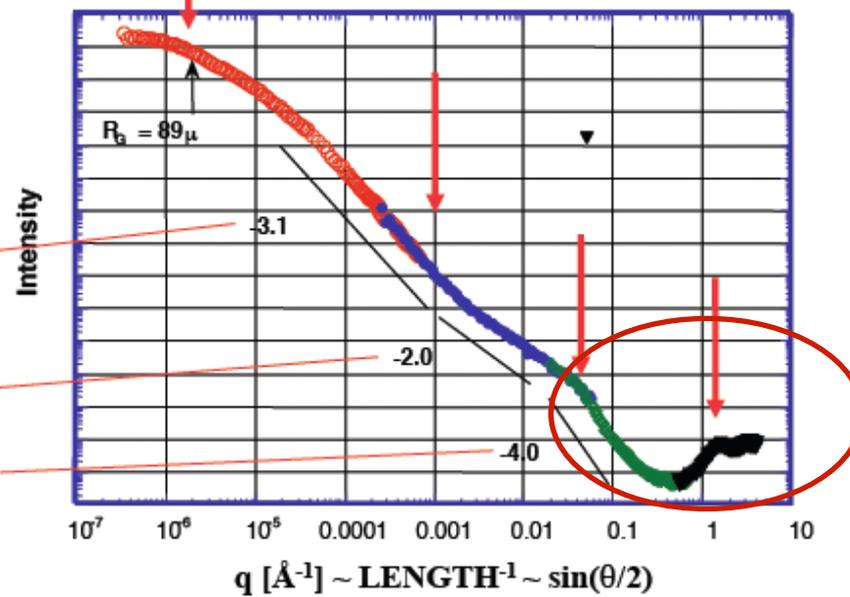
✓ **Examples of Applications for Material Studies (through the talk)**

Interference Effects
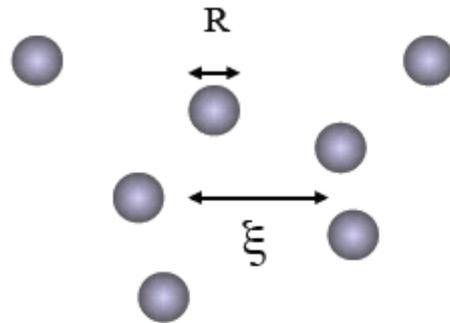
Gas like
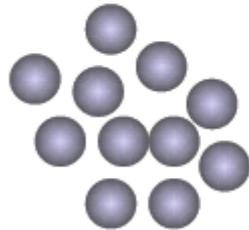
liquid like
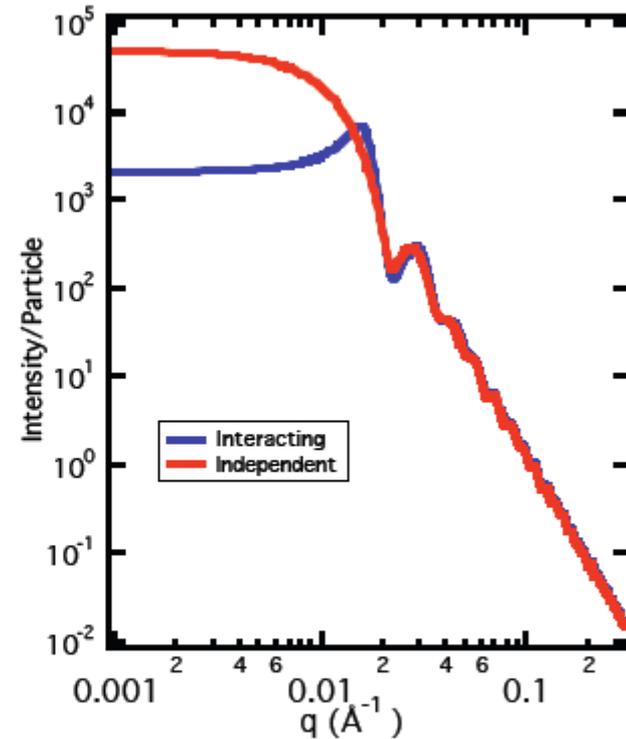
**Interaction potential
Form factor and Structure Factor**

X-ray Scattering from Structures

- Can easily infer amount of order:
  - Amorphous
  - Polycrystalline
  - Single crystal
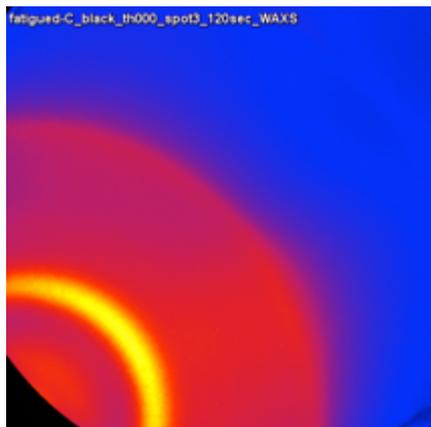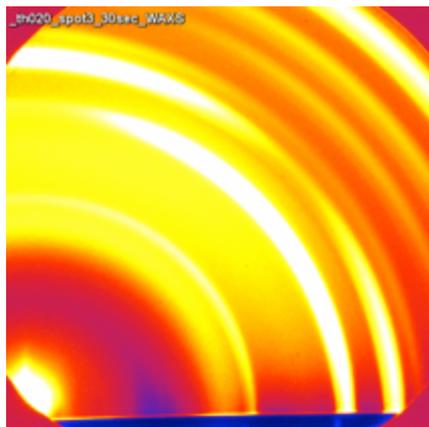
| disordered | some ordering | oriented, textured | single crystal |

less order ←——————————————→ more order
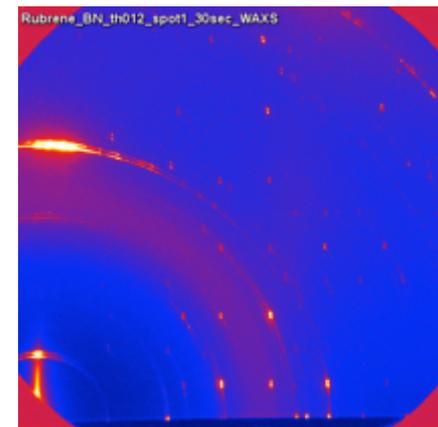
X-Ray diffraction:
Revealing order at scales 1-1000Å

principe

X-Ray beam

$\lambda = 1.5$Å

2Θ

d

λ

Θ Θ

d

λ

Bragg $\Rightarrow$ **nλ = 2 d sinΘ**

$$d \cdot q = 2\pi$$

d-space $\longleftrightarrow$ q-space

Fourrier Transform

time (t) $\longleftrightarrow$ pulsation (ω)

1) Peak positions

I

d

t

d_0

FT

$2\pi / d_0$

q

ω

= Spatial frequency analyzer

2) Peak intensities

I

d

t

d_0

$2\pi / d_0$

q

ω

= Harmonic analyzer

3) Peak line shapes

d

t

FT

q

ω

= Quality analyzer
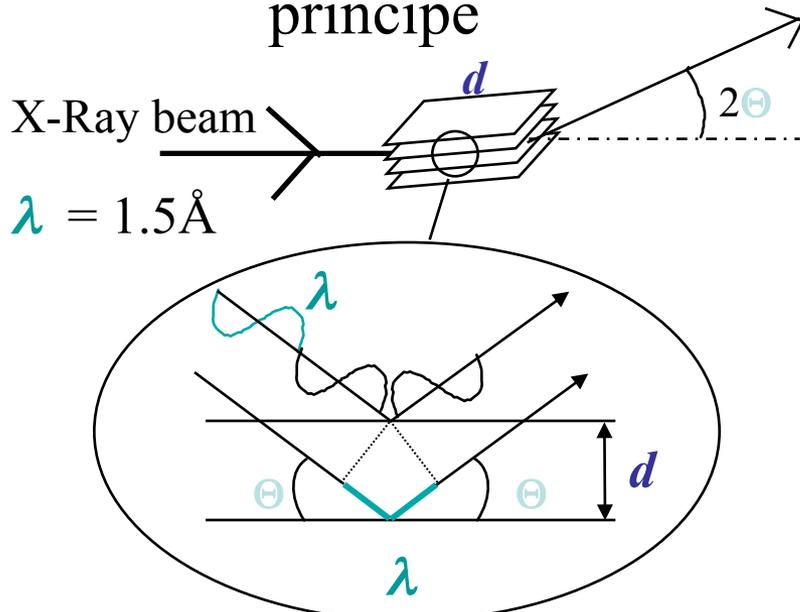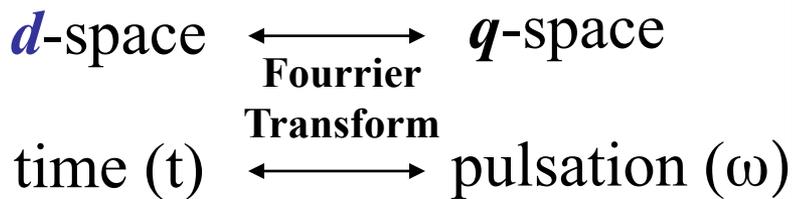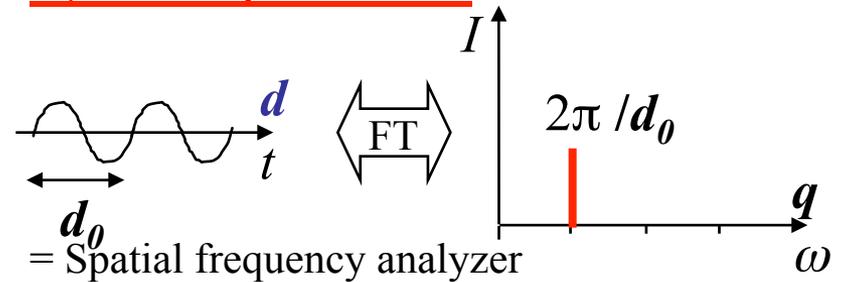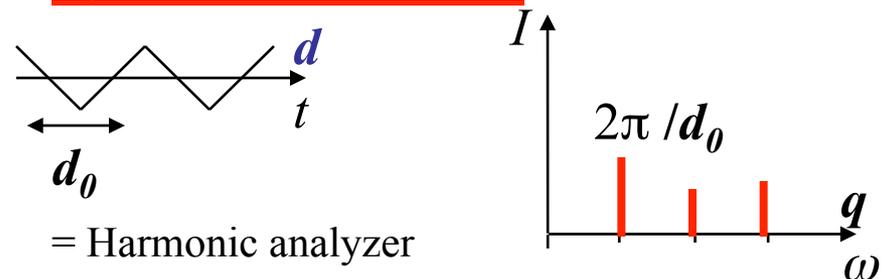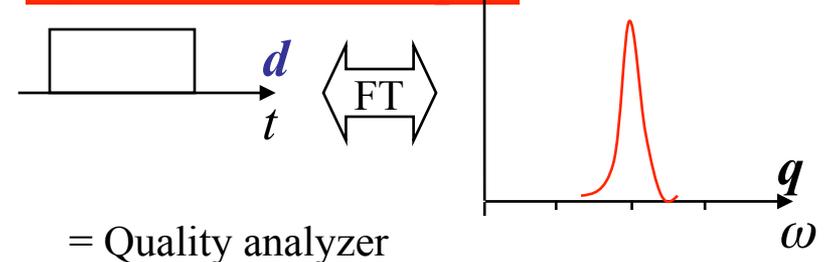
Long and Short range Positional Order

Diffractions peak position ratios for common lattices

- Lamellar symmetry: 1, 2, 3, 4, 5, …
- Cubic symmetry: 1, √2, √3, 2, √5, ...
- Hexagonal symmetry: 1, √3, 2, √7, 3, ...

Solid

Liquid

g(r)

r

a

Long Range Order

g(r)

r

a
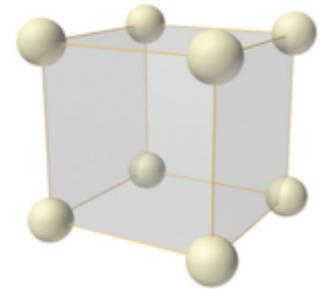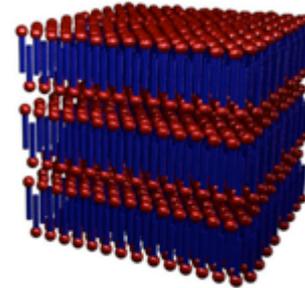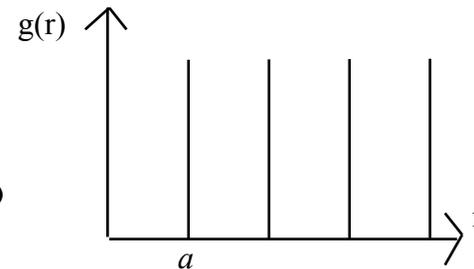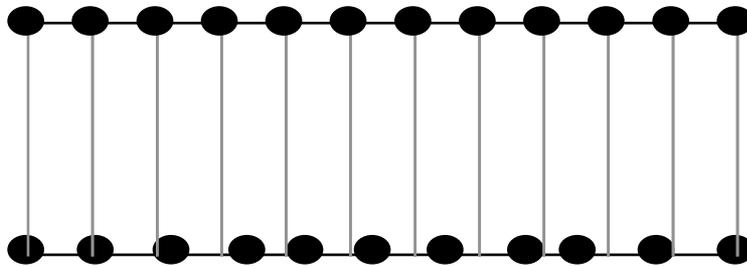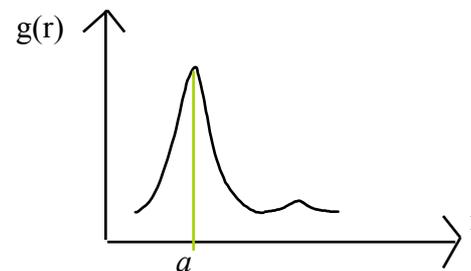
Short Range Order

Lamellar and Columnar Mesophases: X-ray patterns

d_{100}

$$q_{n00} = 2\pi n/d_{100}$$

I

n=1

n=2

n=3

0 1 2 3

q

A d_{100}

d_{110} B

a

I

A

B

0 1 $\sqrt{3}$ 2

q

$$q_{100} = 2\pi/d_{100}$$

$$d_{100} = \sqrt{3}/2.a$$
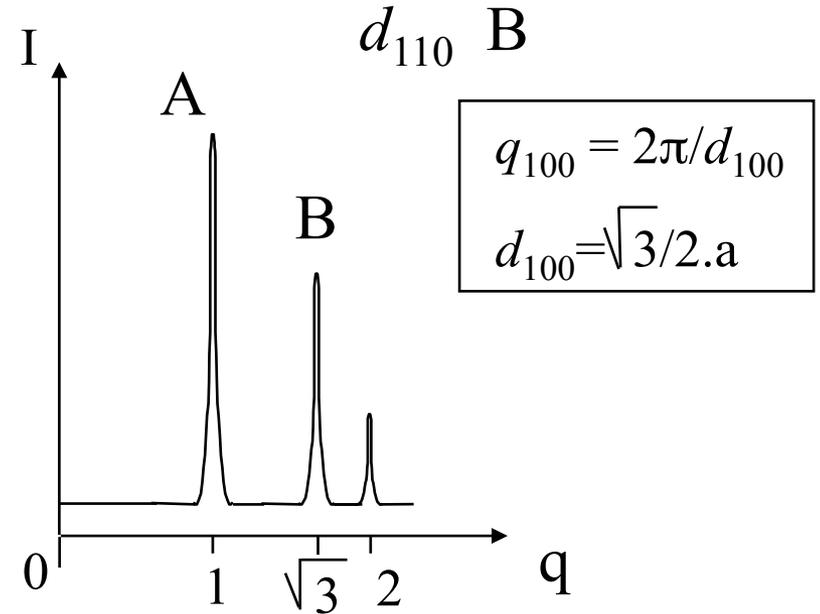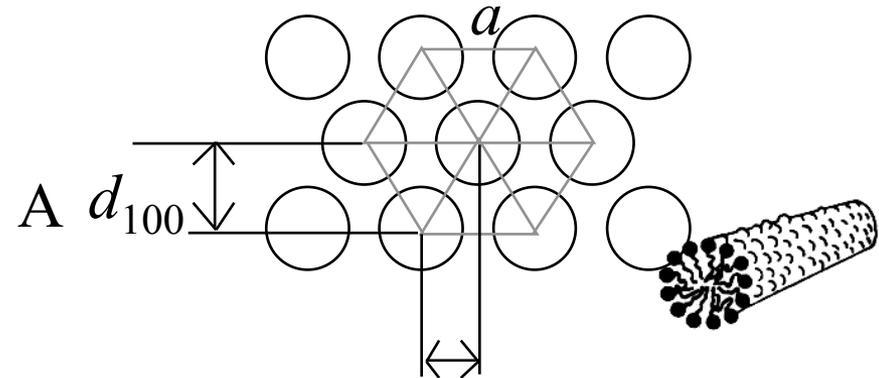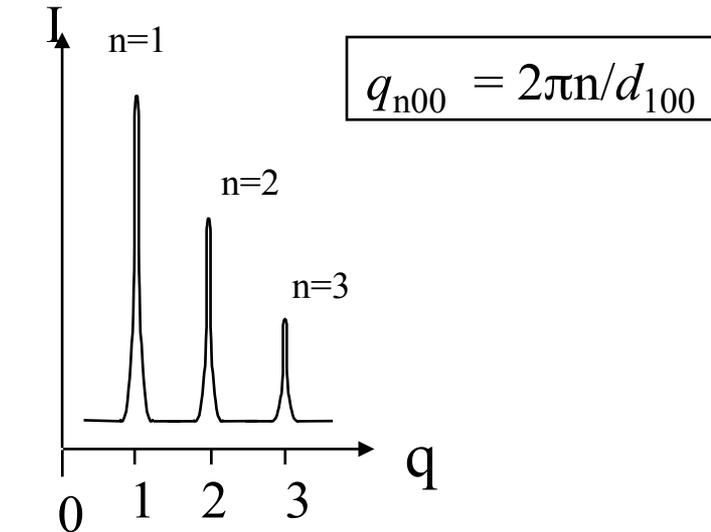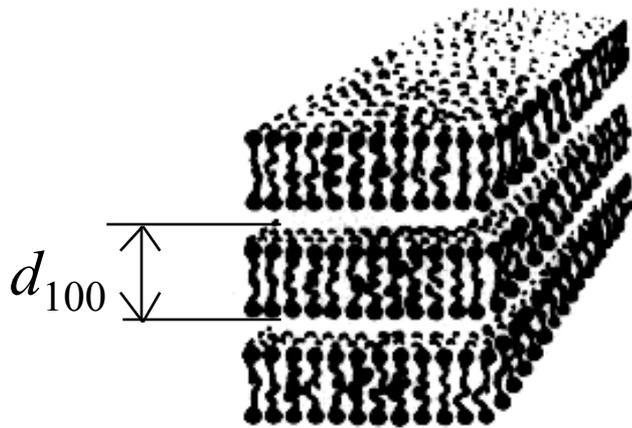
2D Lattice Distorsion

Molten
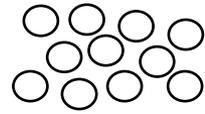
Hexagonal
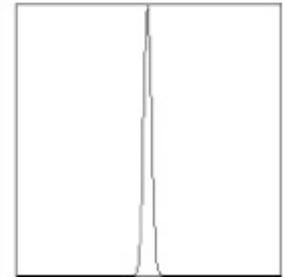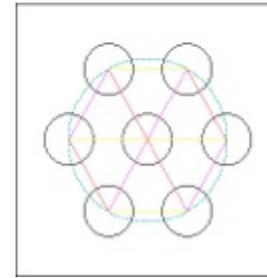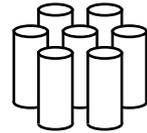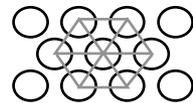
Orthorhombic
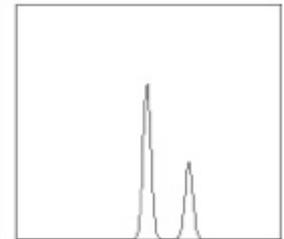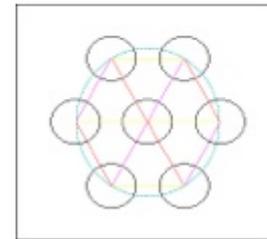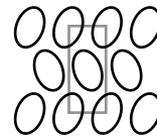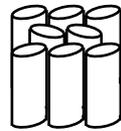
Monoclinic

Powder sample

H_{II}

100
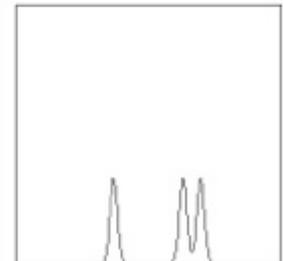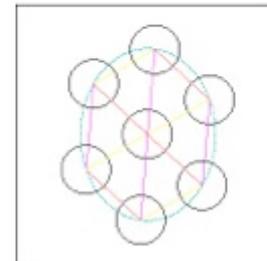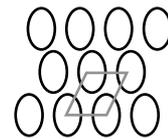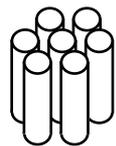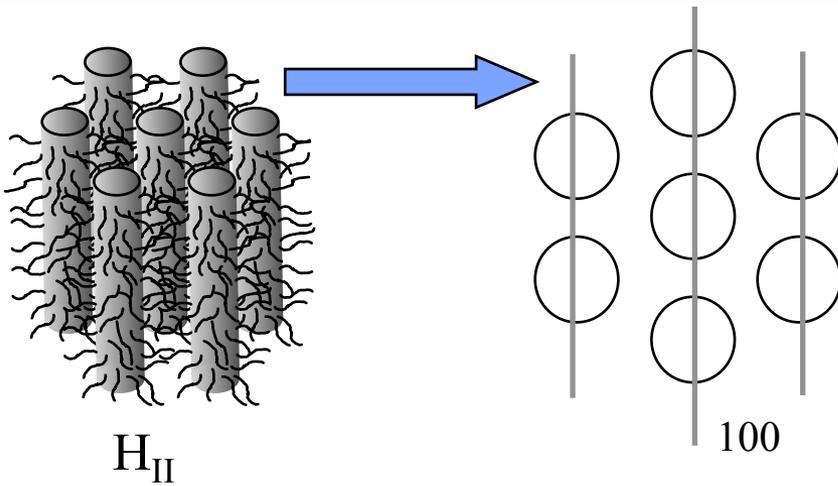
Many small single crystallline domaines
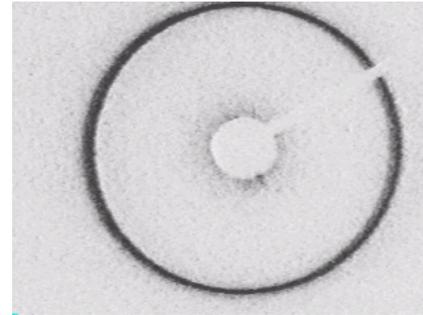
Single Crystal
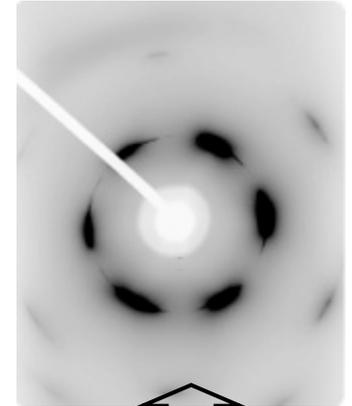
Azimuthal Integration
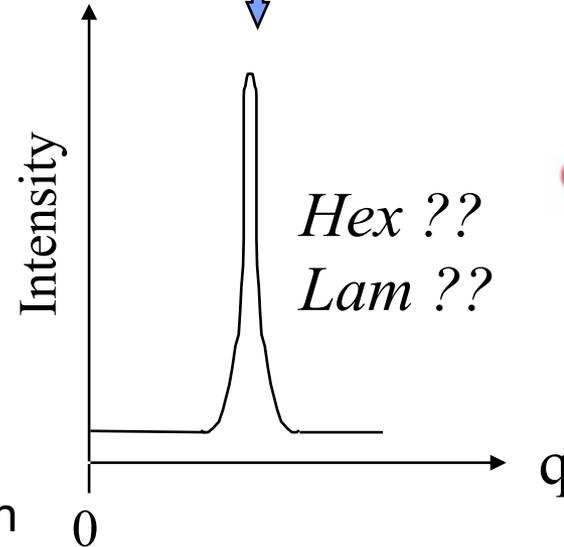
FT

Scherrer formula for estimation of domain sizes

$$D = \frac{K\lambda}{\beta \text{Cos}\theta}$$

Resolution corrected FWHM
K is ~1, depends on domain shape and strain

Intensity

Hex ??
Lam ??

q

0

Assembly of Nanoparticle Systems with DNA

Particle's cores
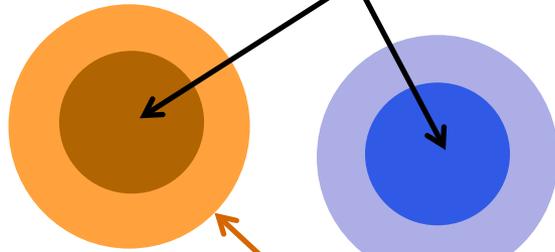
Shells from DNA
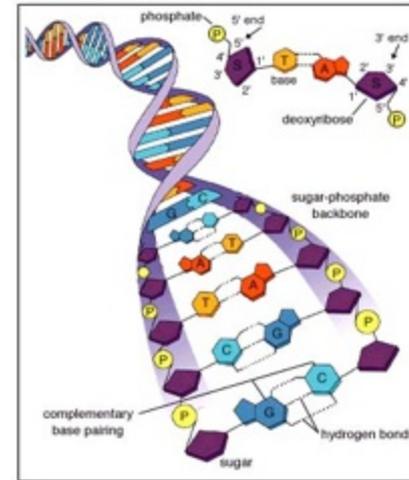
http://www.mhhe.com/biosci/esp/2001_gbio/
folder_structure/ge/m4/s1/

http://en.wikipedia.org/
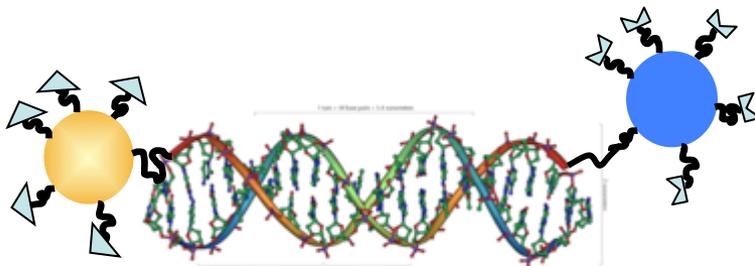
Challenges

?
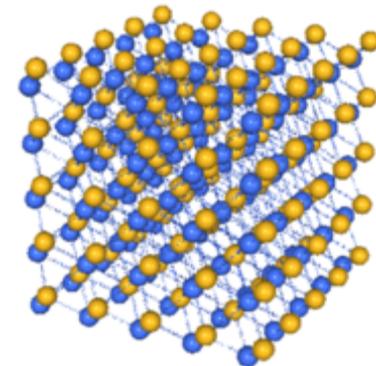
DNA-guided 3D Ordering of Nanoparticles
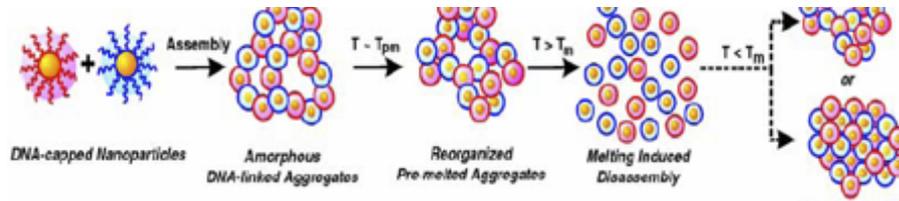
- **Even for the "right" potential assembly is locked in disordered metastable state**

Ordered

Order onset

Molten

Reorganization at T<T$_m$

Disordered, as assembled

D. Nykypanchuk, M. Maye, D. Van der Lelie, and O. Gang, *Nature, 451, 549 (2008)*

DNA-guided 3D Ordering of Nanoparticles

Hybridization

n_S

Spacer n_H

10 nm Au particle
50 DNAs per particle

Structure factor
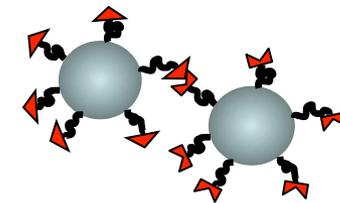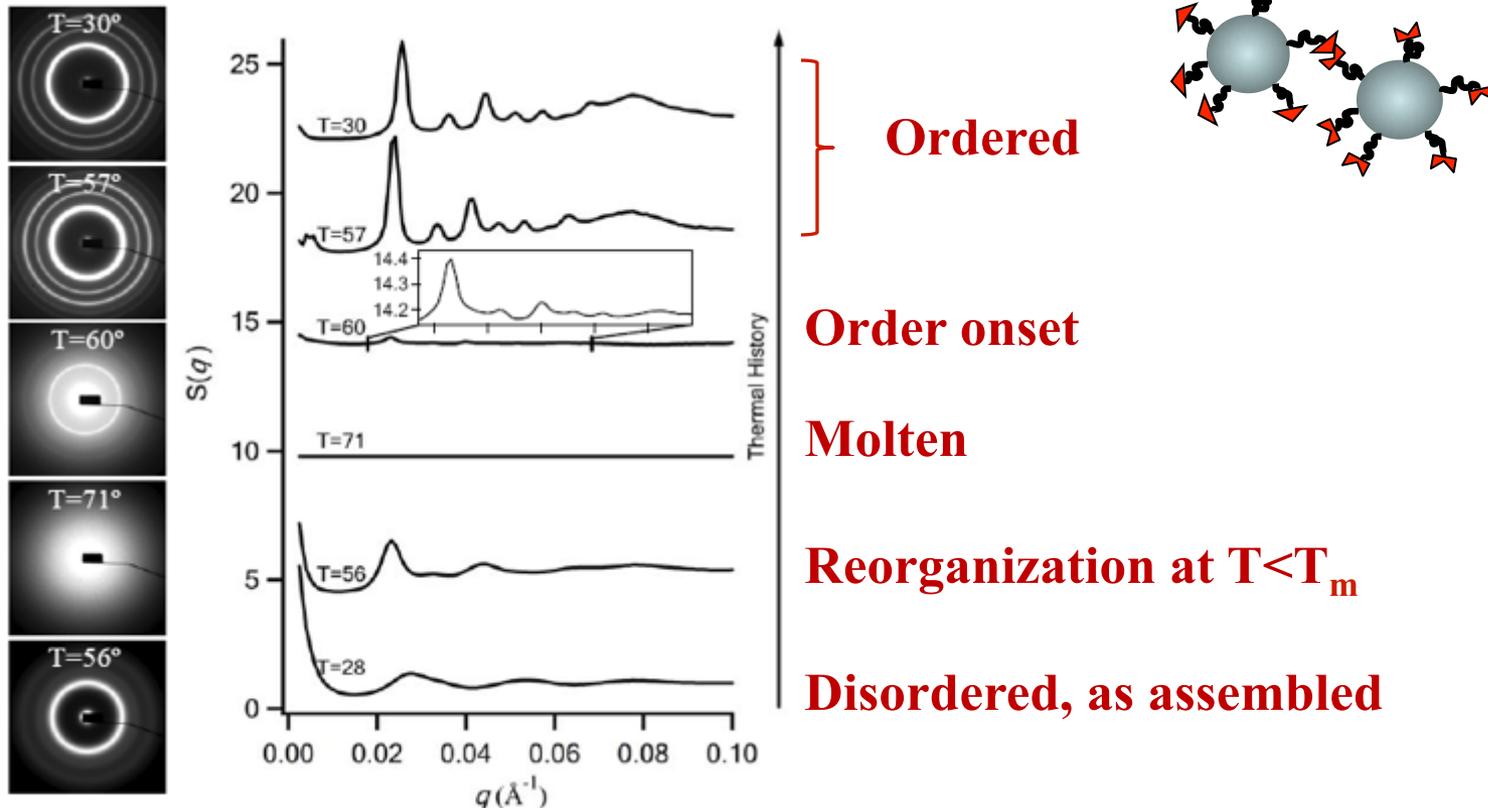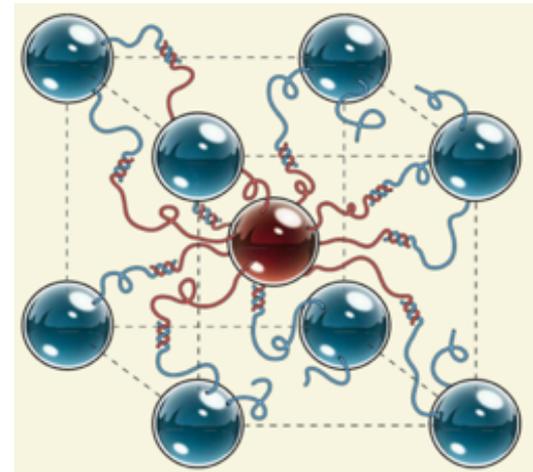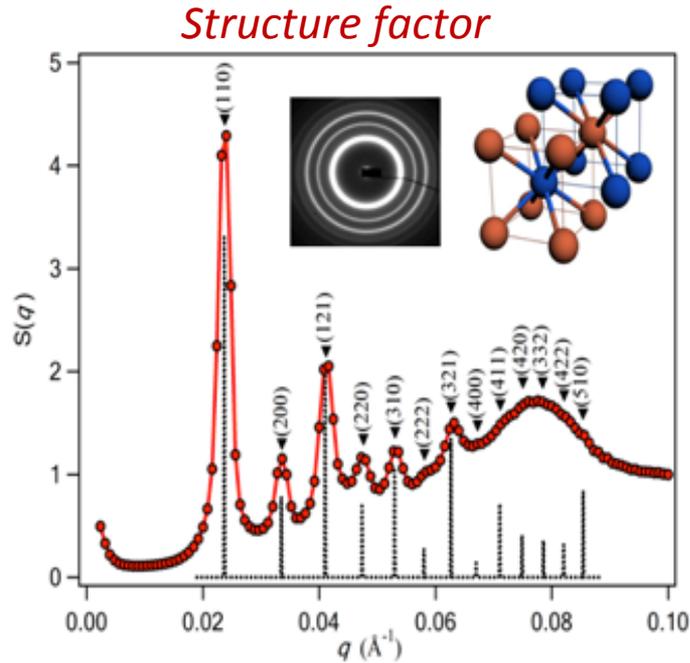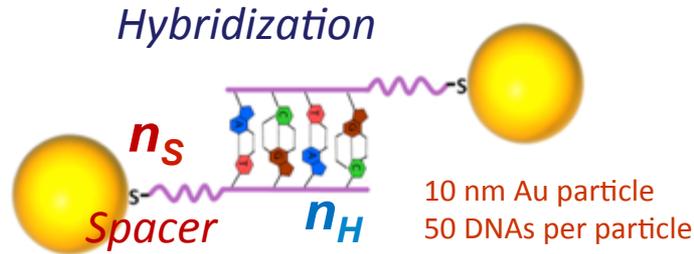
body centered cubic (BCC)

D. Nykypanchuk et al, Nature, 451, 549 (2008); H. Xiong et al, JACS (2008);
H. Xiong et al, PRL (2009)

Compositional Order in Binary Systems

CsCl structure
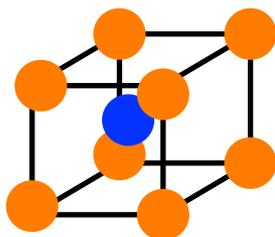
Different electron density
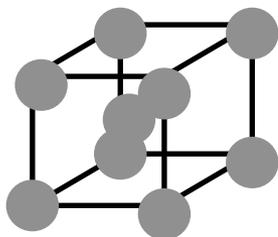
Positional Order -> Correlation length ξ
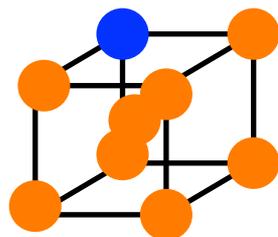
Compositional Order ?
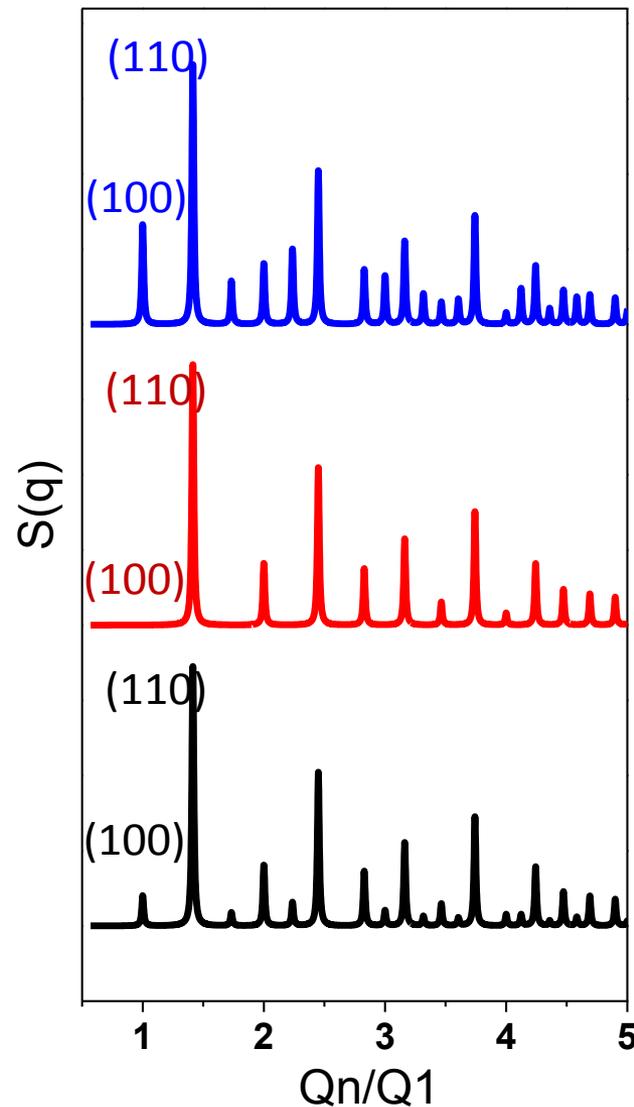
QD (CdTe)   Au

f= 30   f= 50

Longer ssDNA

Softer shell
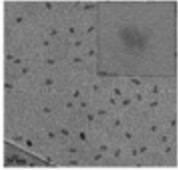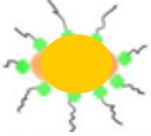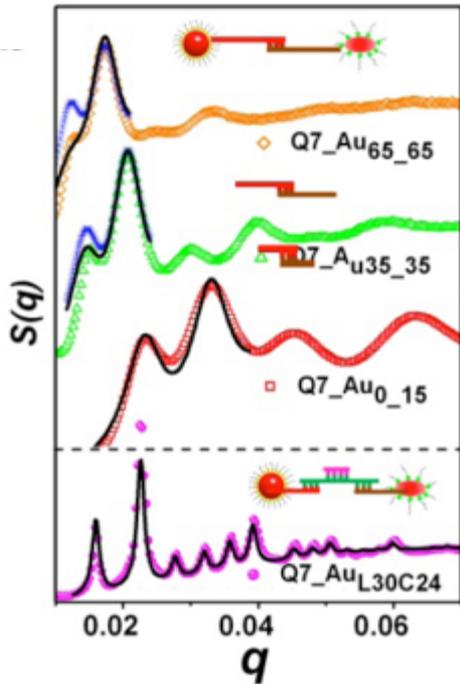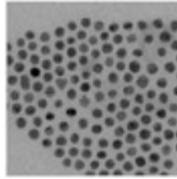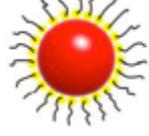
Compositional disorder

Compositional disorder $\eta=(r_A-F_A)(1-F_A)$

r_A : fraction of A sites occupied by A particles

F_A : fraction of A particles in the lattice

Compositional disorder continuously increases with the ssDNA shell thickness

Y. Zhang et al., Nature Nanotechnology, 8 (11), p865 (2013)

Scattering from Nanoparticle Lattices

Structure Factor
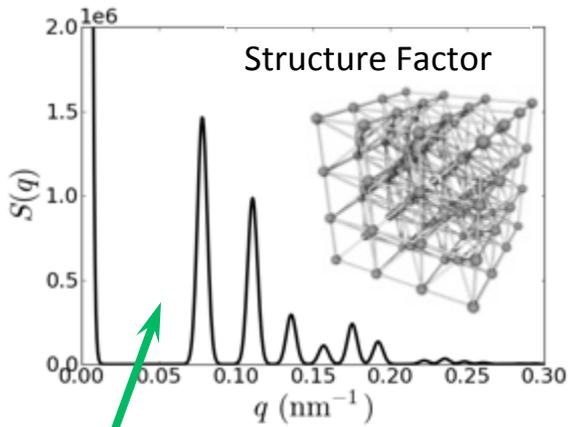
Lattice Unit Cell
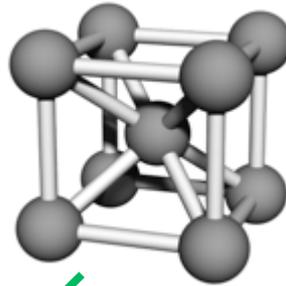
Peak Shape
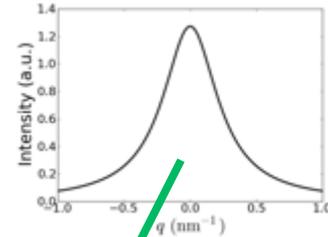
Debye-Waller (thermal disorder)

Plane Wave

$$S(q) = \frac{c}{\ldots} \sum^{m_{hkl}} \left| \sum^{n_c} F_i(M \cdot q_{hkl}) e^{2\pi i(x_j h + y_j k + z_j l)} \right|^2 e^{-\sigma_D^2 q_{hkl}^2 a^2} L_{hkl}(q - q_{hkl})$$

Isotropic Form Factor
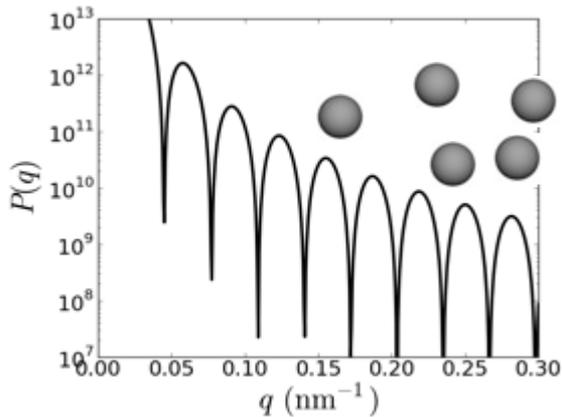
Reciprocal-space Peaks

Particle Form Factor

BCC

Yager et a., J. of Appl. Cryst, 47, 118 (2014)
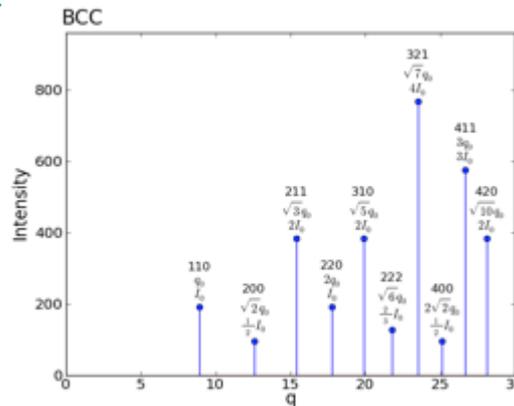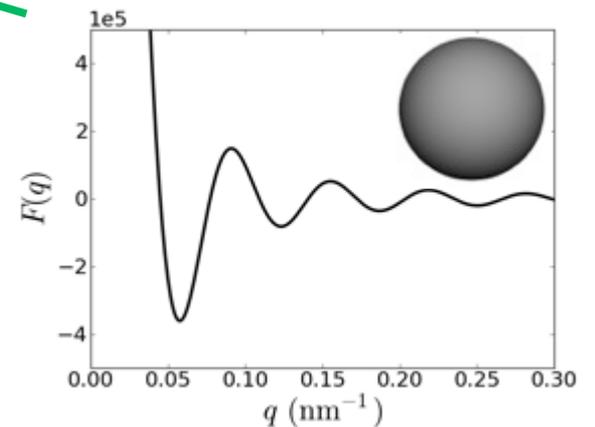
Cube-Directed Assembly of Spheres
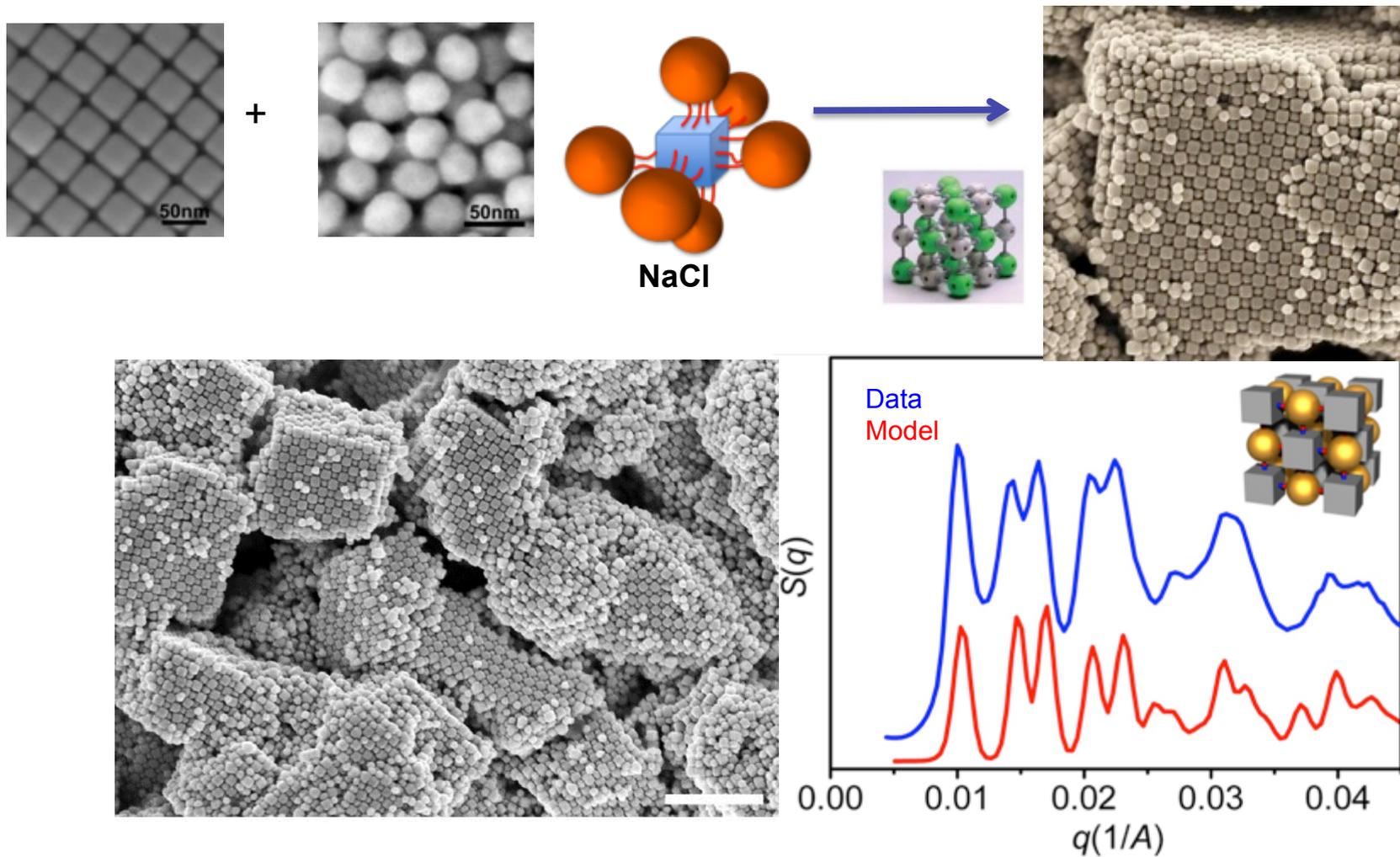
NaCl

Data
Model

$S(q)$

$q(1/A)$

F. Lu, et al, (2015), Nature Communications

Outline

✓ **Why Scattering and its Basics**

✓ **Small Angle X-ray Scattering (SAXS)**

    ✓ **Scattering from Individual Objects**

    ✓ **Scattering from Lattices and Complex Organizations**

✓ **Surface Scattering**

    ✓ **Grazing Incidence Small Angle X-ray Scattering (GISAXS)**

    ✓ **X-ray Reflectivity (XRR)**

✓ **Instrumentation and data processing**

✓ **Examples of Applications for Material Studies (through the talk)**

X-RAY METHODS AT GRAZING INCIDENCE

● **STRUCTURE OF THIN LAYERS ON SUBSTRATE**

diffracted beam (GID)

Crystalline properties

reflected beam

density profile

depth resolution 10nm-200nm

depth

$<10\,nm$

1 α_i/α_c

Diffuse scattering (GISAXS)

Morphology of nano islands
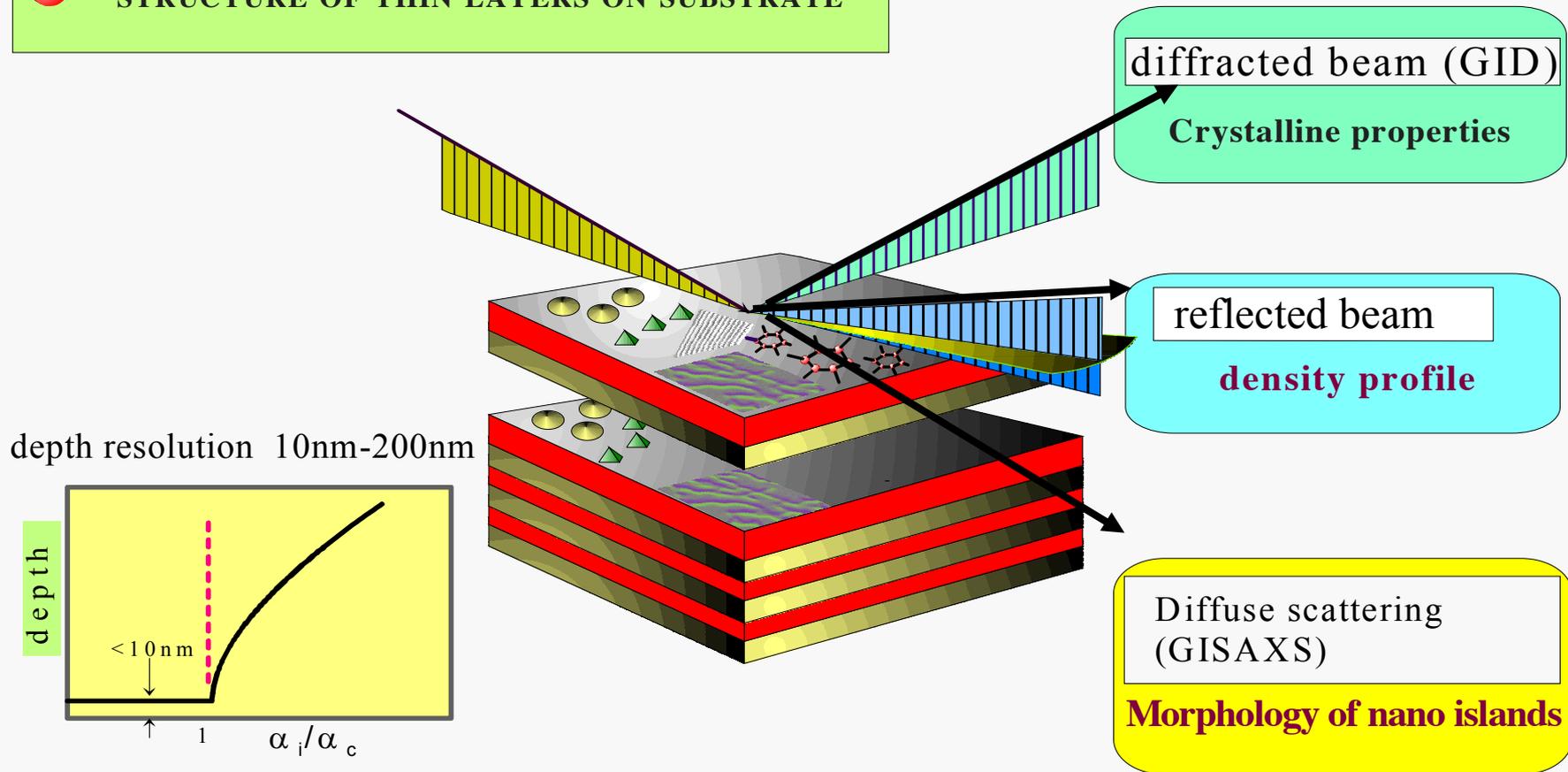
Reflectometry

- X-rays are incident at low angles

- Constructive / Destructive interference

- Measure Reflectivity (I/I_o) vs Q_z

- Penetration through material

$$\vec{k}_{in} - \vec{k}_{out} = \vec{Q}_z$$

Q_z

$\vec{k}_{in}$

$\vec{k}_{out}$

Interference

Substrate
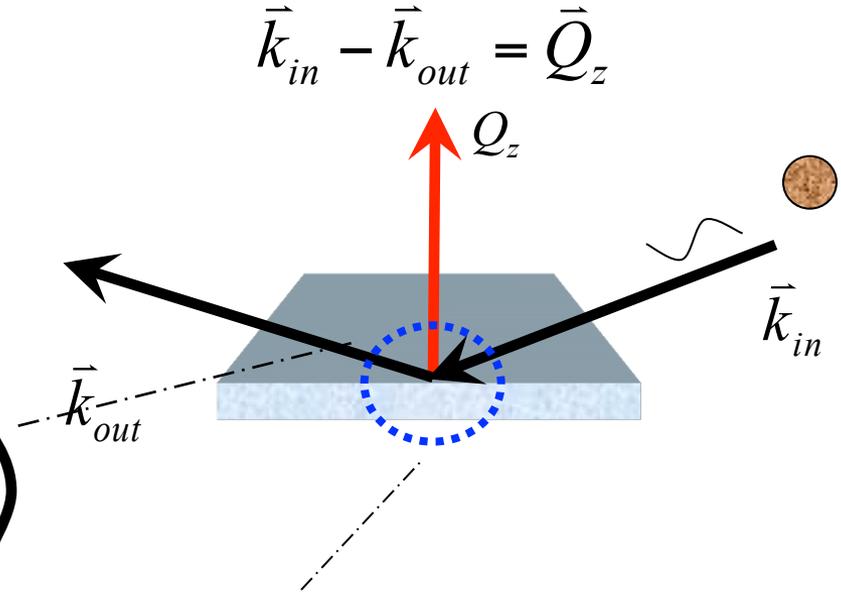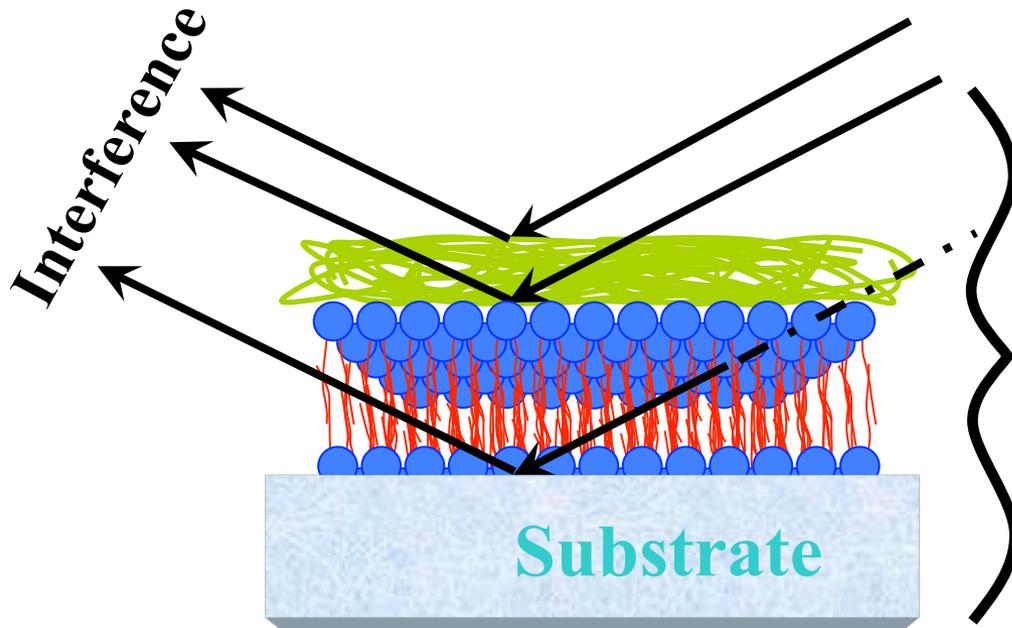
- From Reflectivity *vs.* Q_Z
  - Thickness (Angstrom resolution)
  - Roughness
  - Density
  - Surface coverage

Off-specular scattering
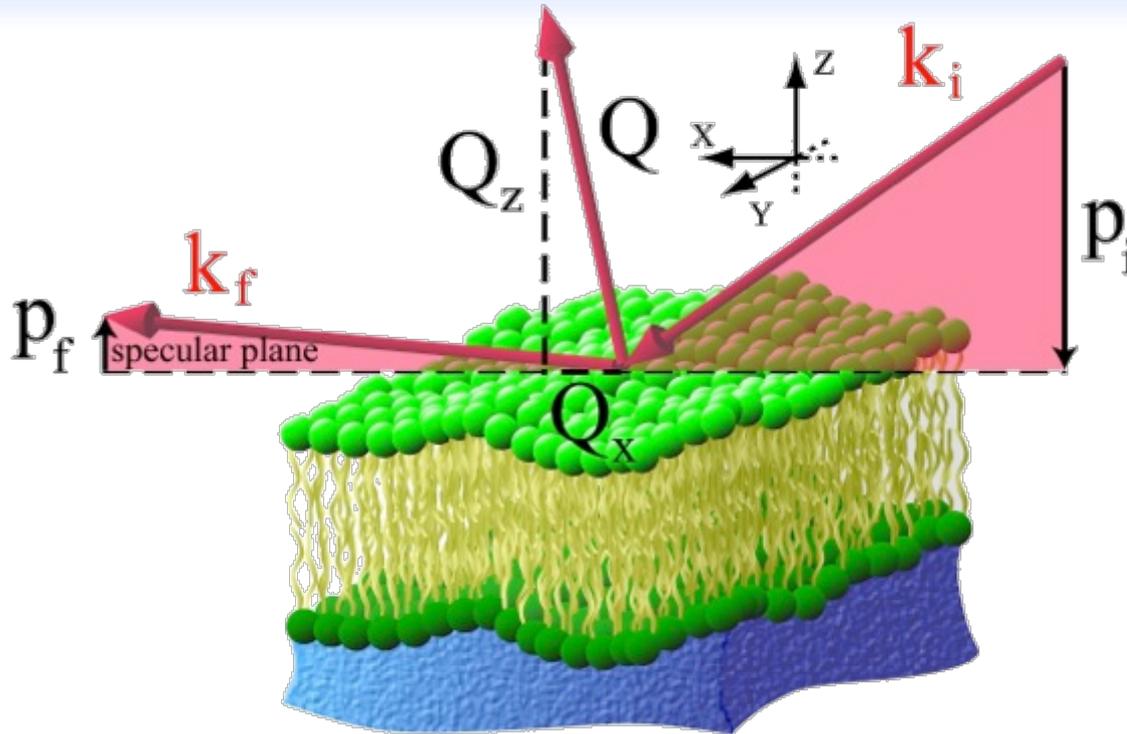
- Probes in-plane structure on surface and interfaces (with Q_x)

- In-plane length-scales (correlations) from ~100 nm to >40 μm

- Roughness correlation from layer to layer

- Use of Distorted Wave Born Approximation to model 2D map

Reflection and refraction – Perfect surface

$n = 1$

k_i

E_0

α_i

$n = 1 - \delta + i\beta$

Minus!! **Dispersion** **Absorption**

k_f

E_r

$\alpha_f = \alpha_i$

α_t

k_t E_t
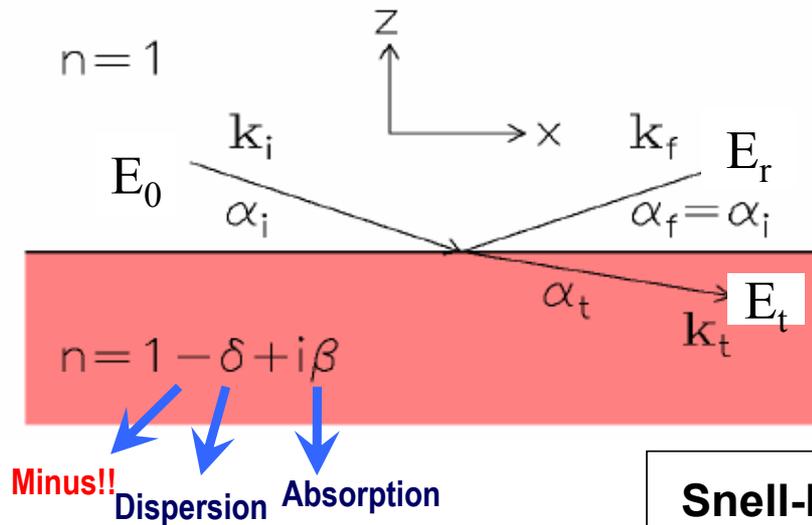
$$\delta = \frac{\lambda^2}{2\pi} r_0 \rho \approx 10^{-4}..10^{-6}$$

$$\beta = \frac{\lambda}{4\pi} \mu \approx 10^{-6}..10^{-9}$$

Snell-Descartes law: $\cos \alpha_i = n \cos \alpha_t$

transmitted wave only if $\cos(\alpha_t) \leq 1$, i.e. $\alpha_i \geq \alpha_c$

If $\alpha_i \leq \alpha_c$,
- Incident wave totally externally reflected.
- Transmitted wave exponentially damped with z.

α_c critical angle for total external reflection of X-rays

$$\alpha_c = \sqrt{2\delta} = \sqrt{\frac{r_0}{\pi} \times \lambda \times \sqrt{\rho}} \approx 0.1 \text{ to } 0.5°$$

Grazing Incidence Small Angle X-ray Scattering (GISAXS)

- Can look at surfaces exposed to liquid, vapor, etc.
- Can apply temperature, shear, electric-field, etc.
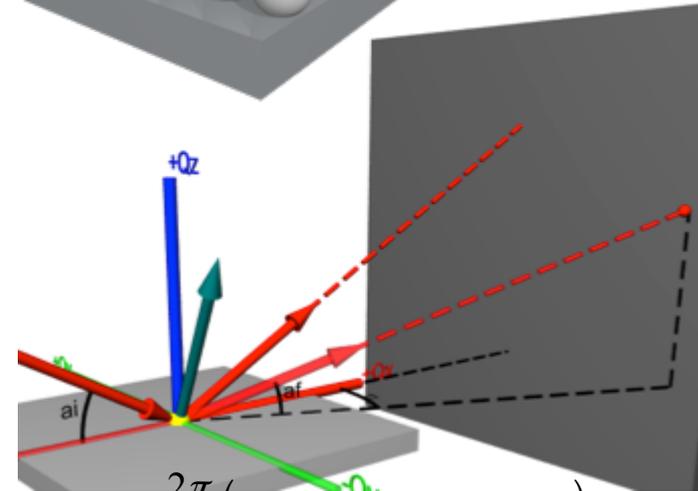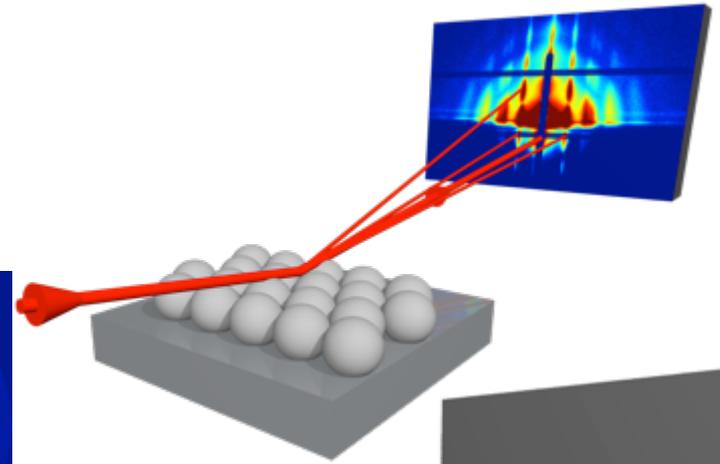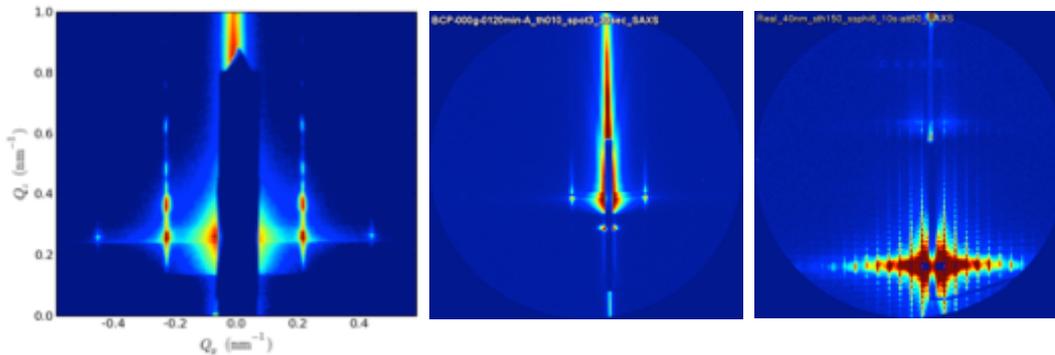
- Scattering measurement: symmetry, spacing, order, grain size, orientation
- Reflection angle provides limited depth-profiling
- Beam projection onto sample (~few mm and more) averages over large area
- Quantitative modeling of GISAXS (multiple reflections, etc.) is non-trivial

$$Q_x = \frac{2\pi}{\lambda}\left(\cos\theta_f \cos\alpha_f - \cos\alpha_i\right)$$

$$Q_y = \frac{2\pi}{\lambda}\sin\theta_f \cos\alpha_f$$

$$Q_z = \frac{2\pi}{\lambda}\left(\sin\alpha_f + \sin\alpha_i\right)$$

Grazing Incidence Diffraction
⇒ Structure parallel to surface (2D diffraction)
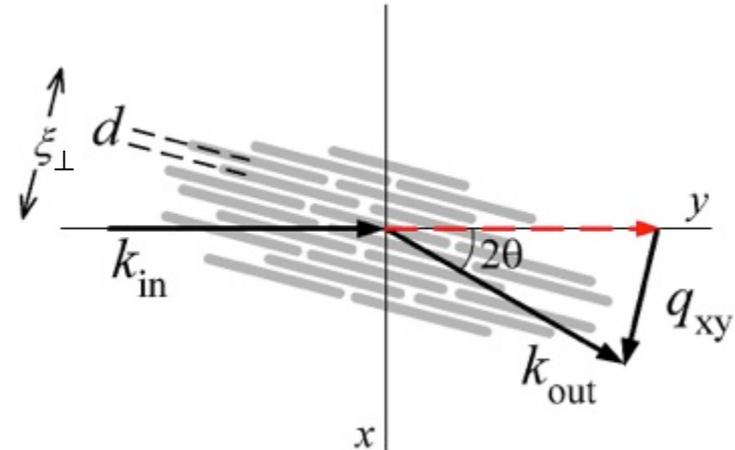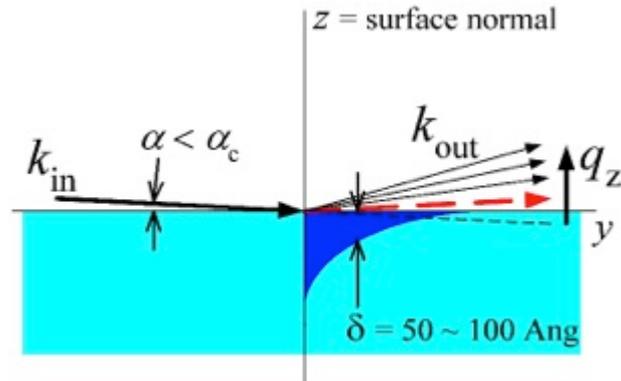
- Evanescence
  ⇒ Scattering mostly from surface

- Lateral periodicity d ⇒ Peak at $q_{xy} = 2\pi/d$

- In-plane structure of 2D lattice is determined from the diffraction peaks, similar to 3D

- Lateral correlation length $\xi_\perp$
  ⇒ Resolution-corrected HWHM$\{q_{xy}\}$ ~ $1/\xi_\perp$

- q_z-dependence (e.g., Bragg rods):
  ⇒ Molecular form factor, molecular tilt, etc.

X-ray Specular Reflectivity
⇒ Structure normal to surface

$$q_z = (4\pi/\lambda)\sin(\alpha)$$

k_{in} k_{out} q_z

$n = 1$ α α y

$n < 1\ (\delta n \sim 10^{-5})$
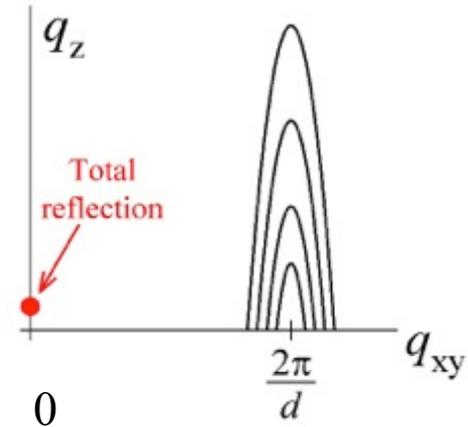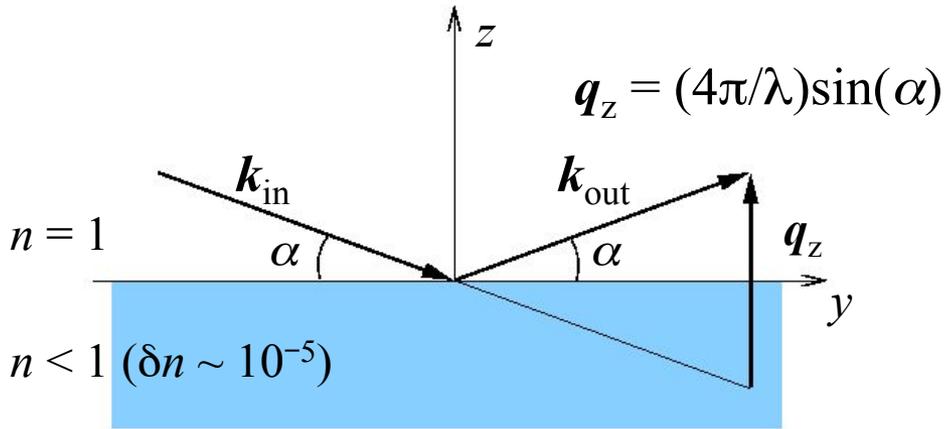
X-Ray Reflectivity: Principle

Visible Light Reflectivity: $\dfrac{n_1}{n_2}$ $n_2 > 1$ $n_1 < n_2$
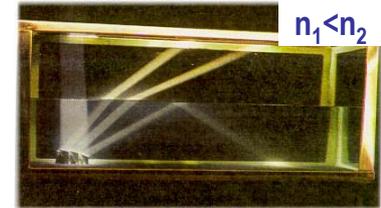
X-Ray Reflectivity: $\dfrac{n_1}{n_2}$ $n_2 < 1$ $n_1 > n_2$
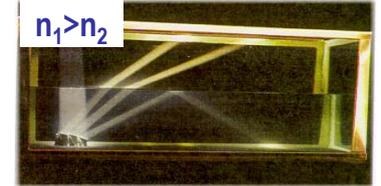
adapted M. Tolan Univ. Dortmund

- <u>Ideally sharp and flat interface:</u> ⇒ Fresnel reflectivity

$$R_F(q_z) = \left| \frac{q_z - \sqrt{q_z^2 - q_c^2}}{q_z + \sqrt{q_z^2 - q_c^2}} \right|^2 = \begin{cases} 1 & \text{for } q_z < q_c \\ \sim (q_c/2q_z)^4 & \text{for } q_z \gg q_c \end{cases}$$

- <u>Real interface (roughness, diffuseness, layers, etc.):</u>

$$R(q_z) \approx R_F(q_z) \left| \int dz \frac{d}{dz}\left[\frac{\langle \rho(z) \rangle}{\rho_\infty} \right] \exp(iq_z z) \right|^2$$

X-ray Specular Reflectivity
⇒ Structure normal to surface

Reflectivity

Reflectivity   Density Profile
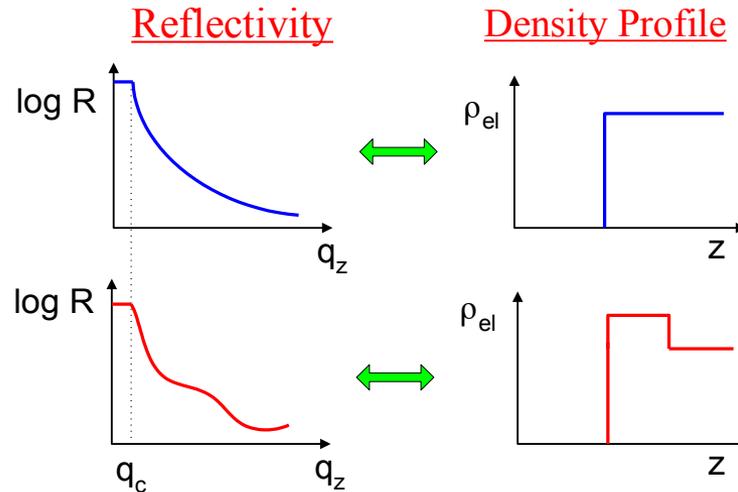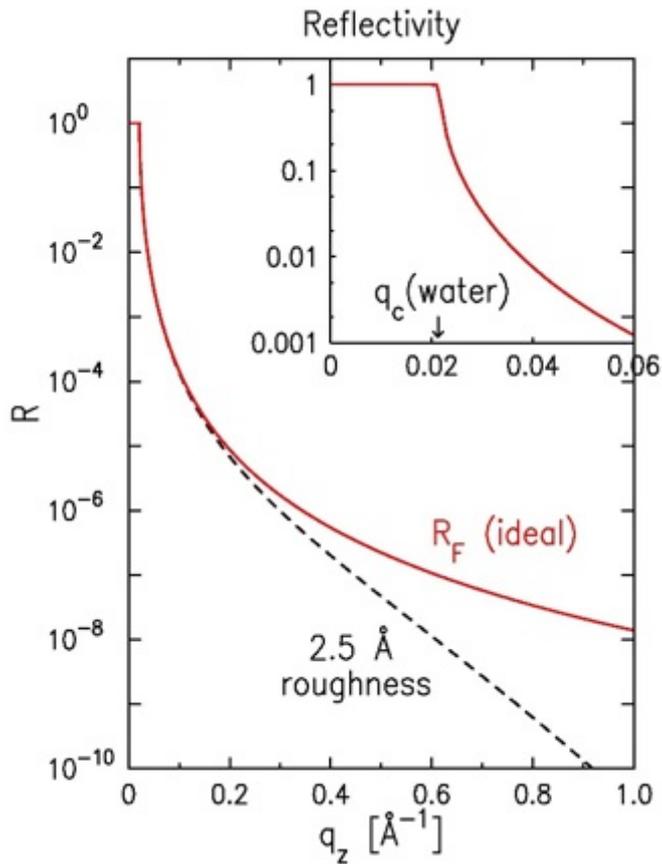
Modeling is needed to reconstruct the electron density profile

➢ XR: low incident angles (<5°)

➢ Relatively large surface areas are probed

➢ XR: Electron density profile normal to the surface

➢ Large dynamical range of profile measurements: thickness 0.1- hundred nm, relative contrast ~ few %

➢ Liquid surfaces can be investigated!

Features - Footprint effect

In the regime of total external reflection, some intensity is lost as the footprint on the surface is too large
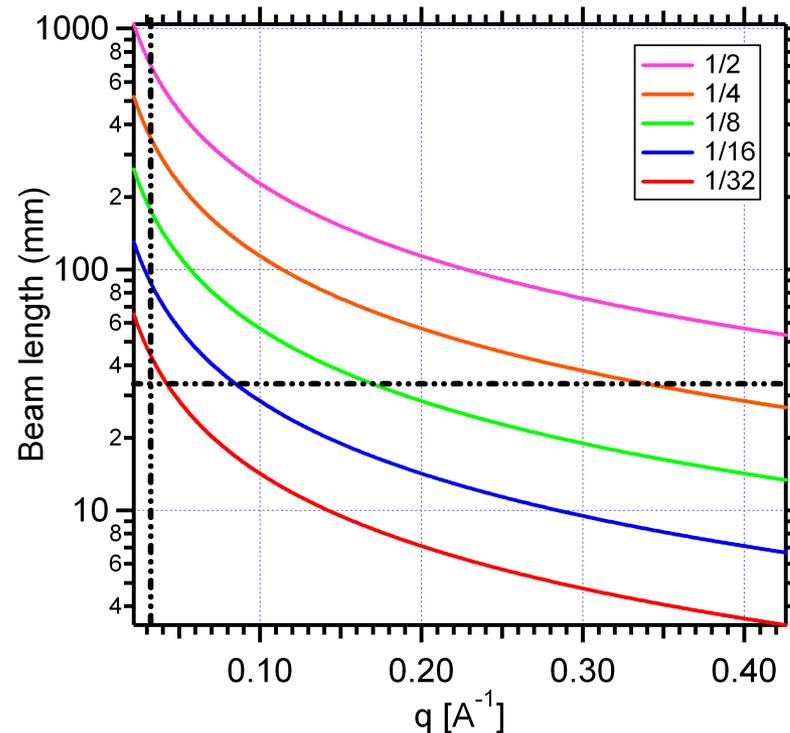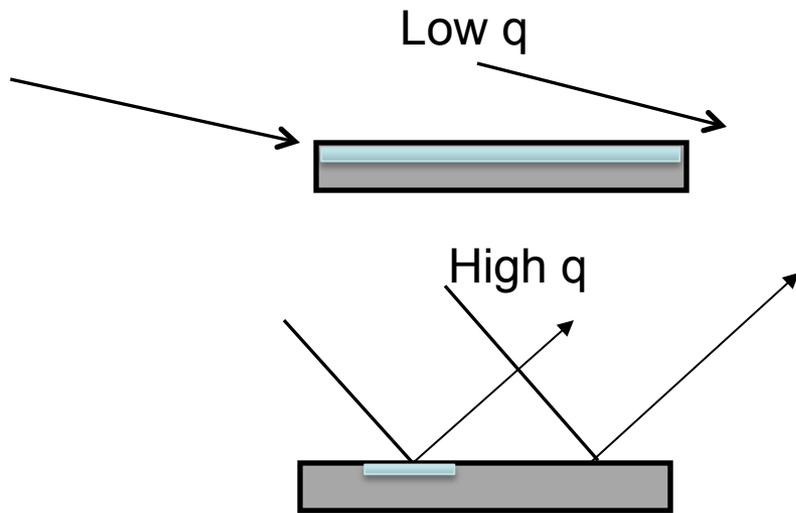
Foot print depends on beam width & sample geometry

What affects reflectivity?

Smooth surface

Maximum specular reflection

Rough surface

Non-specular reflection
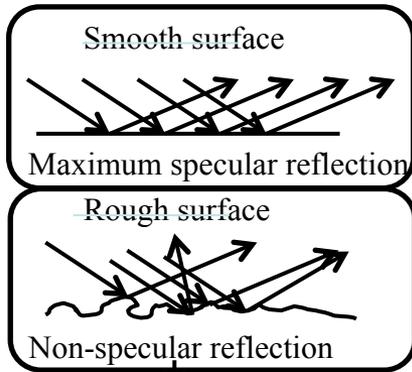
Loss of intensity and sharpness

Effect of roughness depends on coherence length l_c

$$l_c = \frac{\lambda}{2\alpha}$$

Only If roughness features $< l_c$, reflectivity profile is affected

$\sigma \sim 5A$
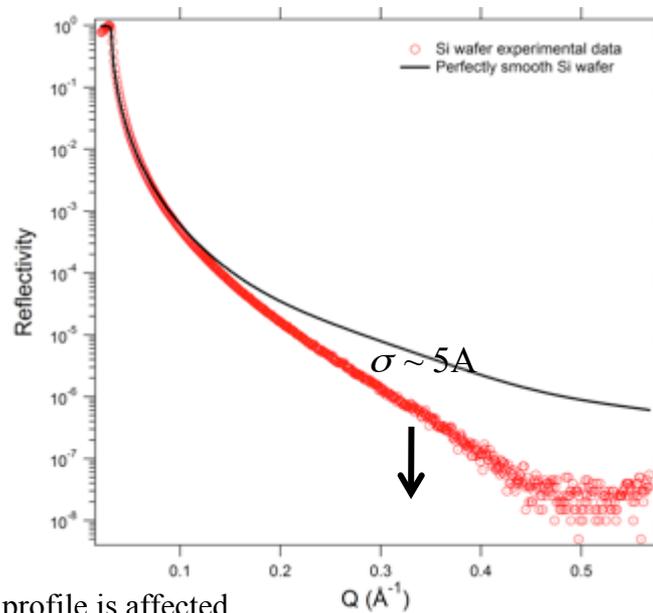
Large Q: roughness

Small (very) Q: Absorption effect and footprint

Total External Reflection Regime

$Q_z^{-4} = (4\pi/\lambda \sin \alpha_i)^{-4}$

$\beta/\delta=0$
$\beta/\delta=1/50$
$\beta/\delta=1/10$
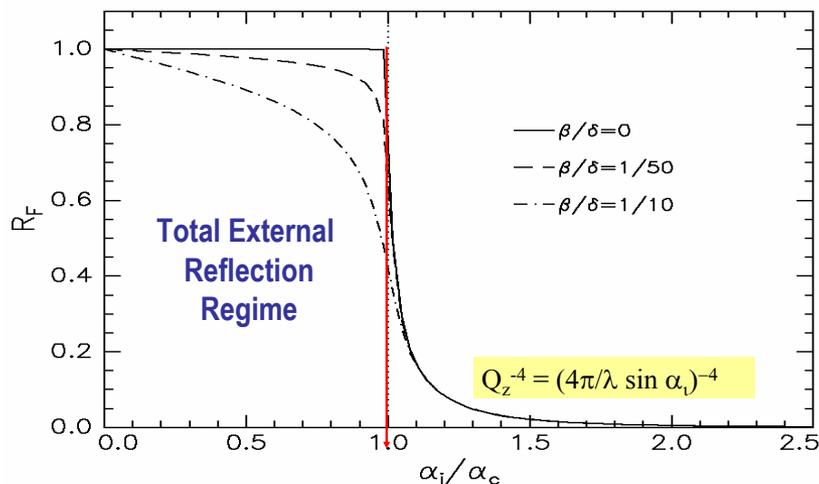
X-ray reflectivity for layered system

Simple estimation of film thickness

Fringes with uniform spacing

Thickness of the layer :

$$t = \frac{2\pi}{\Delta q_z}$$

Multilayer films require detailed modeling accounting for each interface

Multiple scattering (dynamical calculation)

Kiessig fringes

Multiple Interfaces
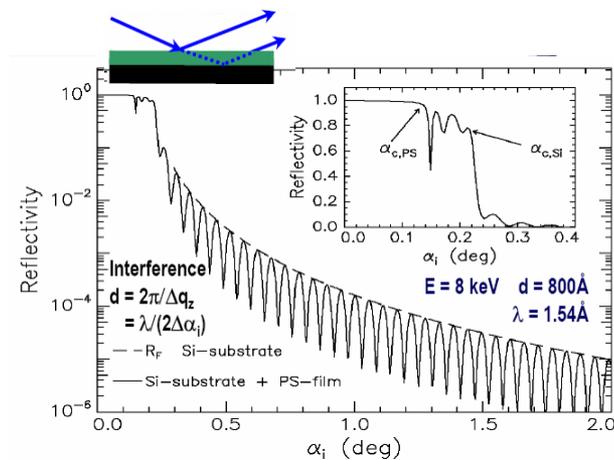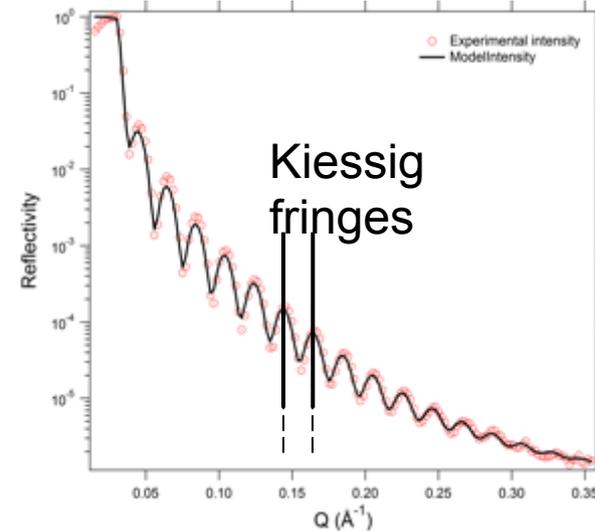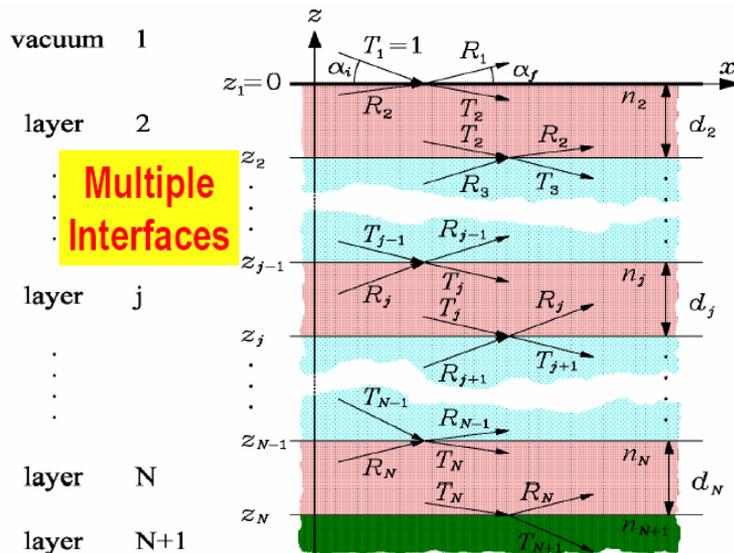
➜ Reflectivity used as an everyday laboratory tool to measure the thickness of layers deposited on a substrate

Structure of 2D nanoparticle/DNA monolayer

High energy (19keV) X-ray probes normal surface structure in-situ at liquid-solid interface
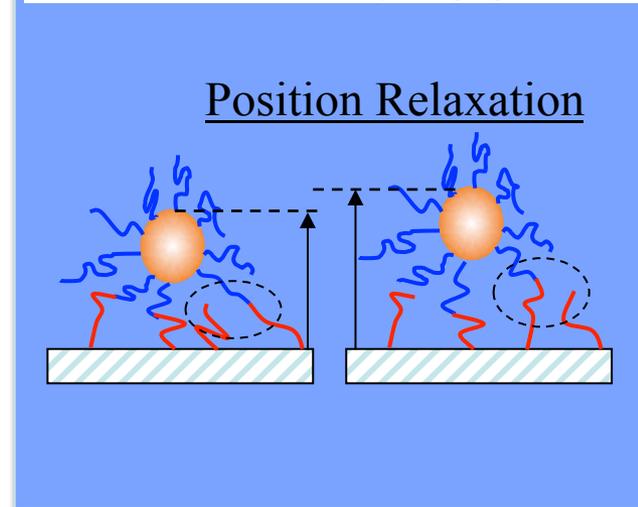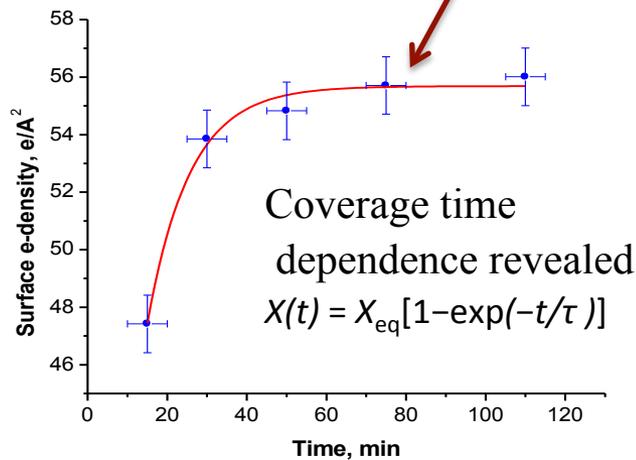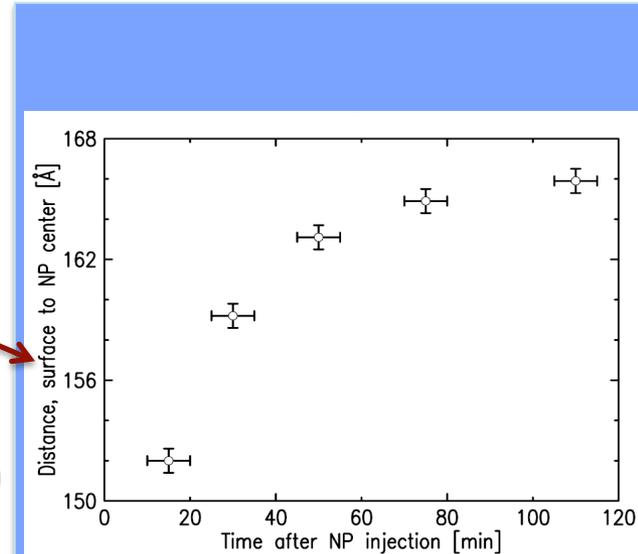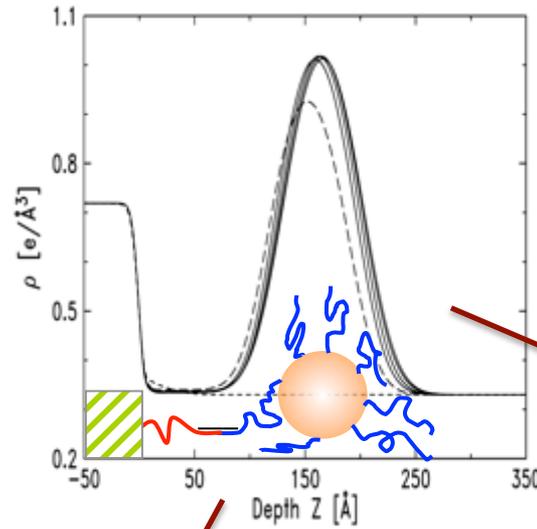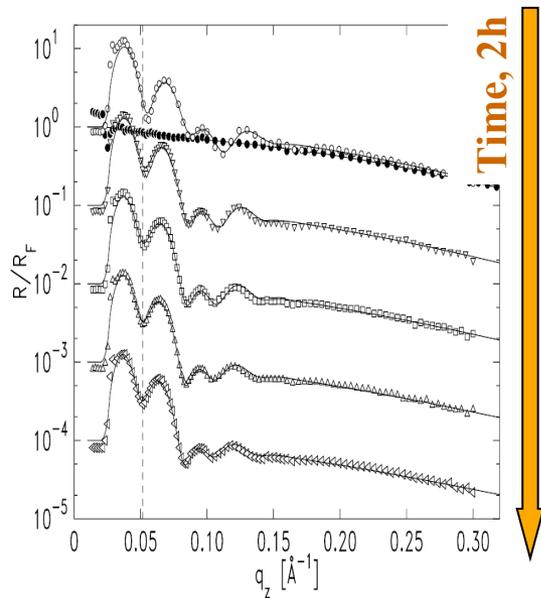
Time, 2h

Position Relaxation

Coverage time
dependence revealed
$X(t) = X_{eq}[1-\exp(-t/\tau)]$

O. Gang, D. Nykypanchuk, M.M. Maye (2007)

Outline

Synchrotron: NSLS II

- NSLS II $912M+
- 791 m circumference
- 58 beam ports
- 3 GeV, 500 mA

Coherent Hard X-ray Scattering (CHX) Beamline

- Each x-ray beam is ~10^{13} ph/s
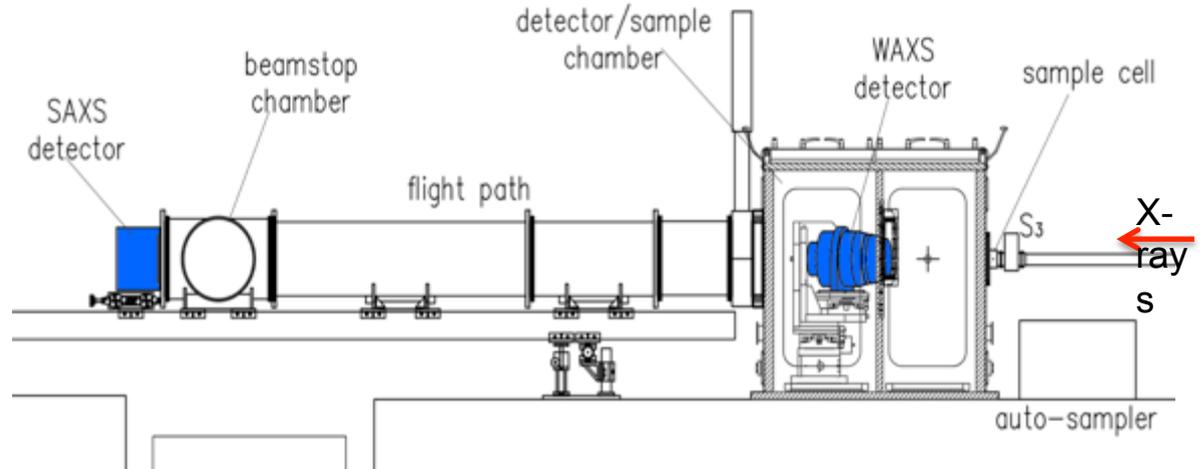
L. Yang, "Using an in-vacuum CCD detector for simultaneous small- and wide-angle scattering at beamline X9" J. Synch. Rad. 2013

• SAXS instruments in general use a series of slits to define beam size and minimize parasitic scattering

• A SAXS detector and an in-vacuum WAXS detector can provide a continuous reciprocal space coverage from molecular to micron sizes

Following appropriate data reduction and calibration procedure

Number of different approaches, often specific to the used area detector & instrument design
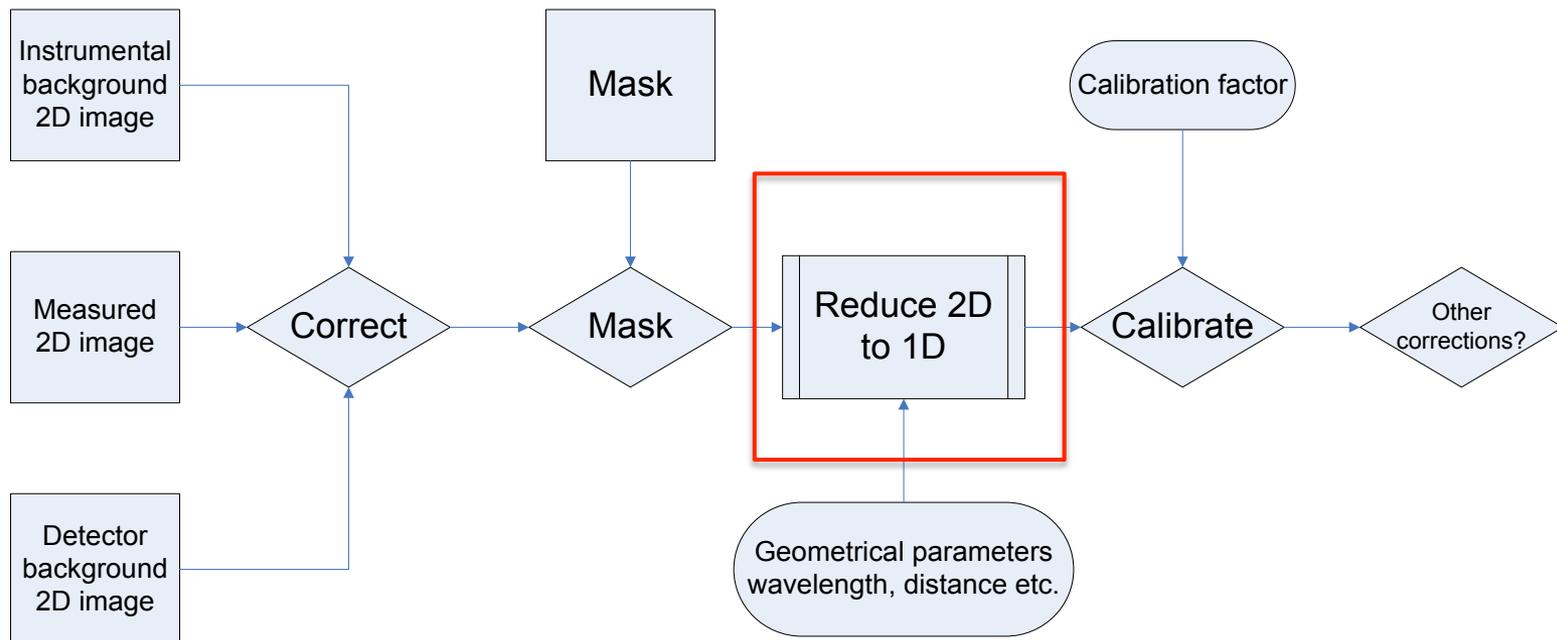
Data2D = (Sa2D − Dark2D) − C * (Bckg2D − Dark2D)

C ~ sample transmission, measurement times, incoming intensity etc.

Parameters that define scattering geometry
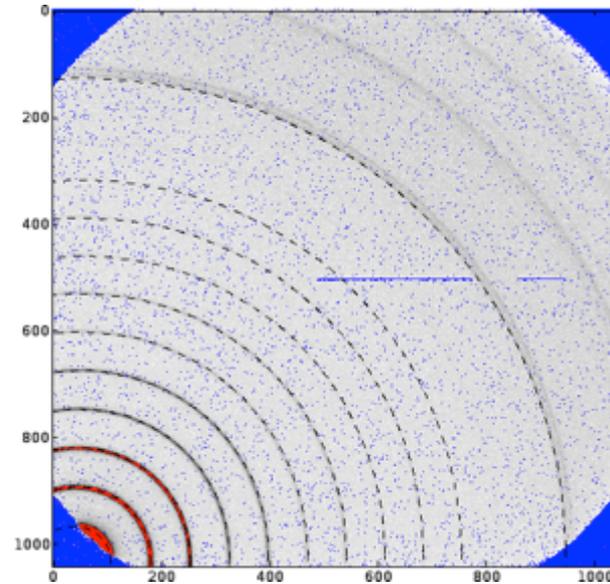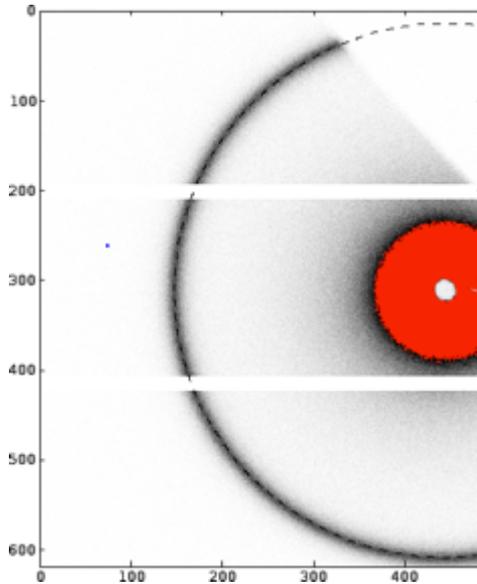
- Some area of 2D detector has to be masked for data reduction
- Calibration of distances and x-ray energy is crucial for the correct conversion to *q*

$$q = \frac{4\pi}{\lambda}\sin\theta$$

```
es.wavelength = 0.886          # X-ray wavelength (Å)
es.bm_ctr_x = 425              # pixel position of the X-ray beam
es.bm_ctr_y = 480              #
es.ratioDw = 49.8              # this is the sample-to-detector distance divided by
                               #         the width of the detector
es.det_orient = 0              # orientation of the detector
es.det_tilt = 0                #         0, 0, 0 for the SAXS detector
es.det_phi = 0                 #
```

2D to 1D

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

To...
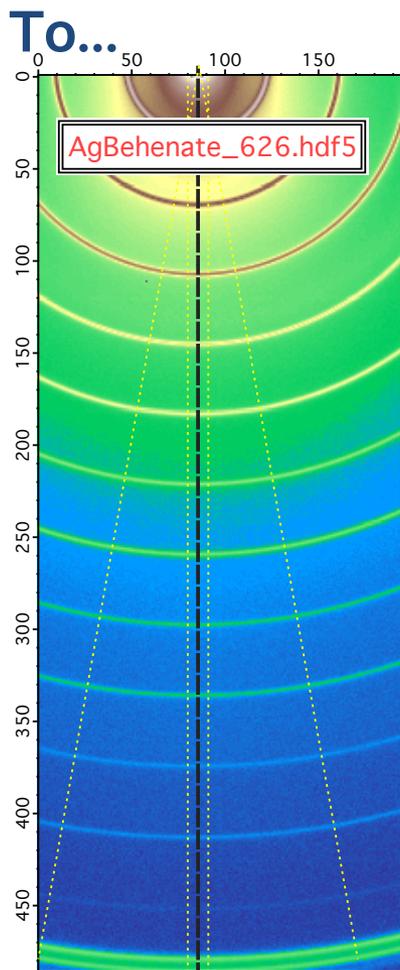
Convert this

Into this
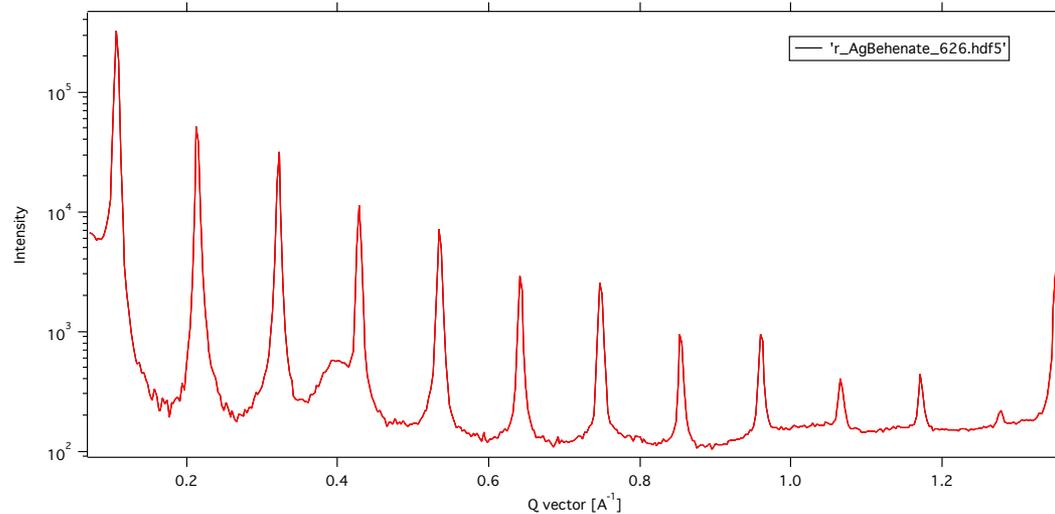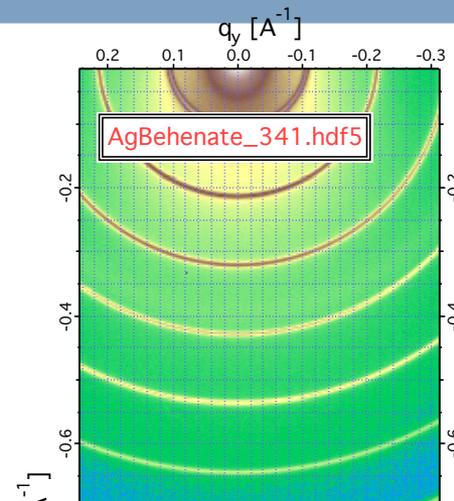
Some of the tools to convert 2D data to 1D data

- Ideally – tools should be provided with instrument
  - Like ESRF (software is mostly specific for their data)
    - http://www.sztucki.de/SAXSutilities/ (Michael Sztucki, processing of SAXS data)
    - http://www.esrf.eu/computing/scientific/SAXS/ (Peter Boesecke, manipulation of 2D data)
- **Fit2D** - http://www.esrf.fr/computing/scientific/FIT2D/ free, in use for very long time (= debugged), large user base, _very_ capable
  - However, not very user friendly and cumbersome for data analysis of large number of data sets – need to learn how to write scripts.
  - Ideal for processing large sets of samples (scripting).
  - Available for many platforms
- **Datasqueeze** - http://www.datasqueezesoftware.com/, $100/$50 for user license, Windows/Linux/MacOS.
- **Nika** – Igor Pro (6.0, Mac & Windows) based package (http://usaxs.xor.aps.anl.gov/) – free but need Igor Pro license (http://www.wavemetrics.com/), $550/$395 for user license.
  - Igor Pro scripts are open source and can be modified by anyone. – Open source

Advanced X-Ray Scattering at NSLS II

- Complex Materials Scattering (CMS) 2016: unique, automated high-throughput material exploration

- Soft Matter Interfaces (SMI) 2016-17: unique, high-performance undulator-based

- Wide energy range (2 to 24 keV) will enable new resonant scattering experiments on hybrid (soft/hard) materials

- Wide q-range for studies of hierarchical materials

- Microbeams (~2 μm) for mapping of heterogeneous samples

- High-flux and fast detectors for kinetic, in-situ, and in-operando experiments

SMI
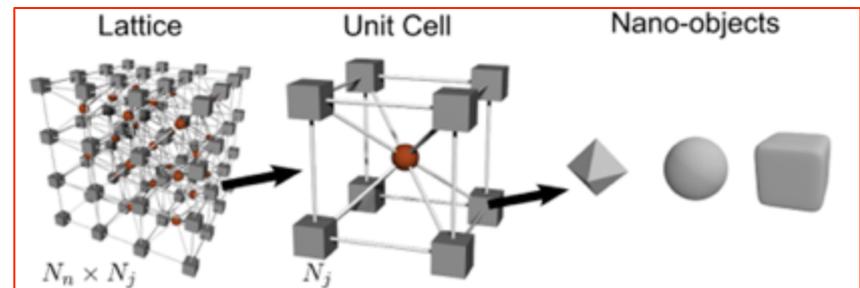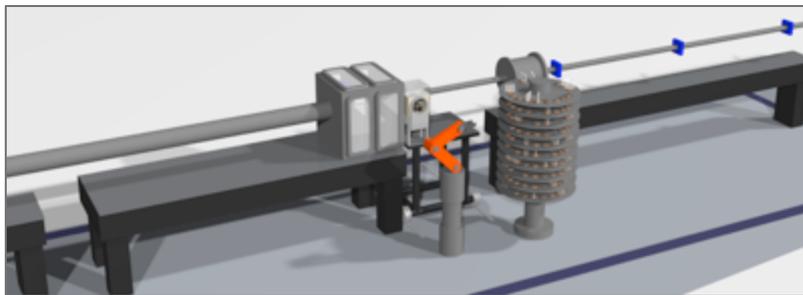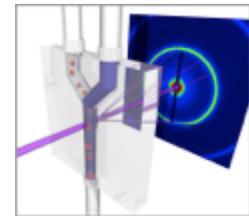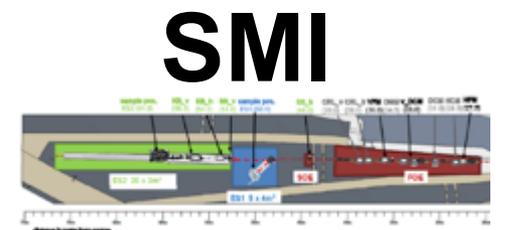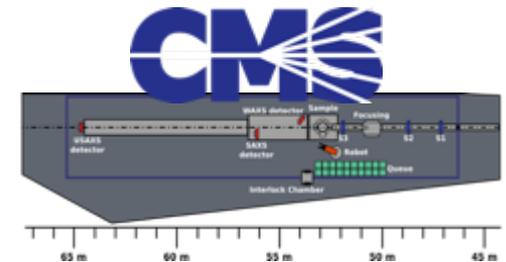
Useful Material

- Heimo Schnablegger & Yashveer Singh, "The SAXS Guide"
- O. GlaQer & O. Kratky, "Small-Angle X-ray Scattering", 1982, available free on line.
- Ryong-Joon Roe, "Methods of X-ray and Neutron Scattering in Polymer Science"
- D. Svergun and M. Koch, "Small-angle sca8ering studies of biological macromolecules in solu@on", Rep. Prog. Phys. 66 (2003) 1735–1782.
- Software: Irena, Nika

<u>Acknowledgments</u>

Assignment

1. Derive a radius of gyration for the shell of given thickness and diameter.

2. Your colleague obtained x-ray reflectivity (right) and grazing incidence diffraction (left) data from the nanoparticle monolayer at different salt conditions and for the underlying lipid layer. Provide your interpretation of the monolayer structure and its evolution using the plots. Does monolayer have in-plane order? What kind? How do the order and the correlation length (assume no contribution from resolution) change with salt increase? What is the thickness of the monolayer? Can you tell anything about nanoparticle shell from this estimation?

Small Angle X-Ray Scattering (SAXS)
from Bulks and Surfaces

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Columbia University, October 28, 2015

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NATIONAL LABORATORY