Investigation of soft matter with x-ray scattering methods

Oliver H. Seeck   (DESY)

1) **What is soft matter?** What are the properties and which properties can be investigated by X-rays: Example bulk polymer small angle scattering

2) **Soft matter and biological multilayer membranes:** Investigation by x-ray reflectivity (Born Approximation)

3) **Soft matter and biological multilayer membranes:** Investigation by x-ray reflectivity (Parratt-, Abeles-Formalism), Examples
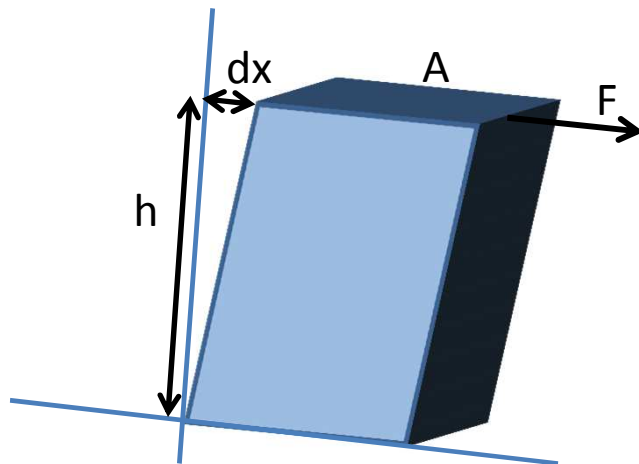
4) **Structured surfaces/gratings and molecular in-plane ordering:** Off-specular diffraction

5) **Capillary waves:** What are capillary waves, correlation functions, power spectral density.

6) **Capillary waves:** Diffuse x-ray scattering

What is soft matter?

"Soft" is a qualitative property

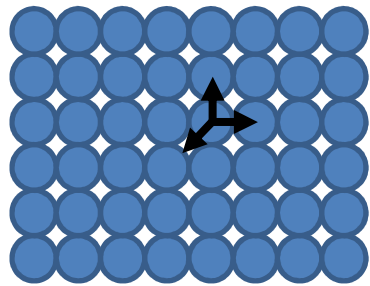The quantitative parameter is the shear modulus G:

$$G = \frac{F/A}{dx/h} \quad \rightarrow \quad \frac{F}{A} = G\,\frac{dx}{h}$$

Shear modulus of metals/glas : some 10 GPa
Shear modulus of soft matter : usually < 0.1 GPa (e.g. polystyrene)
for liquids 0 GPa

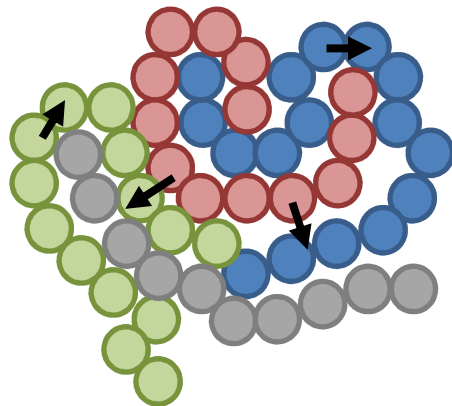When does the shear modulus becomes small (qualitative argument)?

atomic crystal

N : Number of particles

Binding energy between the atoms: some 1/10 eV (~k_BT)
→ Total energy ~ 3N (in 3 dimensions)

organic chain molecules

N_{chain} : Number of particles in chain

Binding energy between the atoms in the chain :
      some 1/10 eV
Binding energy between the chains: some 1/10 eV
→ Total energy ~ $N_{chain}(N/N_{chain})+2N/N_{chain} =N+2N/N_{chain}$
→ Total energy is smaller as compared to 3d-crystal
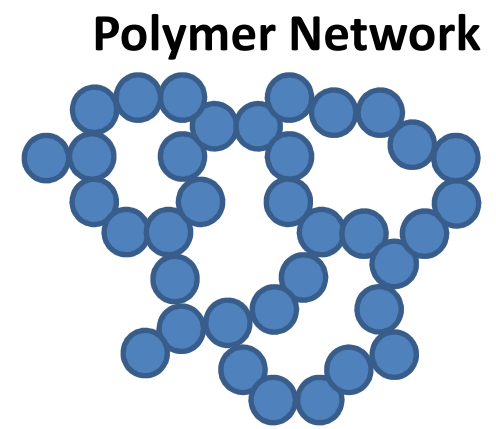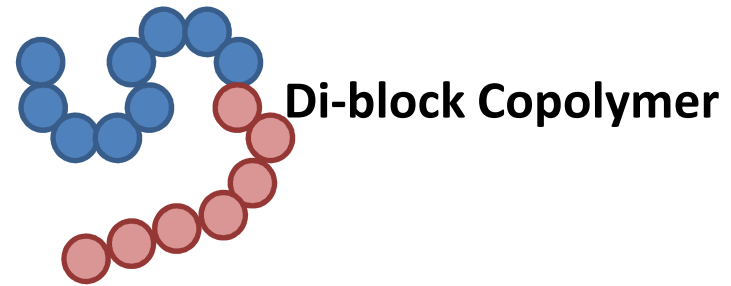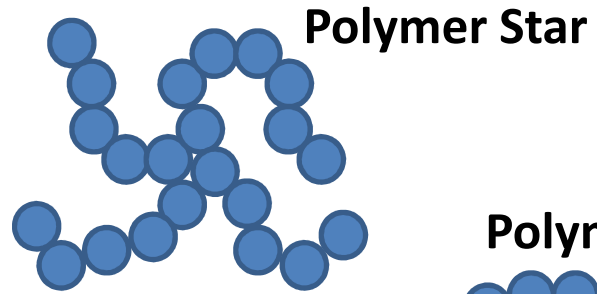   **and** it is mostly concentrating at the chain binding

Material can easily be deformed and is also not easy to crystalize

Types of soft matter
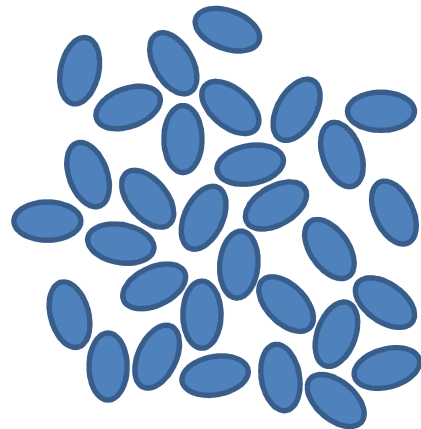
a) Polymer type

Polymer Chain
(as homopolymer)

Polymer Star

Polymer Network

Di-block Copolymer

Polymer Blend

Substrate

Polymer Brush

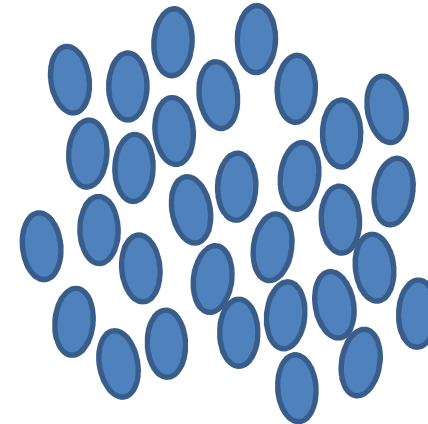Investigation of soft matter with x-ray scattering methods   O. H. Seeck
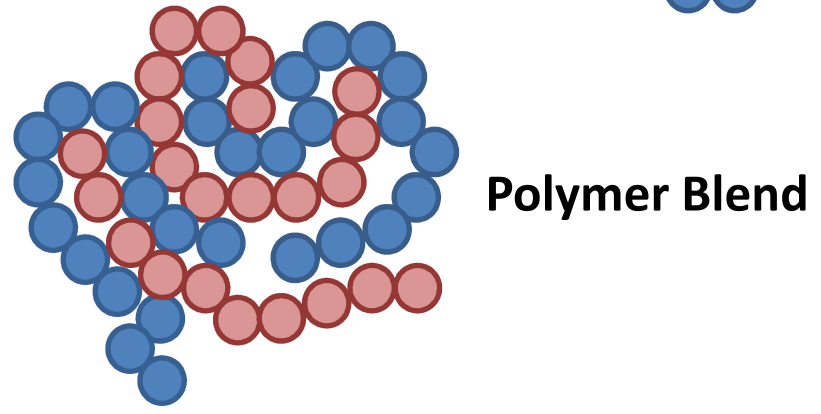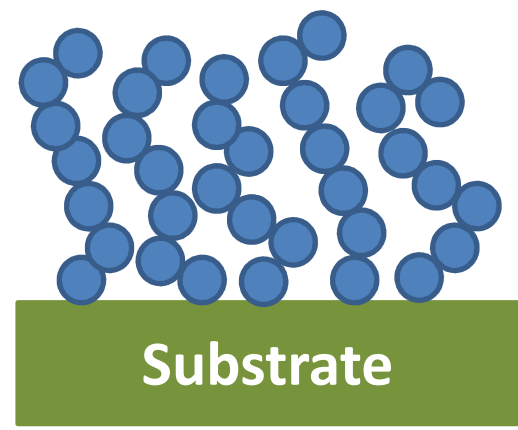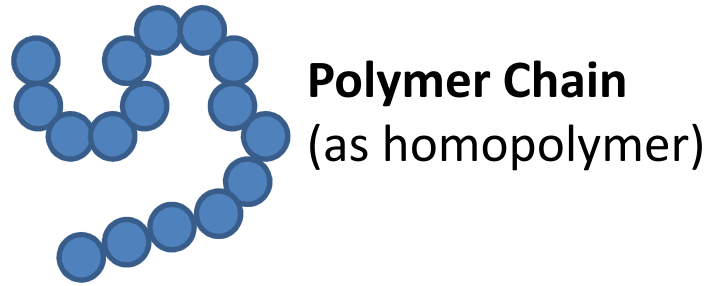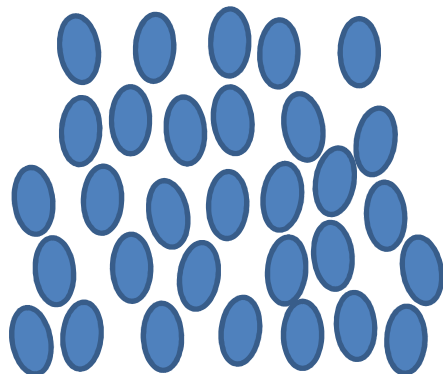
Types of soft matter

Simple liquid
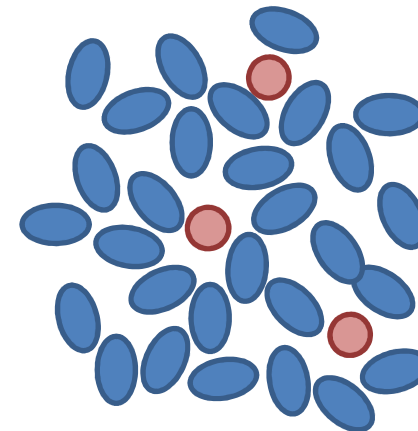- no orientation
- no translational order

Nematic liquid (liquid crystal)
- preferred orientation
- no translational order

Smectic liquid (liquid crystal)
- preferred orientation
- preferred order in layers
- no order between the layers

Solution (molecules)
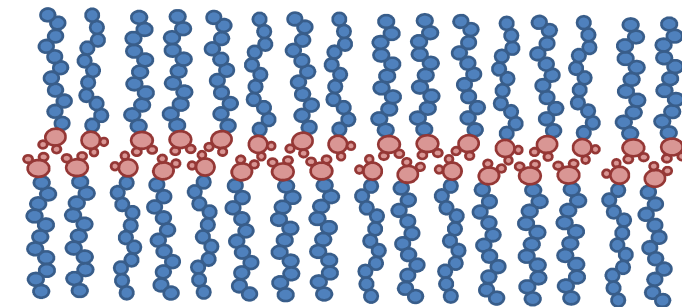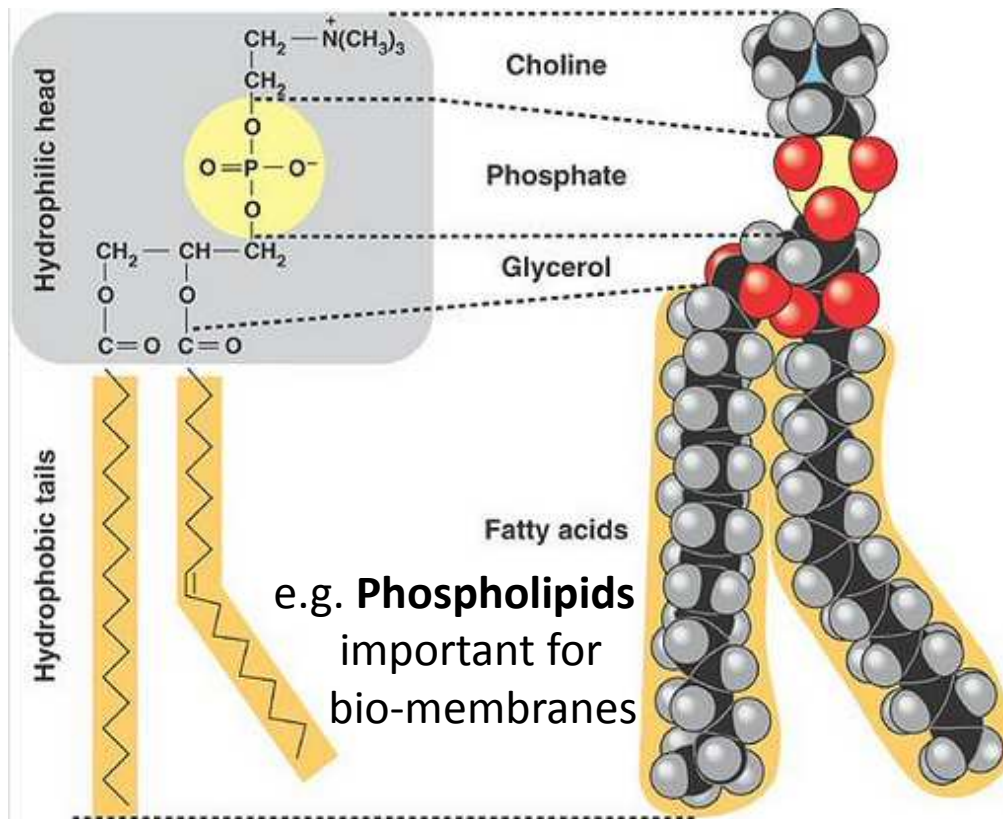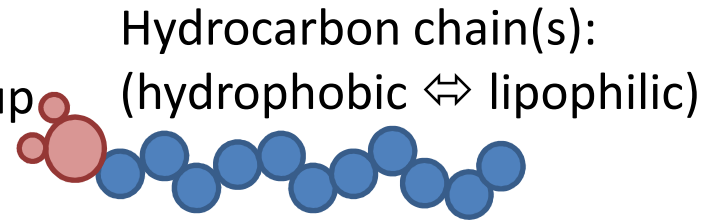**Colloids** (hard or soft particles)

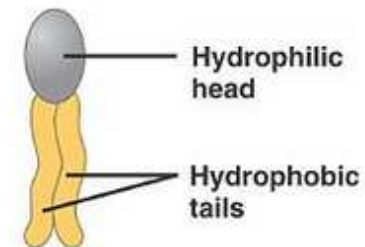# Types of soft matter

Based on amphiphilic (hydrophilic & lipophilic) molecules

Polar head group (hydrophilic)

Hydrocarbon chain(s): (hydrophobic ⇔ lipophilic)

e.g. **Phospholipids** important for bio-membranes

http://aecbio11.wikia.com/wiki/File:Phospholipid_structure.jpg

Phospholipid bilayer forming a membrane

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Types of soft matter

Emulsion

oil

water droplet

water

water droplet
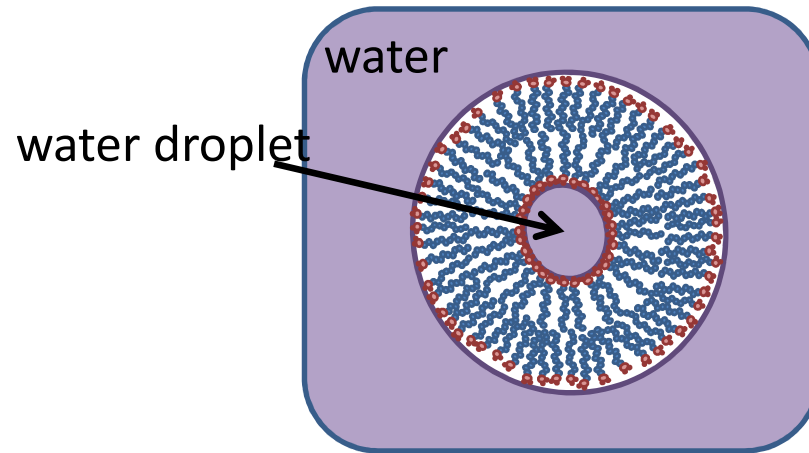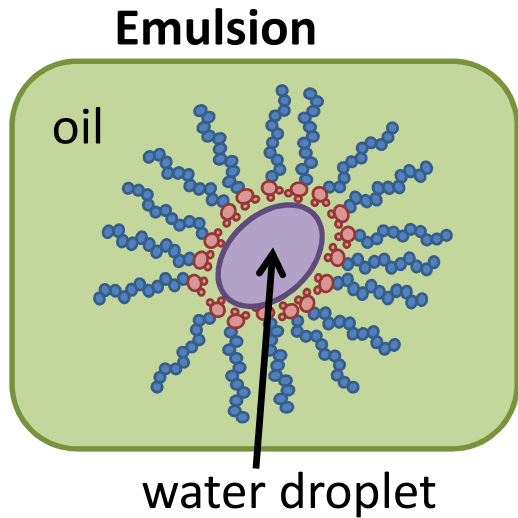
Vesicle
formed by
phospholipids

Rich phase diagrams of ternary (3 substances) amphiphilic systems.

LYOTROPIC LIQUID AND LIQUID CRYSTALLINE PHASES

Drug or Solubilizer/Drug

L3 Phase

Microemulsion

Normal Hexagonal

Reversed Hexagonal

Water

Lipid

Normal Micellar

Reversed Micellar

L3 Phase

Normal Cubic

Lamellar

Reversed Cubic

Microemulsion

Particle Sciences

http://www.particlesciences.com/images/tb/lyotropic-liquid-crystalline-phases.jpg

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Some parameters to quantitatively describe soft matter
(statistical parameters)
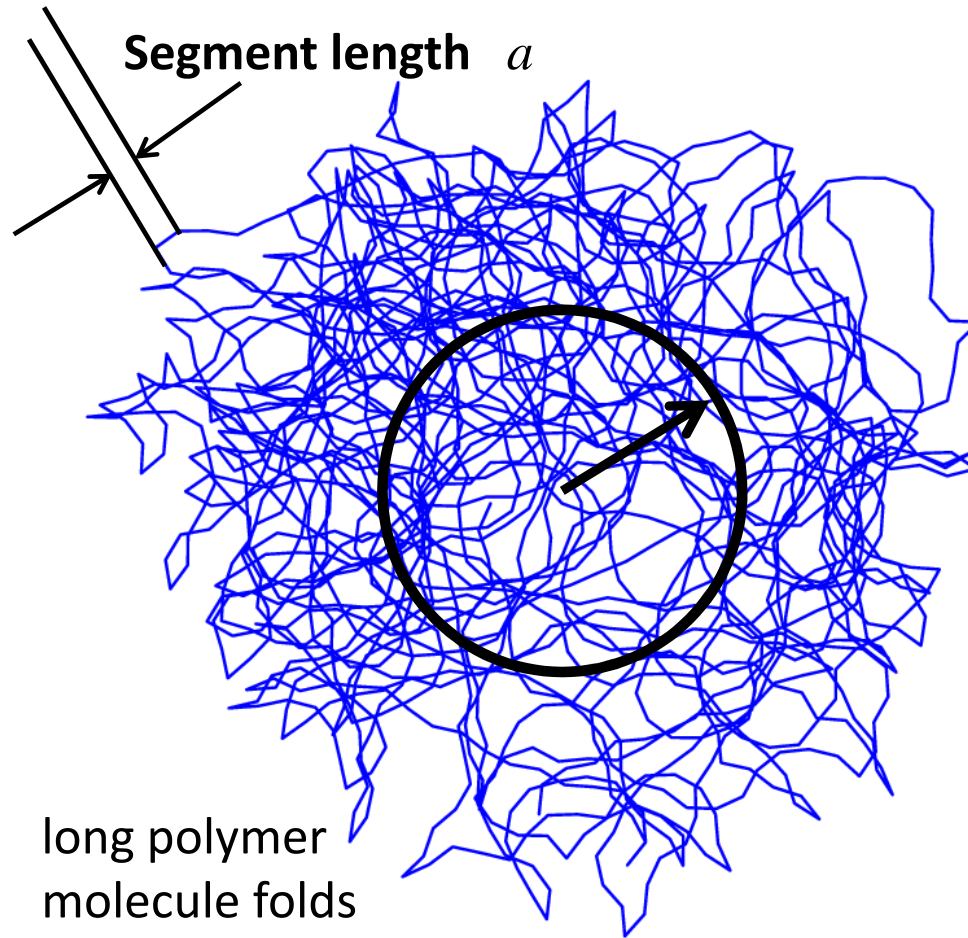
Segment length a

long polymer
molecule folds

Distribution function

2·**Radius of gyration** R_g

$$R_g{}^2 \sim N\,a^2/6$$

Contour length of chain Na
N : **number of segments**
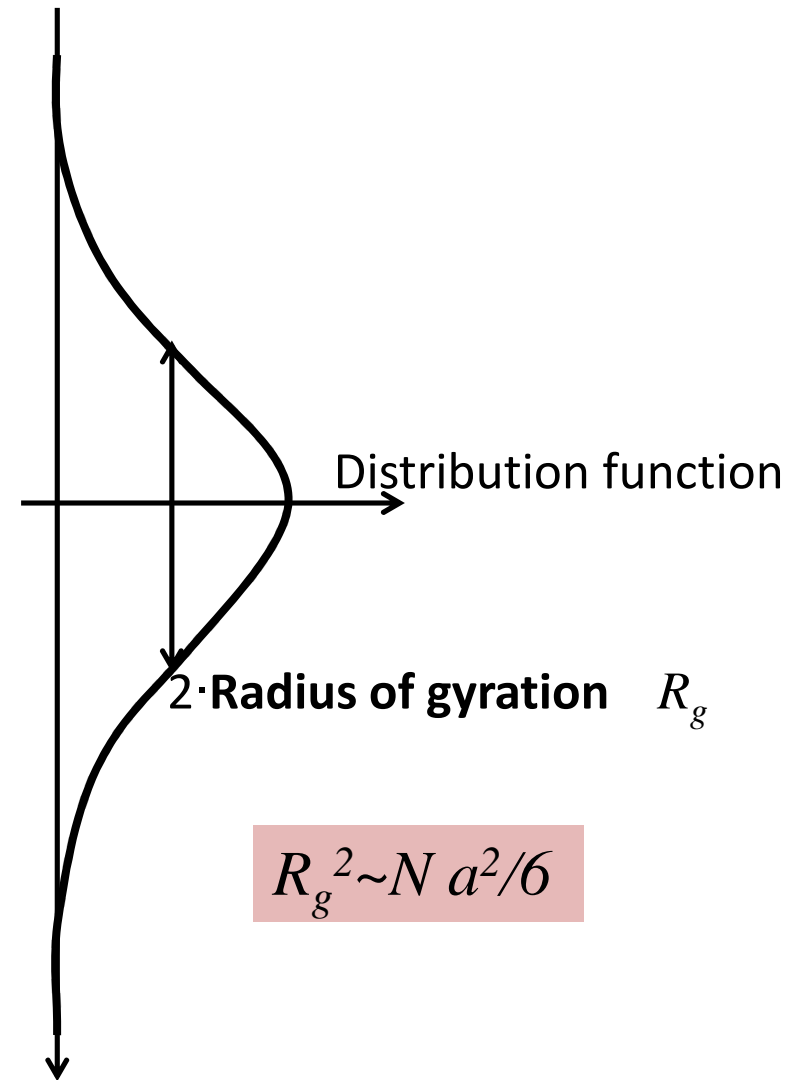
In solution long polymer chains use large space
In the bulk polymers are strongly entangled
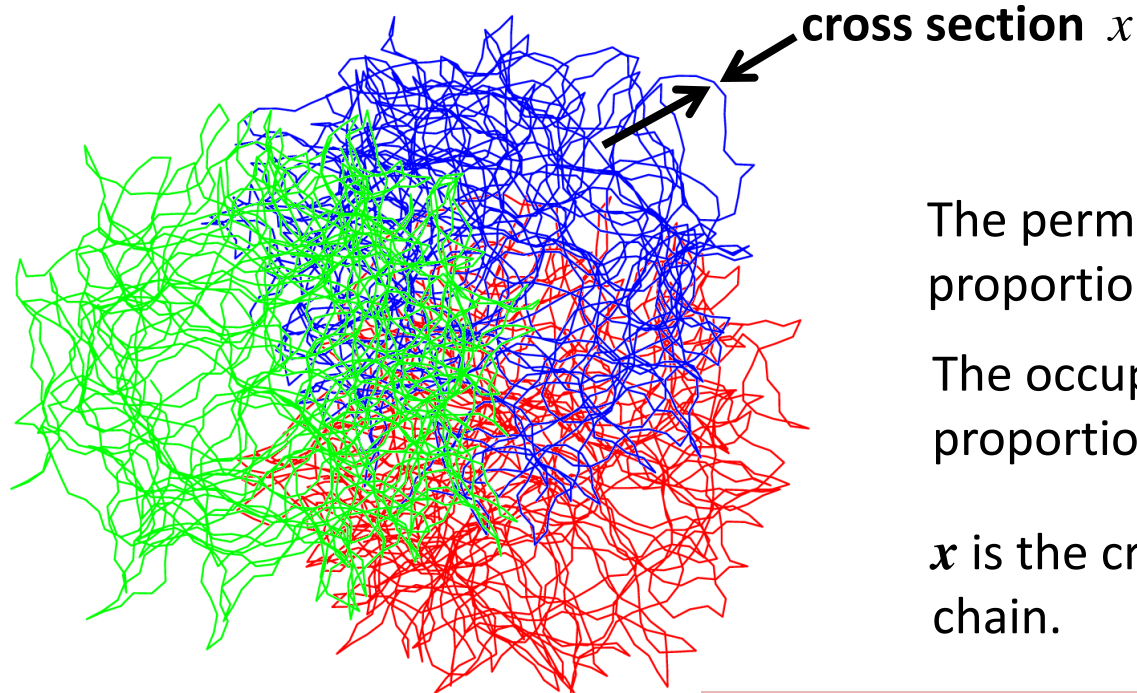
cross section x

The permeated (pervaded) volume is proportional to $R_g{}^3 \sim N^{3/2} a^3$

The occupied volume is proportional to Nax^2

x is the cross section of the chain.

$\rightarrow$ The permeated volume >> occupied volume for large N

This is only realistic in solutions.
In polymer bulk the chains are entangled to preserve the density.

How to determine the relevant parameters by X-rays

$\vec{q}$ Reciprocal wave vector

Incoming X-ray beam

Outgoing beam

Detector

2θ
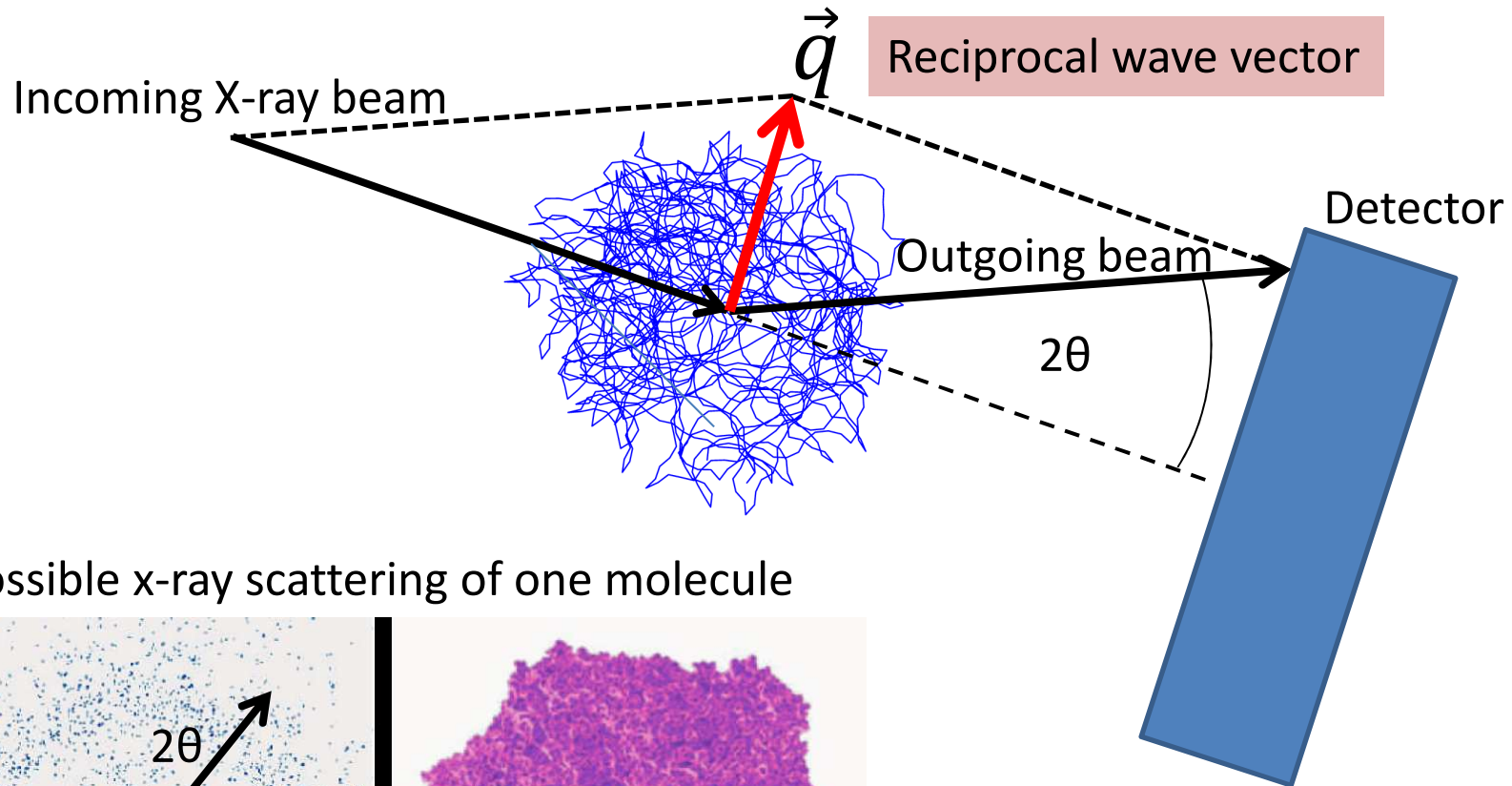
Possible x-ray scattering of one molecule

2θ

Laser polarization

$$A(\vec{q}) \sim \int \rho(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) d^3 r$$

Scattered amplitude in
Born approximation
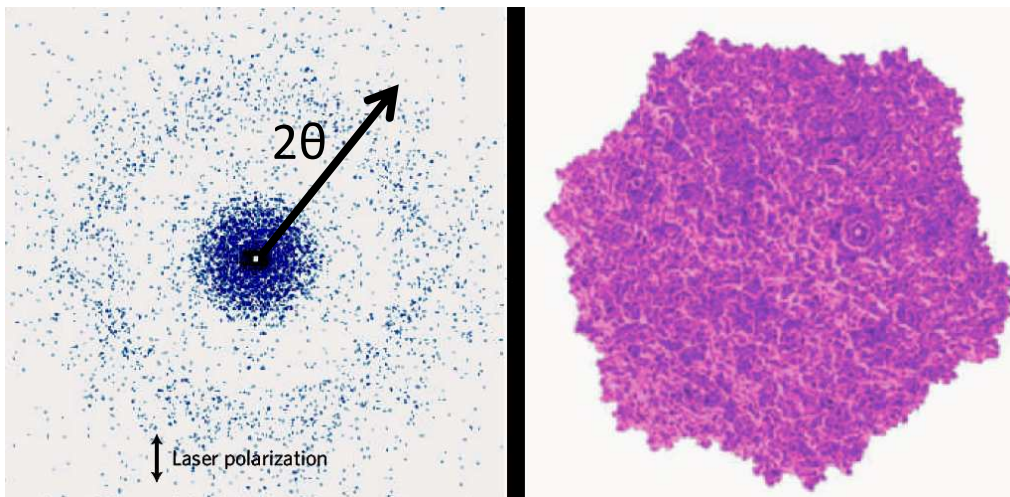
H. Chapman, Nature Materials, **8**, 299 (2009)

Usually, one the scattering cross section of one molecule is not sufficiently large to get a nice scattering pattern (except may be XFELs in the near future)

We need a lot of molecules: If possible: crystallize   Scattered intensity: Many Bragg peaks
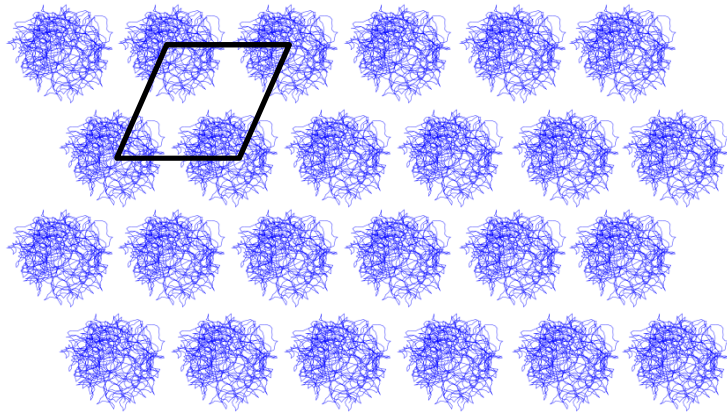
=>
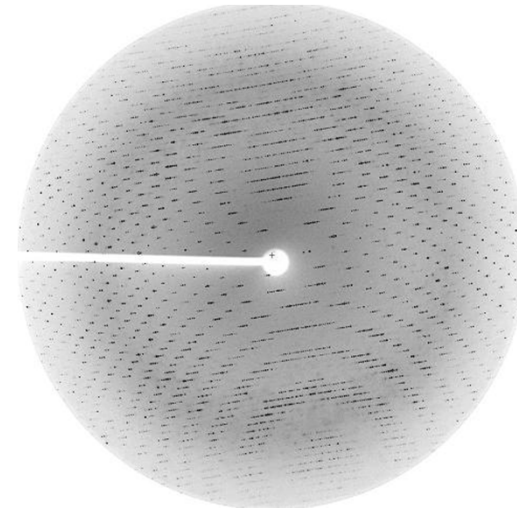
http://chemwiki.ucdavis.edu/Analytical_Chemistry/ Instrumental_Analysis/X-ray_Crystallography

Advantage:

All molecules oriented same =>
amplification of the structure signal at the Bragg-Peaks =>
structure can be determined exactly

Disadvantage:

By far not all molecules can be crystallized
In-vivo or in-vitro measurement not possible

If crystallization is not possible (for whatever reason)

$\vec{q}$

Incoming X-ray beam

Outgoing beam
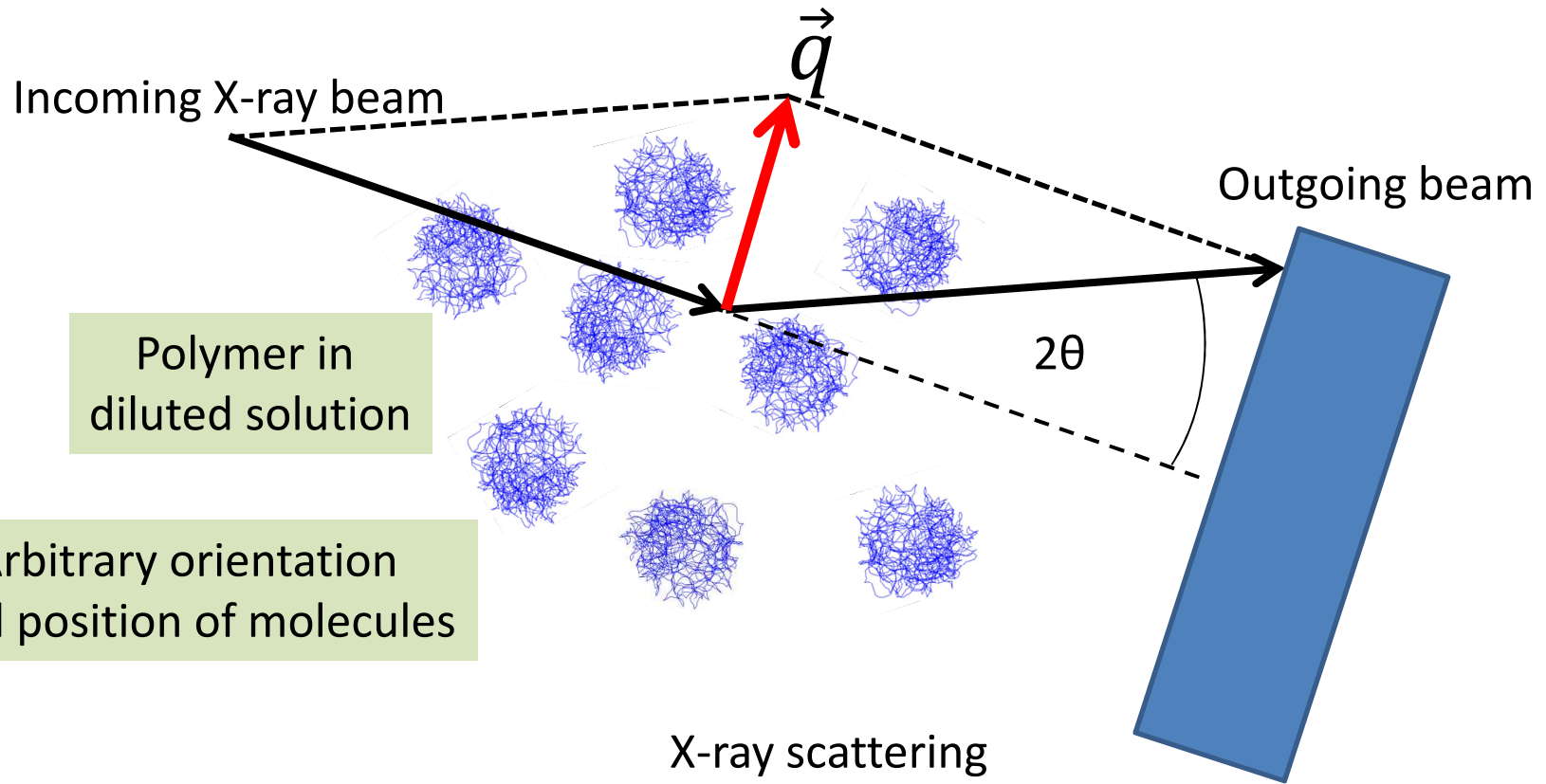
Polymer in diluted solution

Arbitrary orientation and position of molecules

2θ

Laser polarization

X-ray scattering

(a)

=>
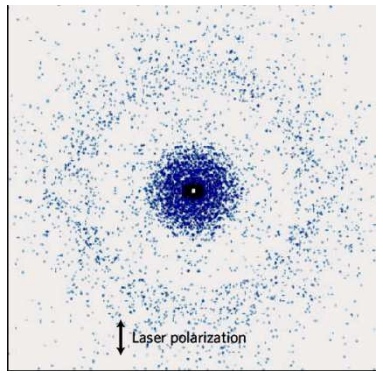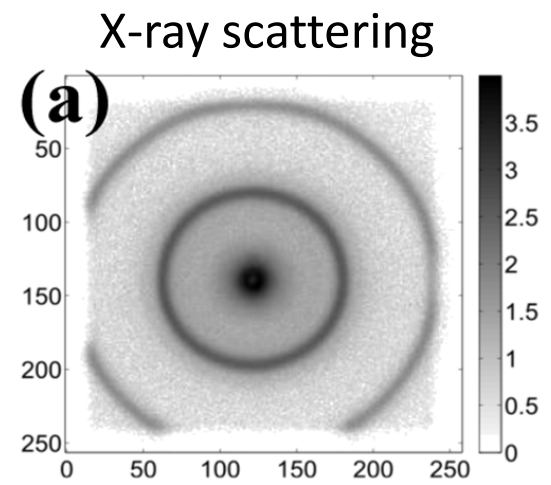
Spiky structure gets lost => Powder like ring structure

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A little bit of scattering theory (partially repeating)

$\vec{q}$

Incoming X-ray beam

Reciprocal wave vector

Outgoing beam

2θ
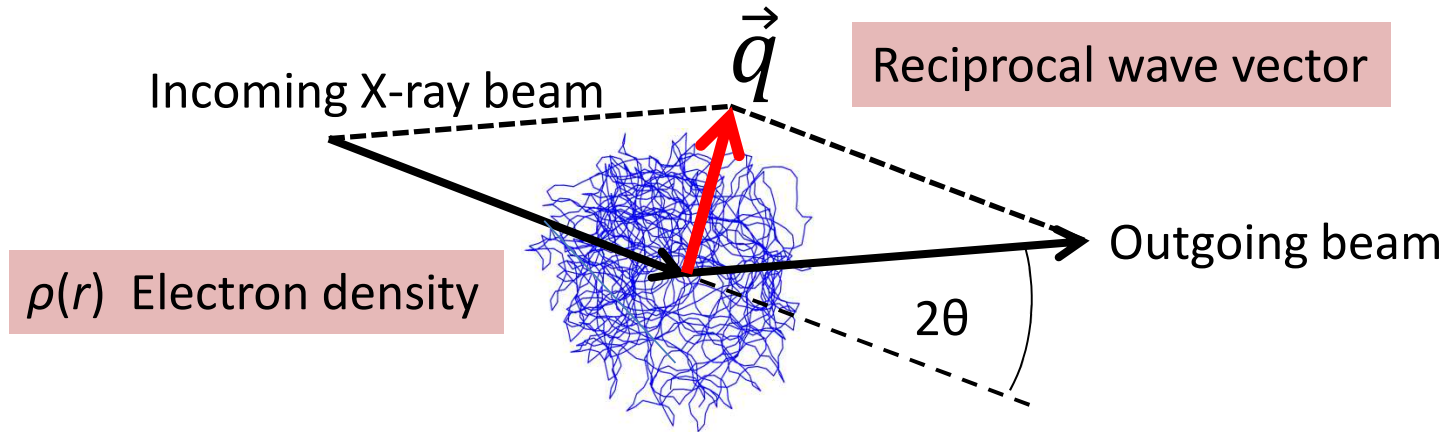
$\rho(r)$ Electron density

Scattered amplitude in Born approximation

$$A(\vec{q}) \sim \int \rho(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) d^3 r$$

Measured intensity

$$I(\vec{q}) = |A(\vec{q})|^2$$

The scattered amplitude is proportional to the Fourier transformation of the electron density ρ

What means Fourier transformation ?

$$F(\vec{q}) = \mathrm{F}(f) = \frac{1}{(2\pi)^{3/2}} \int f(\vec{r}) \exp(-i\vec{q} \cdot \vec{r}) \, d^3r$$

$$f(\vec{r}) = \mathrm{F}^{-1}(F) = \frac{1}{(2\pi)^{3/2}} \int F(\vec{q}) \exp(i\vec{q} \cdot \vec{r}) \, d^3r$$
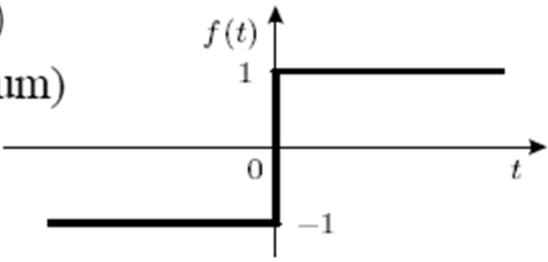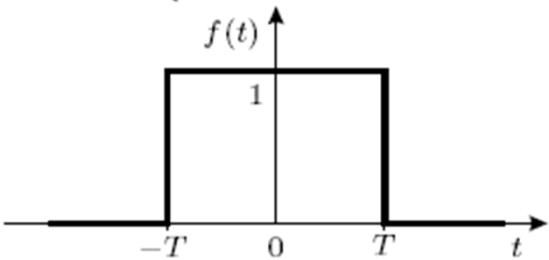
$F(\vec{q})$ is the frequency spectrum of $f(\vec{r})$
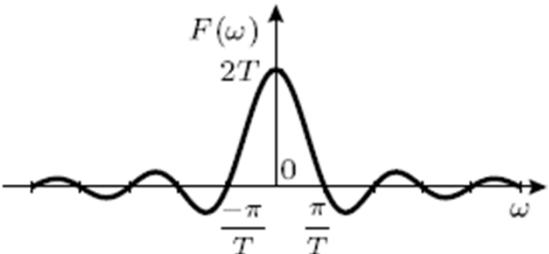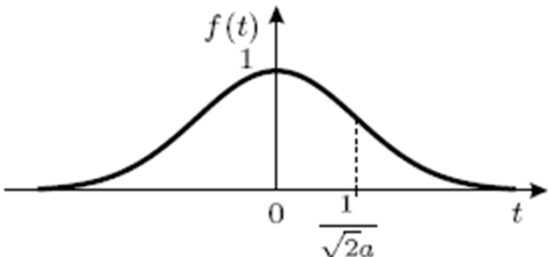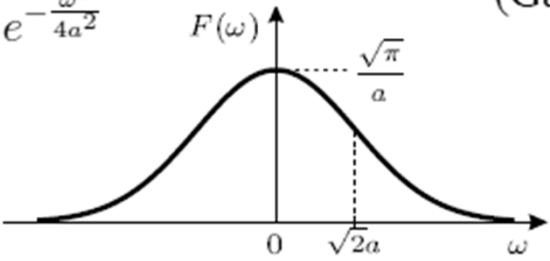
The complex functions $f(\vec{r})$ and $F(\vec{q})$ must be integrable:
- Dropping to zero for large $|\vec{r}|, |\vec{q}|$
  or oscillatory behavior with mean value 0
- Finite number of discontinuities
- If the mean value can be separated (e.g. $f(\vec{r}) = A + \sin(\vec{k} \cdot \vec{r})$):
$$\mathrm{F}(f) = \mathrm{F}(A) + \mathrm{F}\big(\sin(\vec{k} \cdot \vec{r})\big) = A\delta(\vec{q}) + \mathrm{F}\big(\sin(\vec{k} \cdot \vec{r})\big)$$
  where $\delta(\vec{q})$ is the delta function and the last term is integrable

Examples for Fourier transformations

$f(t)$	$F(\omega)$
$\mathrm{sgn}(t)$ (Signum)	$\dfrac{2}{j\,\omega}$
$\mathrm{rect}\left(\dfrac{t}{2T}\right) = \begin{cases} 1 & \text{für} \quad \lvert t \rvert < T \\ 0 & \text{für} \quad \lvert t \rvert > T \end{cases}$	$2T \cdot \dfrac{\sin(\omega T)}{\omega T}$
$e^{-a^2 t^2}$ (Gauß-Funktion)	$\dfrac{\sqrt{\pi}}{a} \cdot e^{-\frac{\omega^2}{4a^2}}$ (Gauß-Funktion)

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In general: small objects in real space are large objects in Fourier space and vice versa

Real space

Fourier space (log-log)
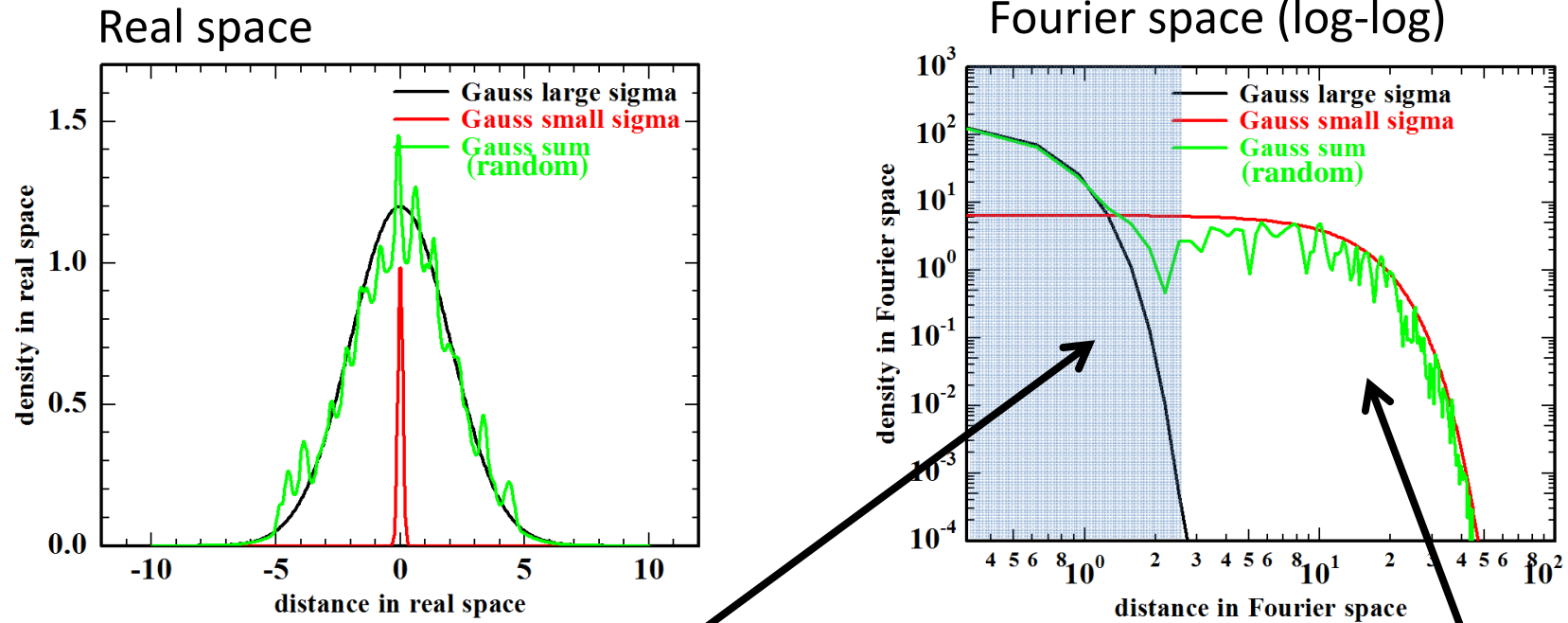
Small angle X-ray scattering (SAXS)

Wide angle X-ray scattering (WAXS)

Small angle scattering contains the shape of molecules

Wide angle scattering contains information about the atoms

Calculations of the intensity $I(\vec{q}) = |A(\vec{q})|^2$

$$I(\vec{q}) \sim \left| \int \rho(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) d^3r \right|^2 = \iint \rho(\vec{r}) \exp(i\vec{q} \cdot \vec{r}) \rho(\vec{u}) \exp(-i\vec{q} \cdot \vec{u}) \, d^3r \, d^3u$$

$$= \iint \rho(\vec{r}) \rho(\vec{u}) \exp(i\vec{q} \cdot ([\vec{r} - \vec{u}]) \, d^3r \, d^3u$$

$$= \iint \rho(\vec{r}) \rho(\vec{r} - [\vec{r} - \vec{u}]) \exp(i\vec{q} \cdot ([\vec{r} - \vec{u}]) \, d^3r \, d^3u$$

$\vec{R} = \vec{r} - \vec{u}$

R is a distance between two objects

$$= \iint \rho(\vec{r}) \rho(\vec{r} - \vec{R}) \exp(i\vec{q} \cdot \vec{R}) \, d^3r \, d^3R$$
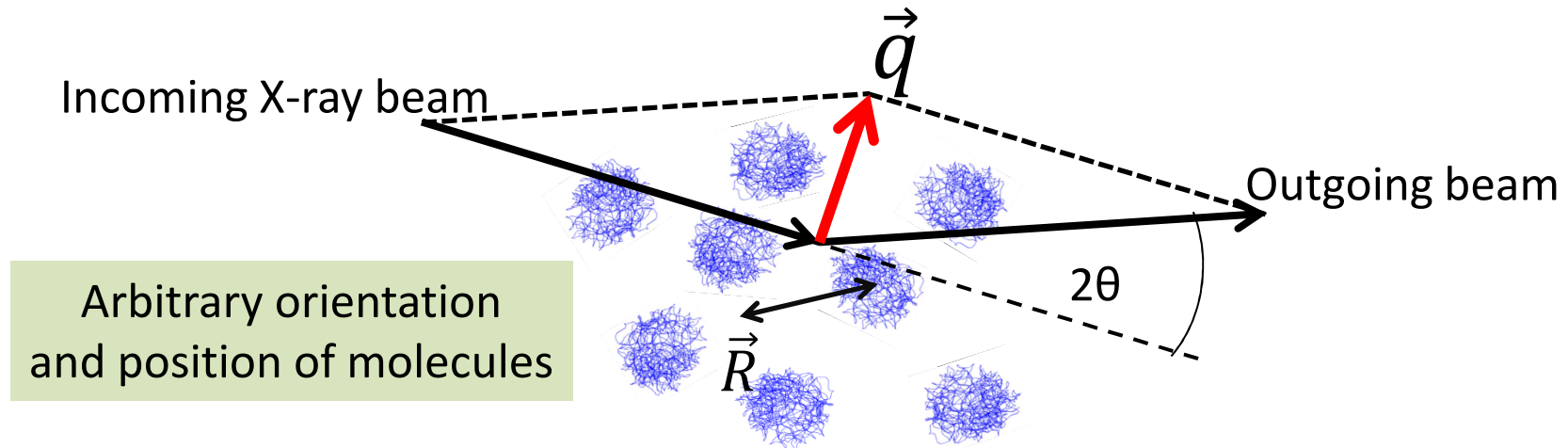
$$= \int \left(\int \rho(\vec{r}) \rho(\vec{r} - \vec{R}) d^3r \right) \exp(i\vec{q} \cdot \vec{R}) \, d^3R$$

$$g(\vec{R}) = \int \rho(\vec{r}) \rho(\vec{r} - \vec{R}) d^3r$$

$$I(\vec{q}) \sim \int g(\vec{R}) \exp(i\vec{q} \cdot \vec{R}) \, d^3R$$

Pair correlation function
Pair distribution function (PDF)

e.g.: Random particles

The PDF only depends on $|\vec{R}|$ in the case of isotropic distribution
=> also the intensity only depends on $|\vec{q}|$

$$g(\vec{R}) = g(R) \underset{\text{isotropic}}{\Longrightarrow} I(\vec{q}) = I(q)$$

Integration with spherical coordinates: $d^3r = R^2 \sin\theta\, d\varphi\, d\theta\, dR$

$$I(q) \sim \int g(R)\exp(iqR\cos\theta)\, R^2 \sin\theta\, d\varphi\, d\theta\, dR = \int R^2 g(R)\frac{\sin(qR)}{qR}\, dR$$

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$$I(q) \sim \int R^2 g(R) \frac{\sin(qR)}{qR} dR$$

Debye formula

$$p(r) \sim \int q^2 I(q) \frac{\sin(qR)}{qR} dq$$

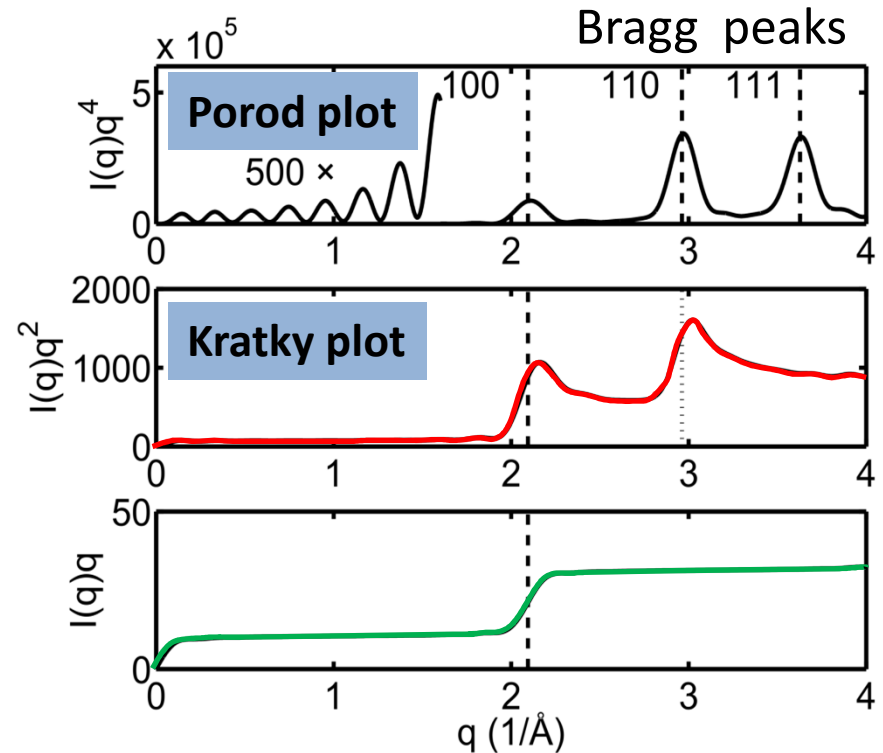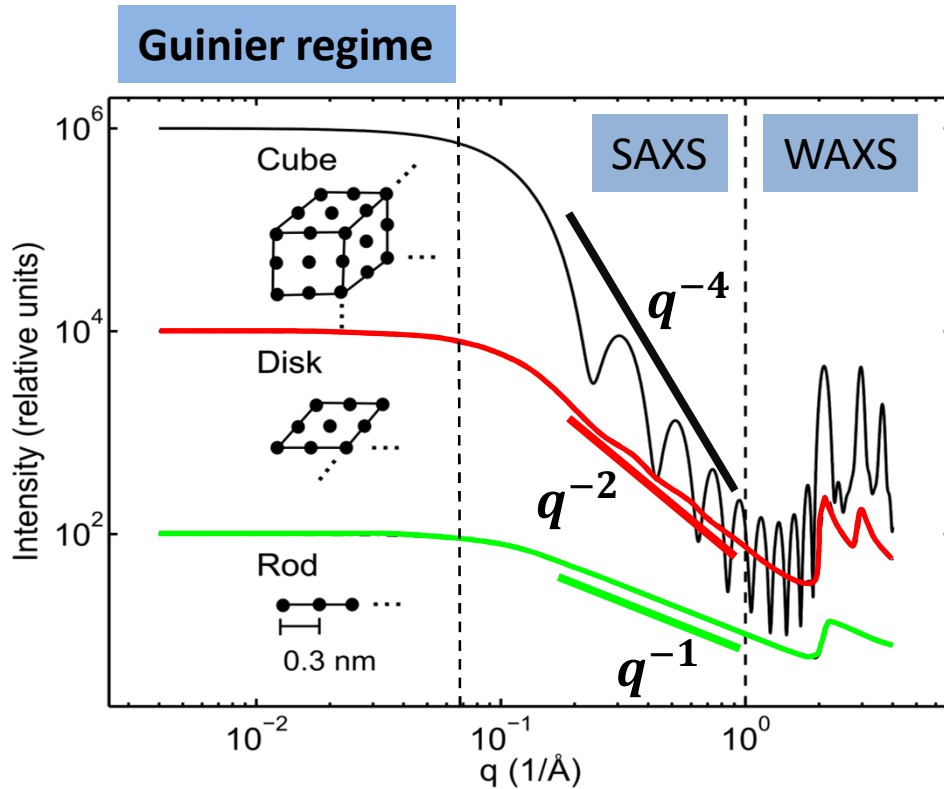The PDF can be determined by a simple back transformation

Distance distribution function

At very diluted samples (e.g. colloids, polymers in solution) the correlation between the particles can be neglected. Then $g(R)$ describes the auto-correlation and the SAXS data just contains the shape information.

In SAXS $I(q)$ and $p(r)$ are characteristic depending on the shape of the particle

Svergun, D. I. and Koch, M. H. J., *Rep. Prog. Phys.*, **66**, 1735 (2003)

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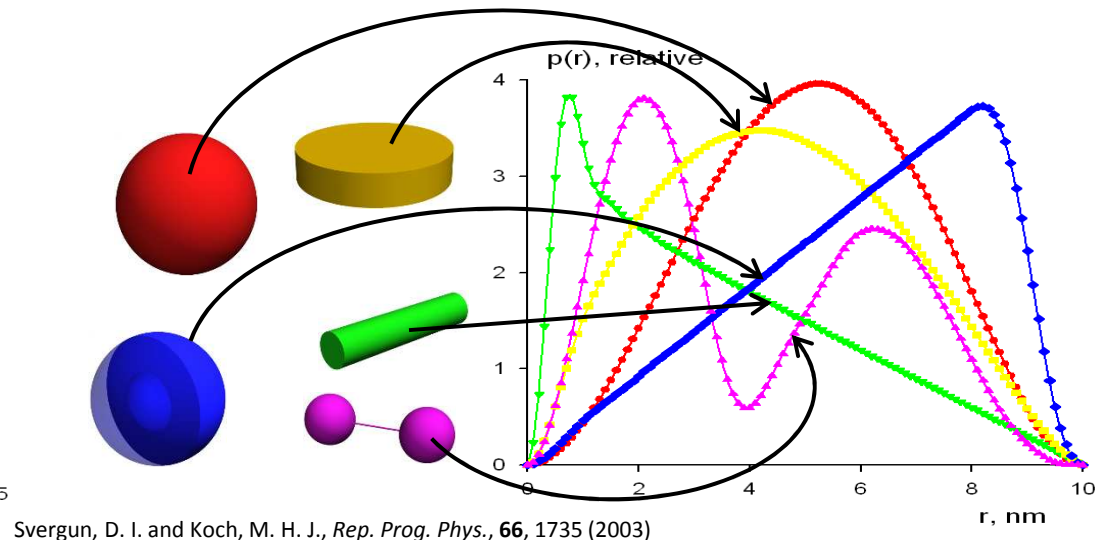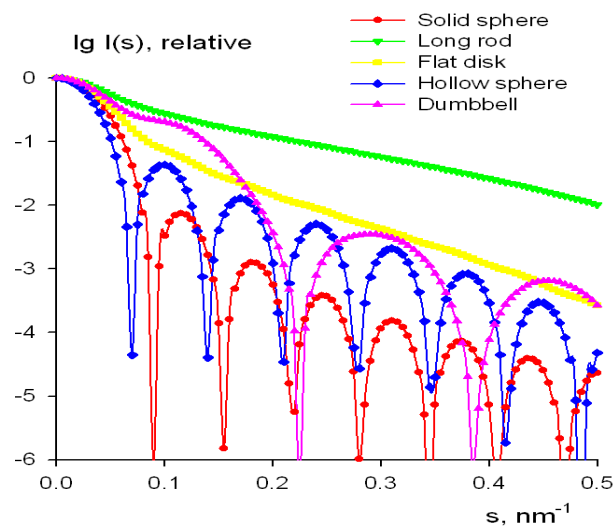
Power laws for the SAXS range

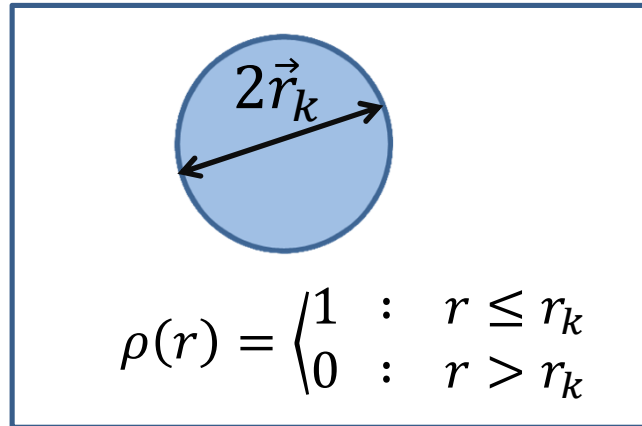For very small q the intensity only depends on R_g, the radius of gyration (**Guinier**)

$$I(q) \sim \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

For larger q but still in SAXS the Intensity is a power law depending on the dimension of the object
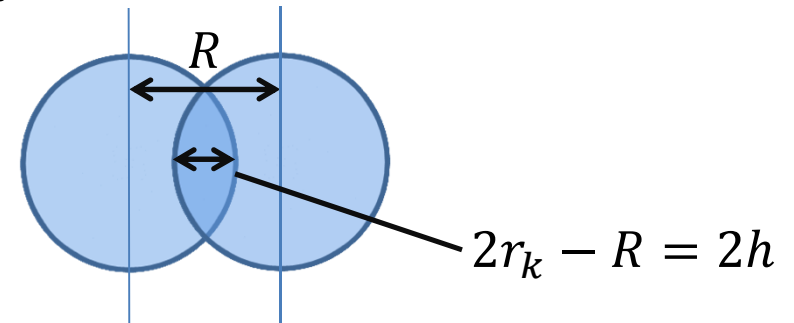
3d objects: $\alpha = 4$ (**Porod law**)
2d objects: $\alpha = 2$
1d objects: $\alpha = 1$
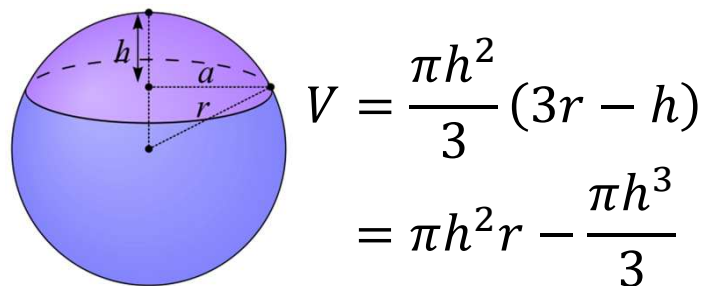
$$I(q) \sim q^{-\alpha}$$

Example: diluted colloid with spherical particles

$2\vec{r}_k$

$$\rho(r) = \begin{cases} 1 & : & r \leq r_k \\ 0 & : & r > r_k \end{cases}$$

$$g(R) = \int \rho(r)\rho(r - R)dr \qquad \text{means}$$

R

$2r_k - R = 2h$

Intersecting volume is (equation for volume of spherical cap)

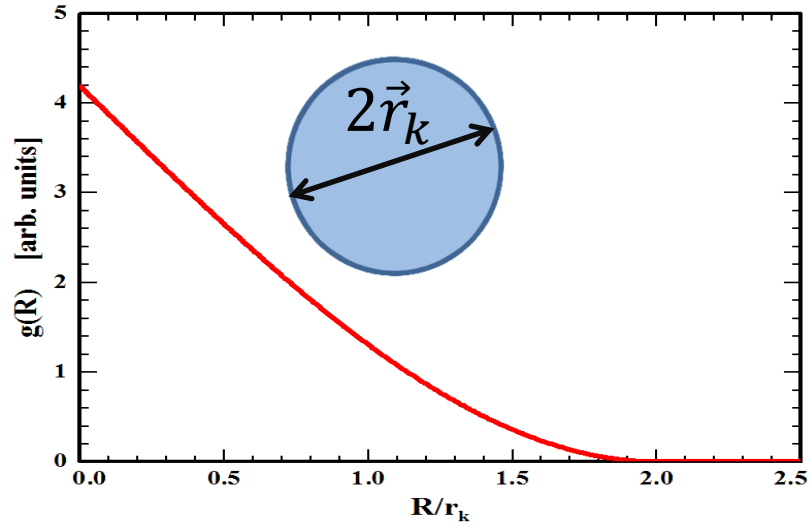$$V = \frac{\pi h^2}{3}(3r - h)$$

$$= \pi h^2 r - \frac{\pi h^3}{3}$$

Intersecting volume
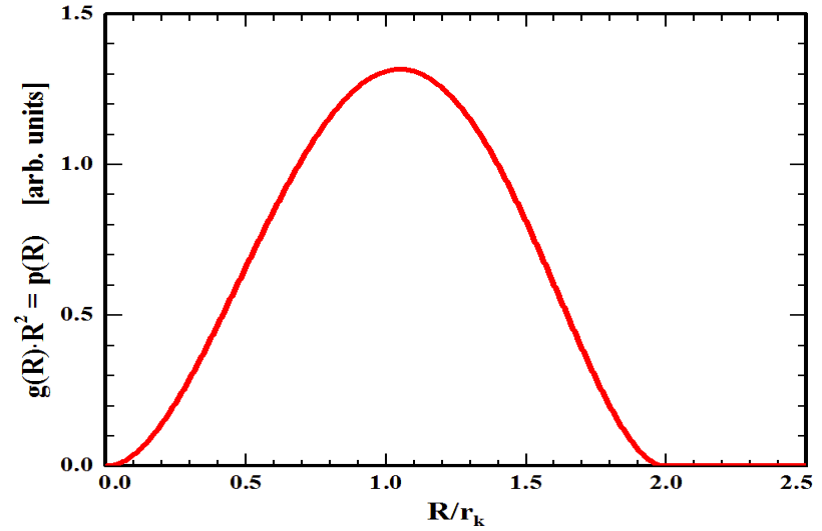
$$g(R) = 2\left(\pi\left(r_k - \frac{R}{2}\right)^2 r_k - \frac{\pi}{3}\left(r_k - \frac{R}{2}\right)^3\right)$$
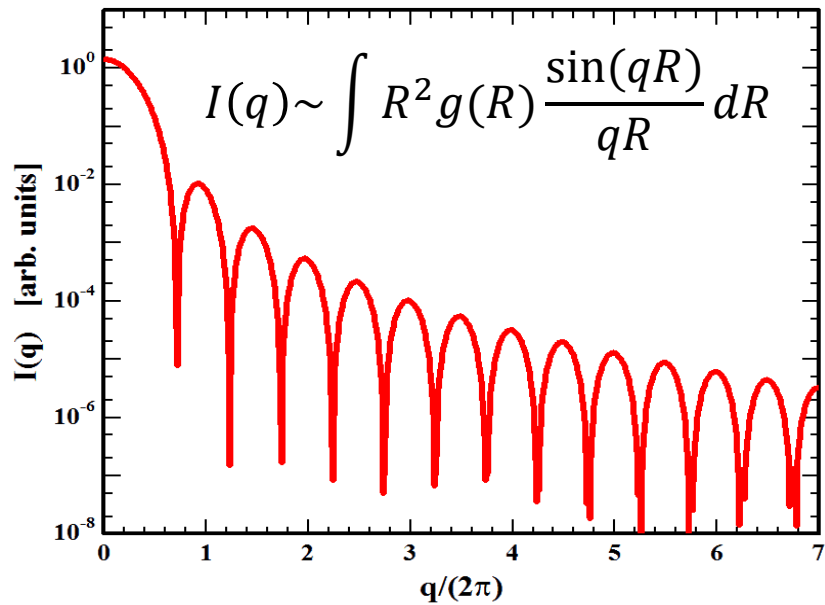
$$g(R) = 0 \quad \text{for} \quad R > r_k$$

$$g(R) = \int \rho(r)\rho(r - R)dr$$

$$p(R) = g(R)R^2 = \int q^2 I(q)\frac{\sin(qR)}{qR}dq$$

$2\vec{r}_k$

Intensity (log representation)

$$I(q) \sim \int R^2 g(R)\frac{\sin(qR)}{qR}dR$$

Intensity (log-log representation)