UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Introduction to X-ray and neutron scattering

Miroslav Šlouf

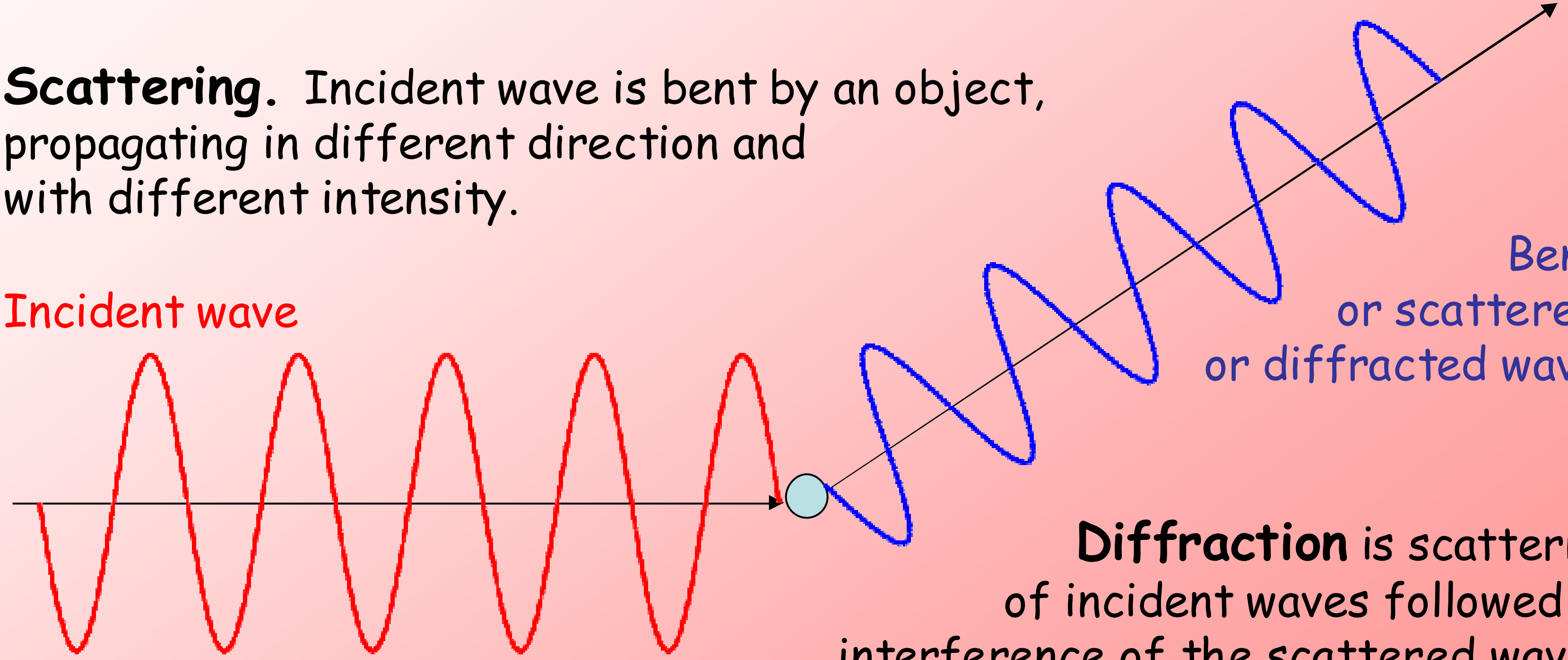
Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06
http://www.imc.cas.cz/unesco/index.html
unesco.course@imc.cas.cz

Introduction to X-ray and Neutron Scattering

Miroslav Šlouf

Institute of Macromolecular Chemistry AS CR; slouf@imc.cas.cz

Scattering. Incident wave is bent by an object, propagating in different direction and with different intensity.



Diffraction is scattering of incident waves followed by interference of the scattered waves.

$\Rightarrow$ diffraction = scattering + interference.

Contents

Introduction

  Diffraction theory

Wide-angle scattering

  Wide-angle scattering on polymers

Small-angle scattering

  Small-angle scattering on polymers

Conclusion

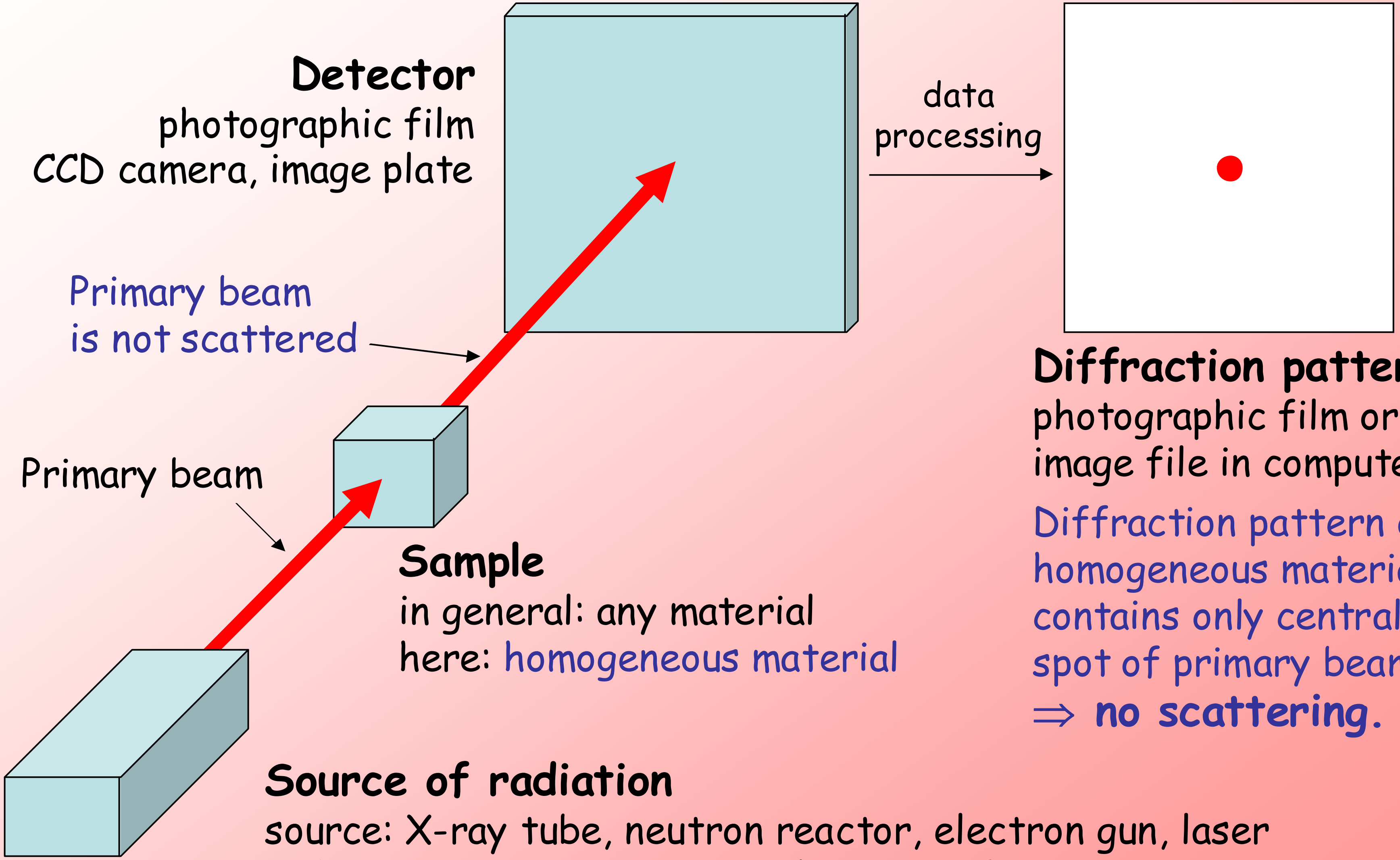
  + many examples

Key shortcuts
WAS = Wide-Angle Scattering
SAS = Small-Angle Scattering
XRD = X-Ray Diffraction
ND = Neutron Diffraction
ED = Electron Diffraction
LS = Light Scattering
SAED = Selected Area Electron Diffraction
SAXS = Small-angle X-ray Scattering

Key symbols
X = scalar (standard font)
X = vector (bold font)
X = complex number (serif font)

Important exception: **A** or A(**q**) = amplitude of diffracted wave, is a complex number. It is denoted either as **A** (correct – complex number) or as A(**q**) (convention).

Scattering by homogeneous materials



Detector
photographic film
CCD camera, image plate

data
processing

Primary beam
is not scattered

Primary beam

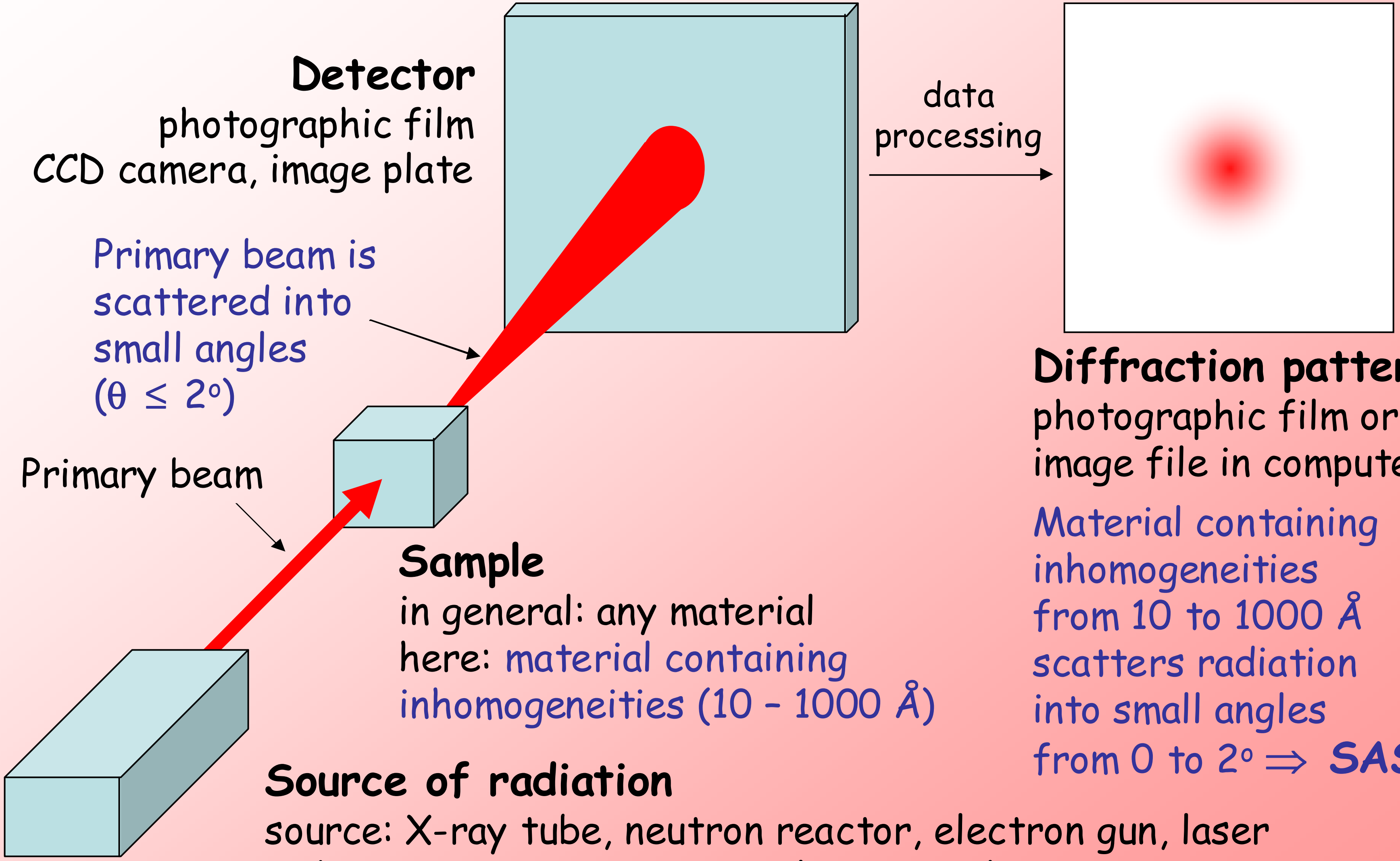
Sample
in general: any material
here: homogeneous material

Diffraction pattern
photographic film or
image file in computer

Diffraction pattern of homogeneous material contains only central spot of primary beam.
⇒ **no scattering.**

Source of radiation
source: X-ray tube, neutron reactor, electron gun, laser
radiation: X-rays, neutrons, electrons, photons

Small-Angle Scattering (SAS)



Detector
photographic film
CCD camera, image plate

Primary beam is
scattered into
small angles
$(\theta \leq 2^\circ)$

Primary beam

Sample
in general: any material
here: material containing
inhomogeneities (10 – 1000 Å)

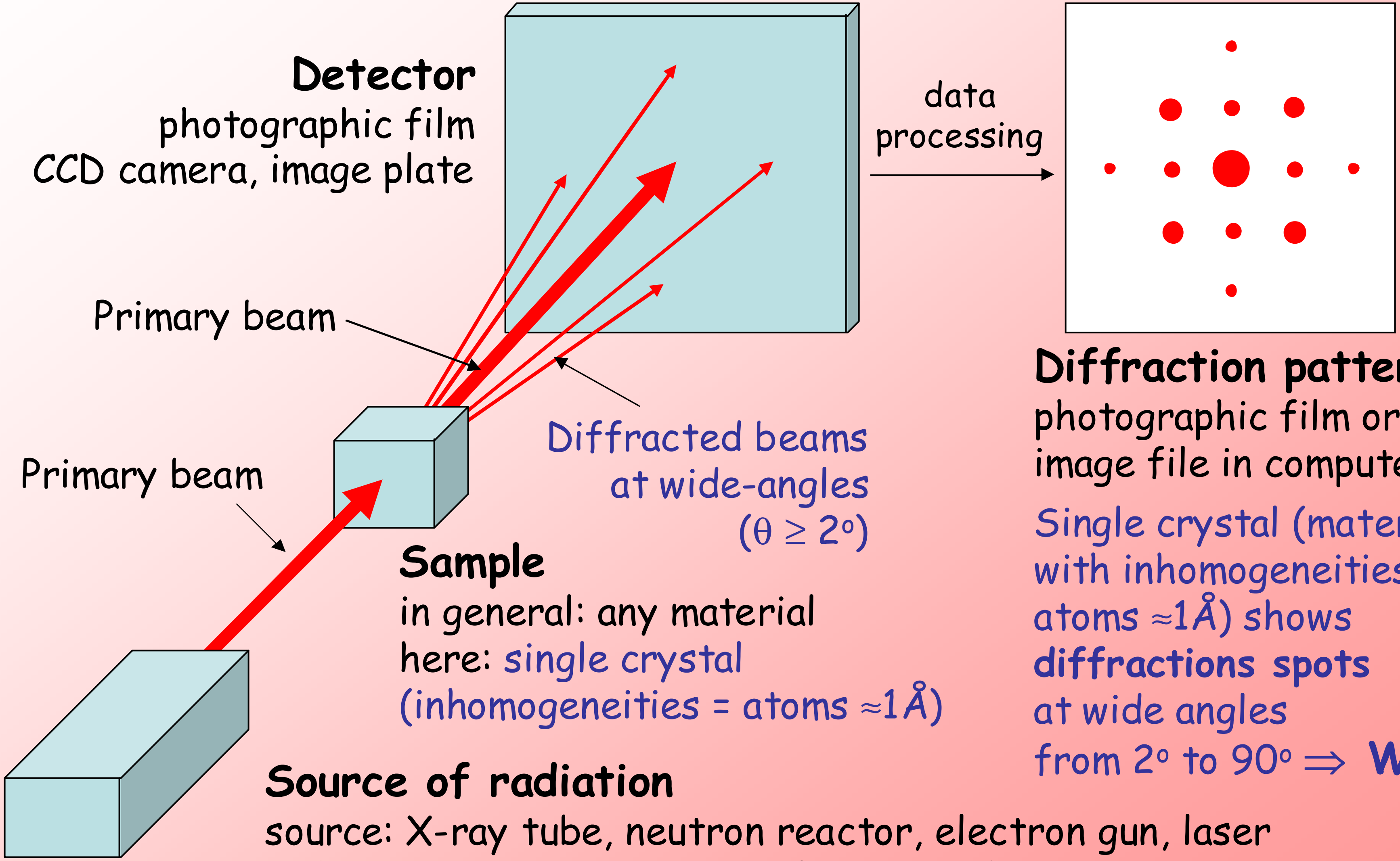
Diffraction pattern
photographic film or
image file in computer

Material containing
inhomogeneities
from 10 to 1000 Å
scatters radiation
into small angles
from 0 to $2^\circ \Rightarrow$ **SAS.**

Source of radiation
source: X-ray tube, neutron reactor, electron gun, laser
radiation: X-rays, neutrons, electrons, photons

Wide-Angle Scattering (WAS)

Case I: Single crystals = Monocrystals



Detector
photographic film
CCD camera, image plate

data processing

Primary beam

Primary beam

Diffracted beams
at wide-angles
(θ ≥ 2°)

Diffraction pattern
photographic film or
image file in computer

Single crystal (material with inhomogeneities = atoms ≈1Å) shows **diffractions spots** at wide angles from 2° to 90° ⇒ **WAS.**

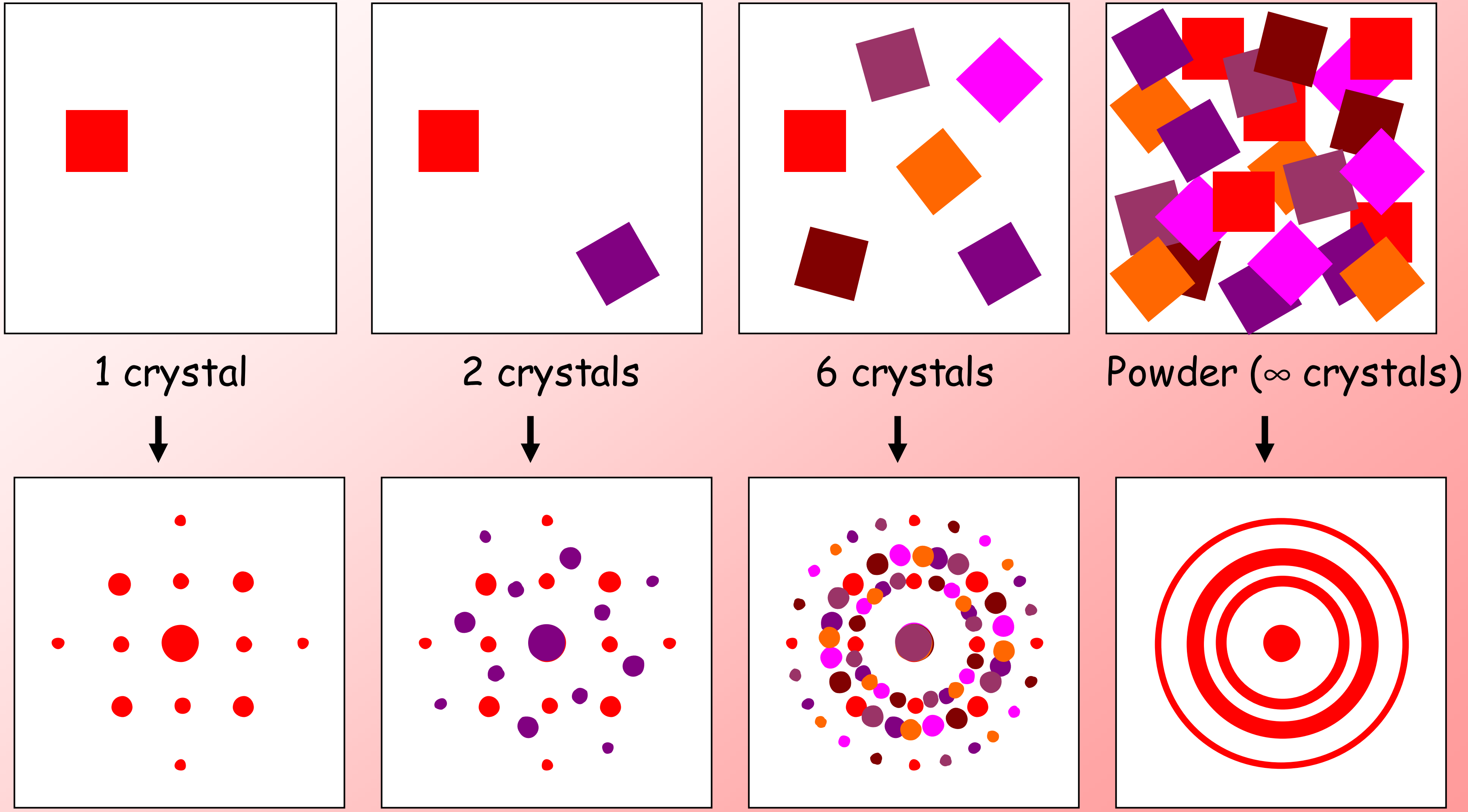
Sample
in general: any material
here: single crystal
(inhomogeneities = atoms ≈1Å)

Source of radiation
source: X-ray tube, neutron reactor, electron gun, laser
radiation: X-rays, neutrons, electrons, photons

Wide-Angle Scattering (WAS)

Case II: Polycrystalline samples - Powders

Polycrystalline samples...



1 crystal

2 crystals

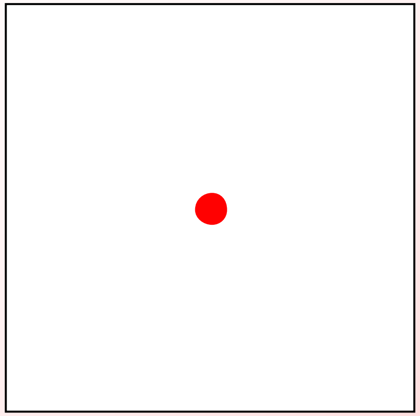
6 crystals

Powder (∞ crystals)

Diffraction patterns...

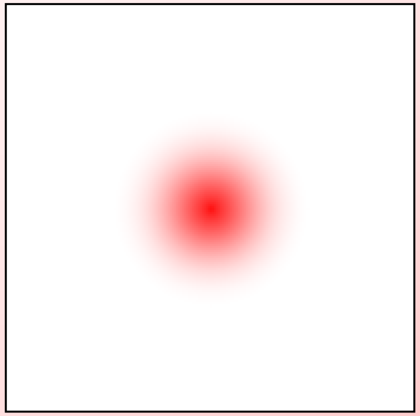
Summary1: Scattering of materials.

Homogeneous material



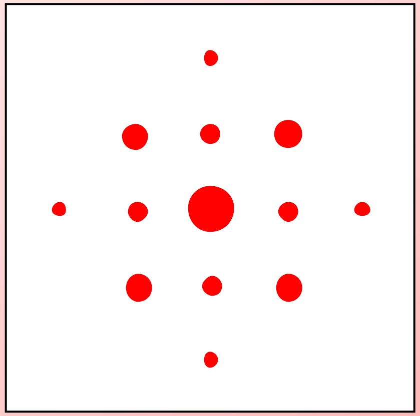
- No scattering
- No diffraction pattern
- Completely homogeneous material is only vacuum!

Material with inhomogeneities from 10 to 1000Å



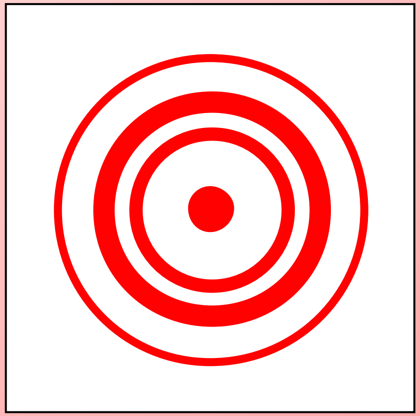
- Small-Angle Scattering (SAS)
- Diffuse spot in small-angle region (from 0 to 2°)
- Polymer materials: polymer solutions, block copolymers

Single crystal (inhomogeneities are atoms ≈ 1Å)



- Wide-Angle Scattering (WAS)
- Sharp spots in wide-angle region (from 2 to 90°)
- Polymer materials: polymer single crystals (very rare)

Polycrystalline material (inhomogeneities are atoms ≈ 1Å)



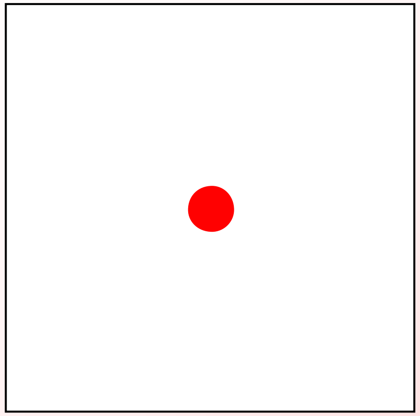
- Wide-Angle Scattering (WAS)
- Sharp rings in wide-angle region (from 2 to 90°)
- Polymer materials: semicrystalline polymers (frequent)

Above are general rules: exceptions do exist!

Example 0: Diffraction patterns.

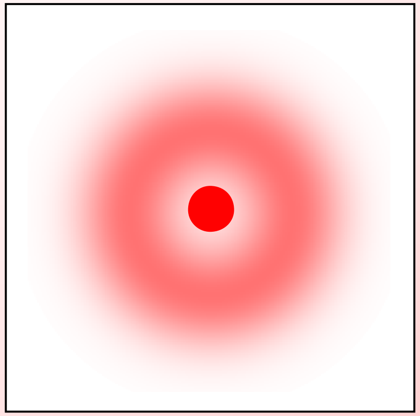
Summary2: Scattering of polymers.

Homogeneous material



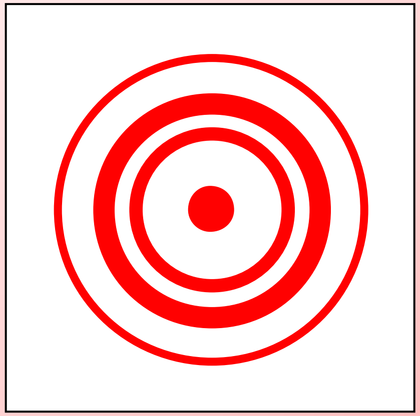
- No scattering
- No inhomogeneities.
- No diffraction pattern.
- This occurs only in vacuum!

Amorphous polymer



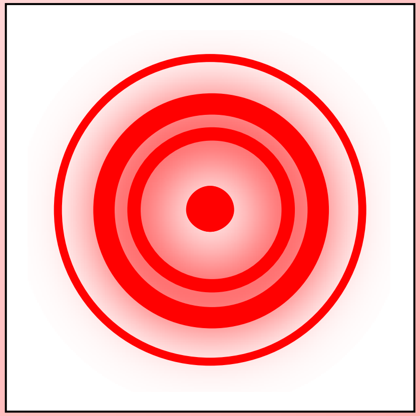
- WAS
- Inhomogeneities are atoms.
- No periodicity ⇒ **amorphous hallo**.
- Amorphous polymers are quite common.

Crystalline polymer



- WAS
- Inhomogeneities are atoms.
- Crystal periodicity ⇒ **sharp rings**.
- Completely crystalline polymers are very rare!

Semicrystalline polymer

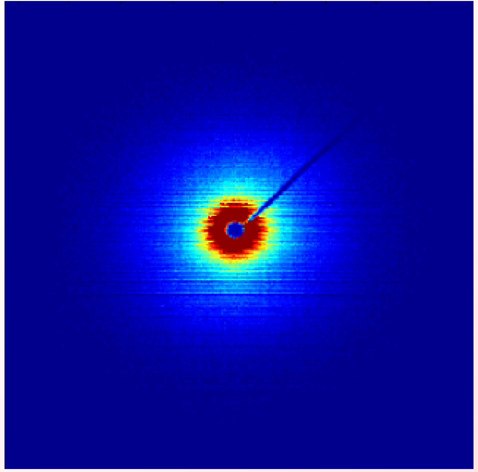


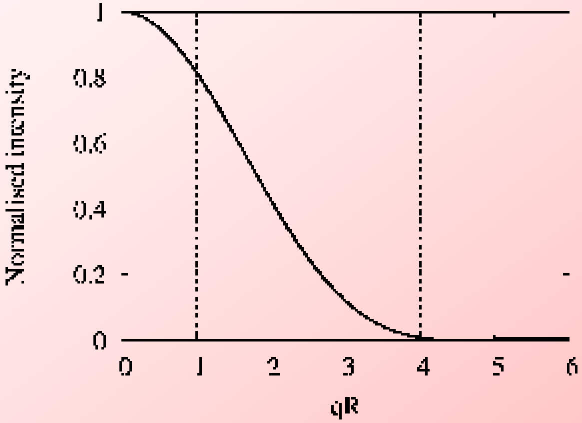
- WAS
- Inhomogeneities are atoms.
- **Sharp rings and amorphous hallo**.
- Semicrystalline polymers are common.

Common synthetic polymers are either amorphous or semicrystalline.
Low molecular weight substances are often completely crystalline.

Various forms of diffraction patterns

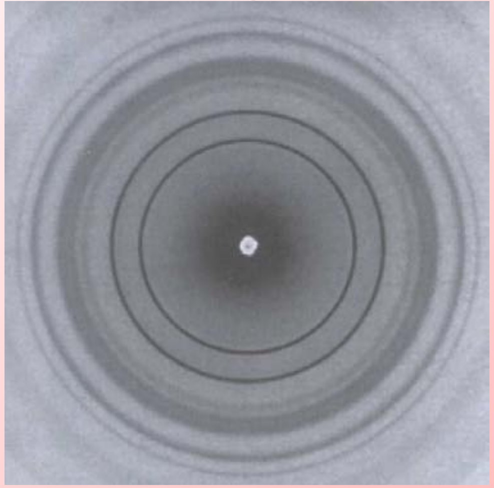
Small-Angle Scattering

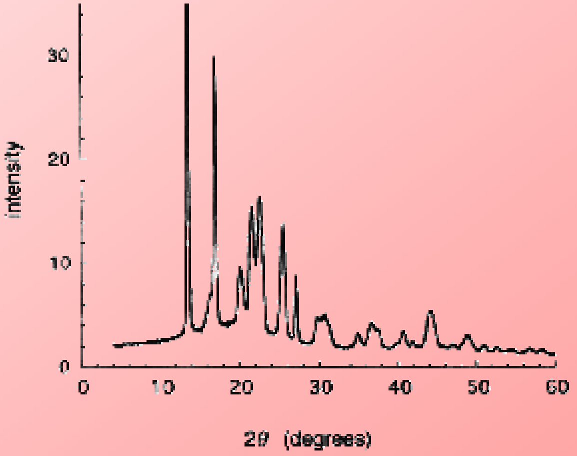




q[A]	I(q)
8.160E-03	31.074
9.111E-03	22.633
1.006E-02	16.947
1.101E-02	12.904
1.196E-02	10.099
1.291E-02	8.018
1.386E-02	6.646

Wide-Angle Scattering



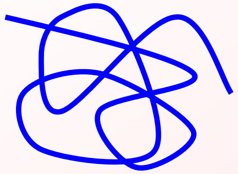


h	k	l	Ihkl
0	0	1	32.8
0	1	1	5.6
1	0	1	29.9
0	0	2	8.5
0	1	2	12.3
2	0	1	12.5
2	1	1	11.1

Some polymer structures,

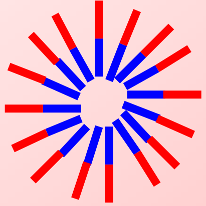
which can be studied by SAS and WAS.

[1] Polymer molecules in solution



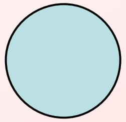
random coil
size: 10^1 - 10^2 Å
Small-Angle Scattering

[2] Polymer micelles



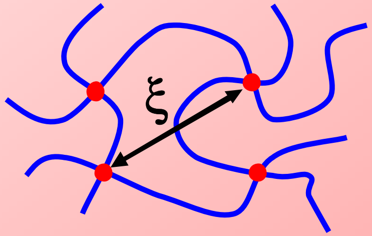
micelle of diblock copolymer
size: 10^1 - 10^3 Å
Small-Angle Scattering

[3] Polymer particles



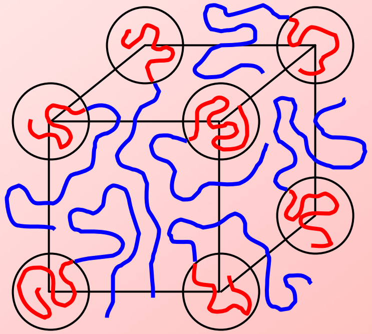
polystyrene microspheres
size: 10^2 - 10^5 Å
Small-Angle Scattering

[4] Polymer networks



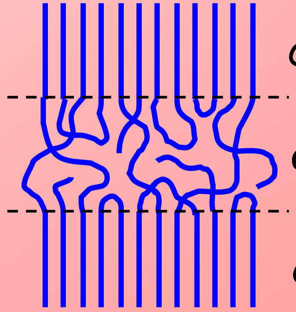
crosslinked polymer
average ξ: 10^1 - 10^3 Å
Small-Angle Scattering

[5] Block copolymer structures



cubic structure
distance between phases: 10^1 - 10^2 Å
Small-Angle Scattering

[6] Semicrystalline polymers



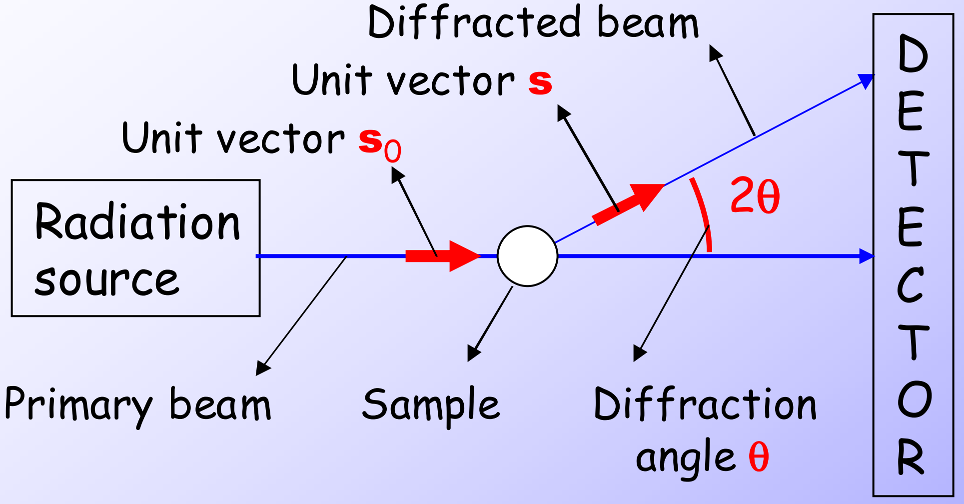
crystalline
amorphous
crystalline

crystalline lamellae
⇒ WAS
long period
⇒ SAS

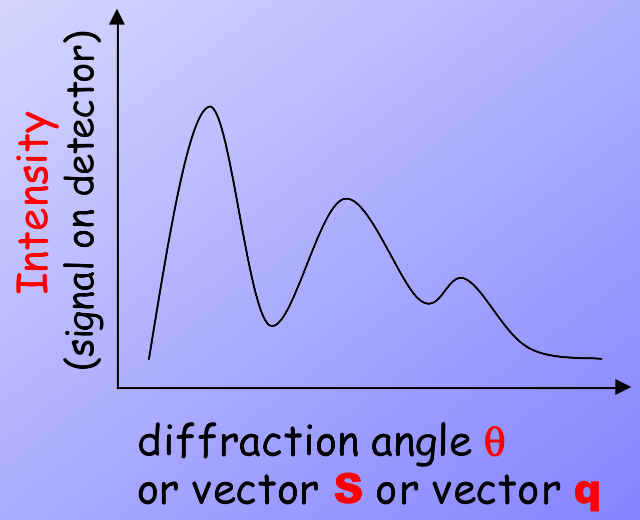
Diffraction theory.

(1) Geometry of diffraction experiment.

Diffraction experiment



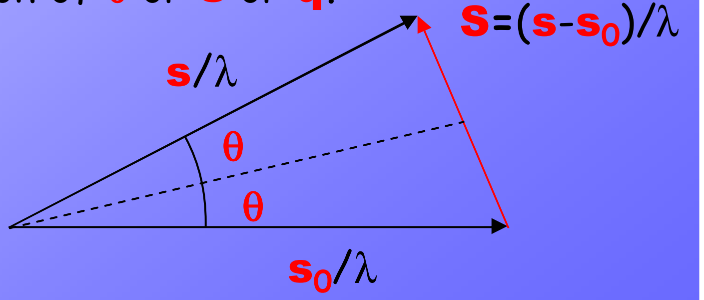
Final diffractogram



Relationships θ × **S** × **q**

During diffraction experiment we measure I as a function of θ or **S** or **q**.

Vectors $\mathbf{s}$ **and** $\mathbf{s}_0$ are unit vectors: $|\mathbf{s}| = |\mathbf{s}_0| = 1$.
Scattering vector $\mathbf{S}$ is defined as $\mathbf{S} = (\mathbf{s}-\mathbf{s}_0)/\lambda$.
Scattering vector $\mathbf{q}$ is defined as $\mathbf{q} = 2\pi\mathbf{S}$.



Magnitude of $|\mathbf{S}| = S = 2 \times \sin(\theta) \times |s/\lambda| = 2\sin\theta/\lambda$
Magnitude of $|\mathbf{q}| = q = |2\pi S| = 4\pi\cdot\sin\theta/\lambda$

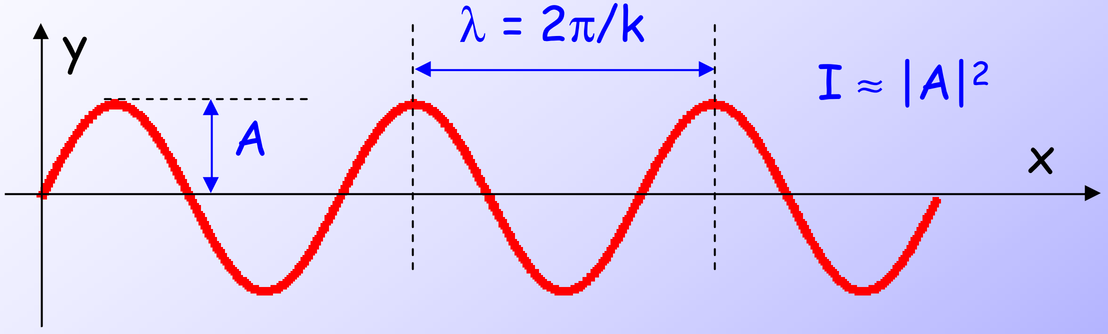
It holds: $\theta \approx S \approx q$, i.e. high θ means also high S and high q and vice versa.

Diffraction theory.

(2) Waves & intensity of waves.

Verbally: wave is a move of oscillations through space.

Graphically:



$\Psi(x,t)$ = wave
I = intensity of the wave
A = amplitude
λ = wavelength
v = speed of propagation
ω = angular speed (of oscillations)
k = ω/**v** = wave vector
Φ = initial phase

Mathematically:

(1) $\Psi(\mathbf{x},t)=A\cos[\omega t-\mathbf{kx}+\Phi]$ ..plane wave propagating in arbitrary direction **x**
(2) $\Psi(\mathbf{x},t)=A\exp[i(\omega t-\mathbf{kx}+\Phi)]$ ..equation (1) in exponential form
(3) $\Psi(x,t)=A\exp[i(\omega t-kx+\Phi)]$ ..plane wave propagating along axis x
(4) $\Psi(x,t)=\underline{A\exp[i\Phi]}\exp[i(\omega t-kx)]$ ..equation (3) re-written with complex amplitude

$\mathbf{A} = A\exp[i\Phi]$ = complex amplitude of the wave

(5) $I \approx |\mathbf{A}|^2$ ..intensity of the wave is proportional to the square of the amplitude
⇒ during diffraction experiments we measure intensity of the waves I.
⇒ during derivations we calculate A, which are related to experimental I.

Example 1: Wave equation, wave propagation, wave intensity.

Diffraction theory.

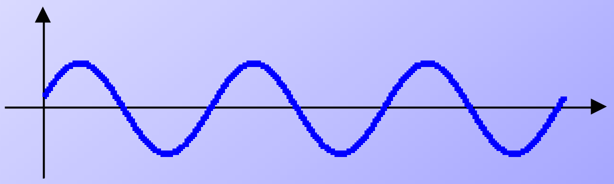
(3) Interference = wave addition.

$\Psi_1(x,t) = A_1\exp[i(\omega_1 t - k_1 x + \Phi_1)]$

$\Psi_1(x,t) = A_1\exp[i\Phi_1]\exp[i(\omega t - kx)]$

Here: $\Phi_1 = \pi/12$, $\omega_1 = \omega$, $k_1 = k$

Wave $\Psi_1(x,t)$ with complex amplitude: $\mathbf{A_1} = A_1\exp[i\Phi_1]$.

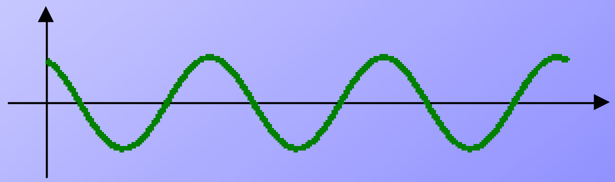


$\Psi_2(x,t) = A_2\exp[i(\omega_2 t - k_2 x + \Phi_2)]$

$\Psi_2(x,t) = A_2\exp[i\Phi_2]\exp[i(\omega t - kx)]$

Here: $\Phi_2 = 5\pi/8$, $\omega_2 = \omega$, $k_2 = k$

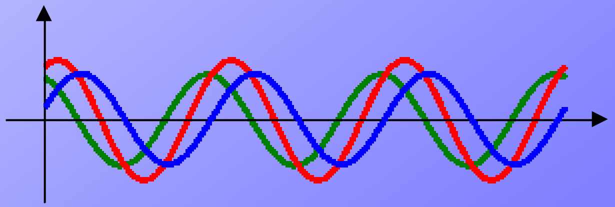
Wave $\Psi_2(x,t)$ with complex amplitude: $\mathbf{A_2} = A_2\exp[i\Phi_2]$.



$\Psi_3(x,t) = \Psi_1(x,t) + \Psi_2(x,t)$

$\Psi_3(x,t) = \{A_1\exp[i\Phi_1] + A_2\exp[i\Phi_2]\}\times\{\exp[i(\omega t - kx)]\}$

$\Psi_3(x,t) = \{A_1\exp[i\Phi_1] + A_2\exp[i\Phi_2]\}\times\{\exp[i(\omega t - kx)]\}$



Wave $\Psi_3(x,t) = \Psi_1 + \Psi_2$ with complex amplitude: $\mathbf{A_3} = \mathbf{A_1} + \mathbf{A_2} = A_1\exp[i\Phi_1] + A_2\exp[i\Phi_2]$.

Conclusion – interference in SAS and WAS:

[1] Interfering waves are plane and monochromatic ⇒ v, ω, k are the same.

[2] Interfering waves may differ in amplitude and phase ⇒ A and Φ may be different.

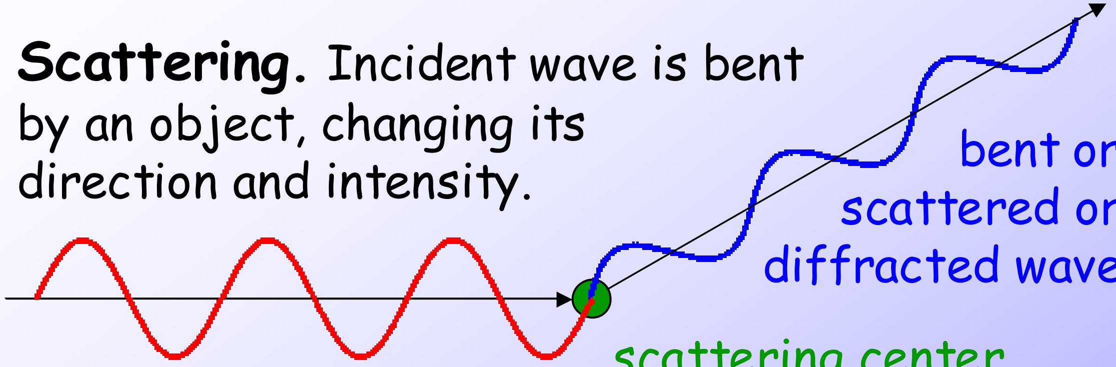
[3] Amplitude of resulting wave is complex, depending on phases of the interfering waves.

Example 2: Wave interference, equivalence of [cos-waves] and [exp-waves].

Diffraction theory.

(4) Scattering = wave bending.

Scattering. Incident wave is bent by an object, changing its direction and intensity.



Wave-particle duality.
Particles may have wave aspect and vice versa.
Examples:
light × photons
electron beam × electrons
De Broglie waves:
$\lambda = h/mv$

Incident wave	Incident particle	λ [Å]	Scatterer	Methods
X-ray beam	X-ray photon	0.5-2	electron	XRD, WAXS, SAXS
neutron beam	neutron	0.5-6	atom nucleus	(ND), WANS, SANS
electron beam	electron	0.001-2	el. potential	(ED), SAED, CBED...
light beam	photon	4..8000	different n	(LS), SALS, WALS...

Scattering by one volume element dr

$I(\mathbf{q}) \approx |A(\mathbf{q})|^2$ ...intensity of the scattered wave depends on its direction $\approx \theta \approx \mathbf{S} \approx \mathbf{q}$

$A(\mathbf{q})$ = const × number_of_scatterers_in_unit_volume × volume_element

$A(\mathbf{q}) = b \times n(\mathbf{r}) \times d\mathbf{r}$ ...b = diffraction length = different for X-rays, neutrons, electrons..

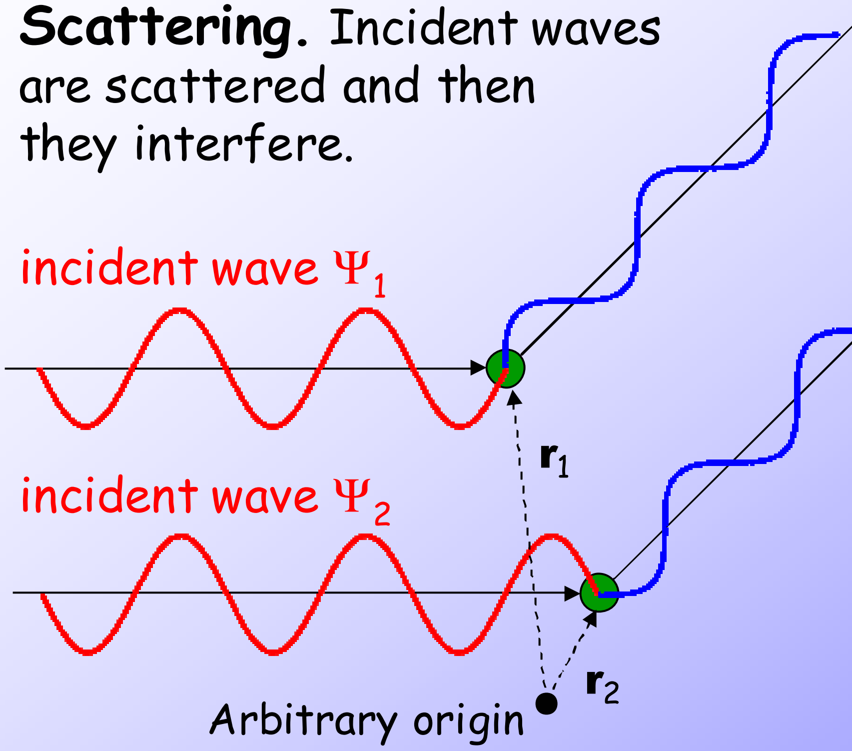
$A(\mathbf{q}) = \rho(\mathbf{r}) \times d\mathbf{r}$ ...$\rho(\mathbf{r}) = b \times n(\mathbf{r})$ = electron density in XRD, nuclear density in ND...

Example 3: Scattering by one atom in XRD, ND, ED.

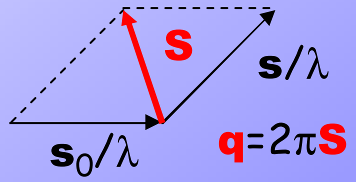
Diffraction theory.

(5) Diffraction = scattering + interference.

Scattering. Incident waves are scattered and then they interfere.

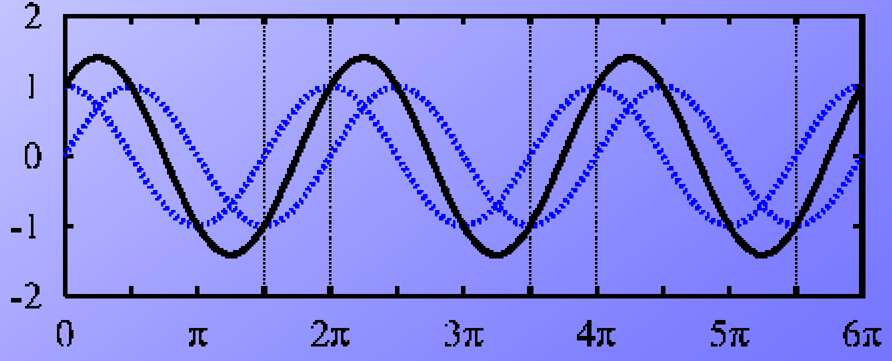


Scattering vector $\mathbf{q}=2\pi\mathbf{S}$ characterizes direction of the scattered wave.



Interference: $\Psi_3 = \Psi_1 + \Psi_2$

Ψ_3 = resulting wave after interference of Ψ_1 and Ψ_2.



Diffraction – we measure amplitude A_3 of the diffracted wave Ψ_3:
We have already shown that: $A_3 = A_1\exp[i\Phi_1]+A_2\exp[i\Phi_2]$
It can be also shown that: $A_3 = A_1+A_2 = A_1\exp[i\mathbf{qr}_1]+A_2\exp[i\mathbf{qr}_2]$.

Example 4: Scattering by two electrons, justification of $\mathbf{A_3} = A_1\exp[i\mathbf{qr}_1]+A_2\exp[i\mathbf{qr}_2]$

Diffraction theory.

(6) Key formula of diffraction theory.

We have already derived:

(1) $I(\mathbf{q}) \approx |A(\mathbf{q})|^2$ ..intensity of wave

(2) $A(\mathbf{q}) = \rho(\mathbf{r})d\mathbf{r}$ ..scattering by 1 volume element

(3) $A(\mathbf{q}) = A_1\exp[i\mathbf{q}\mathbf{r}_1]+A_2\exp[i\mathbf{q}\mathbf{r}_2]$ ..scattering by 2 volume elements

this is a "summation with phases"

Generalization of (3):

(4) $A(\mathbf{q}) = \Sigma A_j\exp[i\mathbf{q}\mathbf{r}_j]$ ..scattering by N volume elements

summation runs from j=1 to N

Combination of (2) and (4):

(5) $A(\mathbf{q}) = \Sigma\rho(\mathbf{r}_j)\times\exp[i\mathbf{q}\mathbf{r}_j]\times d\mathbf{r}$ ..scattering by N volume elements

summation runs from j=1 to N

Generalization of (5):

(6) $A(\mathbf{q}) = \int\rho(\mathbf{r})\times\exp[i\mathbf{q}\mathbf{r}]\times d\mathbf{r}$ ..key formula of diffraction theory

scattering by ∞ volume elements
i.e. scattering by any object
integration runs through the object volume V

By means of equations (6)+(1) it is possible to calculate any diffraction pattern if we know the structure ≈ $\rho(\mathbf{r})$.

Example 5: Illustration of equation (6).

Example 6: Relationship $I(\mathbf{q}) \times \rho(\mathbf{r})$.

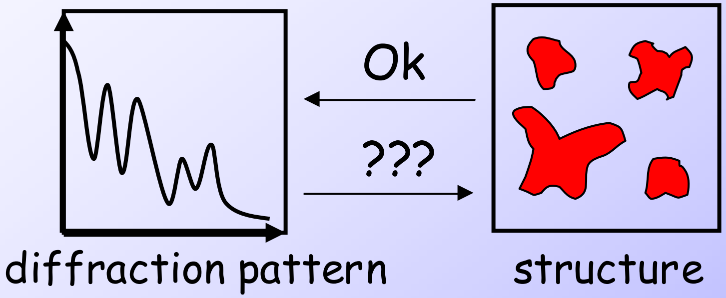
Diffraction theory.

(7) Phase problem.

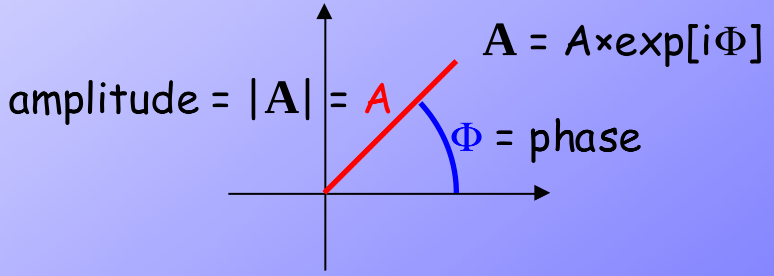
Verbally:

We can calculate diffraction pattern from known structure but we cannot calculate structure from diffraction pattern directly.

Schematically:



Amplitude and phase of complex numbers:



Mathematically:

(1) $I(\mathbf{q}) \approx |A(\mathbf{q})|^2$ ..intensity of wave

(2) $A(\mathbf{q}) = \int \rho(\mathbf{r}) \times \exp[i\mathbf{q}\mathbf{r}] \times d\mathbf{r}$ ..scattering by any object

(3) $\rho(\mathbf{r}) = 1/(2\pi)^3 \times \int A(\mathbf{q}) \times \exp[-i\mathbf{q}\mathbf{r}] \times d\mathbf{q}$ ..Fourier theorem applied on (2)

$I(\mathbf{q})$ represents diffraction pattern, $\rho(\mathbf{r})$ represents structure.

Calculation of $I(\mathbf{q})$ from known $\rho(\mathbf{r})$: Ok ⇒ eq.2 gives $A(\mathbf{q})$, eq.1 gives $I(\mathbf{q})$.

Direct calculation of $\rho(\mathbf{r})$ from known $I(\mathbf{q})$: impossible ⇒ eq.1 gives only $|A(\mathbf{q})|$, not $A(\mathbf{q})$.

Note: Fourier theory & Fourier theorem ⇒ textbooks, wikipedia...

Wide-angle scattering

[1] WAS is connected with crystals.
In other words: diffraction by crystals is observed in wide-angle region.

[2] Simplified model for diffraction by crystals is Bragg Law.
Bragg Law gives distance of the diffraction rings/spots from the centre.

[3] Precise model for diffraction by crystals is Kinematic diffraction theory.
KDT gives not only distance, but also position and intensity of rings/spots.

[4] Polymers usually do not crystallize very well and so their diffraction patterns are not as clear as those of low molecular weight compounds. Nevertheless, WAS on polymers still can yield a lot of information about their structure.

WAS: Crystals

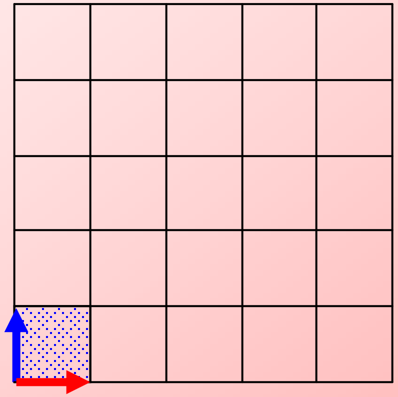
(1) Crystal structure.

Crystals of low molecular weigh compounds (cesium chloride)

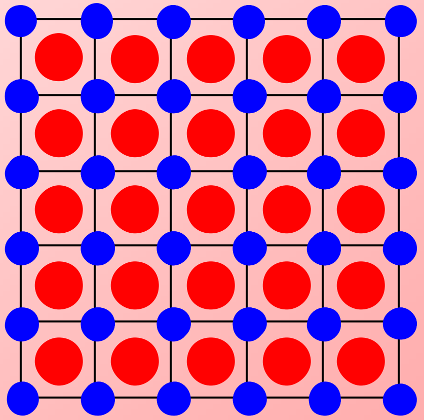
dimensions of crystals of low molecular weight compounds **around 1 mm**

crystal of low molecular weight compound

Crystal



Unit cells



Crystal structure

Crystals of synthetic polymers (polyethylene)

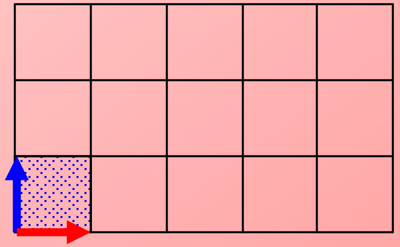
dimensions of crystals of polymers **around 1 μm**

amorphous region

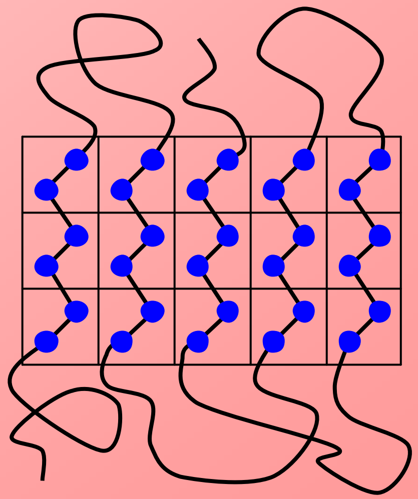
polymer crystalline lamella

amorphous region

amorphous region

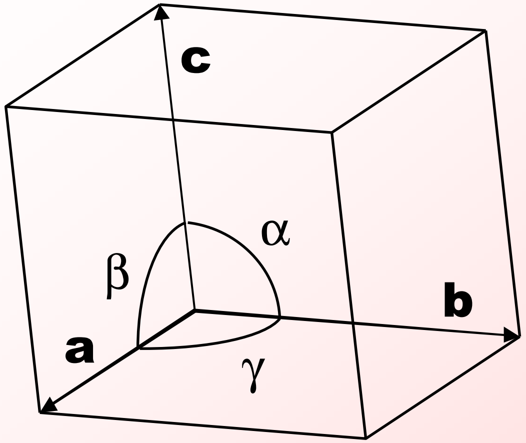


amorphous region



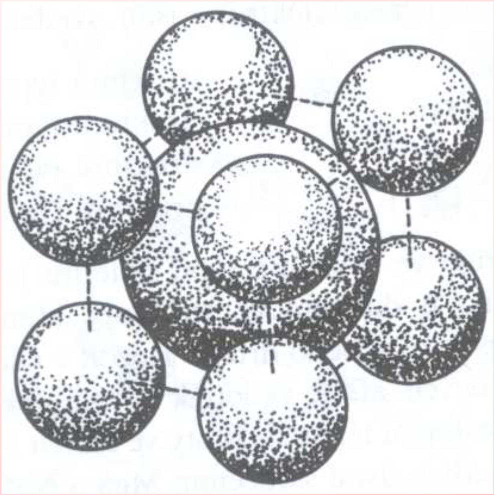
WAS: Crystals

(2) Unit cells.

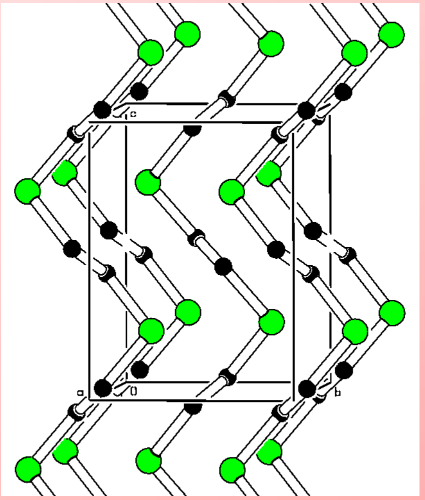


Seven crystal systems

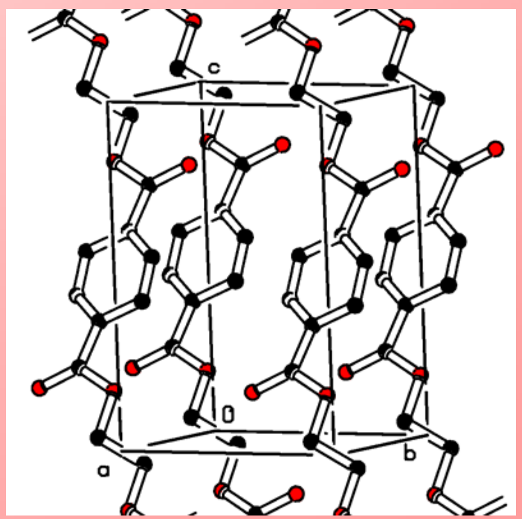
System	Unit cell parameters
cubic	$a = b = c; \alpha = \beta = \gamma = 90^\circ$
hexagonal	$a = b; \alpha = \beta = 90^\circ; \gamma = 120^\circ$
tetragonal	$a = b; \alpha = \beta = \gamma = 90^\circ$
trigonal	$a = b = c; \alpha = \beta = \gamma \neq 90^\circ$
orthorhombic	$\alpha = \beta = \gamma = 90^\circ$
monoclinic	$\beta = 90^\circ$
triclinic	no constraints



Cubic unit cell and structure of CsCl



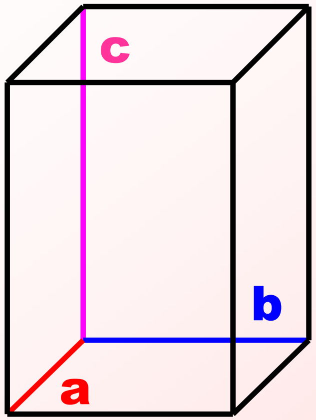
Poly(thioethylene) orthorhombic



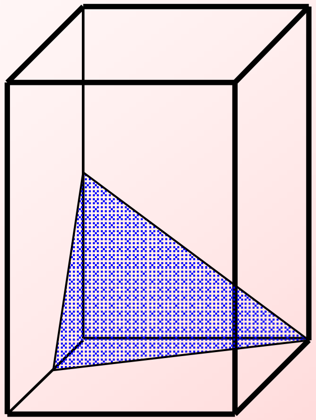
Poly(ethyleneterephtalate) triclinic

WAS: Crystals

(3) Crystallographic planes.



Unit cell

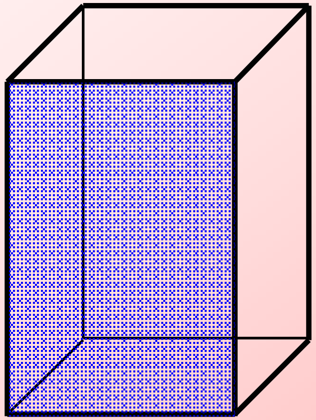


Any plane in crystal

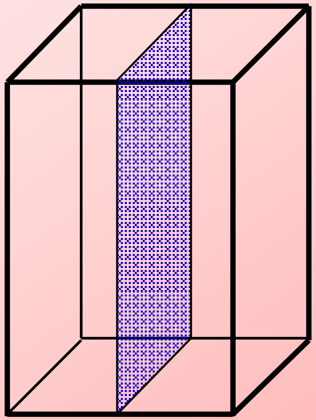
Crystallographic planes are denoted by means of Miller indices [hkl].

Blue plane crosses vector **a** in 1/3 ⇒ h = 3.
Blue plane crosses vector **b** in 1/1 ⇒ k = 1.
Blue plane crosses vector **c** in 1/2 ⇒ l = 2.

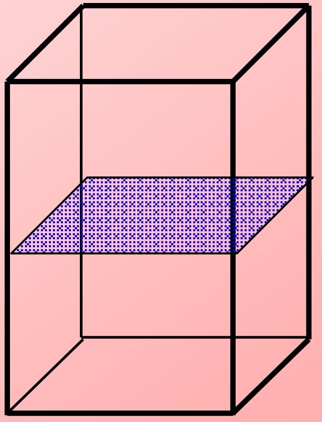
Miller indices of the plane are [312].



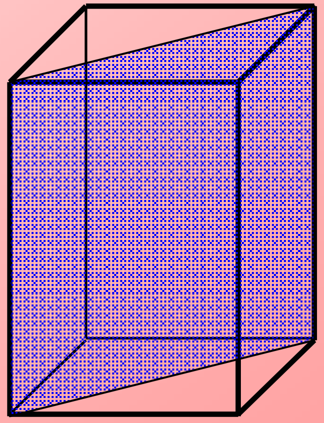
[100]



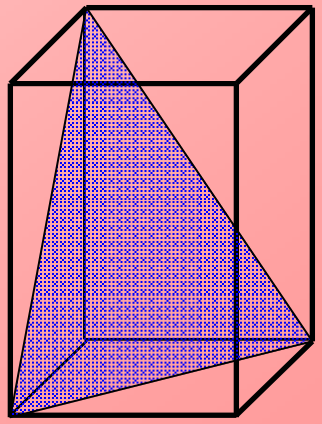
[020]



[002]



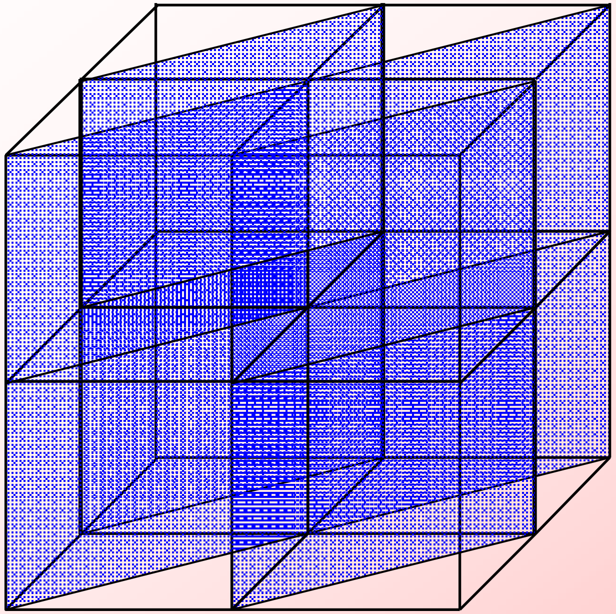
[110]



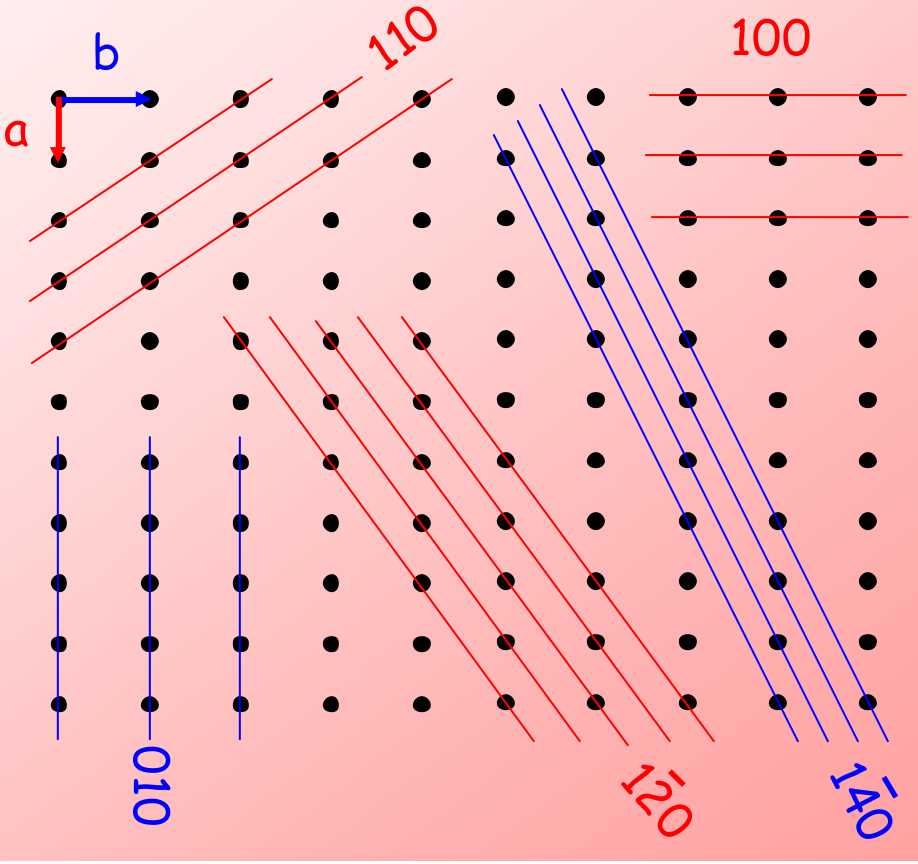
[111]

WAS: Crystals

(4) Crystallographic planes in crystals.



Planes [110] in cubic crystal



Distance between parallel crystallographic planes is denoted as d_{hkl}.
$d_{hkl} = f(h,k,l,a,b,c,\alpha,\beta,\gamma)$

$$\frac{1}{d_{hkl}^2} = \left[\frac{h^2 \sin^2\alpha}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2 \sin^2\gamma}{c^2} + \frac{2hk}{ab}(\cos\alpha \ \cos\beta - \cos\gamma) + \frac{2kl}{bc}(\cos\beta \ \cos\gamma - \cos\alpha) + \frac{2lh}{ca}(\cos\gamma \ \cos\alpha - \cos\beta) \right] \Big/ (1 + 2 \cos\alpha \ \cos\beta \ \cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma)$$

WAS: Bragg Law

Bragg Law represents simplified model of diffraction by crystals.

Assumptions:

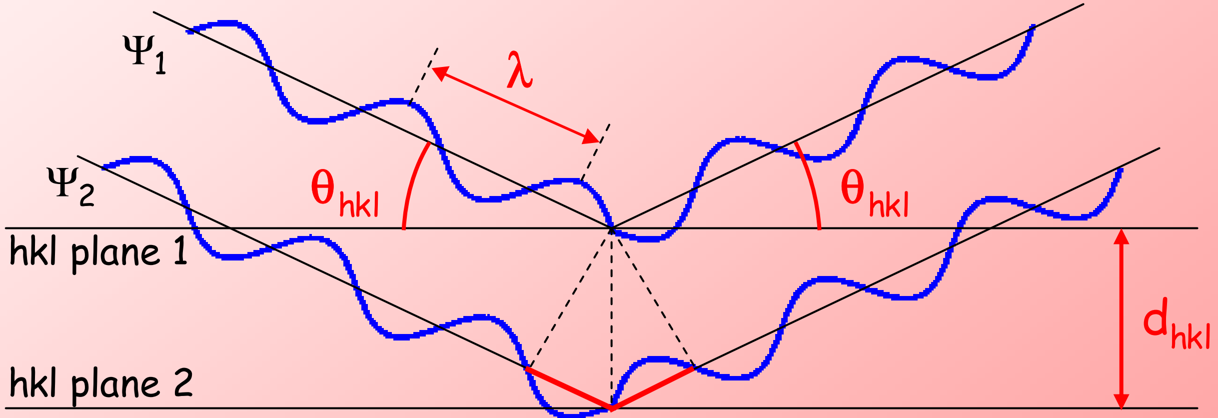
[1] Crystallographic planes are semitransparent mirrors. This is incorrect: the planes are just geometrical constructions representing the periodicity of the crystal.

[2] Waves are reflected by these crystallographic planes. This is incorrect: in fact the waves are scattered by atoms and then they interfere – i.e. they are diffracted.

[3] Maximum interference (= diffraction peak) occurs, if phase difference of reflected waves is 0, 2π, 4π.. = 2n×π (n = integer), i.e. if the path difference is 0, λ, 2λ.. = n×λ. This is true: diffraction peaks are really observed under these conditions.

[Conclusion] Although the assumptions are not completely true, the results are correct!

Graphically:



2 × (d_{hkl} × sinθ_{hkl}) = path difference between Ψ_1 and Ψ_2

Mathematically:

$$\underbrace{2d_{hkl}\sin\theta_{hkl}}_{\text{path difference between waves }\Psi_1\text{ and }\Psi_2} = \underbrace{n\times\lambda}_{\text{integer multiplication of wavelength}}$$

Example7: Bragg Law and diffraction pattern.

WAS: Kinematic diffraction theory

[1] KDT completely describes diffraction by crystals; it holds:

$I(\mathbf{q}) \approx |A(\mathbf{q})|^2$ $A(\mathbf{q}) = \int\rho(\mathbf{r})\exp[i\mathbf{qr}]d\mathbf{r}$ ..key formula of diffraction

$I_{hkl} \approx |F_{hkl}|^2$ $F_{hkl} = \Sigma f_j\exp[i\mathbf{q}\mathbf{r}_j]$ ..diffraction by single crystal.

analogy

F_{hkl} = **structure factor** → gives information about crystal structure
f_j = scattering factor and $\mathbf{r}_j$ = position of the j-th atom in the unit cell
Σ runs from j=1 to N, where N = number of atoms in the unit cell

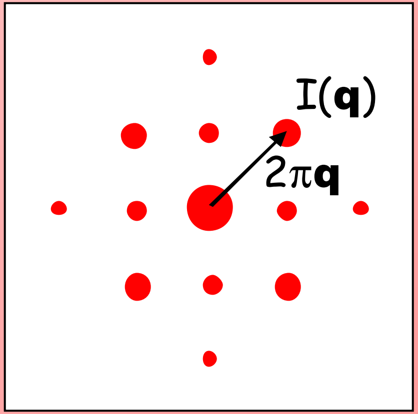
[2] Other KDT results:

(a) diffraction occurs only if: $\mathbf{aS} = h$, $\mathbf{bS} = k$, $\mathbf{cS} = l$ ...Laue's conditions
(**a**,**b**,**c** = unit cell vectors, **S** = scattering vector, h,k,l = integers)
⇒ it implies that single-crystal diffraction pattern contains spots

(b) diffraction occurs only if : $2d\sin\theta = n\lambda$ ..Bragg Law
⇒ it means that Bragg Law is a special case of KDT

[3] KDT completely describes:

(a) position of the diffraction spots – given by **q**
(b) intensity of the diffraction spots – given by I(**q**)

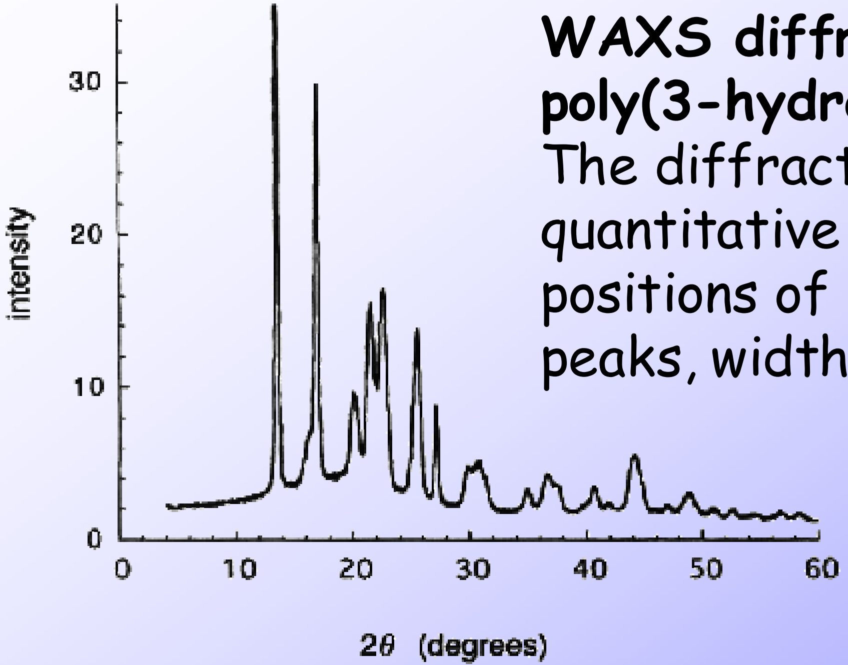


[4] KDT enables:

(a) calculate single-crystal diffraction pattern
(b) calculate powder diffraction pattern, which is even simpler
(c) calculate crystal structure from diffraction pattern – structure analysis

Example8: Structure analysis.

WAS on polymers: survey of possibilities



WAXS diffraction pattern of poly(3-hydroxybutyrate)
The diffraction pattern contains a lot of quantitative information, such as positions of diffraction peaks, intensities of peaks, width of peaks, amorphous hallo...

What can be determined from WAS pattern?
[1] Position of peaks → unit cell parameters a,b,c,α,β,γ.
[2] Positions and intensities of peaks → crystal structure.
[3] Width of peaks → crystal imperfections, crystallite size.
[4] Semicrystalline polymers → degree of crystallinity.
[5] Anisotropic samples → orientation.

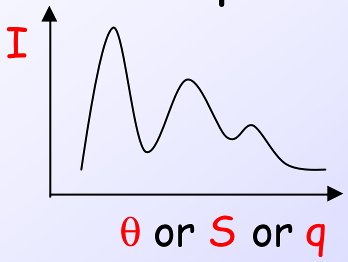
WAS on polymers.

(1) Determination of unit cell parameters = indexing.

We have already learnt the principle!

[1] Diffraction pattern is a function I = I(θ) or I($\mathbf{S}$) or I($\mathbf{q}$).

Slide 11



[2] Relationship between θ (or $\mathbf{S}$ or $\mathbf{q}$) and d_{hkl} → Bragg Law.

Slide 23

$$2d_{hkl}\sin\theta_{hkl} = n\lambda$$

[3] Values of d_{hkl} are associated with unit cell parameters $a,b,c,\alpha,\beta,\gamma$.

$$\frac{1}{d_{hkl}^2} = \left[\frac{h^2\sin^2\alpha}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2\sin^2\gamma}{c^2} + \frac{2hk}{ab}(\cos\alpha\ \cos\beta - \cos\gamma) + \frac{2kl}{bc}(\cos\beta\ \cos\gamma - \cos\alpha) + \frac{2lh}{ca}(\cos\gamma\ \cos\alpha - \cos\beta)\right] / (1 + 2\cos\alpha\ \cos\beta\ \cos\gamma - \cos^2\alpha - \cos^2\beta - \cos^2\gamma)$$

Slide 22

[Conclusion] Indexing = finding of Miller indexes h,k,l and unit cell parameters $a,b,c,\alpha,\beta,\gamma$ from diffraction pattern.

Example9: Indexing.

WAS on polymers.

(2) Determination of crystal structure = structure analysis.

We have already learnt the principle!

[1] Diffraction pattern of crystalline samples is described by kinematic diffraction theory.

Slide 24

[2] Relationship between diffraction pattern and structure of crystalline samples is hidden in structure factors F_{hkl}.

Slide 24

[3] The "only" problem is the Phase problem, but it can be solved if many diffractions are measured.

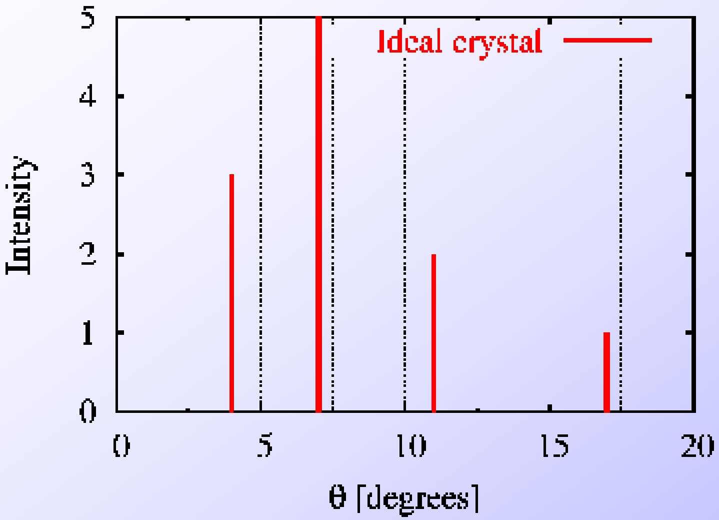
Slides 17, 24

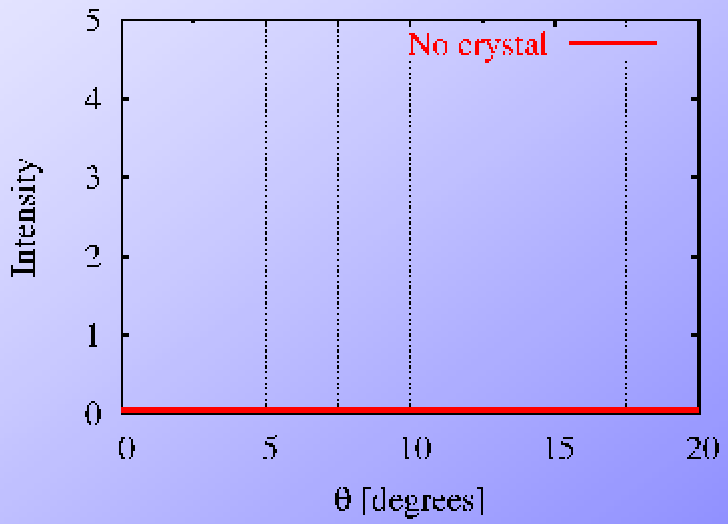
[Conclusion] If we have crystalline sample, we can find positions of all atoms in the crystal. This is called structure analysis.
Low molecular weight compounds usually crystallize quite well → nice diffraction patterns → thousands of diffractions → structure analysis is relatively easy (if we have some knowledge & fast computer).
Polymers usually crystallize badly → poor diffraction patterns → quite often just a few diffractions → structure analysis difficult or impossible.

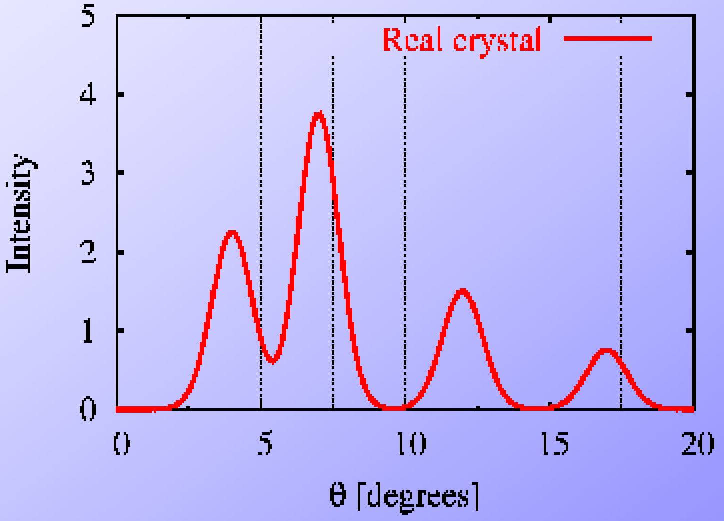
WAS on polymers.

(3) Crystallite size & crystal imperfections.

Simple intuitive model:







Ideal crystal = perfect 3D periodicity
⇒ infinite size ⇒ diffraction width $w_{hkl} = 0$

No crystal = crystal with zero size
⇒ no diffractions, i.e. diffr. width $w_{hkl} = \infty$

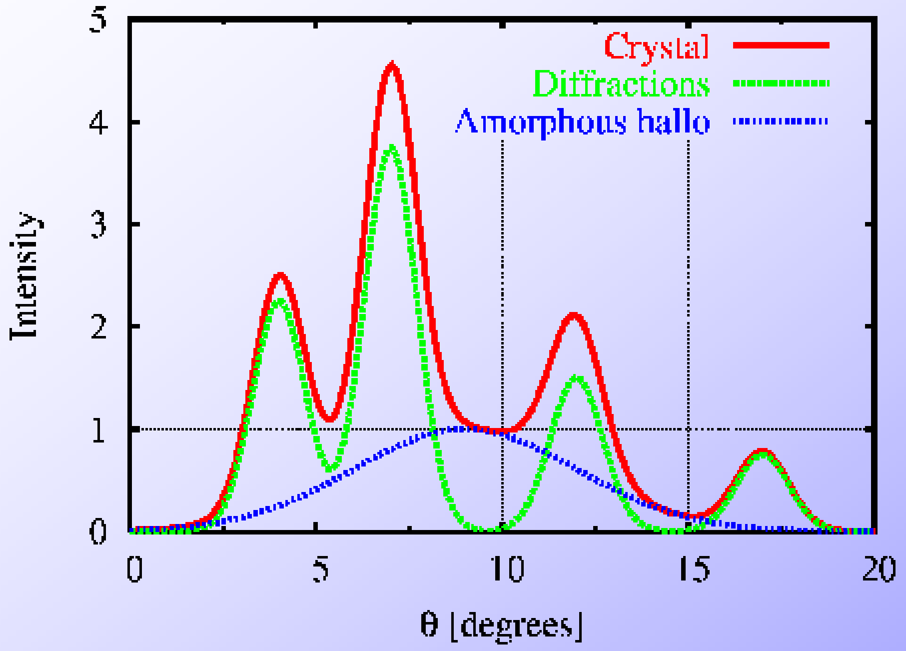
Real crystal = crystal with finite size
⇒ diffraction width $w_{hkl} \approx 2/\varepsilon_{hkl}$, where
ε_{hkl} = size of crystal in direction hkl.

Note: w_{hkl} is also influenced by crystal imperfections and thermal motion of atoms.

WAS on polymers.

(4) Degree of crystallinity.

We have already learned the principle!



Polymers are usually not completely crystalline. Slides 8

This is caused by extremely long polymer molecules. Slide 19

Scattering by crystalline phase: sharp peaks – total intensity I_k.

Scattering by amorphous phase: diffuse hallo – total intensity I_a.

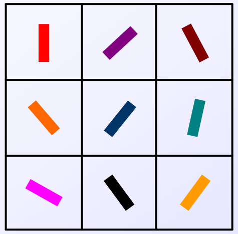
During data processing, it is possible to separate amorphous and crystalline scattering and determined degree of crystallinity:

$$CR = \text{const} \times I_k / (I_k + I_a)$$

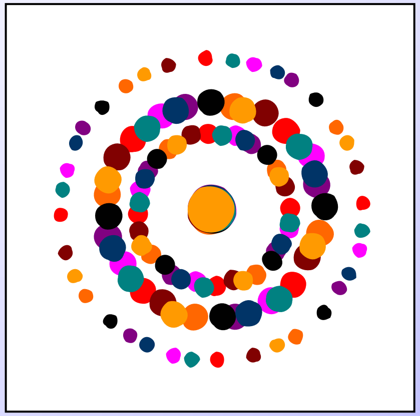
WAS on polymers.

(5) Orientation.

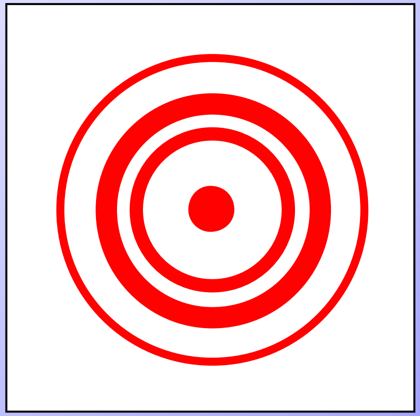
Simple intuitive model:



Polycrystalline sample
(unoriented)

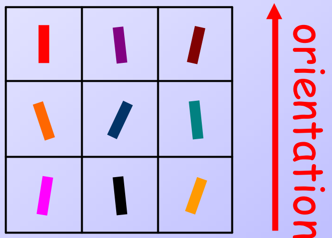


Diffraction pattern

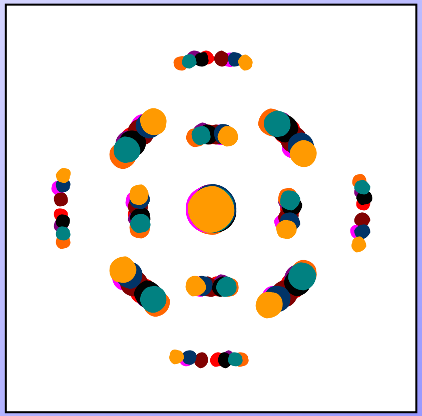


∞ crystals

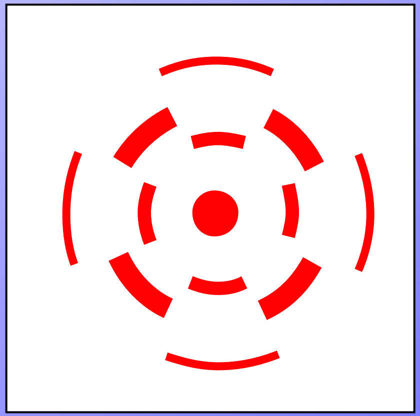
Unoriented
sample:
⇒ rings



Polycrystalline sample
(oriented)



Diffraction pattern



∞ crystals

Oriented
sample:
⇒ half-moons

Small-angle scattering.

Comparison of WAS and SAS.

WAS is connected with crystals.
Intensity is measured at wide diffraction angles $\theta>2^o$.
In WAS diffraction pattern there is a lot of information - many peaks.

- ~5 diffraction peaks enables to identify a known compound
- ~40 diffractions enables to determine unit cell of an unknown compound
- ~1000 diffractions enables to determine structure of an unknown compound

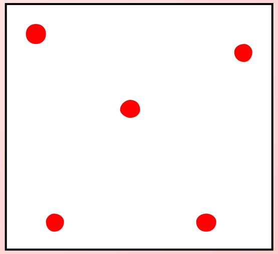
SAS can be applied to any systems with inhomogeneities from 10 to 1000 Å.
Intensity is measured at small diffraction angles $\theta<2^o$.
In SAS diffraction pattern there is little information – only a few peaks.

- SAS diffraction pattern usually contains only one central diffuse peak.
- A lot of different structures may have the same SAS pattern!
- Interpretation of SAS data is not so straightforward as in the case of WAS:
  (a) simple structures: diffraction patterns are pre-calculated
  (b) complicated structures: some knowledge about the structure needed
  (c) general procedure exists: it is not sure that we will find correct structure!

Here are general rules – exceptions do exist!

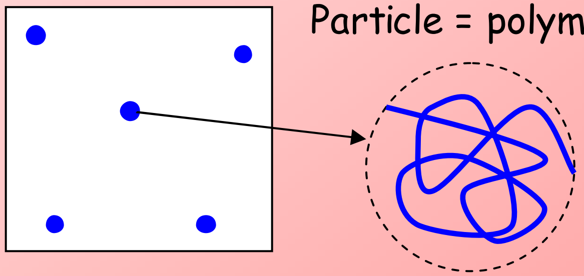
SAS: Which systems can be studied?

[1] Dilute particulate systems.
Examples: polymer micelles, particles...
Parameters: size & shape of particles...



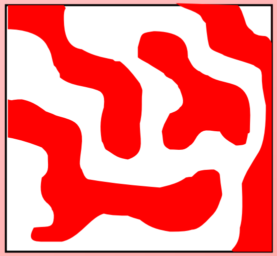
Solution is **diluted**. Particles scatter **independently** on each other.

[2] Liquid and solid solutions.
Examples: polymer molecules in solutions...
Parameters: size & thermodynamic properties...



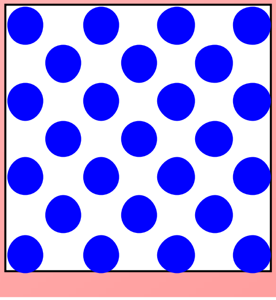
Particle = polymer coil.

[3] Non-particulate two-phase systems.
Examples: polymer blends, semicrystalline polymers...
Parameters: specific surface, thickness of interface...



A mixture of two phases with any structure.

[4] Periodic systems.
Examples: semicrystalline polymers, block copolymers...
Parameters: type of structure, periodicity...



Periodic or quasi-periodic packing of phases.

SAS: Examination in terms of Bragg Law.

Bragg Law, $d \times q = 2\pi n$, relates dimensions
in real space (= direct space, distances d, measured in Å)
and in diffraction space (= reciprocal space, distances q, are measured in $Å^{-1}$).

Note: As it holds: $S = 2d\sin\theta/\lambda$, $q = 2\pi S = 4\pi\sin\theta/\lambda$ and $\theta \in (0^o - 90^o)$,
the values of θ, S and q are all proportional, i.e. small θ means small S and q and vice versa.

Structure	d [Å]	θ [°]	2θ [°]	S [$Å^{-1}$]	q [$Å^{-1}$]
atom	1	30	60	1	6.28
small particle	10	2.9	5.7	0.1	0.628
large particle	1000	0.03	0.06	0.001	0.0628

Note1: Calculation is based on Bragg Law and typical values: n = 1, λ = 1Å.
Note2: Strictly speaking, **Bragg Law can be applied only to periodic systems!**
Note3: Large d ⇔ small θ, S and q – this is reciprocity principle.
Note4: SAXS and SANS are for particles with d = 10 - 1000Å, i.e. $\theta \approx 0 - 2^o$.

Reciprocity principle ensues directly from Bragg Law:
Objects, which are big in real space (i.e. which have a big dimension d)
are small in reciprocal space (i.e. it diffracts at small θ ~ S ~ q) and vice versa.

SAS: Simple structures.

Pre-calculated models. Example: dilute solution of identical spheres.

Dilute solution ⇒ spheres scatter independently ⇒ particulate scattering.

[1] Scattering of sphere with radius R can be derived from key formula:

$$A\left(\mathbf{q}\right)=\int_V \rho\left(\mathbf{r}\right)\exp\left[i\mathbf{qr}\right]d\mathbf{r}$$

[2] The formula is re-written in polar coordinates:

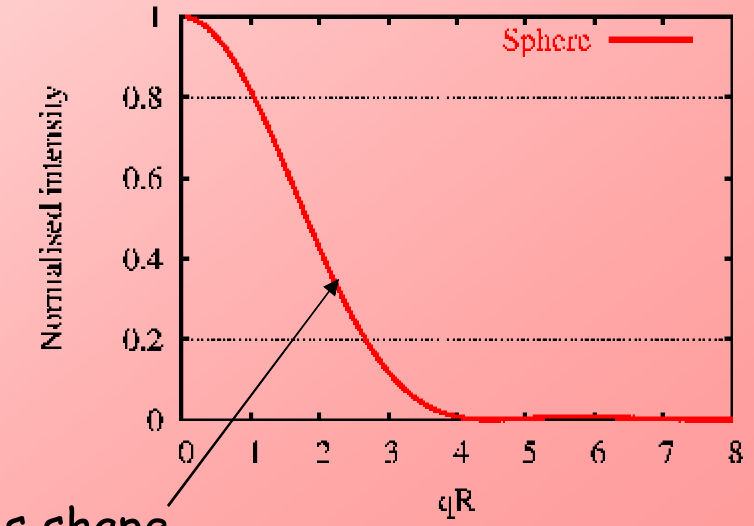
$$A\left(\mathbf{q}\right)=\int_{r=0}^{+\infty}\int_{\Theta=0}^{\pi}\int_{\Phi=0}^{2\pi}\rho\left(r,\Theta,\Phi\right)\,\exp\left[iqr\cos\Theta\right]\,r^2\sin\Theta\,dr\,d\Theta\,d\Phi$$

[3] The rest is only mathematics; results:

$$A\left(q\right)=\rho_0 V\,\frac{3\left(\sin\left(qR\right)-qR\cos\left(qR\right)\right)}{\left(qR\right)^3}$$

$$I\left(q\right)=\left|A\left(q\right)\right|^2=\rho_0^2V^2\,\frac{9\left(\sin\left(qR\right)-qR\cos\left(qR\right)\right)^2}{\left(qR\right)^6}$$

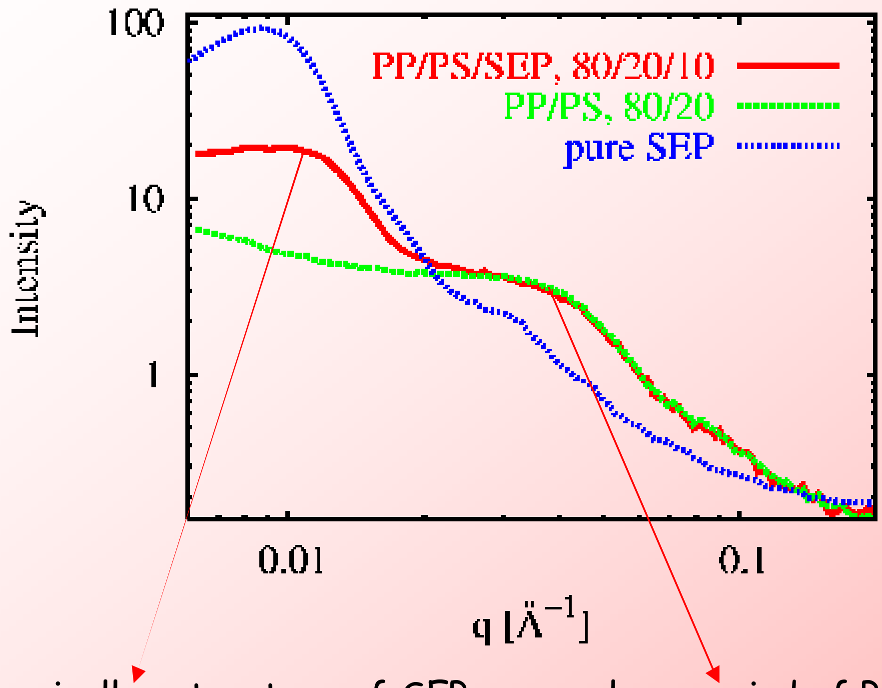
Complete derivation.



Conclusion: If the scattering curve has this shape, scattering objects are homogeneous spheres.

SAS: Complicated structures.

Some knowledge about the system needed. Example: polymer blend.



micellar structure of SEP

long period of PP

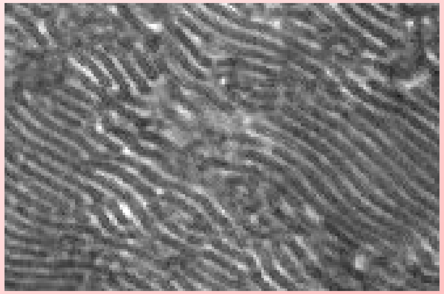
SAXS curve of PP/PS/SEP (80/20/10) polymer blend. More info needed to interpret the diffraction pattern ↓ ↓ ↓

[1] SAXS of PP/PS (80/20) polymer blend.
  ⇒ peak at q ≈ 0.04 = long period of PP

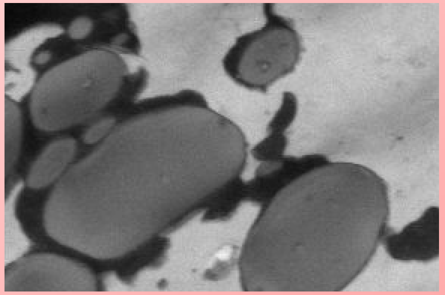
[2] SAXS of pure SEP copolymer.
  ⇒ peak at q ≈ 0.01 connected with SEP

[3] STEM micrograph of SEP and PP/PS/SEP.
  ⇒ SEP has periodic lamellar structure
  ⇒ SEP structure is partially in the blend

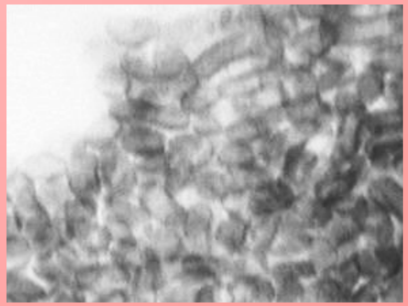
[4] TEM micrograph of PP/PS/SEP blend.
  ⇒ SEP structure changed to micellar



STEM of SEP; 30kx



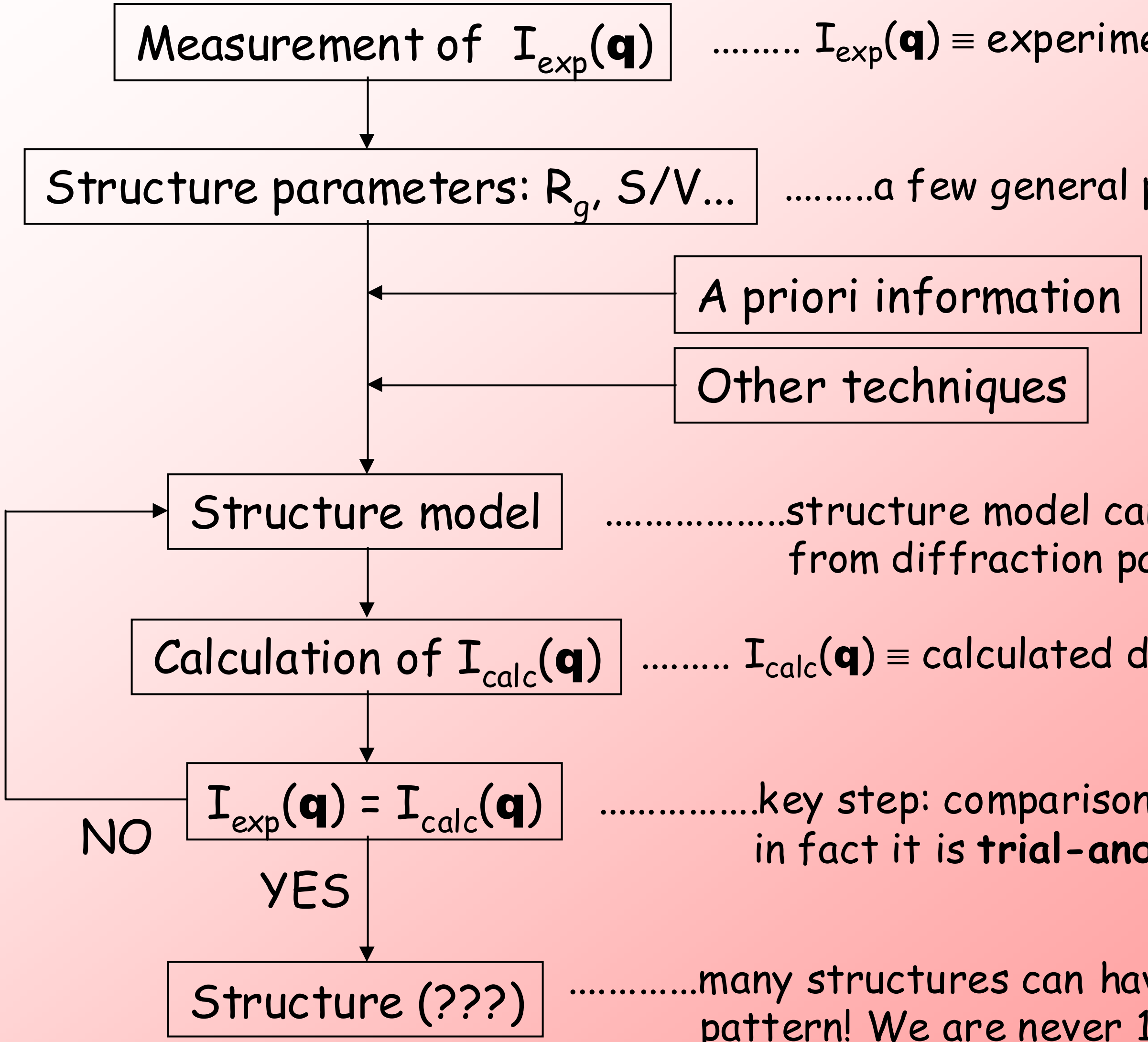
STEM of PP/PS/SEP; 10kx



TEM of PP/PS/SEP; 50kx

SAS: General procedure.

(A general procedure for interpretation of arbitrary SAS data.)



Measurement of $I_{exp}(\mathbf{q})$ ……… $I_{exp}(\mathbf{q}) \equiv$ experimental diffraction pattern

Structure parameters: R_g, S/V... ………a few general parameters can always be calculated. (see next slides).

A priori information

Other techniques

Structure model ………………structure model cannot be calculated directly from diffraction pattern, only estimated.

Calculation of $I_{calc}(\mathbf{q})$ ……… $I_{calc}(\mathbf{q}) \equiv$ calculated diffraction pattern

$I_{exp}(\mathbf{q}) = I_{calc}(\mathbf{q})$ ……………key step: comparison of experiment and model, in fact it is **trial-and-error method**.

NO

YES

Structure (???) …………many structures can have the same diffraction pattern! We are never 100% sure that the final structure is correct!

SAS: Radius of gyration.

Shapes of particles in SAS are often characterised by radius of gyration, R_g:

$$R_g^2 = \frac{\int \mathbf{r}^2 \rho(\mathbf{r}) d\mathbf{r}}{\int \rho(\mathbf{r}) d\mathbf{r}}$$

r = vector with origin in centre of scattering length density
ρ(**r**) = scattering length density.

R_g of particle with constant scattering length density (≡ homogeneous particle):

$$R_g^2 = 1/V \int \mathbf{r} \sigma(\mathbf{r}) d\mathbf{r}$$

σ(**r**) = shape function: equals 1 inside and 0 outside the particle
V = volume of the particle

R_g of some particles with simple shape:

$$R_g = \sqrt{\frac{3}{5}} R$$

Sphere
with radius R

$$R_g = \frac{1}{\sqrt{12}} L$$

Thin rod
with length L

$$R_g = \frac{1}{\sqrt{2}} R$$

Thin disc
with radius R

Conclusion: from R_g it is possible to calculate dimensions of the particle, on condition that we know its shape.

Note: why as obscure quantity as R_g is used instead of something simpler?
Because R_g can often be determined thanks to Guinier Law (slide 40).

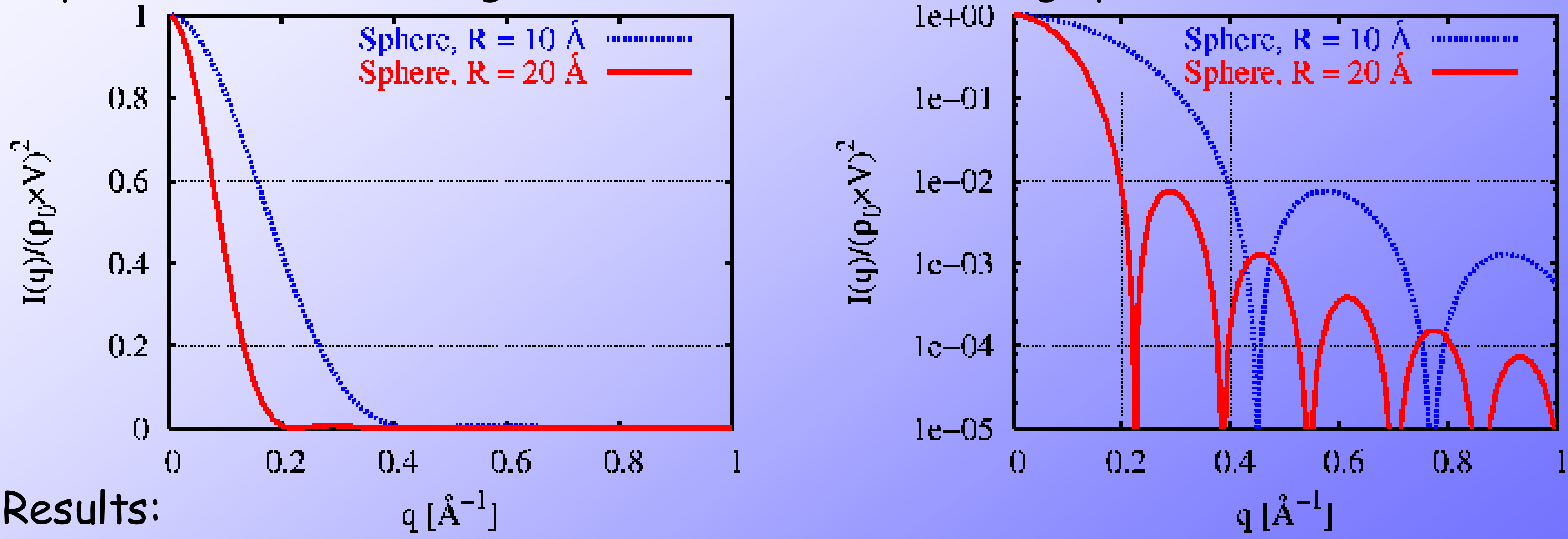
SAS: Size of the particles.

Applies to: Dilute particulate systems.

We have already derived scattering by sphere with radius R:

$$I\left(q\right)=\left|A\left(q\right)\right|^{2}=\rho_{0}^{2}V^{2}\,\frac{9\left(\sin\left(qR\right)-qR\cos\left(qR\right)\right)^{2}}{\left(qR\right)^{6}}$$

Simple model – scattering of two solutions containing spheres with different R:



Results:

[1] different radii are clearly recognizable from I(q)

[2] the differences are more pronounced if I(q) is in logarithmic scale

[3] generalization: analysis of I(q) provides size of arbitrary particles

[4] note: reciprocity principle → smaller sphere ⇔ broader scattering

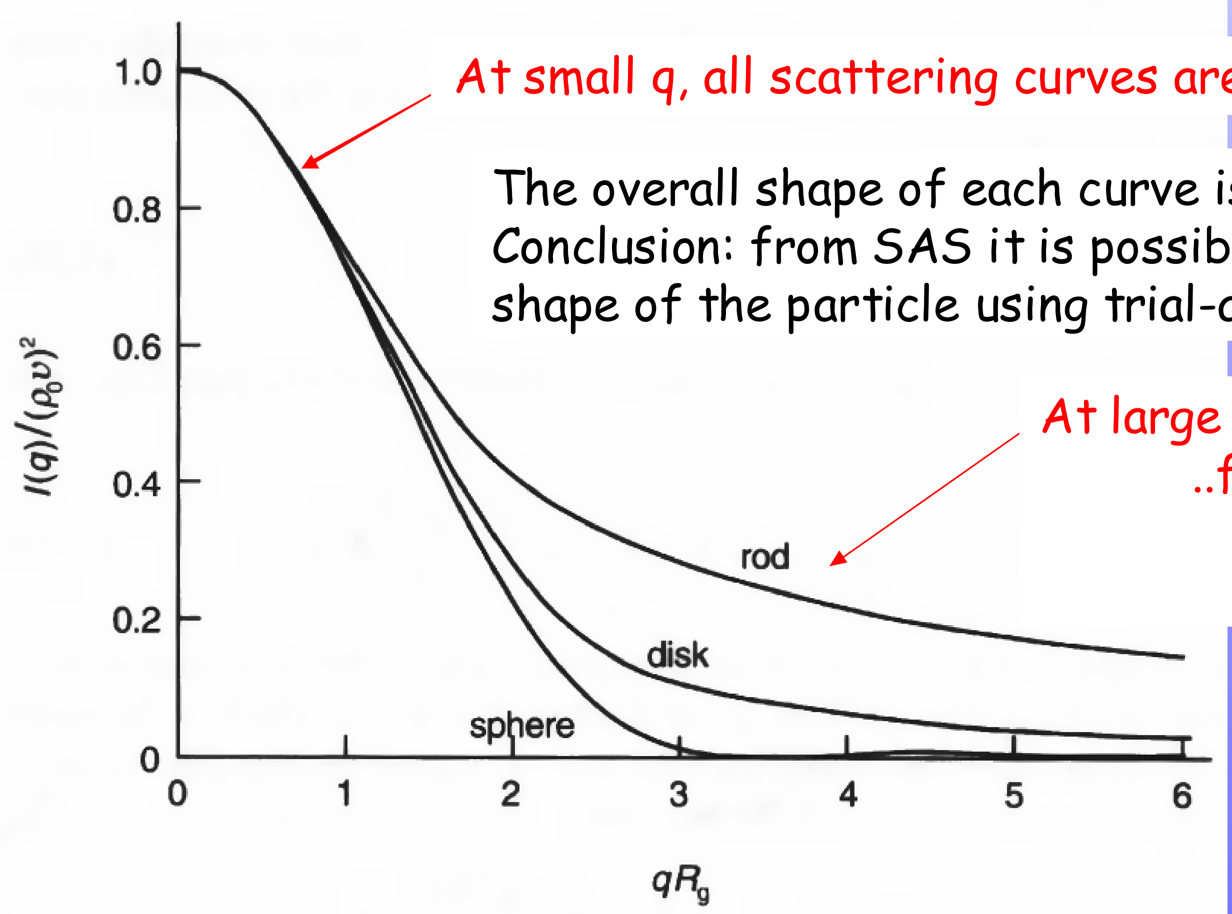
SAS: Shapes of the particles.

Applies to: Dilute particulate systems.

[1] We have already derived particulate scattering of spherical particle.

[2] In an analogous way, scattering of any particle can be derived.

[3] Results for three limiting cases – sphere (3D object), disc (2D) and rod (1D):



At small q, all scattering curves are very close.

The overall shape of each curve is very different.
Conclusion: from SAS it is possible to estimate the shape of the particle using trial-and-error method.

At large q, it holds $I \approx q^{-\alpha}$
..for spheres: $\alpha = 4$
..for discs: $\alpha = 2$
..for rods: $\alpha = 1$

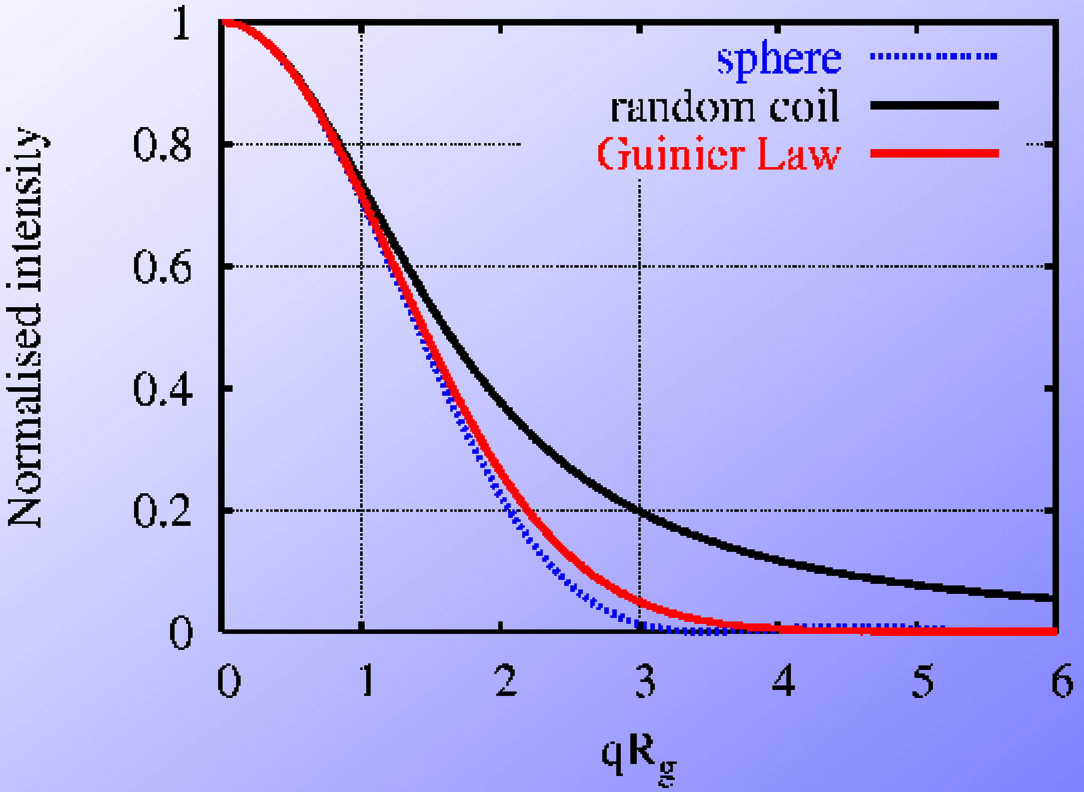
SAS: Guinier Law.

Applies to: Dilute particulate systems.

Verbally: Scattering at small q is always the same, regardless of particle shape!

Mathematically: If ($q < 1/R_g$) then $I(q) = \rho_0^2 V^2 \exp\left(-\frac{1}{3} q^2 R_g^2\right)$ ...Guinier Law.

Graphically: the SAS curves have the same shape for $qR_g < 1$, i.e. for $q < 1/R_g$.



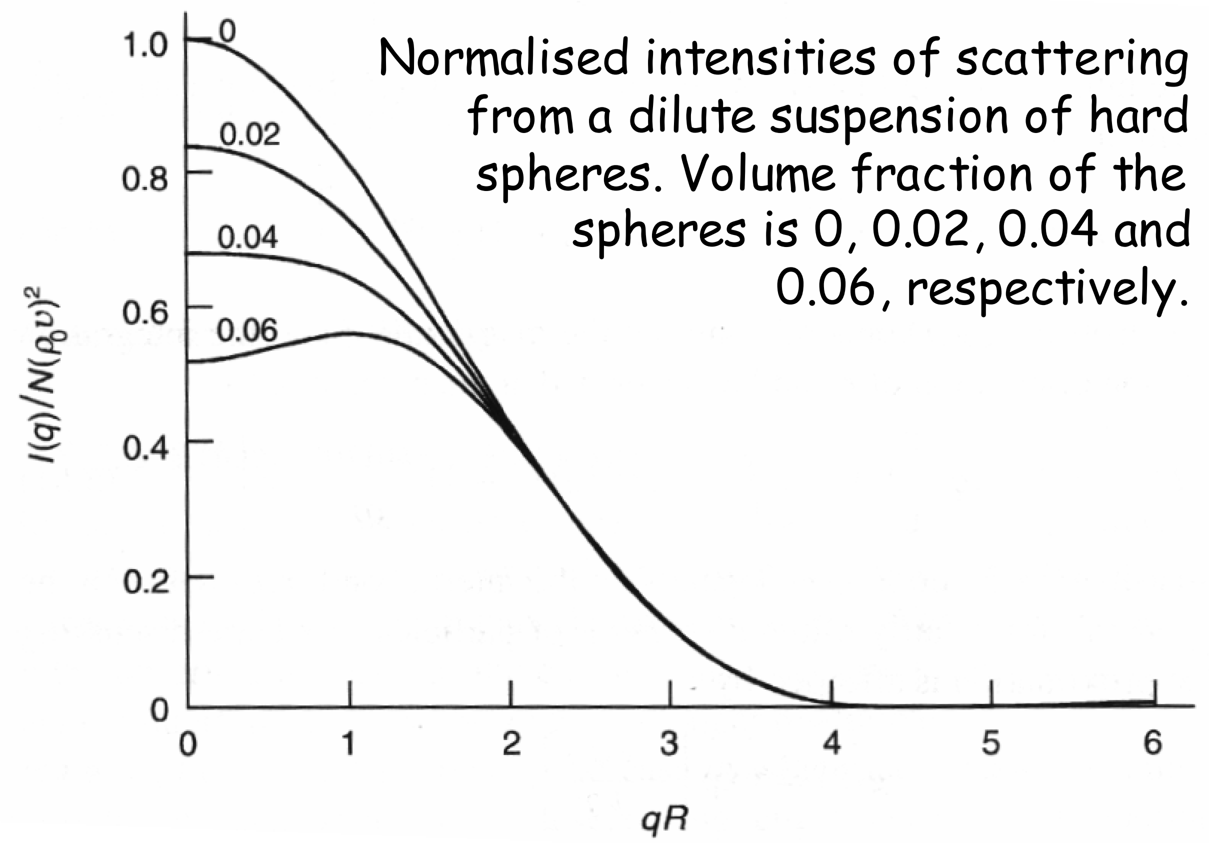
Conclusion:
Radius of gyration, R_g, of any particle can easily be determined from SAS data.

Note1:
This is why R_g is so popular in SAS.

Note2:
Guinier Law holds only in diluted solutions after background correction!

SAS: Dense packing.

Applies to: Dilute particulate system.



Normalised intensities of scattering from a dilute suspension of hard spheres. Volume fraction of the spheres is 0, 0.02, 0.04 and 0.06, respectively.

In diluted solution, particles are so far apart from each other that the interference among the waves scattered by different particles can be ignored, i.e. waves scattered by particles do not interfere. In other words, particles scatter independently, which is called particulate scattering.

In more concentrated solution, the interparticle interference can be no longer neglected, i.e. waves scattered by the particles interfere with each other. The scattering is no longer particulate. This is referred as effect of dense packing.

SAS: Polymers in solution – random coil.

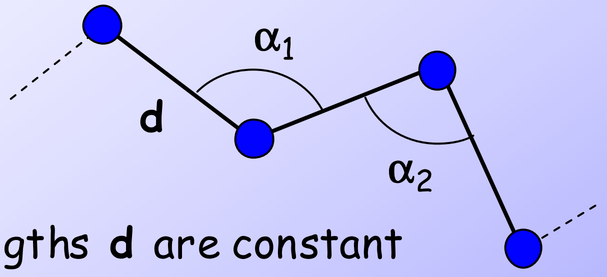
Applies to: Liquid and solid solutions.

Schematic drawing of a polymer molecule in solution.

in solution,
long polymer chain
is twisted into a coil

Simple model describing this shape – random coil (also called Gaussian chain).

Assumptions of the model:



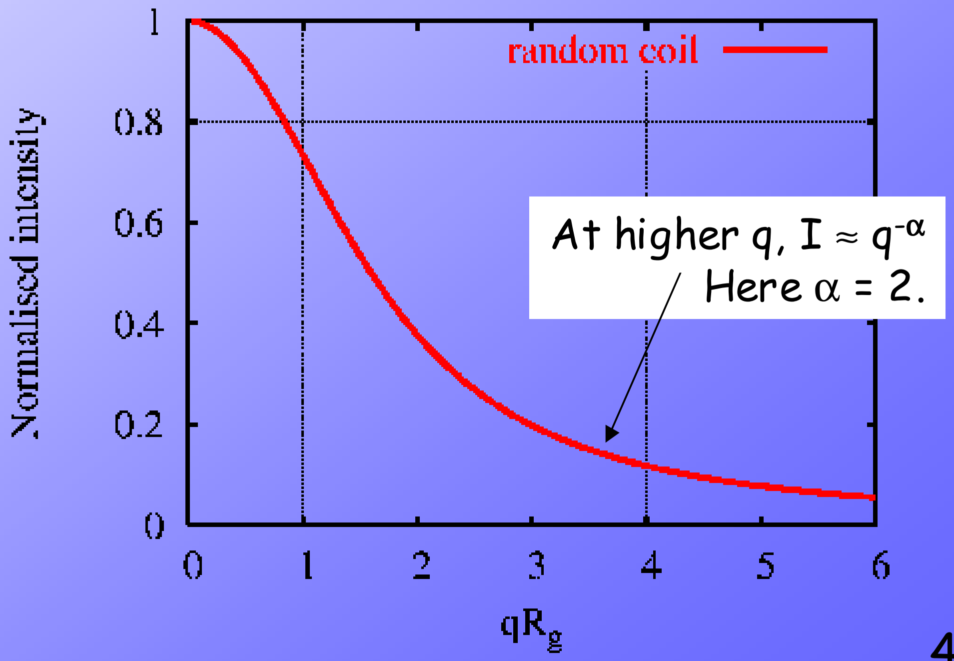
bond lengths **d** are constant
bond angles α = <0;2π>,uncorrelated
$\Rightarrow$ the random chain is very flexible

Results of the model:

Radius of gyration: $\langle R_g^2 \rangle = \frac{nl^2}{6}$

Scattering: $I(q) = \rho_0 V \frac{2\left(e^{-q^2R_g^2} + q^2R_g^2 - 1\right)}{q^4R_g^4}$

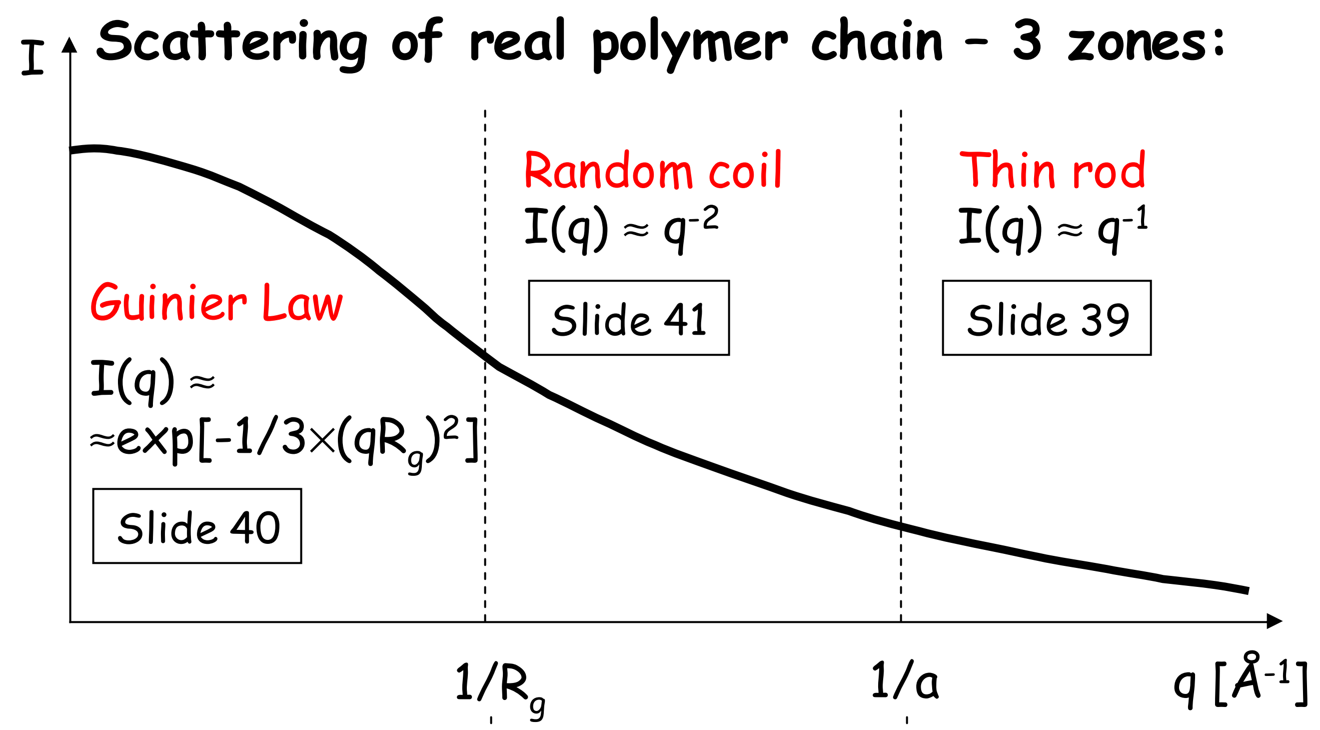
Calculated particulate scattering of random coil:



At higher q, I ≈ $q^{-\alpha}$
Here α = 2.

SAS: Polymers in solution – real coil.

Applies to: Liquid and solid solutions.



Scattering of real polymer chain – 3 zones:

Guinier Law

$I(q) \approx$

$\approx \exp[-1/3 \times (qR_g)^2]$

Slide 40

Random coil

$I(q) \approx q^{-2}$

Slide 41

Thin rod

$I(q) \approx q^{-1}$

Slide 39

Small details at large q – reciprocity principle.

Zone1:

Lowest q ⇔ largest d.
Dimensions: $q^{-1} < R_g$.
We see the whole coil.

Zone2:

Middle q ⇔ middle d.
Dimensions: $R_g < q^{-1} < a$.
We see large parts of of the chain, which are twisted and flexible.

Zone3:

Large q ⇔ small d.
Dimensions: $a < q^{-1}$.
We see small parts of of the chain, which are rigid – as thin rods.

Note:

Dimensions are also characterized by q^{-1}.

SAS: Persistence length.

Applies to: Liquid and solid solutions.

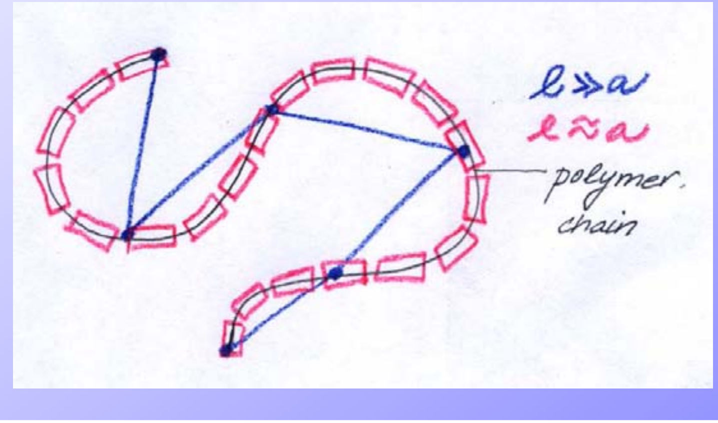
From previous slide – I(q) of real polymer in solution – 3 zones:

[1] At small q, the polymer obeys Guinier law.
[2] At middle q, the polymer behaves as flexible Gaussian chain.
[3] At largest q, the stiff segments of polymer chain behave as a rigid thin rods.

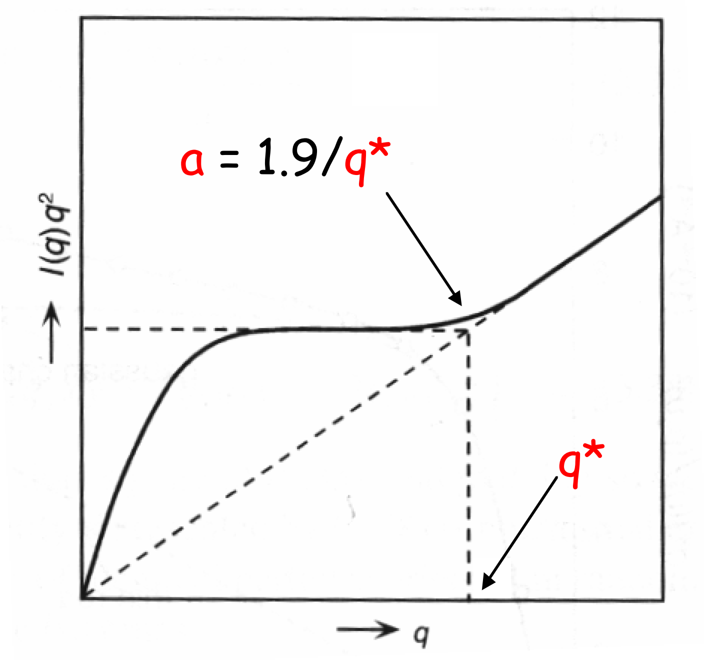
When does the transition between zones [2] and [3] occur?

- Flexible chains: transition at higher q
- Stiff chains: transition at lower q.
- It is connected with constant **a**.

Persistence length a = the length of the largest segment, which enables to describe polymer chain.



Kratky plot – determination of persistence length.



SAS: Porod Law.

Applies to: Non-particulate two-phase systems.

Porod Law: If qR_g >> 1 then $I(q) = 2\pi(\Delta\rho)^2S/q^4$; i.e. $I(q) \approx q^{-4}$.

From Porod law it is possible to derive also:

- specific interface area, calculated from: $I(q)/Q \approx S/V \times 1/q^4$
- average chord lengths, calculated as: $l_1 = 4\Phi_1 V/S$ and $l_2 = 4\Phi_2 V/S$

Non-particulate two phase system.

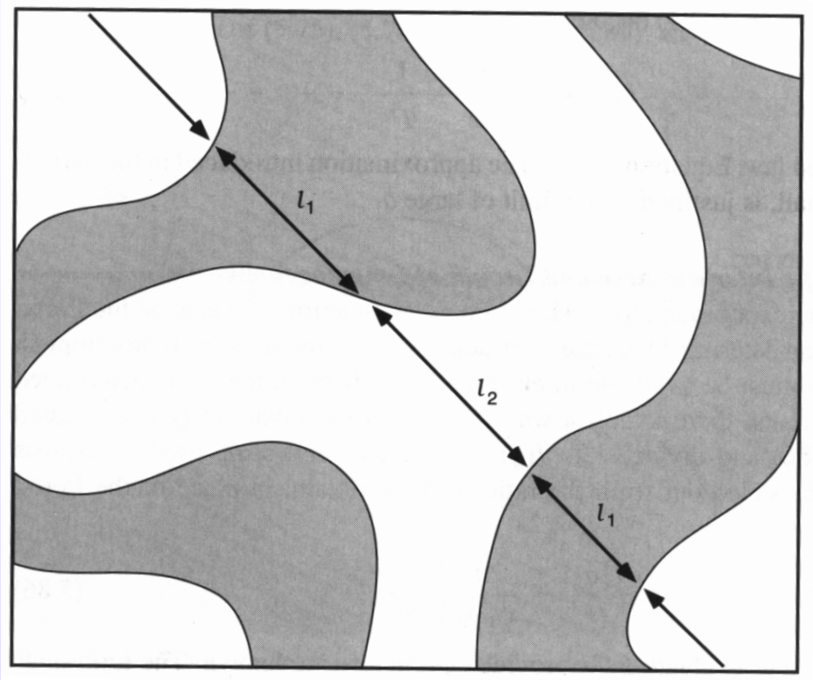
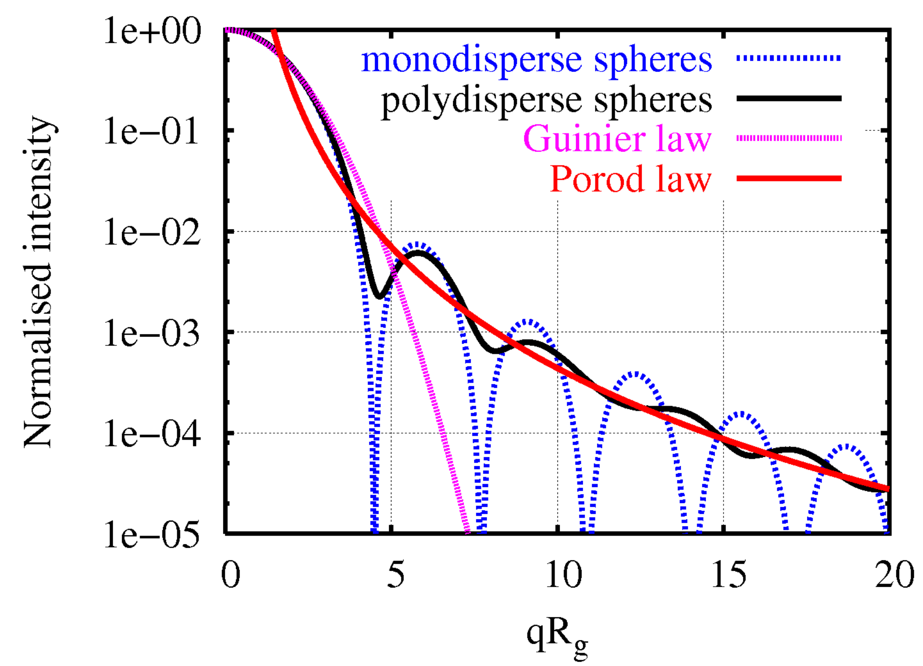


Illustration of Porod Law.

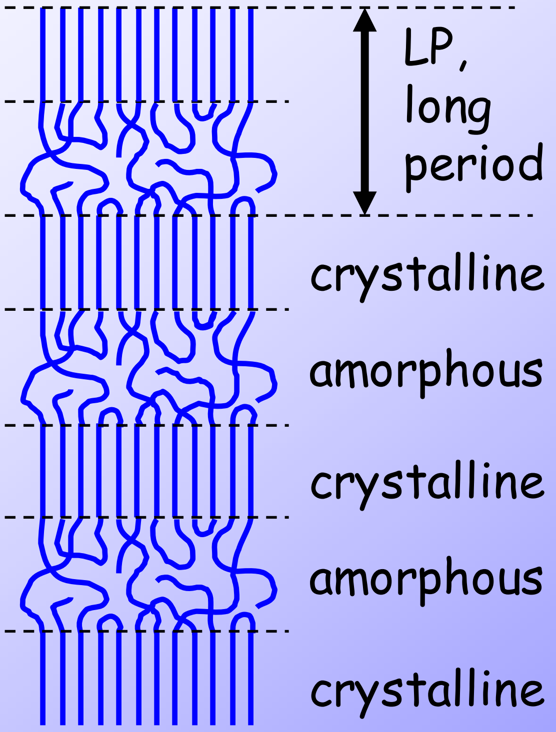


SAS: Long period.

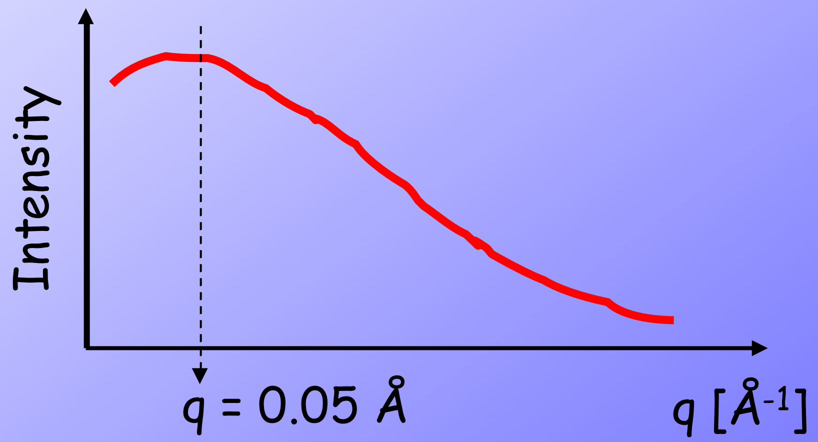
Applies to: Periodic systems.

Synthetic polymers are either amorphous or semicrystalline.
In semicrystalline polymers, amorphous and crystalline parts alternate.
Thickness of the crystalline lamellae: $d \approx 100\text{Å} \Rightarrow q \approx 0.06\text{Å}^{-1}$, $\theta \approx 0.3^{\circ} \Rightarrow$ SAS.

Semicrystalline polymer



Corresponding diffraction pattern



Bragg Law: $dq = 2\pi$

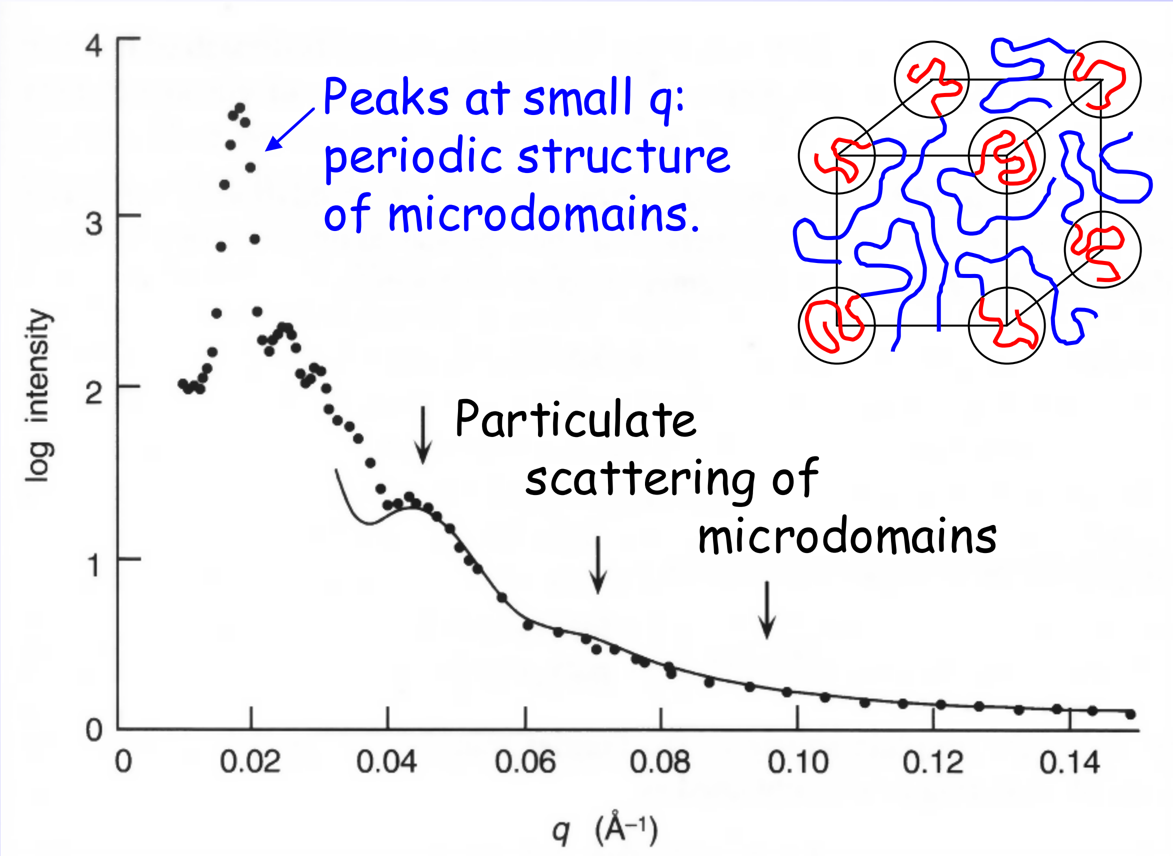
As the structure is periodic, we can use Bragg Law (although it comes from WAS).

Peak at I(q) corresponds to LP.
Here LP = d = $2\pi/q$ = 126 Å.

SAS: Structure of block copolymers.

Applies to: Periodic systems.

SAXS diffraction pattern of a SB diblock copolymer with spherical butadiene microdomains



Black dots: experimental points.
Black line: calculated independent scattering from solid spheres with average radius R=124 Å.

Peaks at small q: scattering, which corresponds to periodic structure of spherical microdomains. Analogy with WAS: larger unit cell + microdomains instead of atoms.

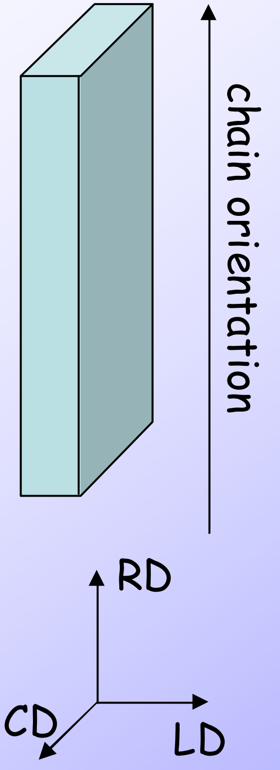
Peaks at higher q: scattering of individual spherical microdomains. Standard SAS scattering of spheres.

Conclusion: SAS of block copolymers yields information about periodicity and type of structure.

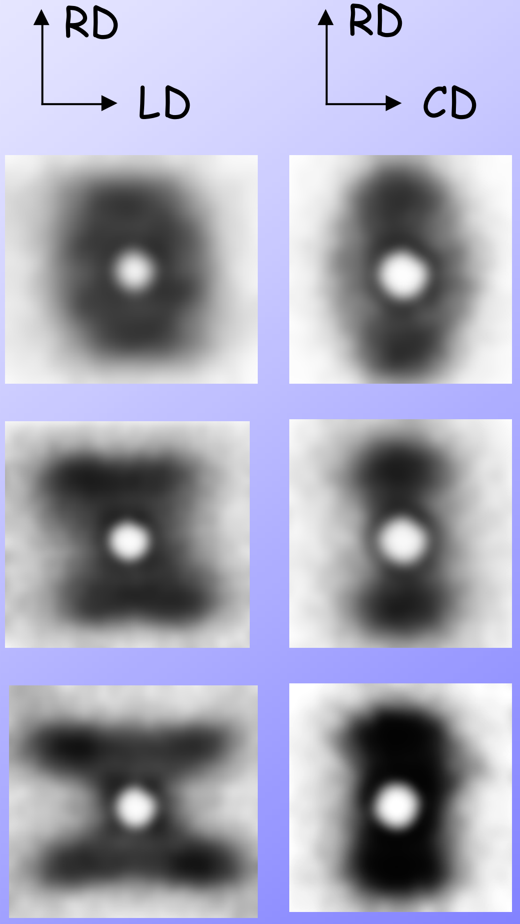
SAS: Orientation.

Applies to: Periodic systems.

Oriented PP
Z.Bartczak:
J.Appl.Pol.Sci
86 (2002) 1396-1404.



SAXS - in two directions

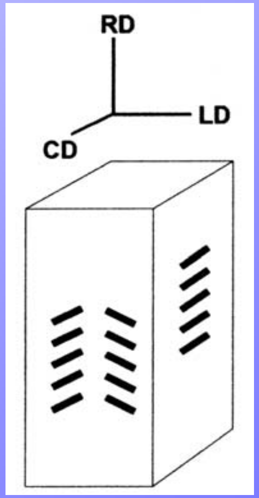


modest orientation

middle orientation

strong orientation

Interpretation:
SAXS shows orientation of crystalline lamellae.



Conclusion:
Oriented sample
⇒ non-spherically symmetric SAS pattern.

Conclusion

Diffraction = scattering + interference.

X-ray, neutron, electron and light diffraction have common principle, which can be represented by the key formula: $A(\mathbf{q}) = \int \rho(\mathbf{r})\exp(i\mathbf{qr})d\mathbf{r}$.

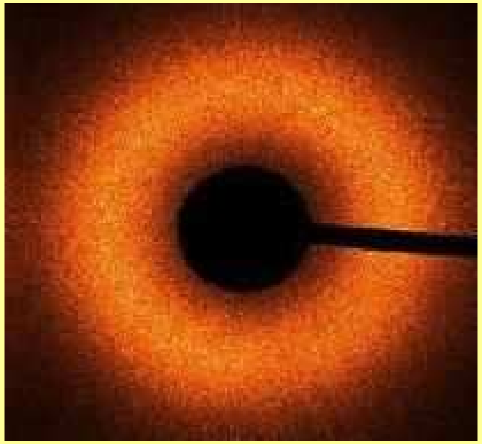
Wide-Angle Scattering is observed on crystals.
WAS may yield: crystal structure, unit cell parameters, degree of crystallinity, crystallite size and orientation...

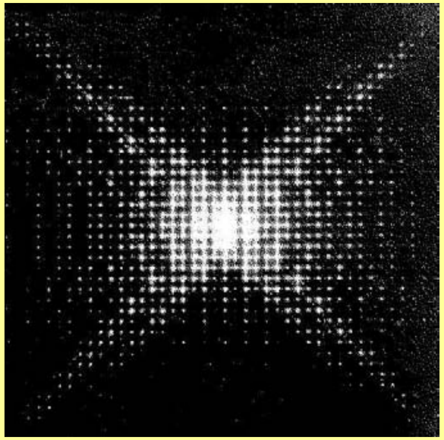
Small-Angle Scattering is observed on systems containing inhomogeneities from 10 to 1000Å. The systems need not be periodic.
SAS may yield: size and shape of particles in diluted solutions, persistence length and other characteristics of polymer molecules, specific interface in non-particulate systems, periodicity, orientation and type of structure in periodic systems...

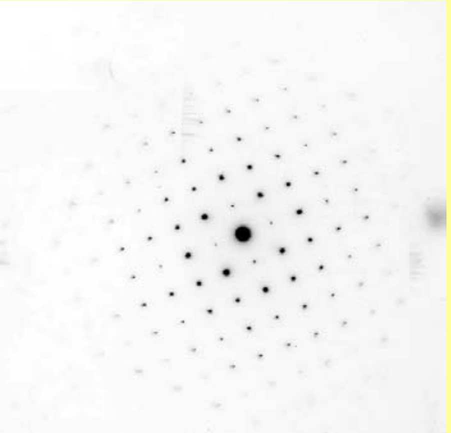
Diffraction on periodic structures in both WAS and SAS can be described by means of simple model, represented by Bragg Law: $2d\sin\theta = n\lambda$.

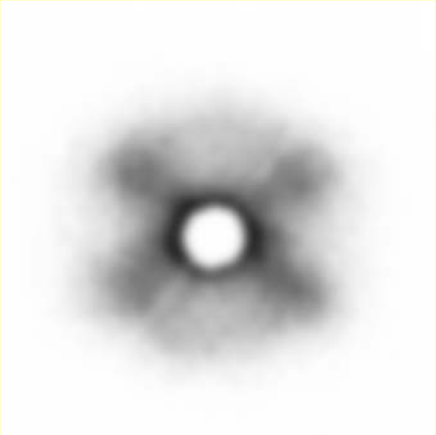
In SAS, Guinier Law often enables to determine radius of gyration, R_g, which is associated with the size of the particle.

Example 0: Various forms of diffraction patterns.

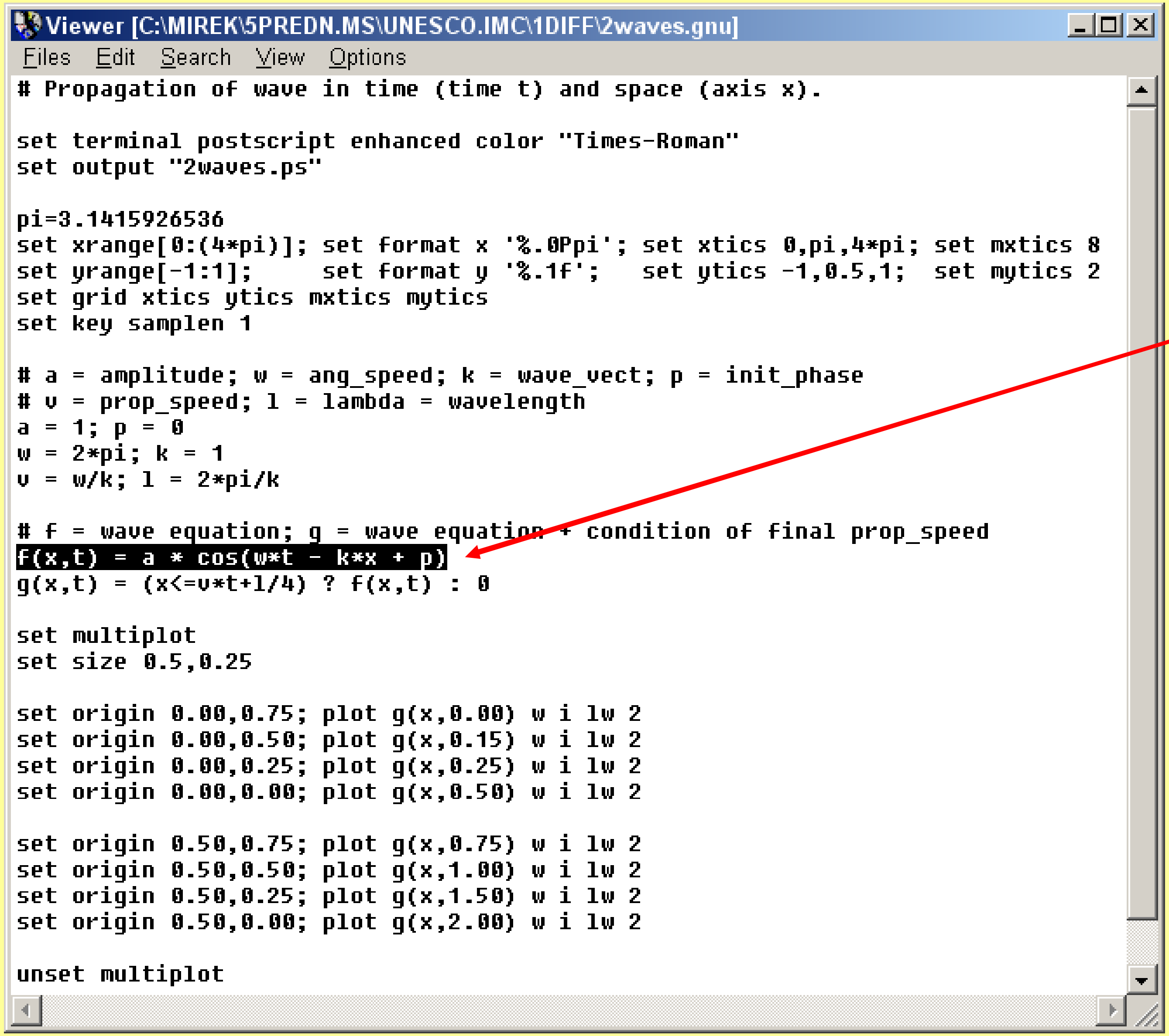

SAS – neutron diffraction


WAS – light diffraction


WAS – electron diffraction


SAS – X-ray diffraction

Example 1/1: Propagation of wave in time and space.



```
# Propagation of wave in time (time t) and space (axis x).

set terminal postscript enhanced color "Times-Roman"
set output "2waves.ps"

pi=3.1415926536
set xrange[0:(4*pi)]; set format x '%.0Ppi'; set xtics 0,pi,4*pi; set mxtics 8
set yrange[-1:1];     set format y '%.1f';   set ytics -1,0.5,1;  set mytics 2
set grid xtics ytics mxtics mytics
set key samplen 1

# a = amplitude; w = ang_speed; k = wave_vect; p = init_phase
# v = prop_speed; l = lambda = wavelength
a = 1; p = 0
w = 2*pi; k = 1
v = w/k; l = 2*pi/k

# f = wave equation; g = wave equation + condition of final prop_speed
f(x,t) = a * cos(w*t - k*x + p)
g(x,t) = (x<=v*t+l/4) ? f(x,t) : 0

set multiplot
set size 0.5,0.25

set origin 0.00,0.75; plot g(x,0.00) w i lw 2
set origin 0.00,0.50; plot g(x,0.15) w i lw 2
set origin 0.00,0.25; plot g(x,0.25) w i lw 2
set origin 0.00,0.00; plot g(x,0.50) w i lw 2

set origin 0.50,0.75; plot g(x,0.75) w i lw 2
set origin 0.50,0.50; plot g(x,1.00) w i lw 2
set origin 0.50,0.25; plot g(x,1.50) w i lw 2
set origin 0.50,0.00; plot g(x,2.00) w i lw 2

unset multiplot
```

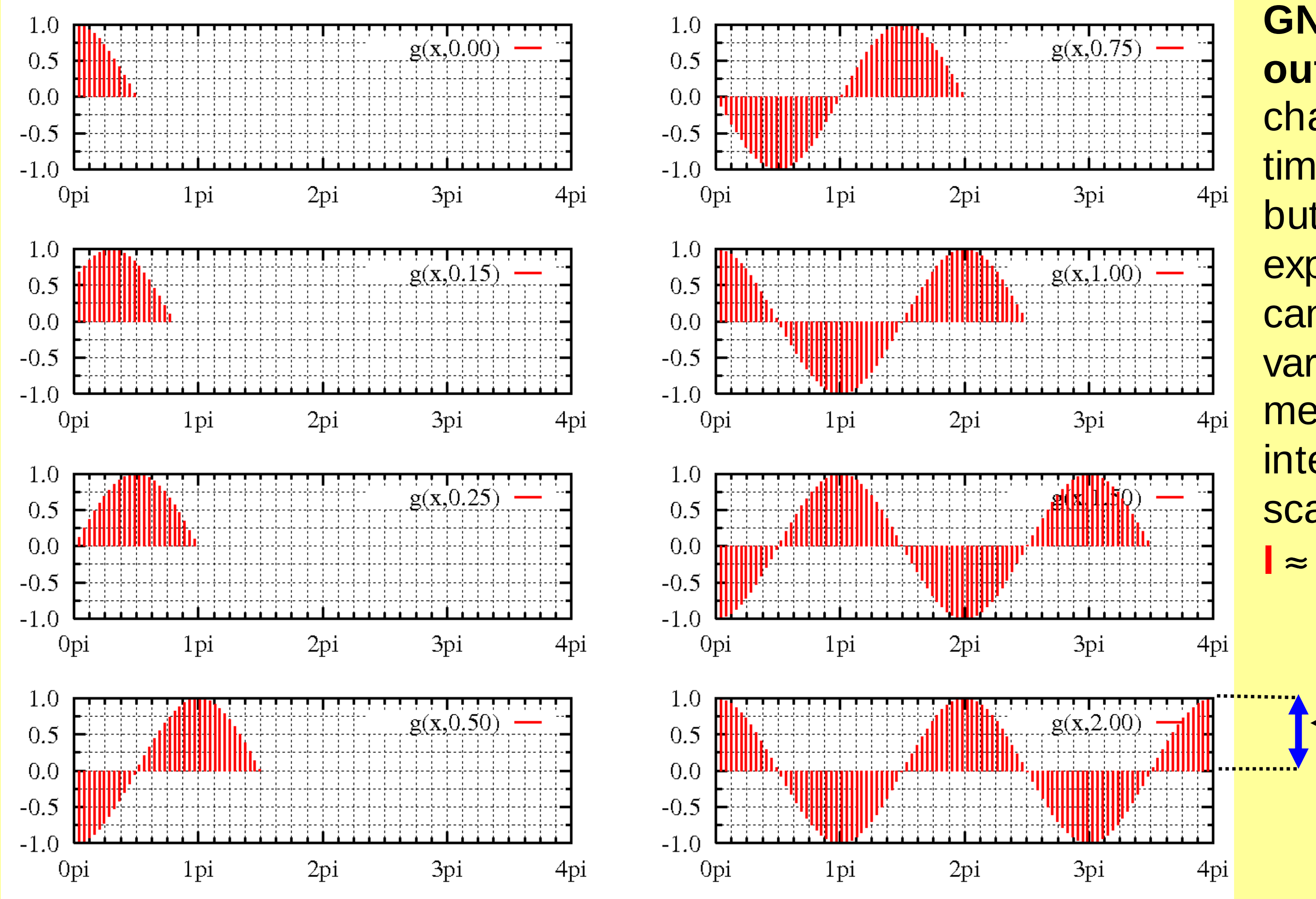
Input for GNUplot.
(freeware program
(for plotting
The script visualizes
wave propagation.

Key part of the script:
cosine wave.

Main problem:
wave = f(a,w,**t**,k,**x**,p)
(that is why the script
(has additional lines

Solution in this script:
a = 1, constant
w = 2π, constant
k = 1, constant
p = 0, constant
t = time, parameter
x = distance, variable

Example 1/2: Propagation of wave in time and space.



GNUplot output: waves change in both time and space, but in scattering experiments we can ignore the variations, as we measure just intensities, **I**, of scattered waves:

$I \approx |A|^2$

absolute value of amplitude

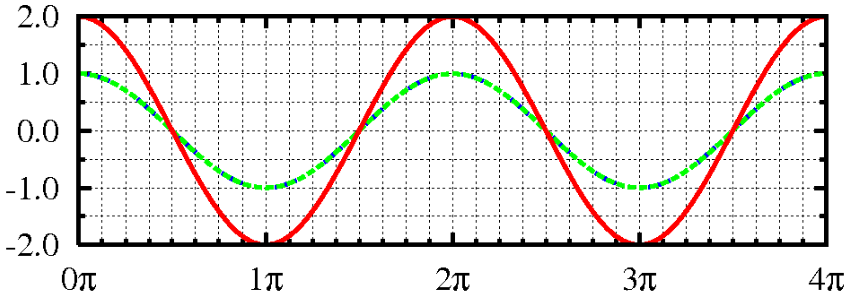
Elastic scattering, scattered wave: $\Psi(x,t) = A * \cos(\omega t - kx + \Phi)$

ω, k ≈ frequency and direction of wave ⇒ constants for given experiment

t, x ≈ time of measurement and detector position ⇒ constants for given experiment

A,Φ ≈ amplitude and phase ⇒ variables, depend on scattering object

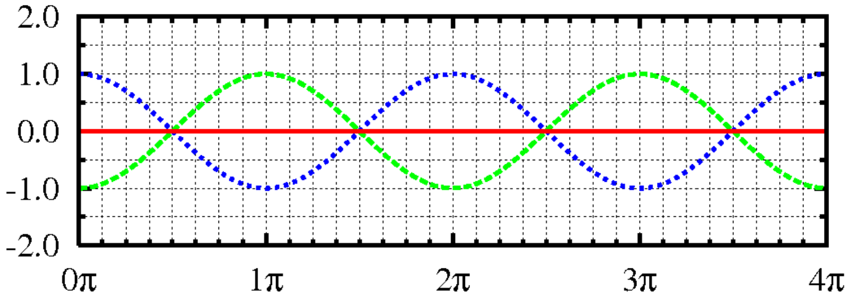
Example 2/1: Interference of [cos-waves] graphically.



Case 1: maximal interference

$\Psi = A * \cos(X+\Phi)$; $X = \omega t - kx$; $A1 = A2 = 1$

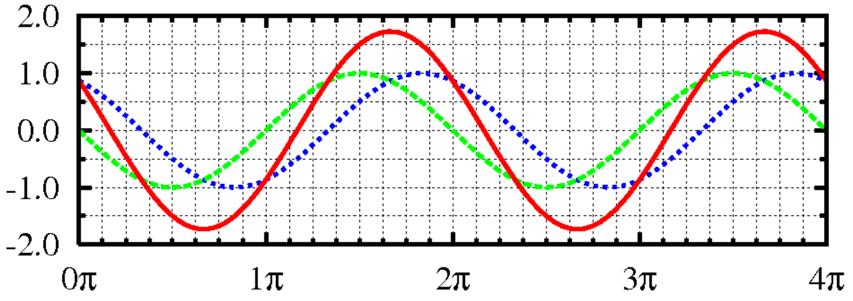
[$\Phi1$ = 0deg and $\Phi2$ = 0deg] $\Rightarrow$ A = 2



Case 2: minimal interference

$\Psi = A * \cos(X+\Phi)$; $X = \omega t - kx$; $A1 = A2 = 1$

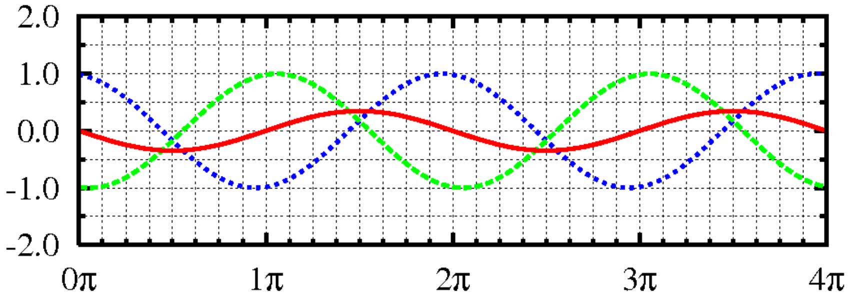
[$\Phi1$ = 0deg and $\Phi2$ = 180deg] $\Rightarrow$ A = 0



Case 3: general case.

$\Psi = A * \cos(X+\Phi)$; $X = \omega t - kx$; $A1 = A2 = 1$

[$\Phi1$ = 30deg and $\Phi2$ = 90deg] $\Rightarrow$ A = 1.73

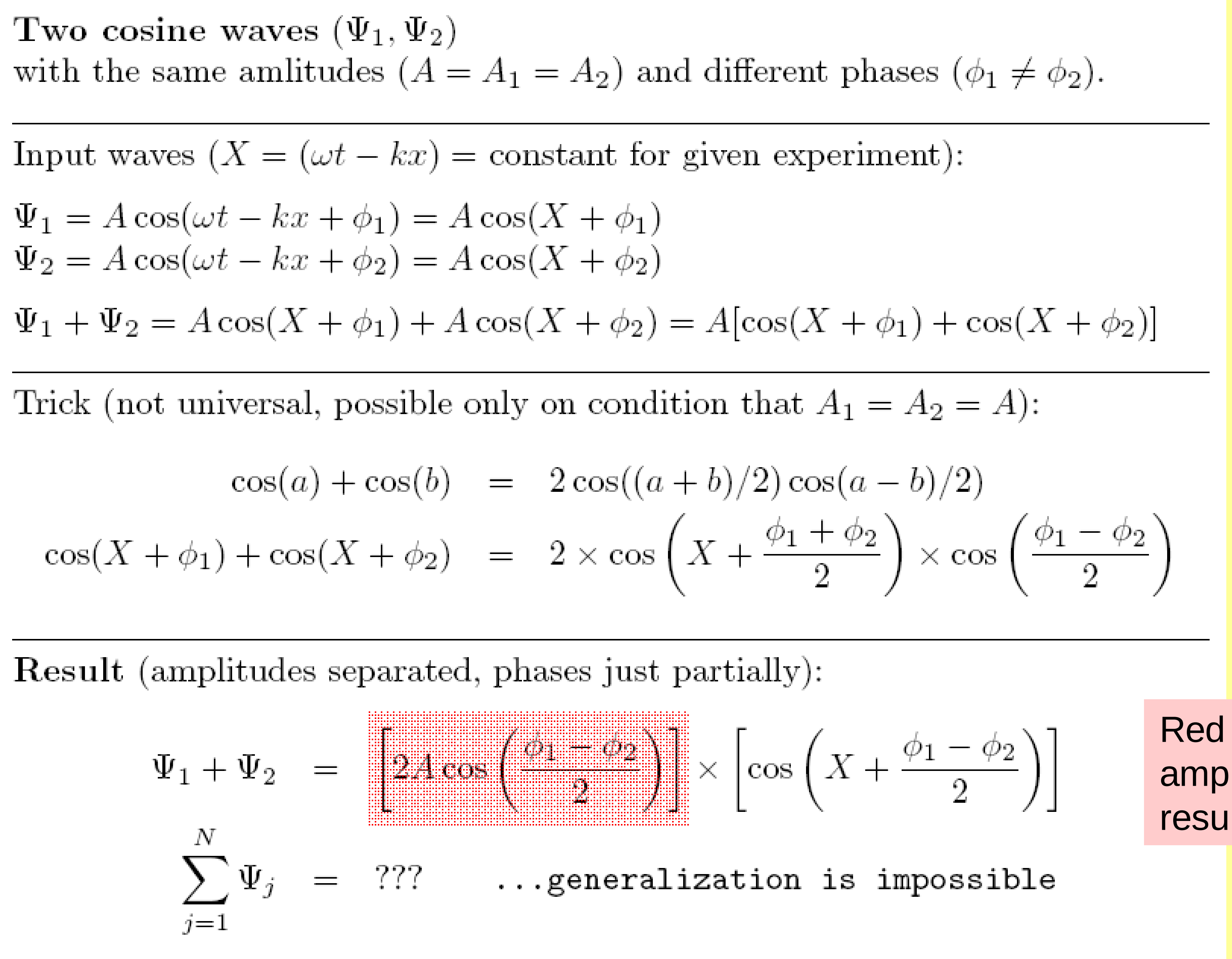


Case 4: general case.

$\Psi = A * \cos(X+\Phi)$; $X = \omega t - kx$; $A1 = A2 = 1$

[$\Phi1$ = 10deg and $\Phi2$ = 170deg] $\Rightarrow$ A = 0.35

Example 2/2: Interference of [cos-waves] mathematically.



Two cosine waves (Ψ_1, Ψ_2)
with the same amlitudes $(A = A_1 = A_2)$ and different phases $(\phi_1 \neq \phi_2)$.

Input waves $(X = (\omega t - kx)$ = constant for given experiment):

$$\Psi_1 = A\cos(\omega t - kx + \phi_1) = A\cos(X + \phi_1)$$
$$\Psi_2 = A\cos(\omega t - kx + \phi_2) = A\cos(X + \phi_2)$$

$$\Psi_1 + \Psi_2 = A\cos(X + \phi_1) + A\cos(X + \phi_2) = A[\cos(X + \phi_1) + \cos(X + \phi_2)]$$

Trick (not universal, possible only on condition that $A_1 = A_2 = A$):

$$\begin{aligned} \cos(a) + \cos(b) &= 2\cos((a+b)/2)\cos(a-b)/2) \\ \cos(X + \phi_1) + \cos(X + \phi_2) &= 2 \times \cos\left(X + \frac{\phi_1 + \phi_2}{2}\right) \times \cos\left(\frac{\phi_1 - \phi_2}{2}\right) \end{aligned}$$

Result (amplitudes separated, phases just partially):

$$\begin{aligned} \Psi_1 + \Psi_2 &= \left[2A\cos\left(\frac{\phi_1 - \phi_2}{2}\right)\right] \times \left[\cos\left(X + \frac{\phi_1 - \phi_2}{2}\right)\right] \\ \sum_{j=1}^{N} \Psi_j &= ??? \qquad \texttt{...generalization is impossible} \end{aligned}$$

Red rectangle: amplitude of resulting wave.

Example 2/3: Interference of [exp-waves] mathematically.

Two exponential waves (Ψ_1, Ψ_2)
with the same amlitudes $(A = A_1 = A_2)$ and different phases $(\phi_1 \neq \phi_2)$.

Input waves $(X = (\omega t - kx) =$ constant for given experiment):

$$\Psi_1 = A\exp(i(\omega t - kx + \phi_1)) = A\exp(i(X + \phi_1))$$
$$\Psi_2 = A\exp(i(\omega t - kx + \phi_2)) = A\exp(i(X + \phi_2))$$

$$\Psi_1 + \Psi_2 = A\exp(i(X + \phi_1)) + A\exp(i(X + \phi_2))$$

No tricks (standard treatment, universal, not only for $A_1 = A_2 = A$):

$$\begin{aligned} \exp(a+b) &= \exp(a) \times \exp(b) \\ A\exp(i(X+\phi_1)) + A\exp(i(X+\phi_2)) &= (A\exp(i\phi_1) + A\exp(i\phi_2)) \times \exp(iX) \end{aligned}$$

Result (amplitudes-and-phases completely separated):

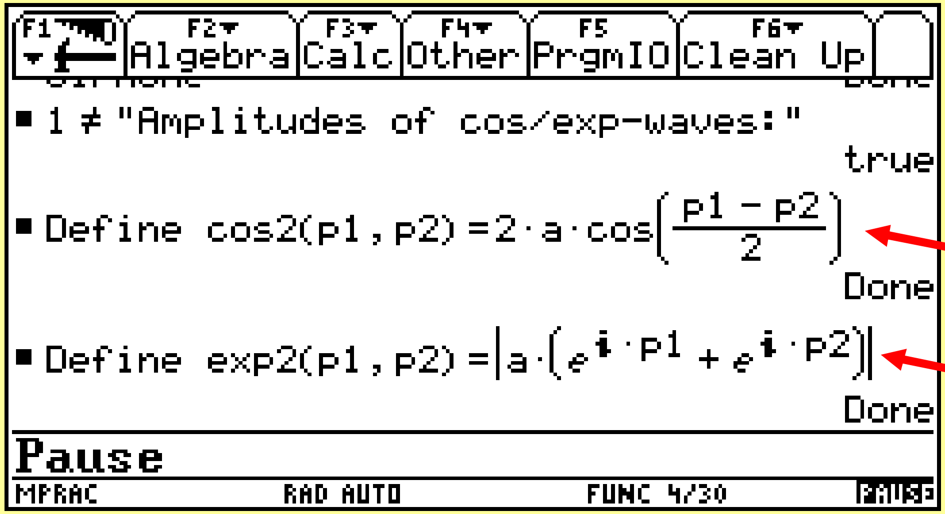
$$\begin{aligned} \Psi_1 + \Psi_2 &= \boxed{[A\exp(i\phi_1) + A\exp(i\phi_2)]} \times [\exp(iX)] \\ \sum_{j=1}^{N} \Psi_j &= \boxed{[A_j\exp(i\phi_j)]} \times [\exp(iX)] \end{aligned}$$

`...generalization is simple`

Red rectangle: (complex) amplitude of resulting wave.

Conclusion: as for calculations, exp-waves are better than cos-waves.

Example 2/4: Equivalence of [cos-waves] and [exp-waves] numerically.



■ 1 ≠ "Amplitudes of cos/exp-waves:" — true

■ Define $\mathrm{cos2}(p1,p2)=2\cdot a\cdot \cos\left(\frac{p1-p2}{2}\right)$ — Done

■ Define $\mathrm{exp2}(p1,p2)=\left|a\cdot\left(e^{i\cdot p1}+e^{i\cdot p2}\right)\right|$ — Done

Pause

Screens of calculator Ti92+ or TiV200 (http://education.ti.com

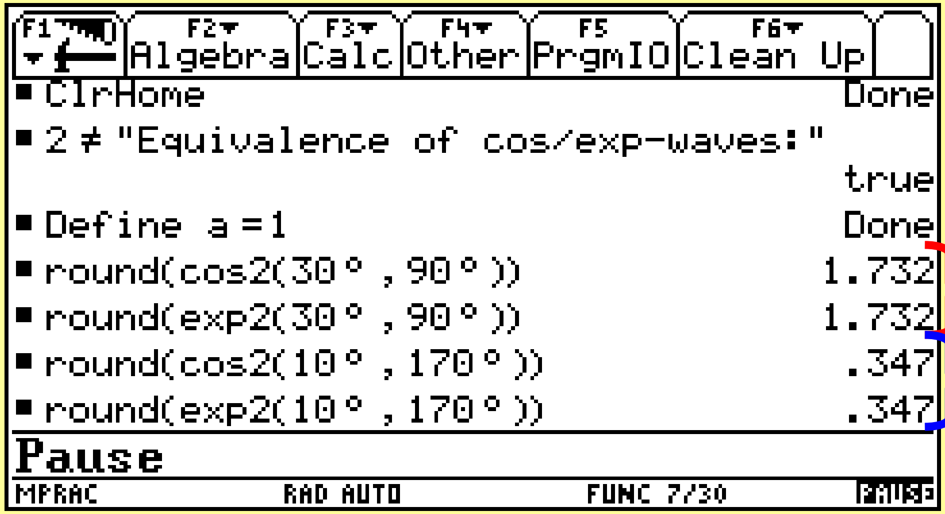
Definition of final amplitude of:

a) two cosine waves

..Example 2/2, amplitude of $\Psi_1+\Psi_2$

b) two exponential waves

.. Example 2/3, |amplitude| of $\Psi_1+\Psi_2$



```
■ ClrHome                                   Done
■ 2 ≠ "Equivalence of cos/exp-waves:"
                                            true
■ Define a=1                                Done
■ round(cos2(30°,90°))                     1.732
■ round(exp2(30°,90°))                     1.732
■ round(cos2(10°,170°))                     .347
■ round(exp2(10°,170°))                     .347
Pause
```

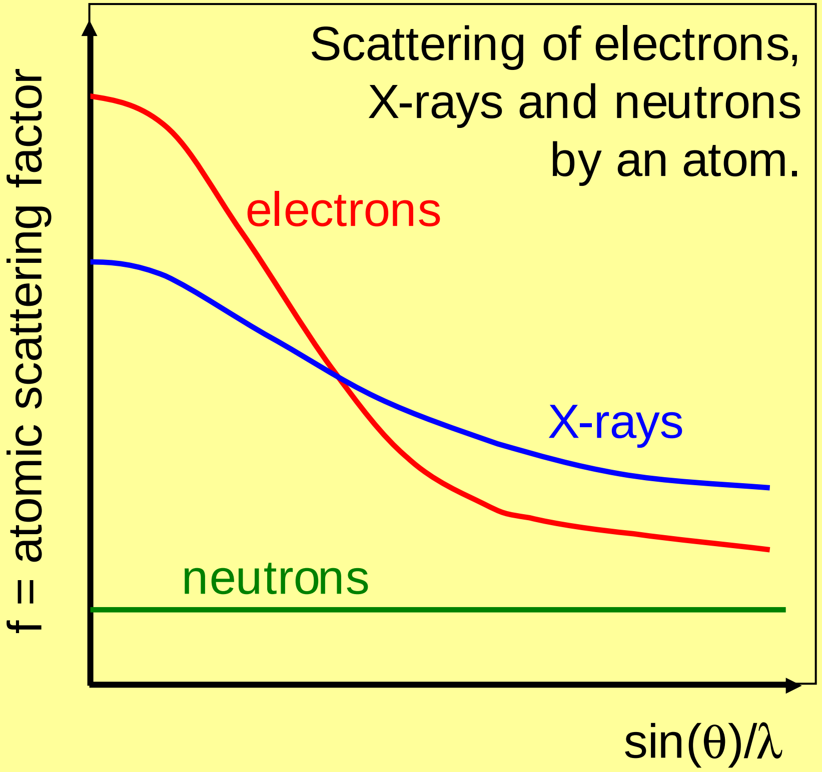
Final amplitude of two waves does not depend on the description. Both [cos-waves] and [exp-waves] yield the same value of final amplitude.

..$\Psi_1+\Psi_2$ from Example 2/1, Case 3.

.. $\Psi_1+\Psi_2$ from Example 2/1, Case 4.

Note: In case of exp-waves, the amplitude is a complex number.
Therefore, we calculate absolute value of amplitude = |amplitude| = real number.

Example 3: Scattering by one center - atom in XRD, ND and ED.



The graph illustrates that scattering by one center/atom can be exactly calculated/measured and tabulated.

(source data → C. Giacovazzo et al:
(Fundamentals of crystallography, p.196-7

The graph shows that for intensity of scattering (given by **f**) it holds:
f(electrons) > f(X-rays) > f(neutrons)

⇒ size of a typical sample:
ED < XRD < ND

Moreover, for atomic scattering factors as a function of atomic number **f(Z)** it holds:

f(electrons) ≈ $Z^{1/3}$
f(X-rays) ≈ Z
f(neutrons) ...no trend

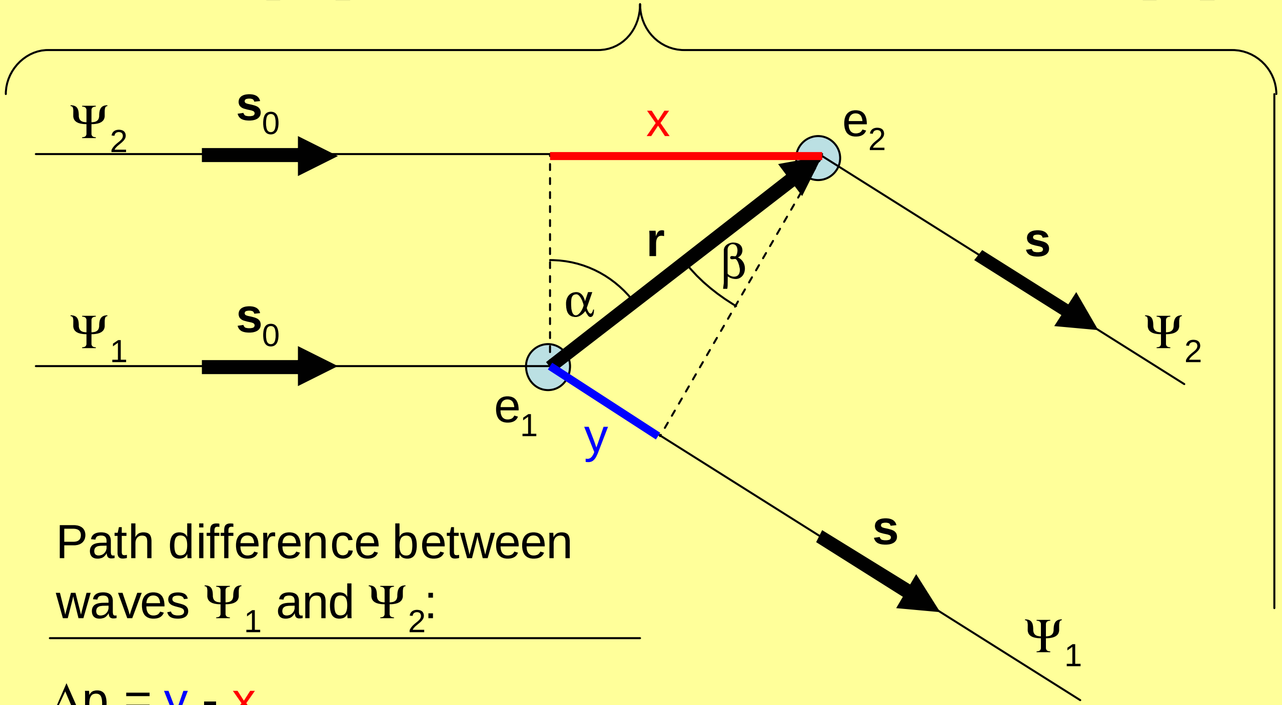
⇒ localization of light elements:
ED > XRD

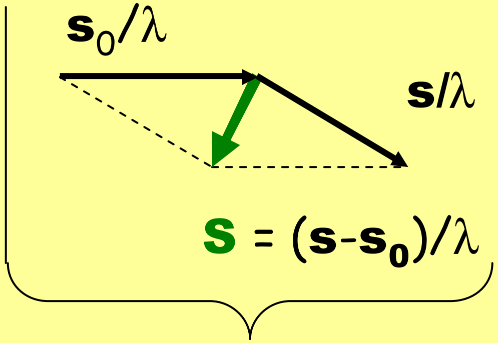
Atomic scattering factor is a measure, how much a single atom scatters given radiation.

sin(θ)/λ ≈ magnitude of scattering vector **S** ≈ magnitude scattering vector **q** ≈ scattering/diffraction angle θ (θ = 0-90°).

Example 4/1: Scattering by two centers - path difference.

2 waves (Ψ_1,Ψ_2), which are scattered by 2 centers (e_1,e_2):





Definition of scattering vector **S**.
(λ = wavelength
(**s**,$\mathbf{s_0}$ = unit vectors

Path difference between waves Ψ_1 and Ψ_2:

$\Delta p = y - x$

$\Delta p = |\mathbf{r}| * \cos(\beta) - |\mathbf{r}| * \cos(\alpha)$

$\Delta p = |\mathbf{r}| * |\mathbf{s}| * \cos(\beta) - |\mathbf{r}| * |\mathbf{s}_0| \cos(\alpha)$.... trick1: **s**, $\mathbf{s_0}$ = scattering vectors of unit length!

$\Delta p = \mathbf{r} * \mathbf{s} - \mathbf{r} * \mathbf{s_0}$ .... trick2: vector multiplication - $|\mathbf{a}||\mathbf{b}|\cos(\gamma) = \mathbf{a} * \mathbf{b}$

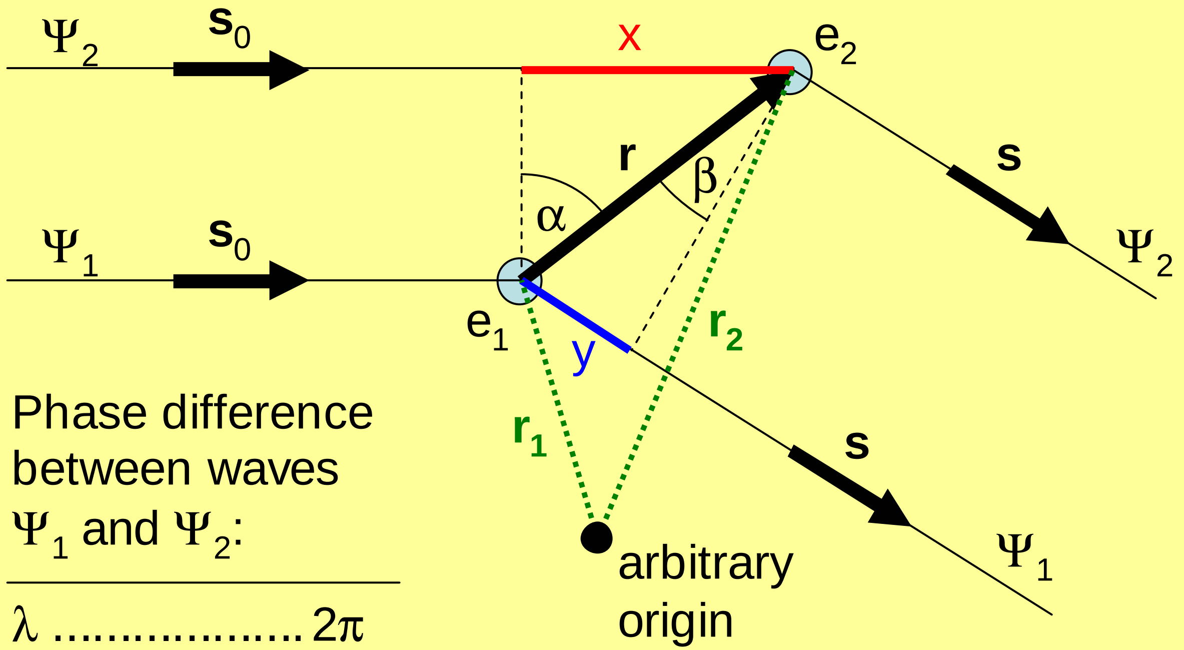
$\Delta p = \mathbf{r}(\mathbf{s} - \mathbf{s_0})$

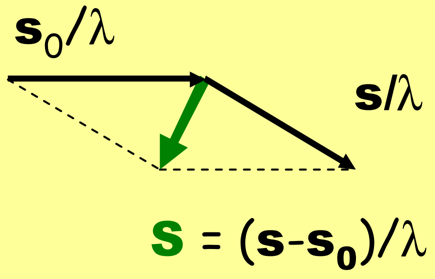
Final result:

The difference between paths of waves Ψ_1 and Ψ_2.
(The additional distance that Ψ_1 has to travel in comparison with Ψ_2)

Example 4/2: Scattering by two centers - path difference.

2 waves (Ψ_1,Ψ_2), which are scattered by 2 centers (e_1,e_2):





Definition of scattering vector **S**.
(λ = wavelength
(**s**,$\mathbf{s_0}$ = unit vectors
($\mathbf{S} = (\mathbf{s}-\mathbf{s_0})/\lambda$
($\mathbf{q} = 2\pi\mathbf{S}$

Phase difference between waves Ψ_1 and Ψ_2:

λ 2π
Δp .... $\Delta\Phi$

$$\Delta\Phi = 2\pi/\lambda * \Delta p = 2\pi/\lambda * \mathbf{r}(\mathbf{s}-\mathbf{s_0}) = 2\pi\mathbf{r} * (\mathbf{s}-\mathbf{s_0})/\lambda = 2\pi\mathbf{r} * \mathbf{S} = \mathbf{q}*\mathbf{r}$$

$\Delta\Phi = \mathbf{qr}$ ..phase of the second wave Ψ_2 with respect to the first wave Ψ_1

Generalization = final result:

$\Phi_1 = \mathbf{qr_1}$ ..phase of the fist wave Ψ_1 with respect to [arbitrary origin]
$\Phi_2 = \mathbf{qr_2}$ ..phase of the fist wave Ψ_2 with respect to [arbitrary origin]

Example 4/3: Scattering by two centers - amplitude of final wave $\Psi = \Psi_1 + \Psi_2$.

Summation of two exponential waves (the same amplitudes):

$$\Psi_3 = \Psi_1 + \Psi_2 = [A\exp(i\phi_1) + A\exp(i\phi_2)] \times \exp(iX)$$

Summation of two exponential waves (different amplitudes):

$$\Psi_3 = \Psi_1 + \Psi_2 = [A_1\exp(i\phi_1) + A_2\exp(i\phi_2)] \times \exp(iX)$$

Derivation from Example 2/3.

Re-writing for two scattered waves ($\Phi_i = \mathbf{q}\mathbf{r}_i$):

$$\Psi_3 = \Psi_1 + \Psi_2 = [A_1\exp(i\mathbf{q}\mathbf{r}_1) + A_2\exp(i\mathbf{q}\mathbf{r}_2)] \times \exp(iX)$$

Combination of Example 2/3 + 4/2.

Complex amplitude of two scattered waves:

$$\mathbf{A}_3 = \mathbf{A}_1 + \mathbf{A}_2 = [A_1\exp(i\mathbf{q}\mathbf{r}_1) + A_2\exp(i\mathbf{q}\mathbf{r}_2)]$$

Final formula: amplitude of 2 scattered waves.

Generalization for N waves with different amplitudes:

$$\Psi = \sum_{j=1}^{N} \Psi_j = \left[\sum_{j=1}^{N} A_j \exp(i\mathbf{q}\mathbf{r}_j)\right] \times \exp(iX)$$

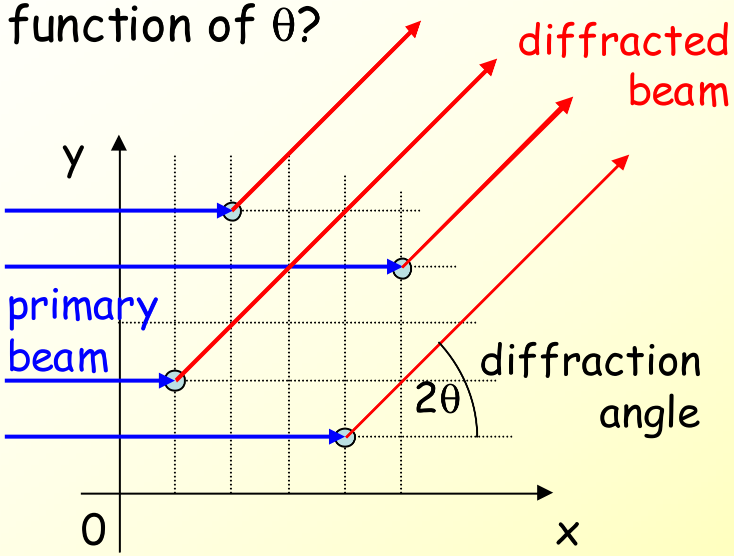
$$\mathbf{A} = \sum_{j=1}^{N} \mathbf{A}_j = \sum_{j=1}^{N} A_j \exp(i\mathbf{q}\mathbf{r}_j)$$

Generalization: amplitude of N scattered waves.

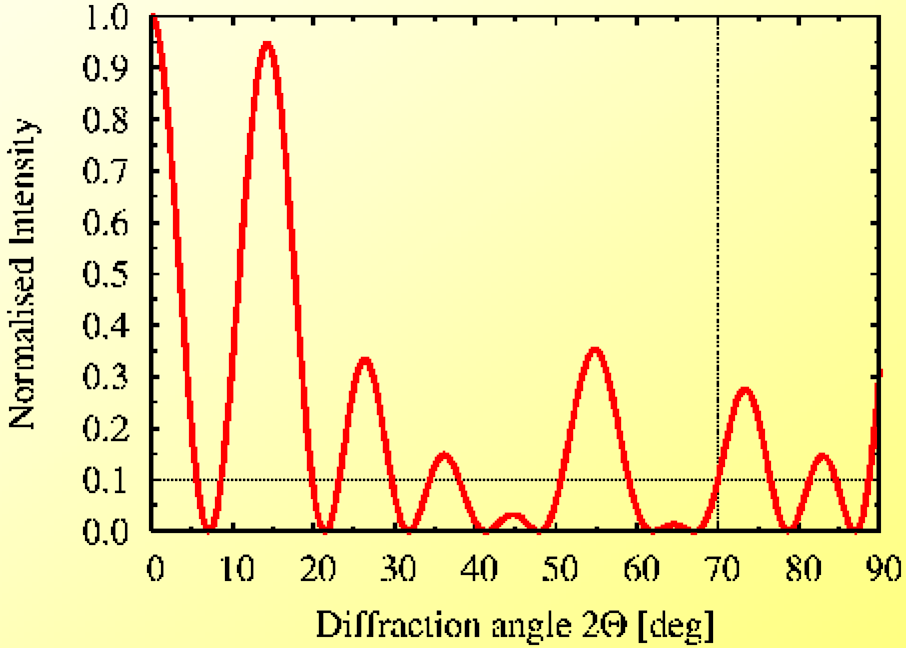
Example5: Key formula of diffraction.

Model

Is the diffracted beam intensity function of θ?



Result



Calculation

We employ the key formula:

$$A(\mathbf{q}) = \int\rho(\mathbf{r})\times\exp[i\mathbf{q}\mathbf{r}]\times d\mathbf{r}$$

..here it changes into summation:

$$A(\mathbf{q}) = \Sigma A_j \exp[i\mathbf{q}\mathbf{r}_j]$$

..and intensity is calculated as:

$$I(\mathbf{q}) \approx |A(\mathbf{q})|^2$$

Conclusions

[1] During the calculation, we used only the formulas derived in this lecture!

[2] The intensity strongly depends on θ: different θ means different vector **q** and different complex amplitudes $A(\mathbf{q})$.

Complete calculation.

Example6: I(**q**) and ρ(**r**).

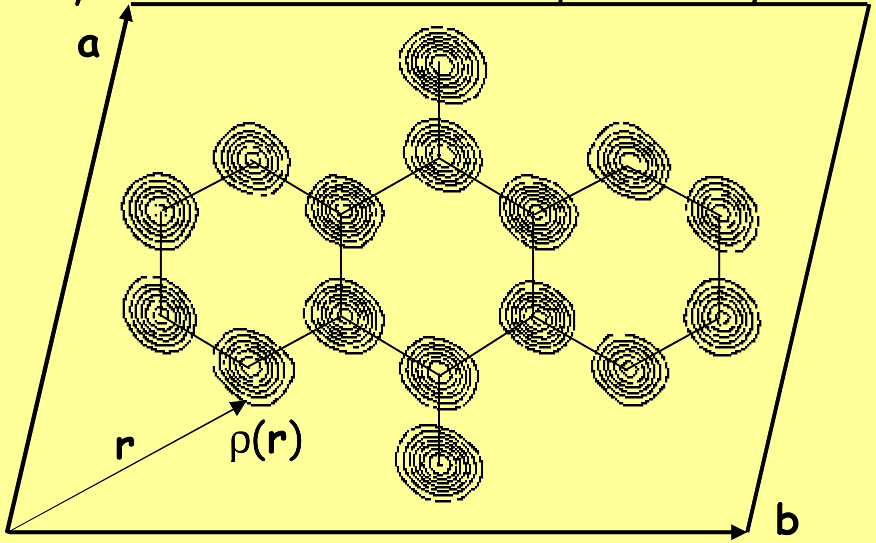
I(**q**) represents diffraction pattern.
I(**q**) is 1D, 2D or 3D function of diffraction vector **q**.

ρ(**r**) represents structure.
ρ(**r**) is 1D, 2D or 3D function of position vector **r**.

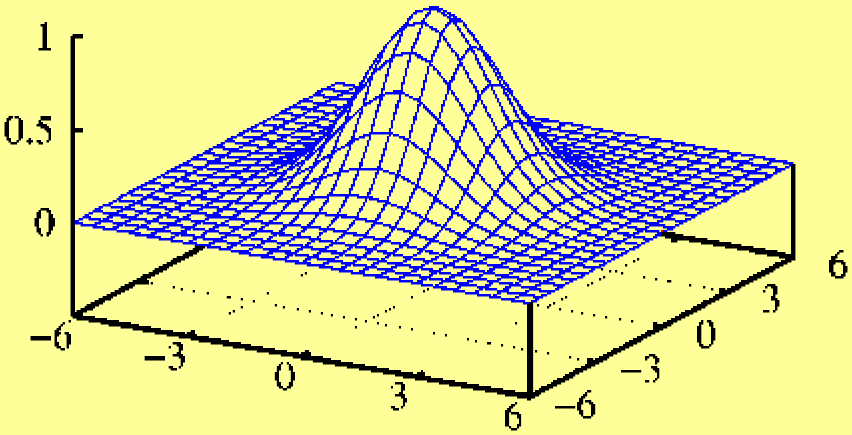
The scattering length density ρ(**r**) gives density of the scatterers.

XRD	ρ(**r**) = electron density	maxima around atoms
ND	ρ(**r**) = nuclear density	maxima at atom nuclei
ED	ρ(**r**) = electric potential density	maxima around atoms
LS	ρ(**r**) = refraction index density	maxima at objects with high n

XRD,WAXS: 2D section of the electron density in a unit cell of anthraquinone crystal

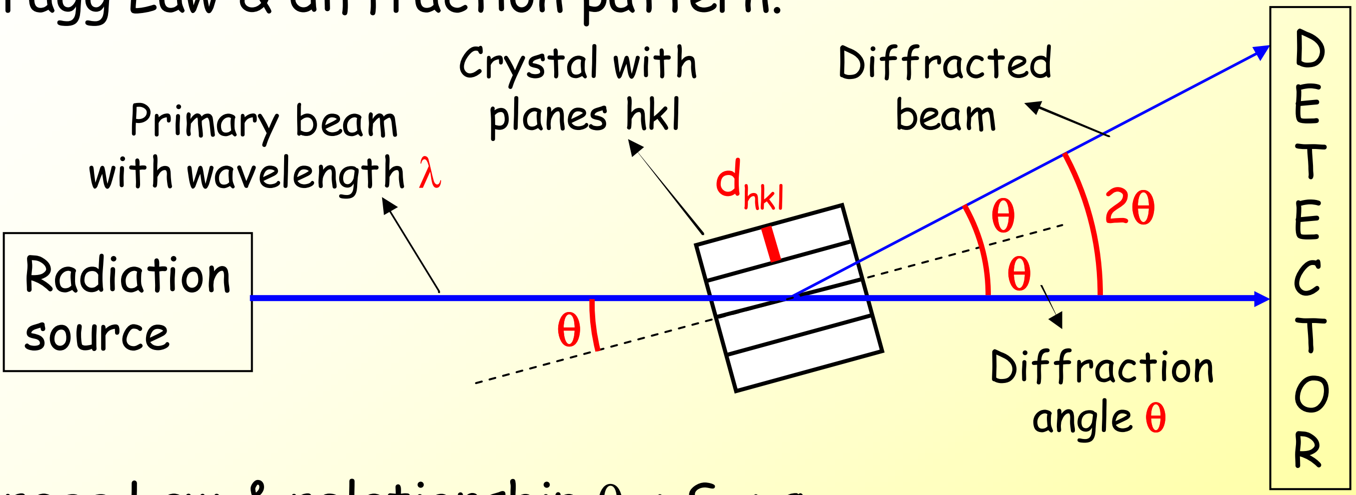


ND, SANS: ρ(**r**) = nuclear density ρ(**r**) in a polymer micelle in solution (origin in the centre of the micelle)



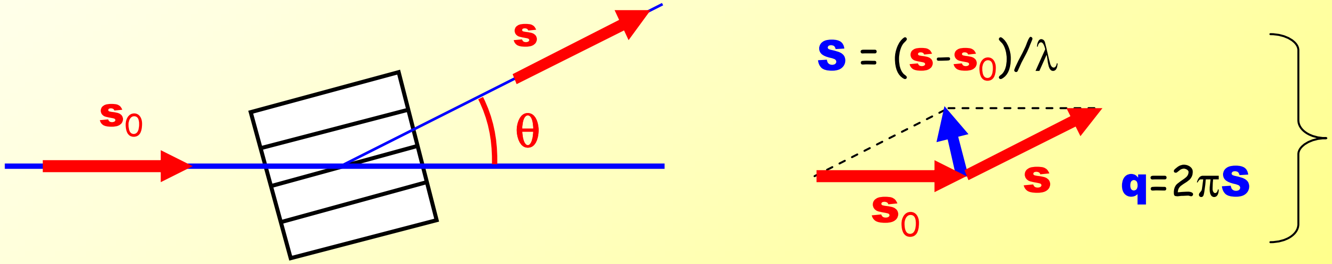
Example7: Bragg Law & diffraction pattern.

Bragg Law & diffraction pattern.



Each plane ≡ one diffraction ring or spot. **Bragg Law** gives the **position** of diffraction ring/spot. It does not say anything about the intensity of the diffraction!

Bragg Law & relationship θ × S × q



Magnitudes of diffraction vectors **S** and **q** increase with increasing diffraction angle θ.

Alternative forms of Bragg Law.

$2d_{hkl}\sin\theta_{hkl} = n\lambda$ ← basic form

$2d\sin\theta = n\lambda$ ← without Miller indexes

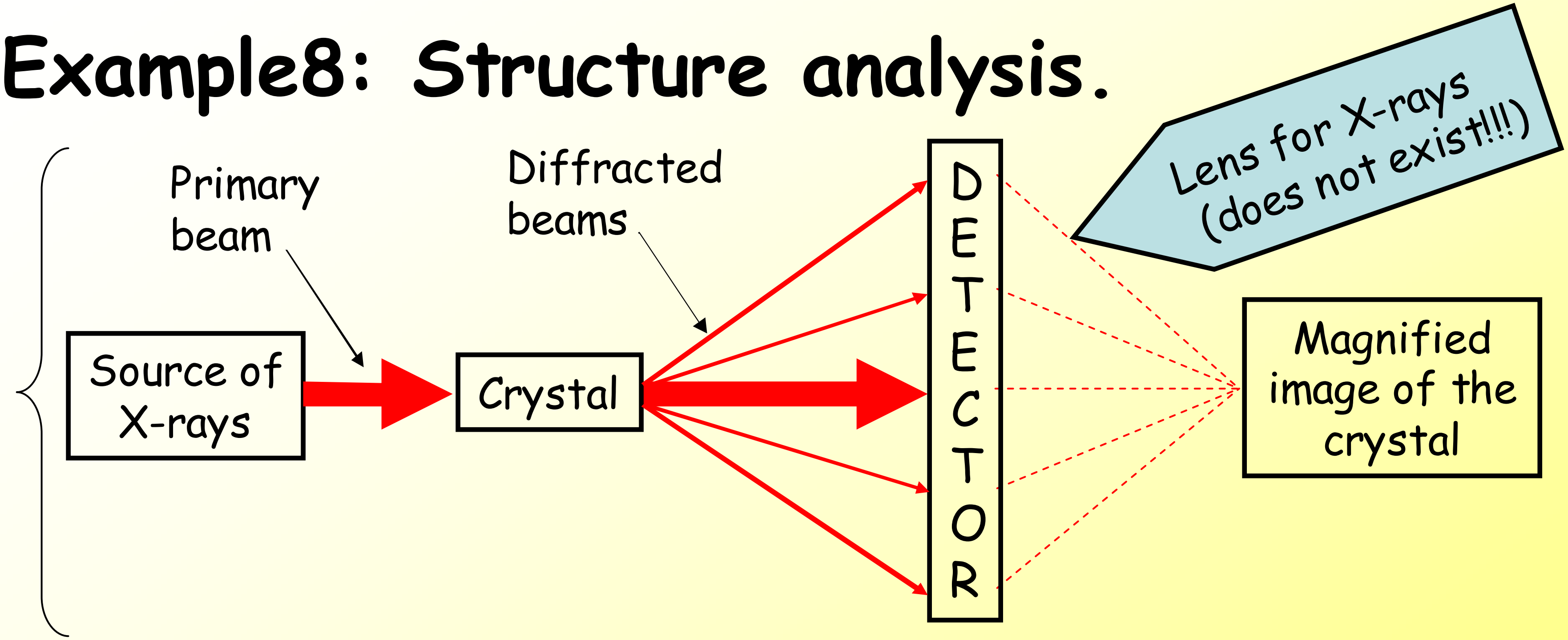
$2d\sin\theta = \lambda$ ← without n: because, for example $2d_{100}\sin\theta_{100}=2\lambda \equiv 2d_{200}\sin\theta_{200}=1\lambda$

$dq = 2\pi n$ ← with q: because $q = 4\pi\sin\theta/\lambda$

$dS = n$ ← with S: because $S = 2\sin\theta/\lambda$

Example8: Structure analysis.

Diffraction experiment


Primary beam

Diffracted beams

Source of X-rays

Crystal

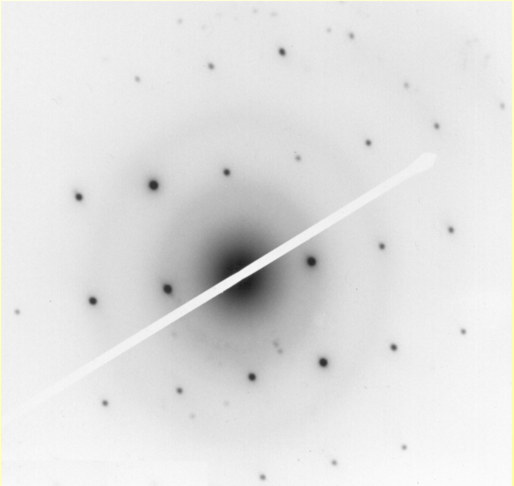
DETECTOR

Lens for X-rays (does not exist!!!)

Magnified image of the crystal

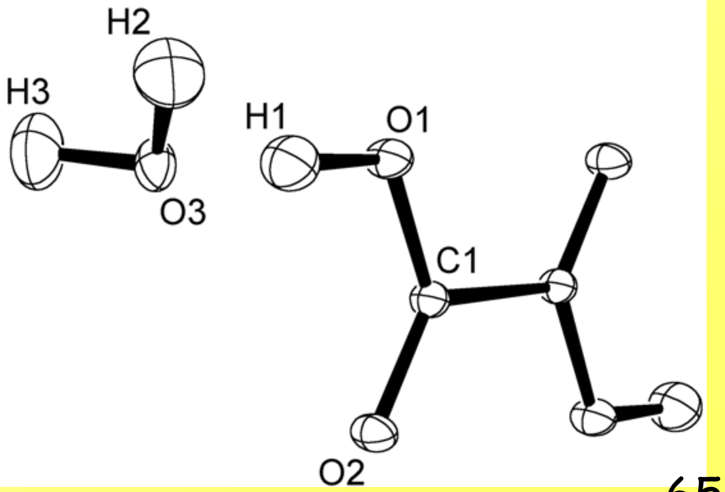
Structure analysis

Image on the detector
≡ diffraction pattern

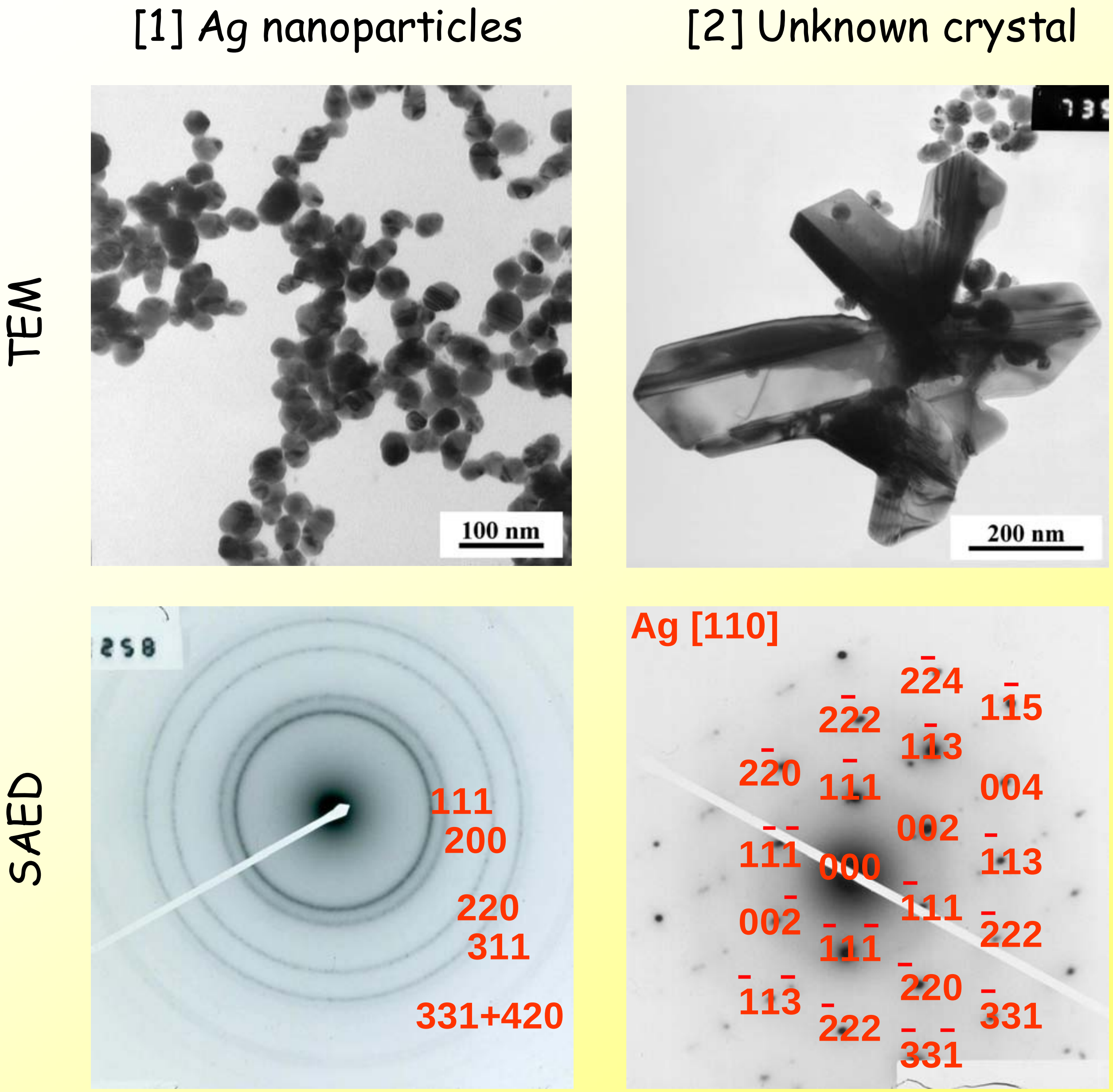


Mathematical calculations.
(instead of lens)

Calculated image of the crystal
≡ CRYSTAL STRUCTURE



Example9: Indexing.



Notes:

Each crystalline substance has a unique unit cell.

Indexing can be employed in two ways:

[1] Identification of a known compound. (Easy: we know a,b,c,α,β,γ and search just h,k,l)

[2] Finding a unit cell of an unknown compound. (Difficult: we search simultaneously a,b,c,α,β,γ and h,k,l).

UNESCO/IUPAC Postgraduate Course in Polymer Science

Thank you for your attention.

- Institute of Macromolecular Chemistry ASCR, Heyrovsky sq. 2, Prague -162 06
- http://www.imc.cas.cz/unesco/index.html
- unesco.course@imc.cas.cz