Polymer systems and phase identification
S4SAS 2014

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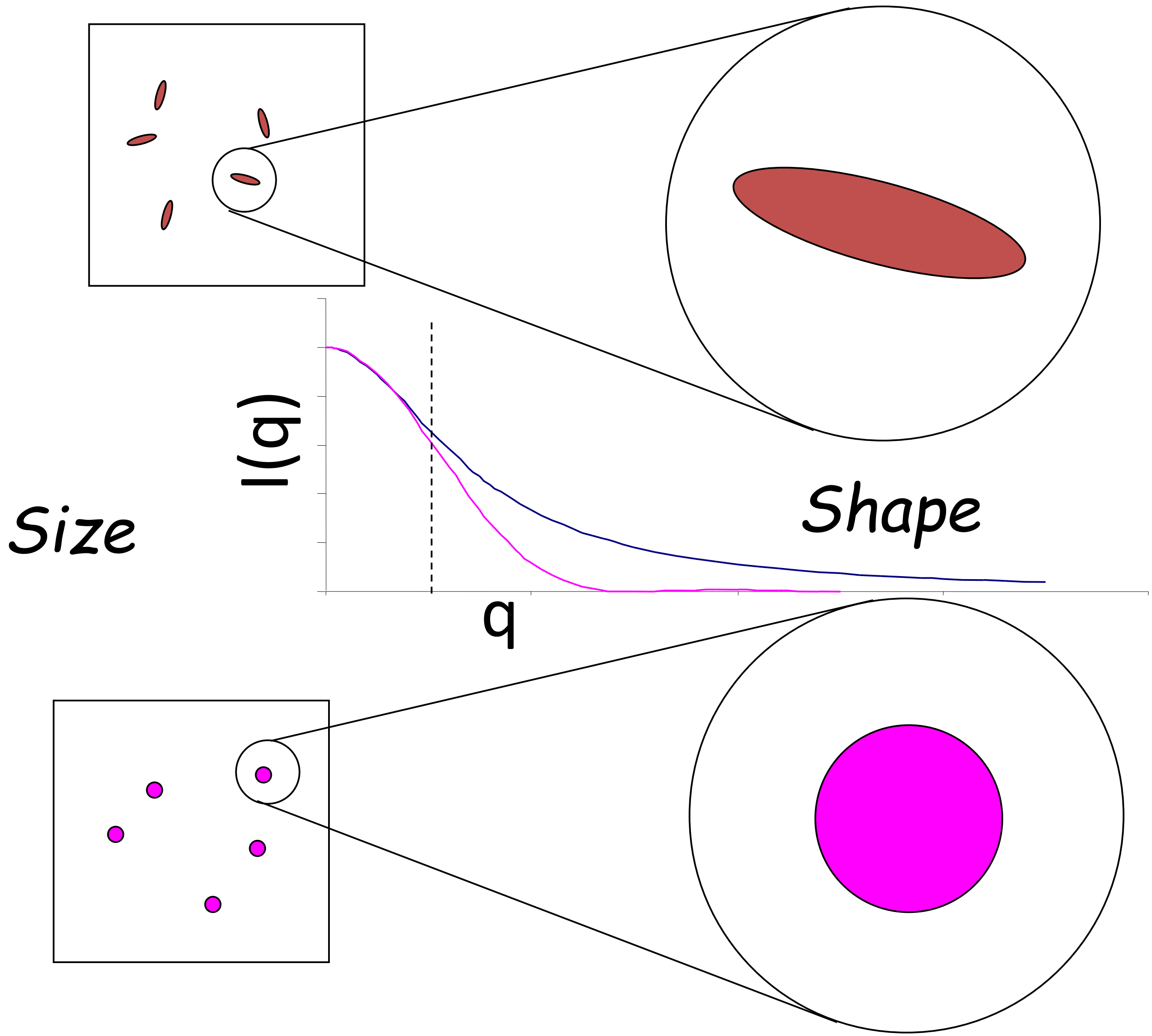
Outline

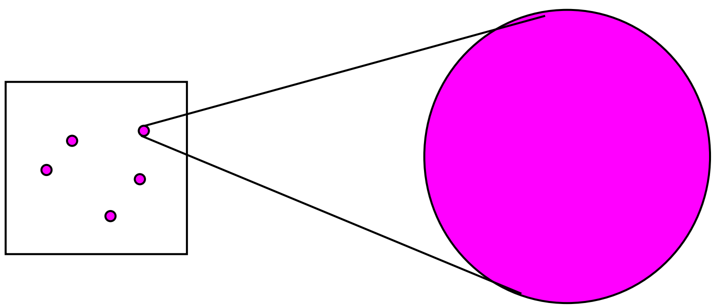
- Solutions, non-crystalline materials
  - Polymer chains, proteins
- Periodic systems
  - Block copolymers
  - Lyotropic liquid systems (surfactants; lipids)
  - Mesoporous materials
- Orientation: powder-like or aligned

Reminder:



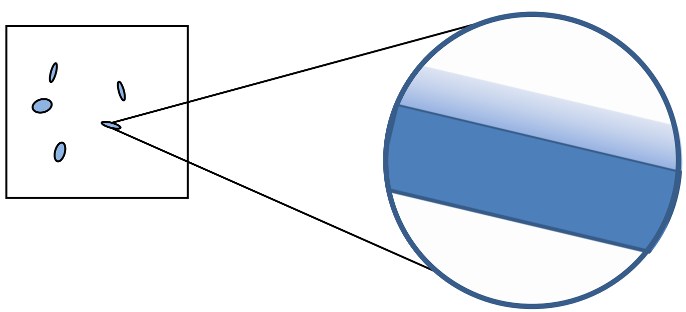
From James' talk:
"Dimensionality" of different shapes

At Rg > q Scattering tends to $I \sim q^{-a}$



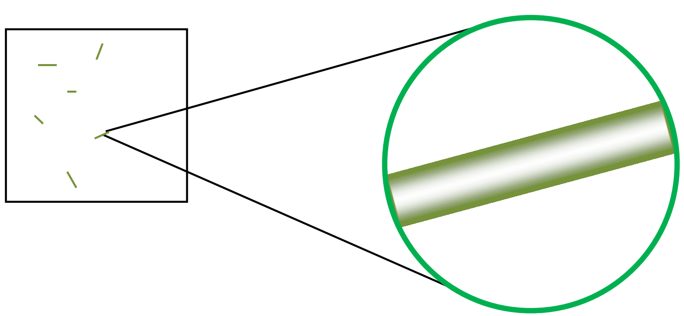
- Spheres (3D): a = 4

  1/q < Rg



- Disks (2D): a = 2

  Thickness < 1/q < Radius

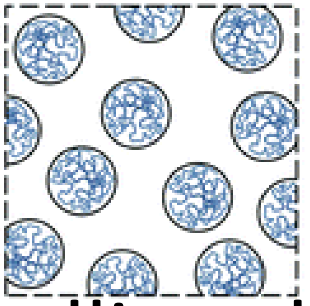


- Rods (1D): a = 1

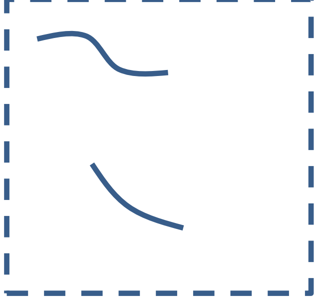
  Radius < 1/q < Length

Dimensionality of a polymer chain in solution

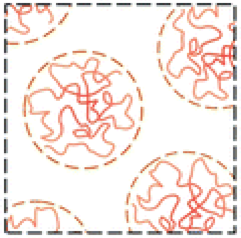
- A (strongly) self-attracting chain would pack itself into a ball; this would make a sphere (3D; a = 4)



- A (strongly) self-repelling chain would stretch out into a completely extended rod (1D; a = 1)

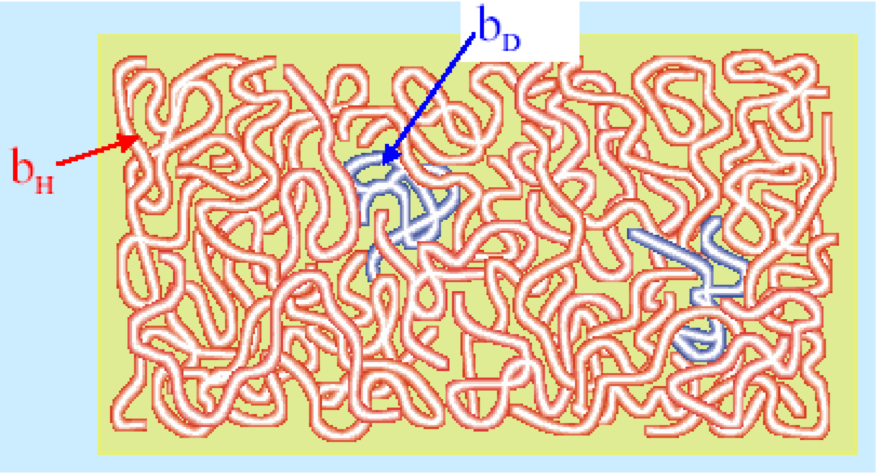


Neither attracting nor repelling?

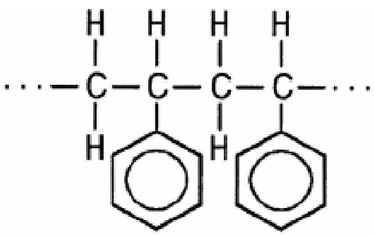


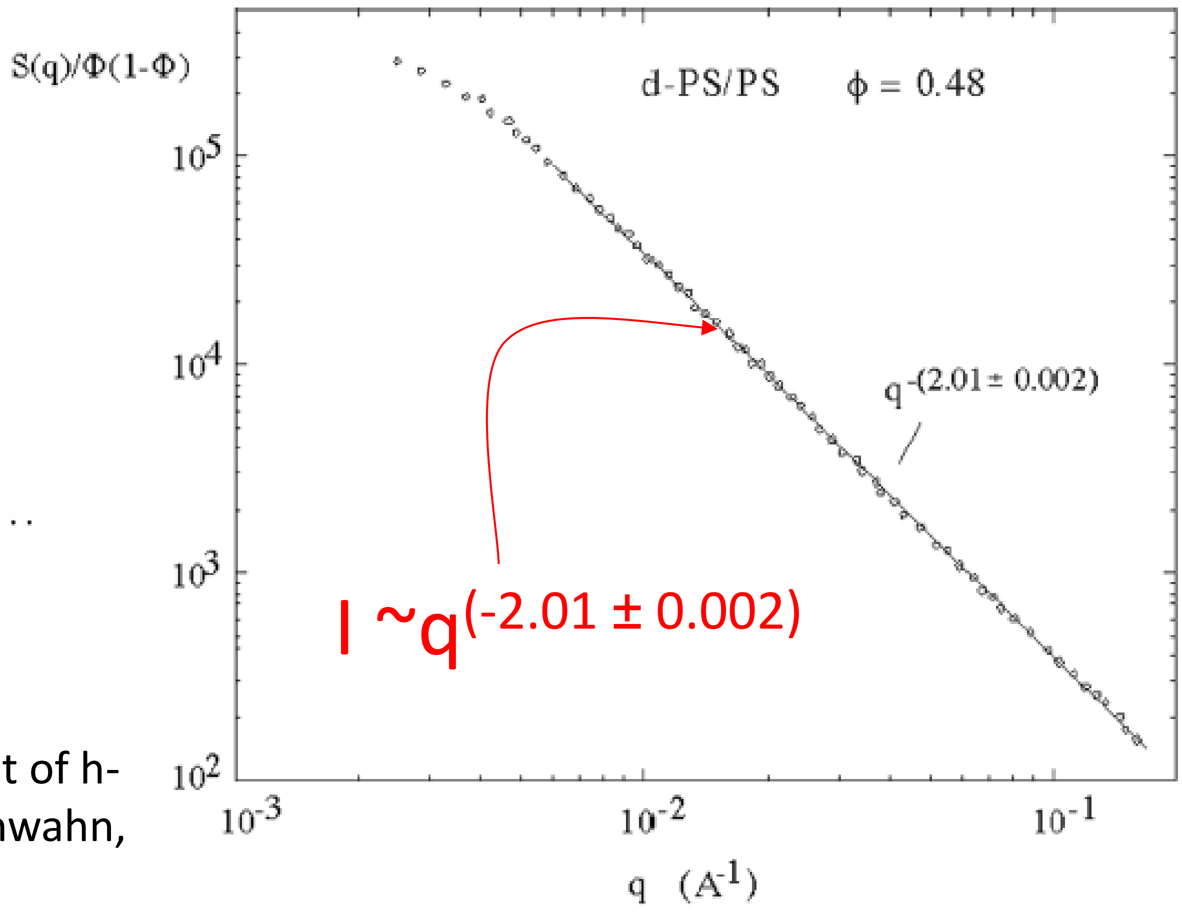
- Polymer in a "theta" solvent
  - Interactions with solvent same as interactions with self
- Polymer in the melt

(use neutrons)



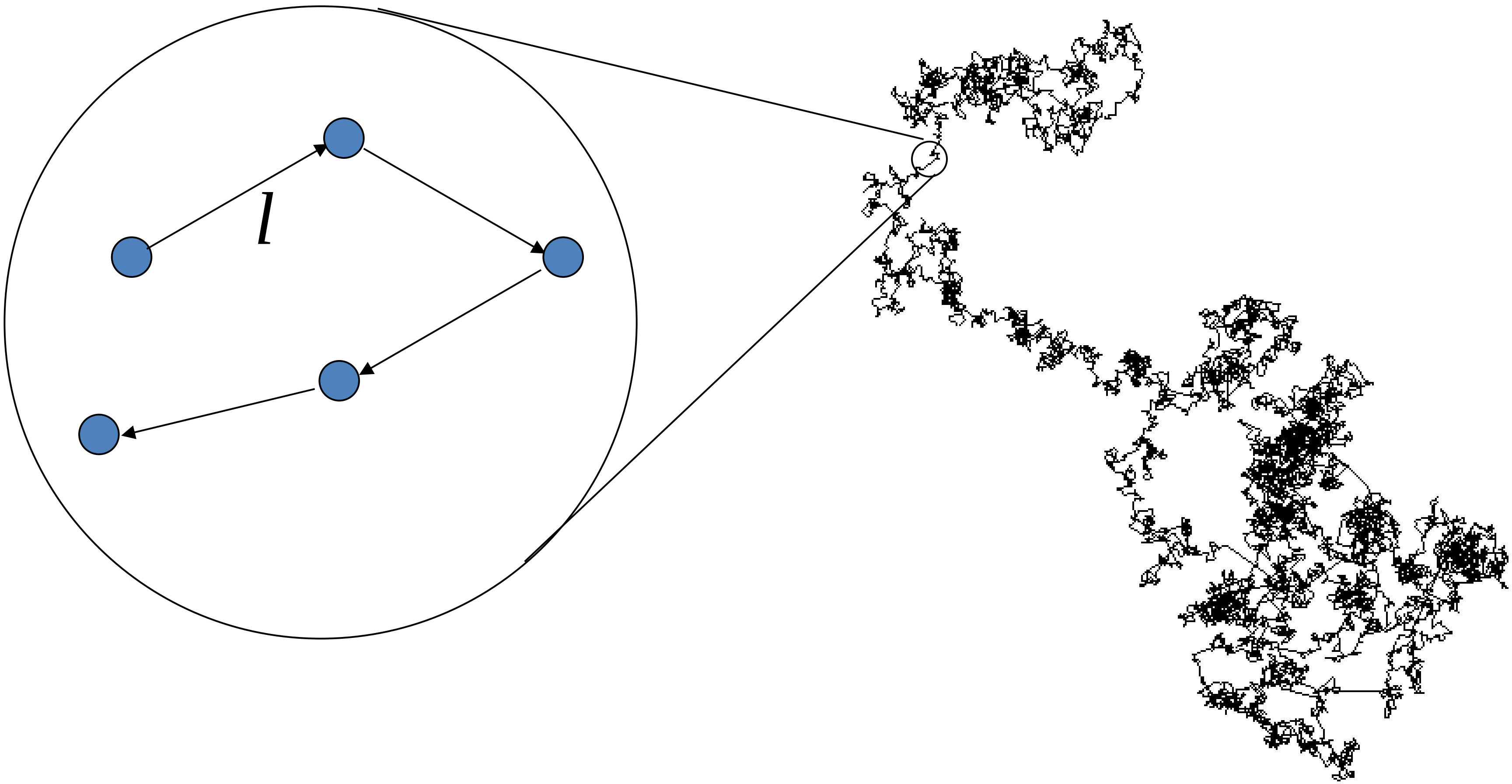
Polymer chains that neither attract nor repel themselves show a = 2. This corresponds to a "random walk" ("Gaussian chain").





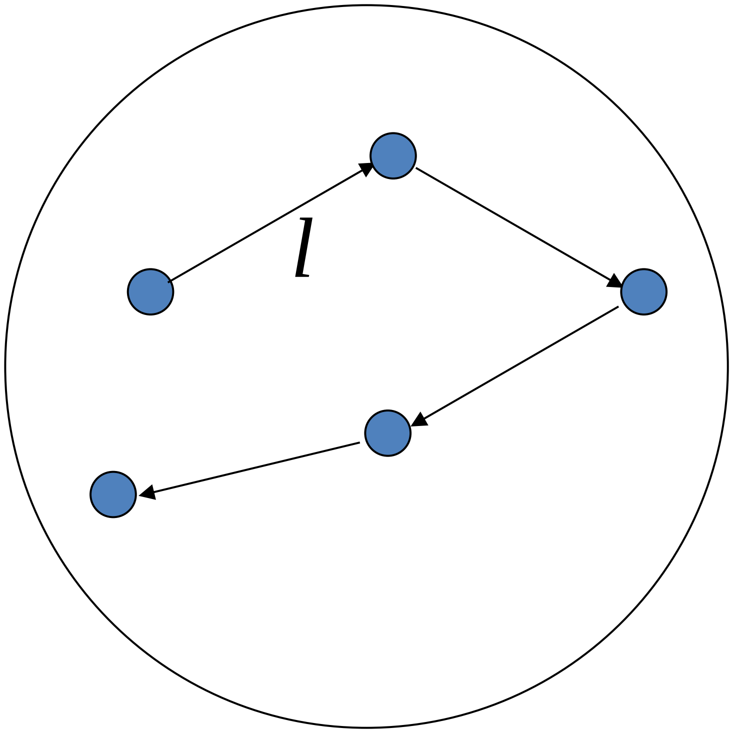
scattered intensity for a melt of h- and d-polystyrene (from Schwahn, 1991 using SANS)

Random walks



Properties of a random walk

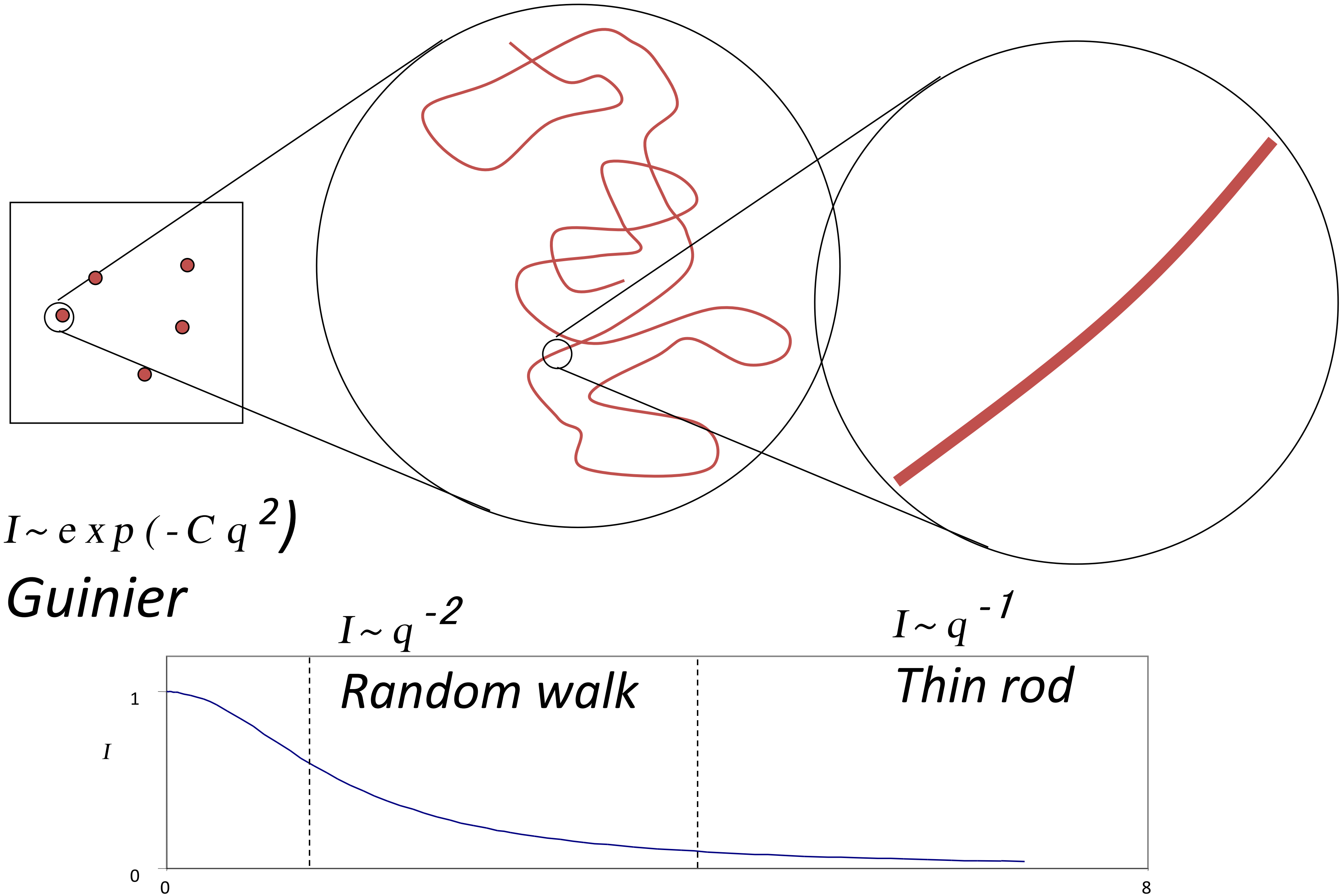
- N "steps" each of length l
- Expected end-to-end distance is $l\sqrt{N}$
- Expected Rg = $l\sqrt{(N/6)}$



Deviations from Random Walk

- (Imagine a length of rubber tubing)
- On a long enough size scale, it can behave randomly
- On a shorter size scale, because the tubing isn’t infinitely flexible, bits of tubing close to each other aren’t independent
- On a size scale less than the “persistence length” the tubing looks like a straight rod.

So, overall ….

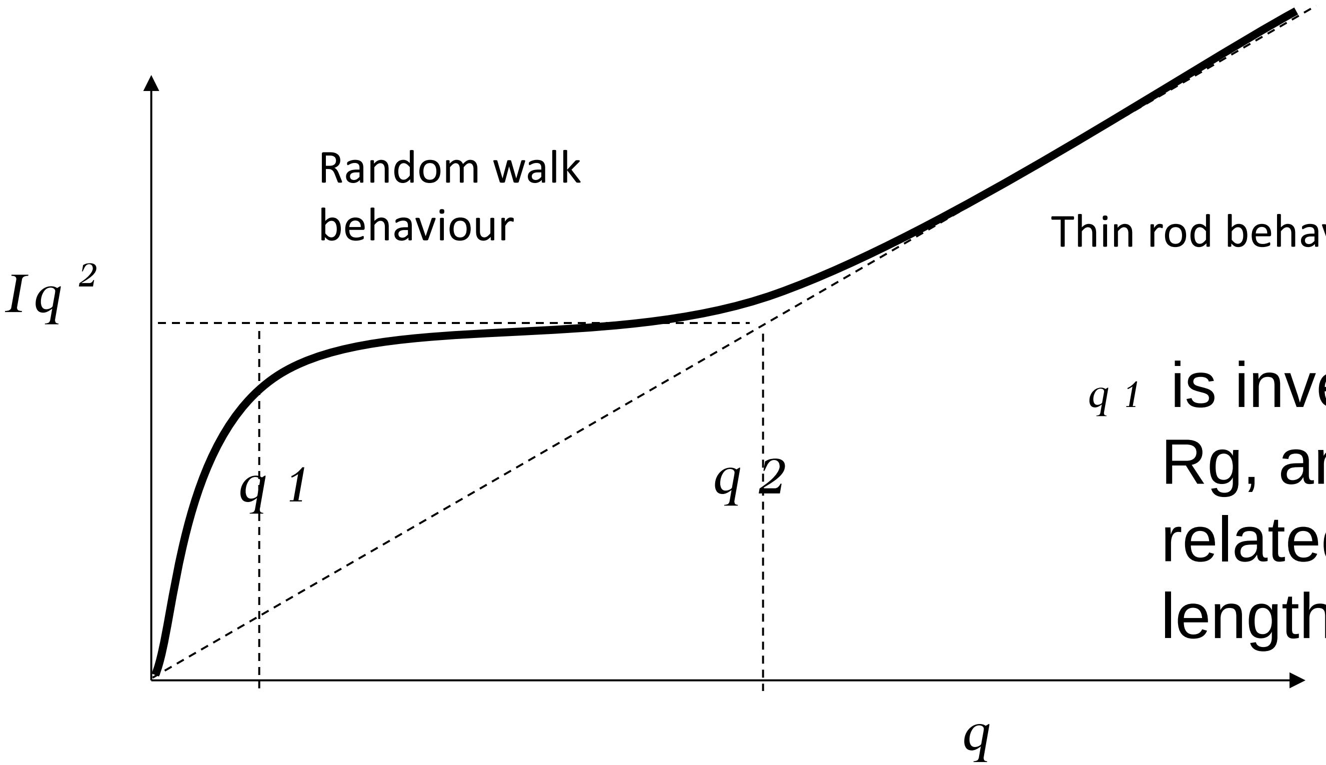


“Worm-like chain” (Kratky and Porod)

Kratky plot (see Rob and James’ talks)

If $I \sim q^{-2}$

$I\,q^2$ is a constant

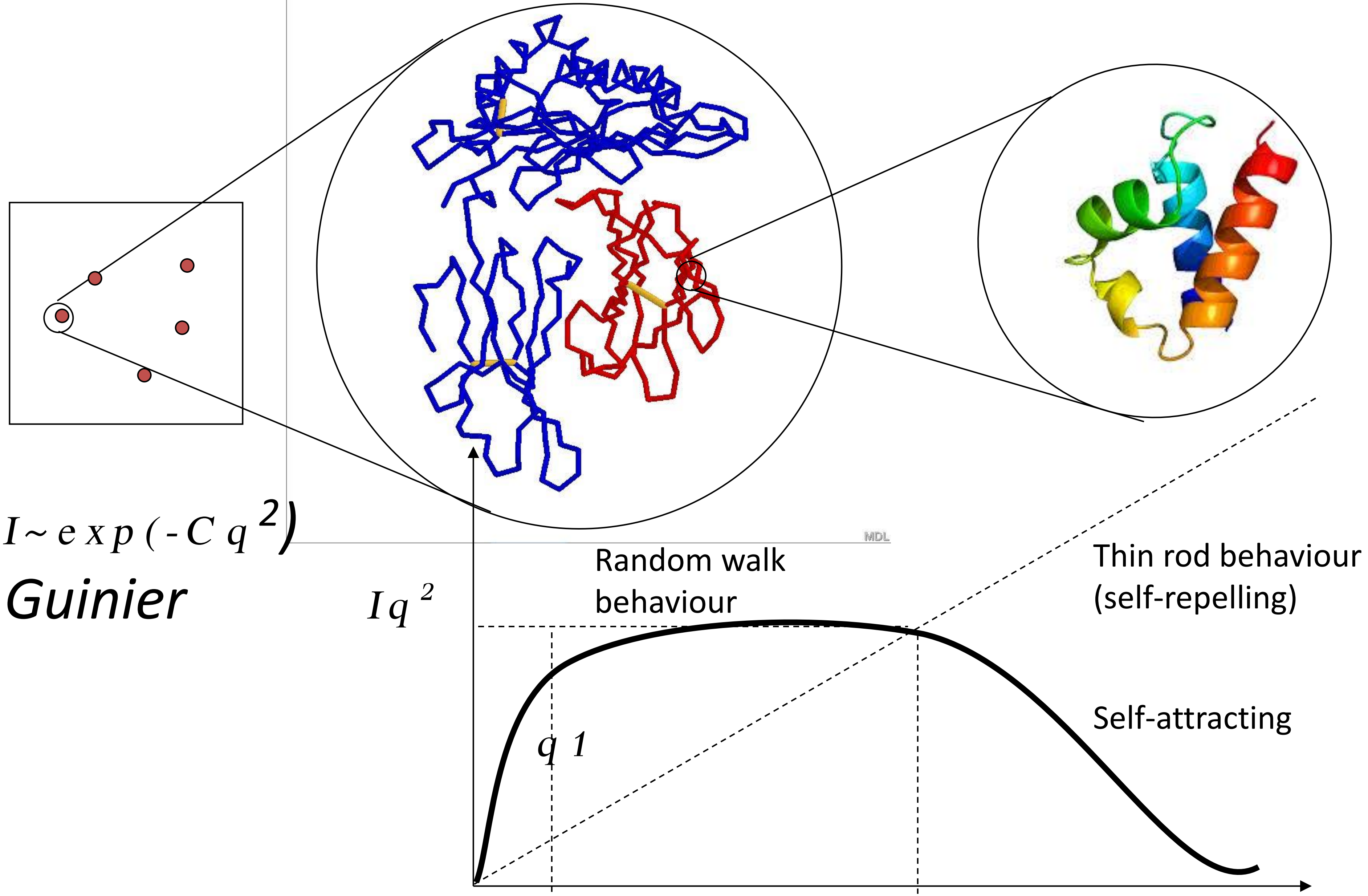


q_1 is inversely related to Rg, and q_2 is inversely related to persistence length

More deviations from Random Walk

- At higher q (short length scale), the Kratky-Porod Worm-like chain acted more like a rigid rod (ie, self-repelling)
- Conversely, folded proteins with internal structure are self-attracting at a short length scale: see Rob’s talk

Self-attracting short-range (eg proteins)

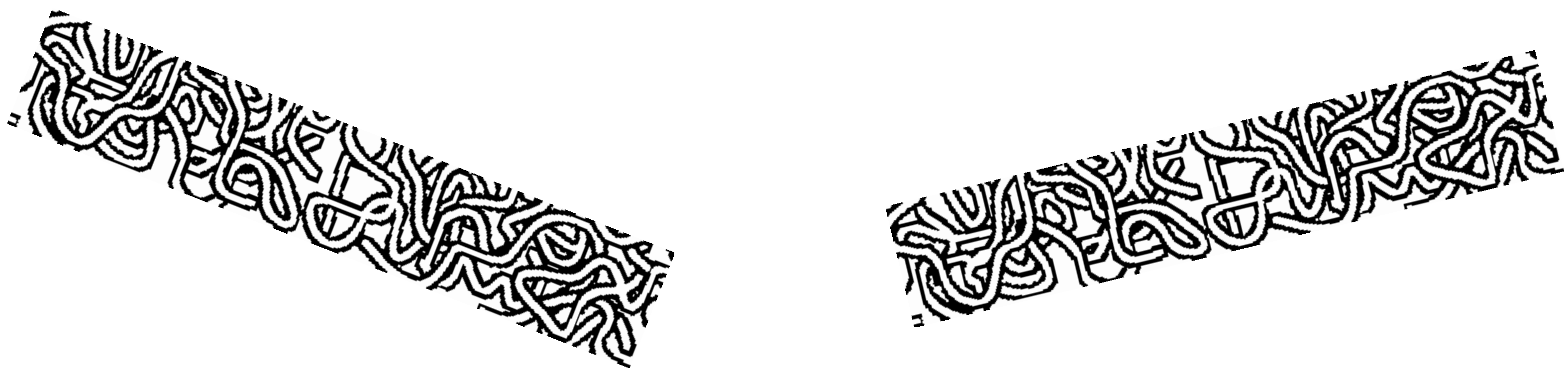


Summary so far

- With solution scattering, you can measure
  - Size (R_g) from Guinier plot in very small angle region. Plot $\ln I$ vs q^2
  - Shape (dimensionality) from plot of $\ln I$ vs $\ln q$
  - Persistence length; flexibility of polymer chain (and extent of "random walk" behaviour) from Kratky plot. Plot Iq^2 against q

Task (1)

- Boffins at the Institute of Studies have, for the first time, used science to produce “Polymer nano-Wotsits”



- In a theta solvent, the polymer adopts a random walk within a cylindrical envelope (as shown).

Discuss what you would expect to see in the scattering pattern.

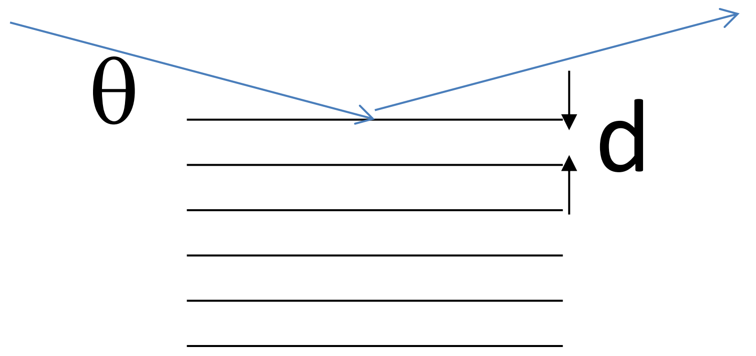
Periodic systems

- Regular repeating features on the 10-100nm size scale are less common, requiring self-assembly:
  - Lipids / detergents (tens of nm)
  - Diblock copolymers (hundreds of nm)
  - *Biological materials (eg keratin, collagen etc) (hierarchical)*
  - Mesoporous materials (silica, metal…)

1D periodicity

- Bragg's law:

  $n\lambda = 2d \sin\theta$



- Simplification:

X-ray reflections from periodicity *across the beam.*

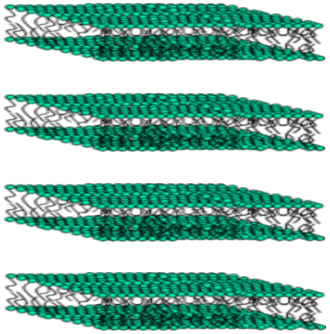
[small-angle]

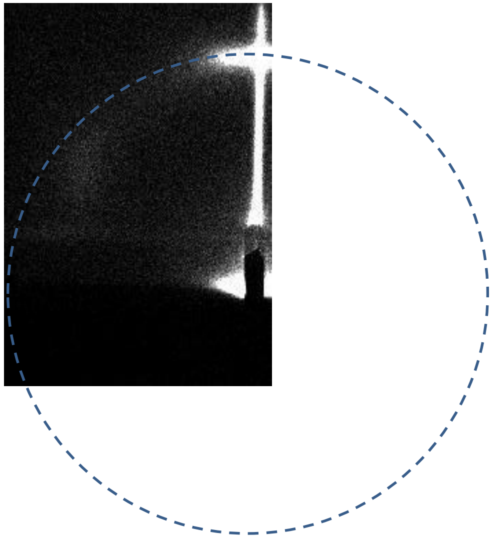
Flash cartoon: powder diffraction

http://www.personal.reading.ac.uk/~scs05ams/xray_cartoon.html

Examples

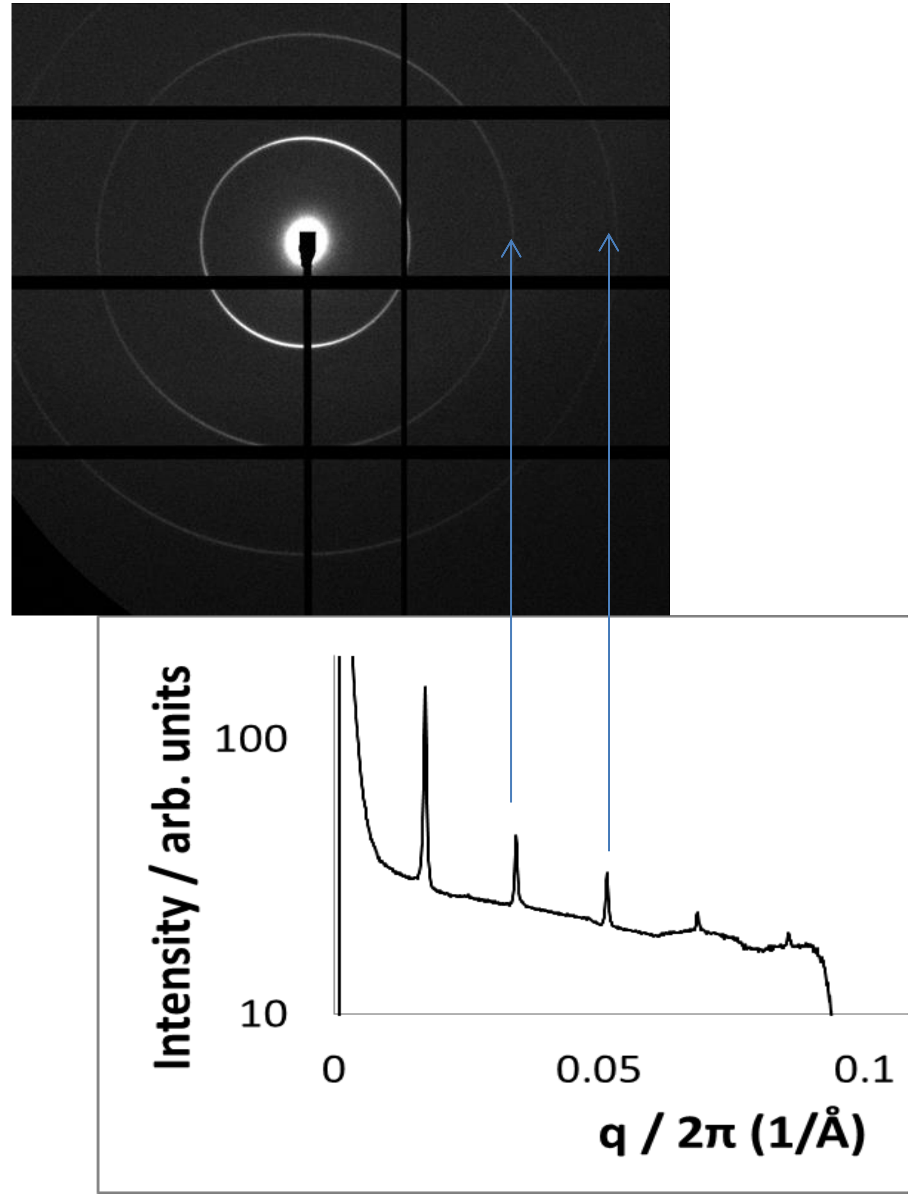
- Lamellar Phase





More complexity

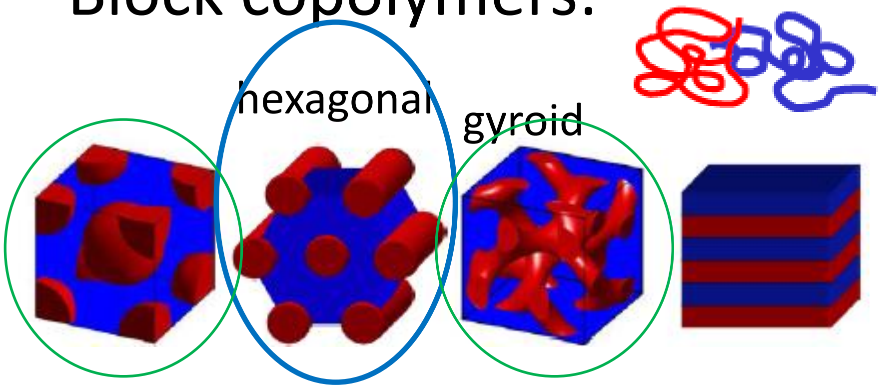
- Bragg Equation: **n**λ = 2d sinθ
  - Higher order reflections n=2,3,4…



- How about 2D or 3D periodicity?
- Block Copolymers / surfactant / lipid phases

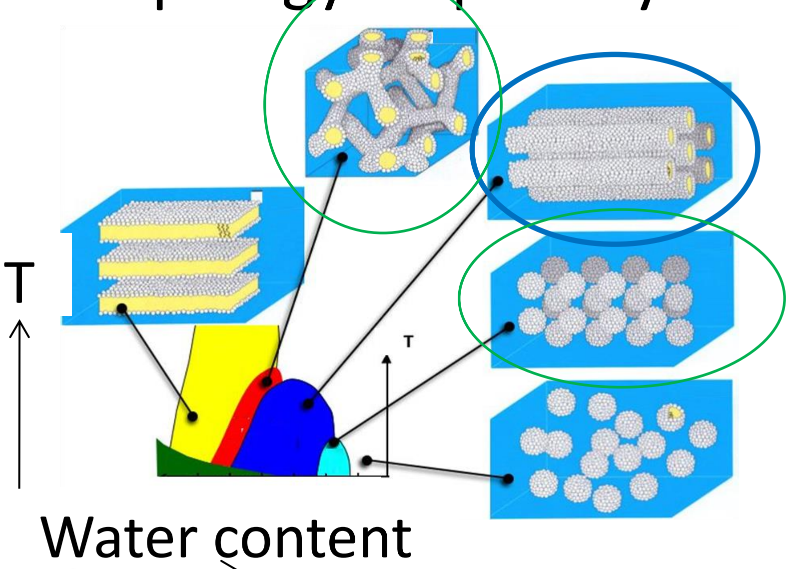
Periodic nanomaterials

- Block copolymers:

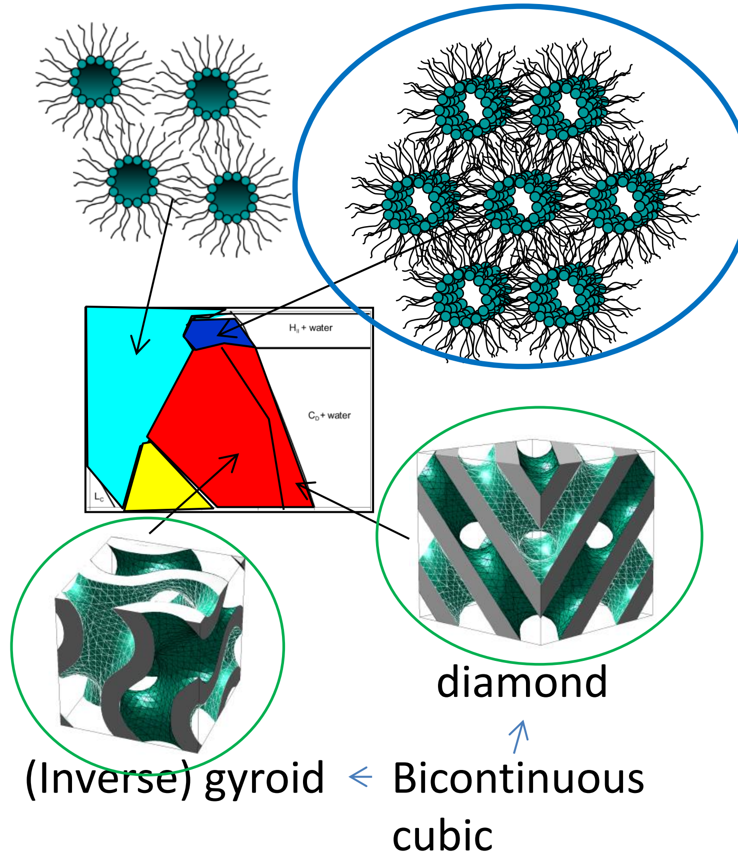


B. W. Boudouris, Purdue

- Surfactants ("normal topology" liquid crystals):



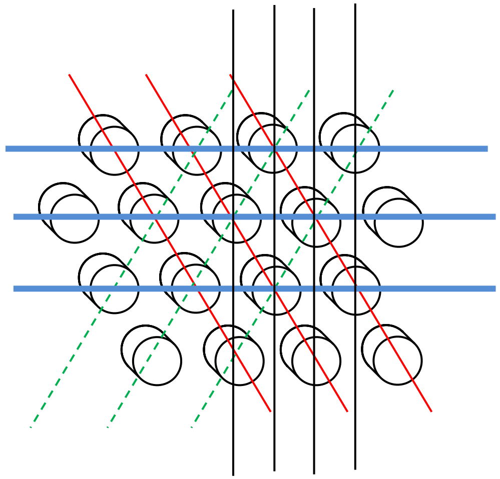
- Lipids ("inverse topology" liquid crystals):



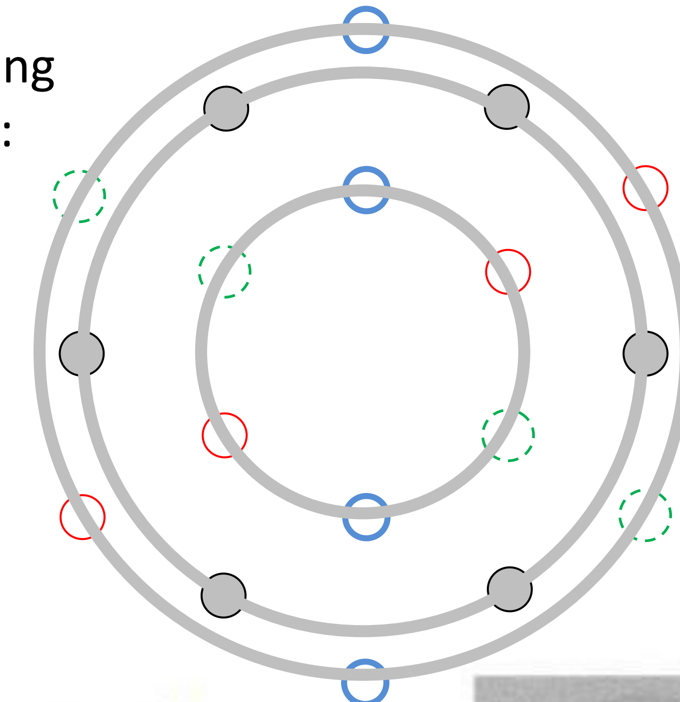
2D periodicity 3D periodicity

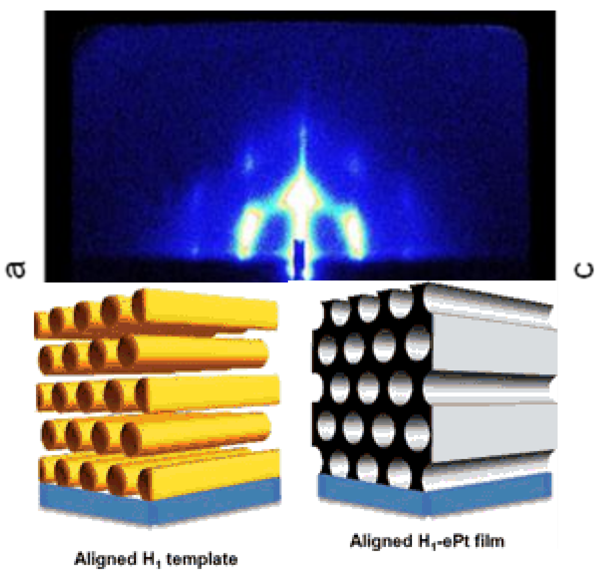
SAXS patterns from hexagonal phase

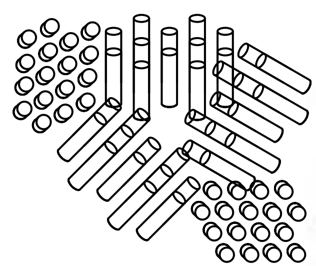
Structure:

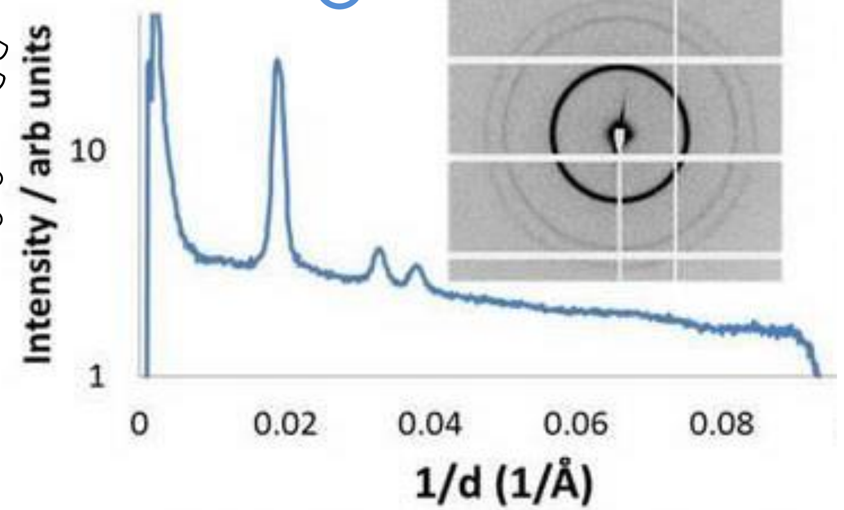


Scattering pattern:



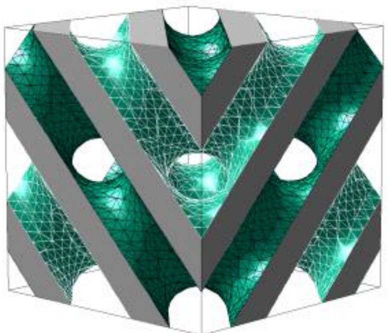




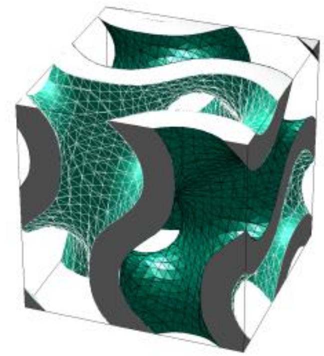


Asghar, Elliott & Squires, J Mat Chem 2012

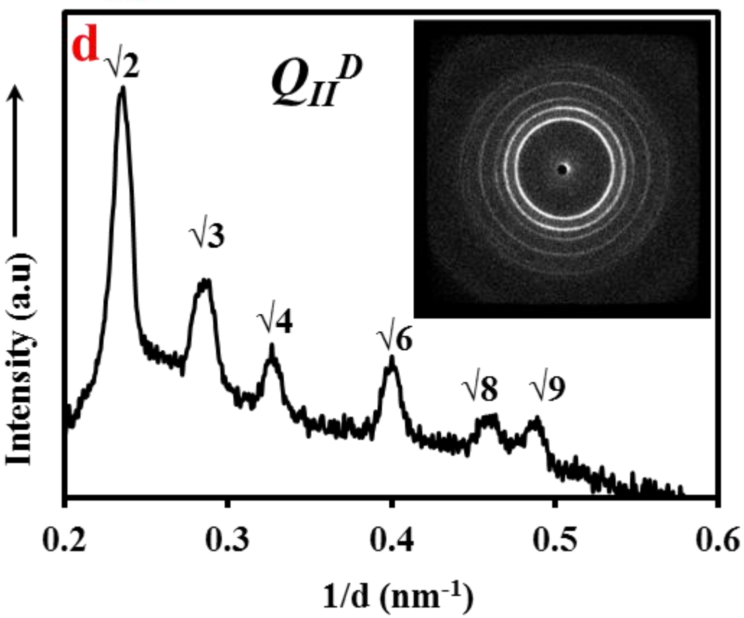
3D periodicity: cubic phases

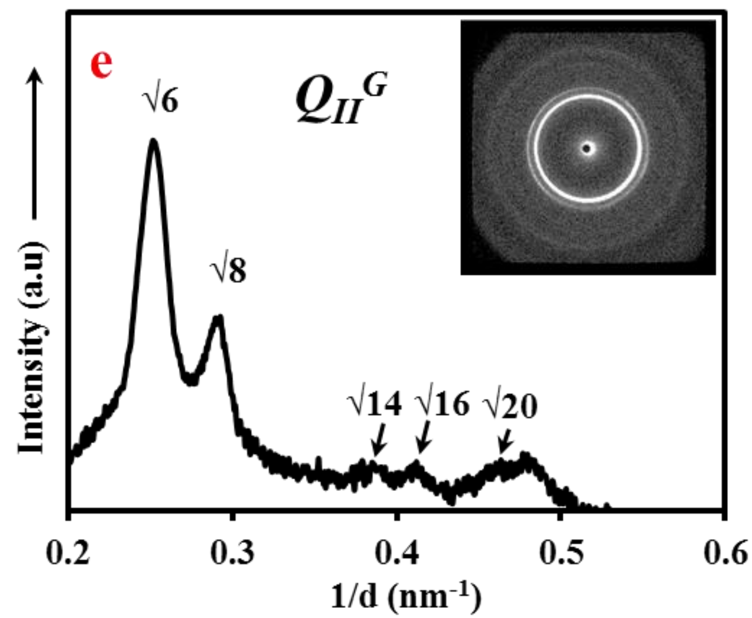


Diamond
Pn3m
(Space group 224)



Gyroid
Ia3d
(Space group 230)





S. Akbar PhD thesis, Reading 2012

- Summary:
  - Positions of reflections
    - Lattice parameter
    - Symmetry

    ie structure factor

- Next:
  - Intensity of reflections
    - Electron distribution
    - What shape is your repeating object

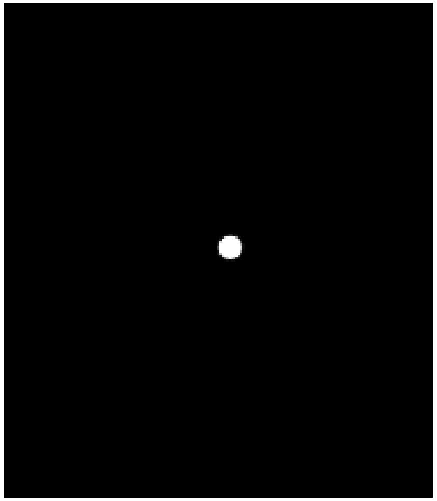
    ie form factor

Pattern is Fourier Transform of Electron density

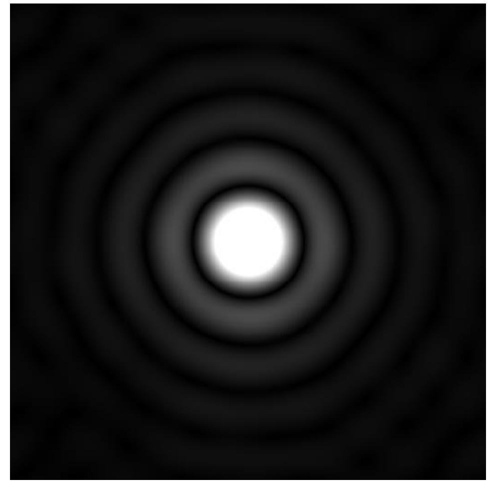
- Any object (=distribution of electron density) gives some sort of scattering pattern.
- This is an image of the Fourier Transform (FT) of the electron density distribution.
- [See previous talks]

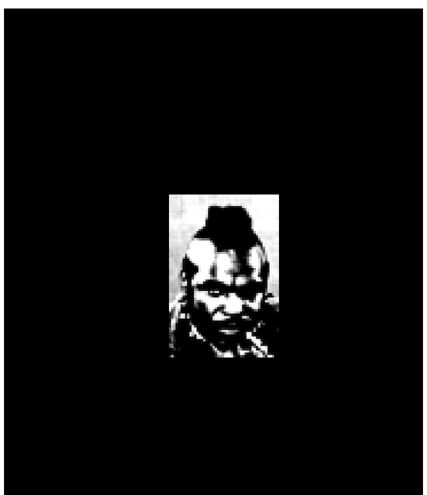
Real Space

Scattering Pattern (Fourier Transform)

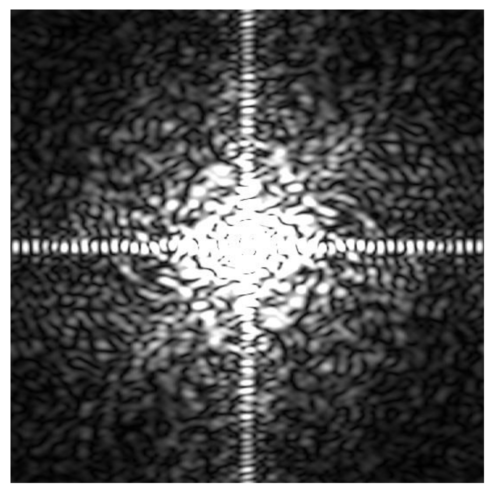


circle





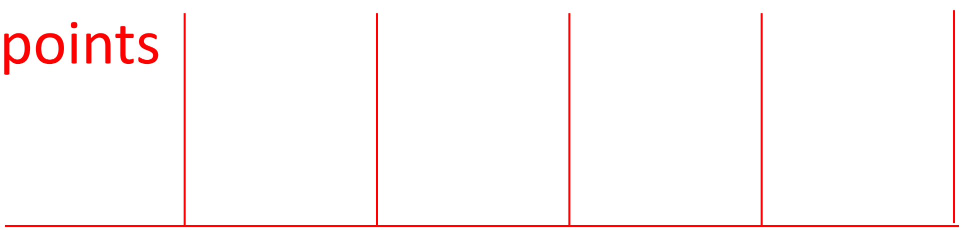
BA Baracus



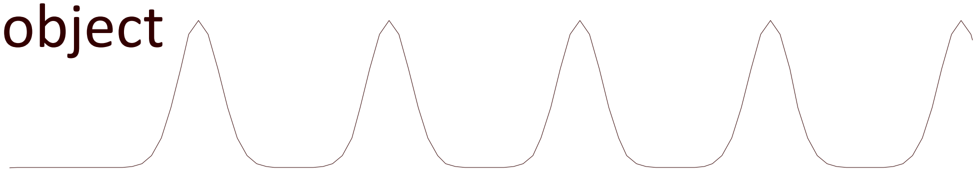
A periodic array of an object [Eg a crystal]

Object:

Lattice of points



1D Crystal of an object

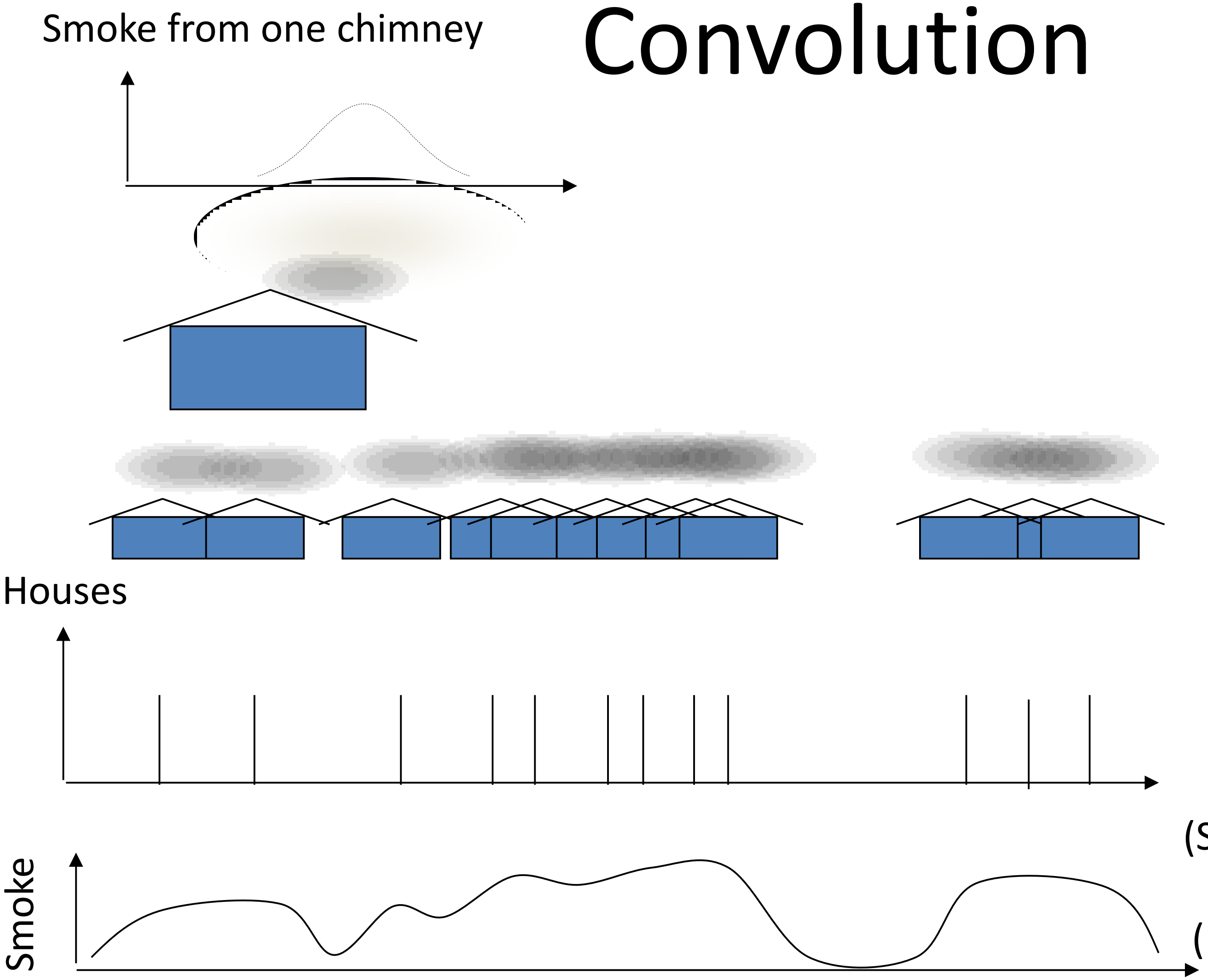


A crystal is the *convolution* of a lattice of points with whatever object is inside a unit cell.

Crystal = Lattice * Object

convolute

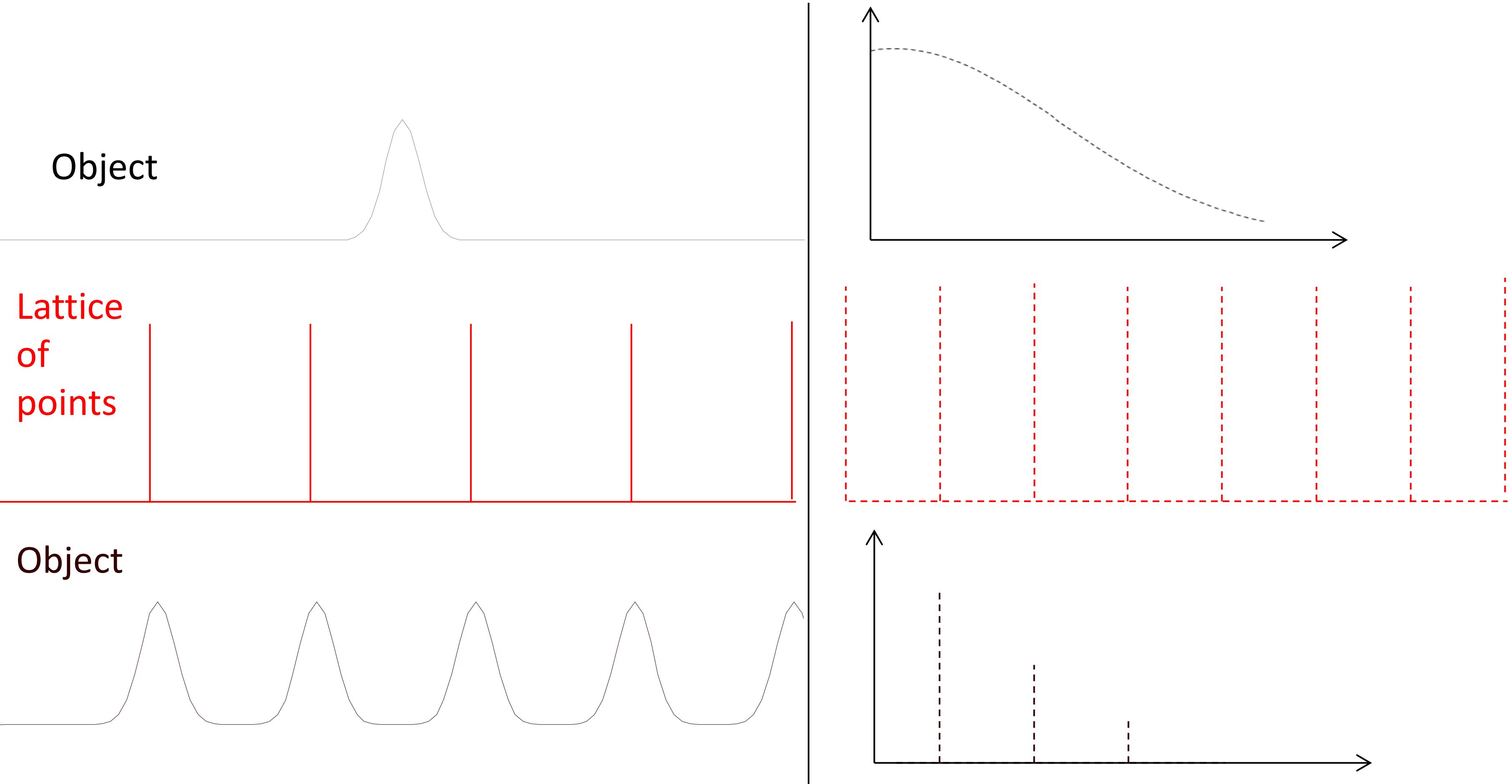
Convolution



(Smoke from one chimney)
*
(Distribution of chimneys)

Real Space

Scattering Pattern (Fourier Transform)

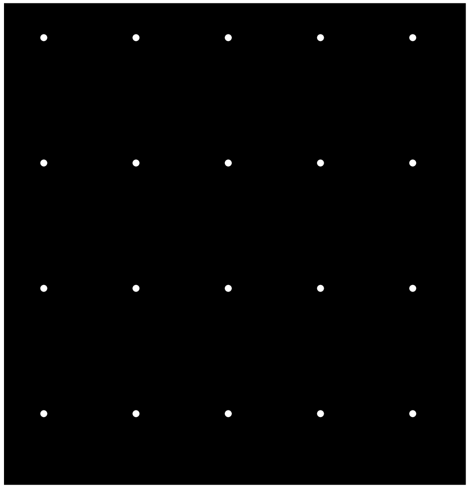


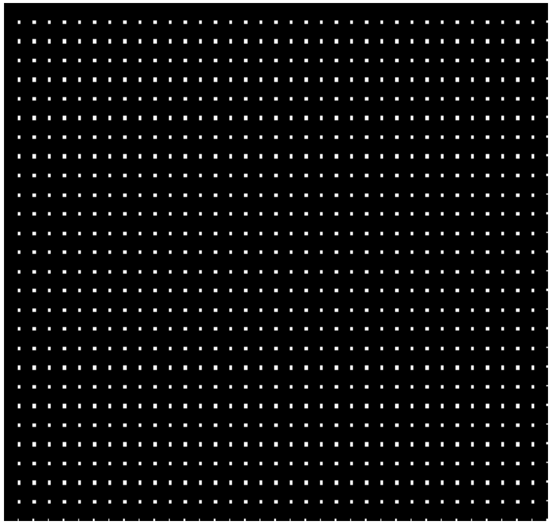
Crystal = Lattice * Object

convolute

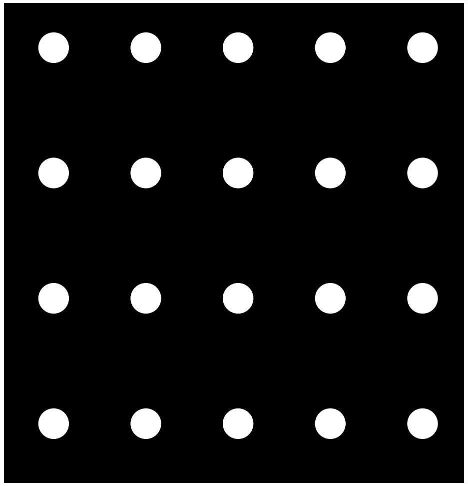
FT(Crystal) = FT(Lattice) x FT(Object)

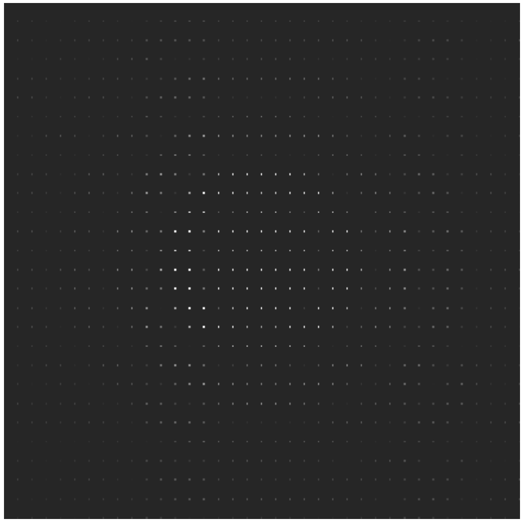
Points



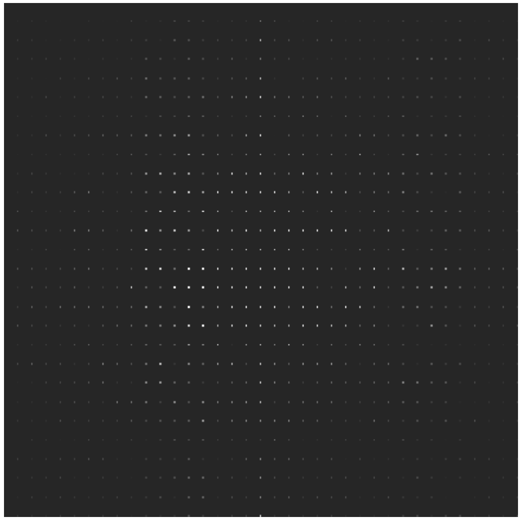


Circles





BA Baracus’s



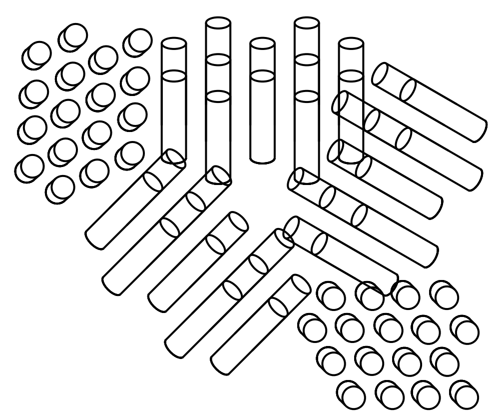
Summary

- *Positions* of spots / peaks →Symmetry of lattice
- *Intensities* of spots / peaks →Electron distribution within one unit cell of lattice

Next:

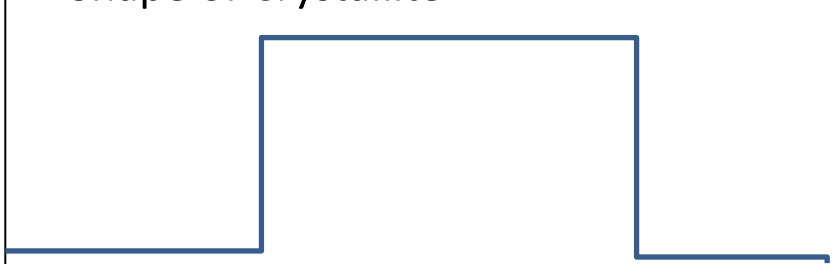
- *Width* of spots / peaks →Finite number of repeats (crystallite size?)

    [or other causes]

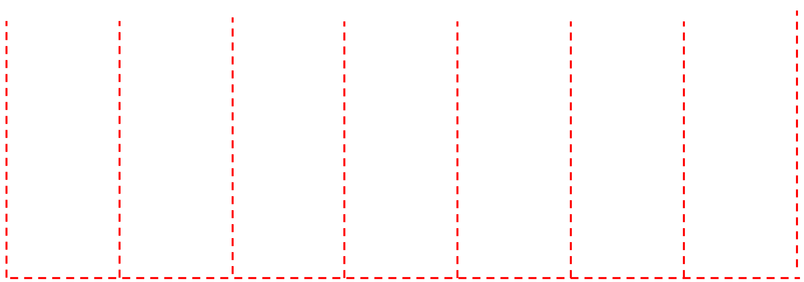


Real Space

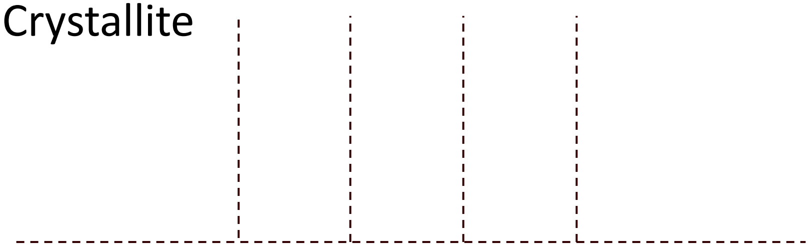
Shape of Crystallite



Infinite Lattice



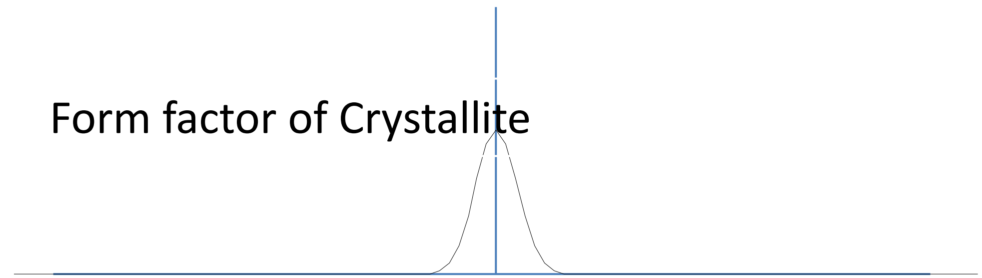
Crystallite



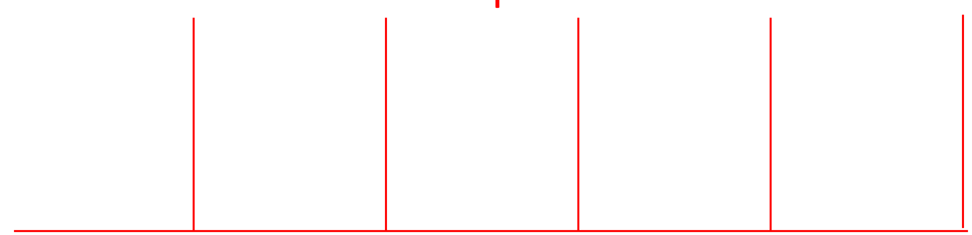
(Crystallite) = (Lattice) x (Crystallite shape)

Scattering Pattern (Fourier Transform)

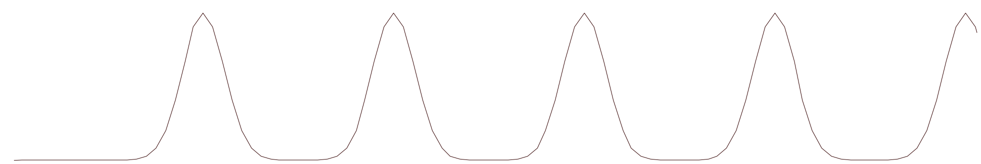
Form factor of Crystallite



FT of infinite Lattice of points



Scattering pattern



FT(Crystallite) = FT(Lattice) * FT(Crystallite shape)

convolute

Crystallite size estimation

- Scherrer equation

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

Dimensionless shape factor (close to 1) → K

Wavelength → λ

Bragg angle → θ

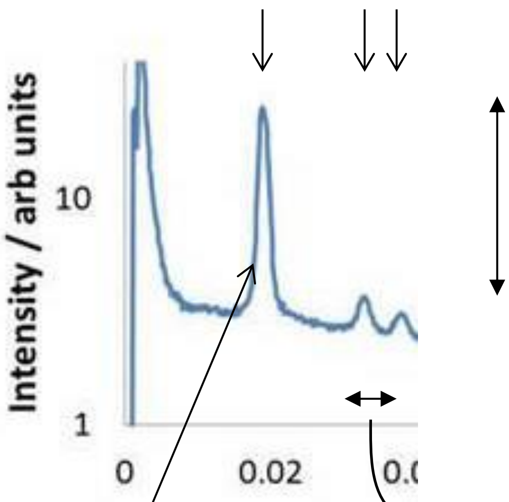
Mean crystallite size (units: as λ) → τ

Line broadening (full width half maximum) (in radians) → β

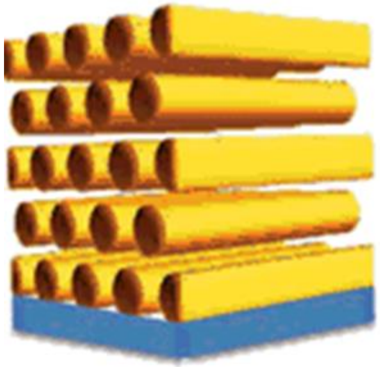
- Note: broadening might also come from *instrument (beam shape); polydispersity*

Summary

Relative positions:
symmetry



Peak heights:
Electron density within unit cell (ie shape / size / composition of each cylinder)

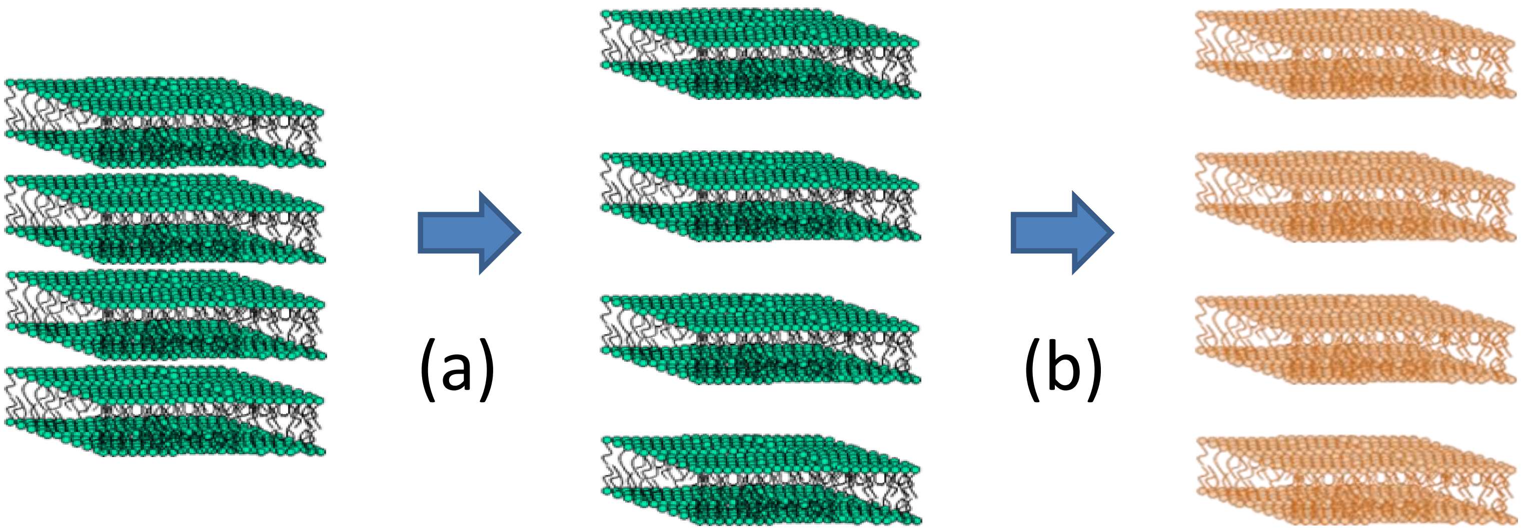


Peak position:
unit cell size (lattice parameter)

Peak widths:
- Finite number of repeats

OR
- Polydispersity
- Instrument: beam broadening

Task (2)



(a) Add water: bilayers move further apart
(b) Add metal nanoparticles that don't change spacing but adhere to interface

Discuss qualitatively what the scattering pattern looks like and how it changes