Obtaining and analysing SAXS data from colloidal structures – basic introduction

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Diamond Light Source

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Small-angle x-ray scattering

- SAXS is used to study structures on length scales 1 – 500nm
- Can be used to study samples in the native state
- Very versatile technique used across physics, chemistry and biology
- Typical systems studied include:
  - Gels
  - Nanoparticles
  - Biological samples
  - Polymers

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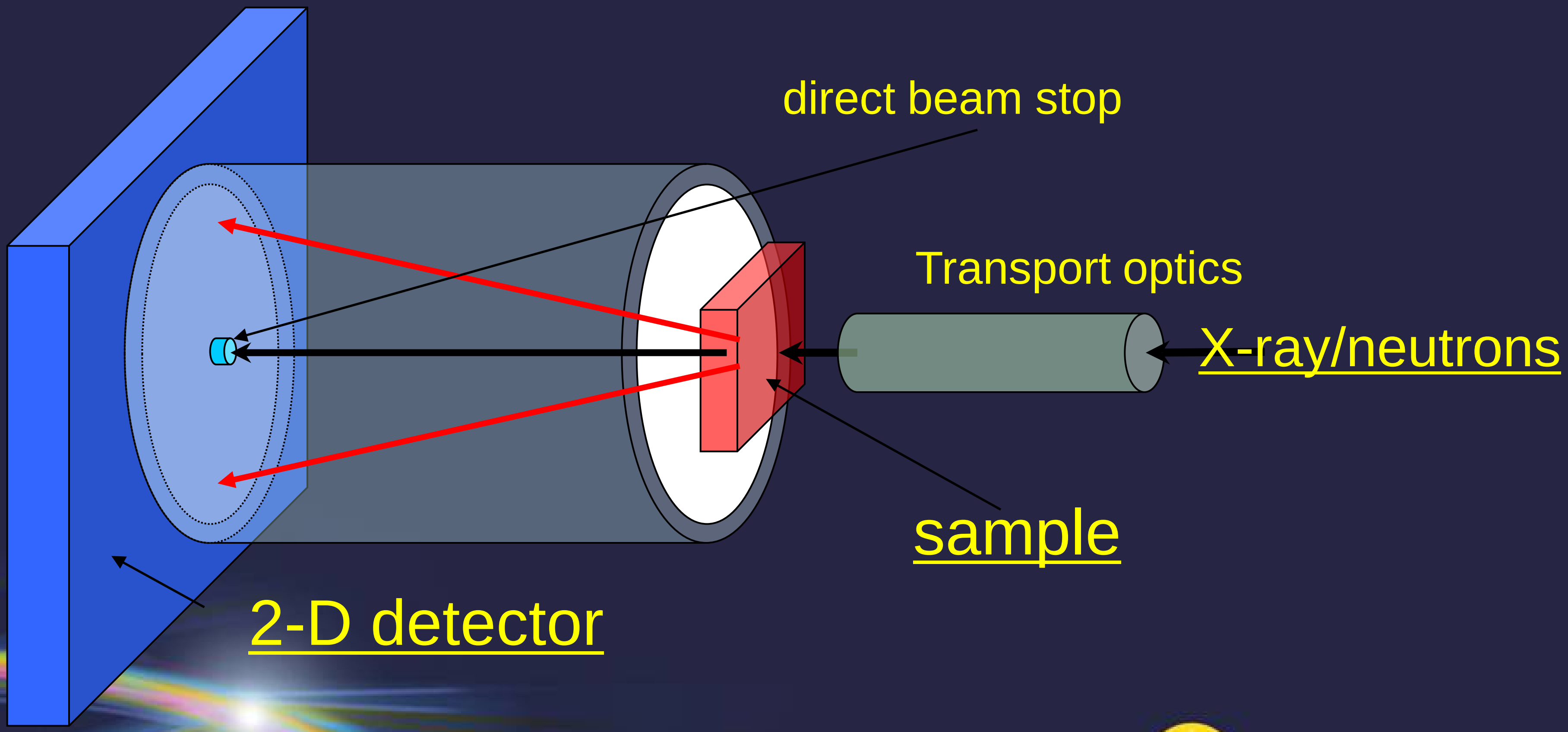
Classic SAXS instrument setup

Measureable region or ‘q-range’ defined by camera length and x-ray wavelength



Sample environments

- For colloidal systems, a variety of sample mounts can be used ranging from quartz capillaries through to flow cells or more complicated components
- Synchrotron SAXS beamlines and SANS instruments often focus on offering time resolved measurements in which the sample can be subjected to shear, temperature and pressure cycles in line
- Diamond offers in-line pressure cell, rheology and linkam heating, stop flow and lego

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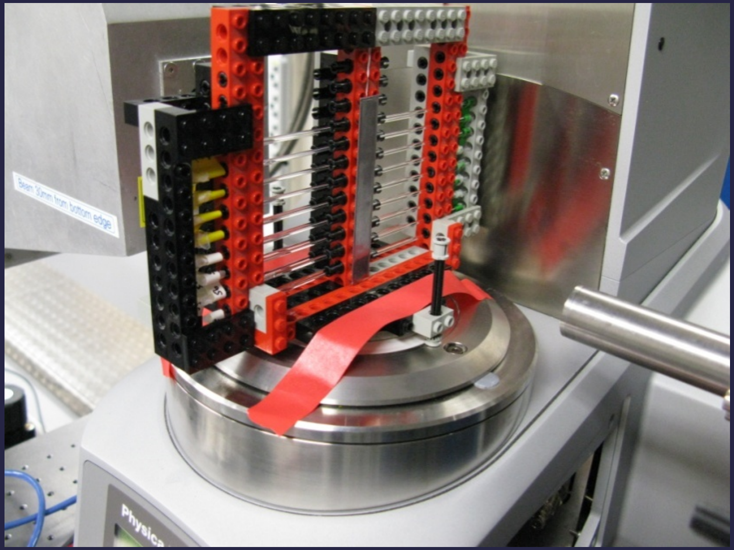
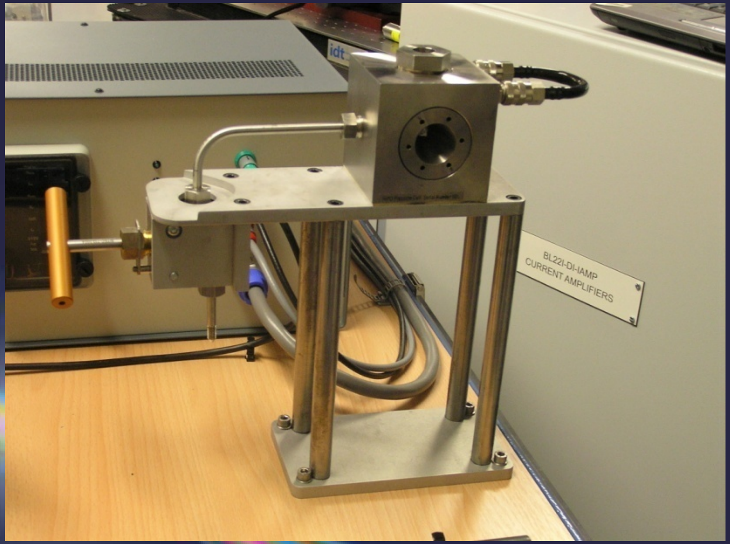
Sample environments

Rheometer

Pressure cell

Lego





SAXS Advantages and Disadvantages

Advantages

- Relatively easy to set the experiment up
- No need to have crystals
- Offers the ability to obtain real time and dynamic measurements
- Few limits on molecular weight

Disadvantages

- Low resolution
- Data analysis can be challenging
- Relatively high concentrations can required

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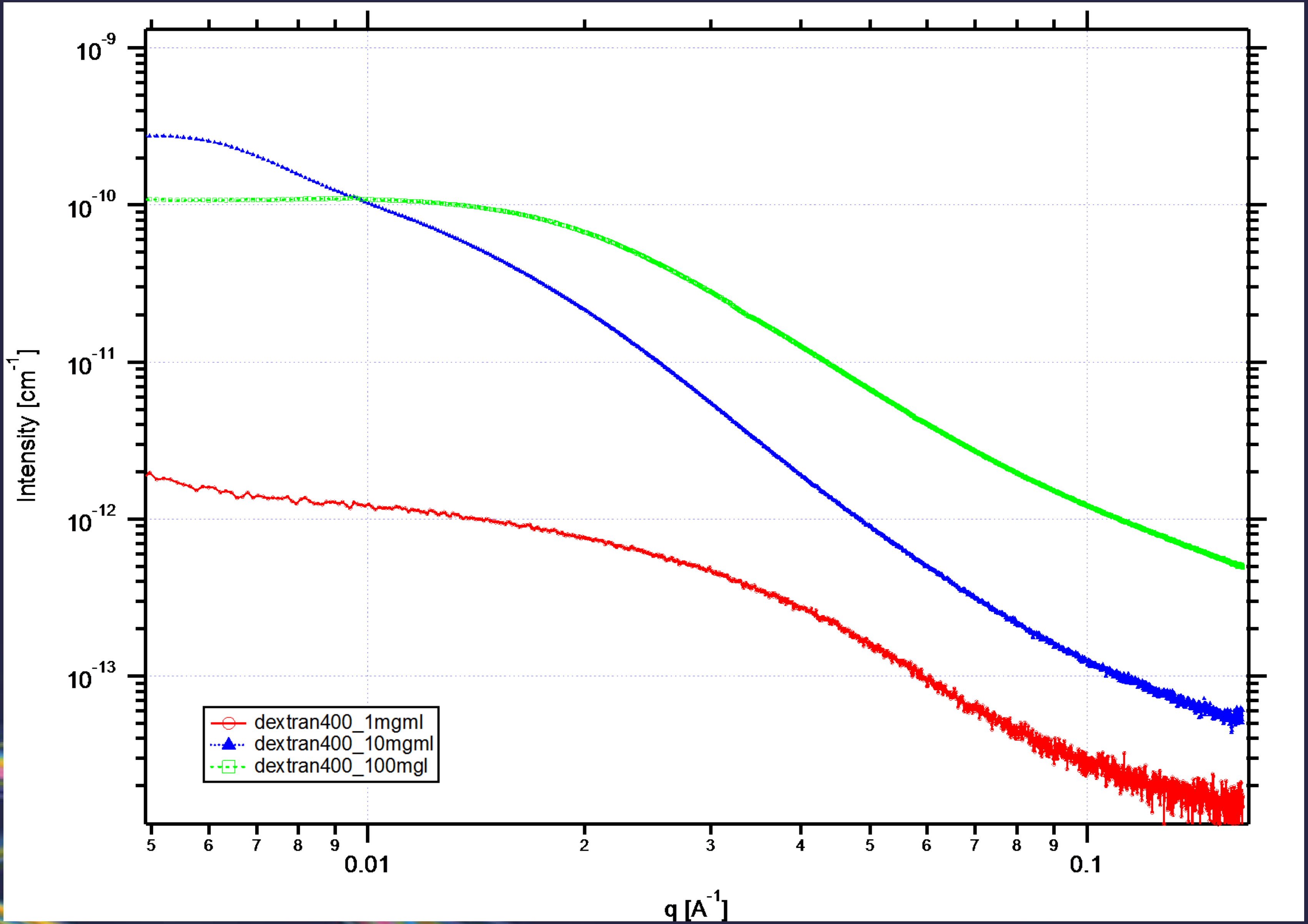
Sample preparation

- Studying your samples in a native state is one of the key attractions of SAXS and SANS, however there are some considerations!
- Sample should not be too thick – you will get problems with multiple scattering and attenuation
- You need to watch out for concentration dependence effects in solution systems (similar to BioSAXS..)
- There needs to be some contrast between regions/objects, inside the sample you're trying to measure!

Sample preparation



Basic SAS equation

$$I(q) = N_V V_p^2 (\rho_p - \rho_s)^2 F(q) S(q) - B$$

Where:

$I(q)$ = scattered intensity

N_v = number of particles

V_p = particle volume

ρ = scattering length densities

$F(q)$ = form factor

$S(q)$ = structure factor

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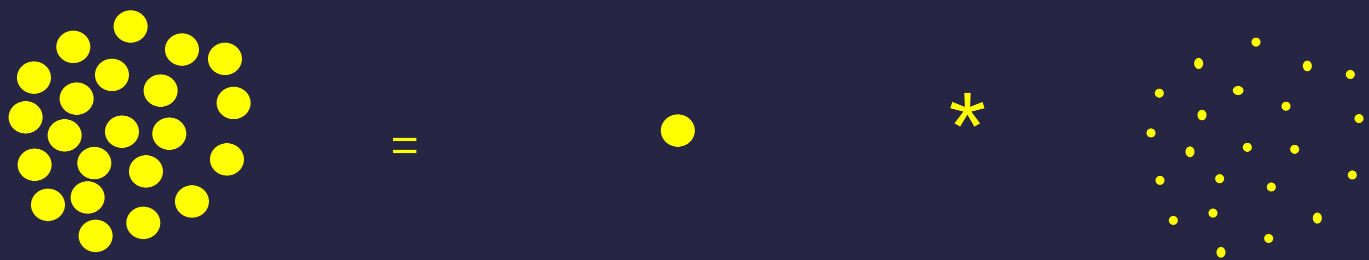
Basic SAS equation



Form factor
of the particle

Structure factor
of the particle

- **Form factor**
  Information on the shape of the objects

- **Structure factor**
  Information on the interactions between objects

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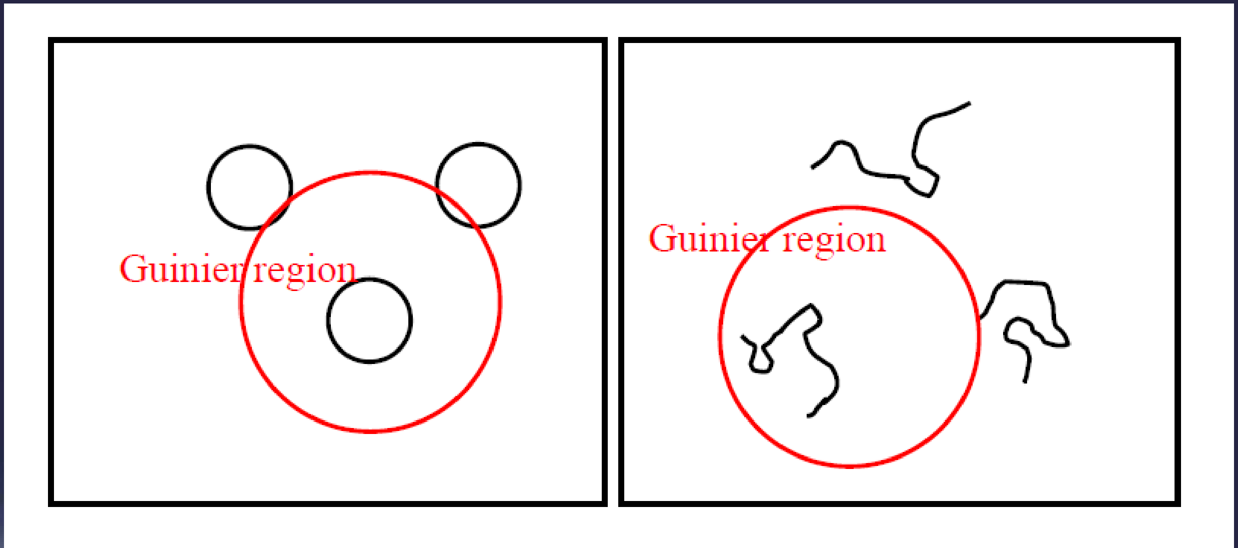
Generic SAXS analysis

- Some basic plots will yield quick structural data –
  - Plot ln[I(q)] against q^2
  - Scattering particles are smaller than the probed length scale in this regime



Generic SAXS analysis

- Some basic plots will yield quick structural data –
  - In the Guinier regime scattering particles are smaller than the probed length scale
  - Guinier plot gives radius of gyration of objects/domains/chain clusters
  - Plot $\ln[I(q)]$ against q^2
  - Gives indication of size with no dependence on model or absolute intensity
  - Be careful of interparticle interference in which case it becomes largely meaningless...

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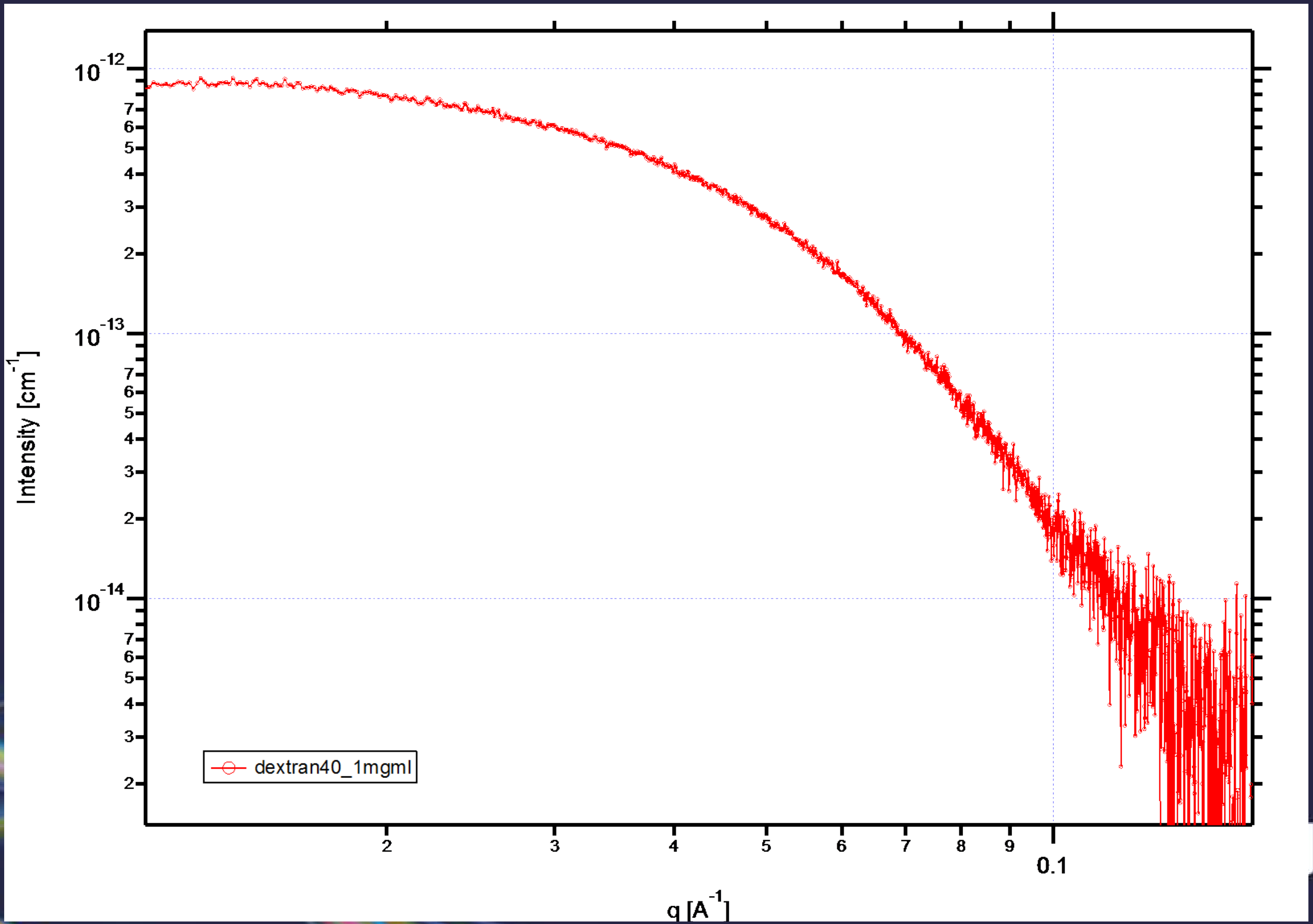
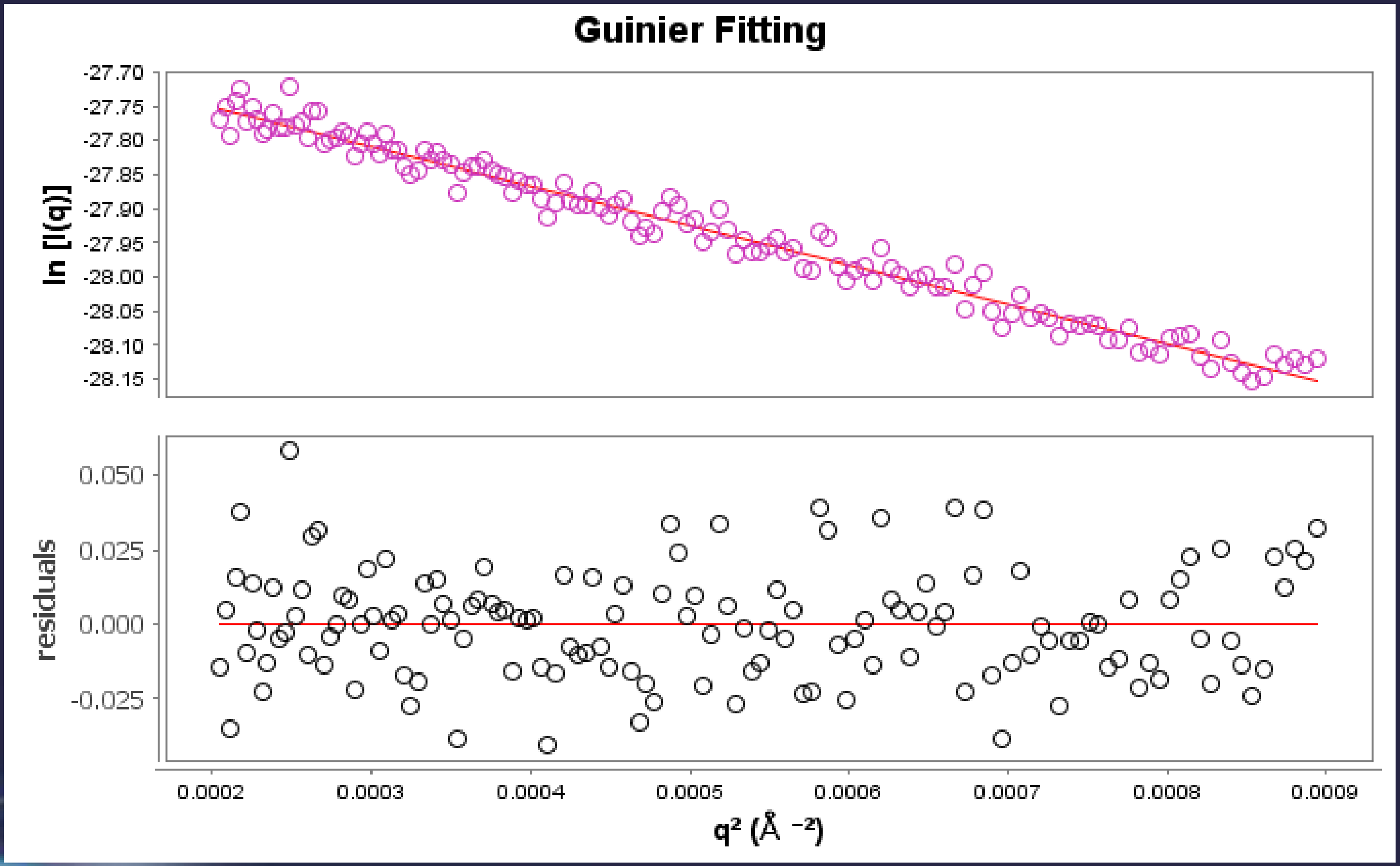
Generic SAXS analysis

- Dextran at low concentration



Generic SAXS analysis

- Dextran at low concentration Rg = 41Å



Radius of gyration

- Radius of gyration is the root-mean square of the distance of all electrons from the centre of gravity
- Well known for many shapes!!
  - Solid sphere radius R:

    $$R_g = \sqrt{(3/5)}\ R$$

  - Thin rod length L

    $$R_g = \sqrt{(1/12)}\ L$$

  - Thin disk radius R:

    $$R_g = \sqrt{(1/2)}\ R$$

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Generic SAXS analysis

- Porod regime gives fractal dimension of the objects and excluded volume
  - In this regime we are probing length scales smaller than the scattering objects
  - Plot your data in Log/Log format
  - The slope varies with different shapes/fractal dimensions
  - Values between -1 and -3 can denote mass fractals
  - Values between -3 and -4 can indicate surface fractals

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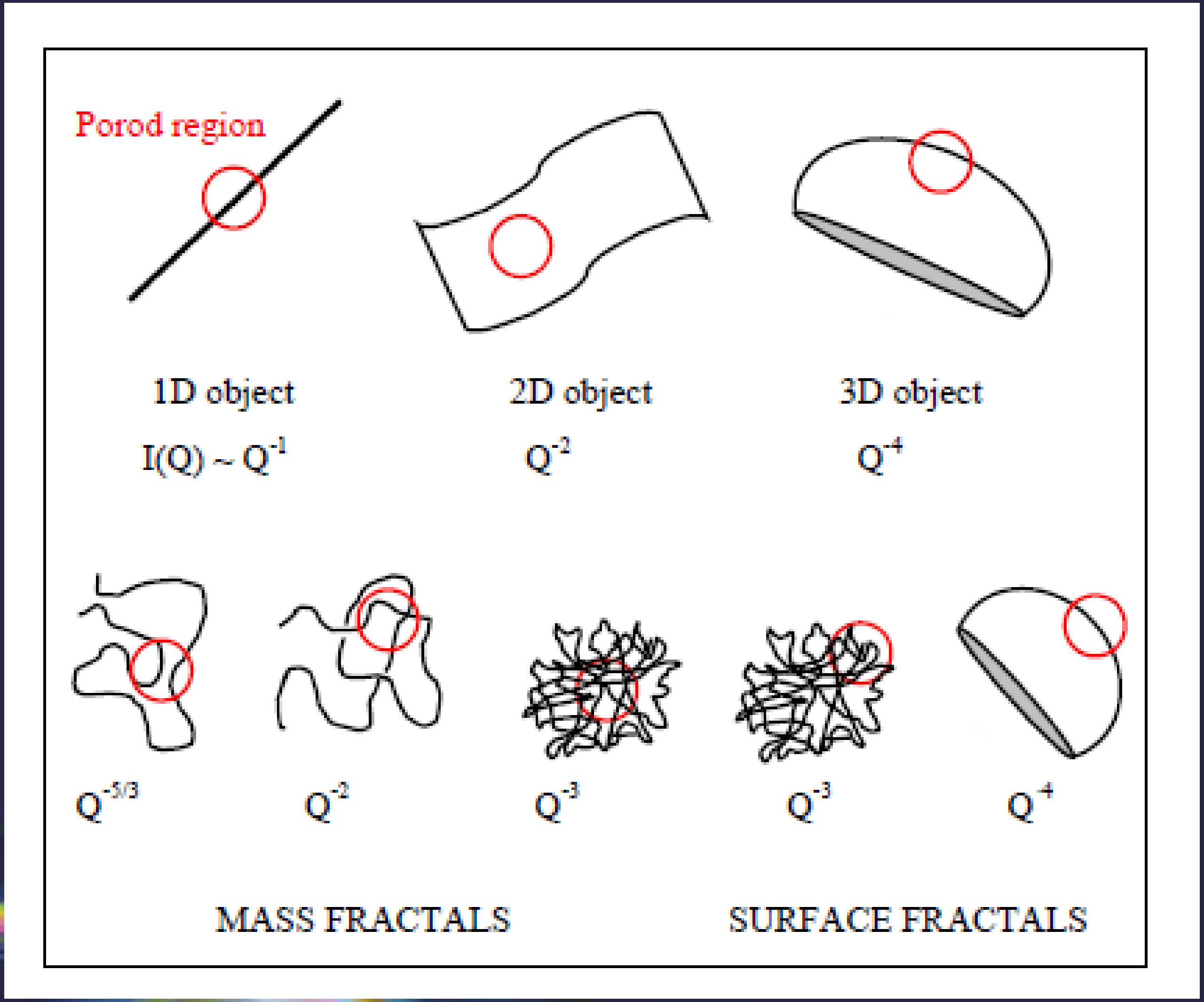
Generic SAXS analysis

- Porod regime gives fractal dimension of the objects and excluded volume
  - Slope of -1 denotes rods
  - If you get -2, indicates disks/lamella
- In the case of fractal structures
  - For classic Gaussian chains, -2
  - A value of -5/3 indicates swollen coils
  - Between -2 and -3 denotes some form of branched system or network

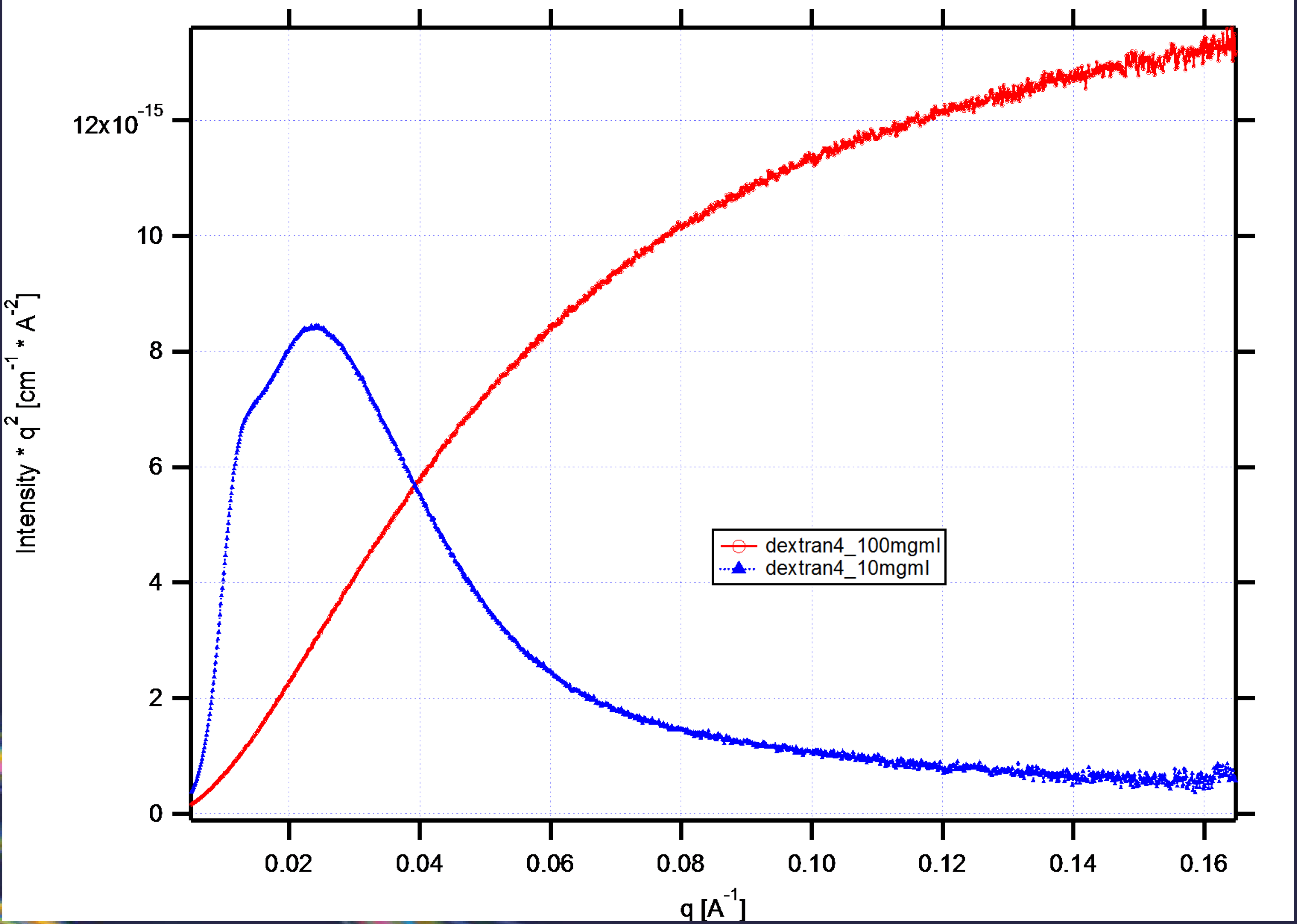
Generic SAXS analysis



Generic SAXS analysis

- Kratky plot
  - You need $I(q)q^2$ versus q
  - Emphasises departures from Gaussian chain behaviour
  - For a given system, you can observe certain behaviour at high q
  - Rod like systems show a linear increase at high q
  - Mass fractals and branched systems reach a maxima and then die off

Generic SAXS analysis



Empirical SAS models

- There are certain very basic empirical SAS models which can be used on systems that are difficult to analyse e.g.
  - Guinier-Porod model (Boualem Hammouda)
  - Unified Model (Greg Beaucage)
- These can be used to build several Guinier and Porod regimes for a given scattering curve
- May be useful for analysing hierarchical systems or mixtures
- There are some more specific ones which are simpler to use!!

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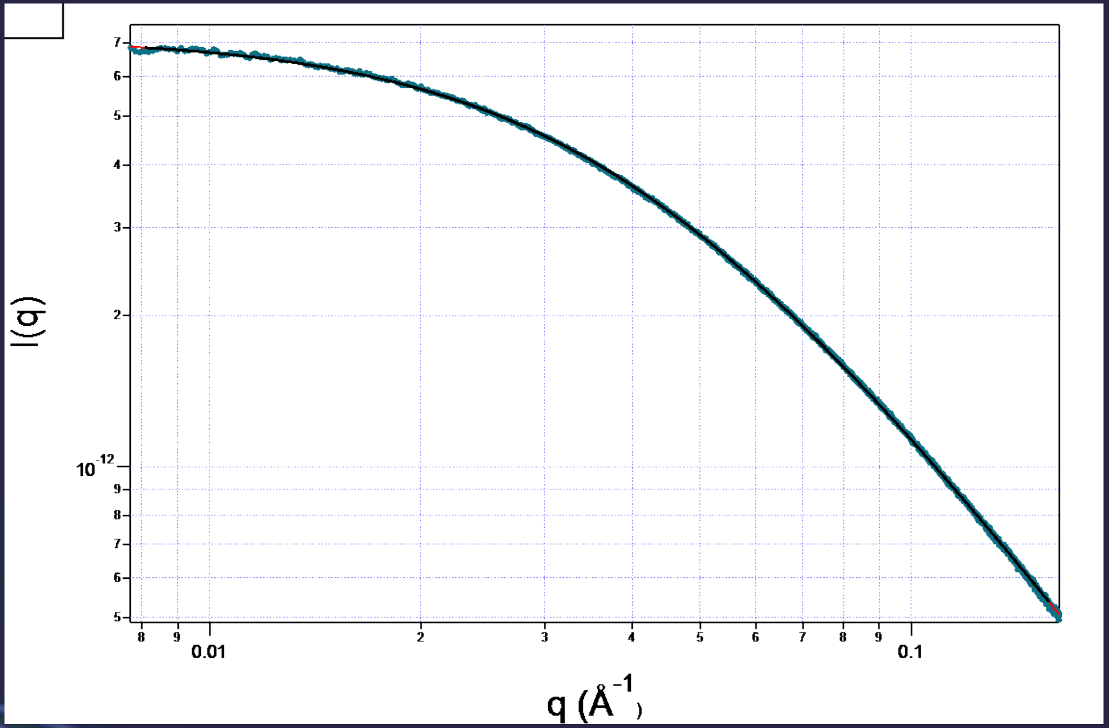
Empirical SAS models

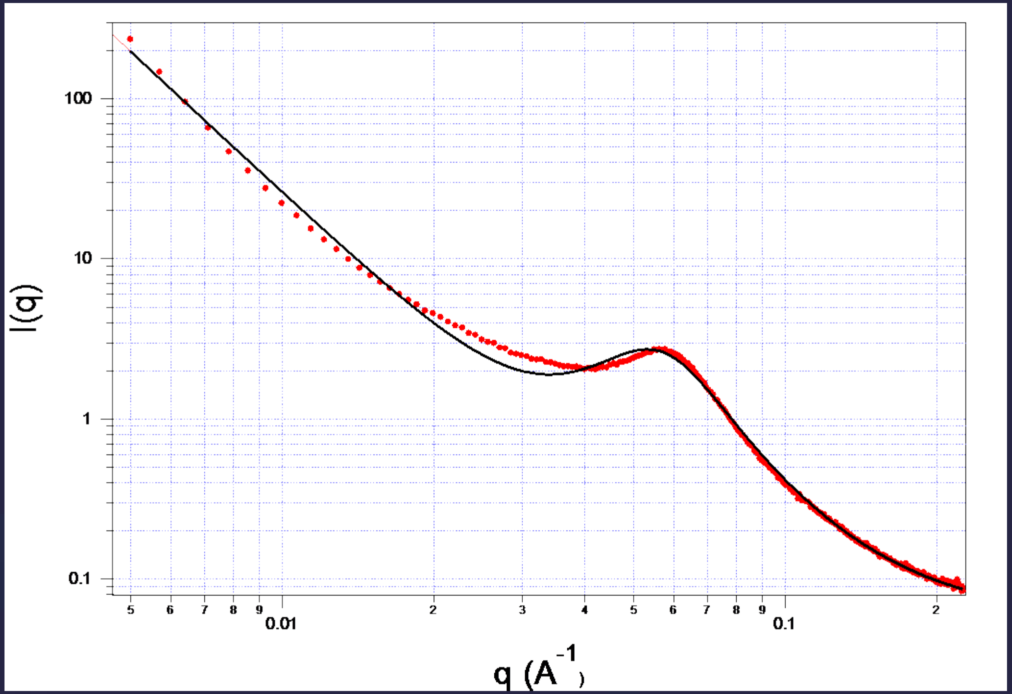
- Correlation length model
  - Gives a correlation within the system which dies out exponentially and the Porod exponent
  - If Porod exponent is 2, this is a Lorentzian function
  - Correlation length should be large for systems like gels
  - P = 1.85
  - ξ = 24 Å



Empirical SAS models

- Broad peak model
  - Very useful indeed for amorphous layered systems
  - Basically bicontinuous structures
  - Will give d-spacing
  - Can be combined with a power law model for fitting

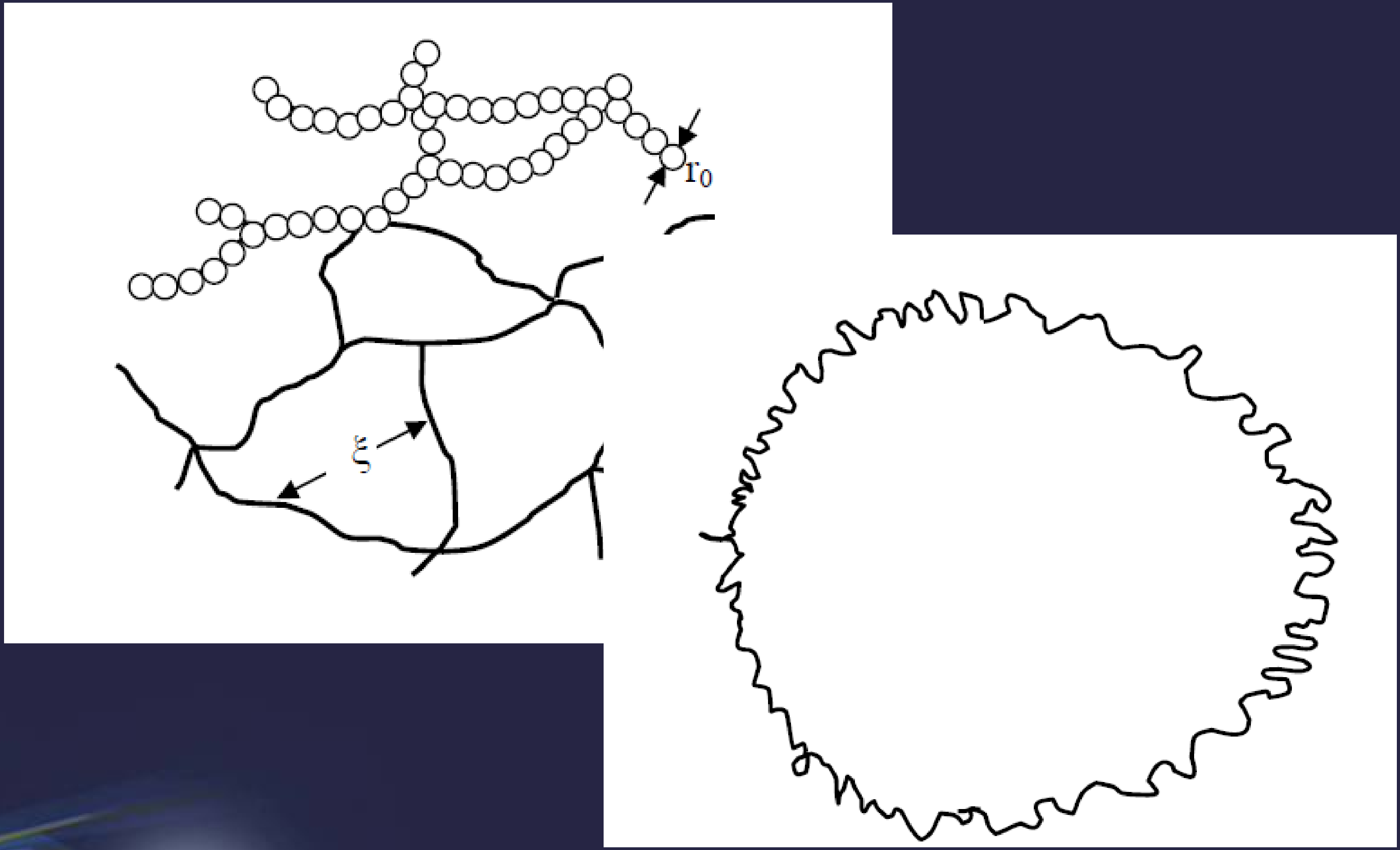
  - d-spacing 116 Å
  - P = 2.9
  - Complex system!



Fractal models

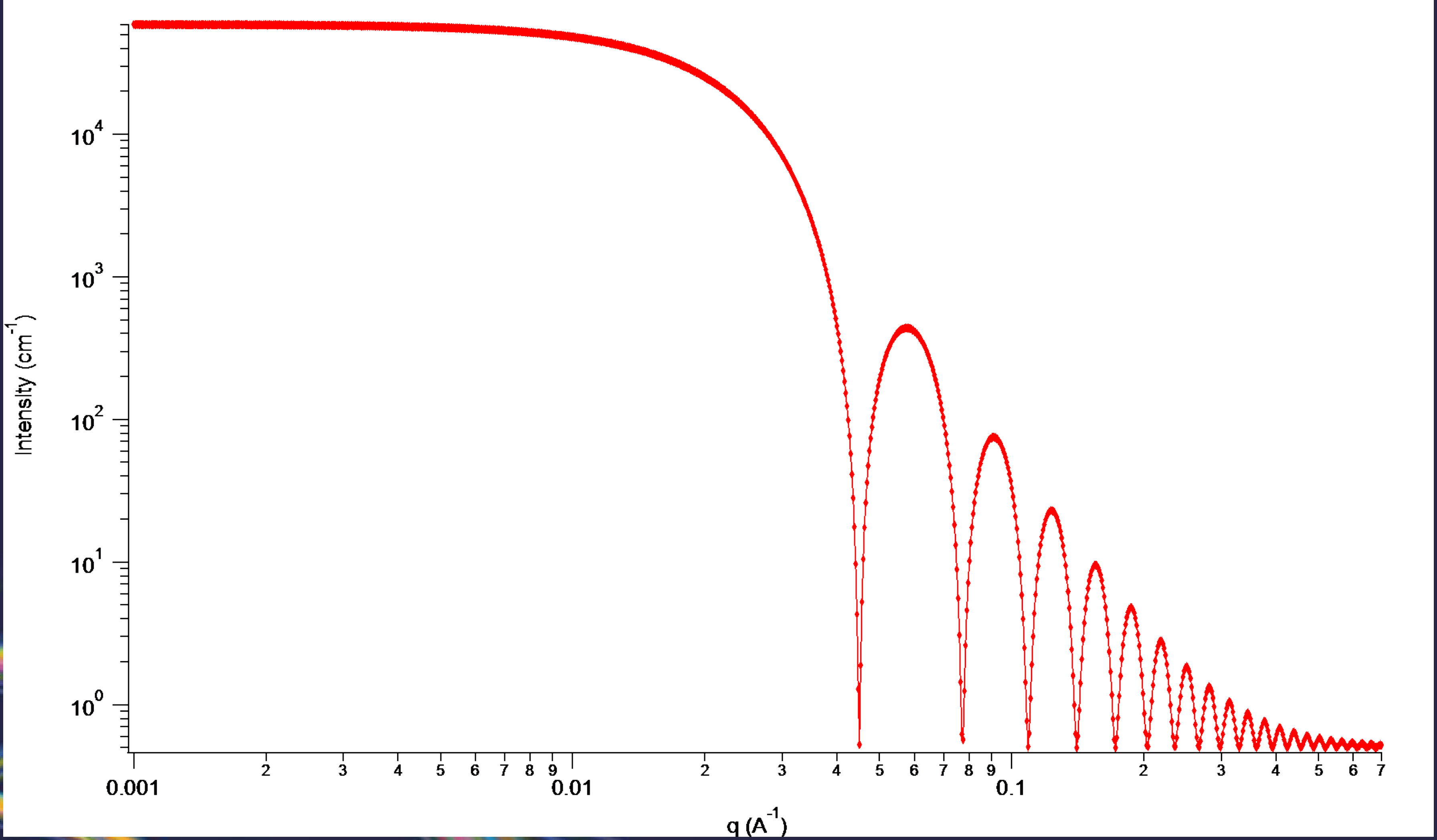
- Structures which branch and/or crosslink into 3-D networks
- Several variations, most commonly used by Teixeira (1988)
  - Structure composed of building blocks usually spheres or cylinders
  - Structures aggregate to form fractal clusters
  - Power law decay corresponds to self-similarity dimension
  - Possible for basic particle to be polydisperse

Fractal models



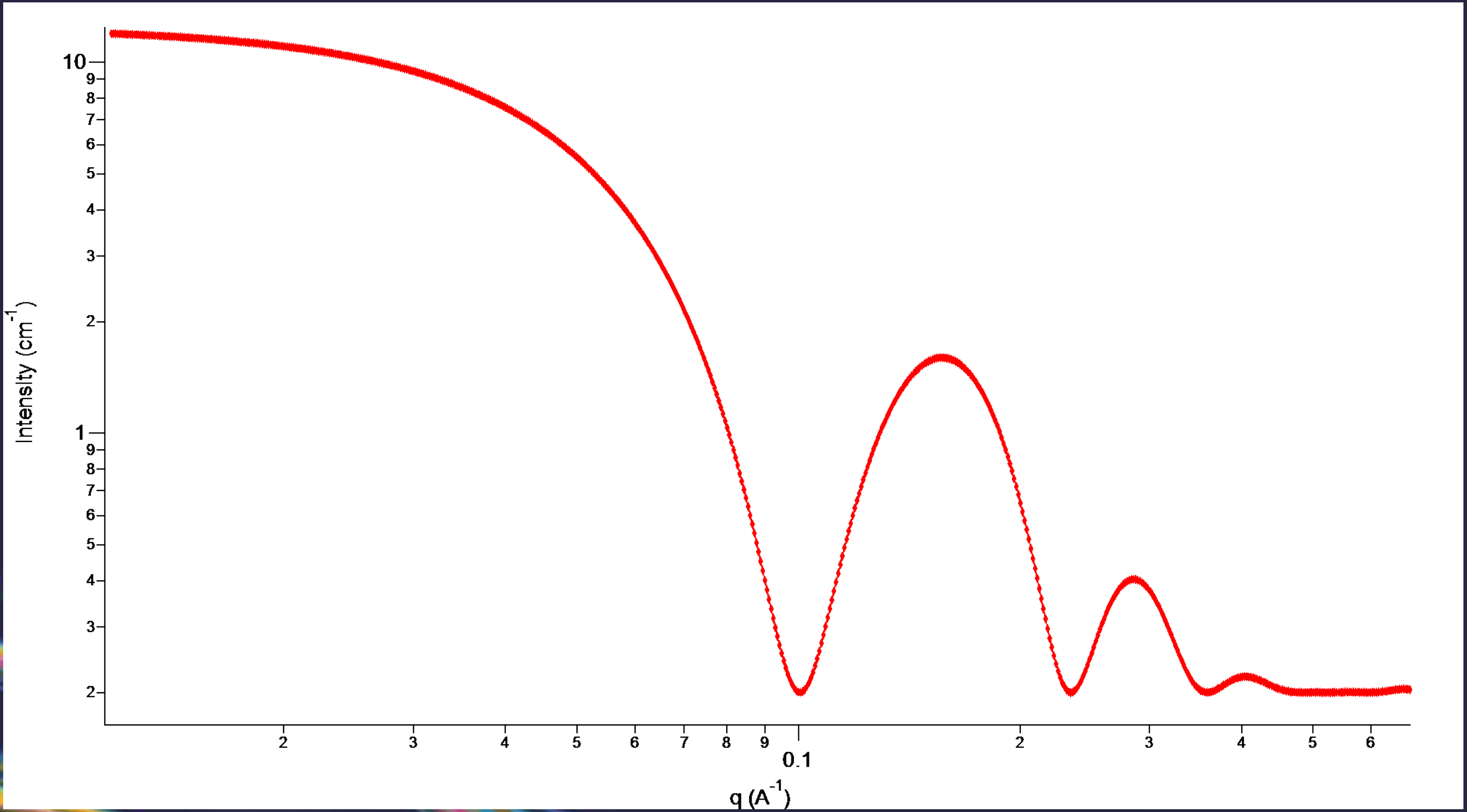
Basic shapes

- Monodisperse Spheres (radius 100Å)



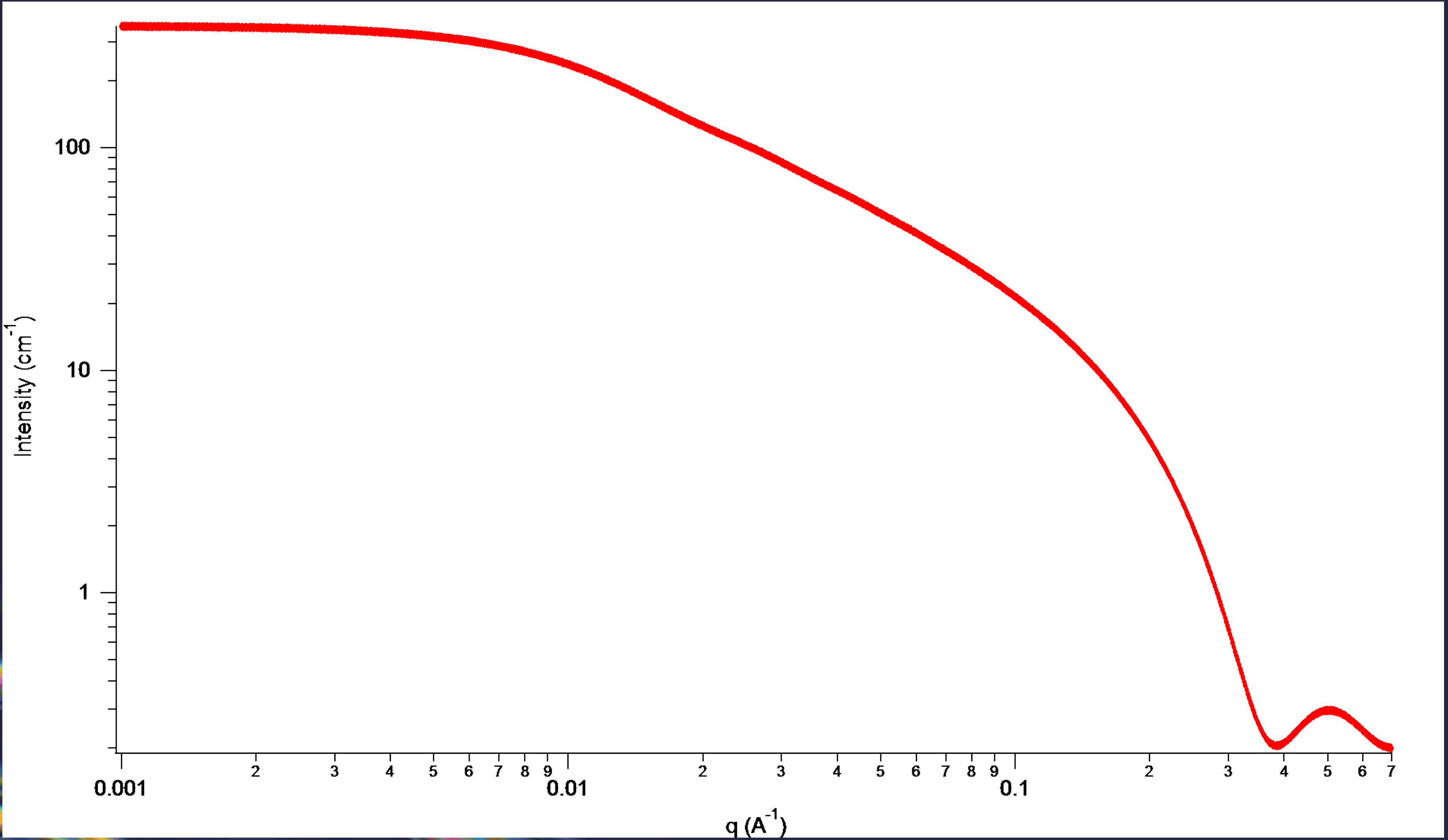
Basic shapes

- Core-shell system (core radius 20Å, shell thickness 12Å)



Basic shapes

- Cylinder/rod like particle (length 400Å, radius 10Å)

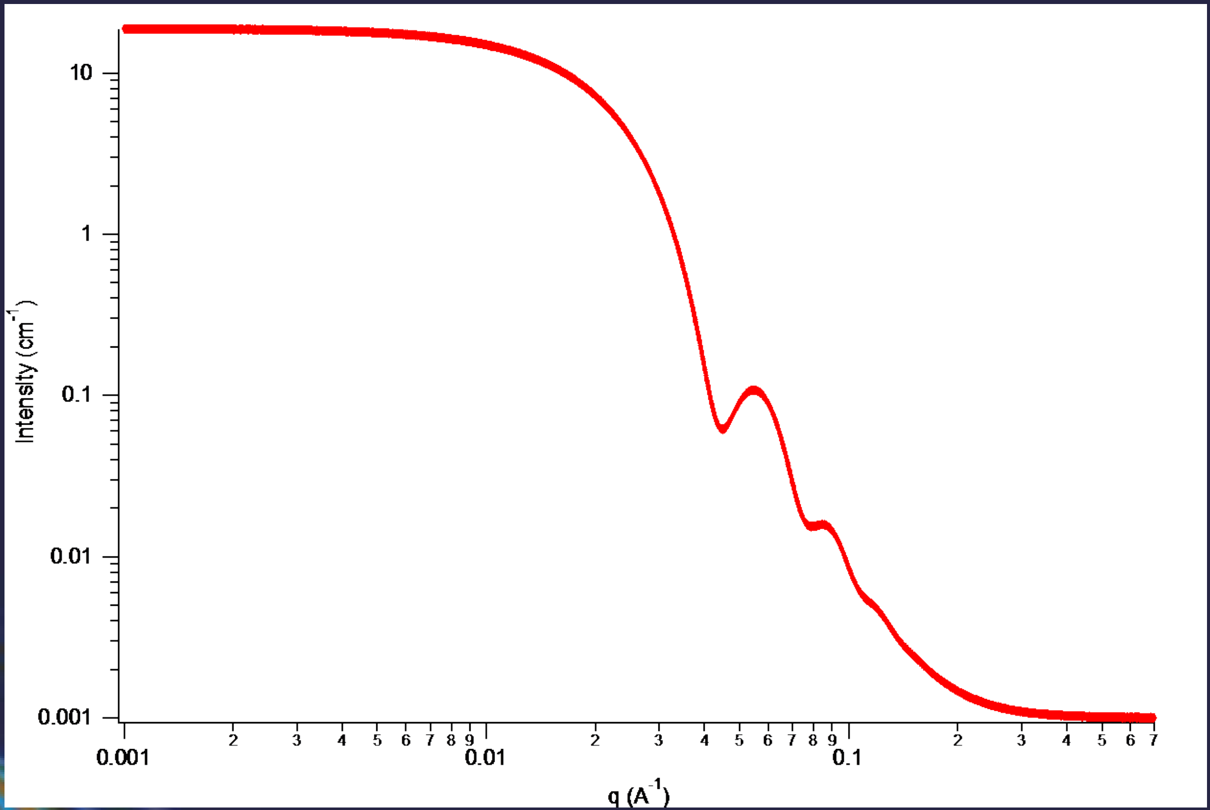


Polydispersity

- Many of your systems will have some polydispersity
- There are ways to account for this in your fitting:
  - Schulz distribution
  - Log-normal distribution
  - Gaussian

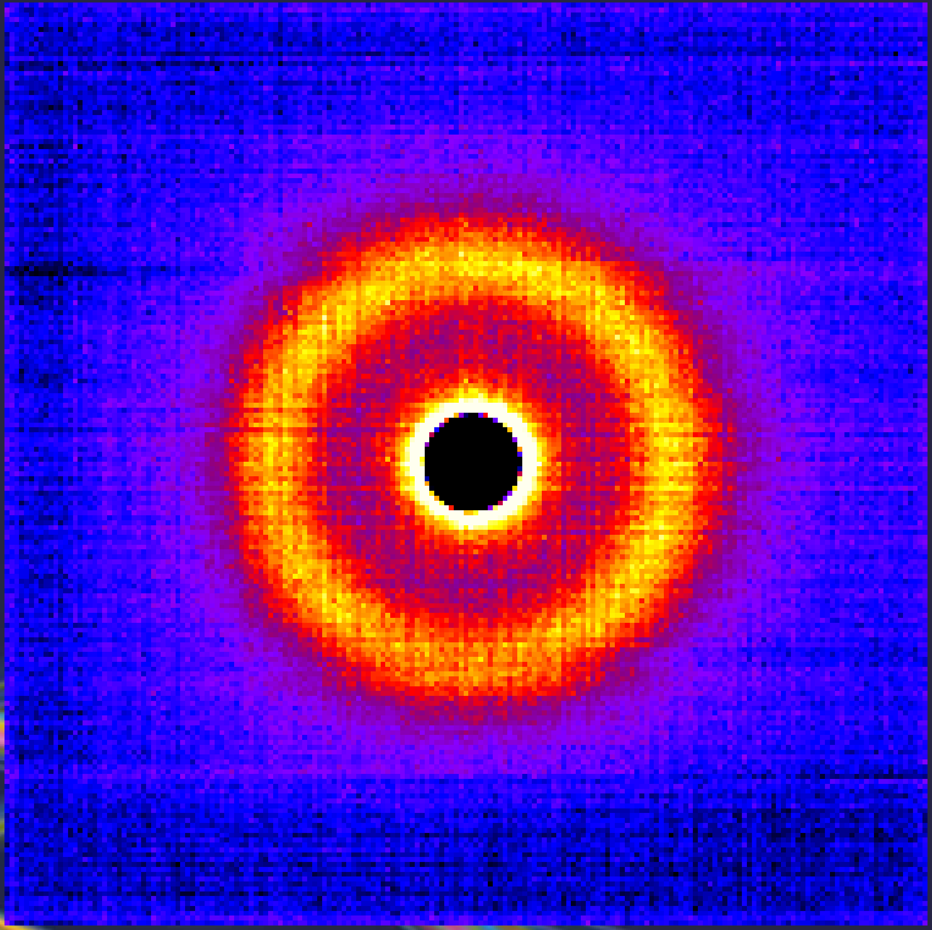
PD = 0.1

Radius = 100Å



Food hydrocolloids

- Starch is the key dietary carbohydrate in the human diet
- Granules are composed of a mixture of lamellar stacks and branched polymers forming fractal structures



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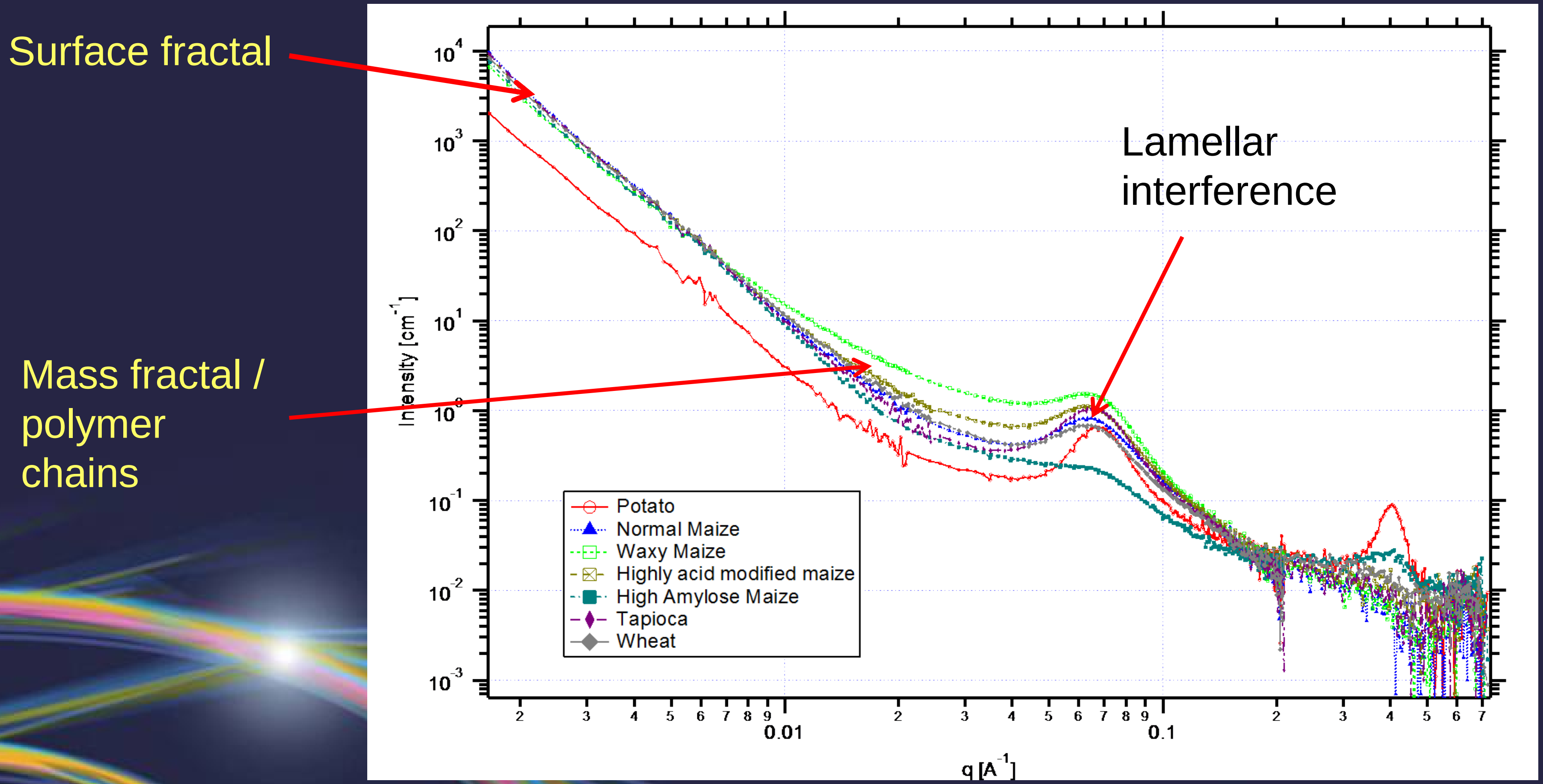
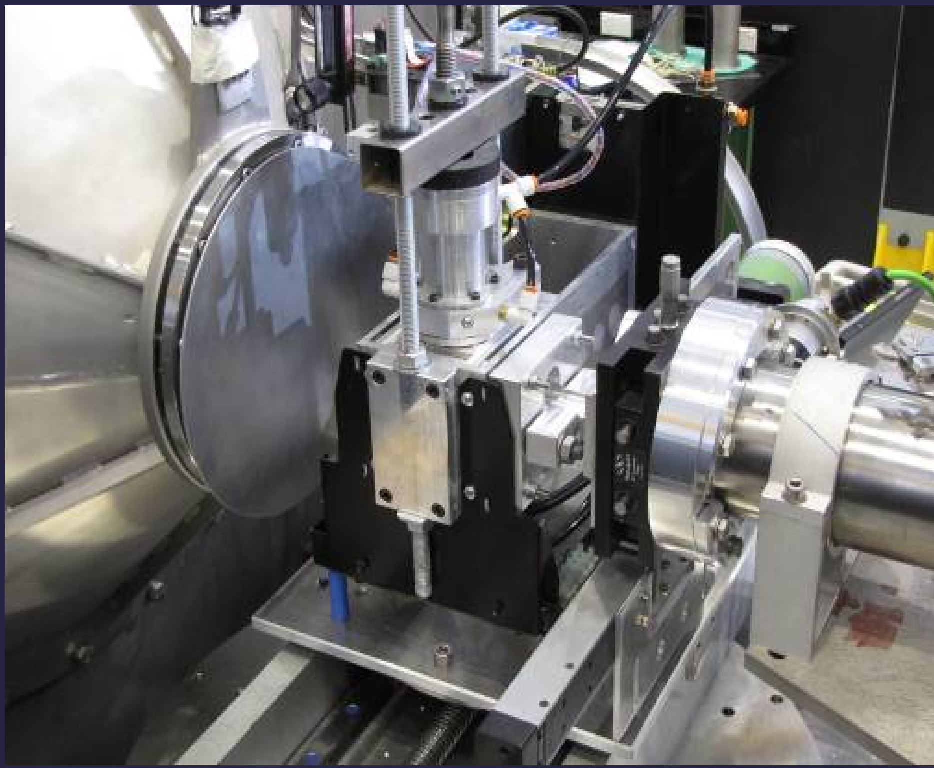


Simultaneous RVA and SANS



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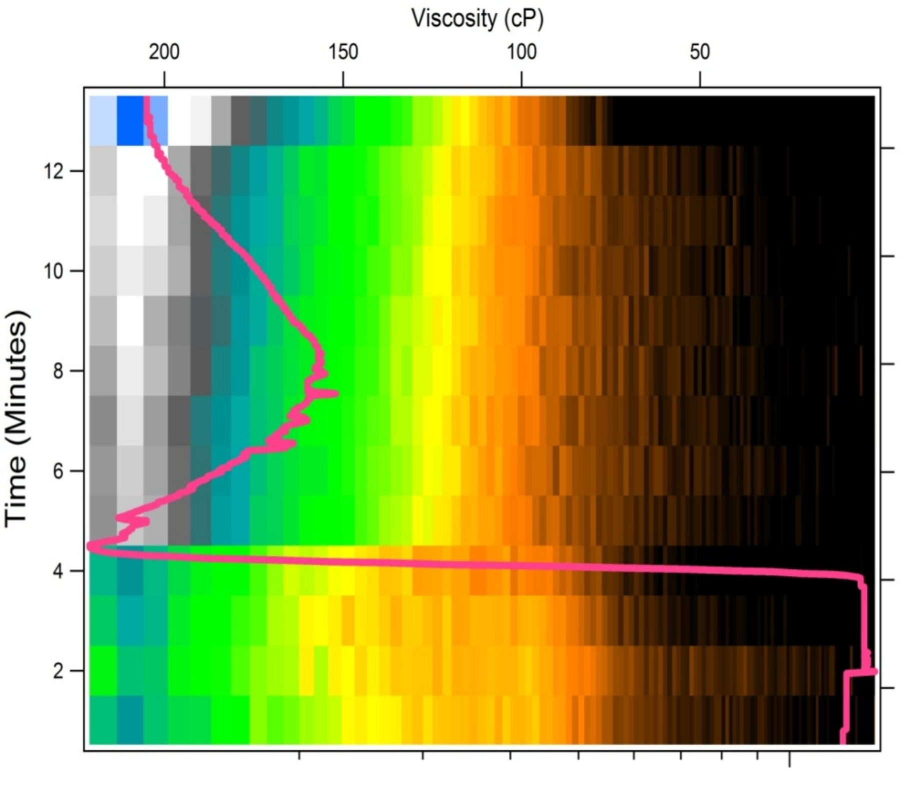
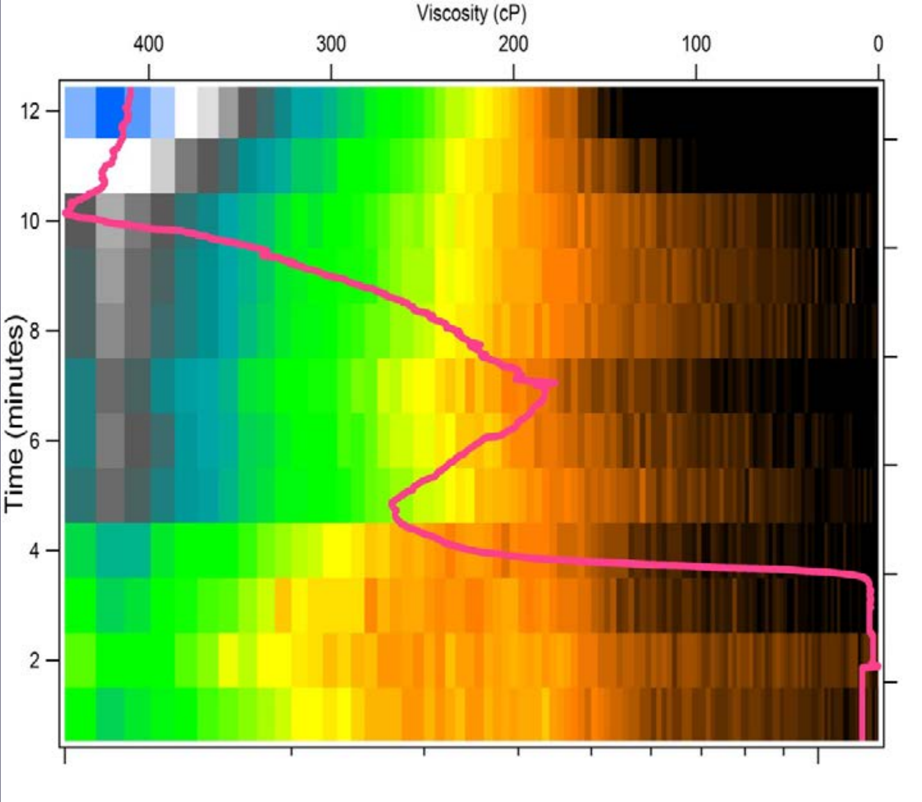
Simultaneous RVA and SANS





Waxy Maize

Tapioca

Analysis

- Lamellar peak disappears after 4 minutes in all of the starches tested
  - This implies a loss of periodic order in the starch structure
  - Very little change in lamellar peak up to this point
  - Correlates exactly with the point in RVA at which the viscosity starts to increase markedly
- After this point the slope of the scattering curve suggests the formation of progressively larger scale structures
  - These structures have the hallmarks of being fractal-type domains with dimensions on the 10’s of nanometer scale

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Advanced Analysis

- Tapioca and Potato pastes seem to form large scale aggregates
  - At least 16nm
  - Low fractal dimension suggesting topologically simple structures
  - Seem to be chain like or linear at the length scales probed here
  - Evidence of another structural level above this
    - Probably worm like structures seen in EM images and detected by USANS at Saclay

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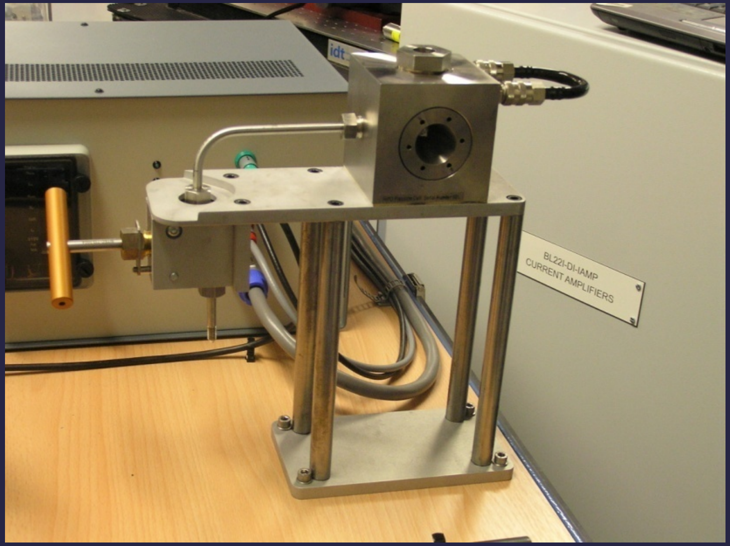
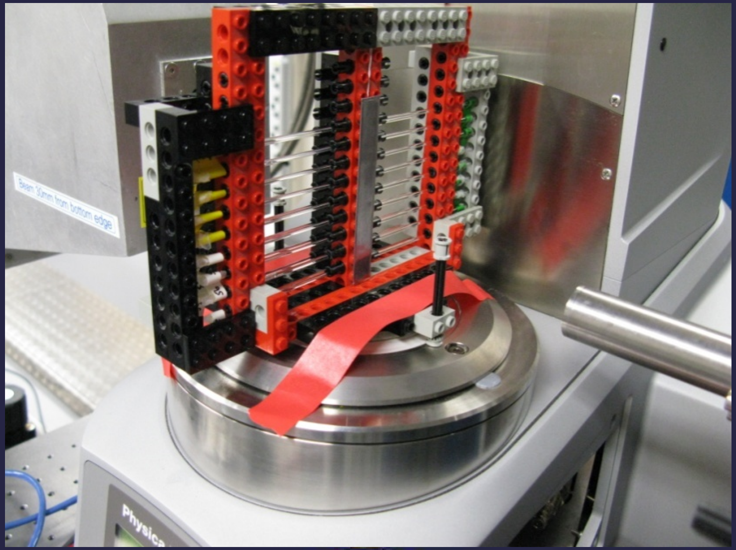
Advanced Analysis

- Maize and Wheat pastes form rather smaller aggregates
  - Dimensions ~8nm
  - Higher fractal dimensions (~2.70) – must be topologically rather complex
  - Aggregates show signatures of either being highly polydisperse or very branched – possibly both!!
  - Waxy maize is an intermediary
    - Monodisperse, large aggregates with considerable branching fraction
  - USANS/USAXS needed to probe higher level structures

SAXS sample environments

- Liquid flow cells
- High pressure cell
- Stop flow
- Rheometer
- Linkam heaters
- Tensile tester
- Syringe pumps
- Lego capillary ladder





Resources

- SasView (NSF)
  - Scattering models for polymers, colloids and particles
  - Handles x-ray and neutron data
- 'SANS Toolkit' – B. Hammouda, NIST
- NIST and APS macros – IGOR (x-rays/neutrons)
- FISH

Further reading

- Small-angle x-ray scattering, eds. O. Glatter, O. Kratky, Academic Press 1982
  - Available as free download
  - *physchem.kfunigraz.ac.at/sm/*
- Structure analysis by small-angle x-ray and neutron scattering, L.A. Feigin, D. I. Svergun, Springer 1987
  - Available as free download
  - *www.embl-hamburg.de/biosaxs/reprints/**feigin_svergun_1987**.pdf*

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Thanks for your attention!