Introduction to scattering techniques

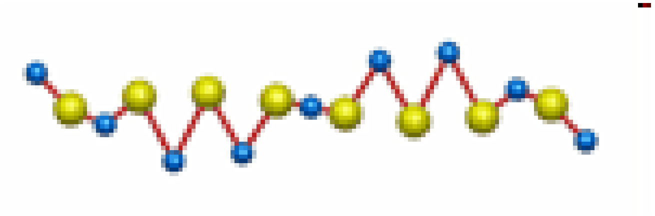
or

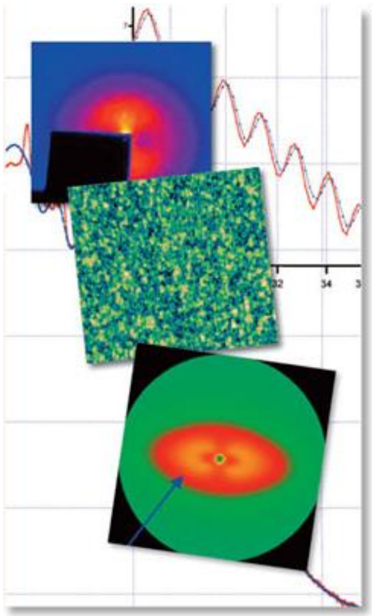
What you always wanted to know about scattering

1- Generalities about scattering techniques

2- Hands on

3- Wrap-up





- Scattering techniques :

  use the scattering of a beam by matter to learn about the structure of the illuminated material

Or

- What can we learn from the materials through the observation of the scattered intensity

What is scattering good at ?

- Methods for looking into microscopic details : microscopy/scattering
- Unfortunately not every thing can be seen through microscopes
- Scattering allows to “see” things through the reverse (Fourier) space / Unfortunately we are not too good at seing in the Fourier space…
- It is an averaging techniques (measure a large number of particles typically $>10^{10}$)

Scattering techniques for material characterization

- Scattering process (ray-matter interaction) to characterize the material structure and dynamics
- Neutron, X-ray, Light
- Scattering for average/instantaneous structure : “static” scattering
- Dynamics : Probing (Brownian) Motion using scattering (Time resolved / Energy resolved)

What can it do for me? How?

- Probing Wave : **<u>Neutrons, X-rays, Light</u>** , also Electrons, microwave, muons , acoustic waves…

- A large class of experimental techniques that use the scattering of a radiation as a probe for structural studies

Microscopic origin of scattering / contrast

- Different rays have different type of interaction with matter

Xrays : a broad range of high energy electromagnetic waves (short wavelength)

scattering experiments are often done with "hard " X-rays wavelength of the order of 0.1 nm

Xrays are scattered by the electrons (Thomson) around atoms

Senses Electron density (density!)

Visible light : much larger wavelength (visible light between 400 nm and 700 nm)

light scattering is resulting from the polarizability of the medium induced dipole and reemission Rayleigh scattering (oscillating dipole picture)

Neutrons : Interaction neutrons with nucleus (Neutrons + Protons)

Best described by quantum mechanics…

X-ray vs neutrons

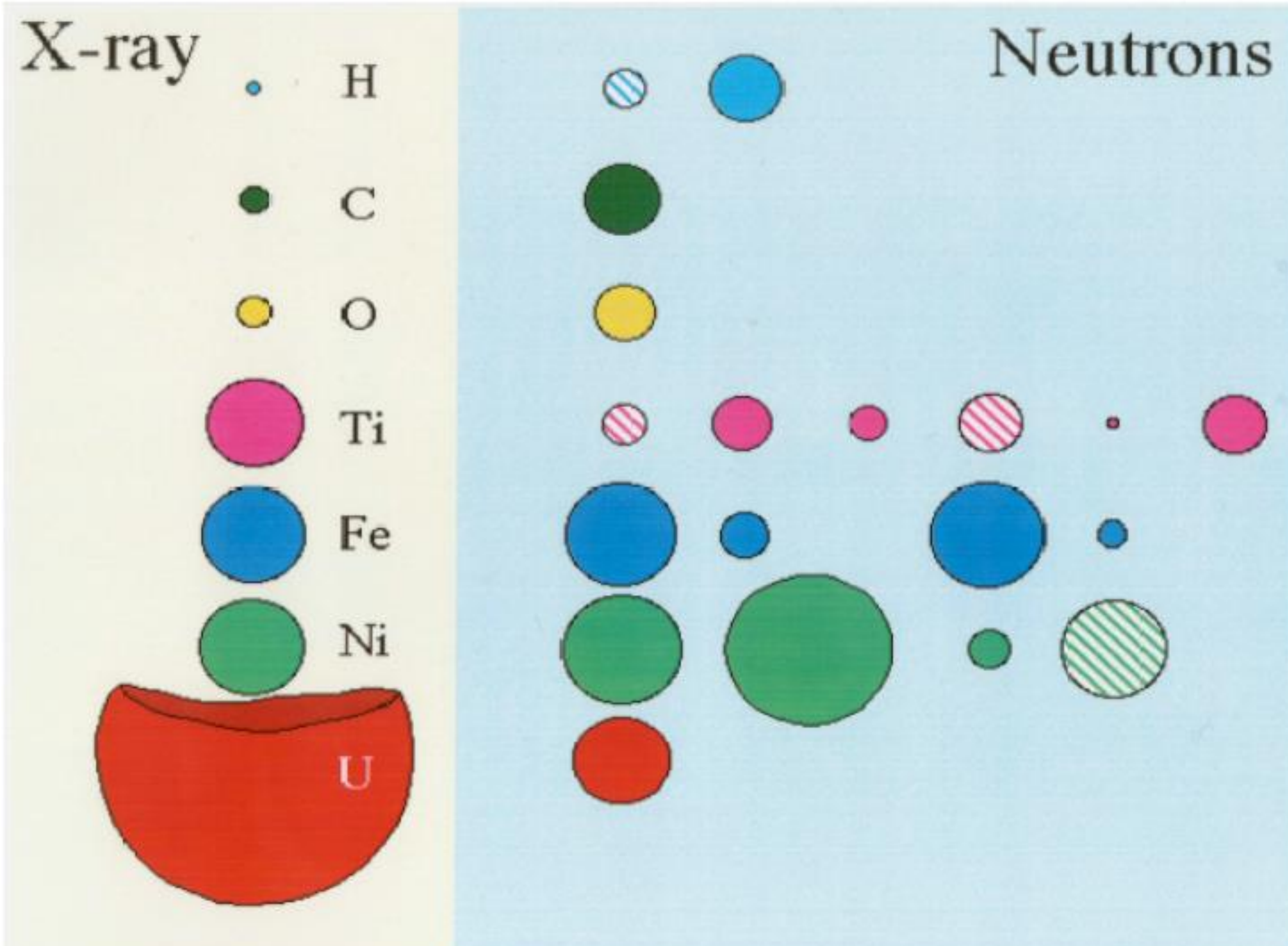
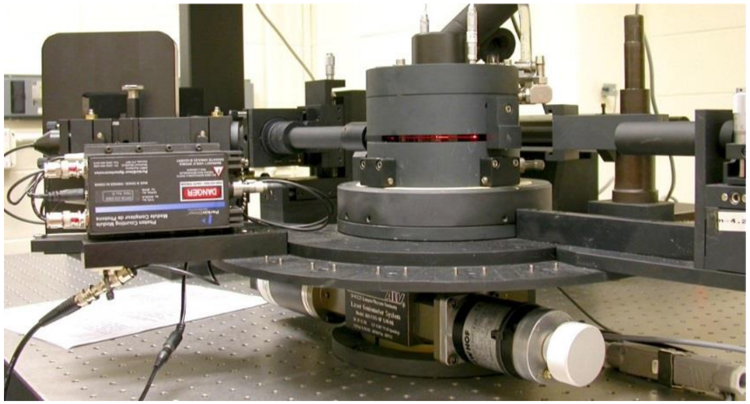
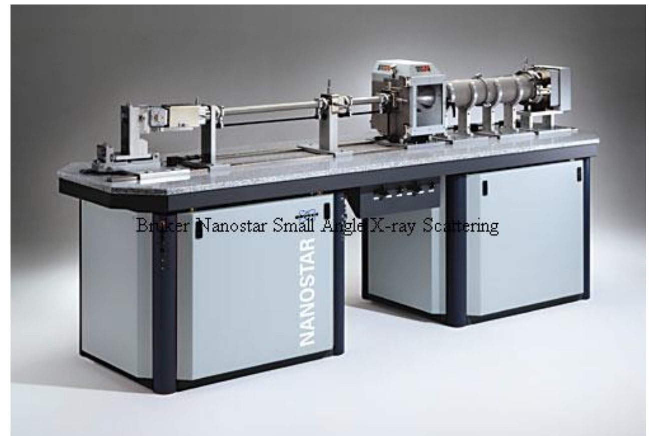
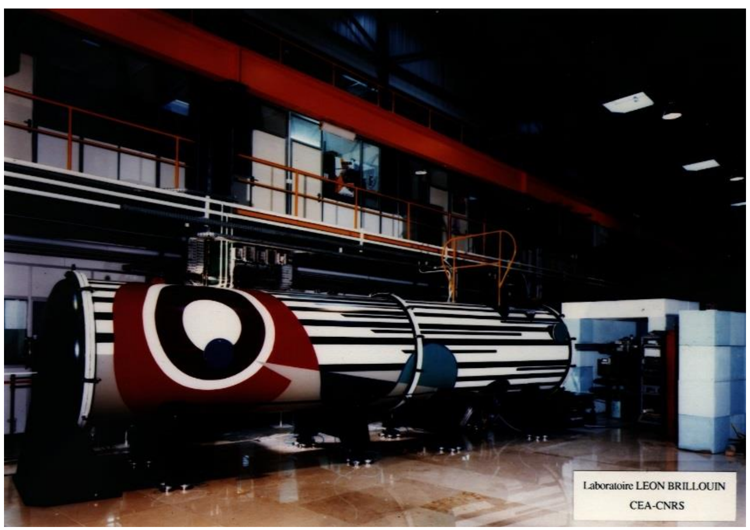


Figure 1.4: Scattering strength of atoms (isotopes) for X-rays and neutrons

Source / Spectrometers





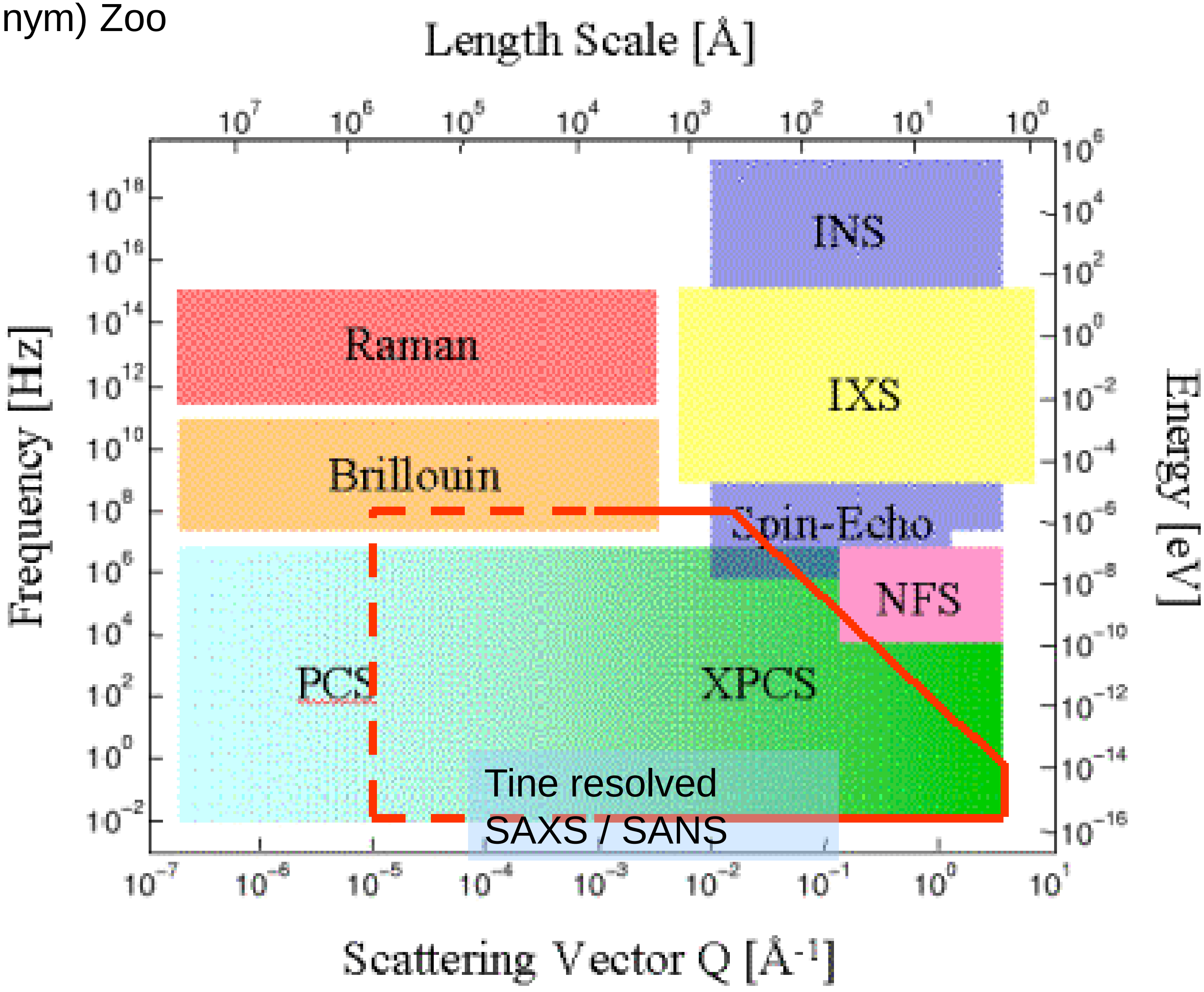


A number of scattering techniques

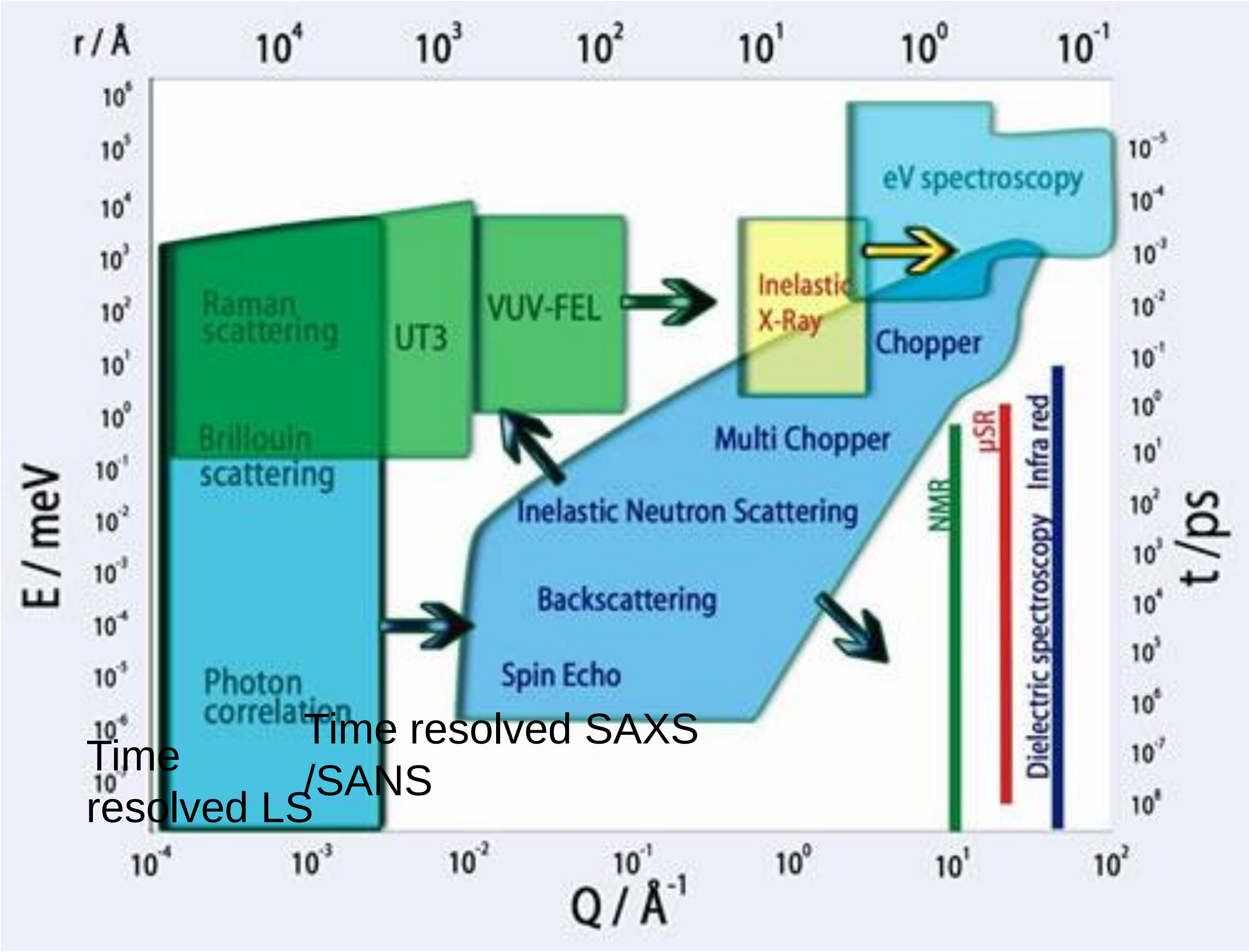
- Many different names (sometimes can prove confusing)
- A broad range of Time (energy) and space (scattering wave vector resolution)
- Distinction between
- "static" : elastic scattering . Structural information

- and "dynamic " : inelastic/quasielestic scattering : dynamic information

The (Acronym) Zoo

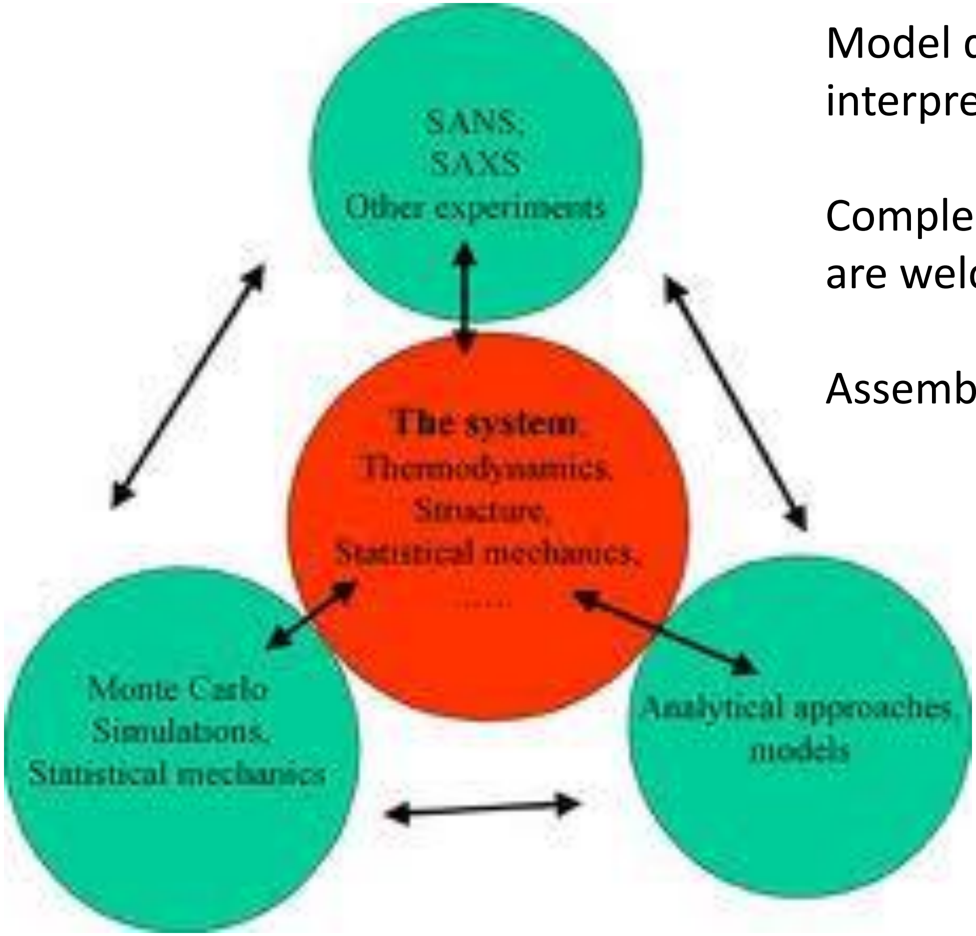


The Zoo



r / Å
10^4 10^3 10^2 10^1 10^0 10^{-1}
E / meV
t /ps
Q / Å^{-1}
Raman scattering
UT3
VUV-FEL
Inelastic X-Ray
eV spectroscopy
Chopper
Brillouin scattering
Multi Chopper
Inelastic Neutron Scattering
Backscattering
Spin Echo
Photon correlation
NMR
μSR
Dielectric spectroscopy
Infra red
Time resolved LS
Time resolved SAXS /SANS

Methods



Model dependent data interpretation

Complementary method are welcomed

Assembling the puzzle

Methodology

- Identified what is it you want to know

(size, structure,…)

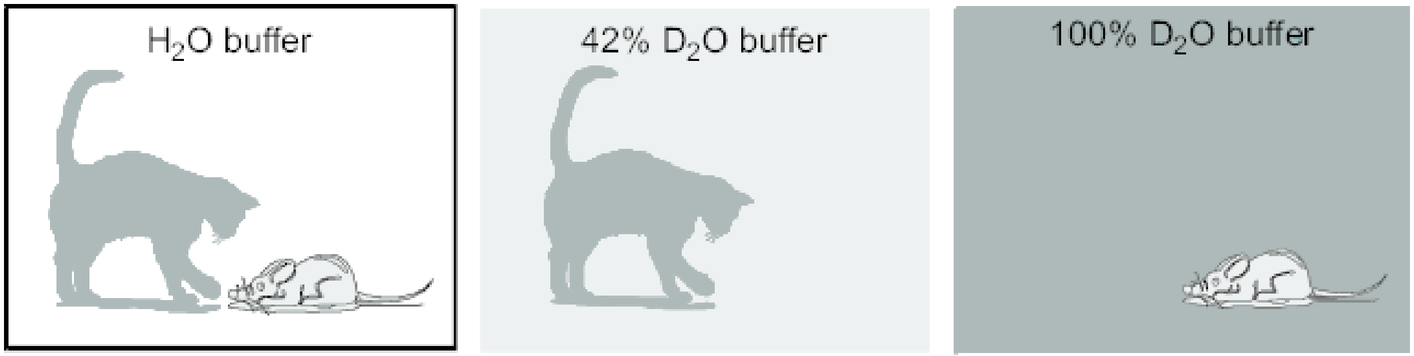
- Select the technique(s) that could best provide the (partial) answer
- Adjust the sample conditions (concentration, contrast conditions,…)
- Experiments in facilities require proposal application

Scattering of polymer melt and solid

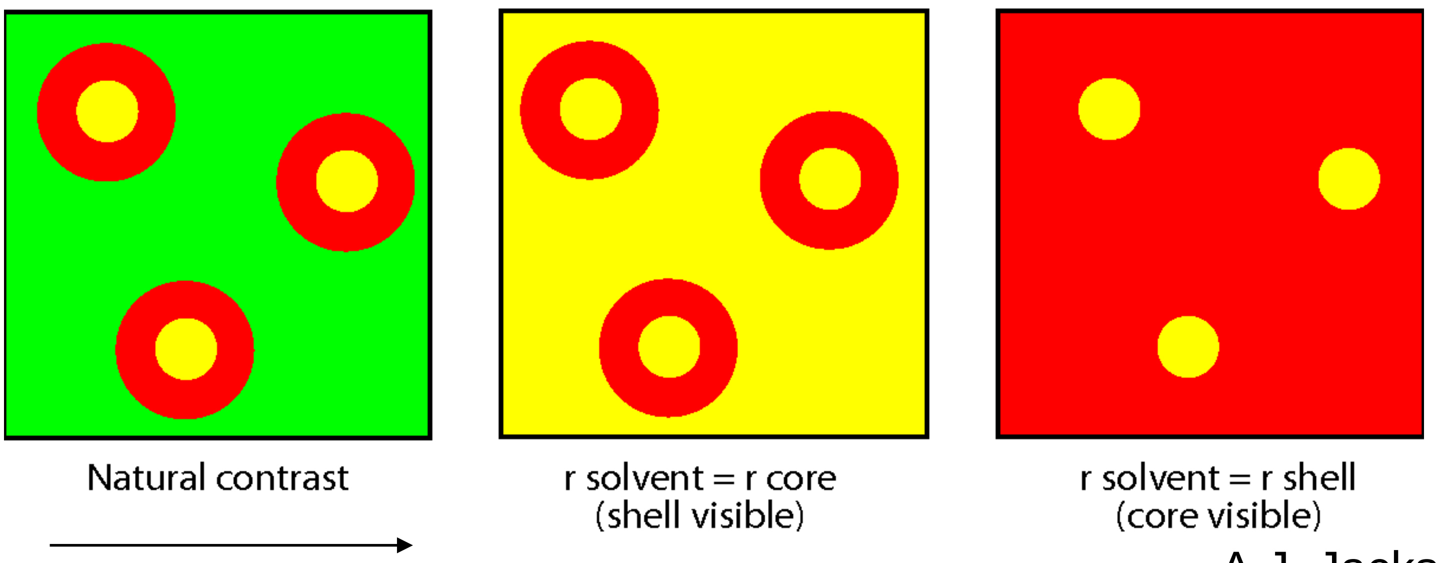
- Pure melt : no contrast / scattering mostly from density fluctuation short length scale not much info on structure of polymer (interesting for glass transition)
- Case of semi-crystalline polymer / strong scattering from crystalline lamellae crystallization kinetics (SAXS-WAXS)

- NEUTRON : the deuteration game
  strong H/D contrast allows to create contrast for neutron scattering without changing too much the polymer (weak chemical difference berween deuterated and hydrogenated polymer.
- This allows to look at chains or part of chains in a melt

The contrast game SANS

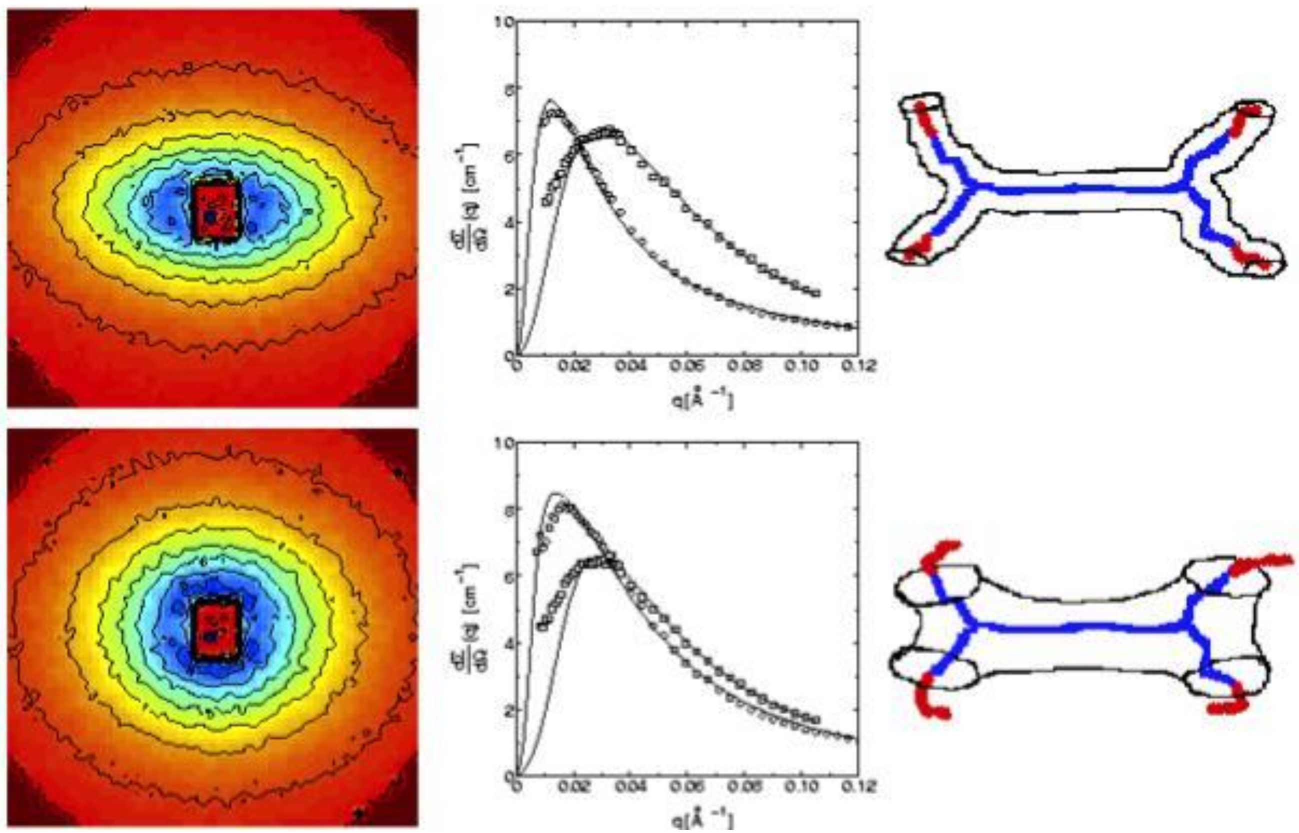


D.J. Callway 2011



A.J. Jackson 2008

Use of H/D contrast for relaxation experiments



(a) Small-angle neutron scattering intensities for a stretched H-polymer sample (two-dimensional detector image). (b) Intensity cuts along the directions parallel to the deformation (open circles) and perpendicular to the deformation (open squares) compared with theoretical calculations for the sample strained to □ = 2 after annealing times “0” and 6 □ 10–2 s at 25□C (the sample was quenched to –85□C). The term d□/d□(q) represents the absolute macroscopic cross section. (c) H in polymer in its confining tube immediately after deformation (the arms are fully confined), and after 6 □ 10^{-2}s, when the arms have relaxed by 12%.

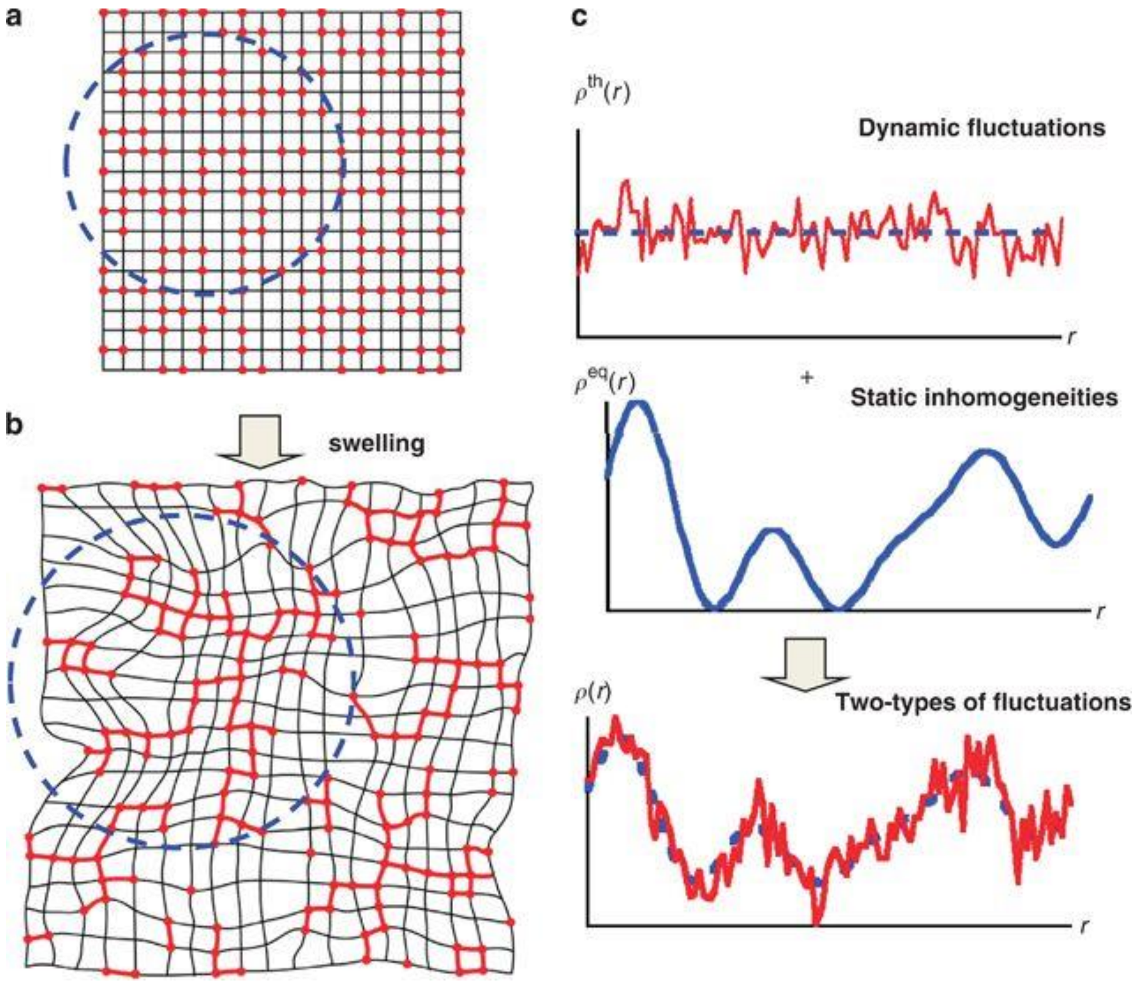
- Static scattering :   SANS, SAXS, LS

I(q) to gain some understanding of the constituants and their structure and interactions

Molecular weight of chains

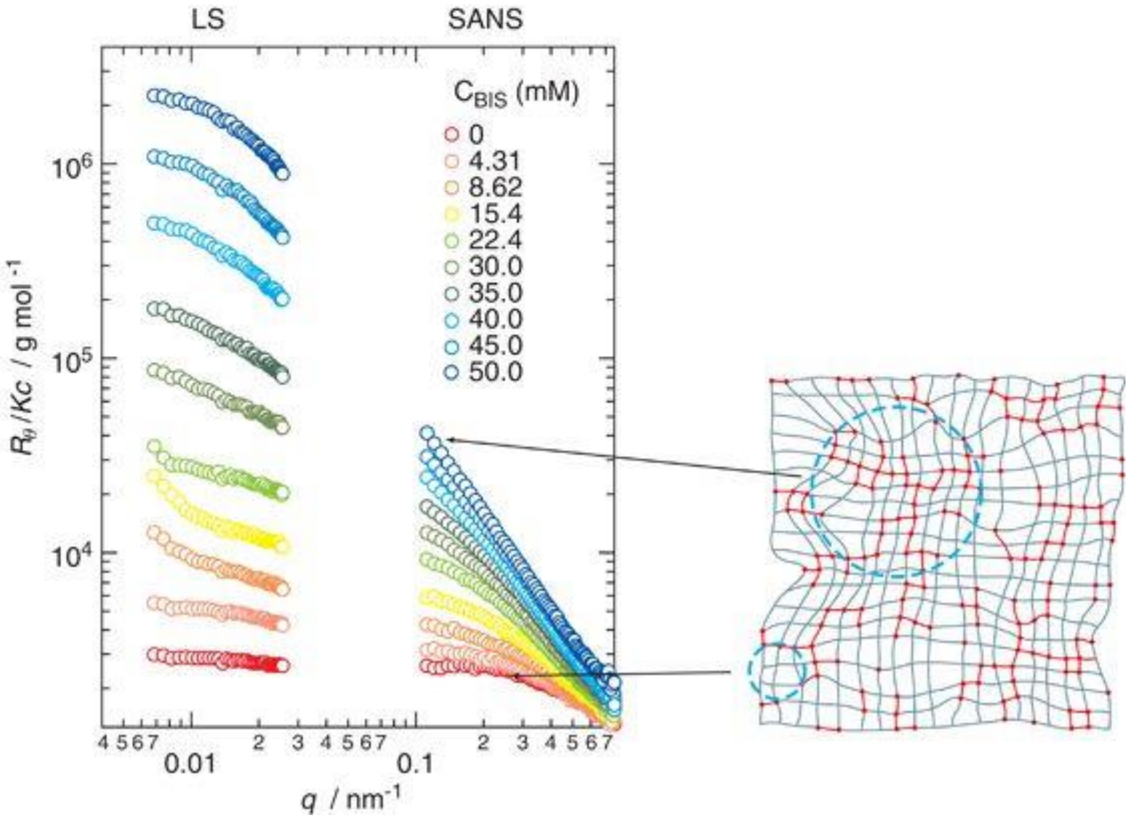
Structure of chains, but also establish phase diagram, etc…

Scattering by network / gels



Swelling heterogeneities

Scattering by network / gels



Mitsuhiro Shibayama

Polymer Journal **43**, 18–34 (2011)

Light scattering

- Strong points :

Home based / cheap instrument Strong sources (laser)

Weak points :

Require almost transparent samples

Limited q-range → limited resolution (a bit better than an optical microscope) due to the long wavelength (500 nm)

What can it do for me ?

- M w, Rh, Rg, A2 , some info about polydispersity

SAXS

- At home : weak source . At synchrotron facilities (1000 times brighter) (1 hr→ 1 s…) extended q-range
- Pb : contrast / beam damages

- What can it do for me ?
- Form factors , structure factors
- Kinetics measurements : high flux → short measurment time (~0.1s) or faster
- Microfocus beam : spatial resolved (μm or even less) /

Spatially resolved SAXS for inhomogeneities

SANS

- Low flux → long counting time (no (very)fast kinetics)
- Advantage : proton/deuterium contrast
- No radiation damage

- What can it do for me ?
- Form factor in concentrated systems (zero average contrast)
- Contrast variation for labelled systems
- Long experiments without raraition damages

references

- A number of school :
  Juelich (http://www.fz-juelich.de/iff/wns_lab_now neutrons) , Bombannes (SCATTERING METHODS APPLIED TO SOFT CONDENSED MATTER , http://www.ill.eu/news-events/events/bombannes2010/),
  Grenoble (Hercules, http://hercules.grenoble.cnrs.fr/accueil.php?lang=en , facility) and others …,
- A number of good text book exist, some from the schools mentioned above Bombanes School / Julich school
- SAXS : historical book SAXS Guinier / SAXS by Porod
- *Dynamic Light Scattering,* Berne and Peccora,(physics oriented)
- Dedicated to Polymer :
  Methods of X-ray and Neutron Scattering in Polymer Science (Topics in Polymer Science), 2000 RJ Roe,
  Polymers and Neutron Scattering, 1997, JS Higgins and H.Benoit
- More practical books from Springer laboratory series
- *Light Scattering From Polymer Solutions And Nanoparticle Dispersions, 2007 ,*W. Schartl (a good introduction) ,
  X-ray scattering of soft matter, 2007, N. Stribeck
- Most polymer physics book have a chapter on scattering

Examples

- How do I measure the size, molecular mass, polydispersity of a given batch of polymer ?
- Polymer characterization by dilute solution (dynamic) light scattering
  static light scattering
  Zimm plot :(1/I vs $q^2+\alpha c$)

M_w, R_g, A_2, from extrapolation $c \rightarrow 0$ and $q \rightarrow 0$

DLS : D → Rh

Case study

- Characterization of dendronized polymers in solutions by scattering :
- Measure of Rg vs M with GPC MALLS , persistence length
- Measure of form factor by SANS, fit with model form factor

Hands on Scattering experiments

- The small angle scattering toy model

Illustration of angular dependence, scattering intensity, contrast, Speckle Dynamics

- SLS /DLS setup x3
  - denpol solution
  - colloidal dispersion
  - polymer solution and gels

Attention Be ware : LASER light

- Static and dynamics

- Xray, neutrons, light

- Angular dependence of intensity

Take home message

- Scattering a range of powerful techniques for structural (including dynamics)
- Broad range of time and spatial resolution
- It measures in the reciprocal space (Fourier transform of the direct space)
- Neutron / Light / X-rays
- Light scattering : probably the simplest techniques , easily available , but with limited resolution (wave-length ~ .5μm)

SLS : measures intensity (in absolute units) and its angular (scattering wave vector) dependence :

I(q→ 0) : molecular mass (Mw)

I(q) → size of the coil R_g

DLS : probes the brownian motion of coil , mostly center of mass diffusion Get a diffusion coefficient D , and an hydrtodynamic radius Rh : an easy size measurements.

SANS : the contrast between H and D for neutrons allows to probe polymer melt . The right q-range for polymer coil

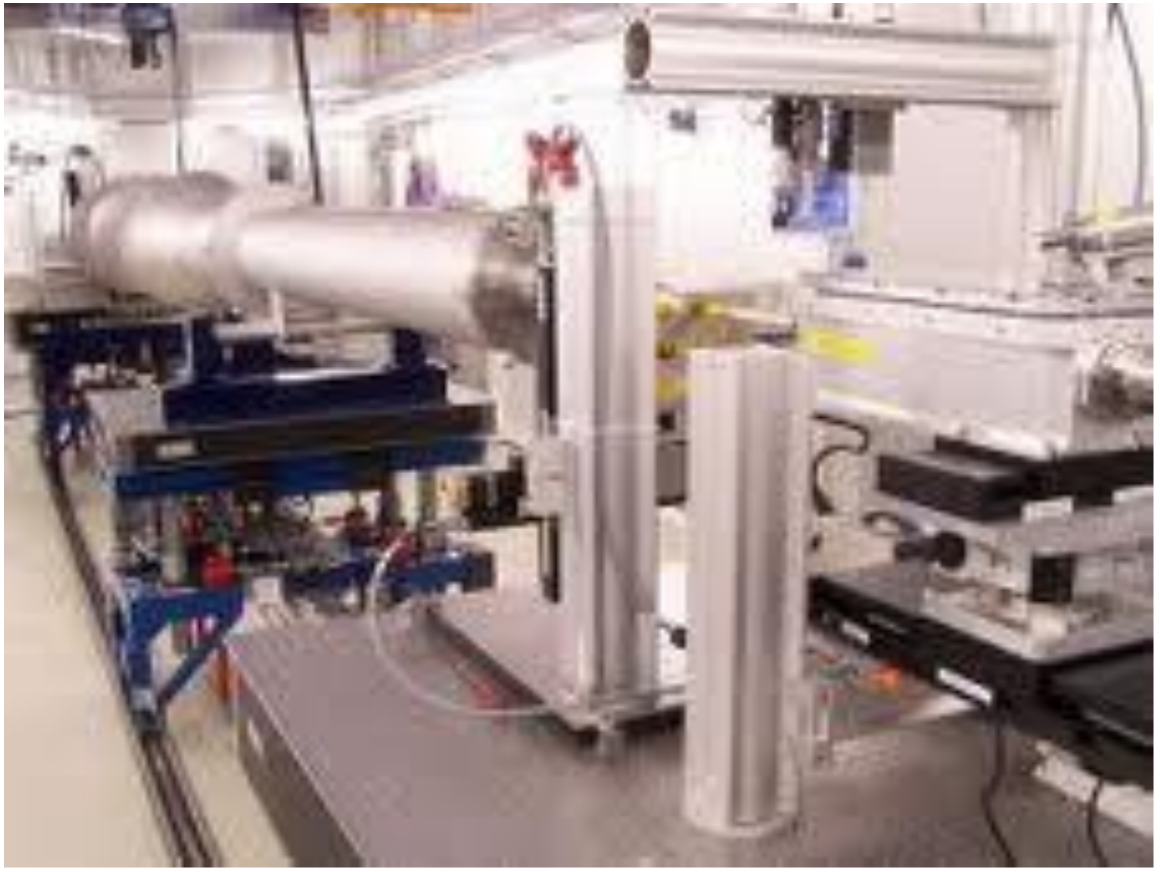
Form factors / Structure factors are measured intensity is also there

Dynamic can be obtained through time resolved measurement

More elaborate techniques for dynamics (NSE, inelastic, quasi-elestic)

SAXS : (WAXS) ideal for measuring crystallization , can also do for solutions right q –range (0.15 nm)

Some dynamics x-rays technique : XPCS (the synchrotron X-ray version of DLS) limited to slow time (>ms)



What does what ?

STATIC STRUCTURE :

- Neutron SANS : contrast (often require deuteration of samples; often the only possibility when it comes melt)

Needs to be done in large facilities, requires research proposal application

- X-ray : SAXS-WAXS : lab based set-up (getting better and better) ; synchrotron experiments : large facilities, research proposal required

- Light scattering : SLS/DLS is good for characterization (GPC-MALLS) , Rh

Hands on…

- The LS basic :
- Angular dependence of intensity
- Value of the intensity
- Diffusion of the particles
- Small Angle Scattering :
- 2D detector : position – angle : multiple q
- Small angle (forward) scattering
- Kinetics measurements I(q,t) ; ex : phase separating systems (equivalent to a movie of phase separation)

Scattering by gels

- Crosslinked vs Semi-dilute solution
- Melt what can be done ?: not so much due to lack of contrast…main fluctuations of density are short range molecular length + (complex longer scale heterogeneities)
- Swollen Gels : swelling heterogeneities (due to the heterogeneities of crosslink)
- (not so clear hoe they relate to the properties …. May be in hydrogel for collapse/swelling kinetics
- Scattering and double network :

What length scales to look for ? (interpenetrating network)