Small angle scattering techniques (neutrons and X-rays) applied to self-assembled systems, polymer networks, and nanocomposites (under deformation)

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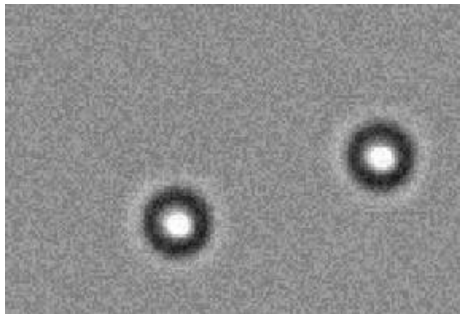
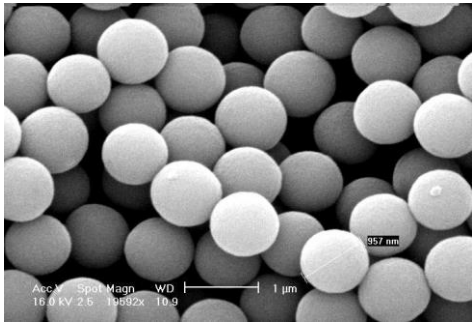
SoftComp SOFT MATTER COMPOSITES

DoDyNet Winter School January 2019

Building blocks of soft matter

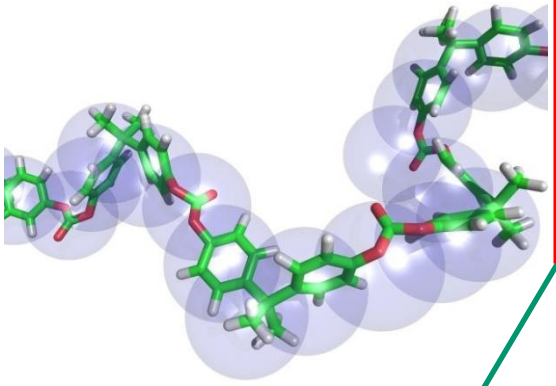


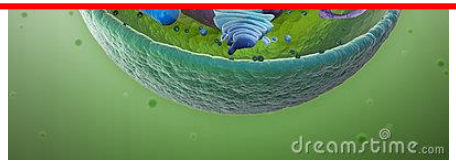


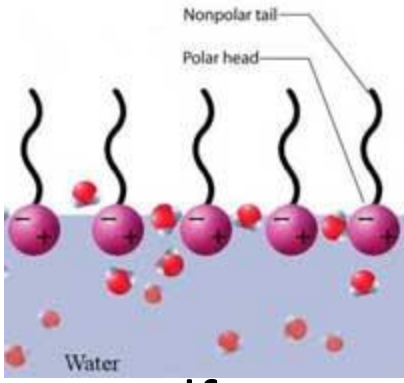
colloids

cells

Order on the mesoscale = can be studied by small-angle scattering (SAS)







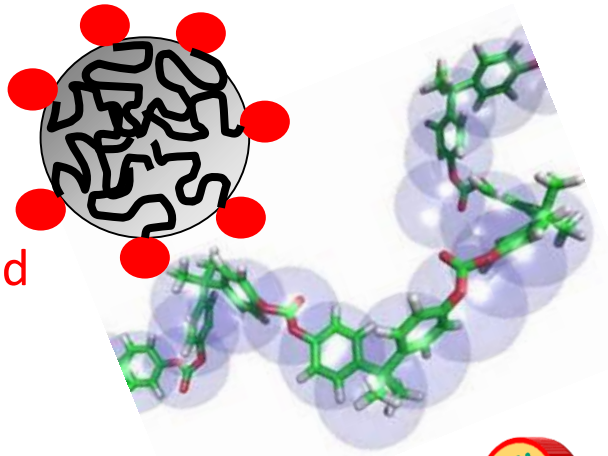
polymers

liquid crystals

self-assembled systems

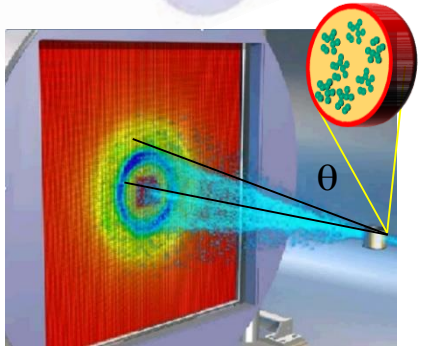
Outline

1) Soft matter as microstructured systems



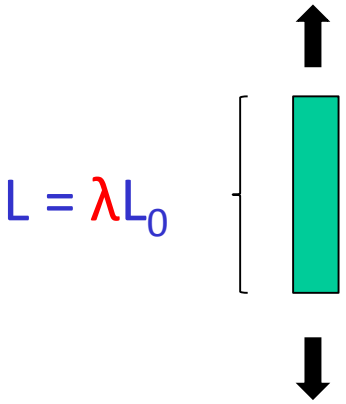
- Surfactant self-assembly
- Polymer systems: molecules, networks, particles and nanocomposites

2) Structural analysis by small-angle scattering



- Principles: contrast, scattering process
- Shape analysis, a 'math-free' Fourier transform
- Applications: micelles, bilayers, polymers, surfaces, aggregates
- Interactions and pair correlation

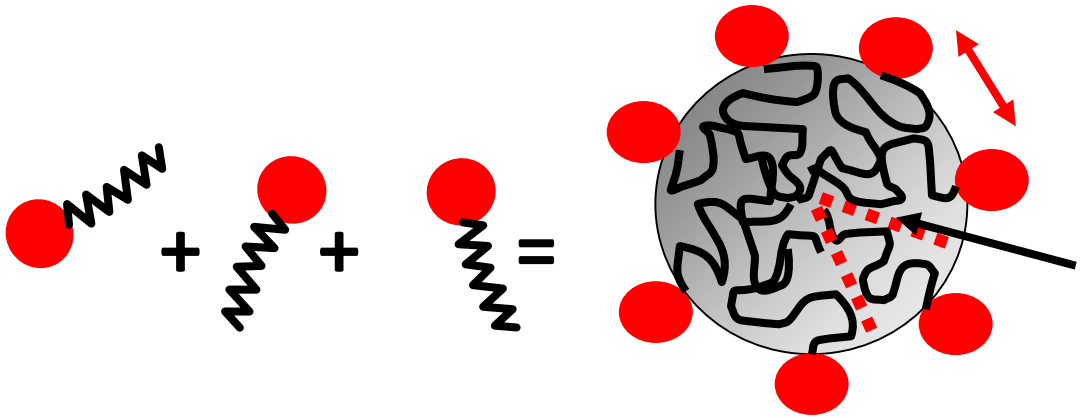
3) Scattering under deformation



- Experiments and geometries
- Affine deformation and networks

Self-assembly

Above the critical micellar concentration (cmc), surfactant molecules self-assemble:



repulsion → surface

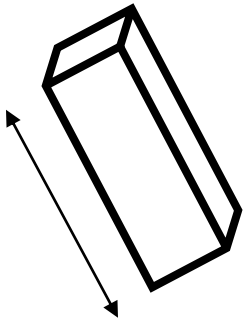
per head group A

hydrophobic attraction

Spontaneous curvature of monolayer: 'geometric' packing constraints

Packing parameter $p = v/l_c A$

$R \leq l_c$ (chain extension)



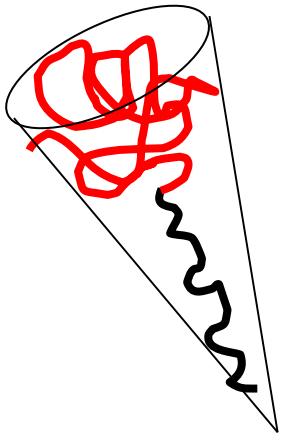
Israelachvili, Mitchell, Ninham, *J Chem Soc Farad Trans* **1976**, I 72,1525

Israelachvili, 'Intermolecular and Surface Forces', Academic Press **1995**

Schematic phase diagram of non ionic surfactants

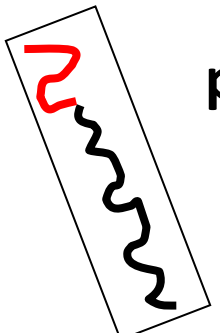
(T=const.)

Surfactant: POE

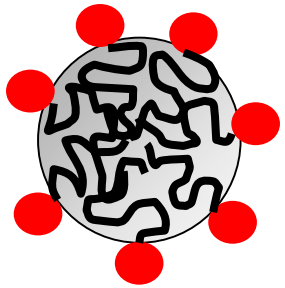


p = 1/3

Cosurfactant: pentanol, hexanol, ….

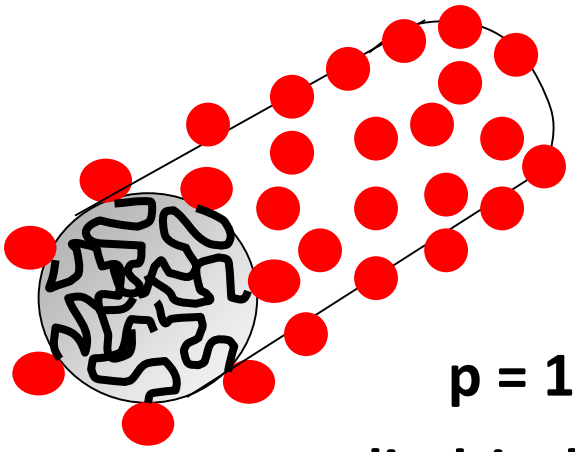


$p = v/l_c A = 1$



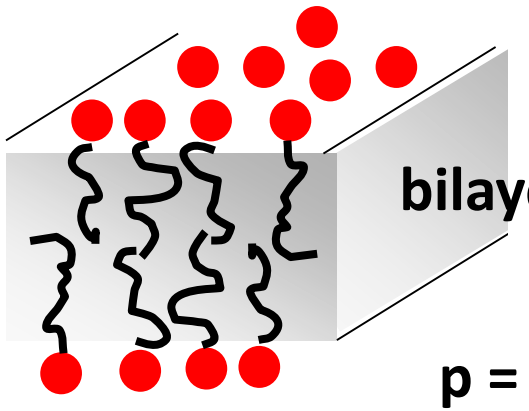
globular micelles

p = 1/3



p = 1/2

cylindrical micelles

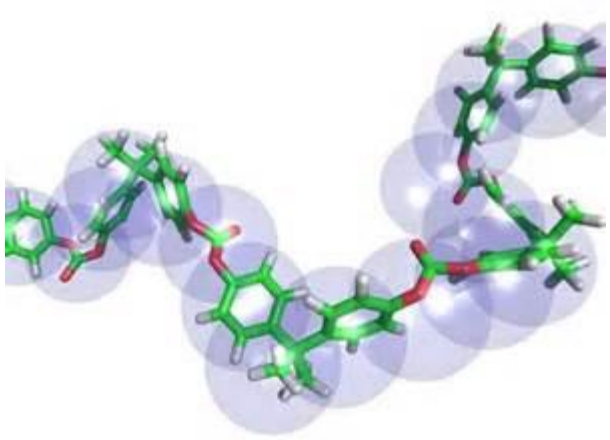


bilayers

p = 1

Polymer chains

Linear polymer chain (e.g. PEO, PE, PS):



Extended length **1.5 microns**
≈ 10^4 bonds ≈ 150 kg/mol

In (theta-)solvent: **R ≈ 15 nm**

- Number of conformations: $3^{10'000} \approx 10^{5000}$
- One picosec/conformation: (much) longer than age of universe

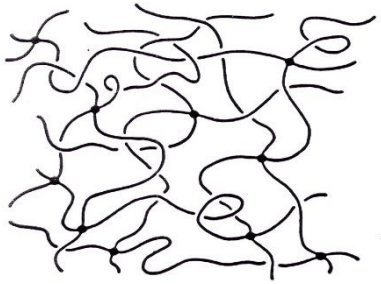
→ statistical description: $\mathbf{R_g = a\ N^{1/2} \sim M^{1/2}}$

How can this be measured?

Polymer systems

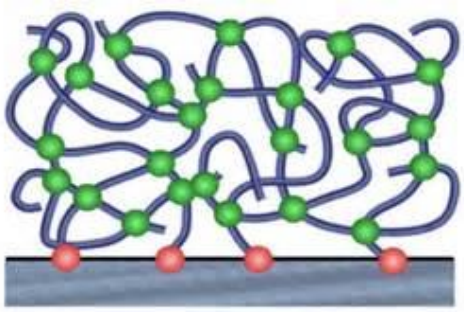
Polymer networks and gels:

with solvent; or dry
(melt or elastomer)



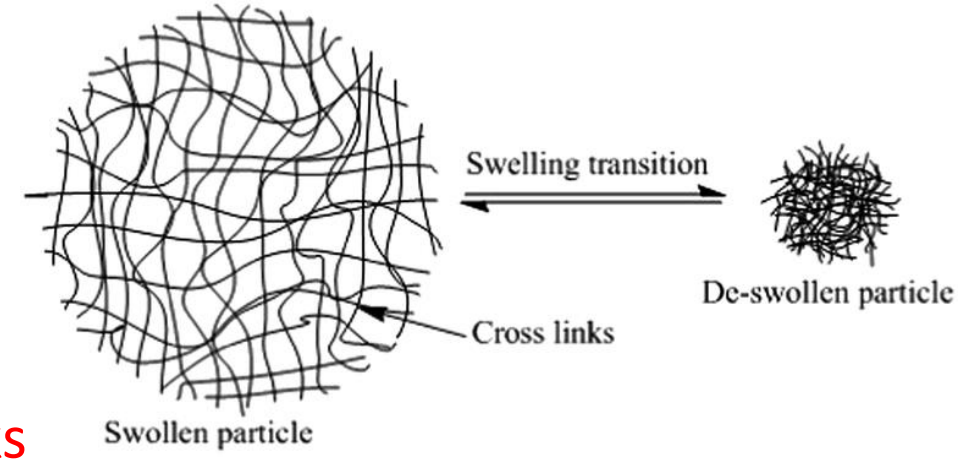
swelling

Polymer brushes:



colloidal stability;
lubrification

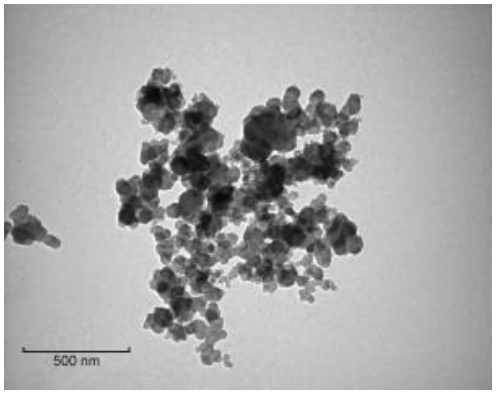
Polymer microgels:

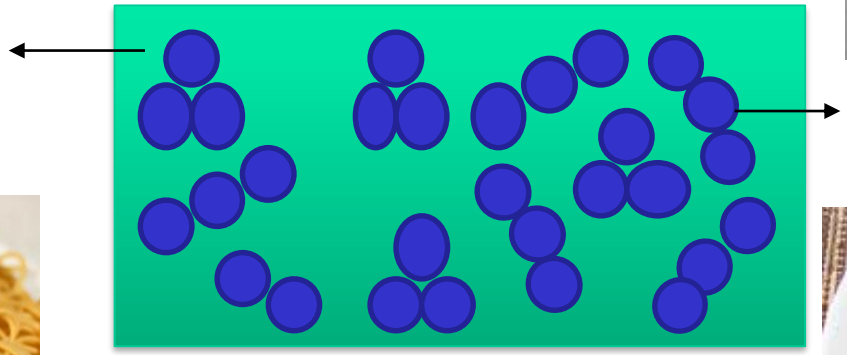


+ others: latex, polymer adsorption, interpenetrated networks

Polymer nanocomposites

multiphase materials
polymer + nanoparticles



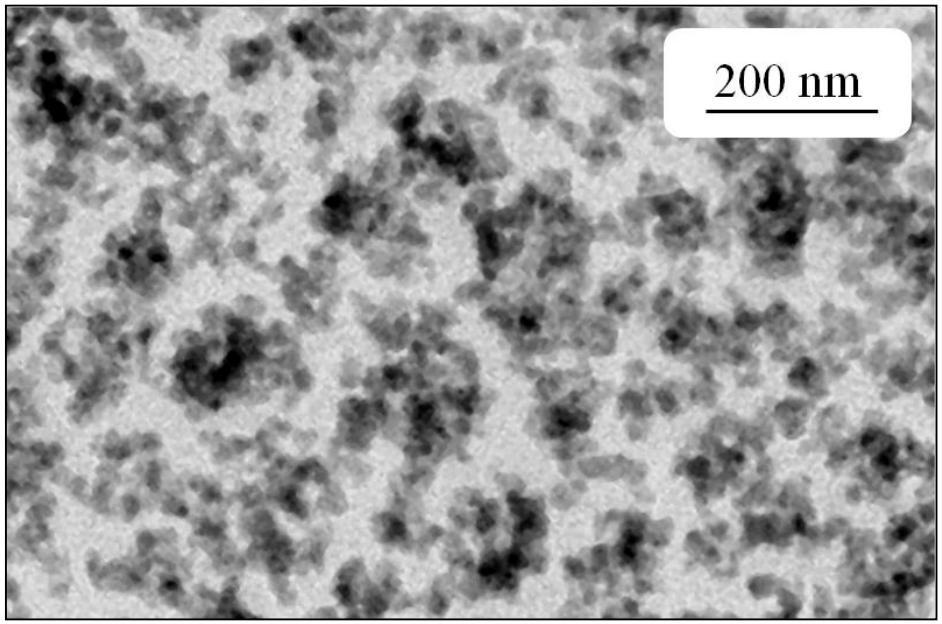


filler
(1 to 100 nm)

What is the structure of nanocomposites ?
Chain structure ? Filler structure ?
How to see one OR the other ?

How to measure structure of soft matter?

With electron microscopy:



Advantages:

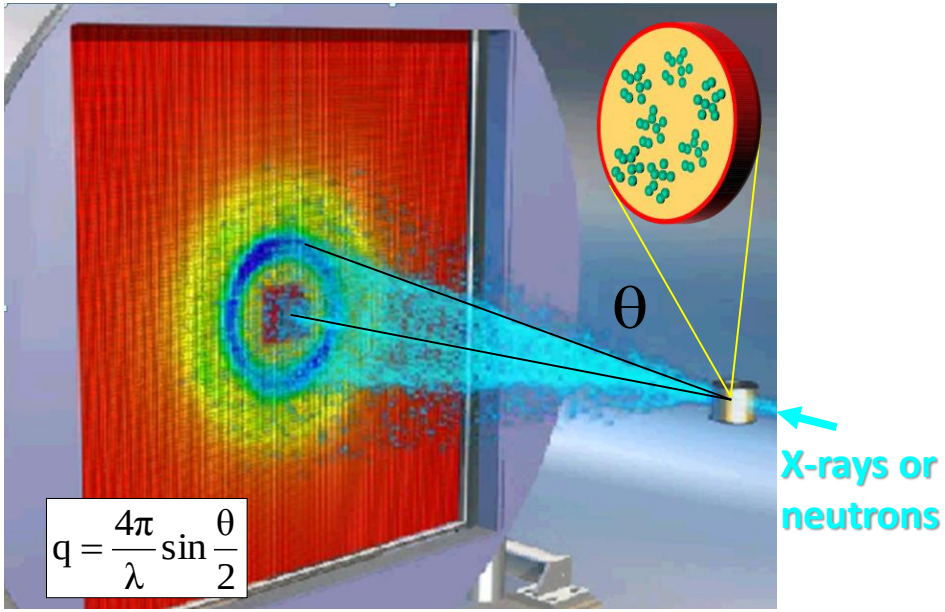
- Analysis is intuitive and simple

Problems:

- Only for filler, not chains
- 3D ?? (if not tomography)
- Statistical relevance ??

How to measure structure of soft matter?

By small-angle scattering:



Advantages:

- Statistically relevant (large sample)
- Fast and simple

Problems:

- Need contrast
- Exact inversion impossible: complex data analysis

→ Combine with other information:

- A priori knowledge of system
- Different techniques, in particular imaging

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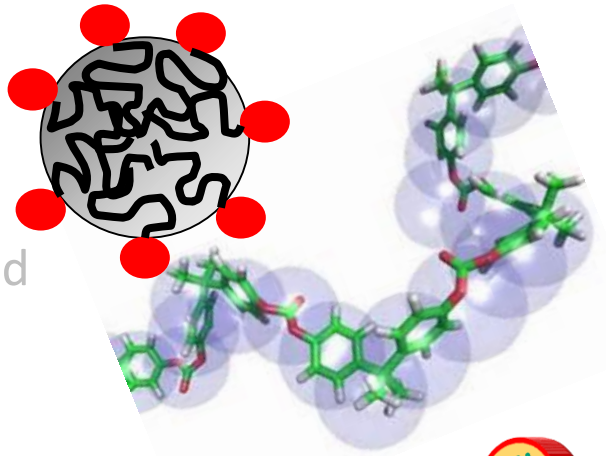

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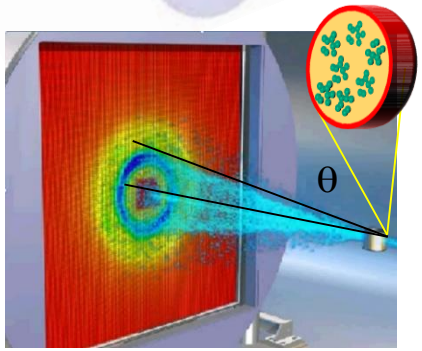
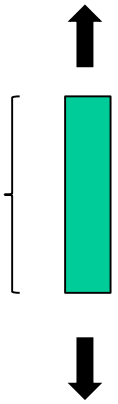


3) **Scattering under deformation**

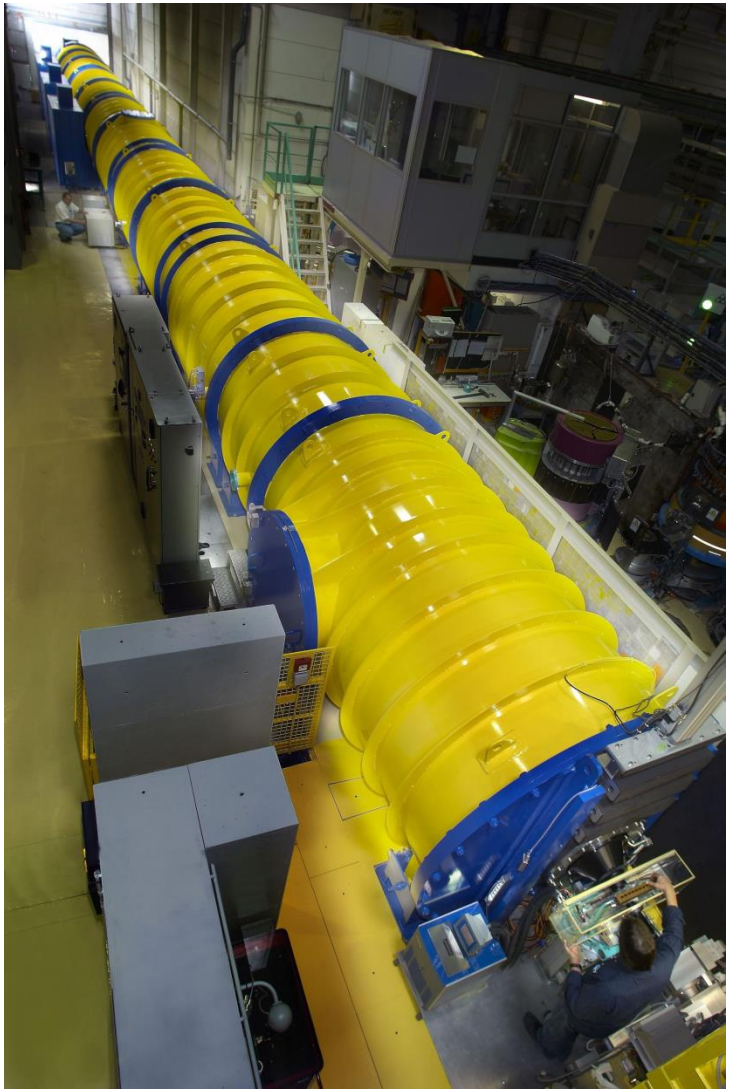
- Experiments and geometries

- Affine deformation and networks

$L = \lambda L_0$

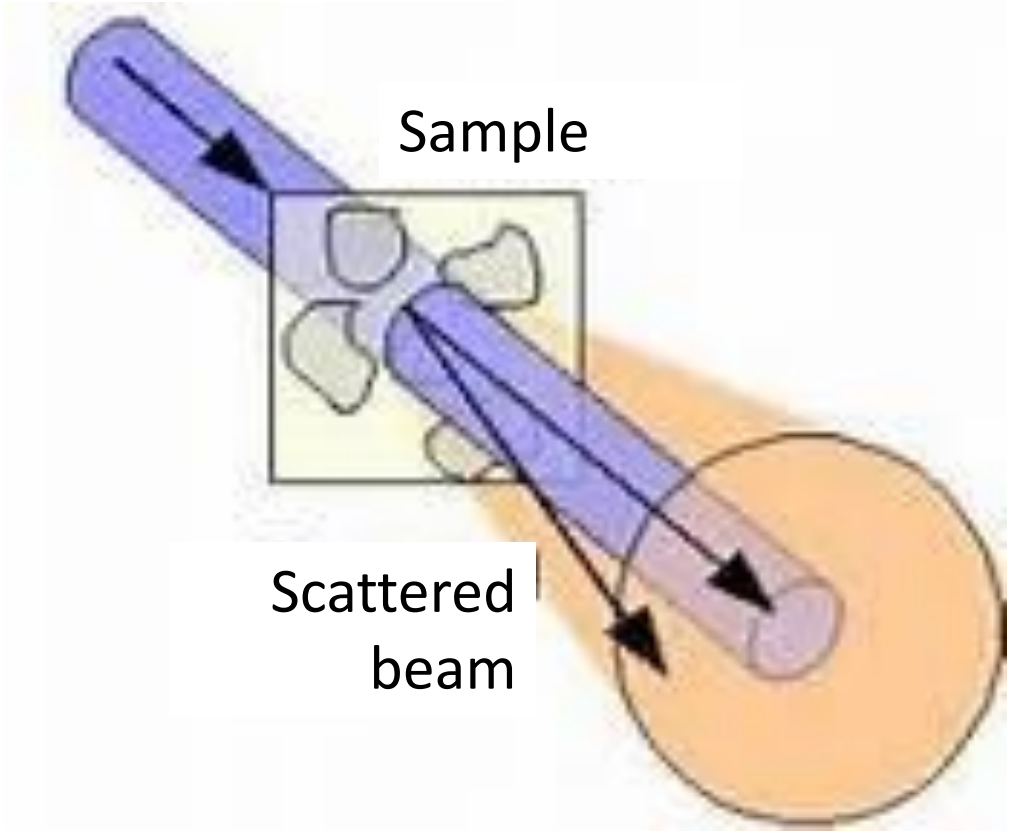


Small Angle (Neutron) Scattering: real instruments



D11, ILL Grenoble

Neutrons
or X-rays



Fourier transform !

Contrast

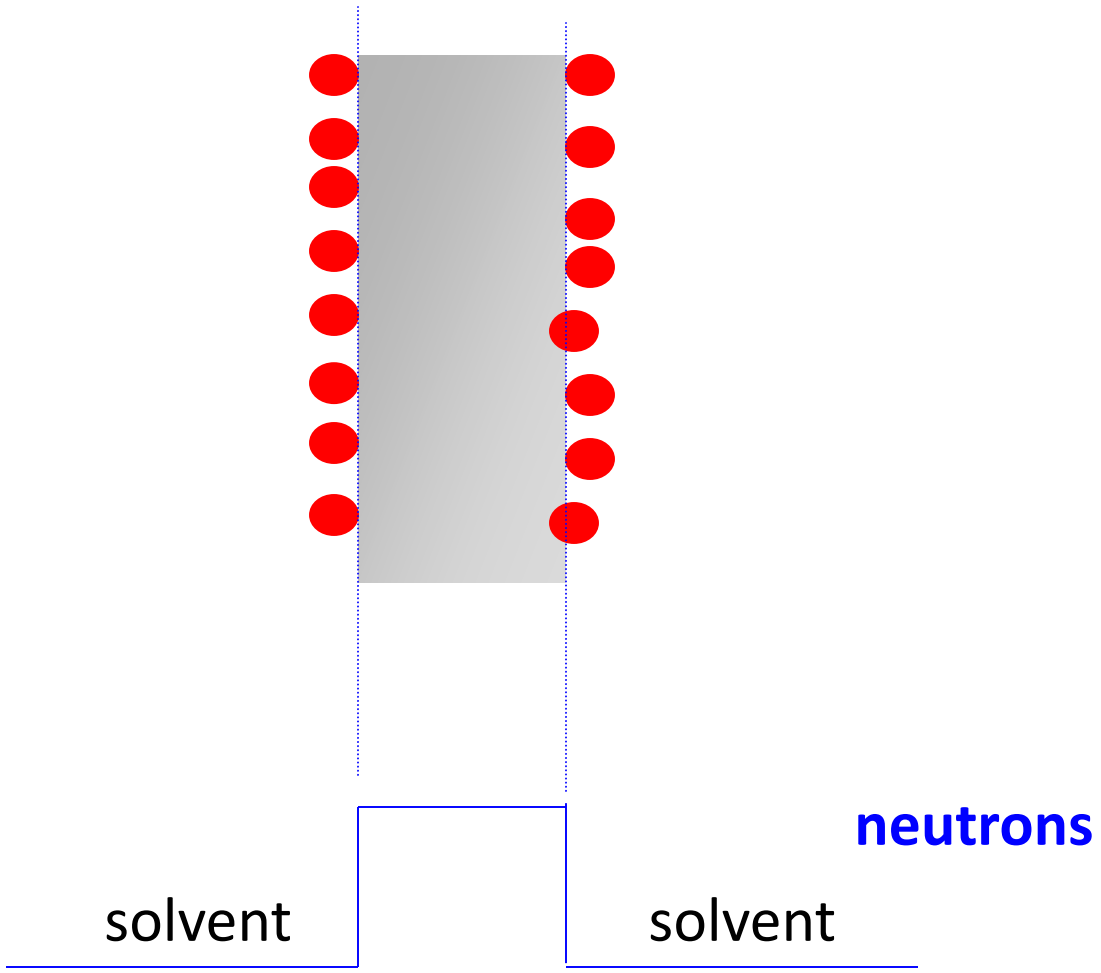
Contrast =

Difference in

scattering length

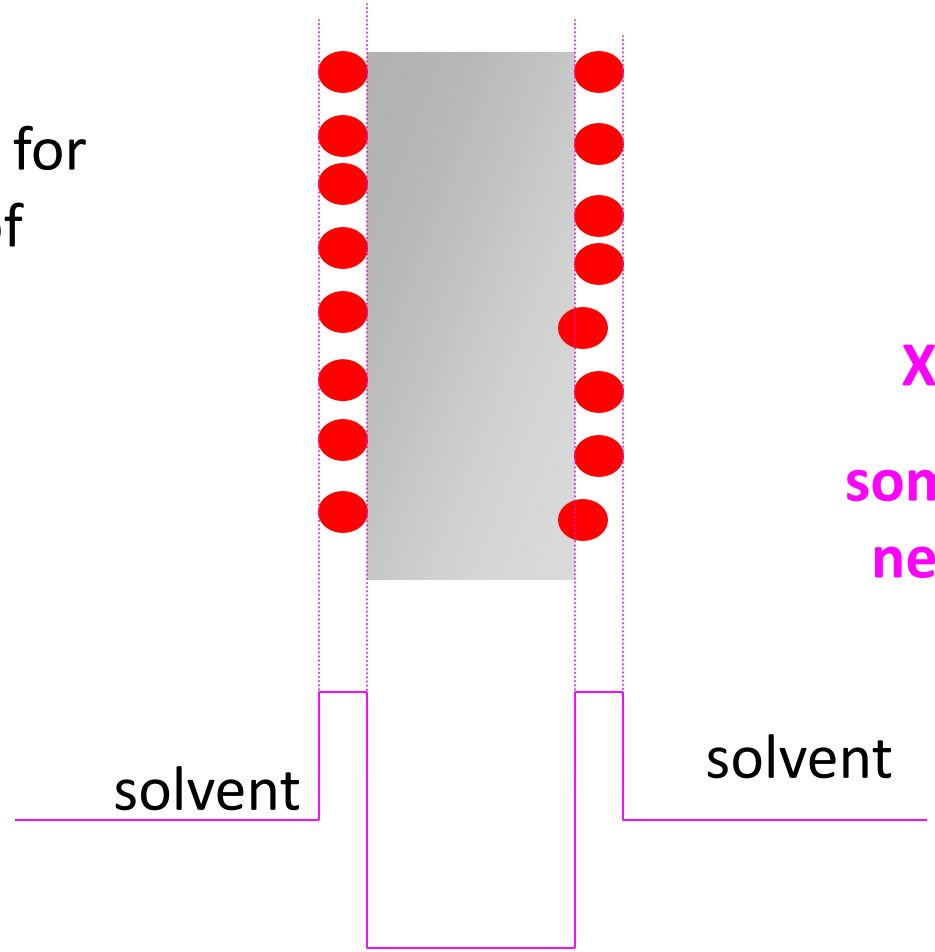
density $\rho = \Sigma b_i/V$

(sld)



Contrast

Core shell models for characterization of hydrophilic shell.

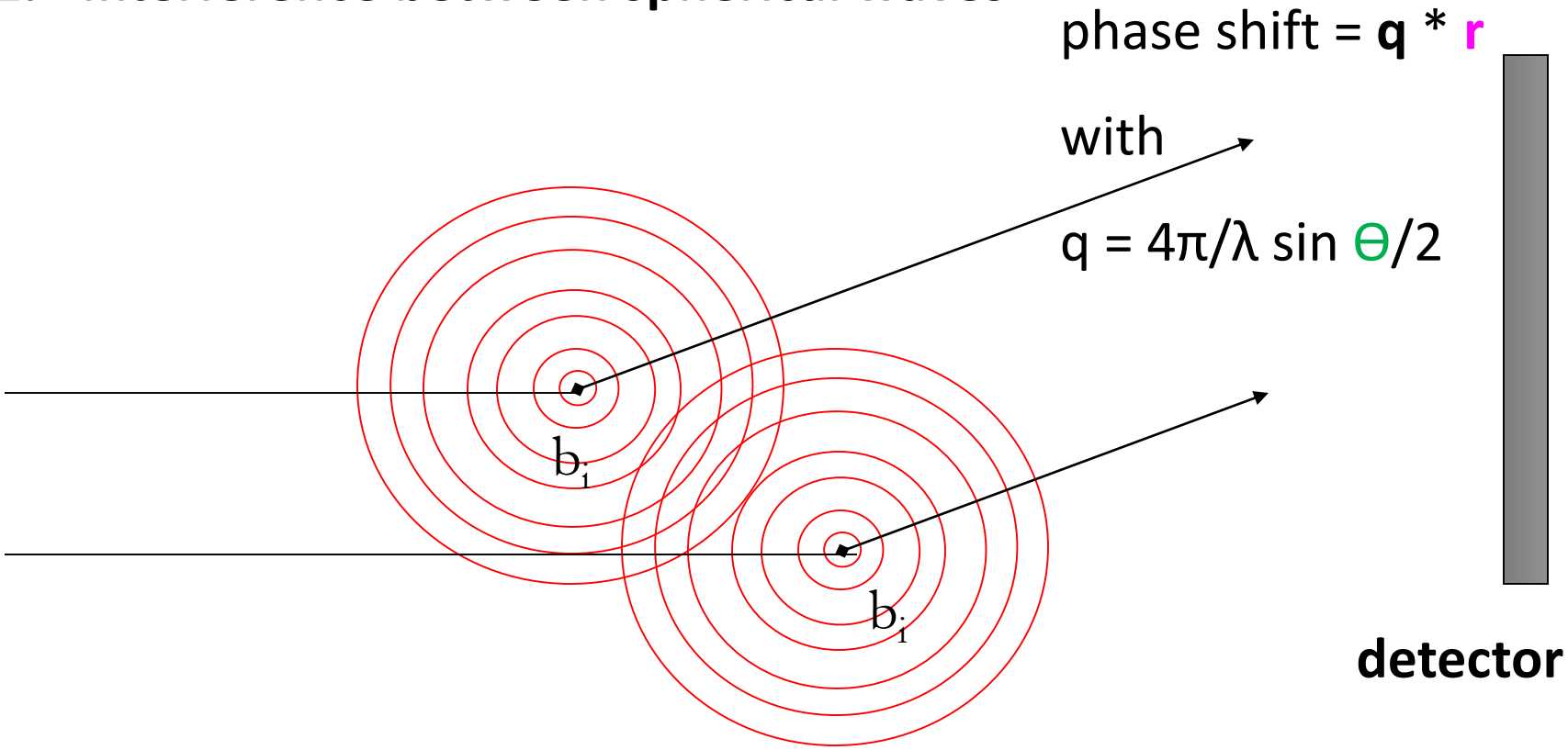


X-rays,

sometimes neutrons

Basic mechanism

1. Interference between spherical waves

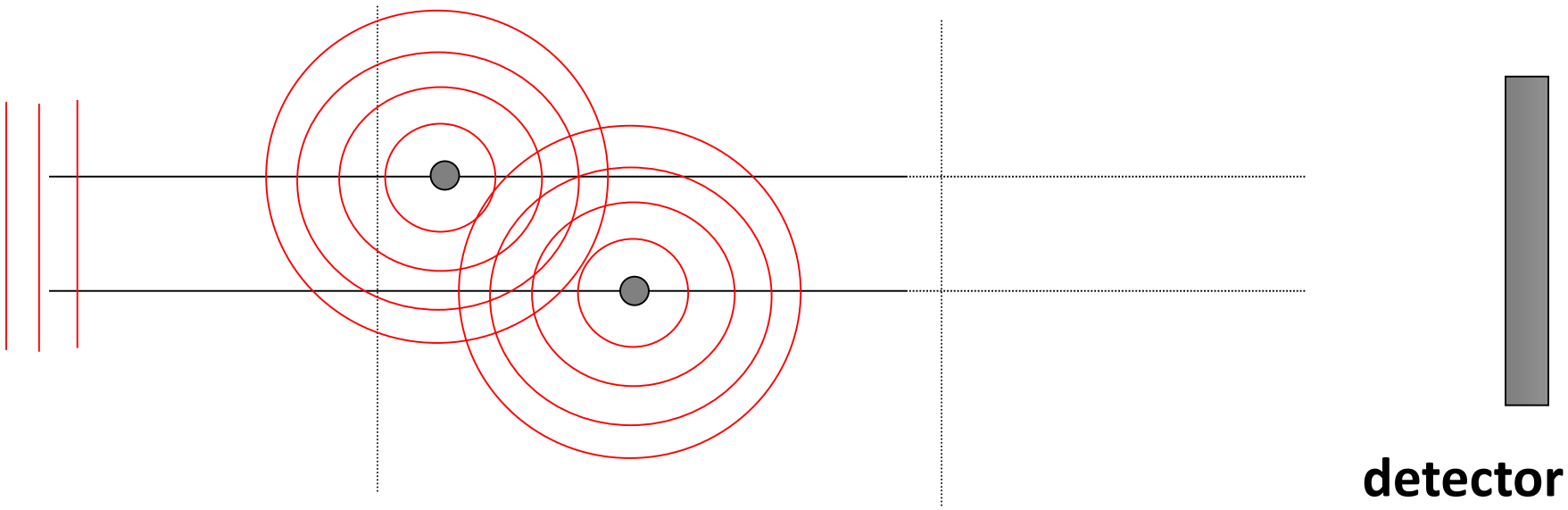


Small distances → large angles

Large distances → small angles

Basic mechanism

2. Forward (q=0) scattering is additive



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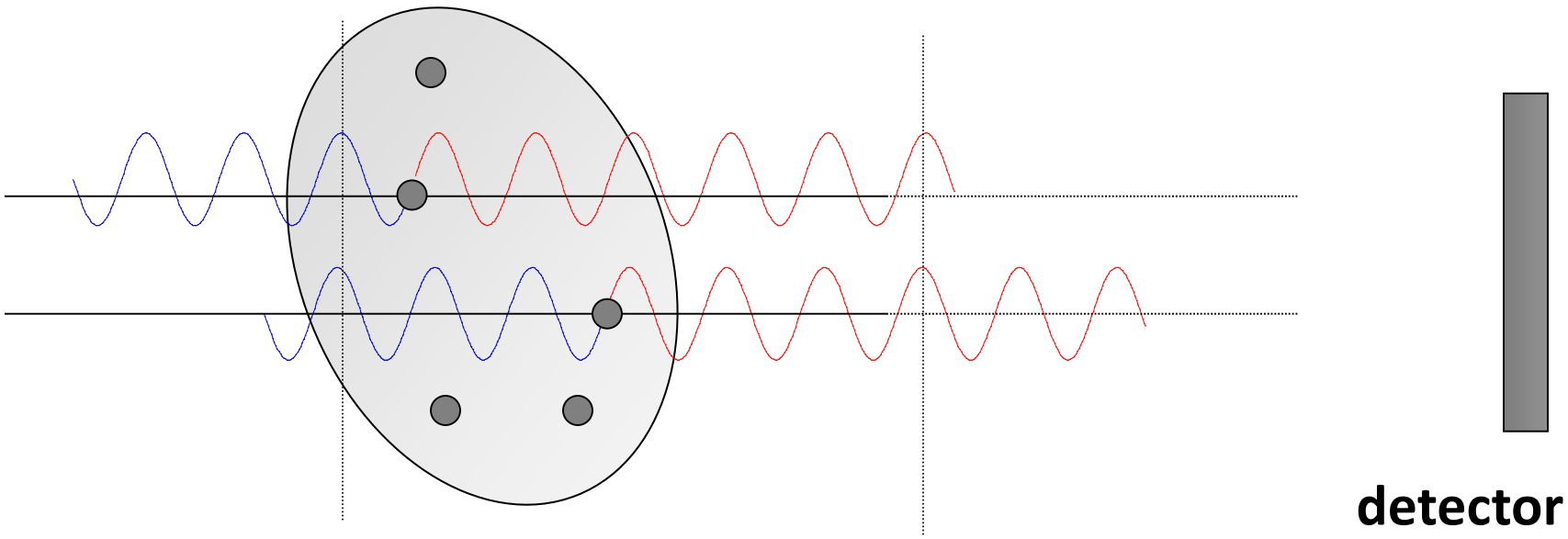


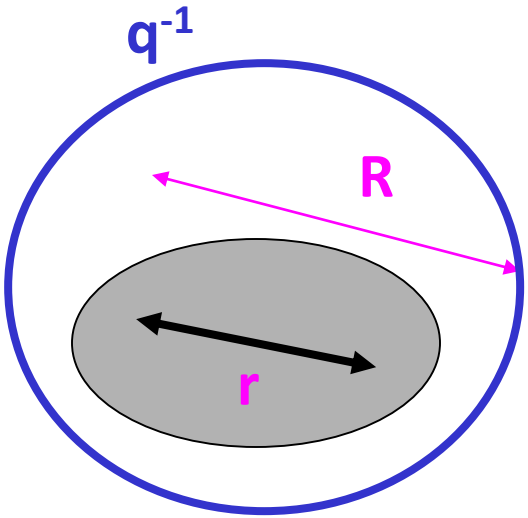
No phase shift → constructive interference on detector

$I(q \to 0) \propto$ concentration * mass

Basic mechanism

3. What mass is measured at q > 0 ?

phase shift = **q** * **r** with $q = 4\pi/\lambda \sin \Theta/2$



$R < q^{-1}$

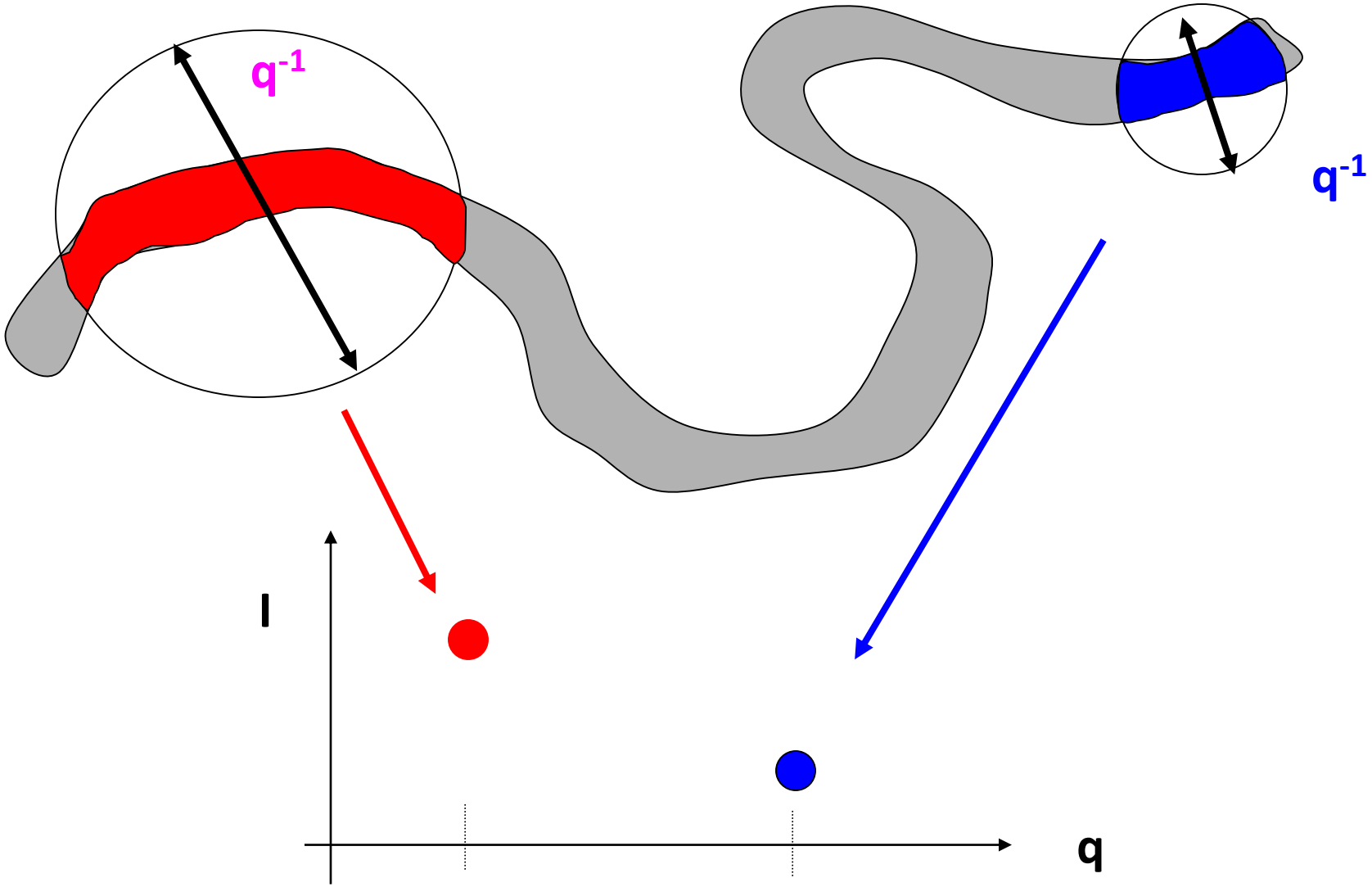
$\rightarrow \quad r < q^{-1}$

$\rightarrow$ qr = phase shift ≈ 0

$\rightarrow$ I(q) = mass inside sphere q^{-1}

General scattering law

$I(q) \propto$ mass inside sphere of radius q^{-1}



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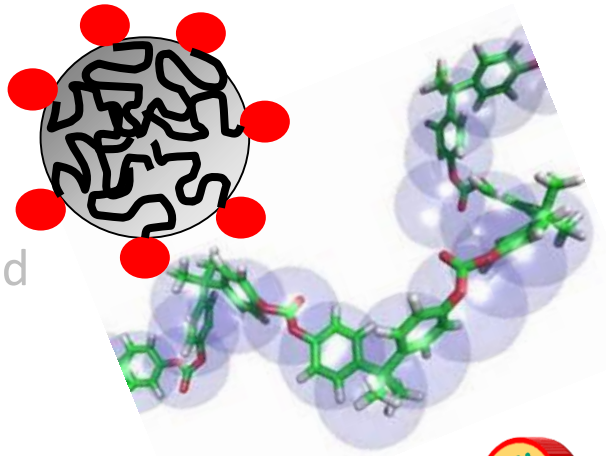
- Polymer systems: molecules, networks, particles and nanocomposites



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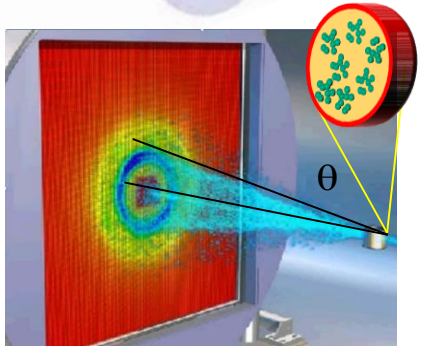

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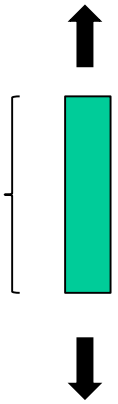
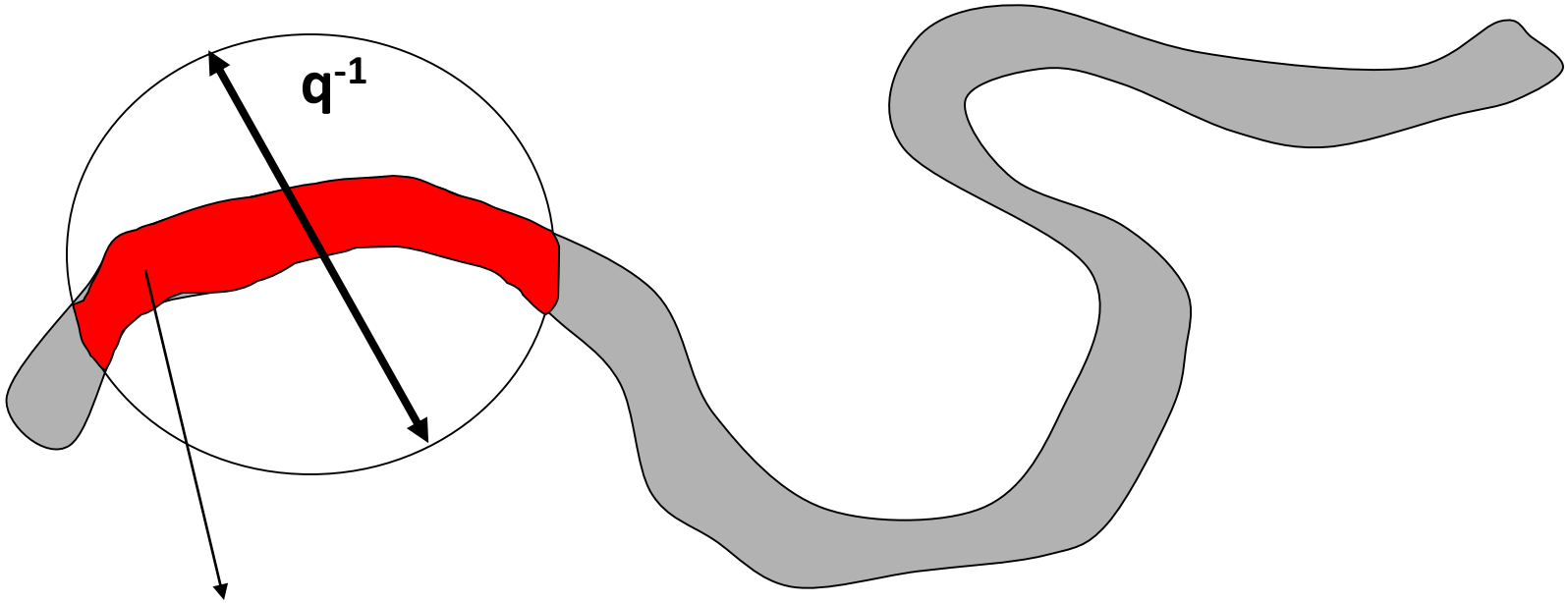
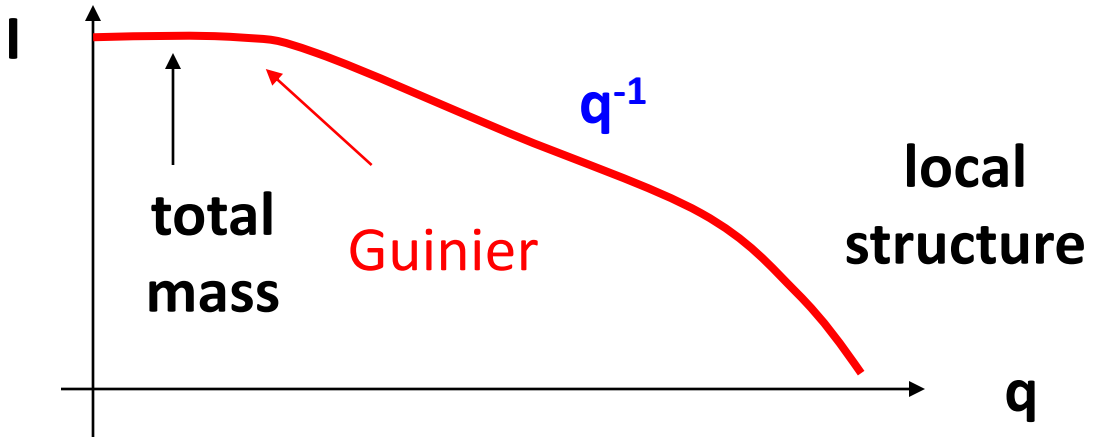


General scattering law: cylinders

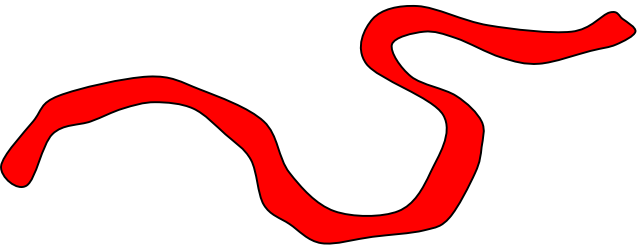


mass inside ≈ cylinder = Section x Length = S q^{-1}

$$I(q) \propto \Phi S q^{-1}$$



Example of cylinders



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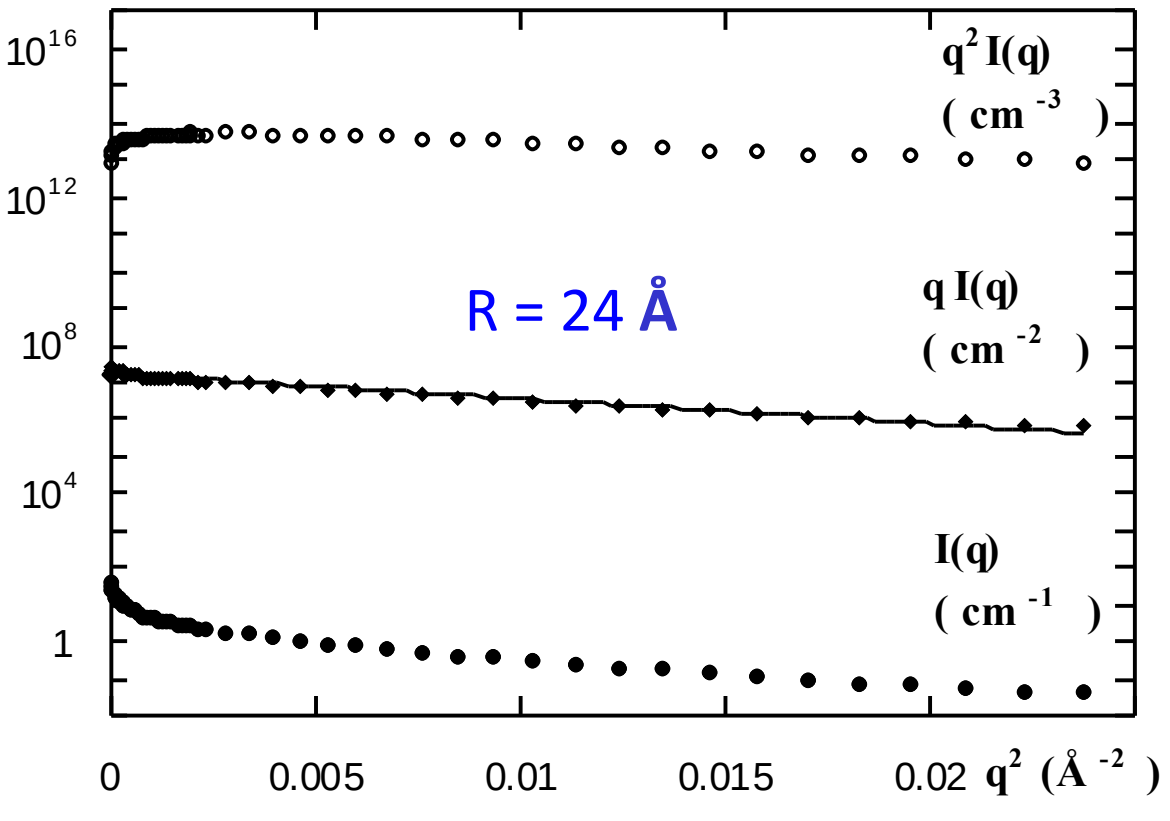
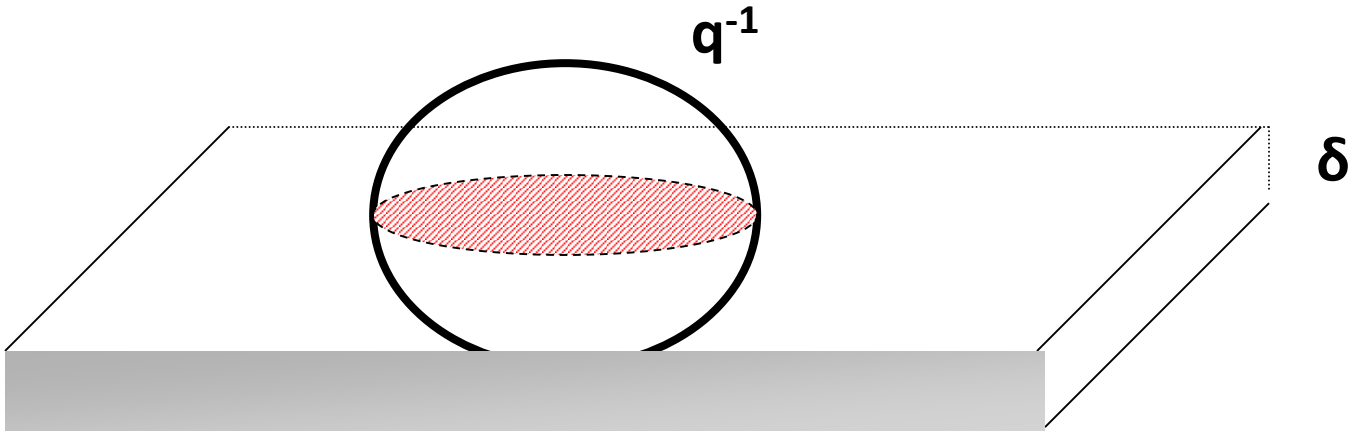


Cylinders, small q : $qI(q) = \pi \Phi \Delta\rho^2 S \exp(-q^2R^2/4)$

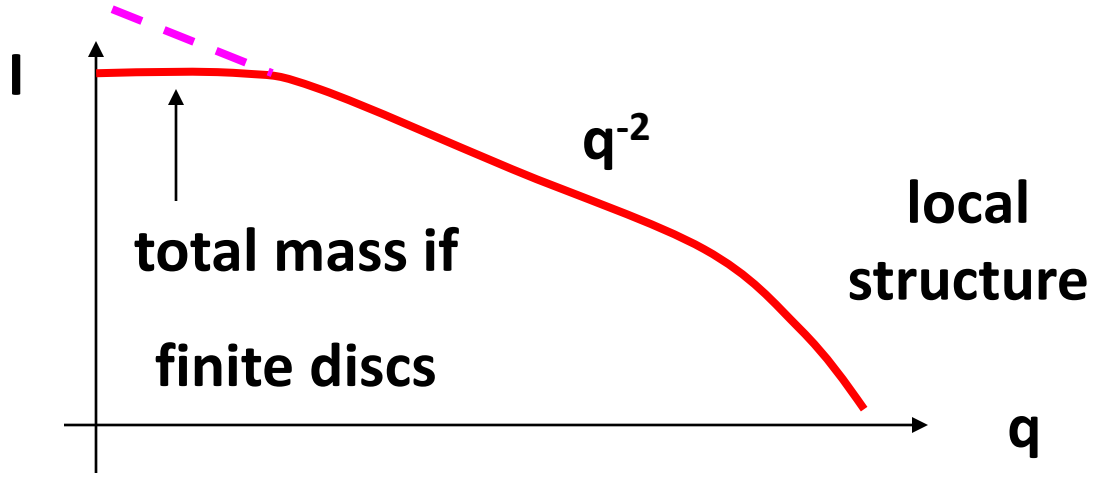
Guinier for cross section

General scattering law for flat bilayers



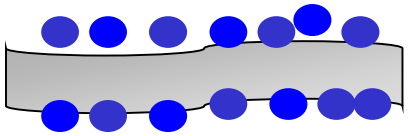
mass inside ≈ cylinder = thickness x surface = $\delta \ \pi q^{-2}$

$$I(q) \propto \Phi \delta \, q^{-2}$$

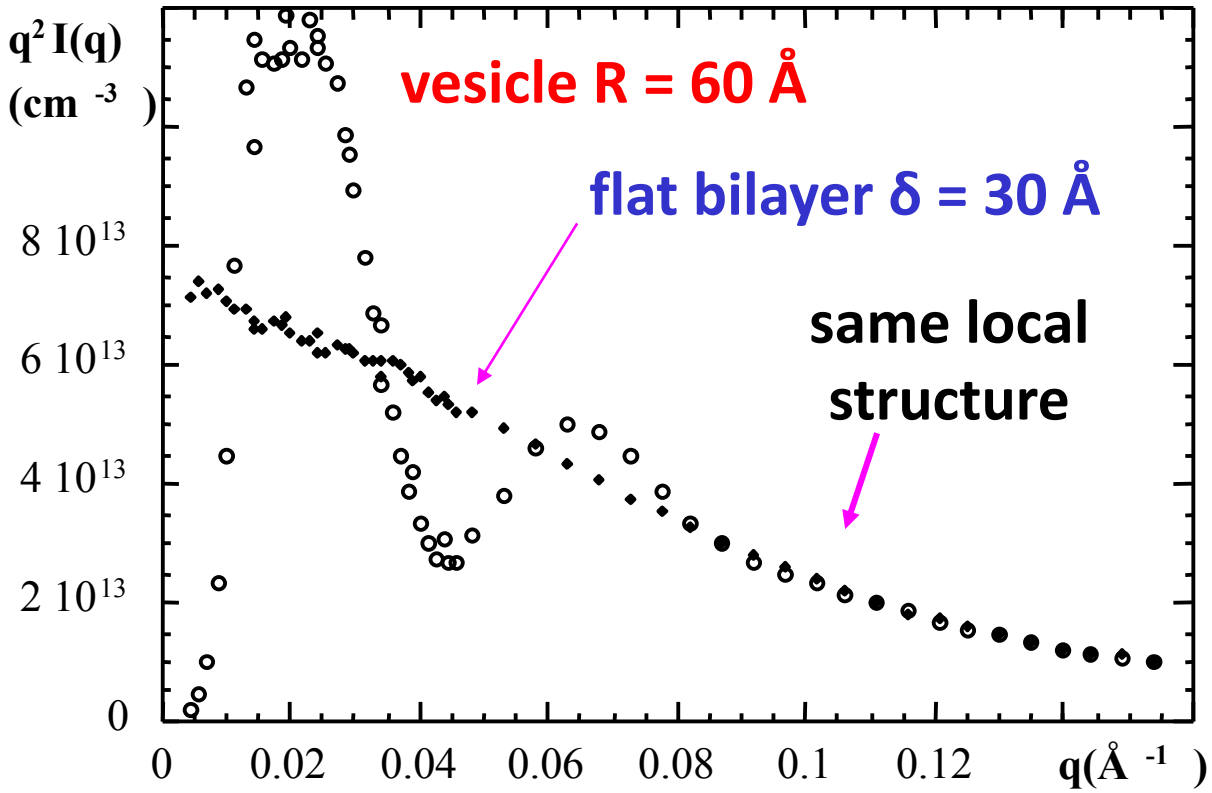


Example: flat vs. curved bilayers

flat bilayer $q^2 I(q) \propto \exp(-q^2\delta^2 / 12)$



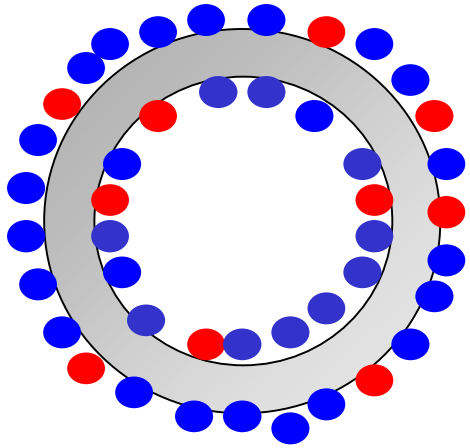
q^{-2} dependence



+ ionic surfactant

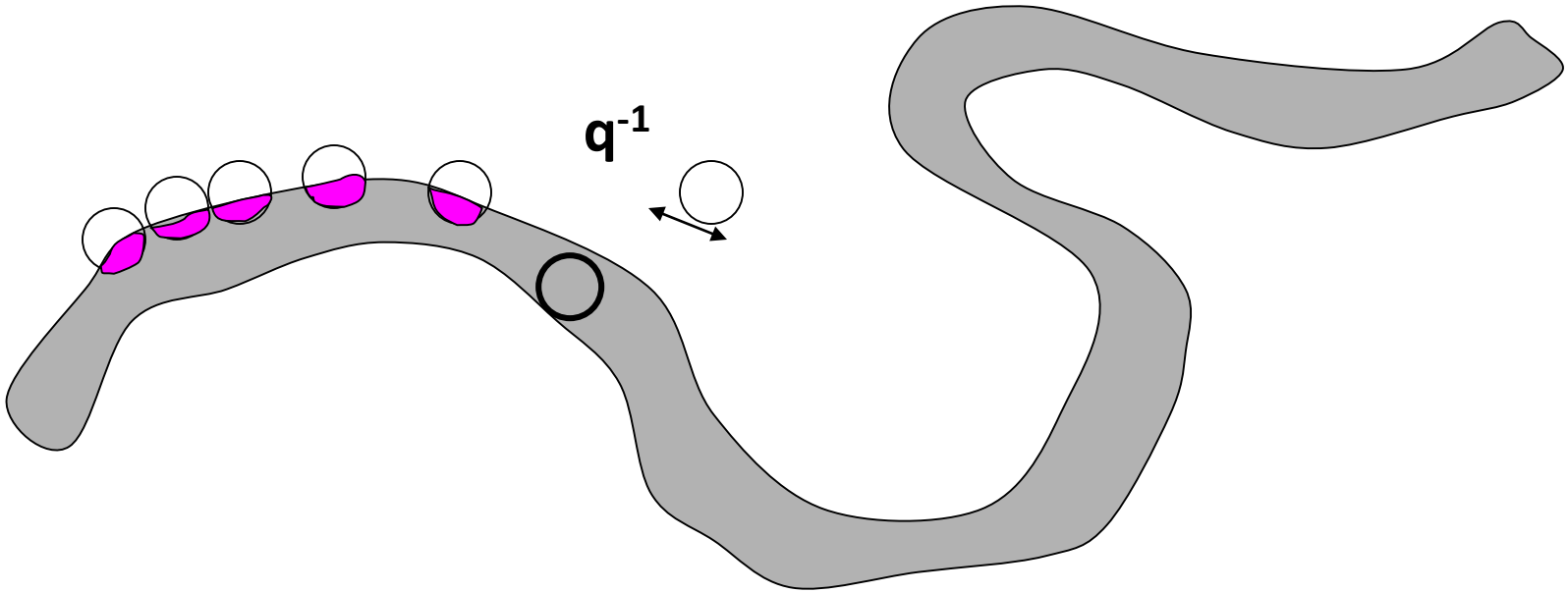
→ Radius

→ Helfrich κ's



Langmuir **1996**, *PRE* **1997**

Smooth surfaces: Porod's law



1. Full or empty spheres do not contribute at $q > 0$.

2. Number of half empty spheres = surface / $\pi R^2 \propto S\, q^2$

3. Each sphere on surface contributes: mass $\propto R^3 \propto q^{-3}$

=> Porod law for smooth surfaces: $I \propto$ number x mass^2

$I \propto A/q^4$ **(A gives specific surface S/V)**

Fractal surfaces: modified Porod's law

B. Mandelbrot: how long is the coast of Britain?

1. Full or empty spheres do not contribute at $q > 0$.

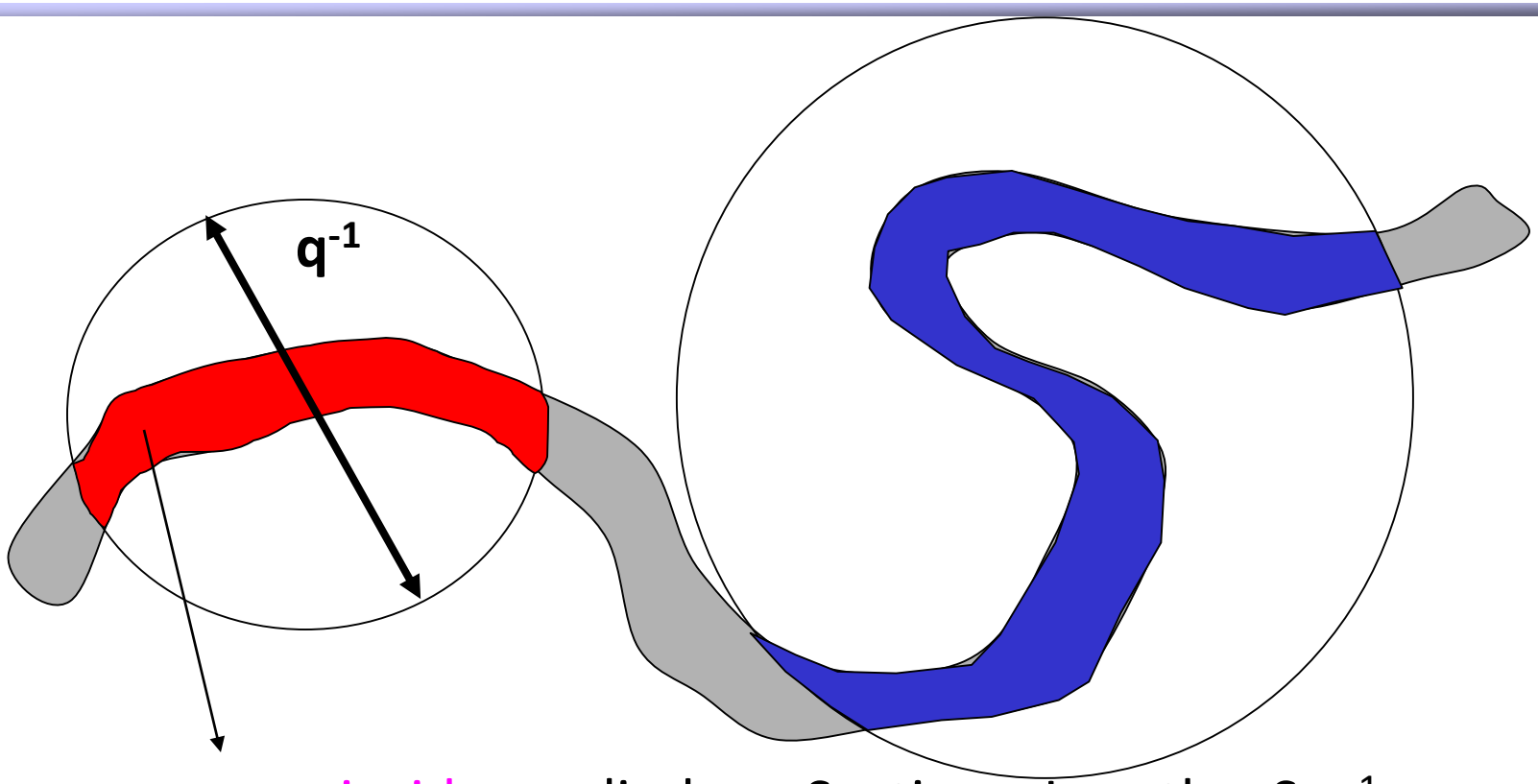
2. Number of half empty spheres $\propto q^D$

3. Each sphere on surface contributes: mass $\propto R^3 \propto q^{-3}$

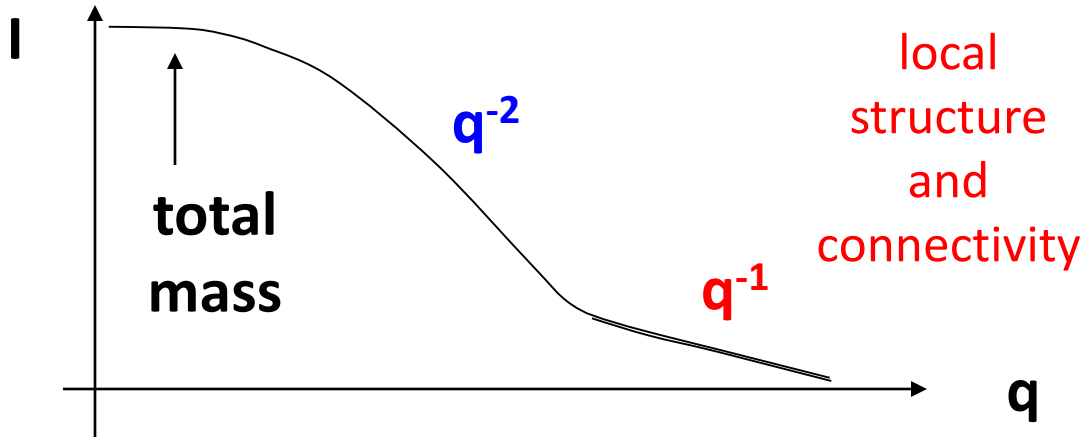
=> Porod law for fractal surfaces: $I \propto$ number x mass^2

$$I \propto A/q^{6-D}$$

Conformation of polymer chains

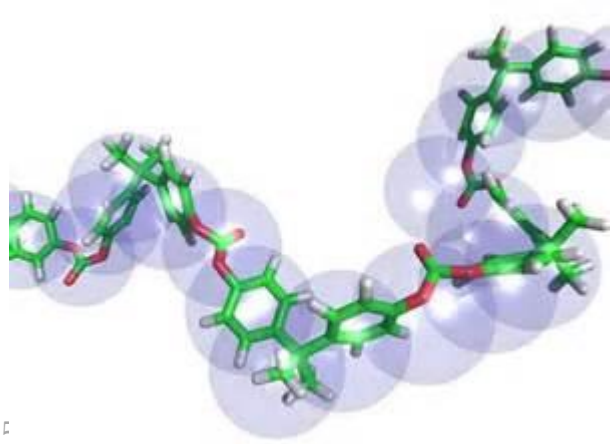


mass inside ≈ cylinder = Section x Length = S q^{-1}



Conformation of polymer chains

Linear polymer chain (e.g. PEO, PE, PS):



In (theta-)solvent: **R ≈ 15 nm**

- Number of conformations: $3^{10'000} \approx 10^{5}$
- One picosec/conformation: (much) longer than age of universe

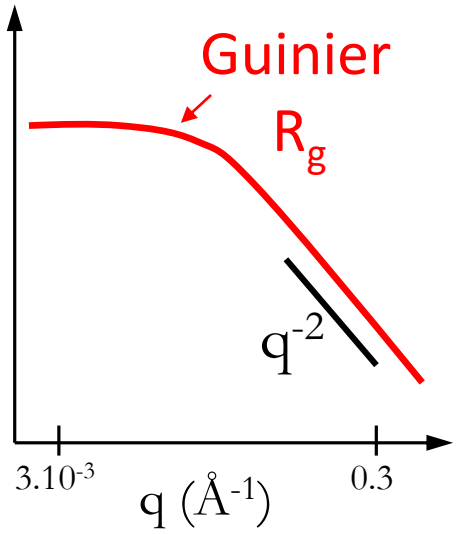
→ statistical description: $\mathbf{R_g} = a\, N^{1/2} \sim \mathbf{M}^{1/2}$

→ $\mathbf{I \sim M \sim R_g^{\,2} \sim q^{-2}}$

Debye function of Gaussian chains:

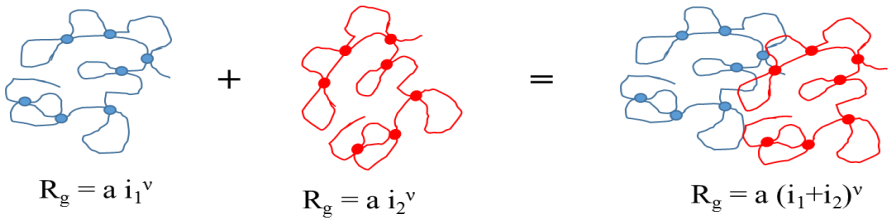
$$P_{Debye}(q) = \frac{2}{q^4 R_g^4}\left(e^{-q^2 R_g^2} - 1 + q^2 R_g^2\right)$$

Now, q^{-2} is chain or sheet?



Conformation of polymer chains

Generalized Gaussian coil



Arbitrary conformation exponent:

→ statistical description: $\mathbf{R_g} = a\ N^{\nu}$

→ fractal dimension: $d_f = 1/\nu$

expresses **solvent** conditions

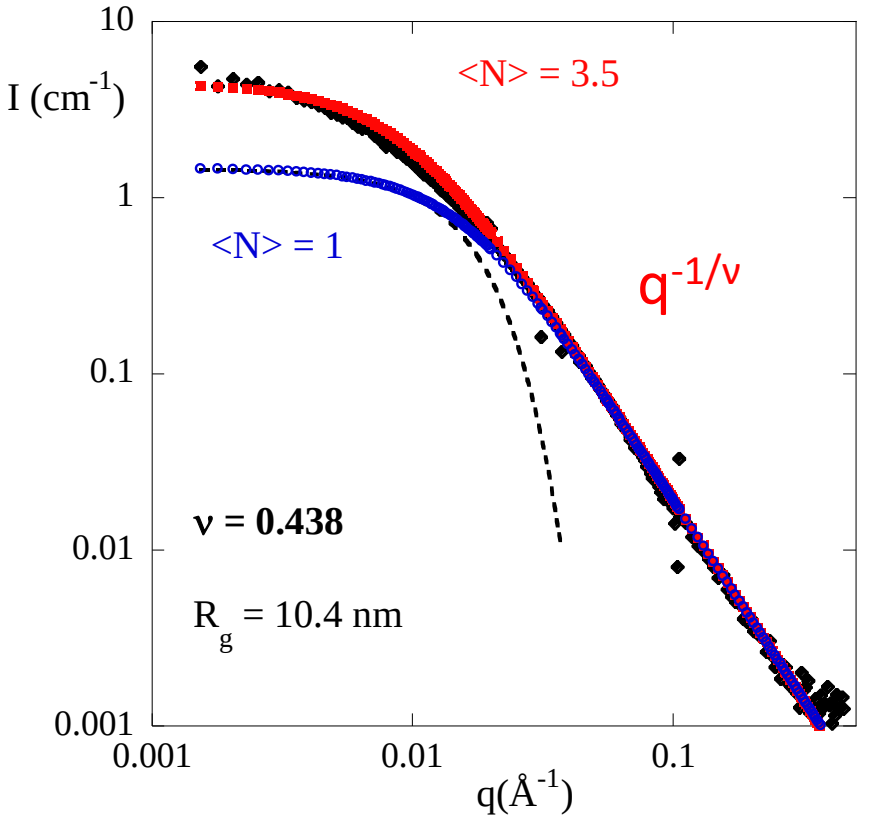
$$P(q, R_g) = \left[\left(\frac{1}{\nu U^{\frac{1}{2\nu}}}\right)\gamma\left(\frac{1}{2\nu}, U\right) - \left(\frac{1}{\nu U^{\frac{1}{\nu}}}\right)\gamma\left(\frac{1}{\nu}, U\right)\right]$$

with

$$U = (2\nu + 1)\cdot(2\nu + 2)\cdot\frac{(qR_g)^2}{6}$$

$$\gamma(a,b) = \int_0^b t^{a-1}e^{-t}dt$$

'Single-chain NP', Arbe, Colmenero, JO

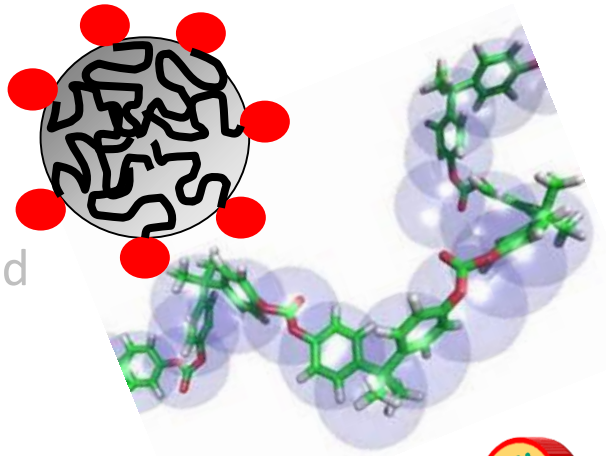


Outline

1) **Soft matter as microstructured systems**

- Surfactant self-assembly

- Polymer systems: molecules, networks, particles and nanocomposites



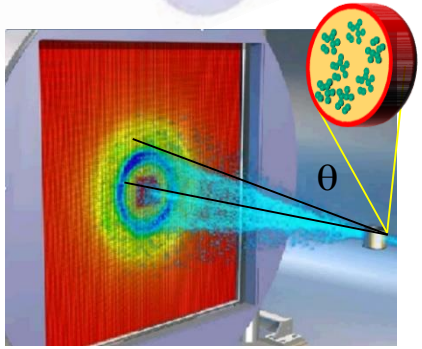
2) **Structural analysis by small-angle scattering**

- Principles: contrast, scattering process

- Shape analysis, a ‘math-free’ Fourier transform

- Applications: micelles, bilayers, polymers, surfaces, aggregates

- **Interactions and pair correlation**

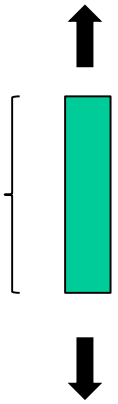


3) **Scattering under deformation**

- Experiments and geometries

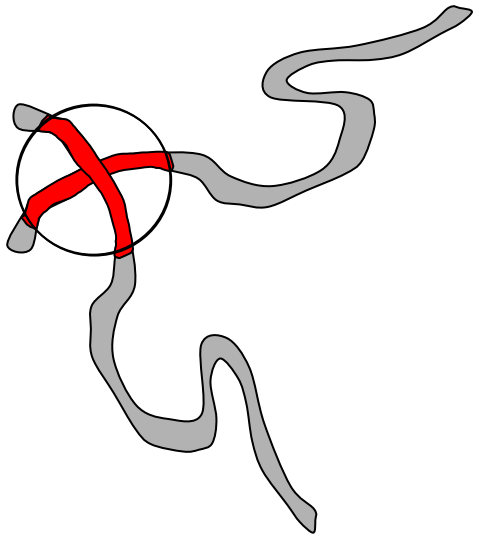
- Affine deformation and networks

$L = \lambda L_0$

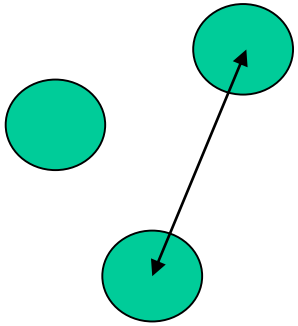


Interactions

From single (finite-size) particle to many:



Interactions easiest with spheres



Spheres described by **form factor P(q)**,
interactions by **structure factor S(q)**

Only for identical objects of spherical symmetry:

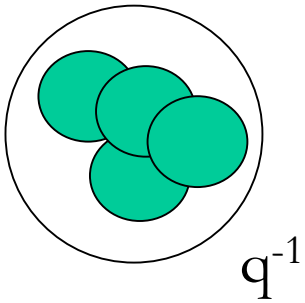
$$I(q) = I_o\, P(q)\, S(q)$$

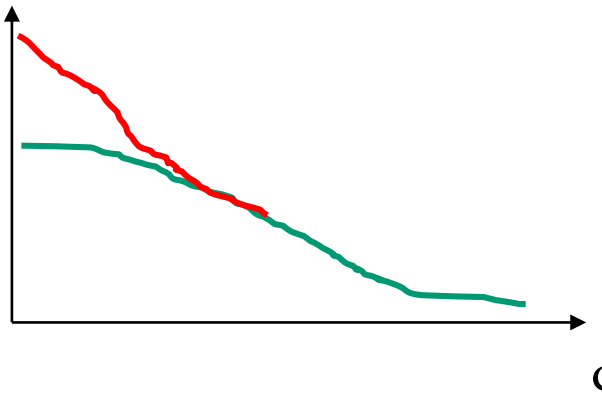
What does S(q) do to scattered intensity?

Interactions and structure factor S(q)

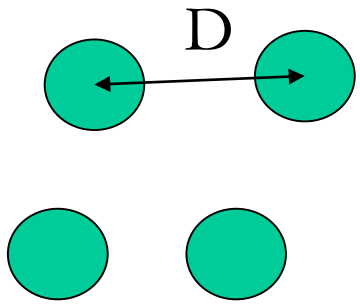
Attractive interactions:

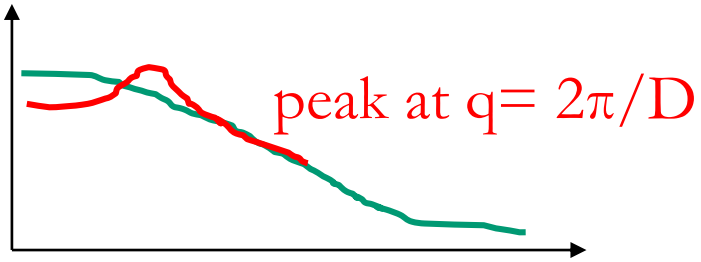
mass increases in q^{-1} sphere



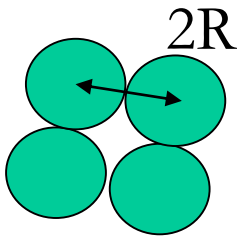


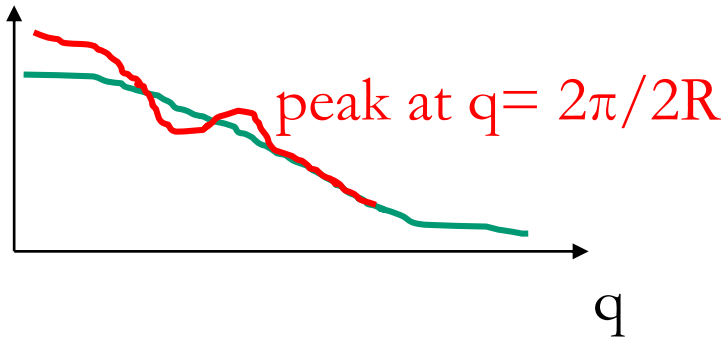
Repulsive interactions:





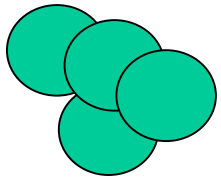
Both:

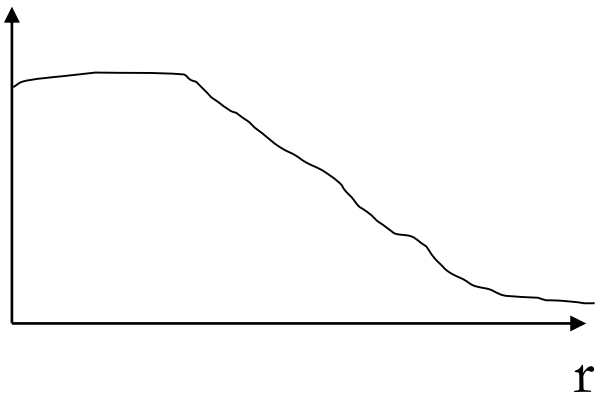




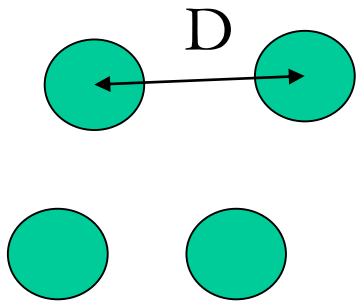
Interactions and pair correlation function g(r)

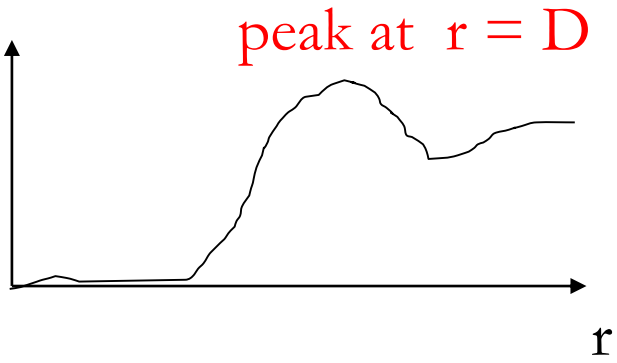
Attractive (soft) interactions:



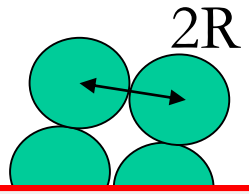


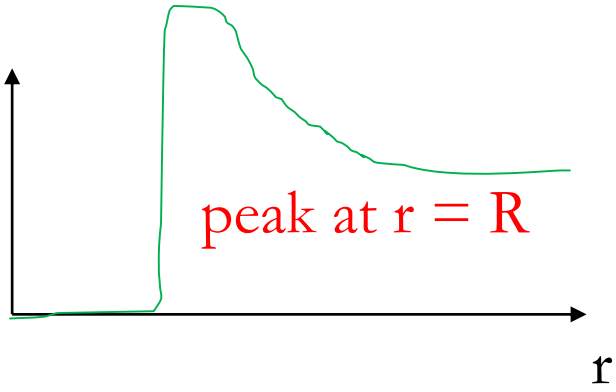
Repulsive interactions:





Both:





g(r) is the Fourier transform of S(q)

$$S(q) = 1 + 4\pi \frac{N}{V} \int_0^\infty [g(R) - 1] R^2 \frac{\sin qR}{qR} \, dR$$

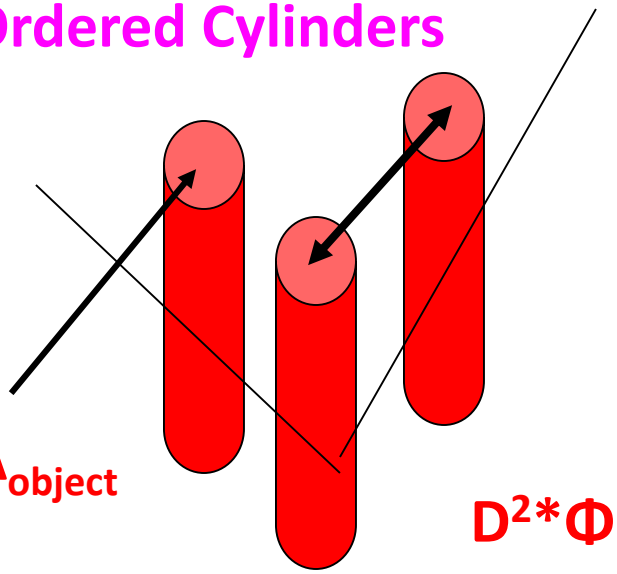
Interactions in practice: dilution laws to follow structure peaks

Globular objects

Conc.

Cubic model: $D^3 * \Phi = V_{object}$

Ordered Cylinders



A_{object}

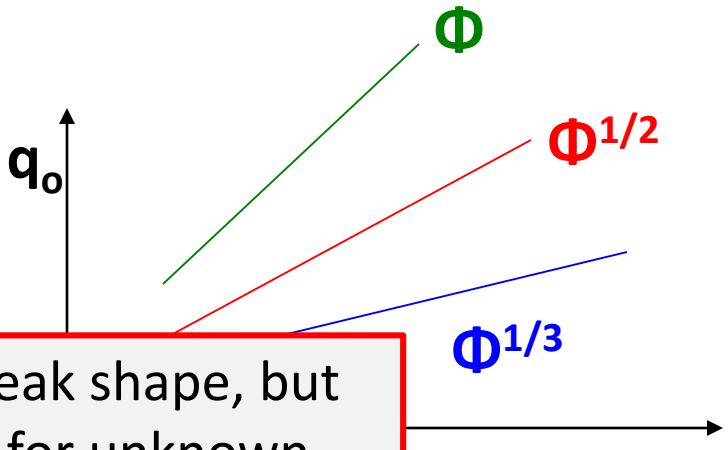
$D^2 * \Phi = A_{object}$

Flat bilayers

D

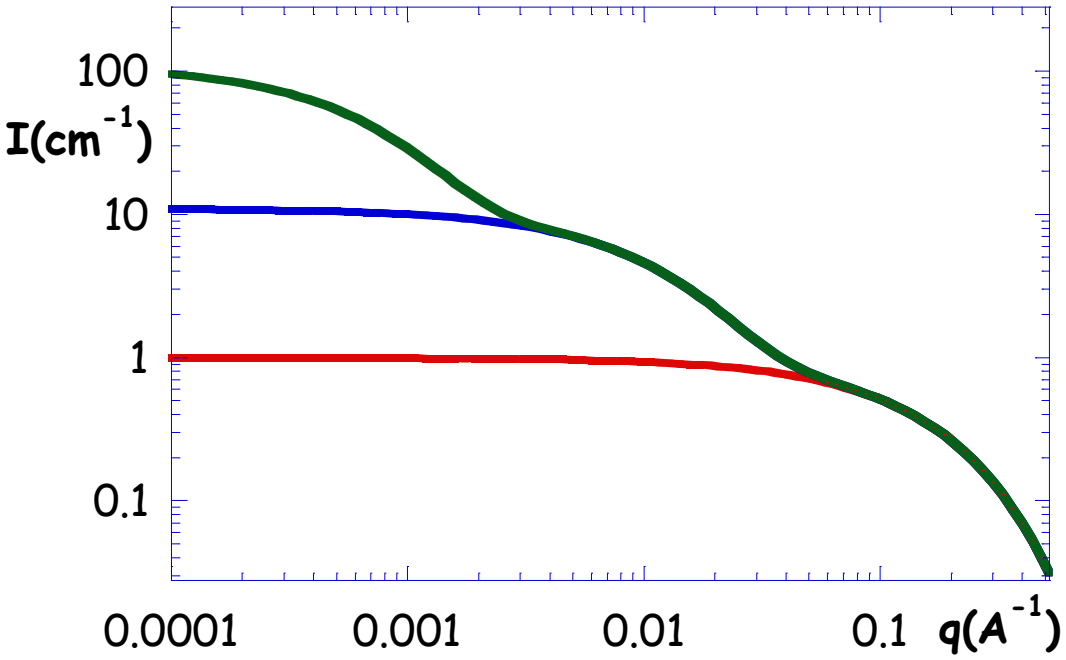
$D * \Phi = \delta$

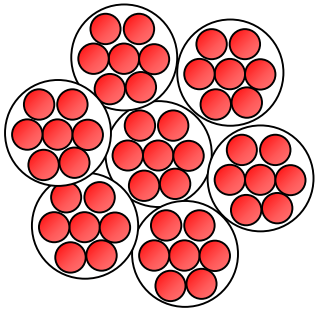
δ



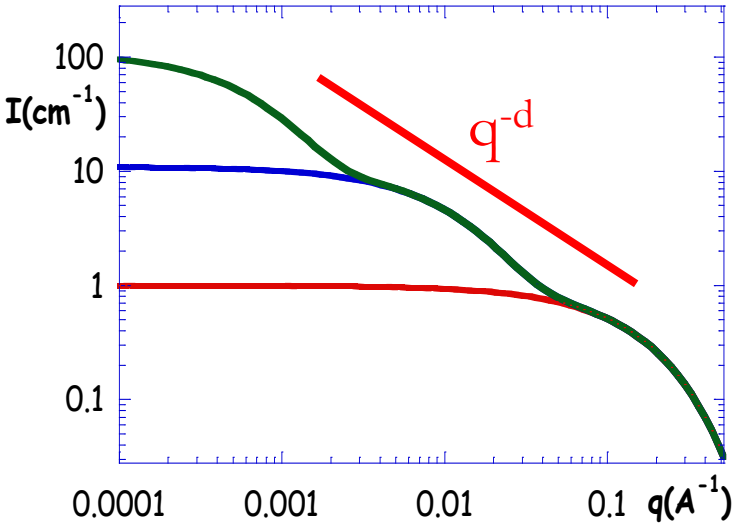
Dilution laws: Don't calculate peak shape, but see how it moves. Very useful for unknown structures (cf. microemulsions).

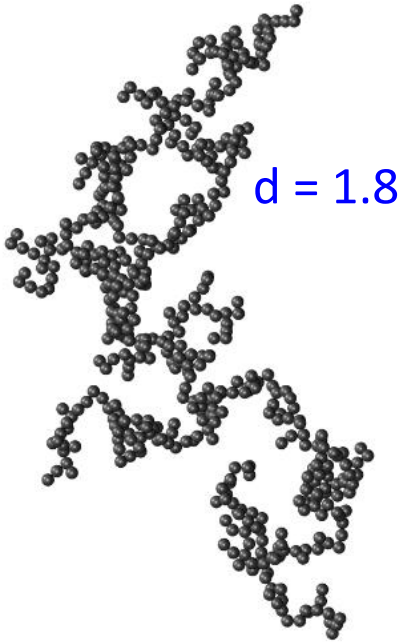
Scattering from hierarchical systems: nanoparticle aggregates

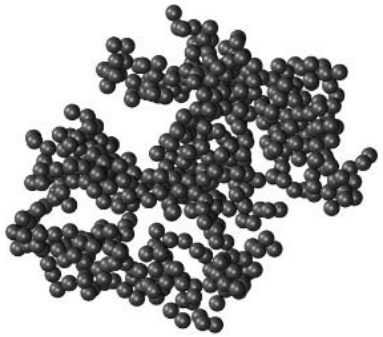




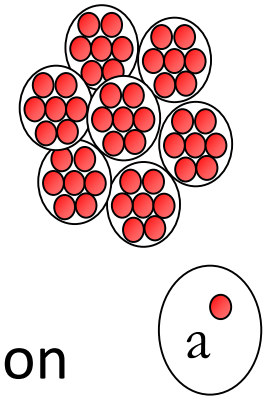
Scattering from hierarchical systems: nanoparticle aggregates







Fractals:



- self-similar
- $N = (R/a)^d$
- d is the fractal dimension

Scattering law:

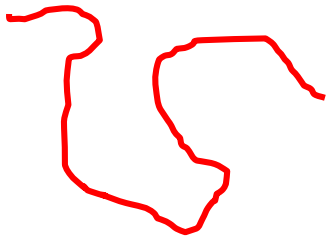
- Mass in sphere of radius q^{-1}
- $N = (R/a)^d$
- **$I(q) \sim$** mass $\sim N \sim 1/(qa)^d \sim$ **$1/q^d$**

Our examples:

- Cylinder q^{-1}
- Sheet or Gaussian polymer q^{-2}
- Chain in good solvent: $q^{-1/\nu}$
- Surface q^{-4} (or surface fractal)

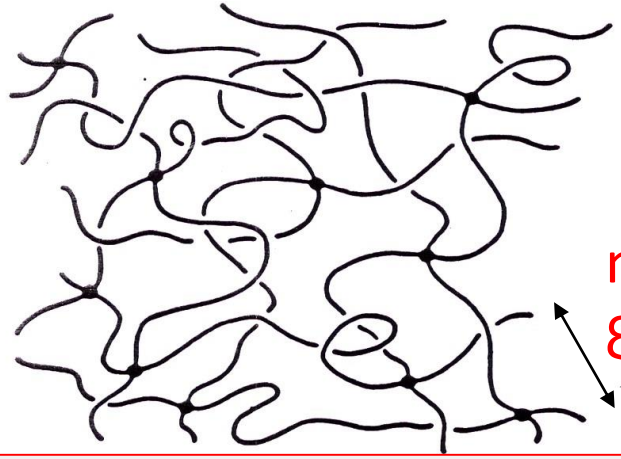
Scattering of polymer networks

- Single chain: g(r) = 1/r and finite size R_g
  => Debye function in q^{-2}, I_0 = chain mass

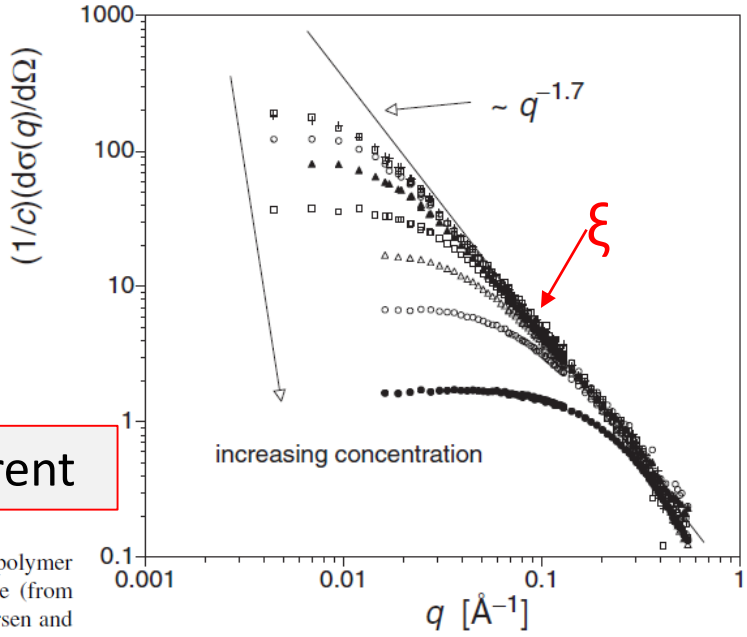


- g(r) of single chain with cut-off: g(r) = 1/r exp(-r/ξ)

Ornstein-Zernike (OZ) $I(q) = \frac{I_0}{1+(q\xi)^2}$ I_0 = fluctuations



mesh size ξ



OZ and Debye look similar, interpretation different

Fig. 20. Normalized scattering intensity $I(q)/c$ as a function of the scattering vector q for different polymer concentrations c for polystyrene in deuterated toluene and $M_w = 120{,}000$ g/mol. The concentrations are (from below) $c = 0.27$, 0.11, 0.054, 0.028, 0.011, 0.0052, 0.0021 and 0.0013 g/ml. The data are taken from Pedersen and Schurtenberger (1999).

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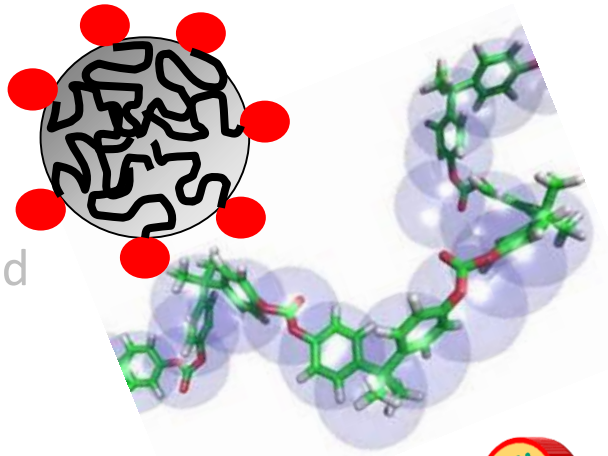
- Surfactant self-assembly

- Polymer systems: molecules, networks, particles and nanocomposites



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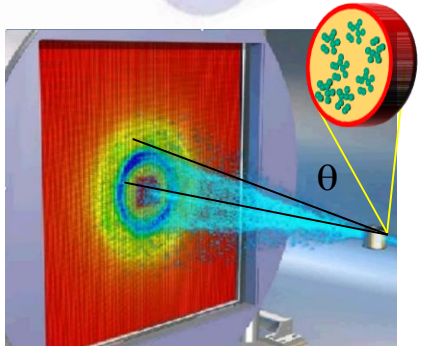


- Principles: contrast, scattering process

- Shape analysis, a ‘math-free’ Fourier transform

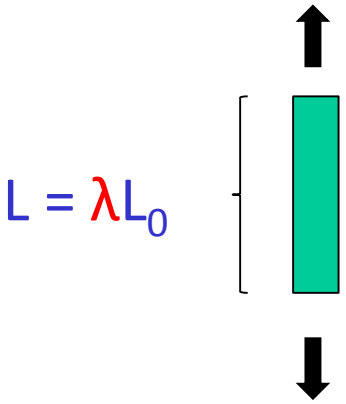
- Applications: micelles, bilayers, polymers, surfaces, aggregates

- Interactions and pair correlation

3) **Scattering under deformation**

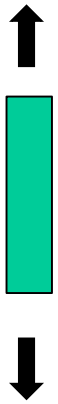
- Experiments and geometries

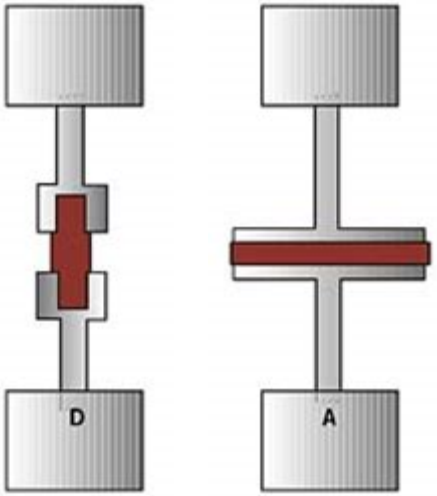
- Affine deformation and networks



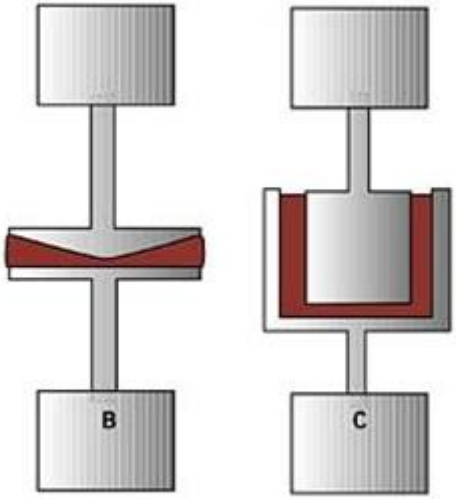
Scattering of samples under deformation

Solids





Liquids



Uniaxial strain

Torsion, shear

Cone-plate, Couette

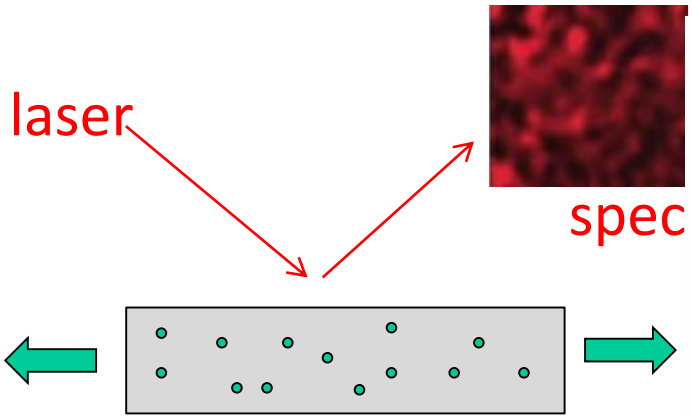
$\lambda = \varepsilon + 1 = L/L_0$ macroscopic deformation γ

elastomers, rubber, gels: polymer networks

polymer or surfactant solutions, soft gels

Scattering experiments

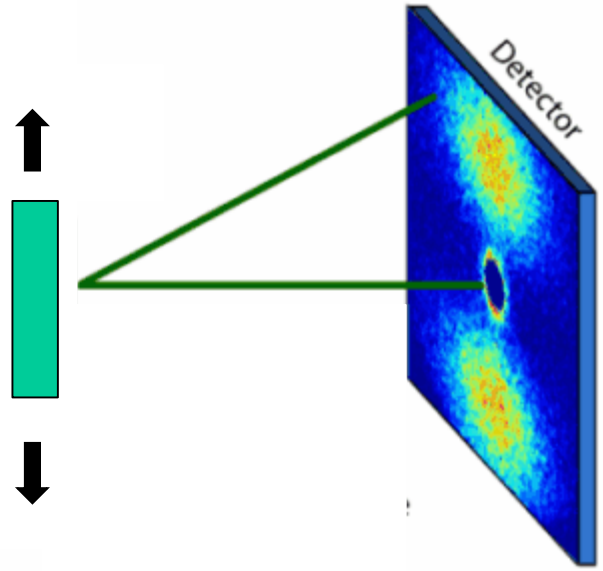
e.g. diffusive wave spectroscopy (DWS) in backscattering



tracer NPs or … PNC

No idea on the structure!
Back-and-forth (echo) tells you, if same structure is retrieved after motion (with L. Cipelletti, U Montpellier).

Small-angle scattering (SAS)
→ single scattering event



$I(q_x,q_y)$ instead of $I(q)$ gives micro-structure in different directions.

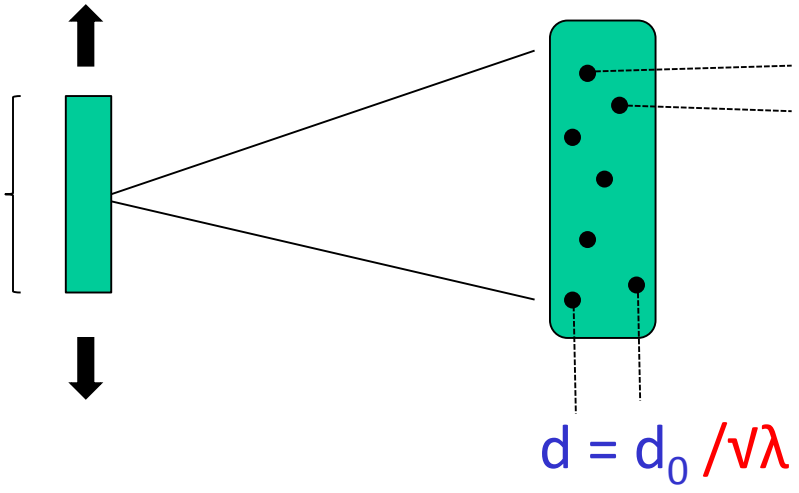
Different scattering experiments and geometries give different information

Affine deformation

Macroscopic strain

$\lambda = L/L_0$

microscopic deformation



What about the other two directions?

In case of volume conservation and symmetry: $V = L_x L_y L_z = L_{0x}\, L_{0y}\, L_{0z}$

$V = \lambda_x L_{0x}\, \lambda_y L_{0y}\, \lambda_z L_{0z}$

$\lambda_x\, \lambda_y\, \lambda_z = 1$

Uniaxial strain in z-direction:

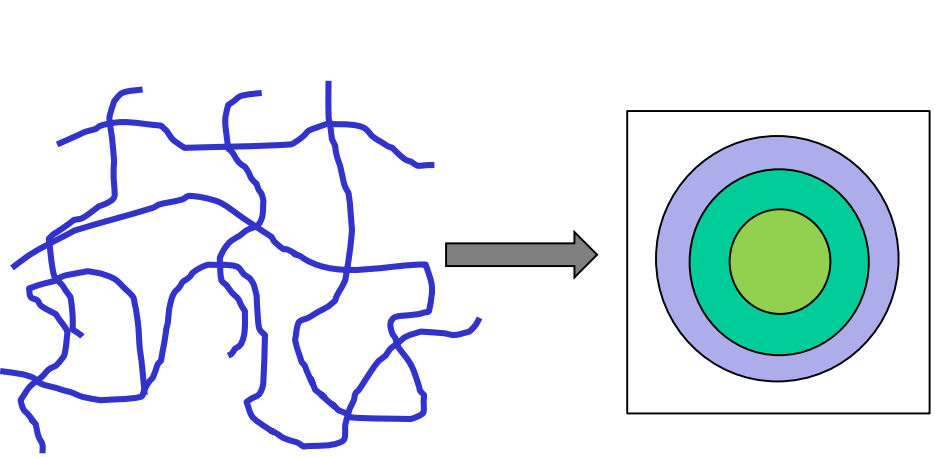
$\lambda_z = \lambda$

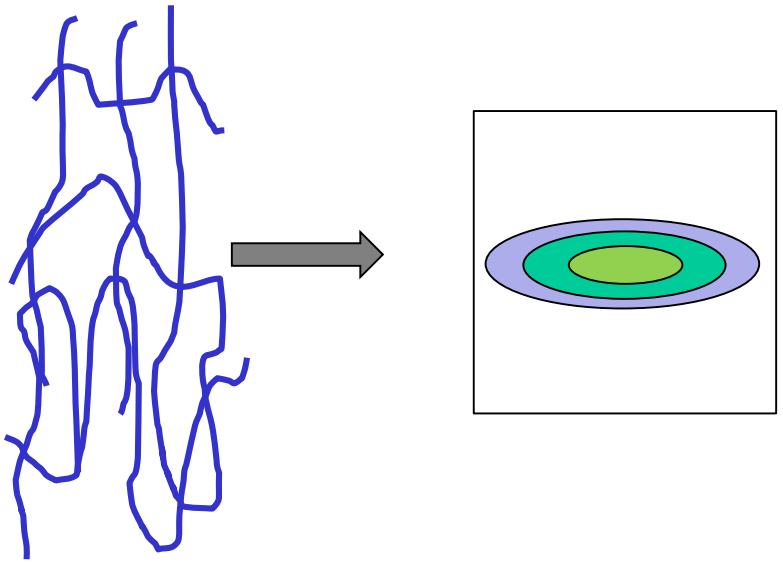
$\lambda_x = \lambda_y = 1/\sqrt{\lambda}$

Affine deformation and scattering

Initial isotropic structure

Deformation: λ, $1/\sqrt{\lambda}$





Radius of ring: q_0

Ellipse : affine deformation of ring:

=> Follow deformation on local scale!

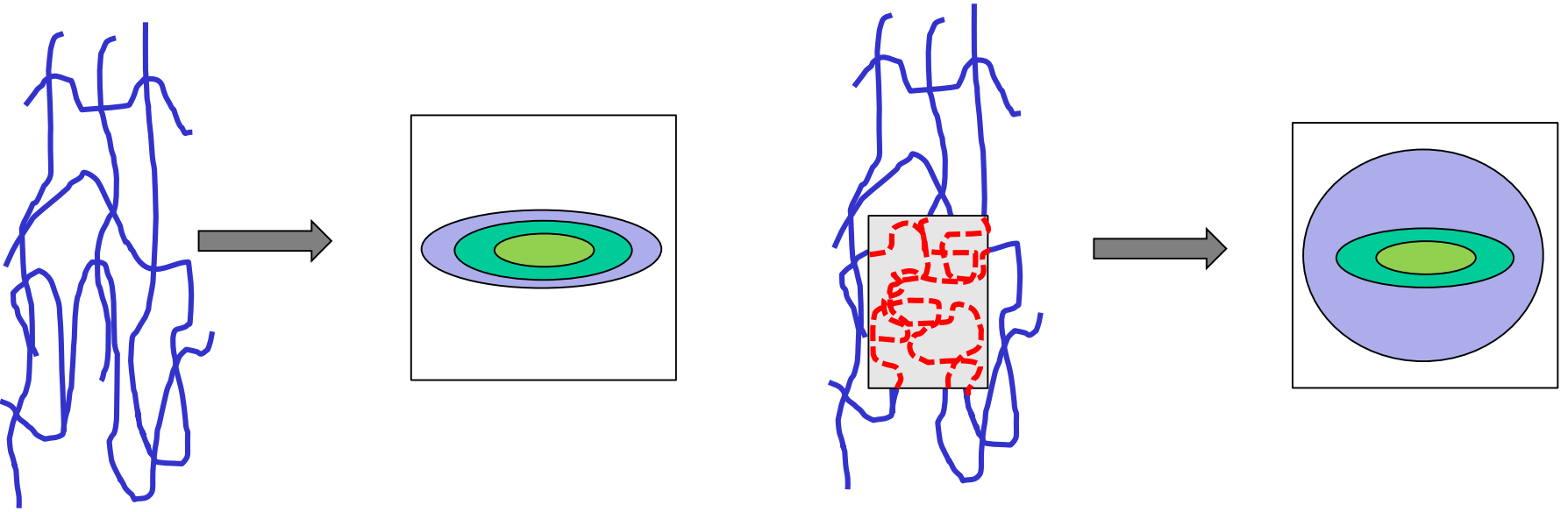
$q_z = q_0 / \lambda$

$q_x = q_0 \sqrt{\lambda}$

Partially affine: Observation of relaxation

Step-strain deformation: λ, $1/\sqrt{\lambda}$

Relaxation at constant strain

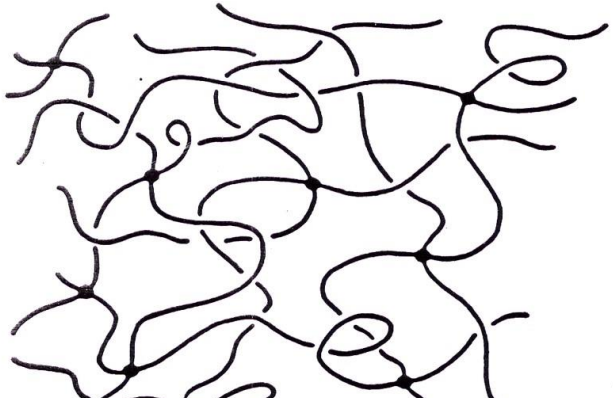


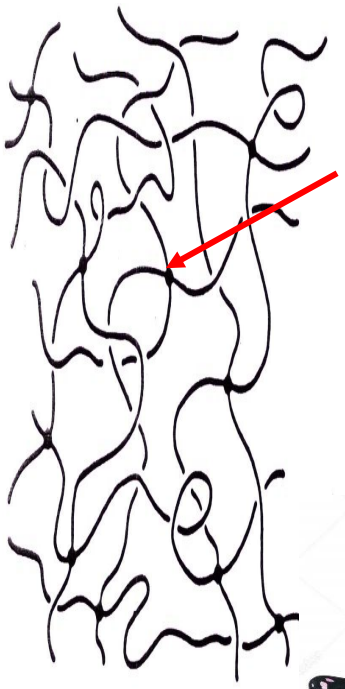
'isotropized'

$\Rightarrow$ Determine q-vector (= typical size) delimiting affineness.

$\Rightarrow$ Gives scale of spatial reorganization (with time).

Studies of network deformation





Displacement of junctions?

Network theories

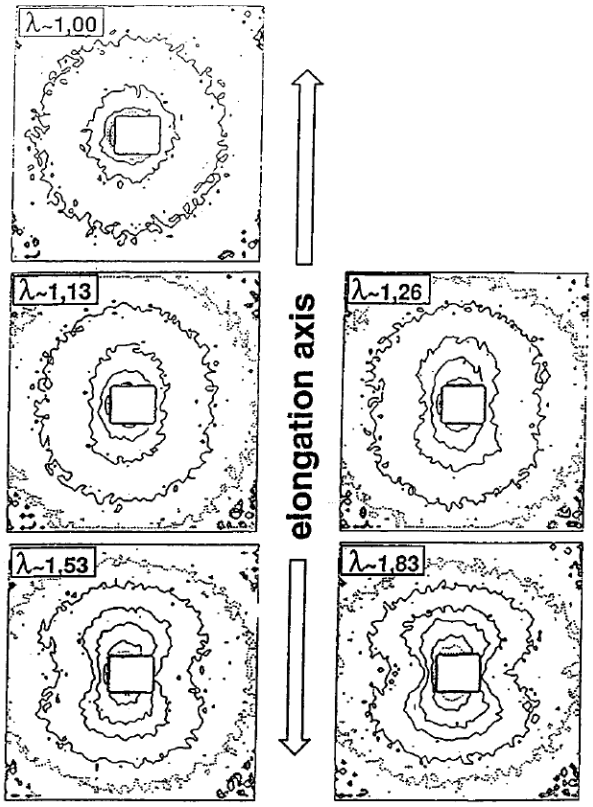


Figure 3. Isointensity curves as a function of the elongation ratio, λ, for the sample at swelling ratio $Q = 23$.

Macromolecules **1996**, *29*, 5574−5584

Small-Angle Neutron Scattering Study of Swollen Elongated Gels: Butterfly Patterns

E. Mendes,*,†,‡ R. Oeser,§ C. Hayes,†,§ F. Boué,|| and J. Bastide⊥,△

Studies of network deformation

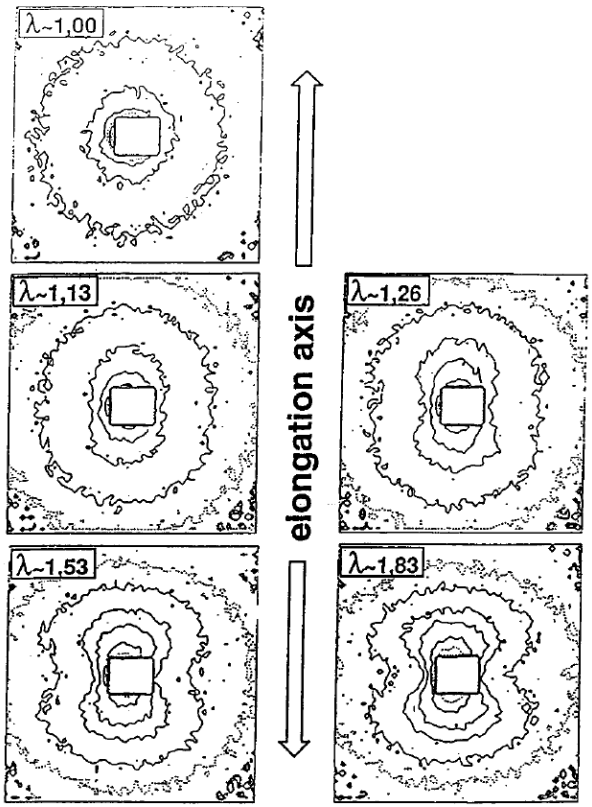


Figure 3. Isointensity curves as a function of the elongation ratio, λ, for the sample at swelling ratio $Q = 23$.

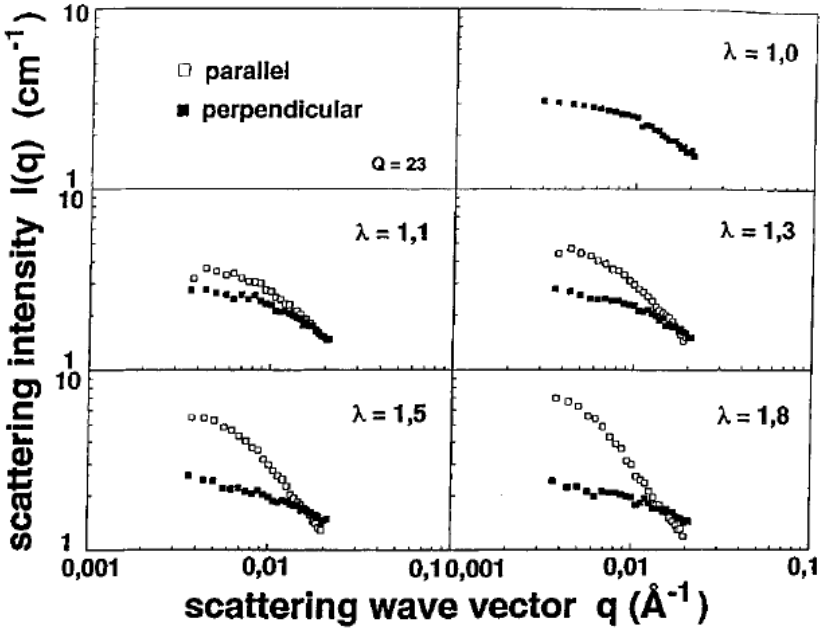


Figure 4. Scattered intensity, $I(q)$ in the parallel and in the perpendicular directions as a function of q, for different elongation ratios, λ. A log−log representation is used. The swelling ratio is $Q = 23$.

OZ: Extract screening length and I_0 (fluctuations) and compare to models (overestimate).

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Studies of network deformation: relaxation

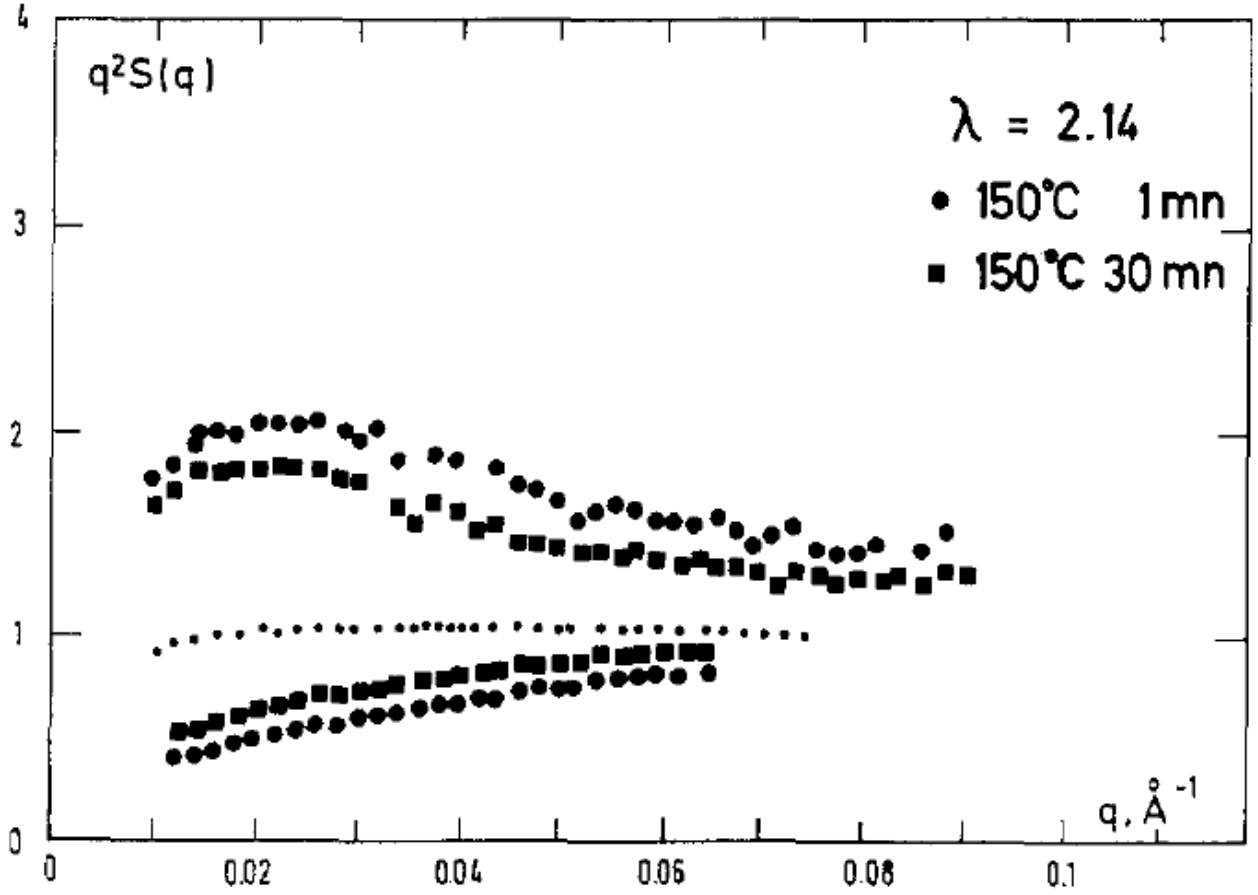
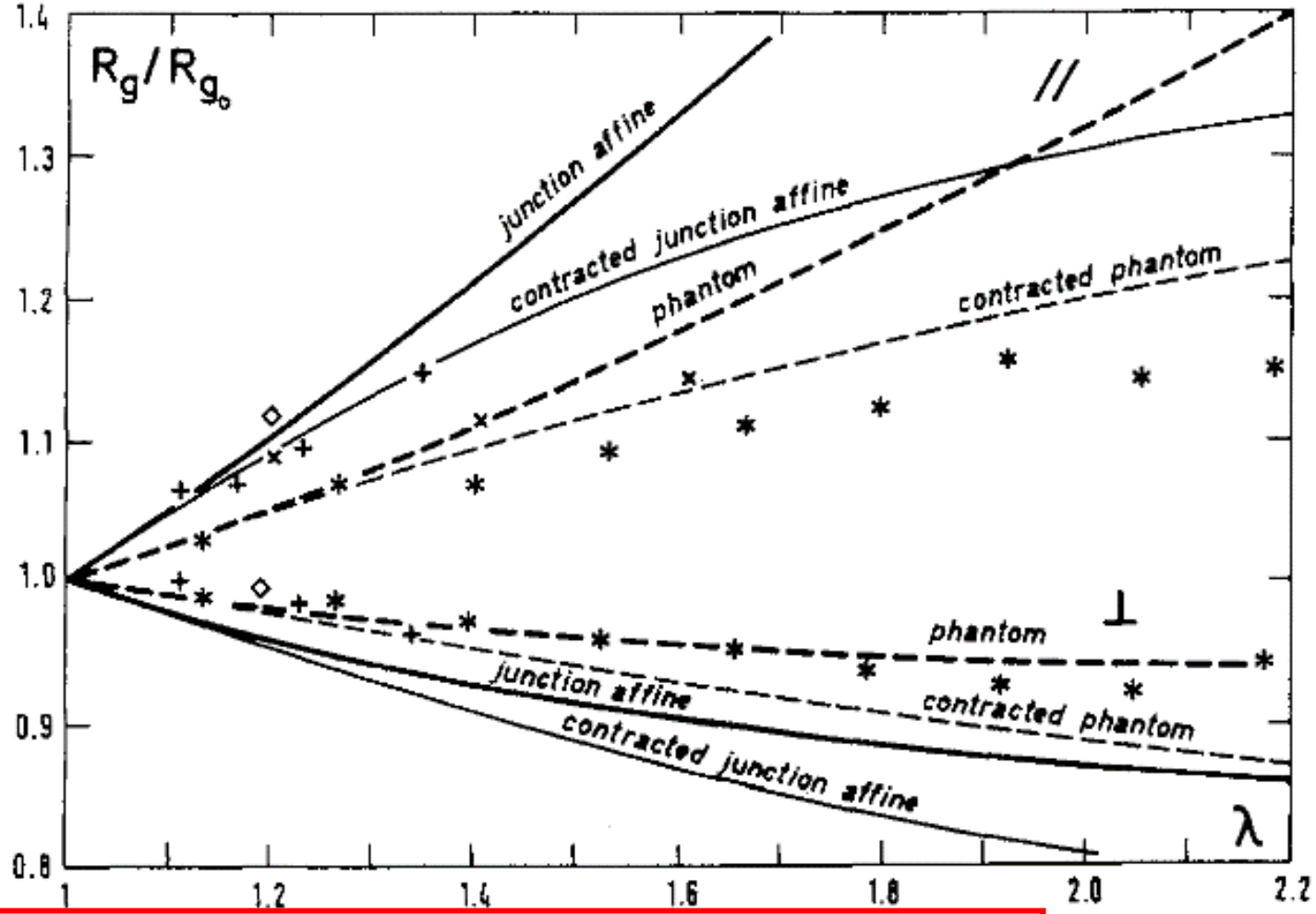


Fig. 5. Relaxation of the form factor of a *y*-rubber stretched 2.14 times between 1 min (●) and 30 min (■) at 150°C

Labelled meshes, in

Progr Colloid & Polymer Sci 75:152-170 (1987)

Studies of network deformation: mechanical models



Phantom network vs. junction-affine
Happy? Good fit? Different deformations in two directions! => Defects

Labelled meshes, in

Progr Colloid & Polymer Sci 75:152-170 (1987)

Outline

Examples

- Chains in polymer nanocomposites.
- Chains in core-shell microgel particles.

Chains can be modelled as sequence of beads/monomers.

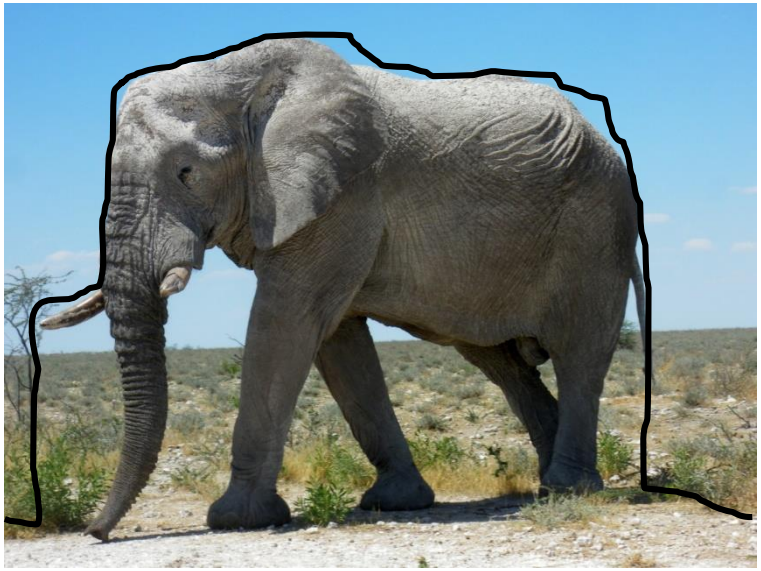
- NPs in polymer nanocomposites: simple RMC
- Aggregates of NPs in polymer nanocomposites: RMC+aggs

- Anisotropy: field- or deformation-induced.

Take home messages

- It is said to take five parameters to fit an elephant.

- A good fit does NOT mean you have produced anything meaningful.



THEREFORE (true for many areas):

- Start with easiest model. Only in case of failure, make it more complex (more parameters, phenomena, …).
- Don’t try to make perfect fits. Better follow signatures (slopes, peaks, …).
- Talk to people with experience in data treatments.
- Use other people’s programs only if you understand what you are doing (namely, the underlying equations).

What (neutron) scattering really is…