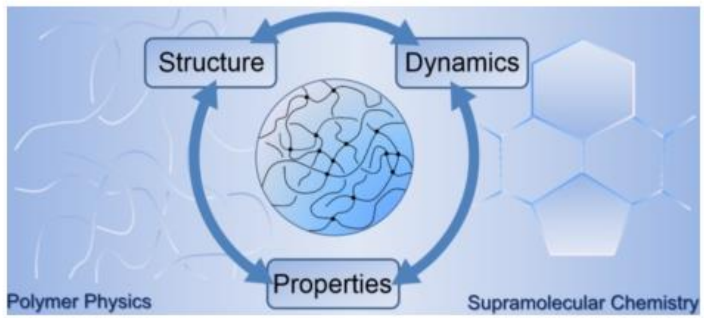
Marie Sklodowska Curie ITN-DoDyNet
Double dynamics for design of new responsive polymer networks and gels



"Structure and diffusion in DDNs at the nano- to micro- scale"

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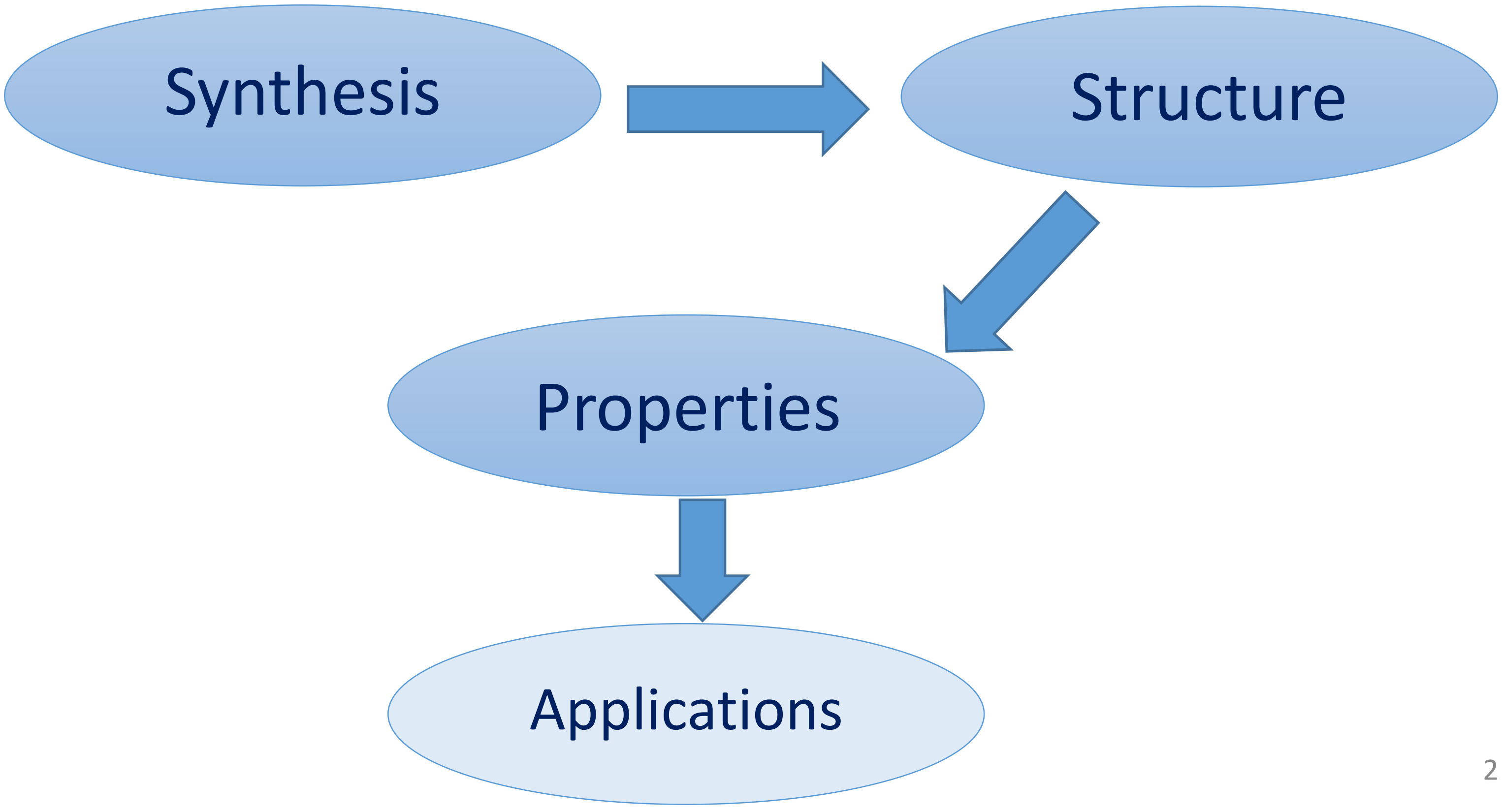
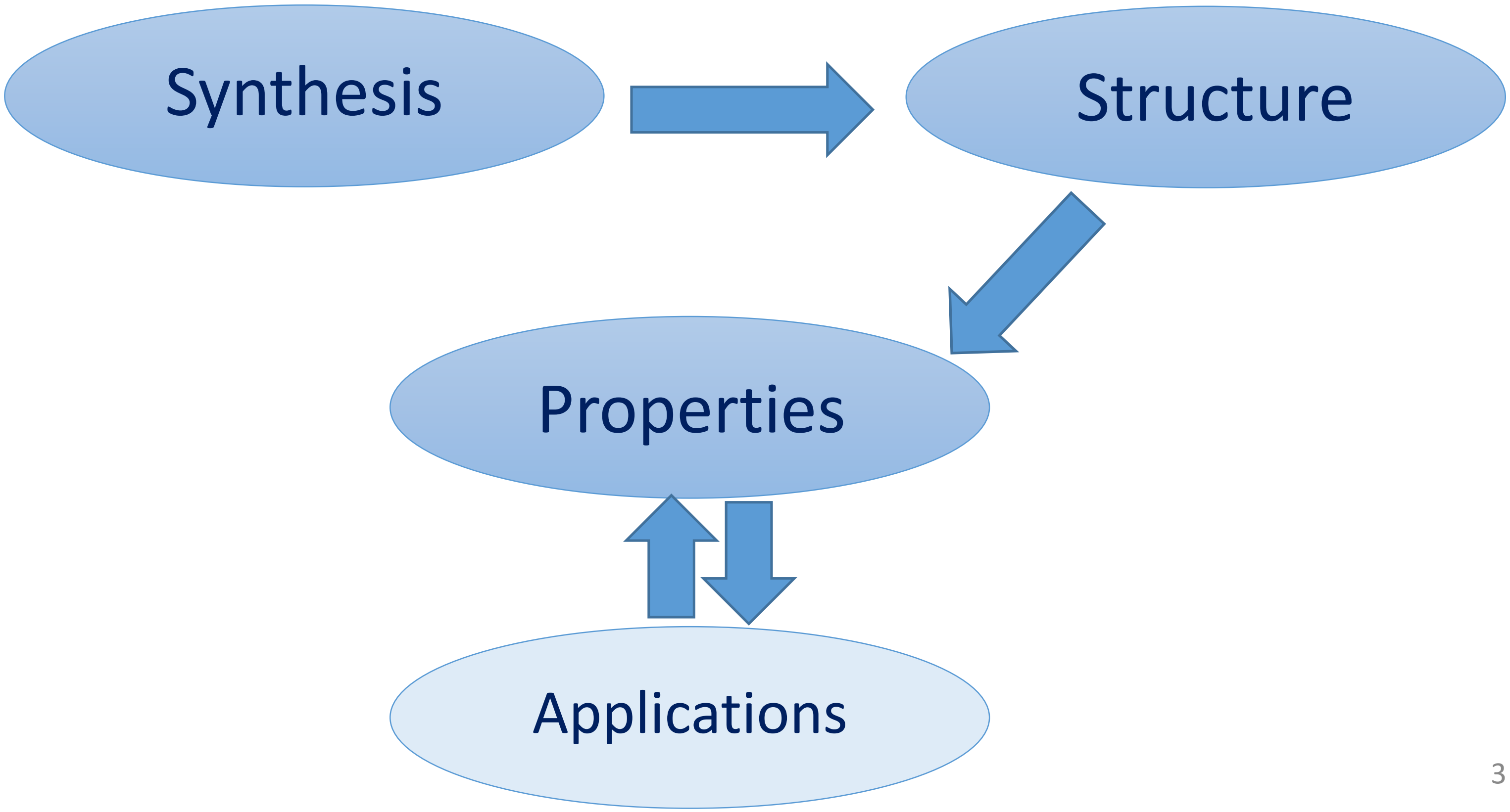
Prof. Dr. Sebastian Seiffert

Institute of Physical Chemistry
Johannes Gutenberg University
Mainz, Germany

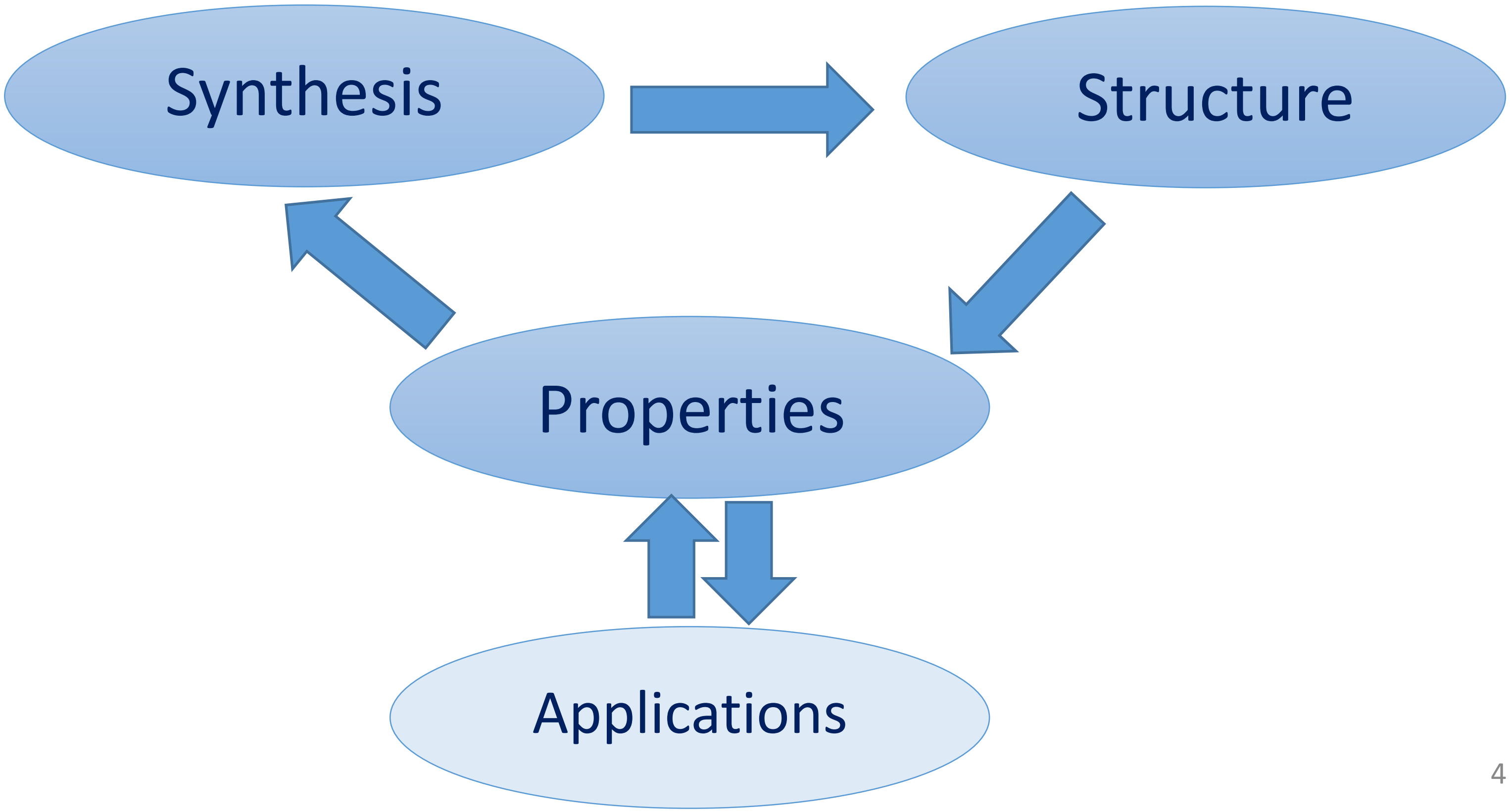
Structure and diffusion in DDNs at the nano- to micro- scale



Structure and diffusion in DDNs at the nano- to micro- scale



Structure and diffusion in DDNs at the nano- to micro- scale



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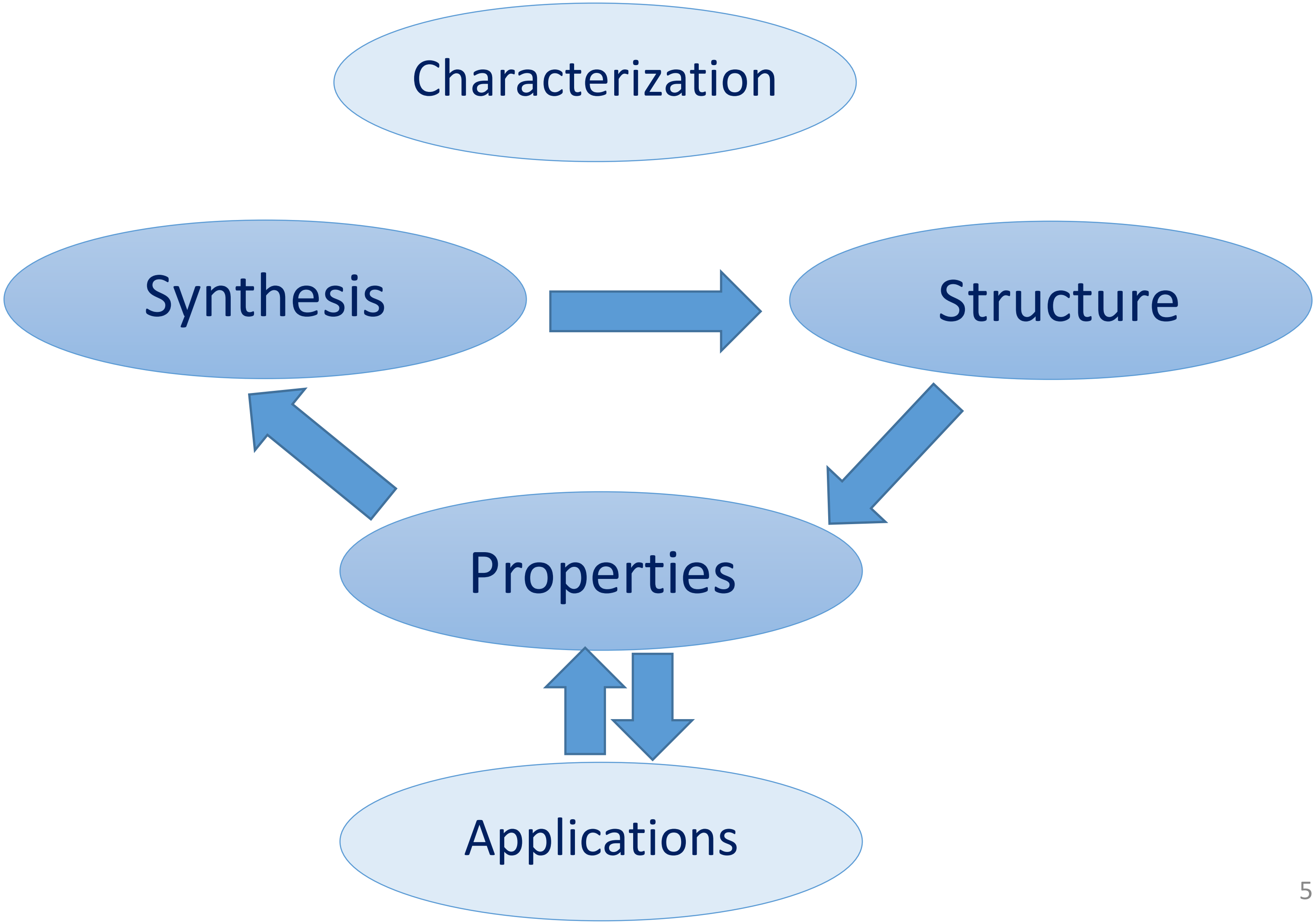
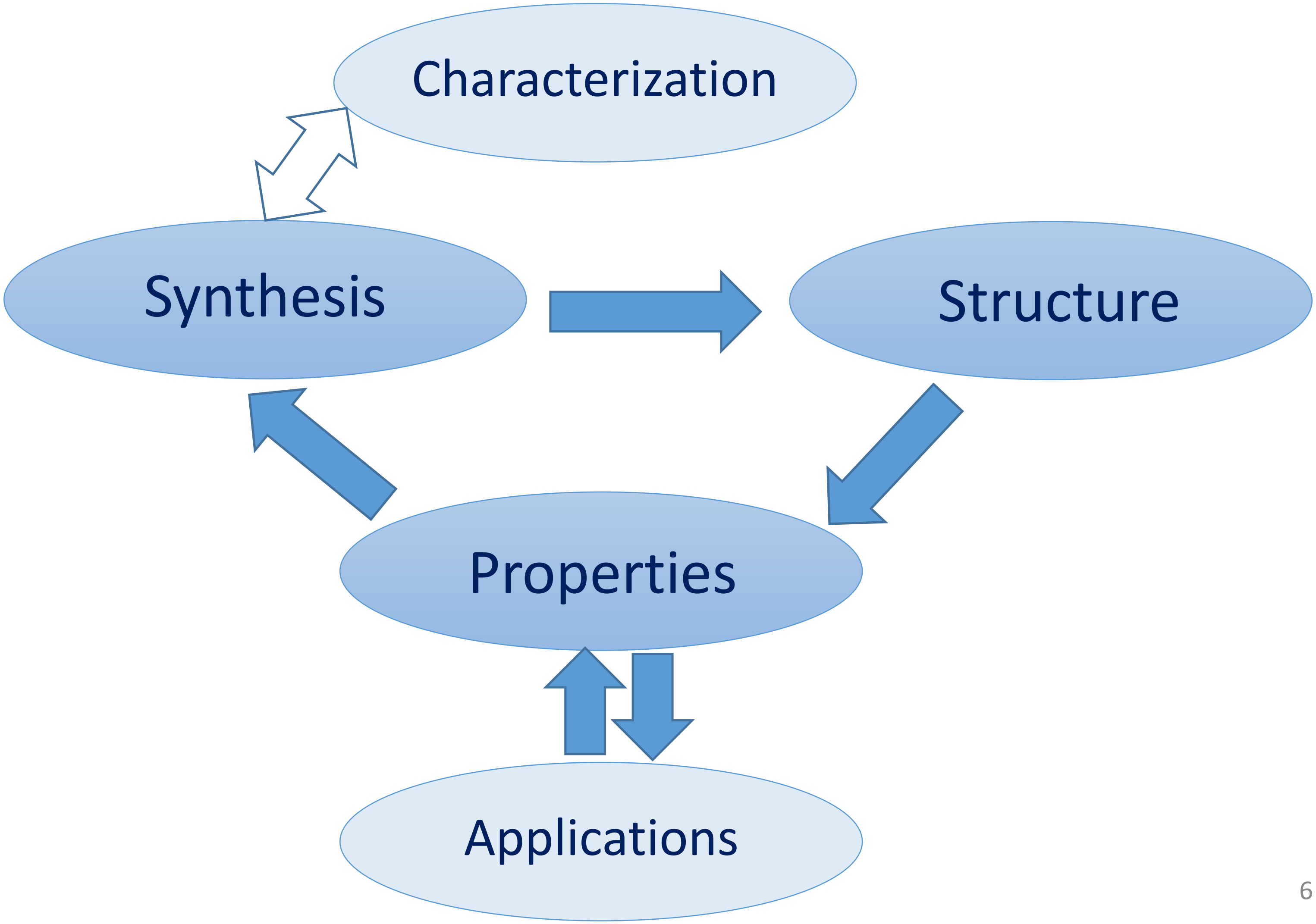
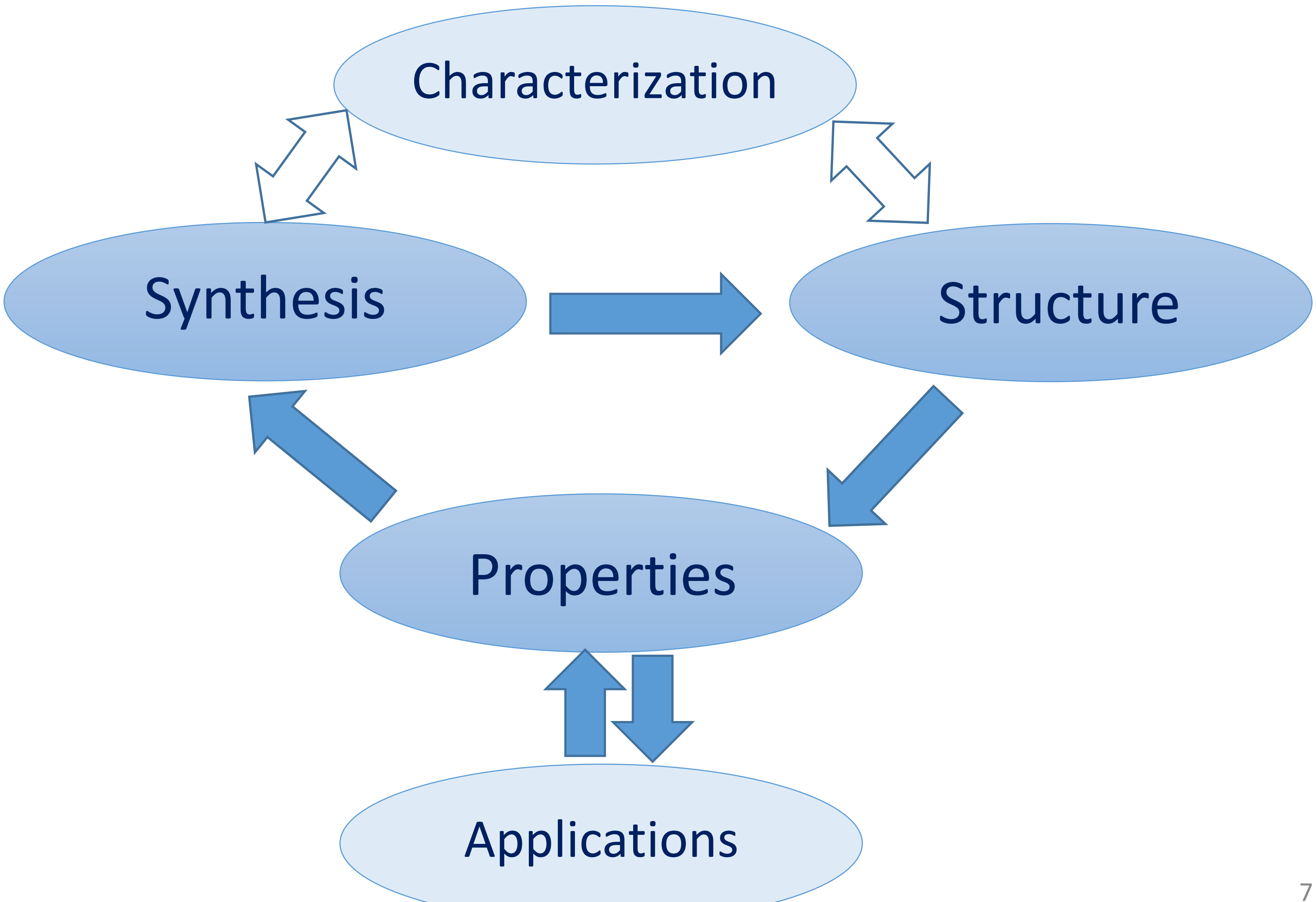


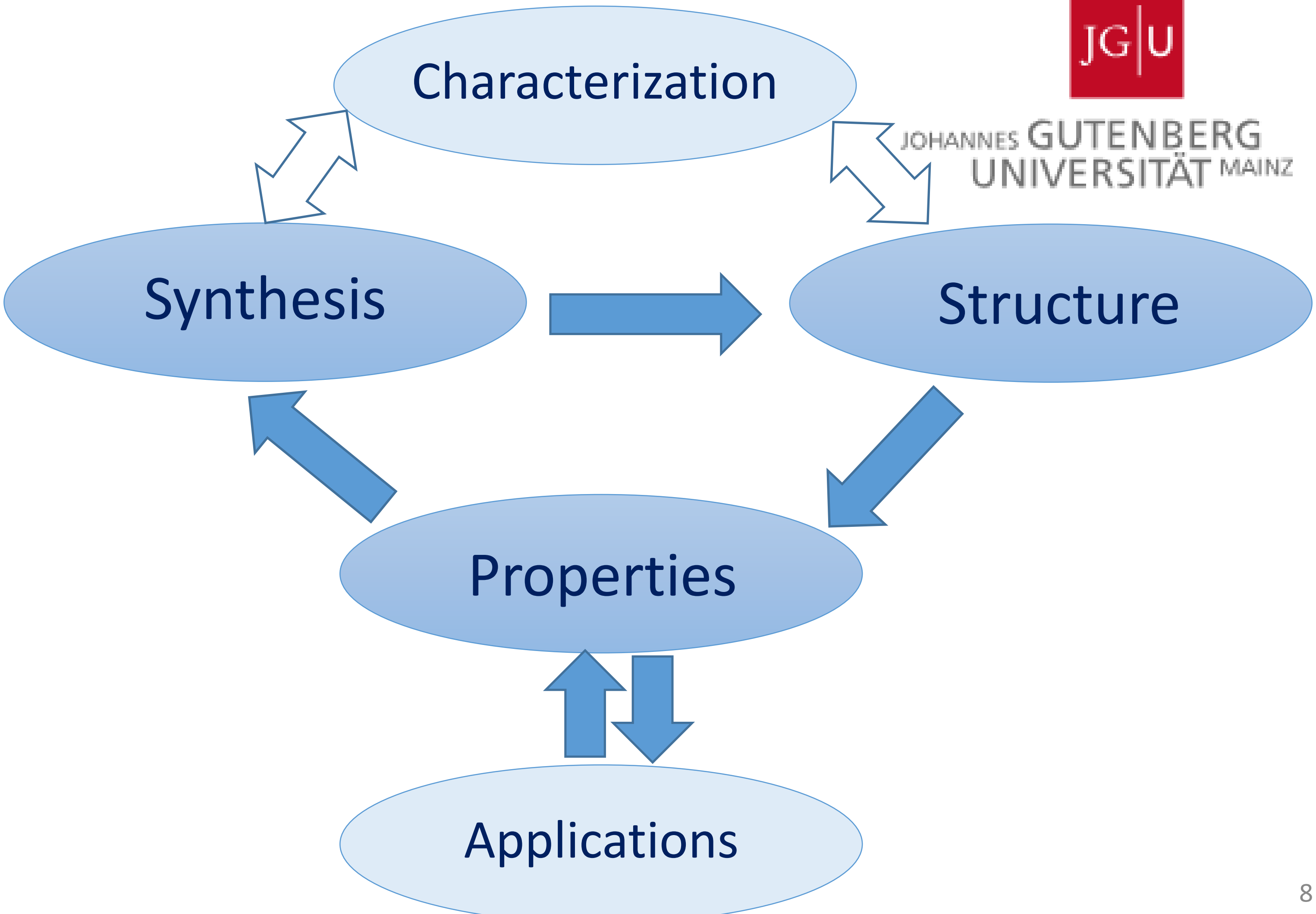
Structure and diffusion in DDNs at the nano- to micro- scale



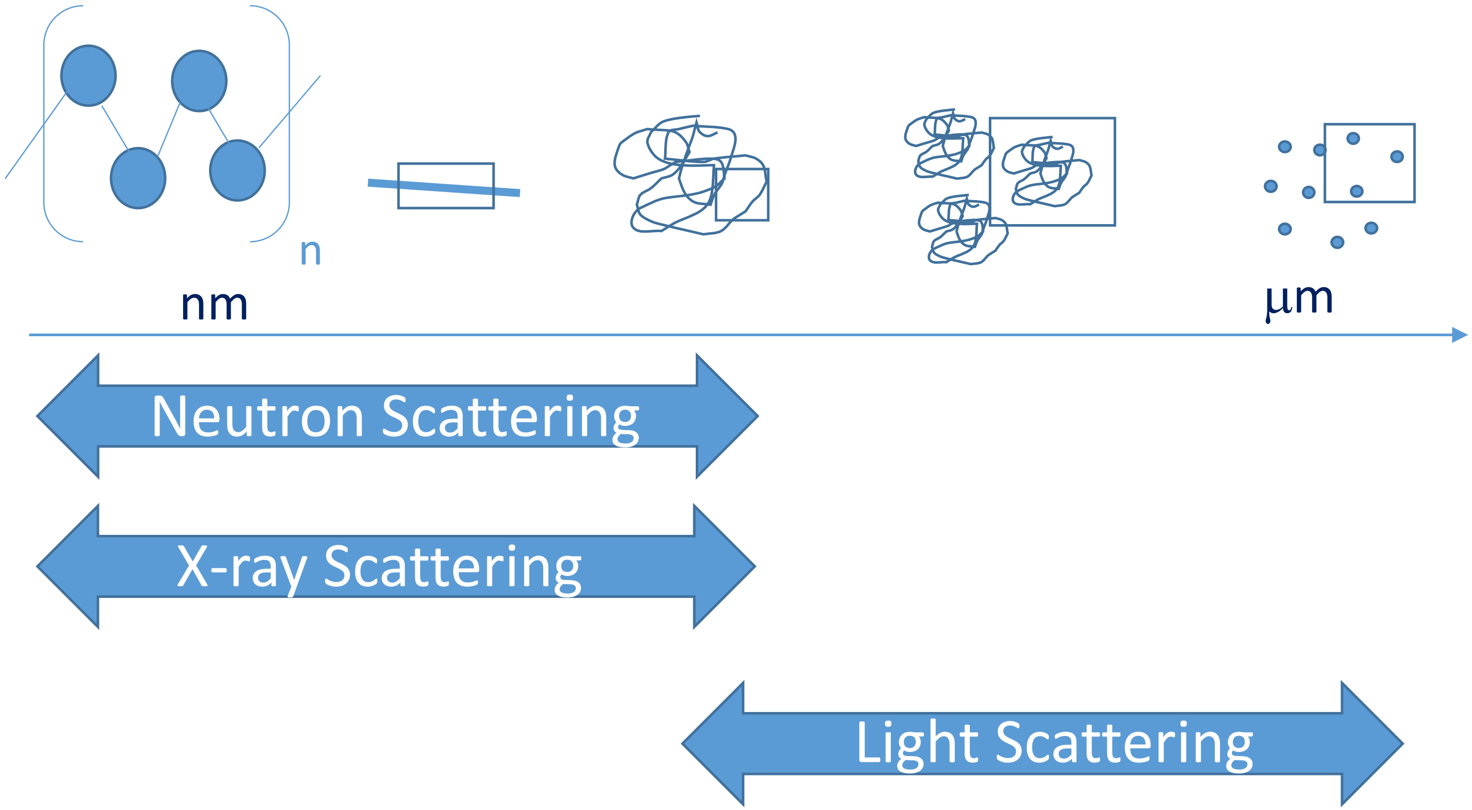
Structure and diffusion in DDNs at the nano- to micro- scale



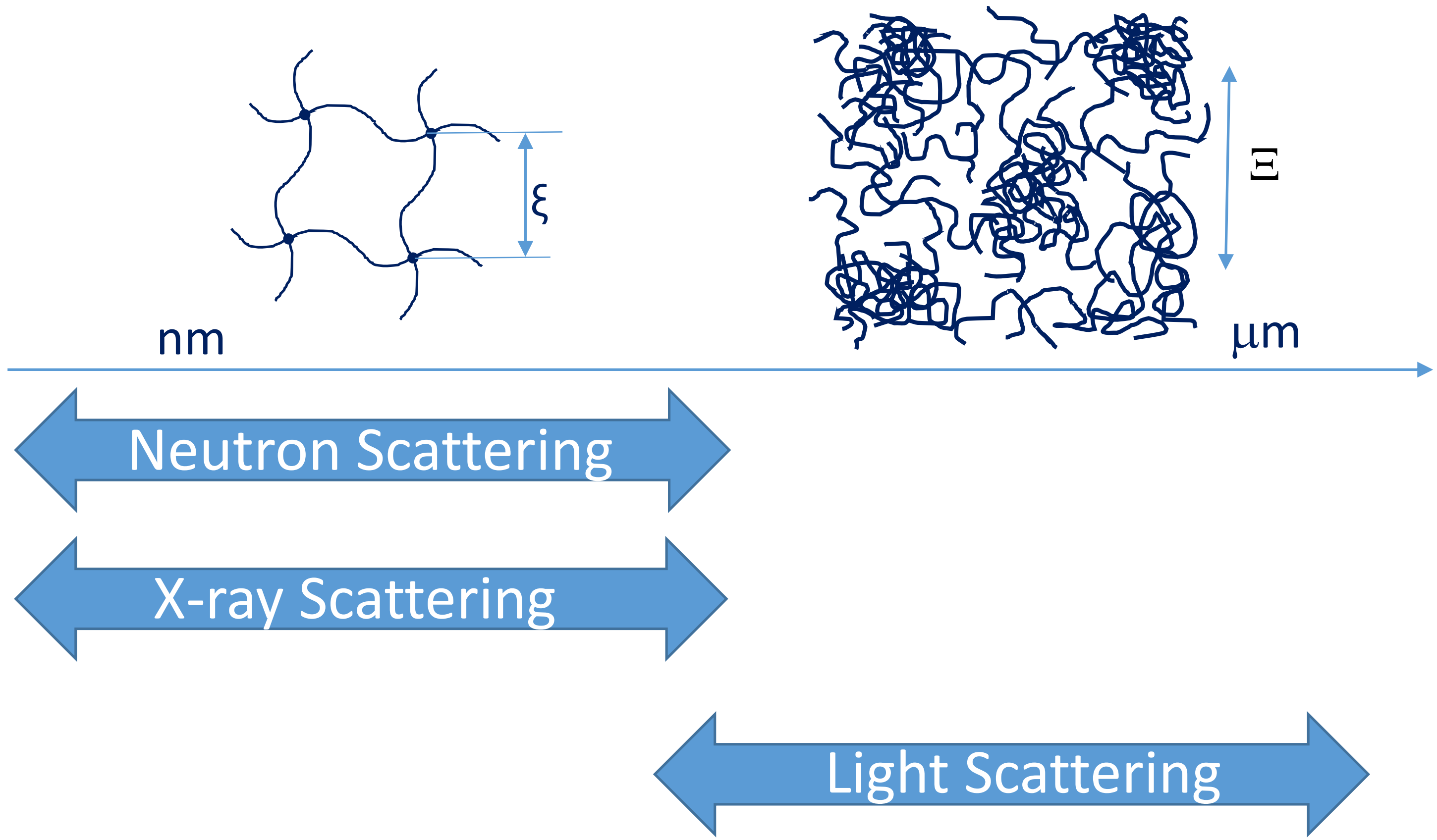
Structure and diffusion in DDNs at the nano- to micro- scale



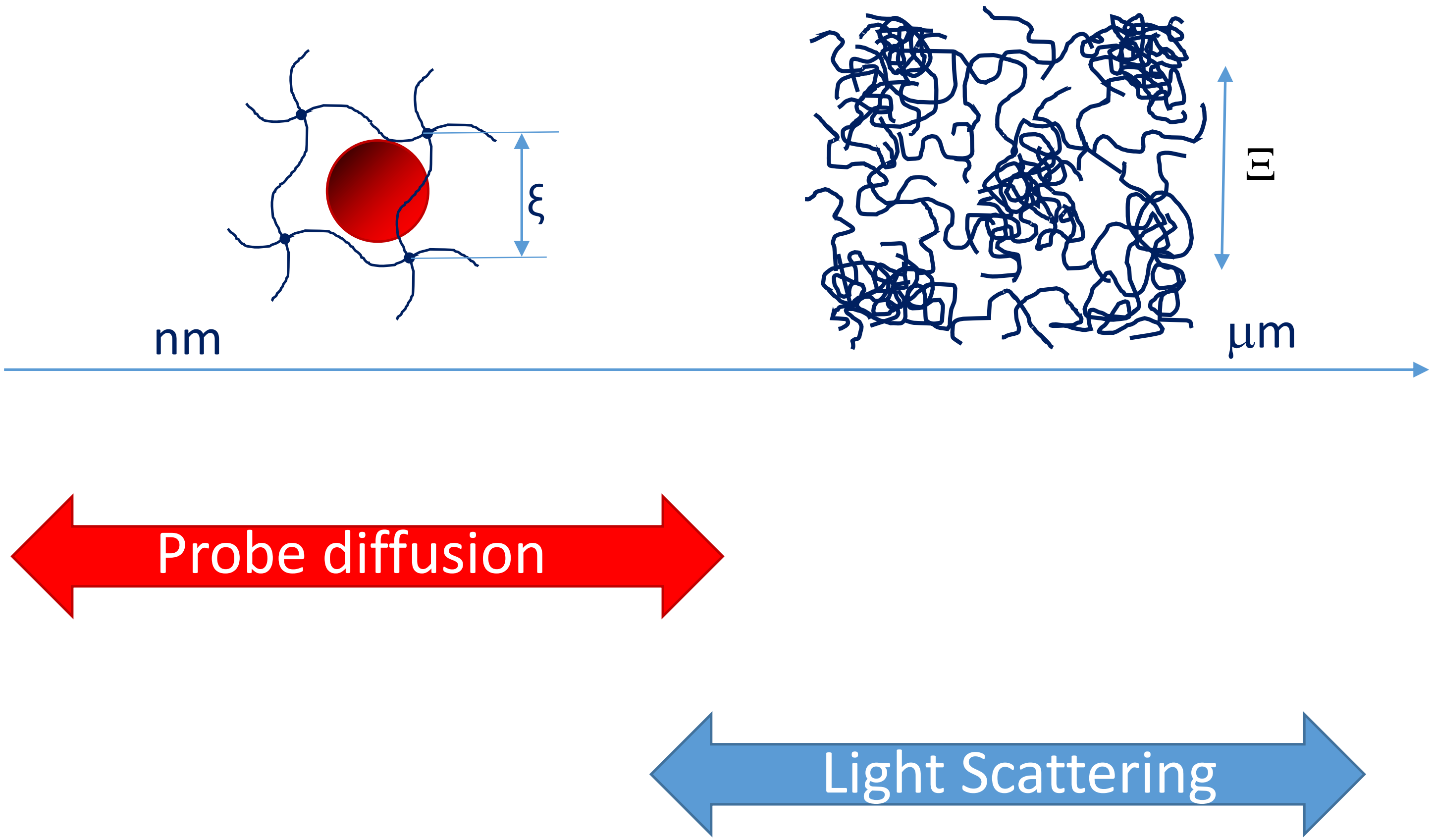
Scattering methods



Scattering methods



Scattering methods



From the nano- to micro- scale

Characterization techniques

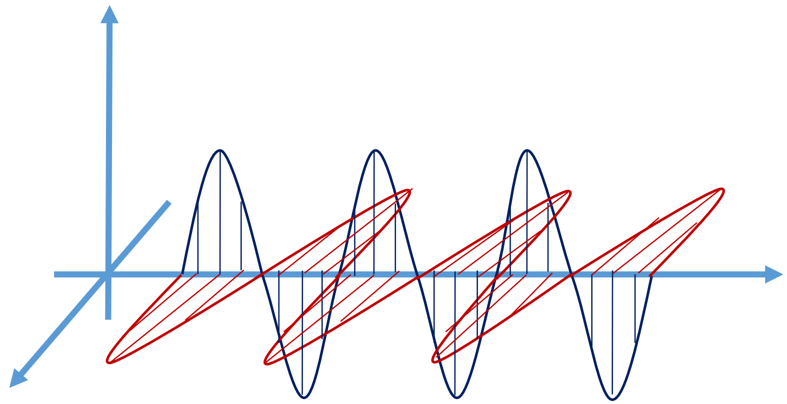
Light scattering

- Static light scattering (SLS)
- Dynamic light scattering (DLS)

Probe diffusion

- Dynamic light scattering
- Fluorescence correlation spectroscopy (FCS)
- Fluorescence recovery after photobleaching (FRAP)

Light Scattering



Light is an electromagnetic wave produced by an electric and magnetic field oscillating perpendicular to each other.

In light scattering only the electric field is considered, because the magnetic field does not interact with organic matter.

The electric field is given by:

$$E(x,t) = E_0 \cos(2\pi\upsilon\left(t - \frac{x}{c}\right)) + \Phi$$

$\upsilon = frequency$ $\quad c = \text{speed of light}$

$E_0 = \text{amplitude field}$ $\quad \Phi = phase$

The intensity of the light will then be:

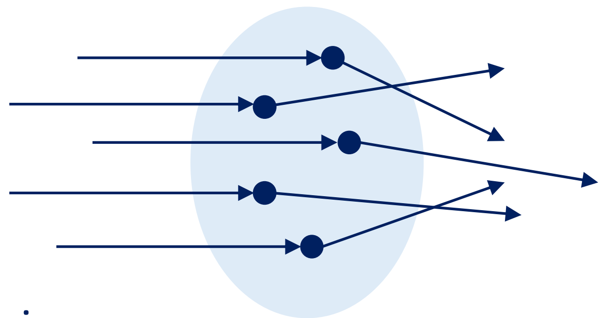
$$I_0(x) = \varepsilon_0 c < E^2(x,t) >$$

$\varepsilon_0 = permettivity\ of\ vacuum$

Light Scattering

When the electric field interacts with the particles, it will induce in them a dipole.

The dipole will oscillate generating other waves itself. This re-emission is the scattering.



There are 3 types of scattering:

- Elastic: if the outgoing wave has the same wavelenght of the ingoing wave
- Quasi elastic: if the outgoing wave has almost the same wavelenght of the ingoing wave
- Inelastic: if the outgoing wave has not the same wavelenght of the ingoing wave

Dynamic and static light scattering are quasi elastic light scattering events.

Light Scattering

Static: measures the average intensity of the scattered light at different angles

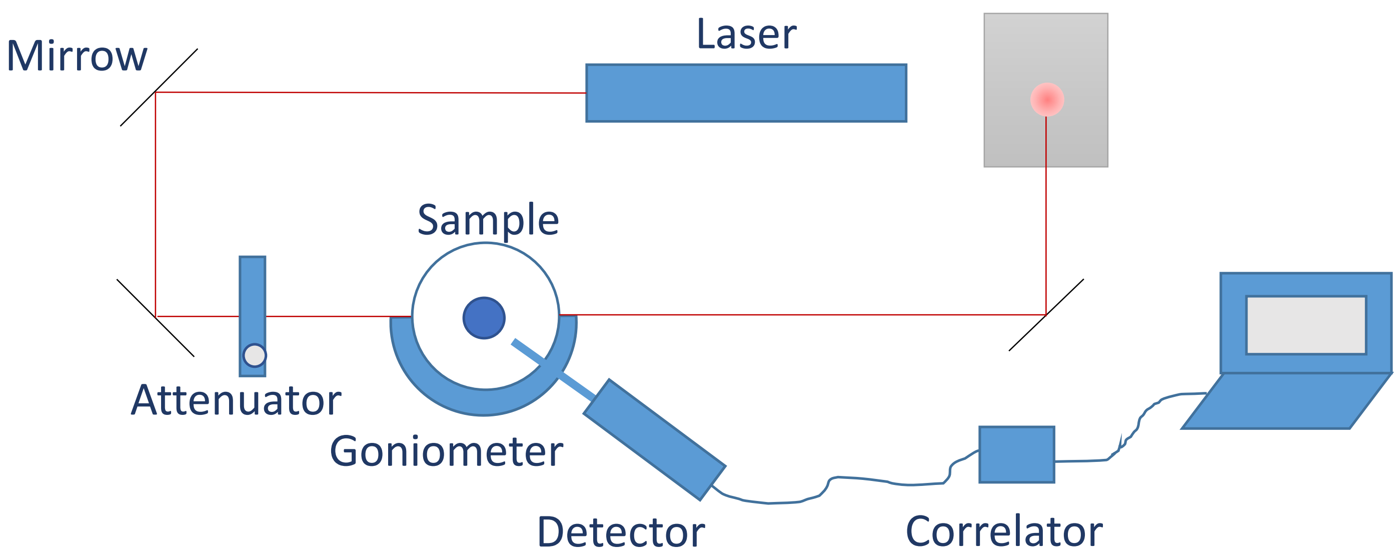
Dynamic: measures the temporal fluctuations of the scattered light

What we need in advance	SLS	DLS
Refractive index solvent	√	√
Viscosity solvent		√
Concentration sample	√	
Temperature sample		√
dn/dc	√	

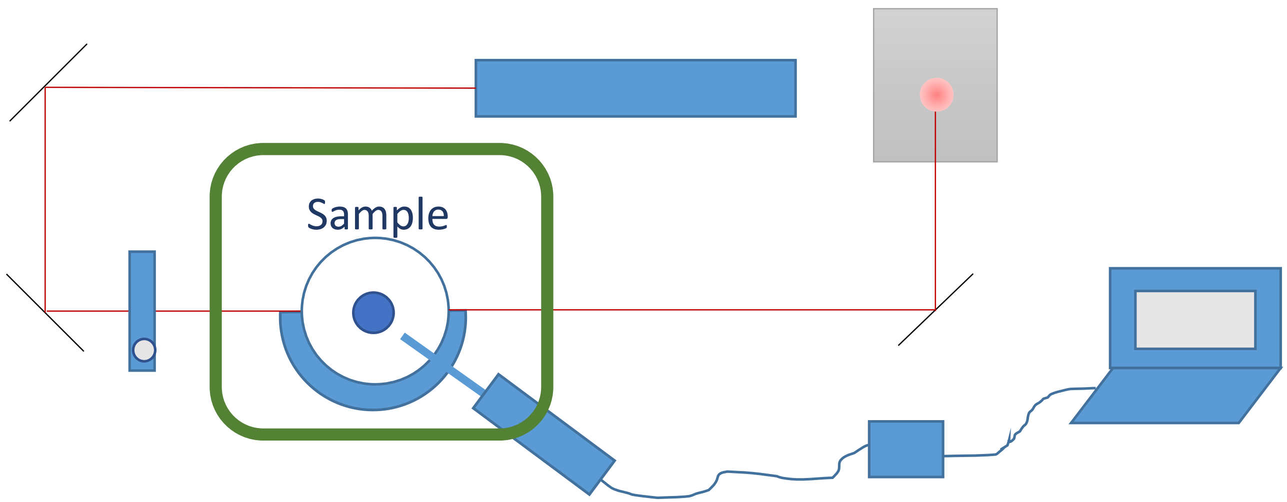
	What can be determined	SLS	DLS
Single chains	Molecular weight	√	
	Radius of gyration	√	
	Hydrodynamic radius		√
	Shape	√	
Networks	Mesh size		√
	Homogeneity		√

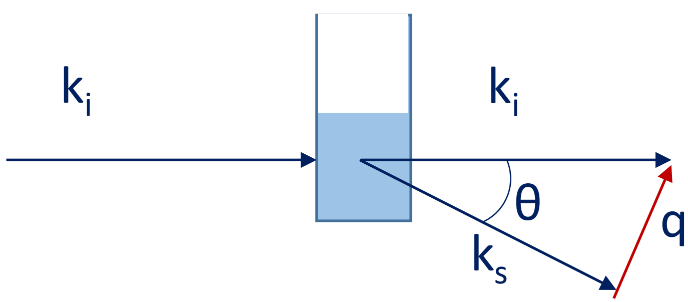
Light Scattering

Setup



Light Scattering

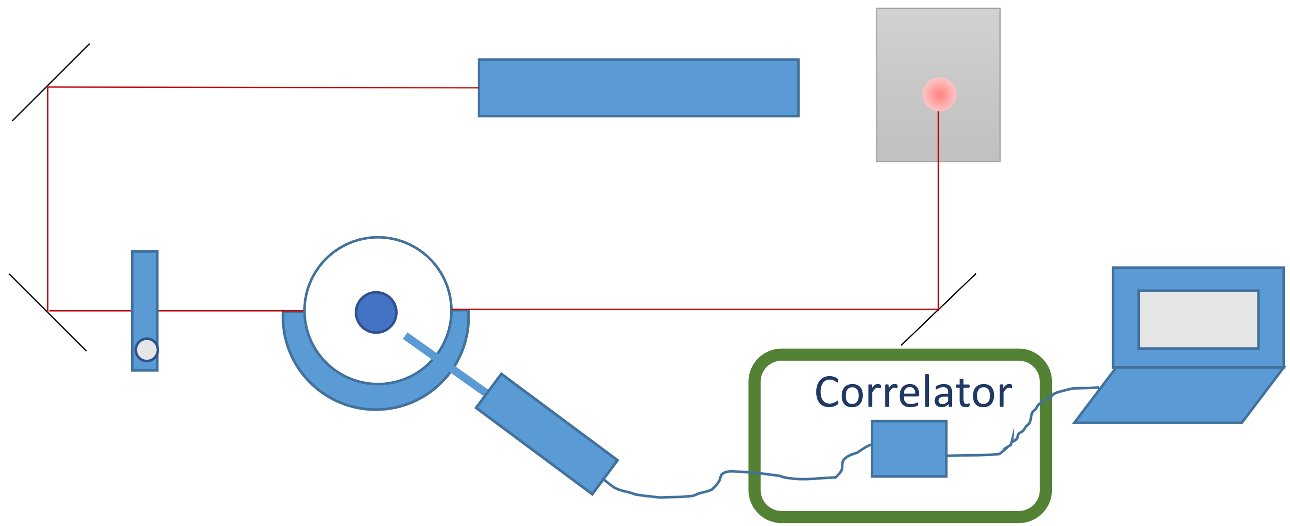




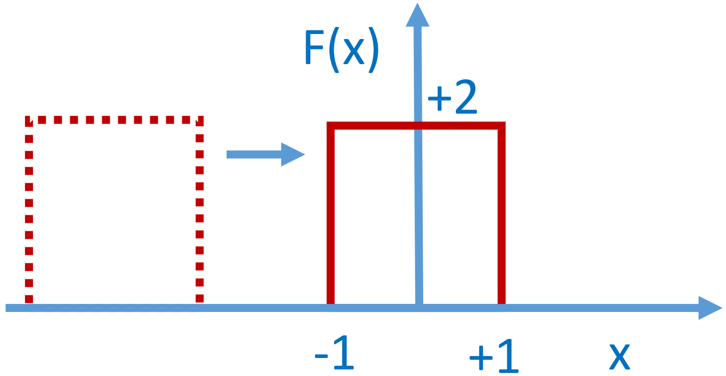
$$q = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right)$$

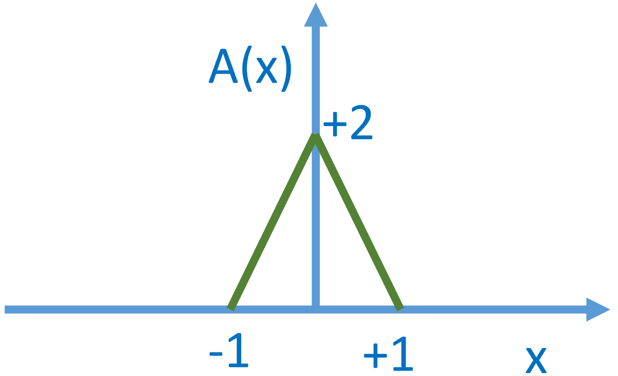
$\mathbf{q}=\mathbf{k}_{incident}-\mathbf{k}_{scattered}$=scattering vector

Dynamic Light Scattering

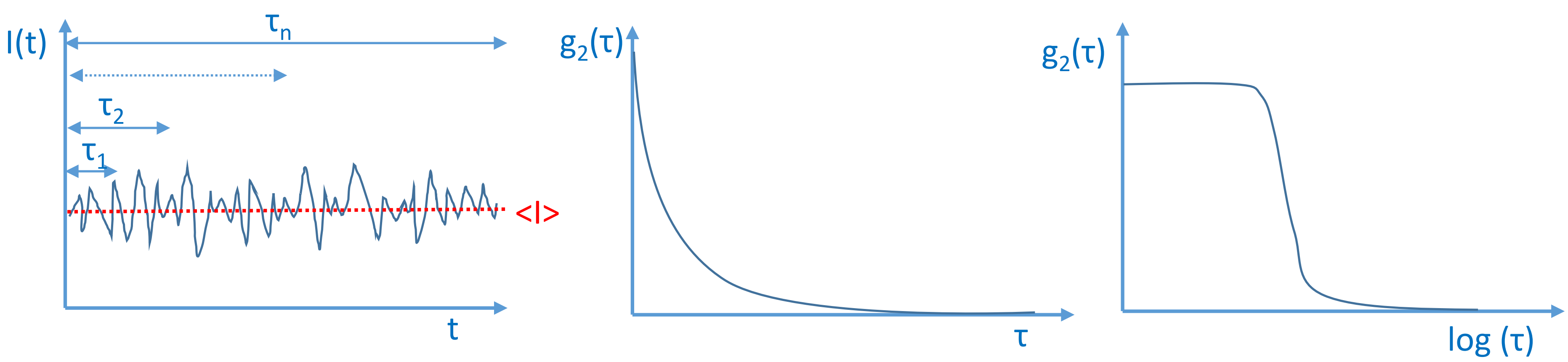


Autocorrelation function: function that relate a copy to the initial function and how it changes in relation to the set parameter





Dynamic Light Scattering



Intensity autocorrelation function $G_2(t) = < I(t)\ I(t+\tau) >$ $g_2(t) = \dfrac{< I(t)\ I(t+\tau) >}{< I(t) >^2}$

Field autocorrelation function $G_1(t) = < E(t)\ E(t+\tau) >$ $g_1(t) = \dfrac{< E(t)\ E(t+\tau) >}{< E(t) >^2}$

$$g_2(t) = 1 + \beta\,[2\,x\,(1-x) g_1(t) + \ x^2\ g_1^2(t)]$$

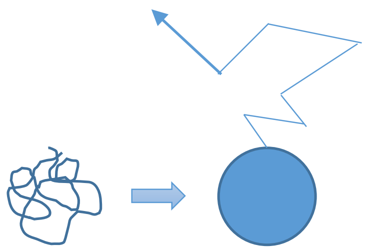
$x = 1$ ergodic systems

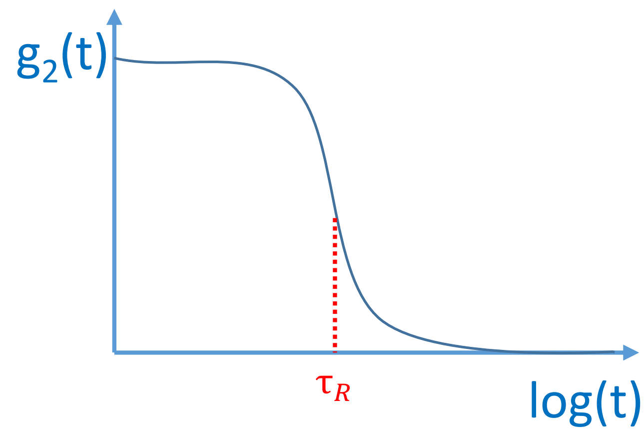
$0 < x < 1$ non-ergodic systems

Siegert relationship: $g_1(t) = \sqrt{\dfrac{g_2(t) - A}{A}}$

Dynamic Light Scattering

- Single chains or nanoparticles

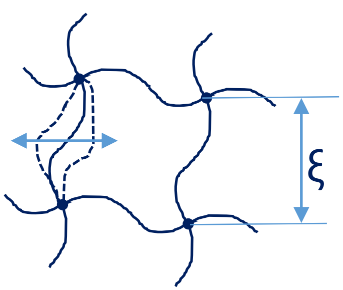


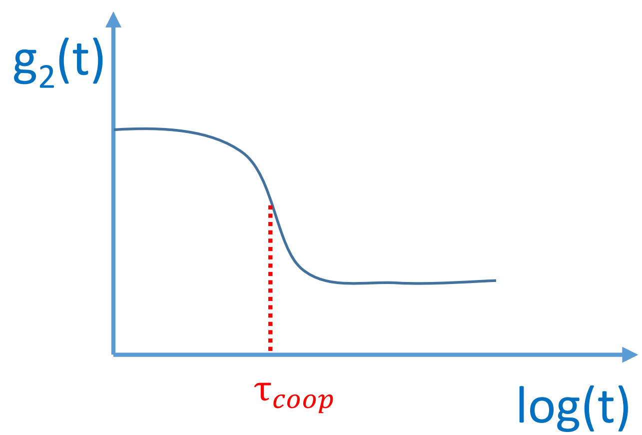


$$\tau_R = \frac{1}{D_{self}q^2}$$

$$D_{self} = \frac{kT}{6\pi\eta R_h}$$

- Networks

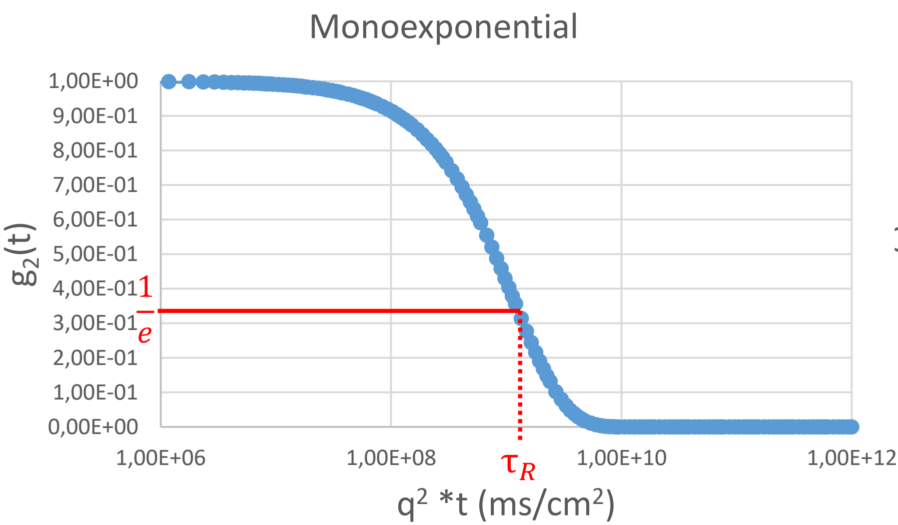


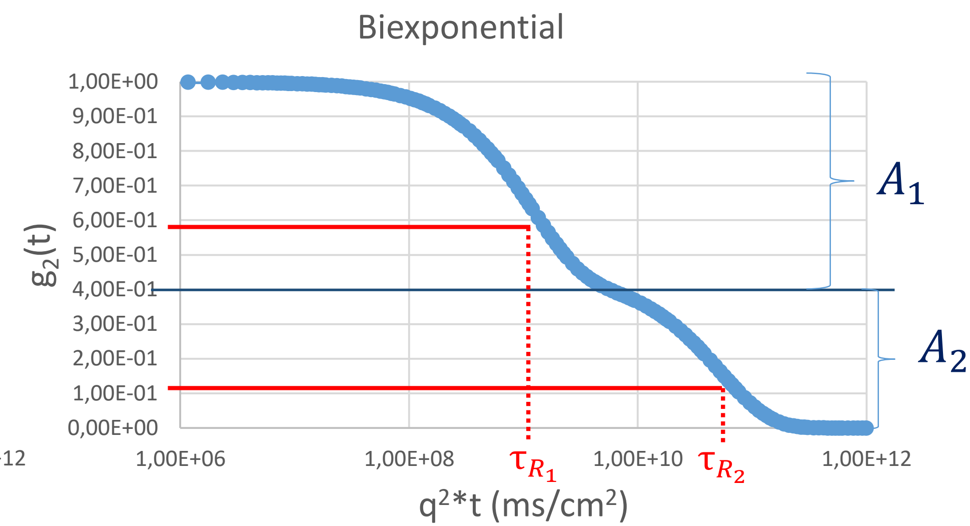


$$\tau_{coop} = \frac{1}{D_{coop}q^2}$$

$$D_{coop} = \frac{kT}{6\pi\eta\xi}$$

Dynamic Light Scattering

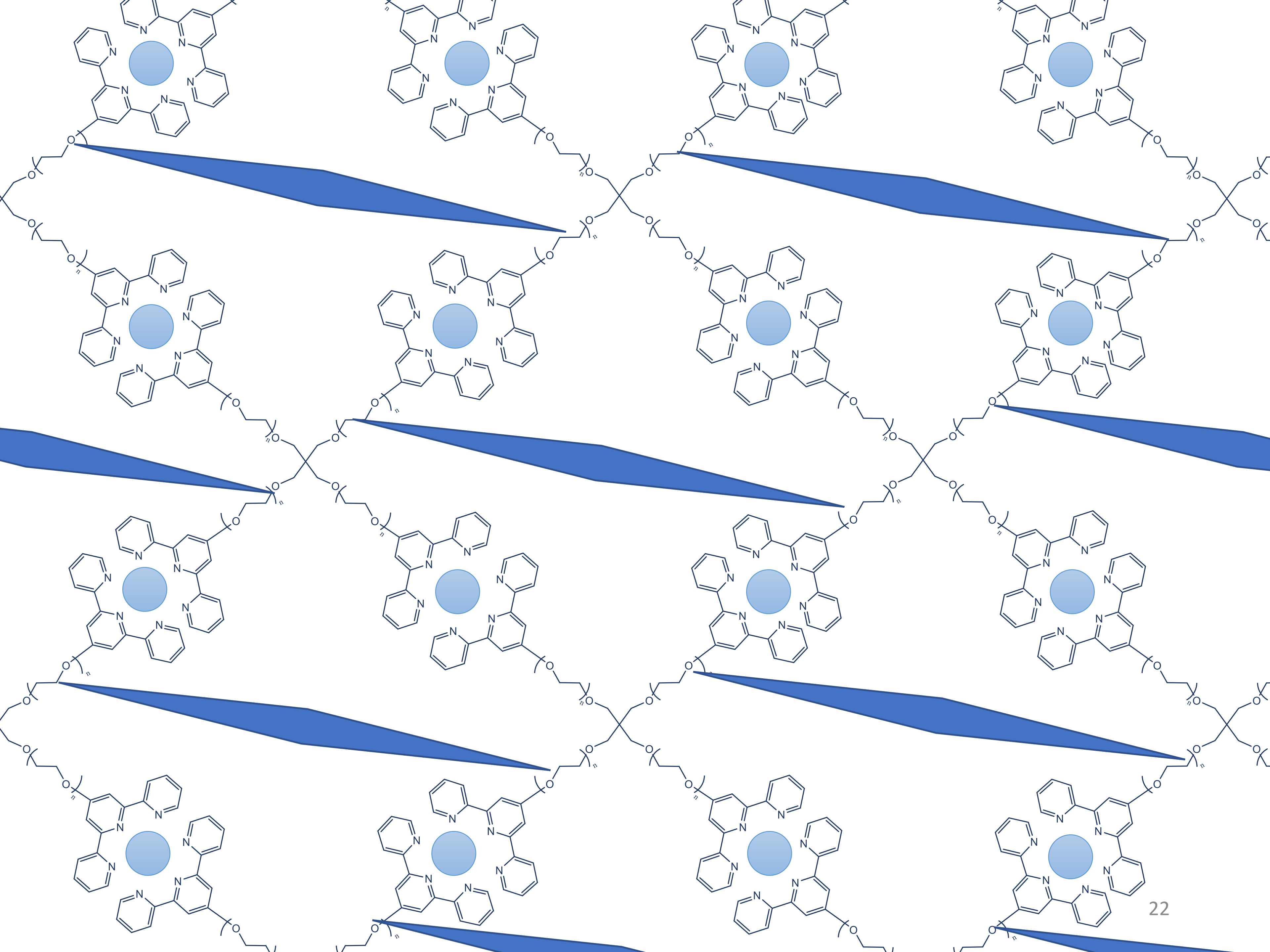




$$g_2(\tau) = A_1 \exp\left(-\frac{1}{\tau_{R_1}}\tau\right) \qquad g_2(\tau) = A_1 \exp\left(-\frac{1}{\tau_{R_1}}\tau\right) + A_2 \exp\left(-\frac{1}{\tau_{R_2}}\tau\right)$$

$$\tau_R = \frac{1}{Dq^2}$$

$$g_2(\tau) = A_1 \exp(-D_1 q^2 \tau) \qquad g_2(\tau) = A_1 \exp(-D_1 q^2 \tau) + A_2 \exp(-D_2 q^2 \tau)$$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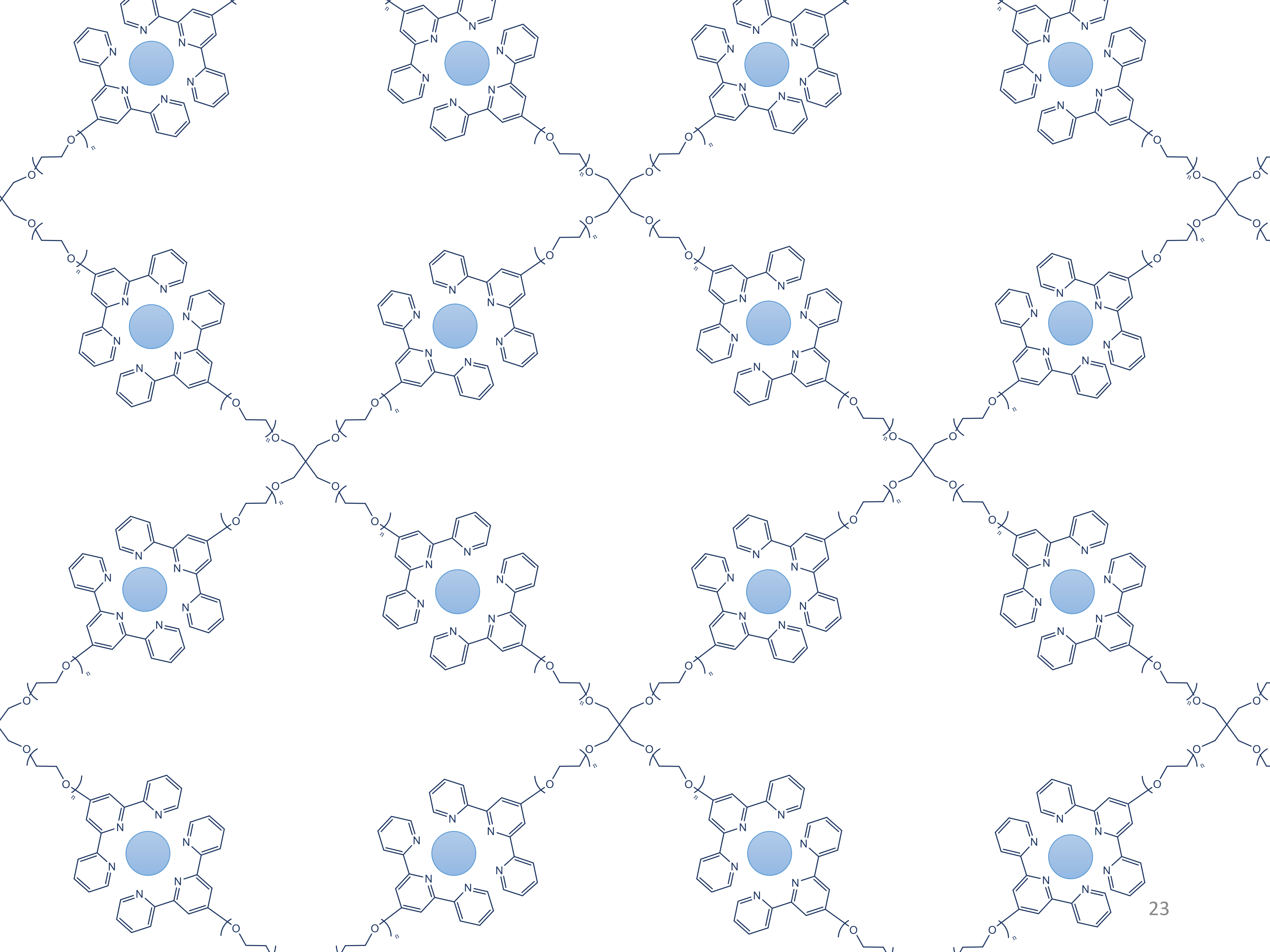
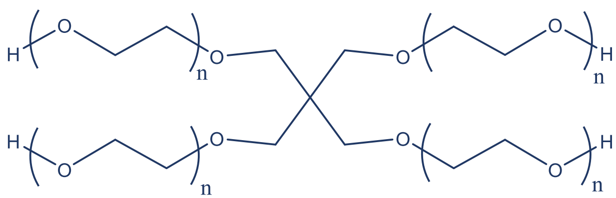


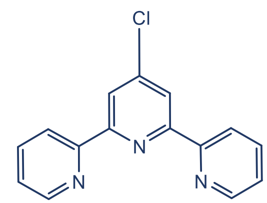
Experimental part

Synthesis



4-arm Poly ethylene glycol (PEG)
10 000 g/mol

+

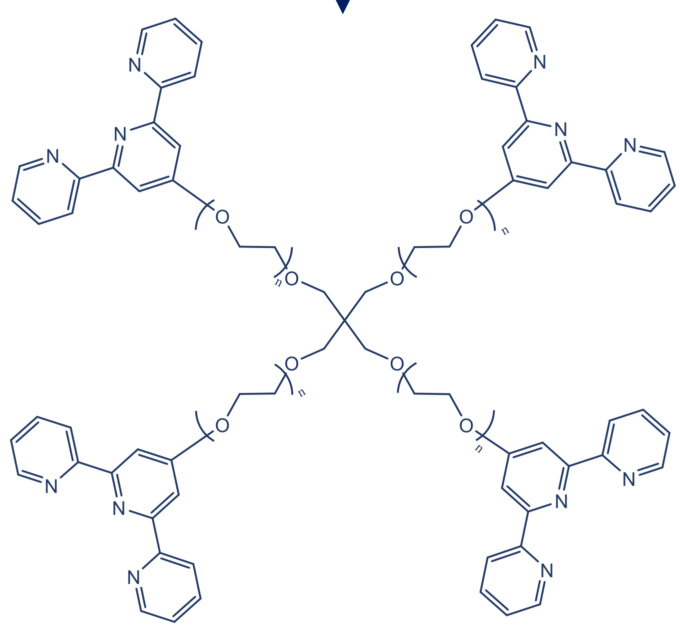


Chloro terpyridine

DMSO (dry)

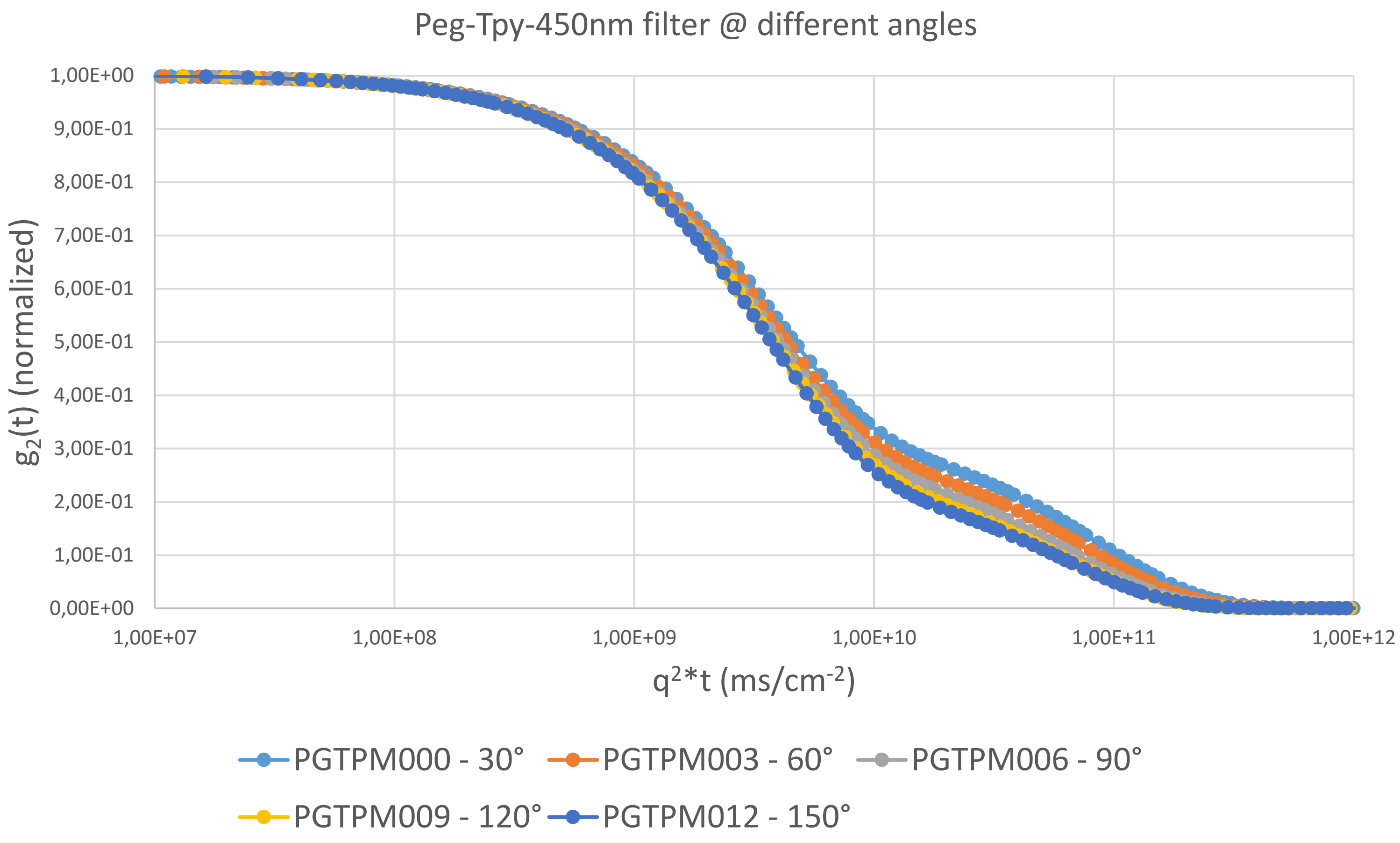
KOH

Kryptand 2.2.2.

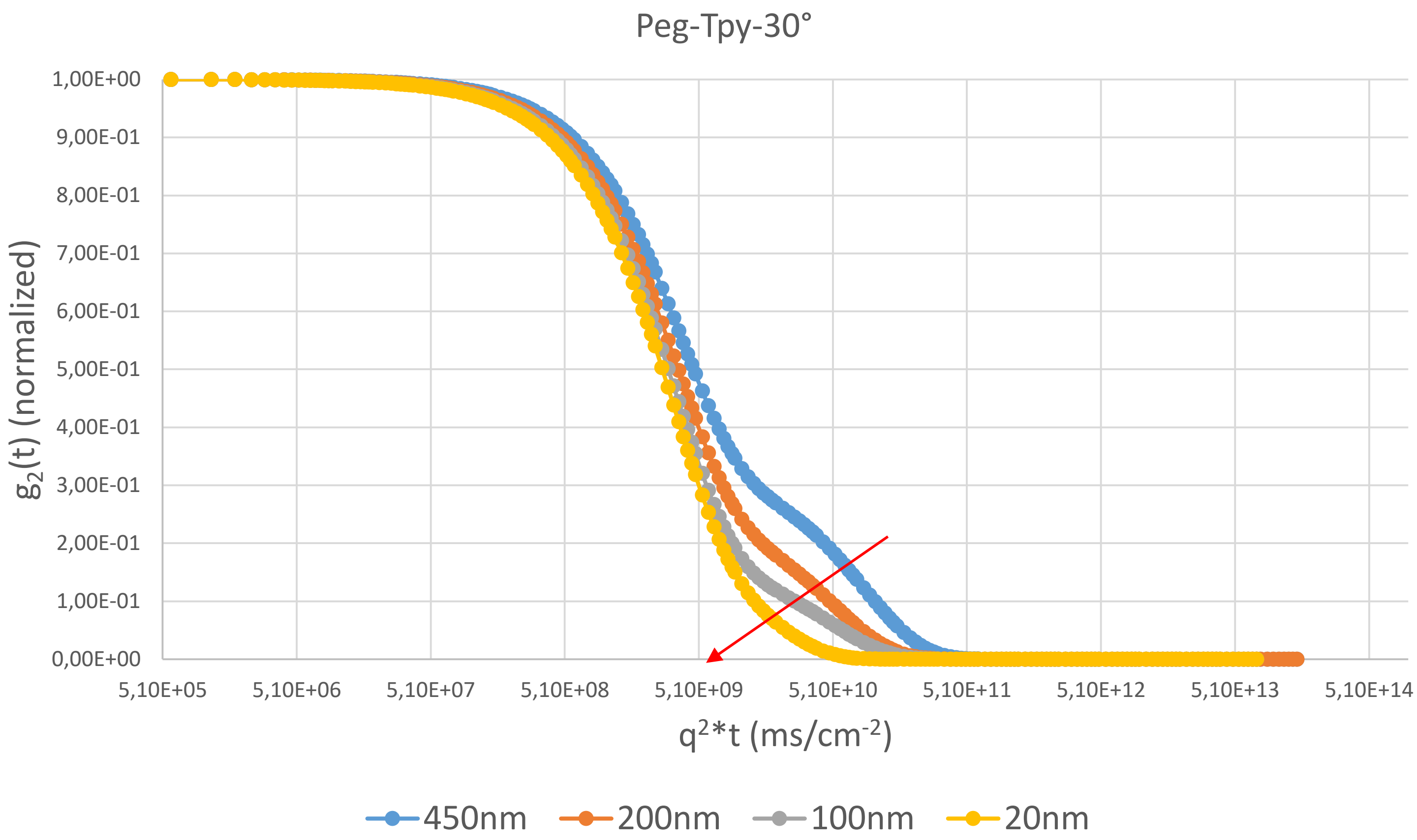


Results

It is biexponential because there are impurities!

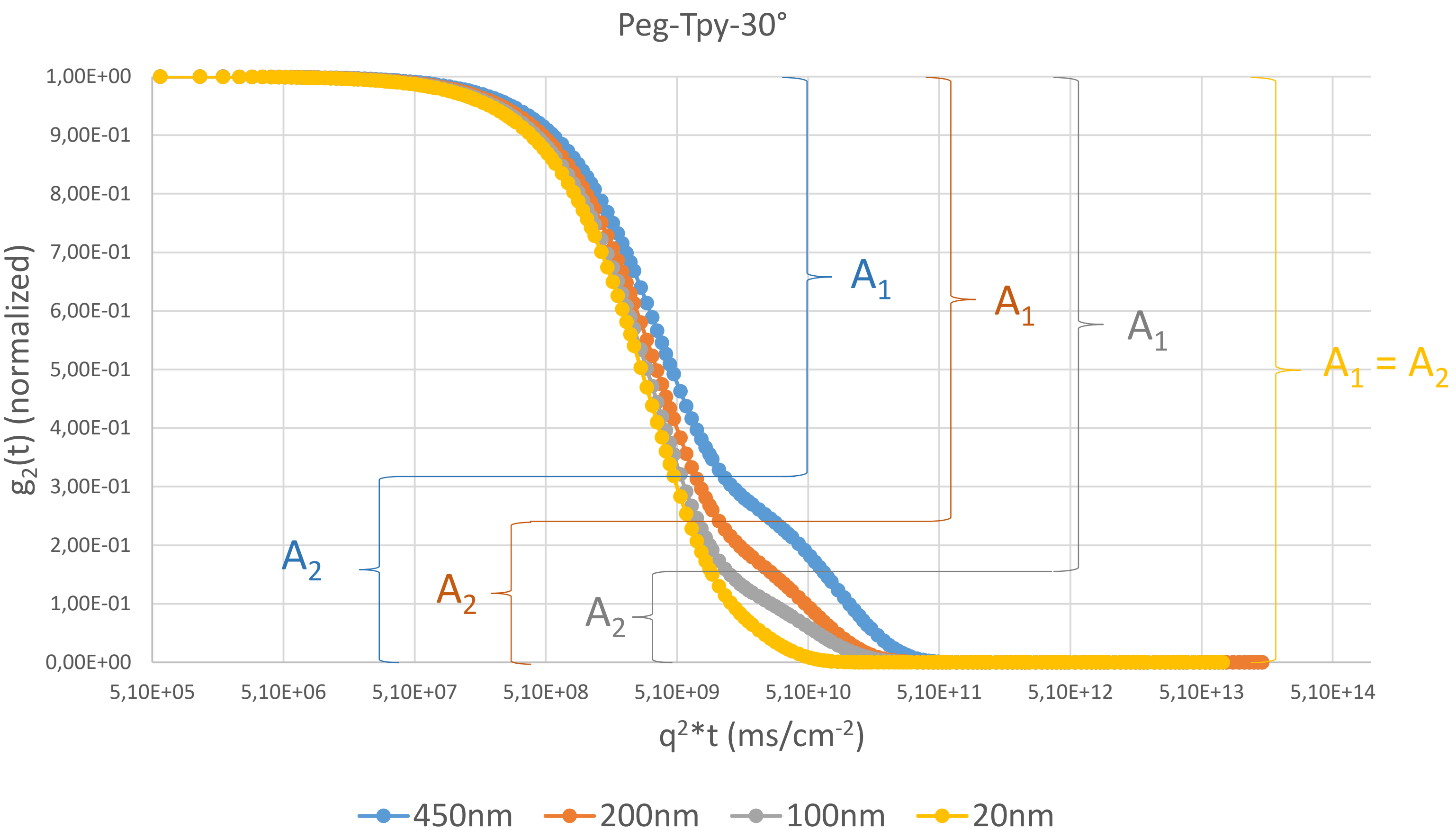


Results



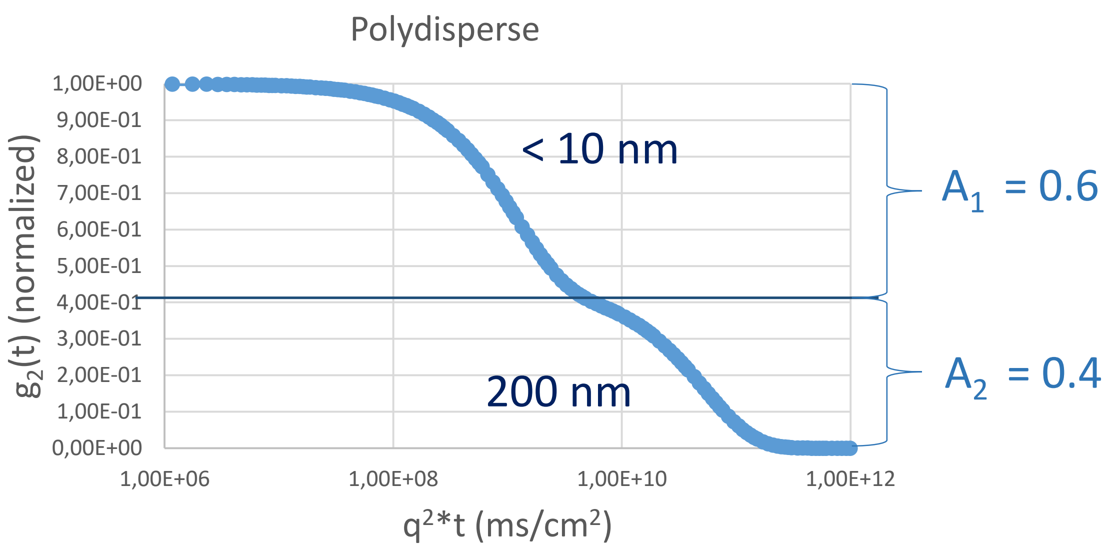
Peg-Tpy-30°
1,00E+00
9,00E-01
8,00E-01
7,00E-01
6,00E-01
5,00E-01
4,00E-01
3,00E-01
2,00E-01
1,00E-01
0,00E+00
g2(t) (normalized)
5,10E+05
5,10E+06
5,10E+07
5,10E+08
5,10E+09
5,10E+10
5,10E+11
5,10E+12
5,10E+13
5,10E+14
q2*t (ms/cm-2)
450nm
200nm
100nm
20nm

Effect of impurities



$$g_2(\tau) = A_1 \exp(-D_1 q^2 \tau) + A_2 \exp(-D_2 q^2 \tau)$$

Effect of impurities



$$M = c\,R^3$$

$$\frac{c_1}{c_2} = \frac{R_1^3}{R_2^3} \qquad c_1 = \frac{R_1^3}{R_2^3} c_2$$

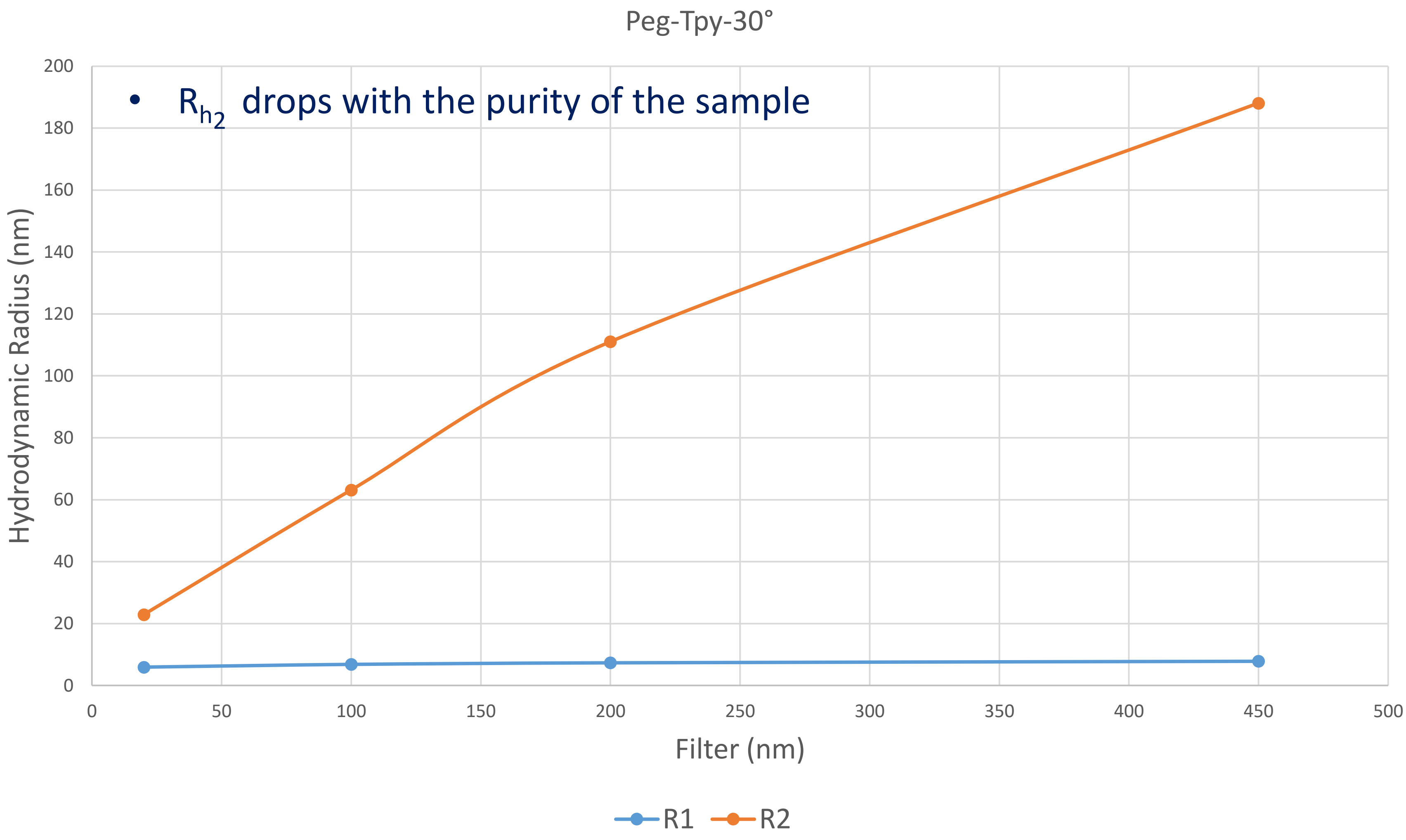
$$x_{c_2}(\%) = \frac{c_2}{c_1 + c_2} * 100 = \frac{c_2}{\frac{R_1^3}{R_2^3} c_2 + c_2} * 100 = 1\%$$

Only the 1% of impurities gives 40% of the scattering intensity!

Hydrodynamic Radius

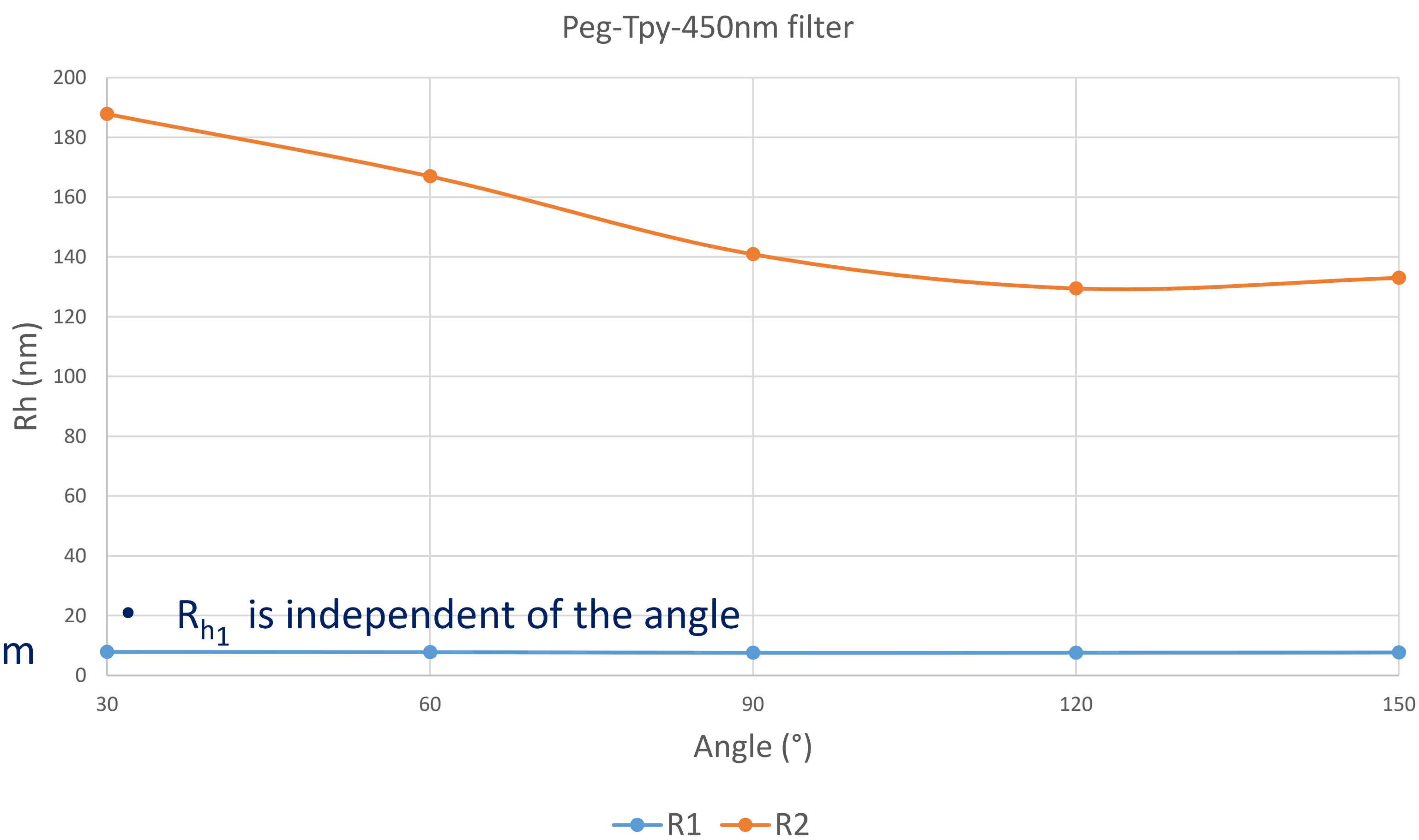
$$R_h = \frac{kT}{6\pi\eta D}$$

- R_{h_2} drops with the purity of the sample



Hydrodynamic Radius

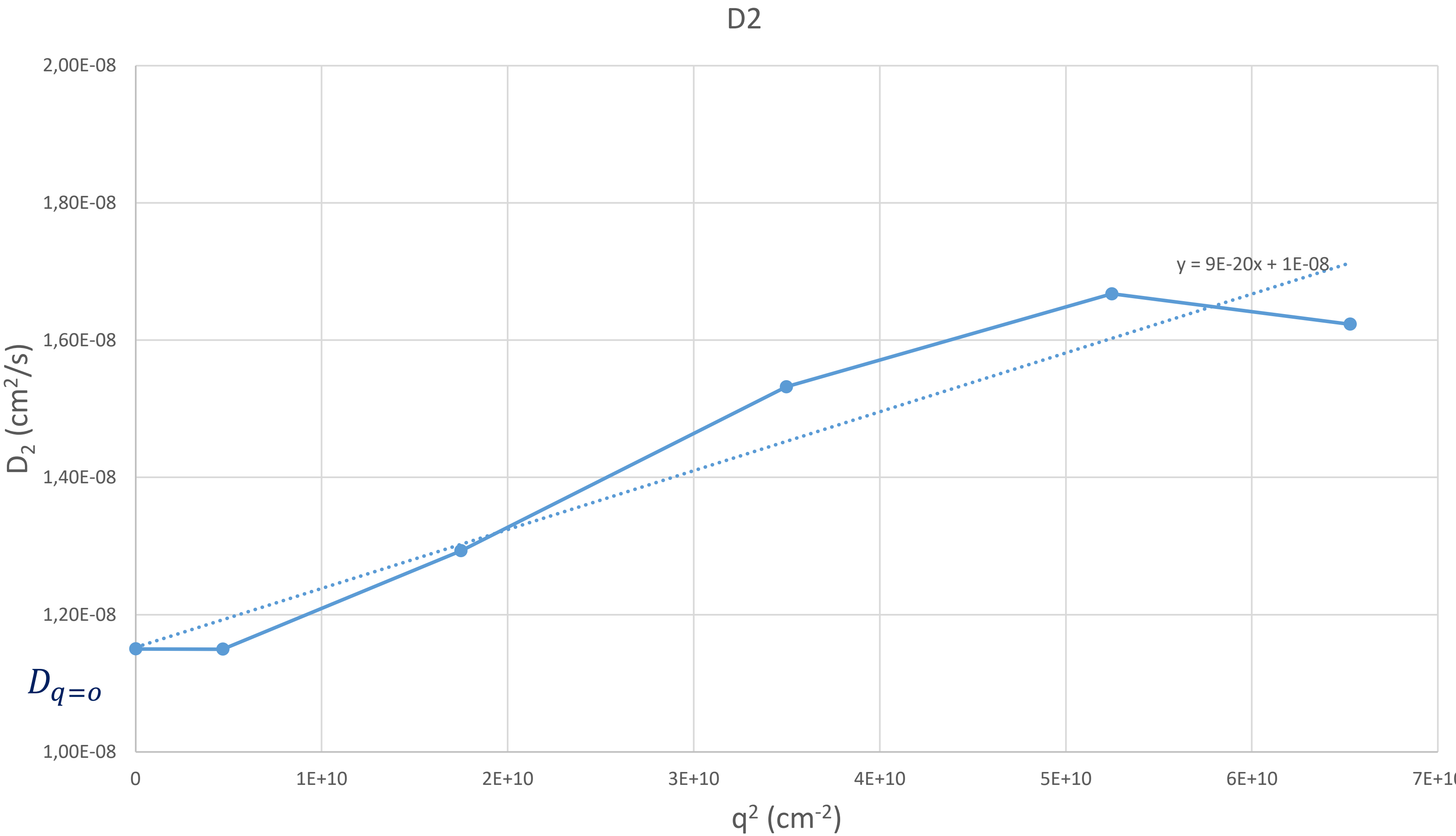
$$R_h = \frac{kT}{6\pi\eta D}$$



- R_{h_1} is independent of the angle

$R_{h_1} < 10$ nm

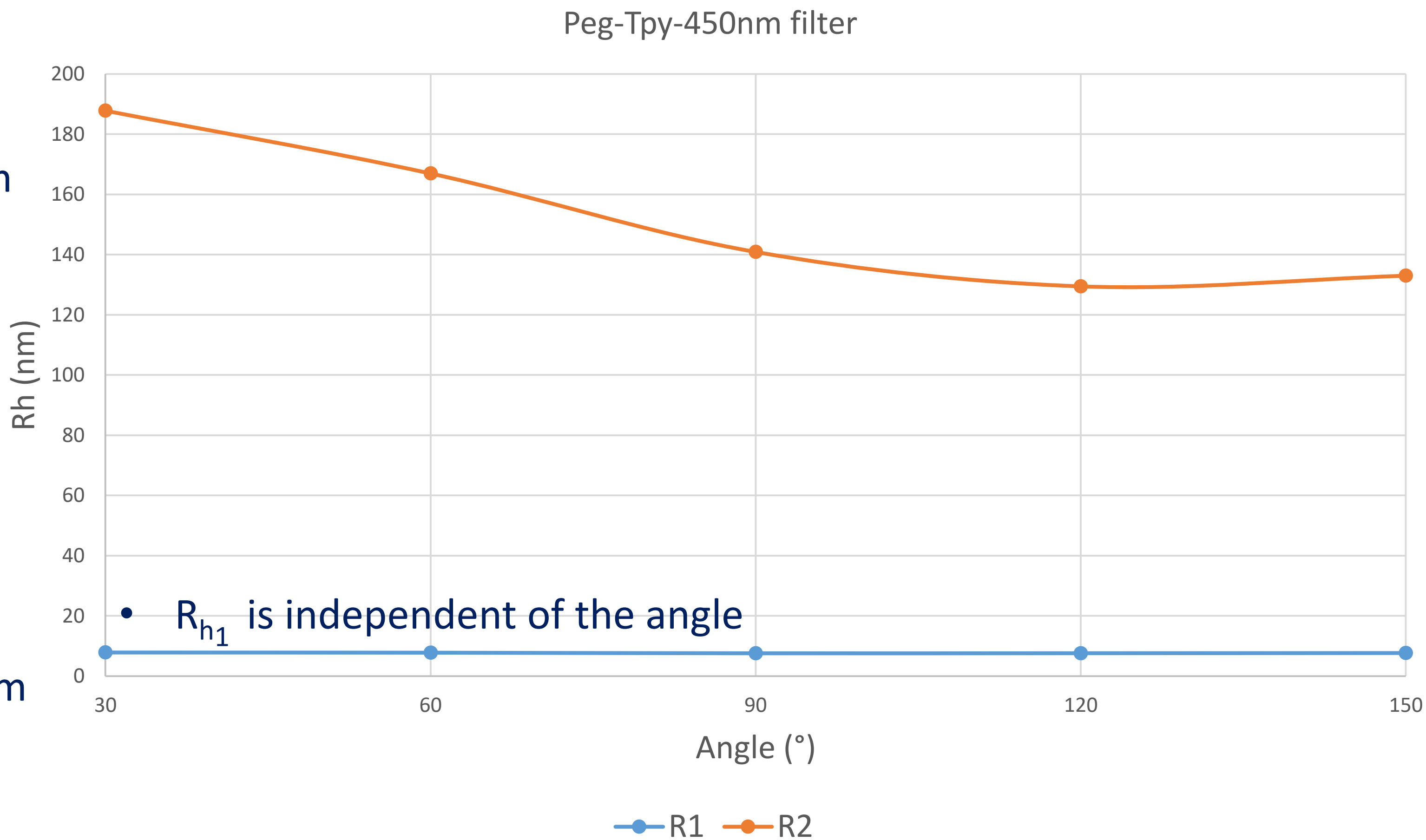
Diffusion coefficient



Hydrodynamic Radius

$$R_h = \frac{kT}{6\pi\eta D}$$

R_{h_2} = 180 nm



- R_{h_1} is independent of the angle

R_{h_1} < 10 nm

Conclusions

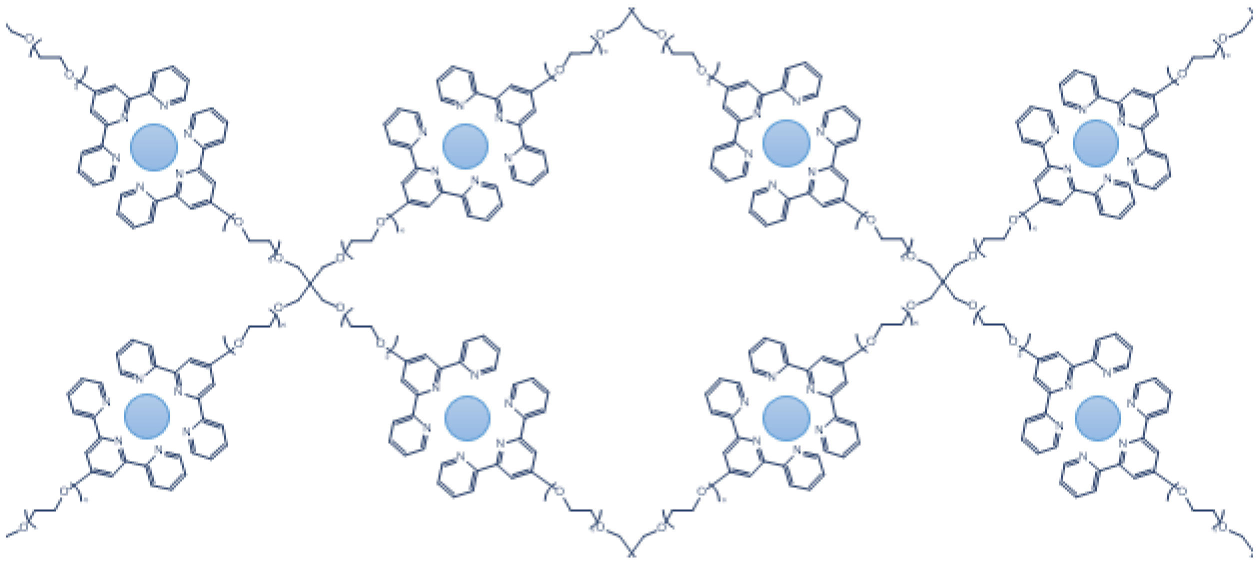
- The presence of impurities brings to bi-exponential curves
- A small concentration of impurities contribute almost half to the intensity
- Measurements of molecules smaller than 10 nm are angle independent

- Purity of sample and environment is necessary

- Preparation of networks in situ is mandatory

Future plans

- Analysis of the supramolecular network



- Analysis of other DoDyNet samples

Thank you for your attention

Questions?