Spin-Echo Small-Angle Neutron Scattering

Wim G. Bouwman

- **In 2 slides**
- Instrument Delft
- Data analysis
- Examples
- Where?

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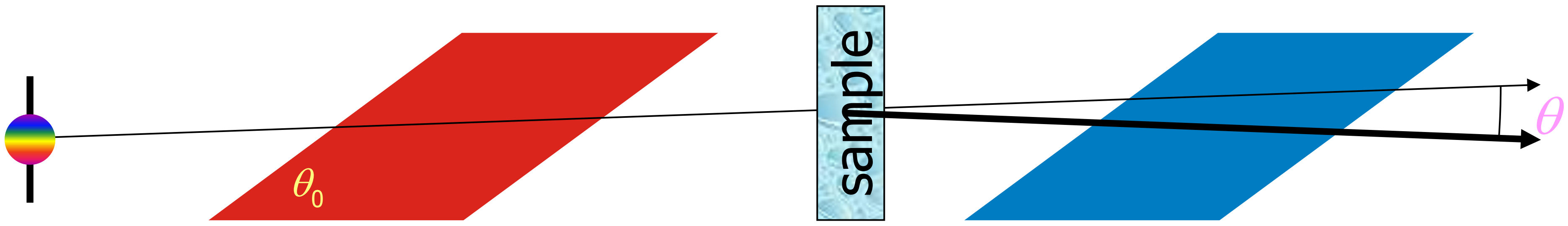
Larmor encoding of scattering angle
spin-echo small angle neutron scattering



- Unscattered beam gives spin echo ϕ = 0 independent of height and angle
- Scattering by sample $\rightarrow$ no complete spin echo
  $\rightarrow$ net precession angle
- High resolution with divergent beam, sensitive to scattering over 3 μrad

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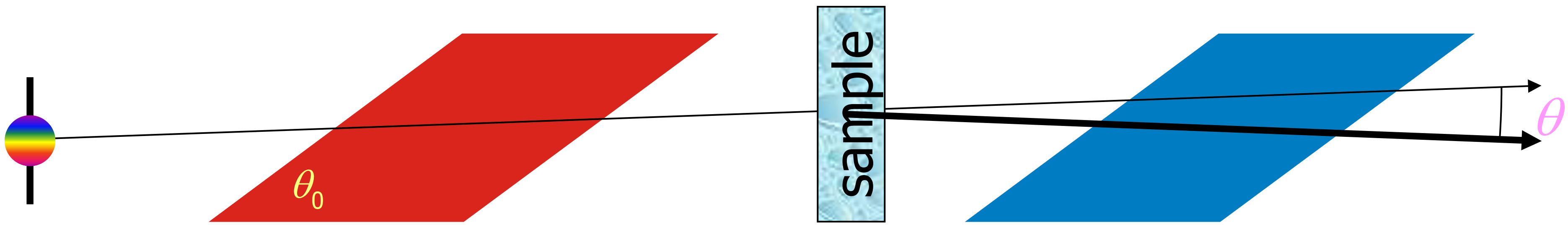
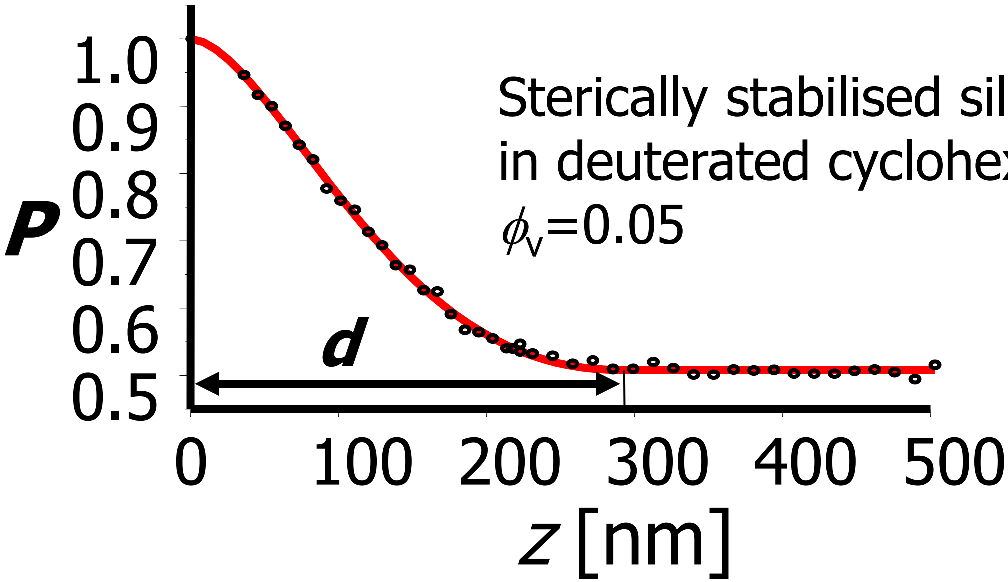
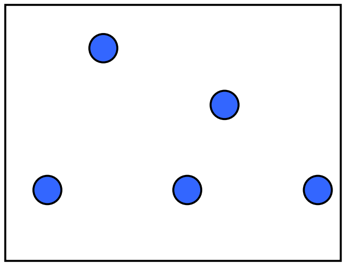
SESANS = Fourier transform scattering ⇒ projected density correlation function 20 nm – 20 μm





Sterically stabilised silica particles d=298 nm in deuterated cyclohexane
ϕ_v=0.05



Outline SESANS

- In 2 slides
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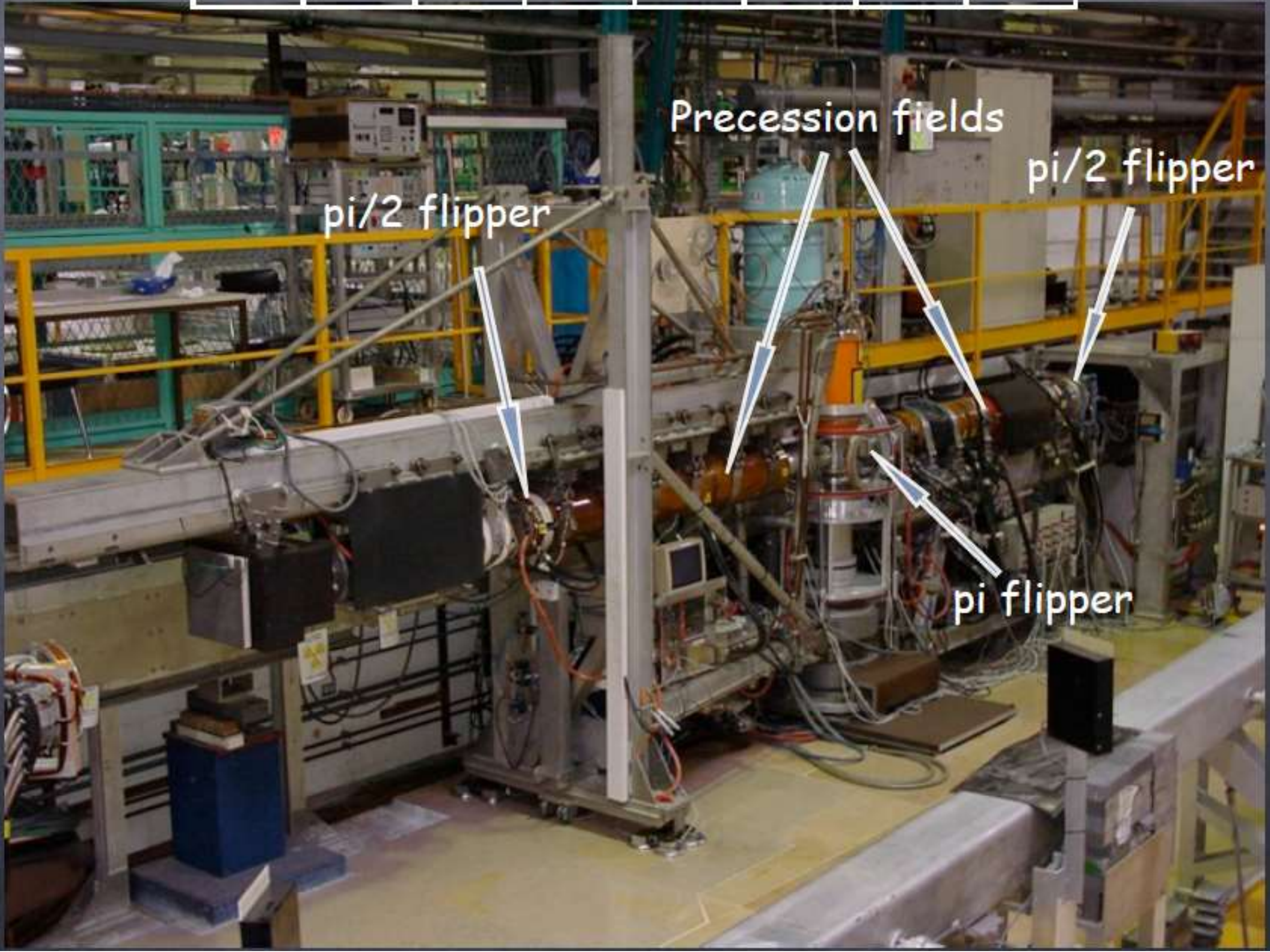
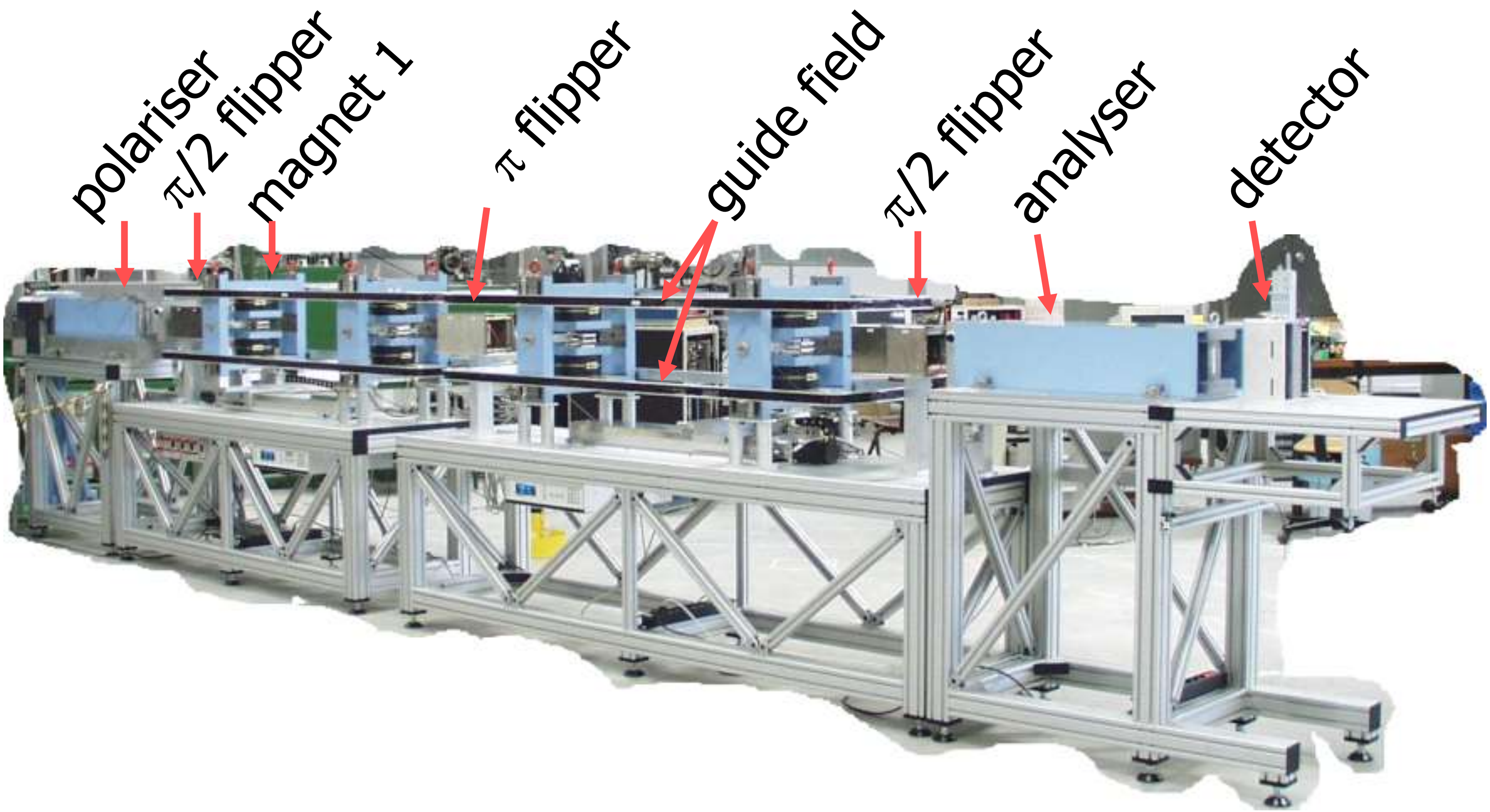
Polarized Neutrons

Fourier time (in nsec):

4Å		6Å		8Å		10Å	
t min	t max	t min	t max	t min	t max	t min	t max
0.01	3.3	0.04	11.1	0.09	26.4	0.18	51.7



SESANS
spin-echo small-angle neutron scattering



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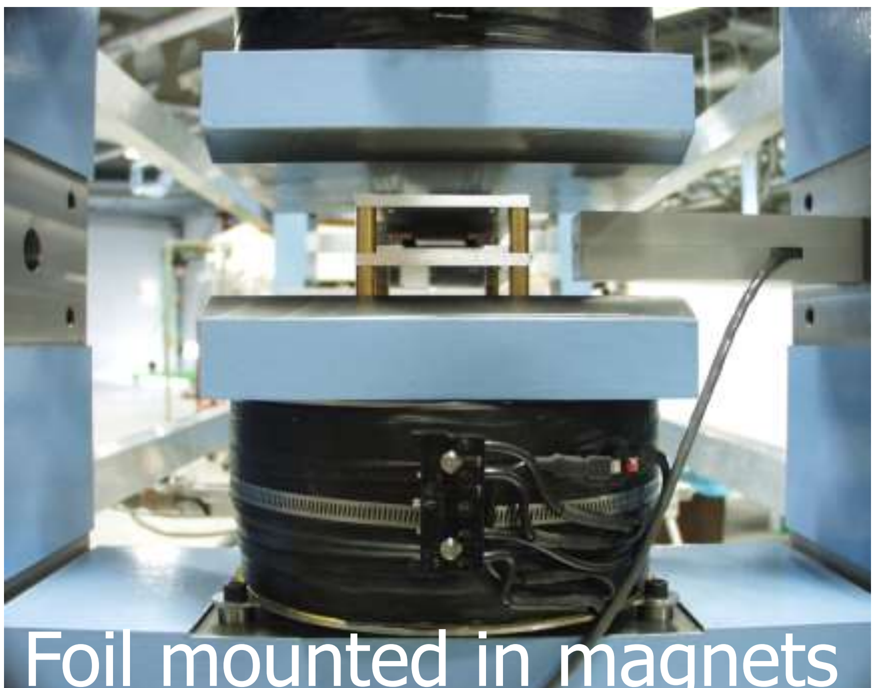
Magnetised foils tuned for π-flip: can be considered reversal field

3 μm permalloy film



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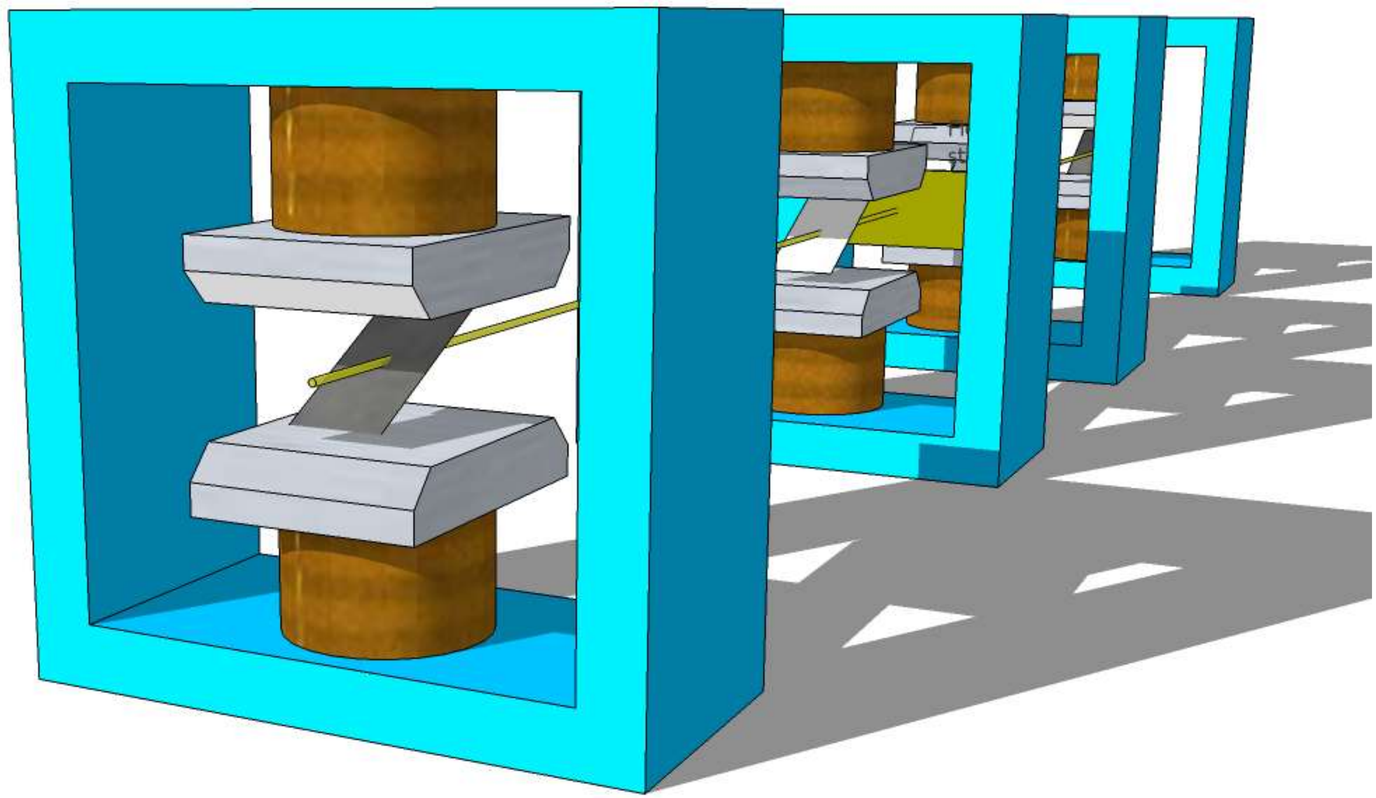
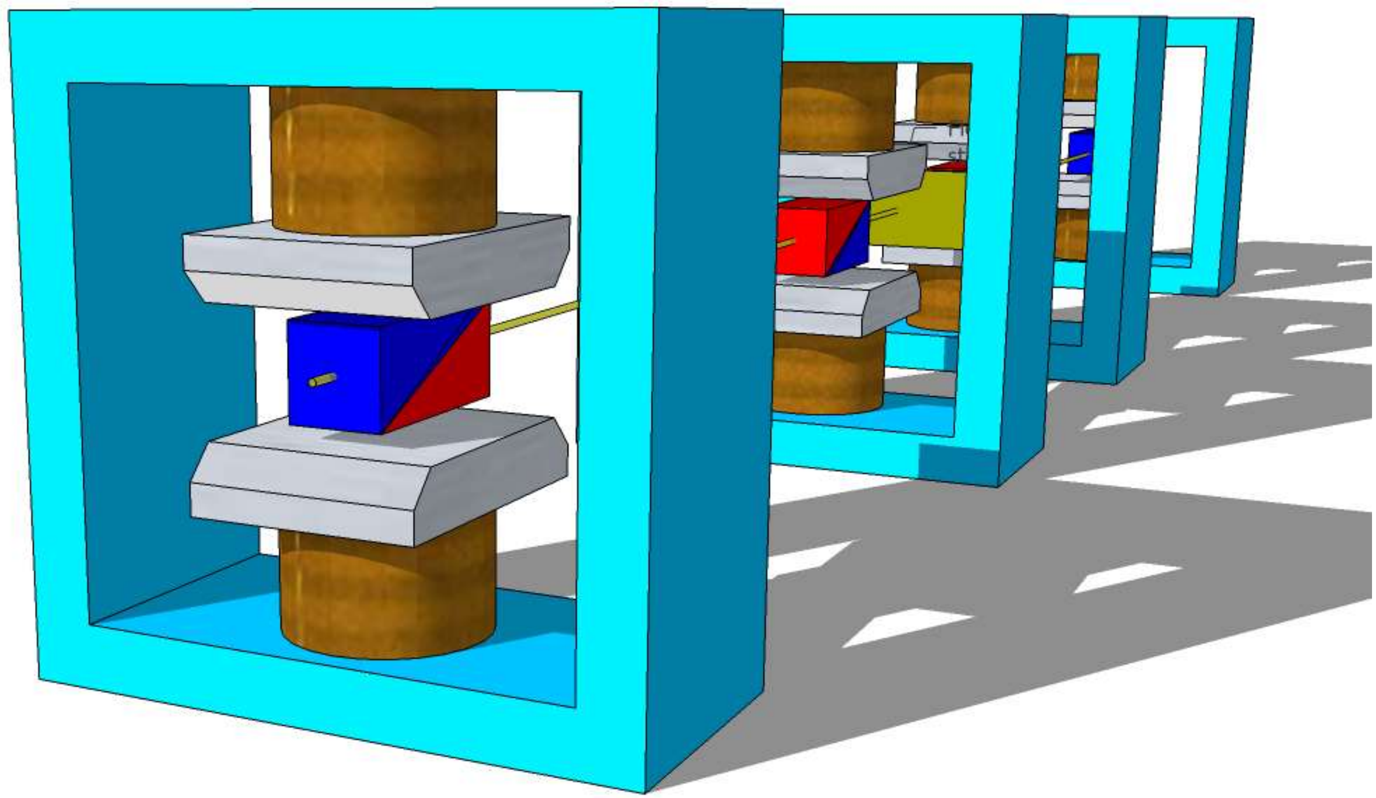
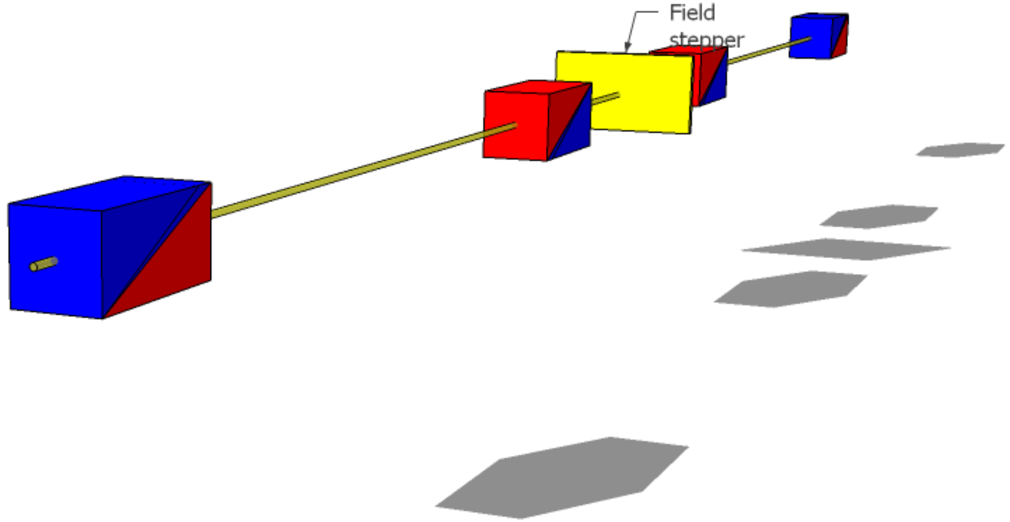
Precesion regions defined by foils and magnets (1)



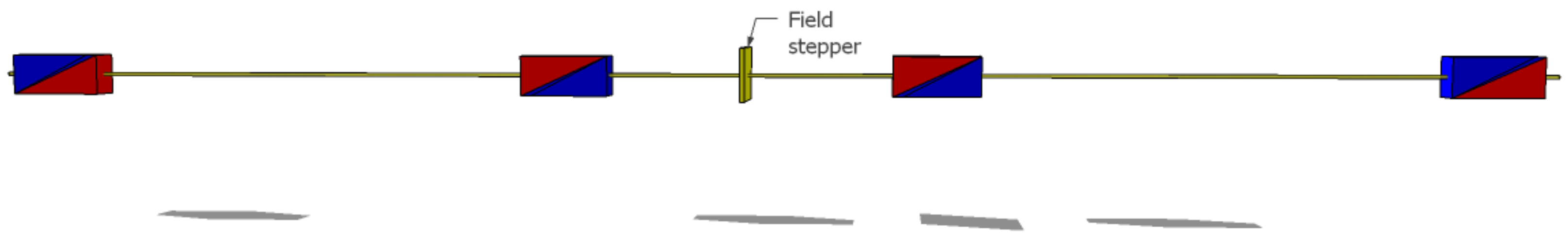
Precesion regions defined by foils and magnets (2)



Precesion regions defined by foils and magnets (3)



Precesion regions defined by foils and magnets (4)



Outline SESANS

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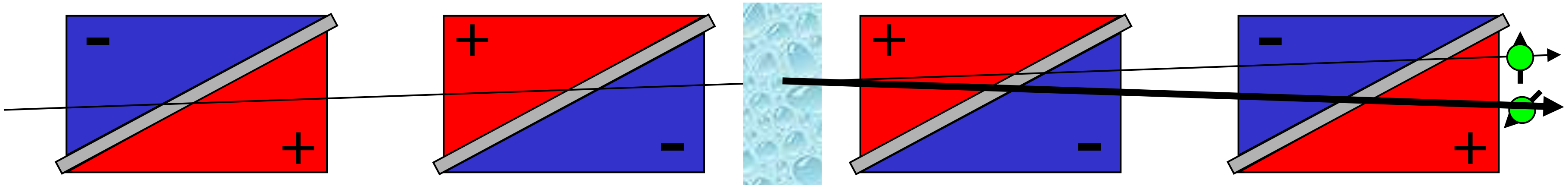
From SANS to SESANS

Precession angle proportional to: $\phi \propto \int BdL$: scattering angle



$$P = \cos(\phi) = \cos(Q_z \delta_z)$$

$$\delta_z = \frac{\gamma_n m \lambda^2 LB \cot \theta_0}{\pi h}$$

$$G(\delta_z) = \frac{1}{k_0^2} \int \frac{d\sigma(\vec{Q})}{d\Omega} \cos(Q_z \delta_z) d\vec{Q}$$

Keller *et al.* Neutron News **6**, (1995) 16
Rekveldt, NIMB **114**, 366 (1996).

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Polarized Neutrons

Echo condition:

$$\int_{\pi/2}^{\pi} B_1 d\ell = \int_{\pi}^{\pi/2} B_2 d\ell$$

The measured quantity is: S(q,t)/S(q,0) where

$$t \propto \lambda^3 \int B d\ell$$

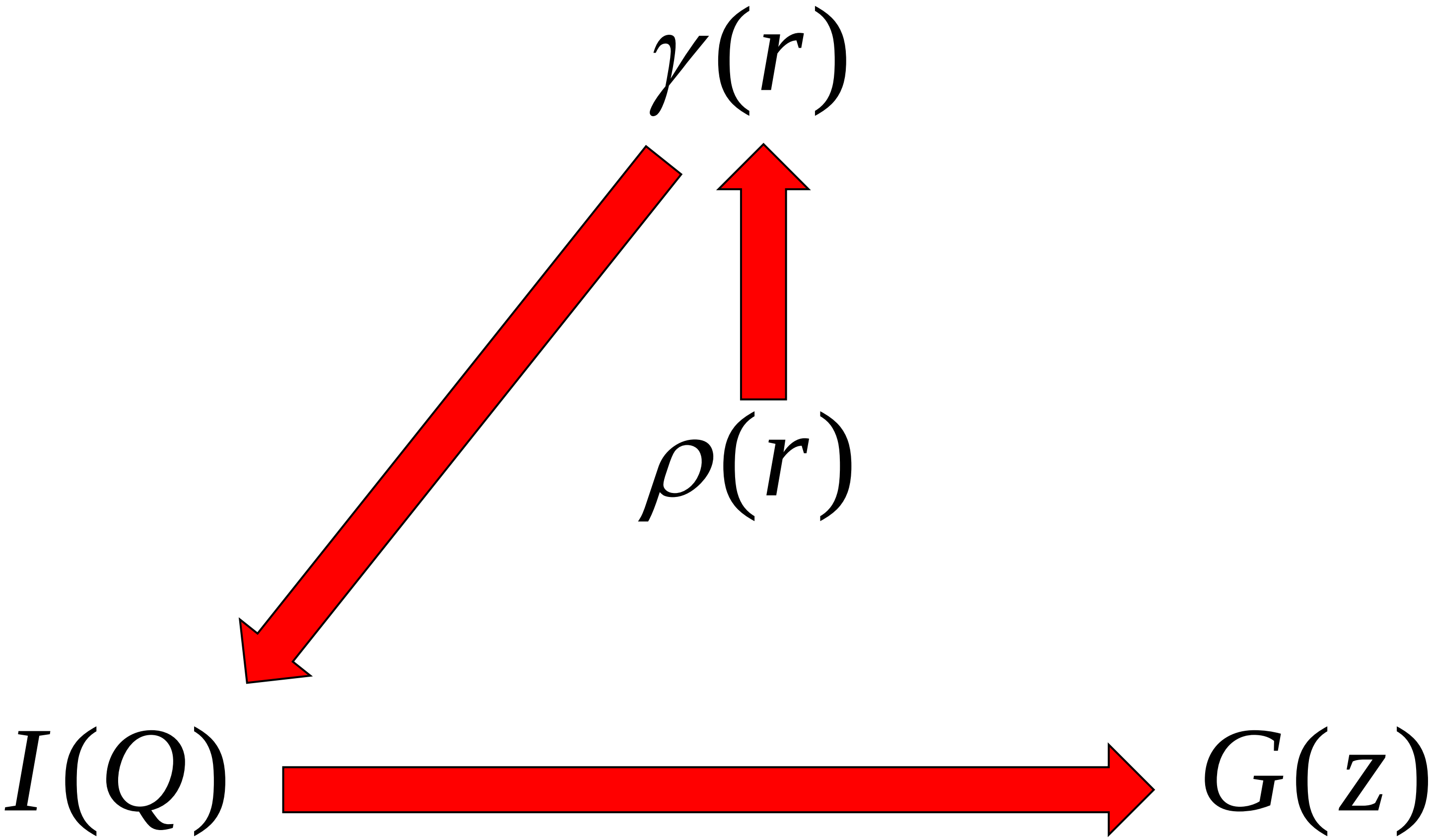
For elastic scattering: $$\varphi_{tot} = \frac{\gamma B_1 l_1}{v_1} - \frac{\gamma B_2 l_2}{v_2} = 0$$

For omega energy exchange: $$\varphi_{tot} = \frac{h\gamma B l}{m v^3}\omega + o\left(\left(\frac{\omega}{1/2 m v^2}\right)^2\right)$$

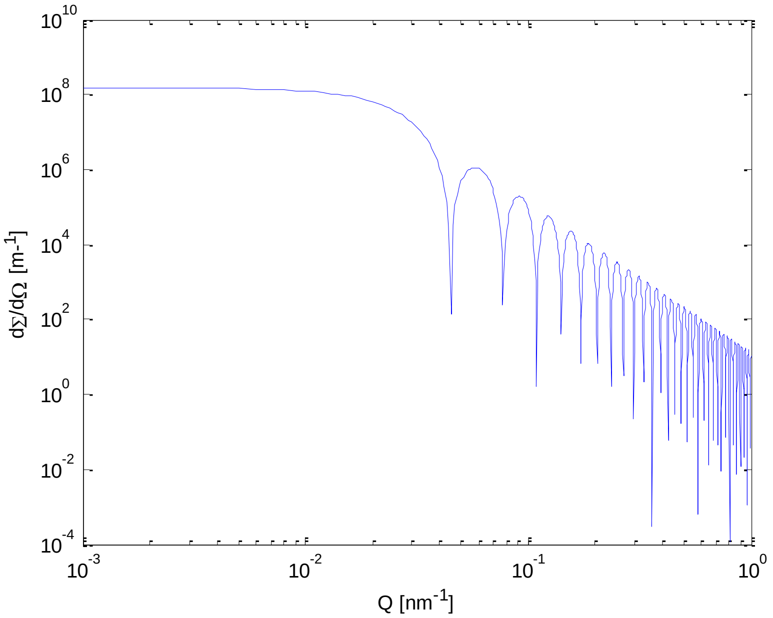
The probability of omega energy exchange: $$S(q,\omega)$$

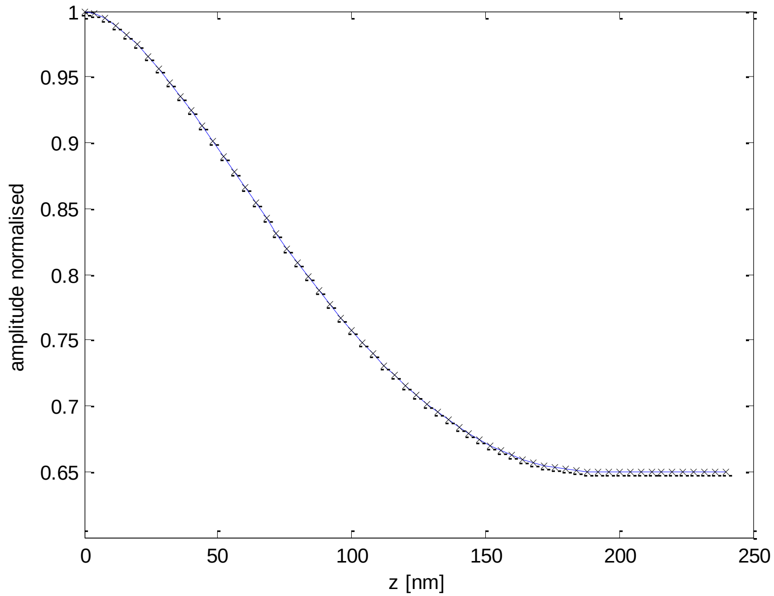
The final polarization: $$\langle \cos\varphi \rangle = \frac{\int \cos(\frac{h\gamma B l}{m v^3}\omega) S(q,\omega) d\omega}{\int S(q,\omega) d\omega} = S(q,t)$$

Density, correlation, SANS, SESANS



SANS to SESANS conversion spheres R=100 nm





$$\tilde{G}(z) = \int_0^\infty J_0(Qz)\frac{d\Sigma}{d\Omega}(Q)QdQ \qquad P(z) = e^{\frac{t\lambda^2}{2\pi}\left(\tilde{G}(z)-\tilde{G}(0)\right)}$$

Dilute Randomly Ordered Uniform Particles (reminder Karen Edler's lecture)

- scattering from independent particles:

$$I(q) = \frac{N}{V}(\rho_p - \rho_s)^2 V_p^2 \left\langle \frac{1}{V_p} \left| \int_{particle} e^{i\boldsymbol{q}.\boldsymbol{r}}\, d\boldsymbol{r} \right|^2 \right\rangle$$

- Assume: i) system is isotropic, then $\langle e^{-iqr} \rangle = \frac{\sin(qr)}{qr}$

  ii) no long range order, so no correlations between two widely separated particles

$$I(q) = I_e(q)(\rho_p - \rho_s)^2 V_p \int_0^\infty \gamma(r) \frac{\sin(qr)}{qr} 4\pi r^2 dr$$

$\gamma(r)$ = correlation function within particle

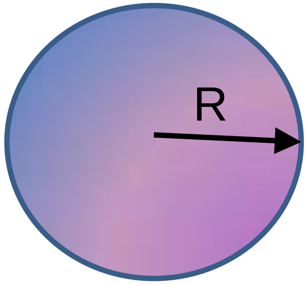
$P(r)=4\pi r^2\gamma(r)$ is the probability of finding two points in the particle separated by r

Spheres (adapted from Karen Edler's lecture)

- Start with form factor:

$$F(q) = \frac{1}{V_p}\int_0^\infty \gamma(r)\frac{\sin(qr)}{qr}4\pi r^2 dr$$

- Now consider radial pair correlation function for sphere, with sharp edges, radius R:



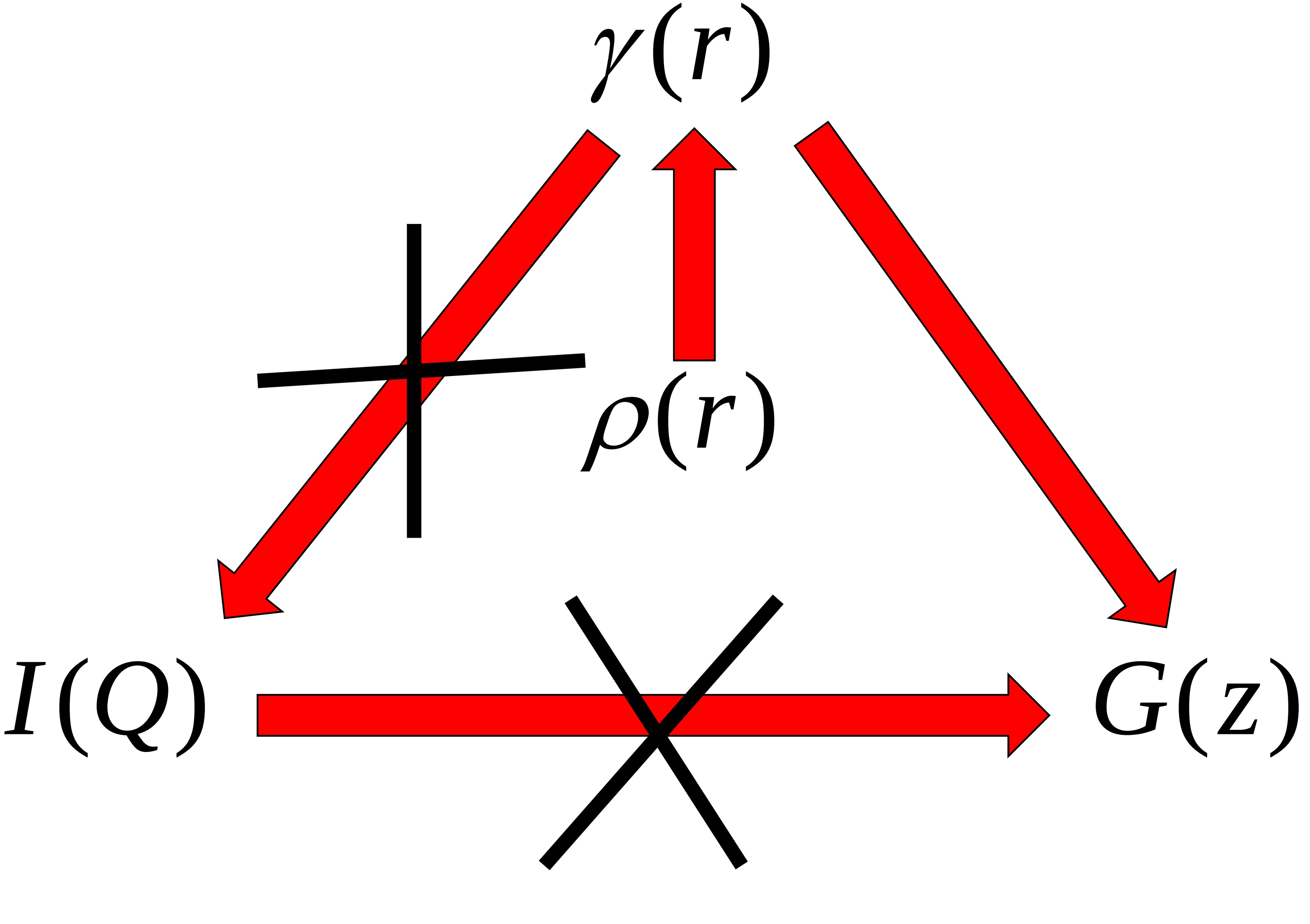
$$\gamma(r) = 1 - \frac{3}{4}\left(\frac{r}{R}\right) + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

$$F(qR) = \frac{1}{V_p}\int_0^\infty \left[1 - \frac{3}{4}\left(\frac{r}{R}\right) + \frac{1}{16}\left(\frac{r}{R}\right)^3\right]\frac{\sin(qr)}{qr}4\pi r^2 dr$$

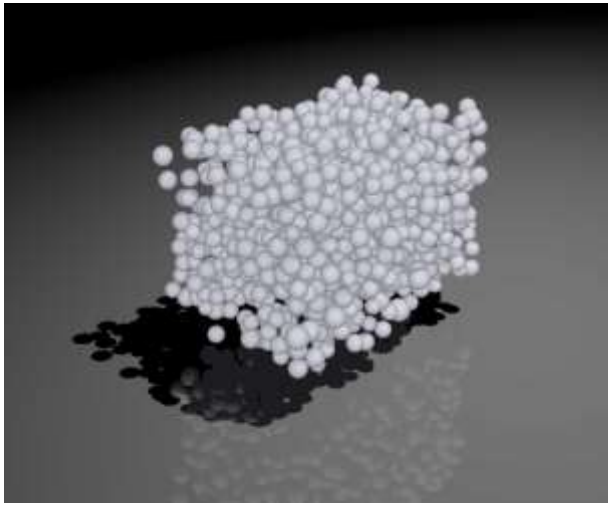
- Integrate by parts three times:

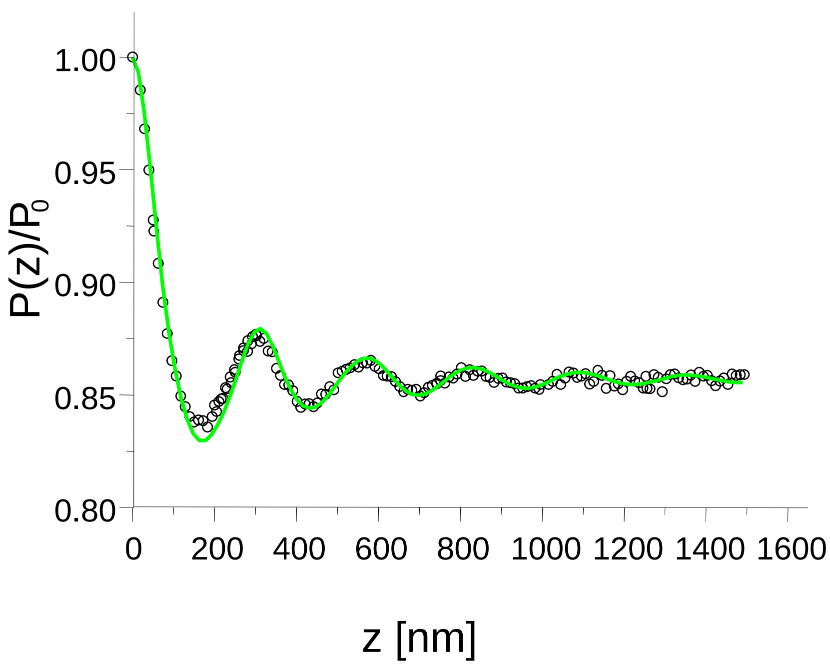
$$F(Q) = \left[\frac{3(\sin(QR_p) - QR_p\cos(QR_p))}{(QR_p)^3}\right]^2$$

Density, correlation, SANS, SESANS



From structure to polarisation





structure

$$\gamma(\mathbf{r}) = \int_V \rho(\mathbf{r}')\rho(\mathbf{r}+\mathbf{r}')d\mathbf{r}'$$

density correlation function

$$G(z) = 2\int_0^\infty \gamma(x,0,z)dx$$

SESANS correlation function

$$P(z) = e^{(G(z)-G(0))}$$

polarisation

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Spheres in SESANS

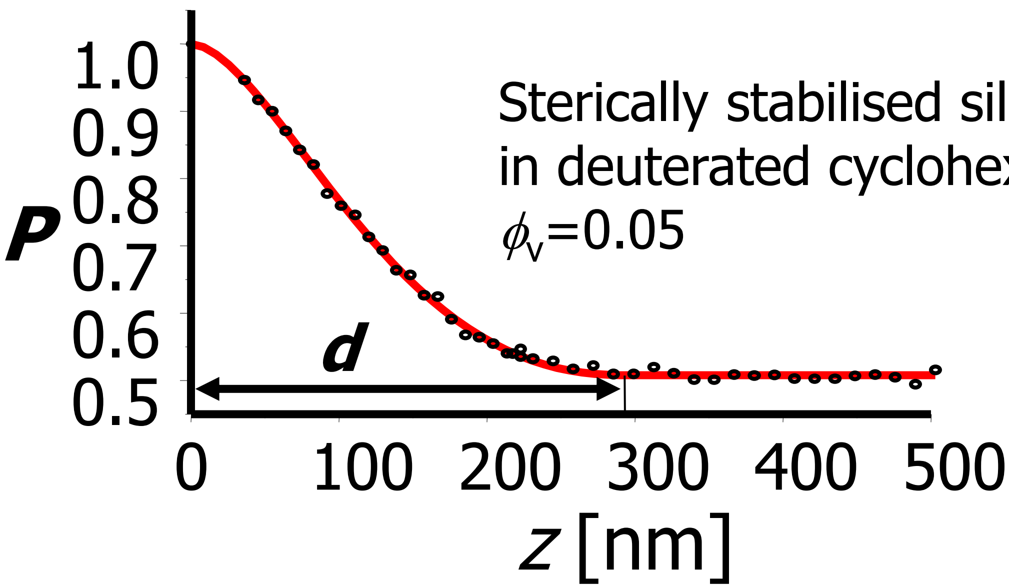
$$\gamma(r) = 1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

$$G(z) = \Re\left(\left[1-\left(\frac{z}{2R}\right)^2\right]^{1/2}\left[1+\frac{1}{2}\left(\frac{z}{2R}\right)^2\right] + 2\left(\frac{z}{2R}\right)^2\left(1-\frac{z}{4R}\right)^2 \ln\left\{\frac{z/R}{2+[4-(z/R)^2]^{1/2}}\right\}\right)$$

$$G(z) = \frac{2}{\xi}\int_z^\infty \frac{\gamma(r)r}{(r^2-z^2)^{1/2}}\,\mathrm{d}r$$

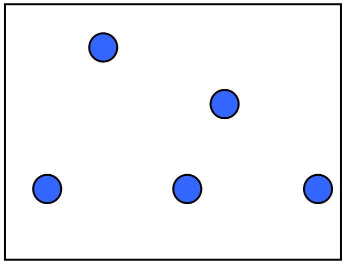
$$G(z) = \exp[-(9/8)(z/a)^2]$$

$$P(z) = \exp\{\Sigma_t[G(z)-1]\}$$



Sterically stabilised silica particles d=298 nm in deuterated cyclohexane

ϕ_V=0.05



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More Complex: Fitting Scattering (Karen Edler)

- observed scattered intensity is Fourier Transform of real-space shapes

$$I(Q) = N_p V_p^2 (\rho_p - \rho_s)^2 F(Q) S(Q) + B$$

where: F(Q) = form factor

S(Q) = structure factor

Form Factor = scattering from within same particle

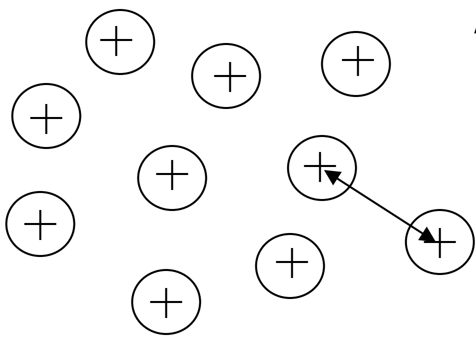
$\Rightarrow$ depends on particle shape

Structure Factor = scattering from different particles

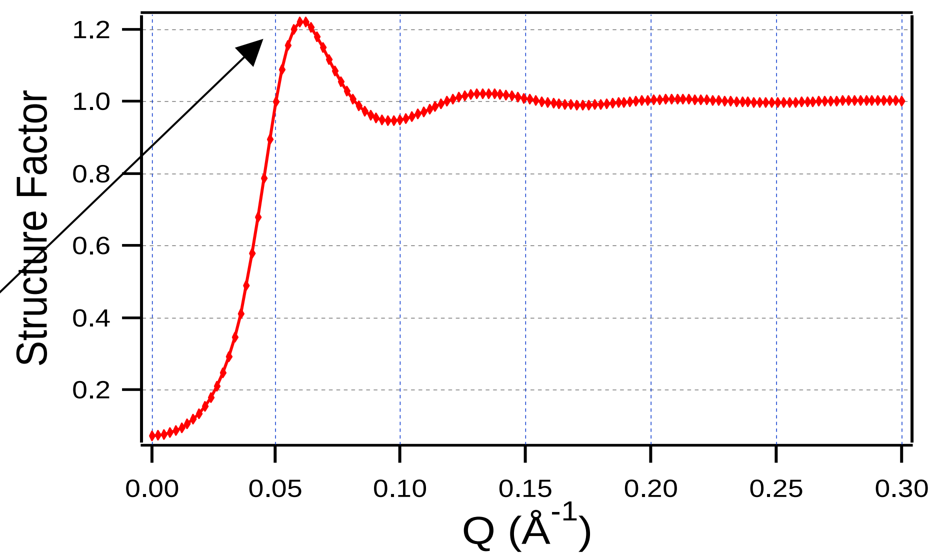
$\Rightarrow$ depends on interactions between particles

Structure Factors (Karen Edler)

- for dilute solutions S(Q) = 1
- particle interactions will affect the way they are distributed in space $\Rightarrow$ changes scattering
- for charged spheres:

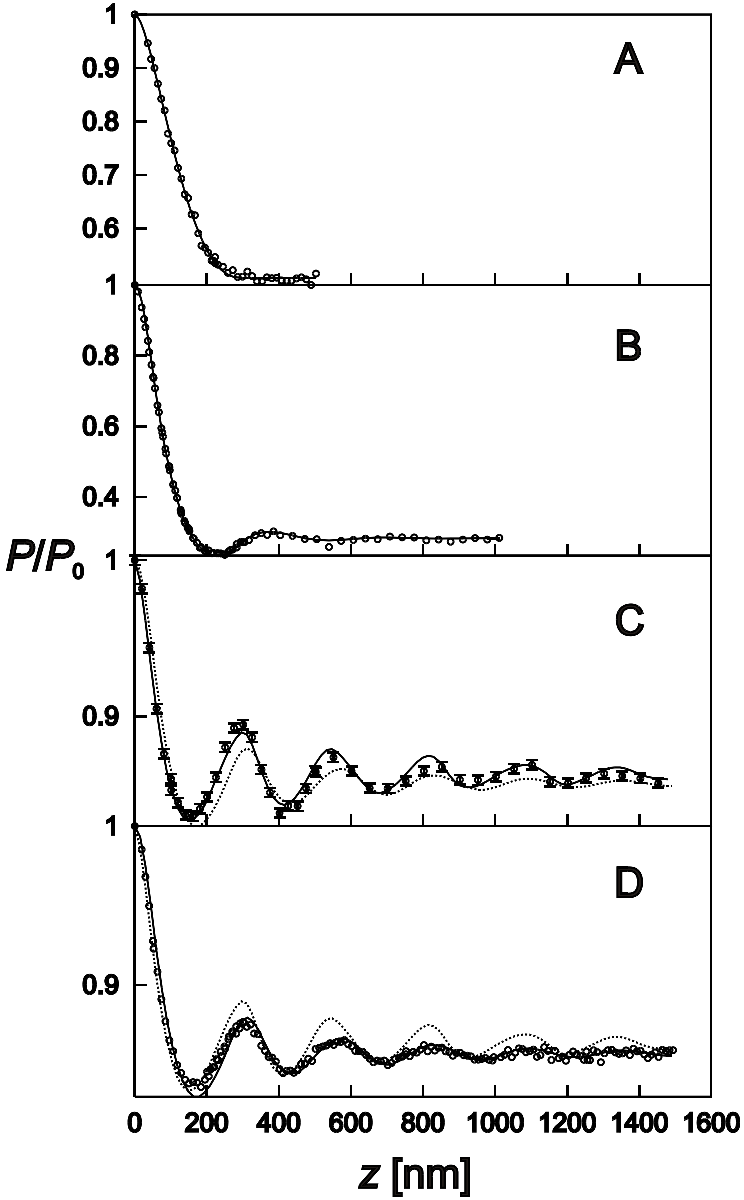


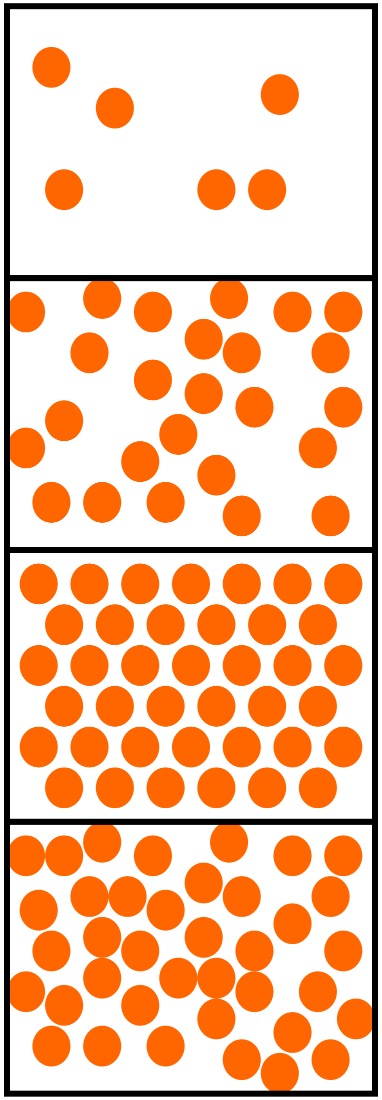
Average distance between nearest neighbours relatively constant = "correlation distance"



Position of first maximum related to correlation distance

Structure factor in SESANS **convolution** product





gas

liquid

crystal

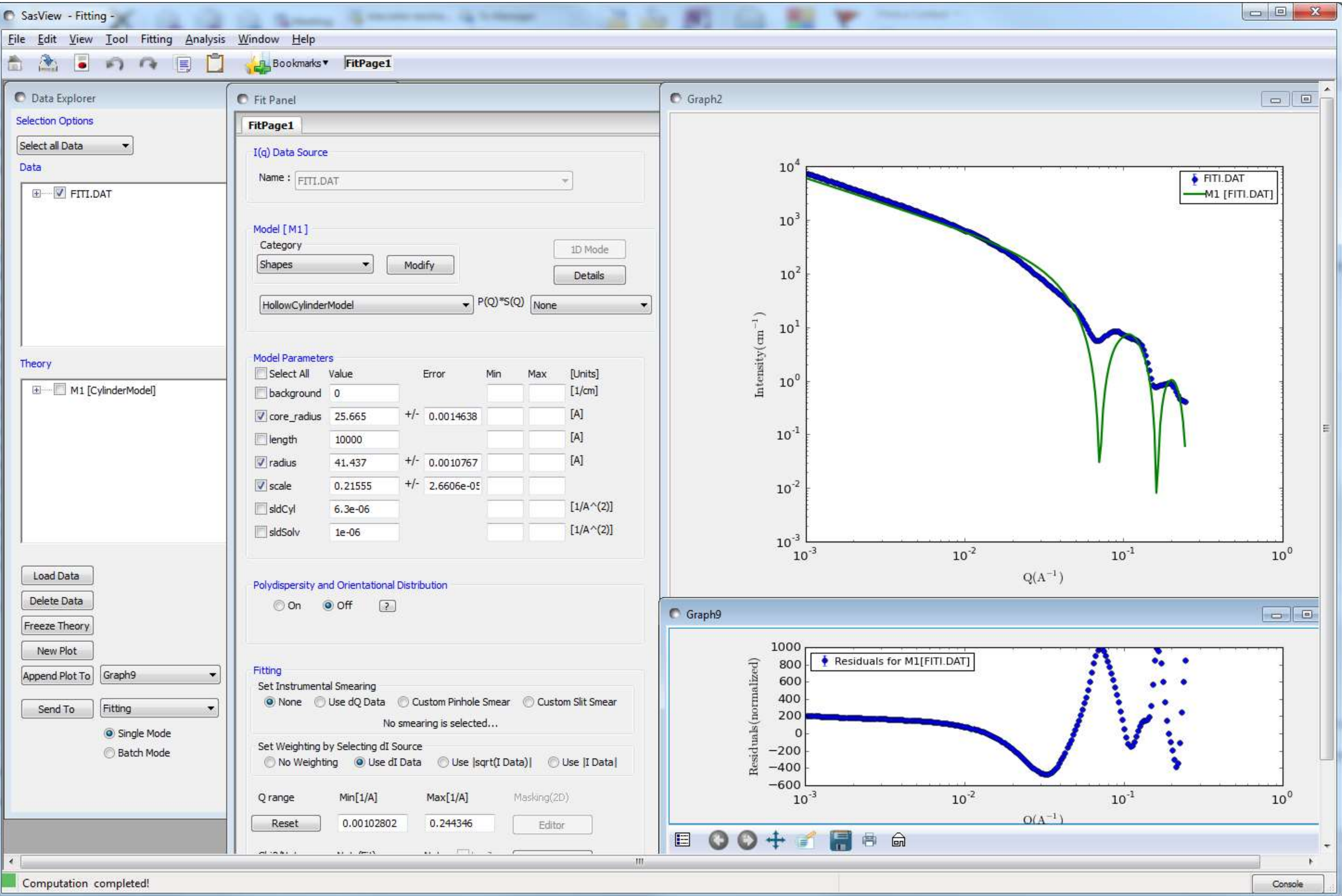
glass

Krouglov et al. J. Appl. Cryst. **36**, 1417-1423 (2003)

Present data analysis

- Mostly ad hoc Matlab written real space models
- Recently started to Hankel transform SANS models

SASVIEW, work in progress



Outline SESANS

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- Data analysis
- **Examples**
- Where?

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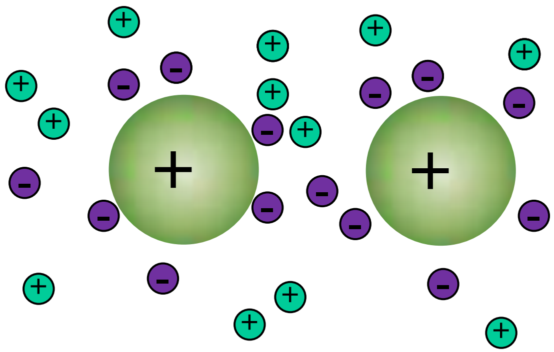
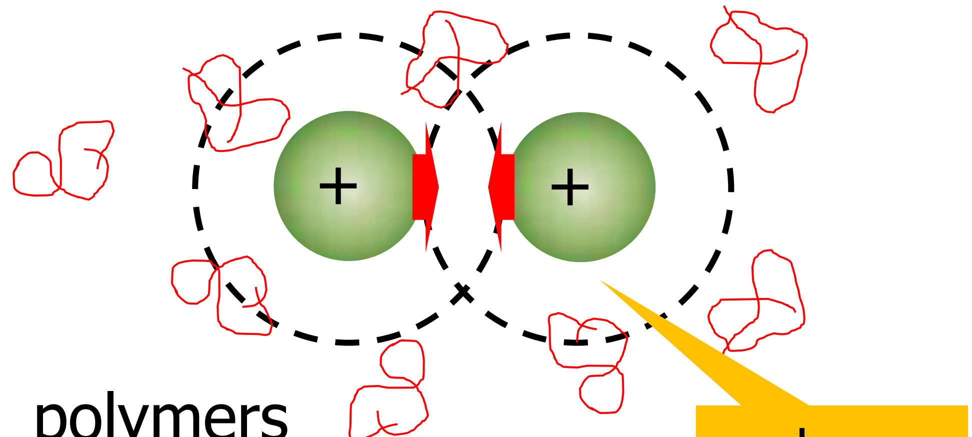
Depletion interactions in charged, aqueous colloid-polymer mixtures (model for e.g. milk)



salt
reduces
repulsion



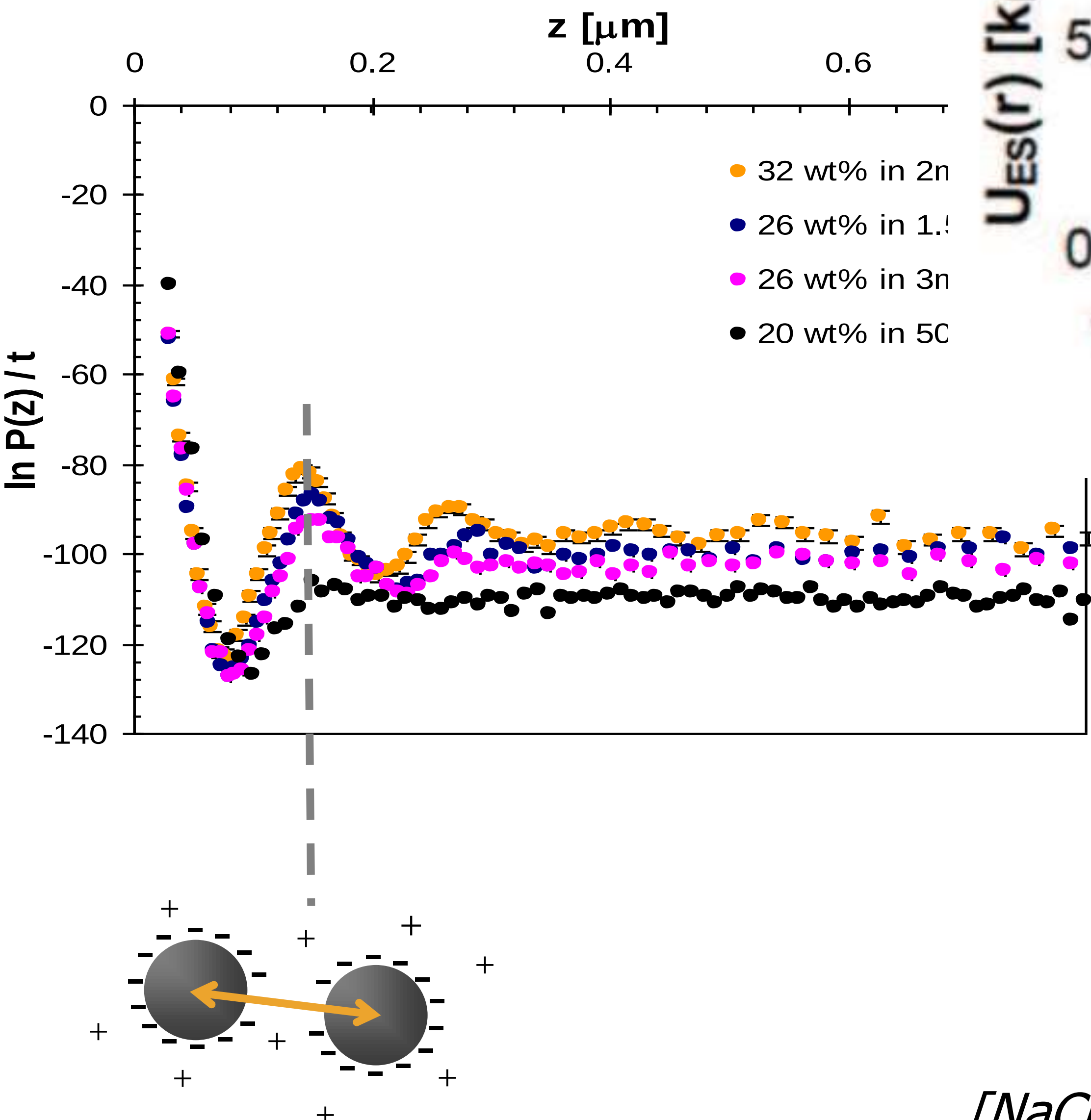
polymers
give
attraction

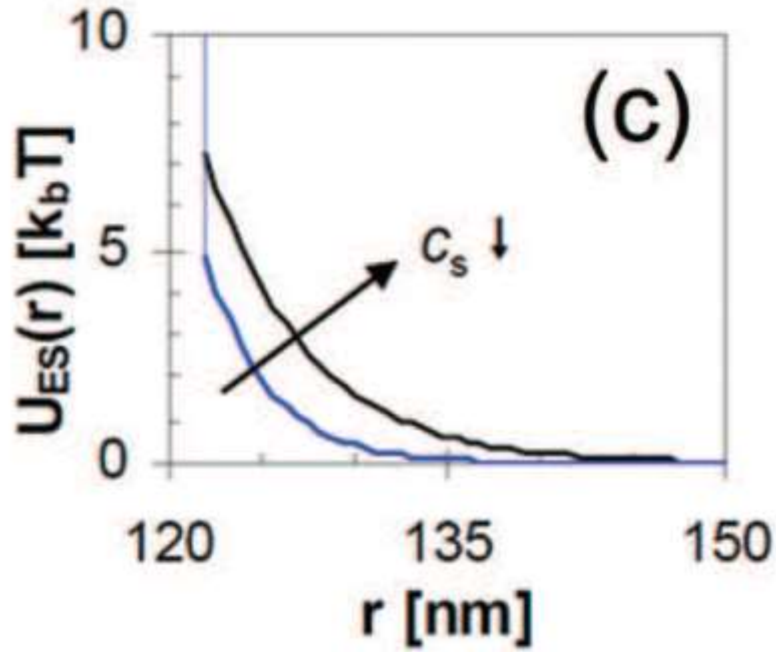
Kitty van Gruijthuijsen

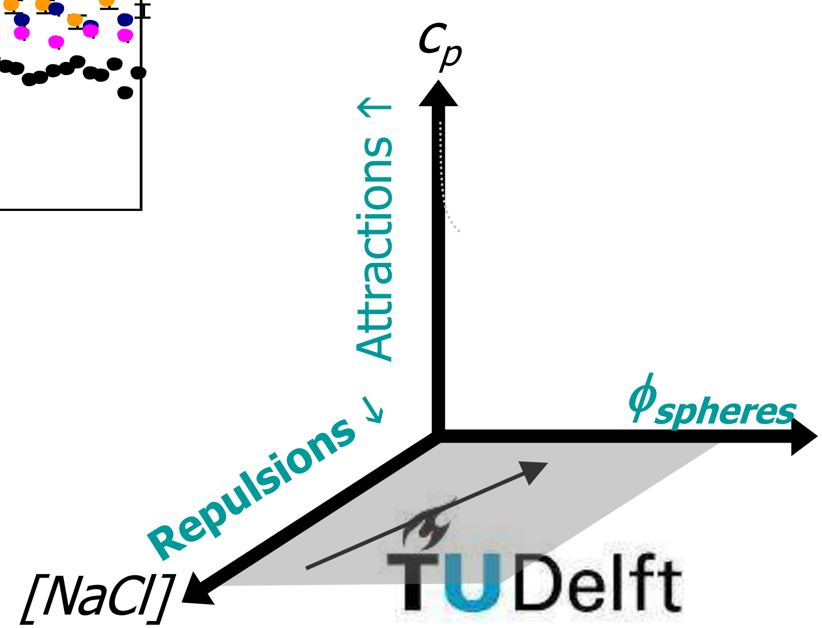
Peter Schurtenberger, Anna Stradner - Lund University

Adolphe Merkle Institute, Université de Fribourg

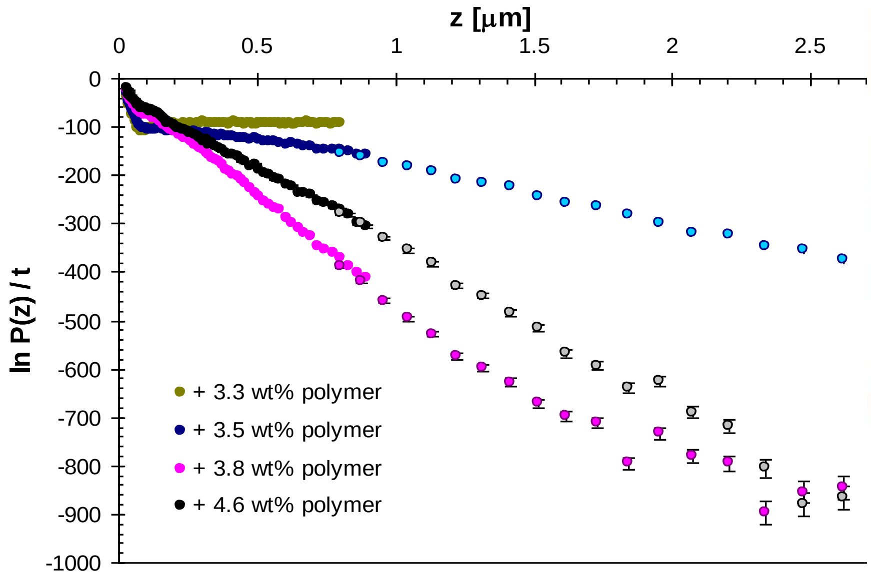
Colloids


z [μm]
0
0.2
0.4
0.6
ln P(z) / t
0
-20
-40
-60
-80
-100
-120
-140
32 wt% in 2n
26 wt% in 1.
26 wt% in 3n
20 wt% in 50

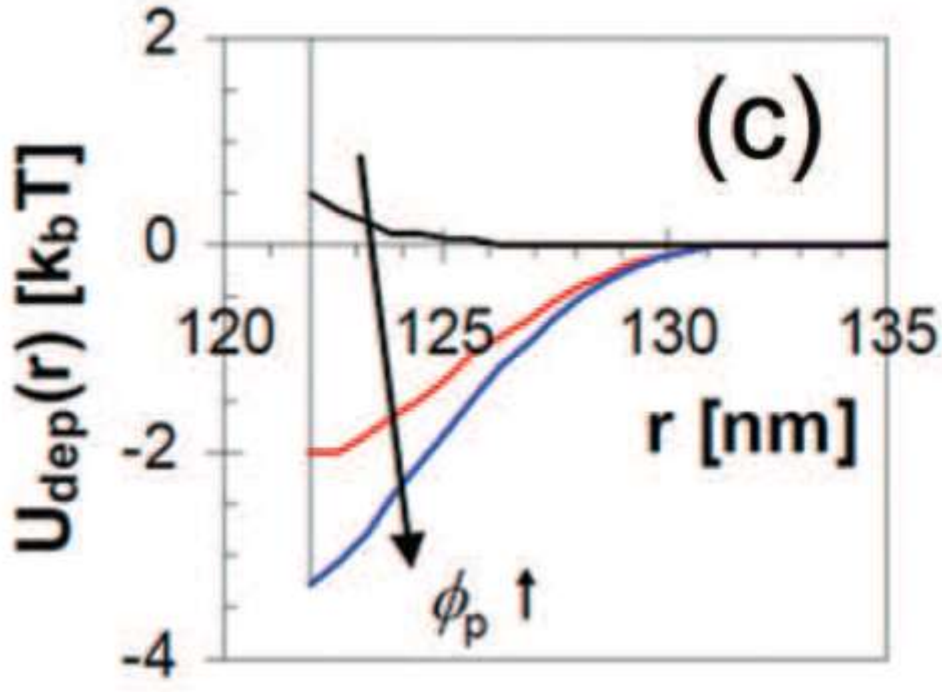

(c)
$U_{ES}(r)$ [k_bT]
10
5
0
c_s ↓
120
135
150
r [nm]


c_p
Attractions ↑
Repulsions ↓
$\phi_{spheres}$
[NaCl]

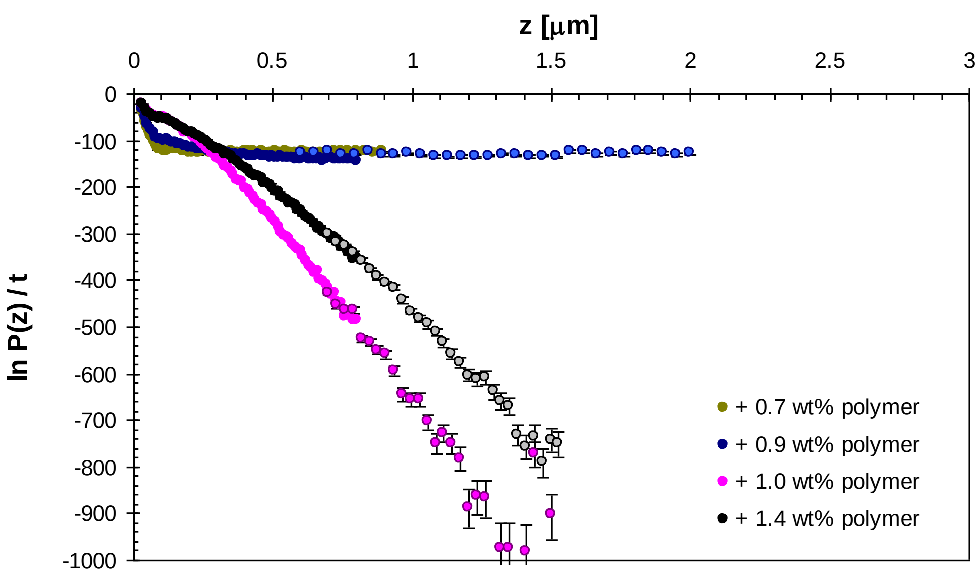
Gels



z [μm]
0
0.5
1
1.5
2
2.5
ln P(z) / t
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
+ 3.3 wt% polymer
+ 3.5 wt% polymer
+ 3.8 wt% polymer
+ 4.6 wt% polymer

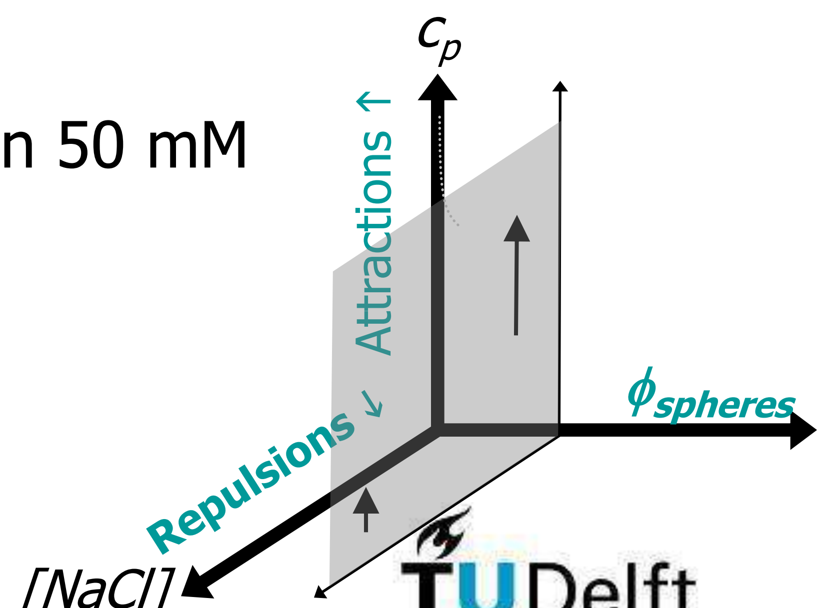


(c)
$U_{dep}(r)$ [k_bT]
2
0
-2
-4
120
125
130
135
r [nm]
ϕ_p ↑



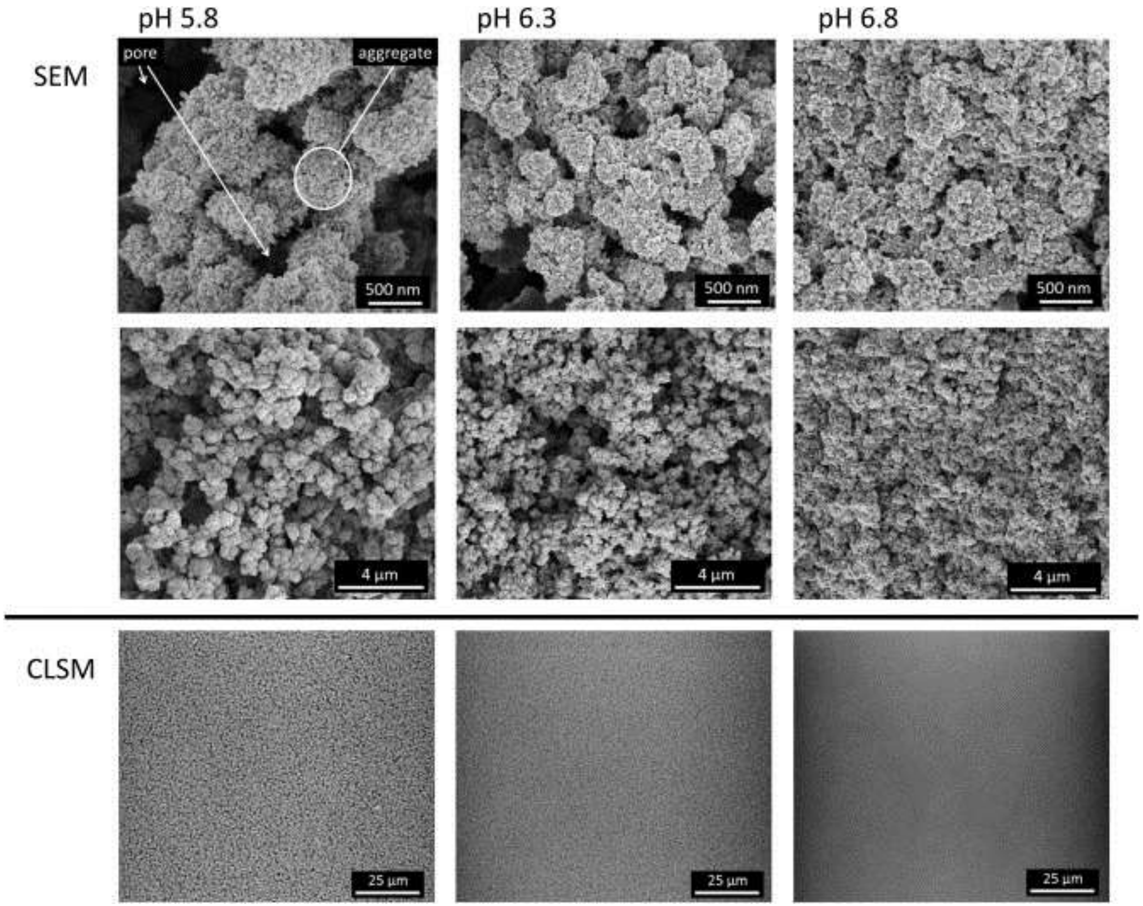
z [μm]
0
0.5
1
1.5
2
2.5
3
ln P(z) / t
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
+ 0.7 wt% polymer
+ 0.9 wt% polymer
+ 1.0 wt% polymer
+ 1.4 wt% polymer

In 50 mM



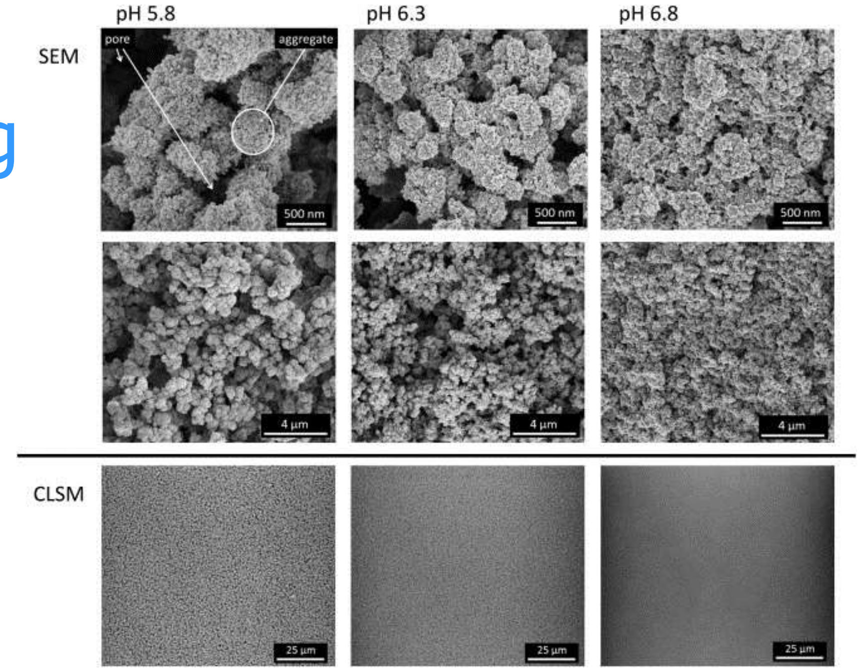
c_p
Attractions
Repulsions
$\phi_{spheres}$
[NaCl]
TU Delft

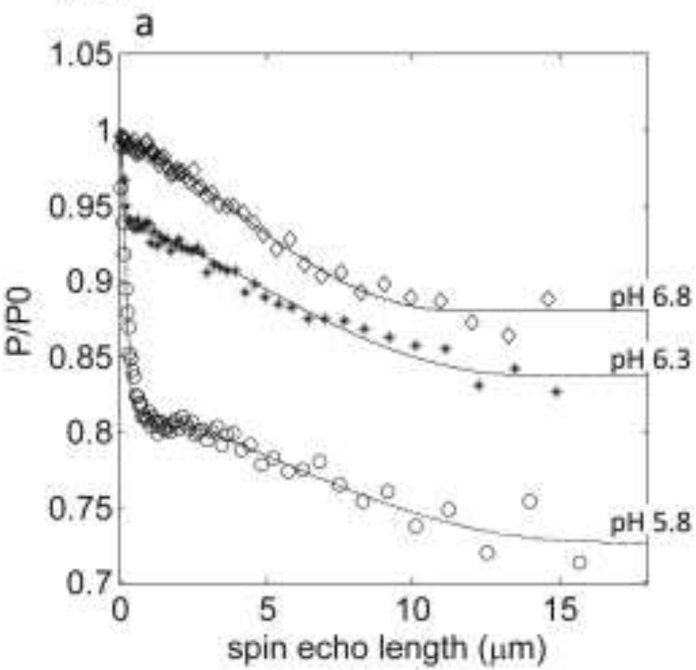
Water holding of ovalbumin gels
Juiciness, release tastants

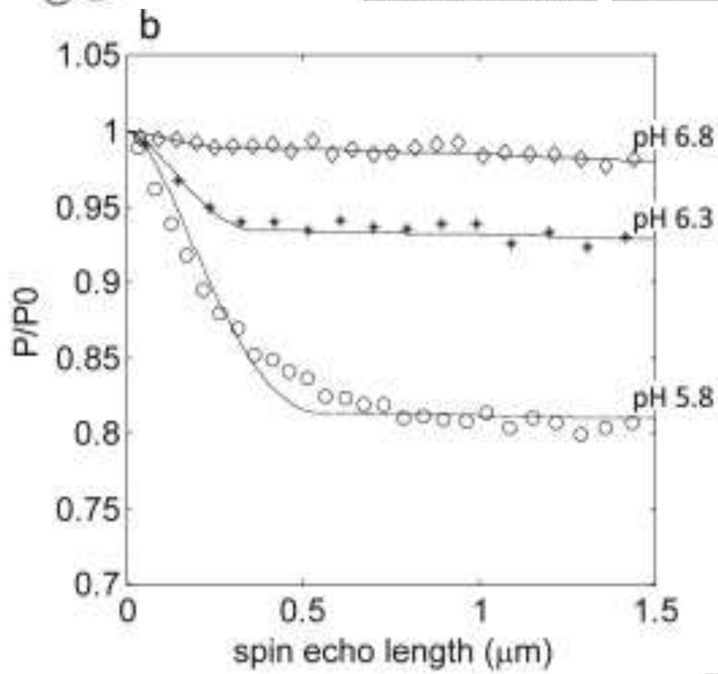


Maaike Nieuwland, TNO & TI Food and Nutrition

Acid reduces water holding





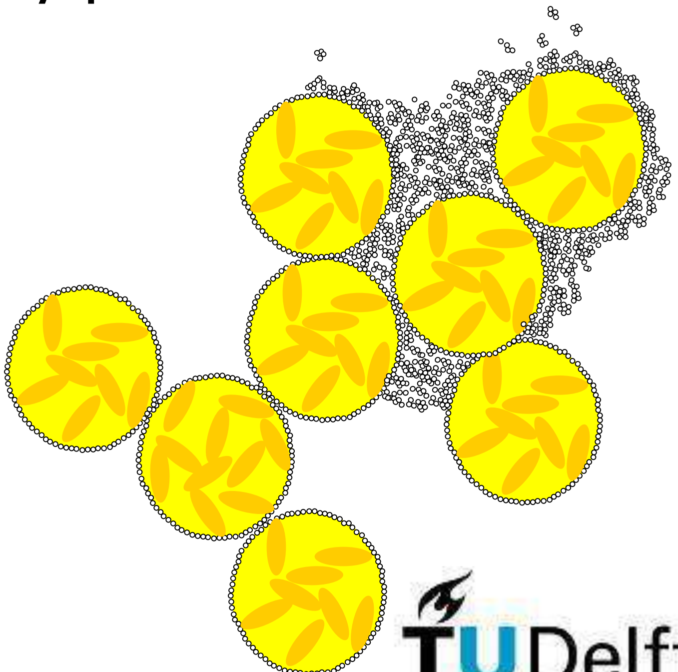


Texture fresh cheeses essential for pleasure eating and shell life time

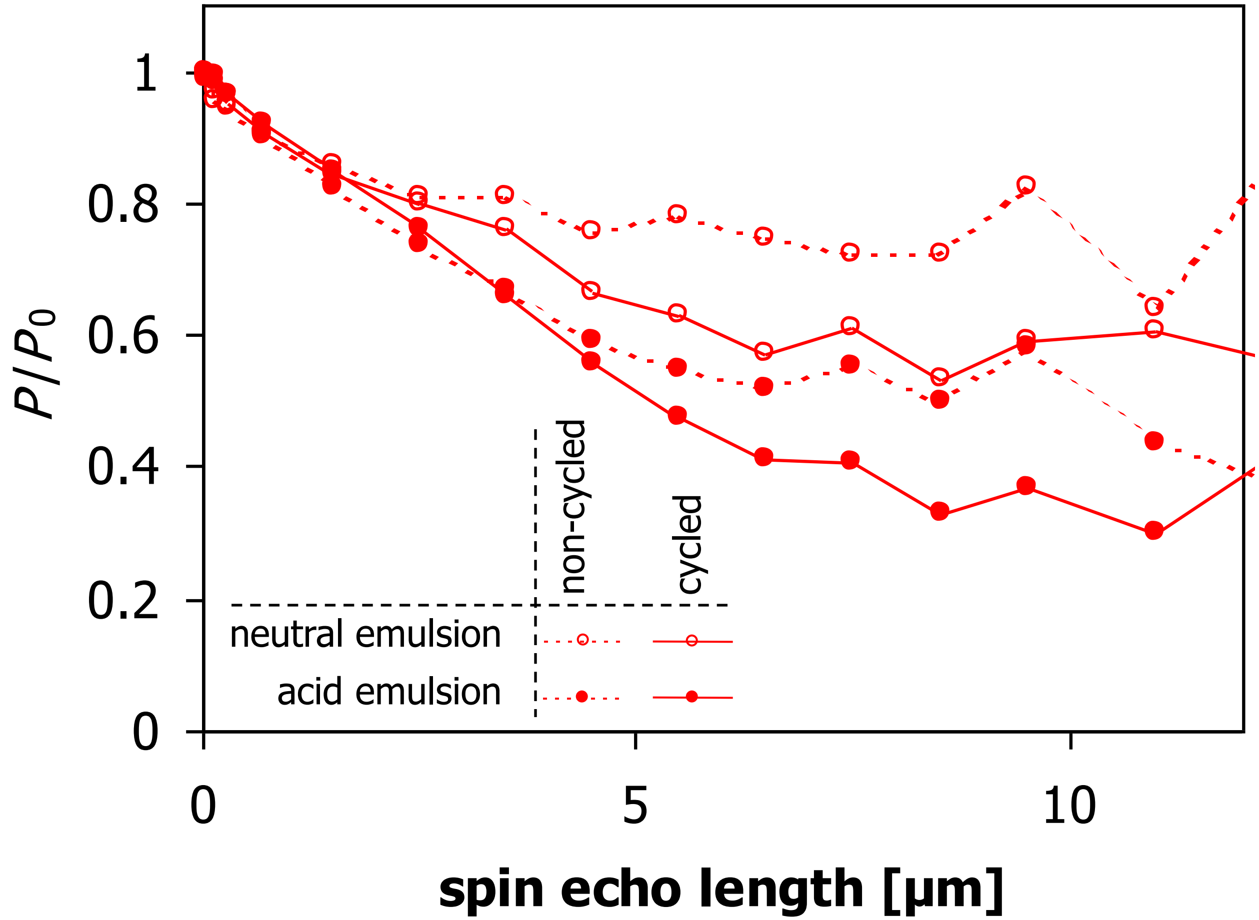
Fresh cheese-type products have a complex microstructure, built from elements of quite different size and properties:

- Fat droplets, stabilised by protein
- Fat droplet aggregates
- Protein aggregates

Arjen Bot

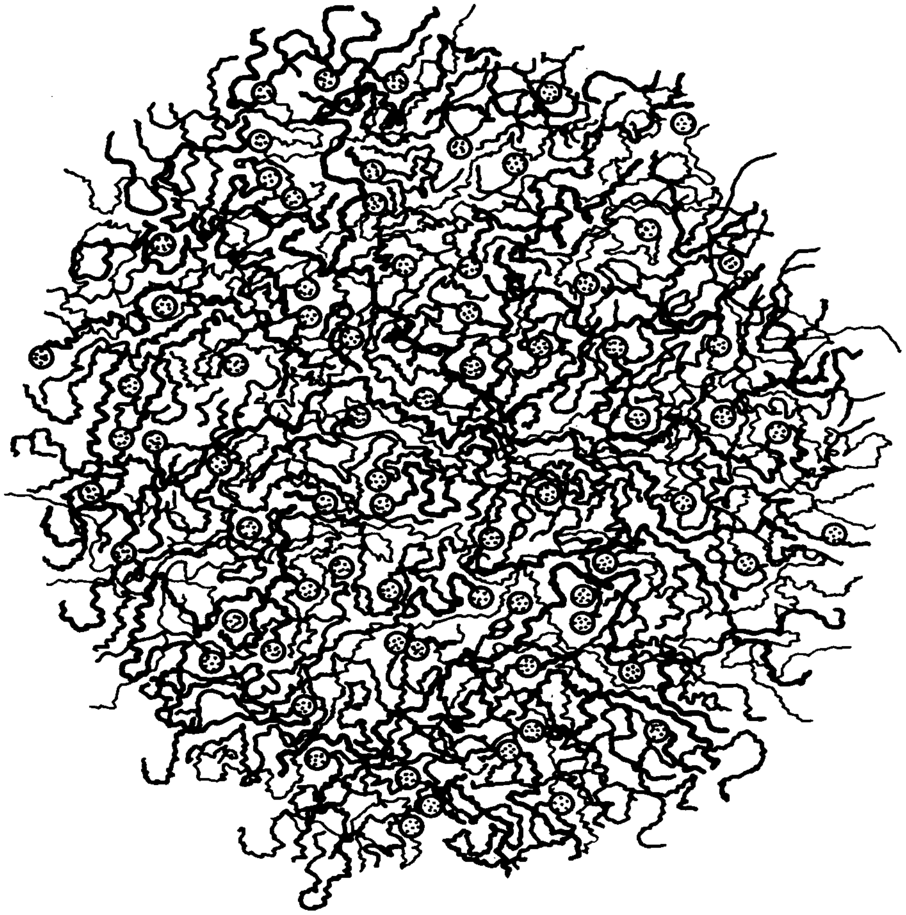


Effect of processing: native vs denatured / neutral vs acidified



Bot et al. Food Hydrocolloids **21** 844–854 (2007)

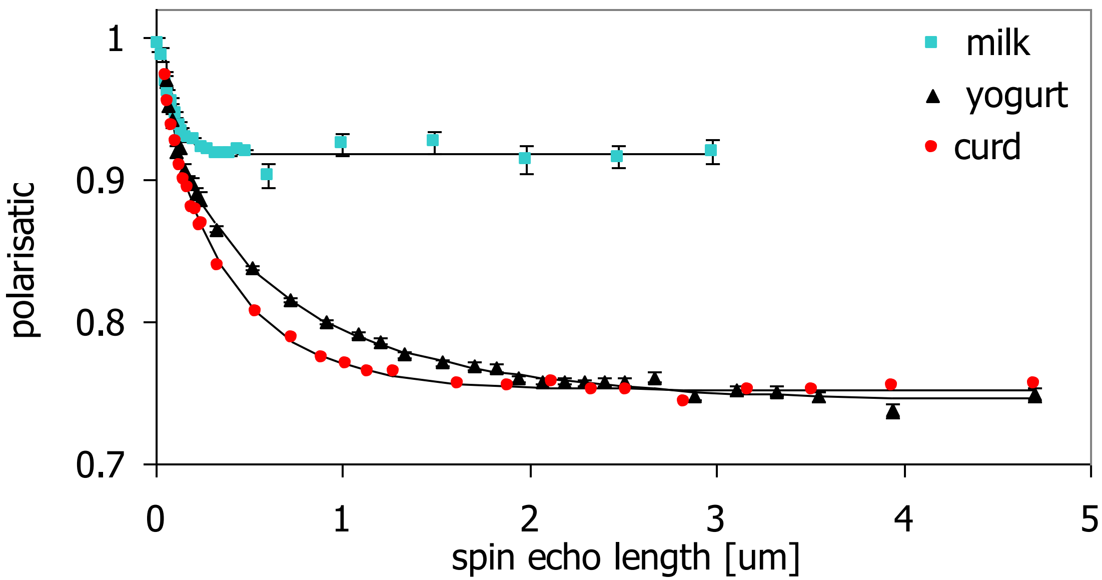
Structure determined of dairy products

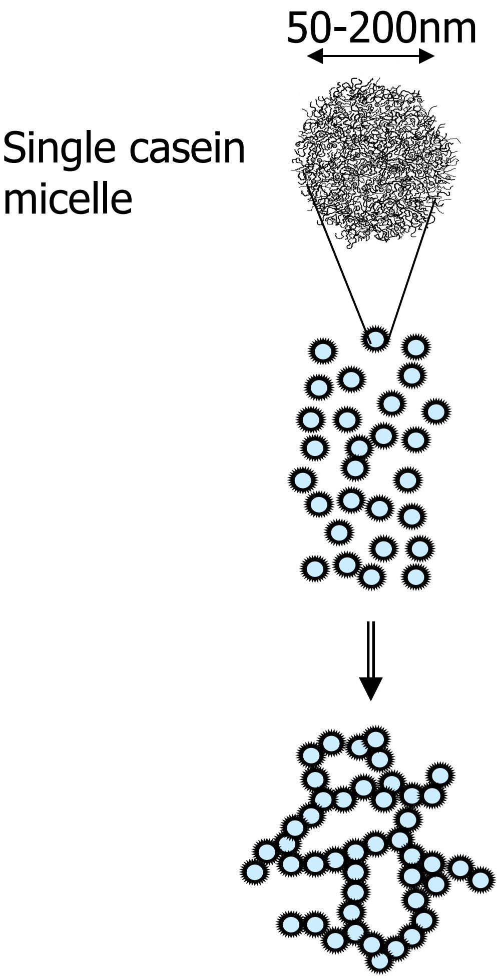


Hans Tromp
NIZO food research
the Netherlands

TU Delft

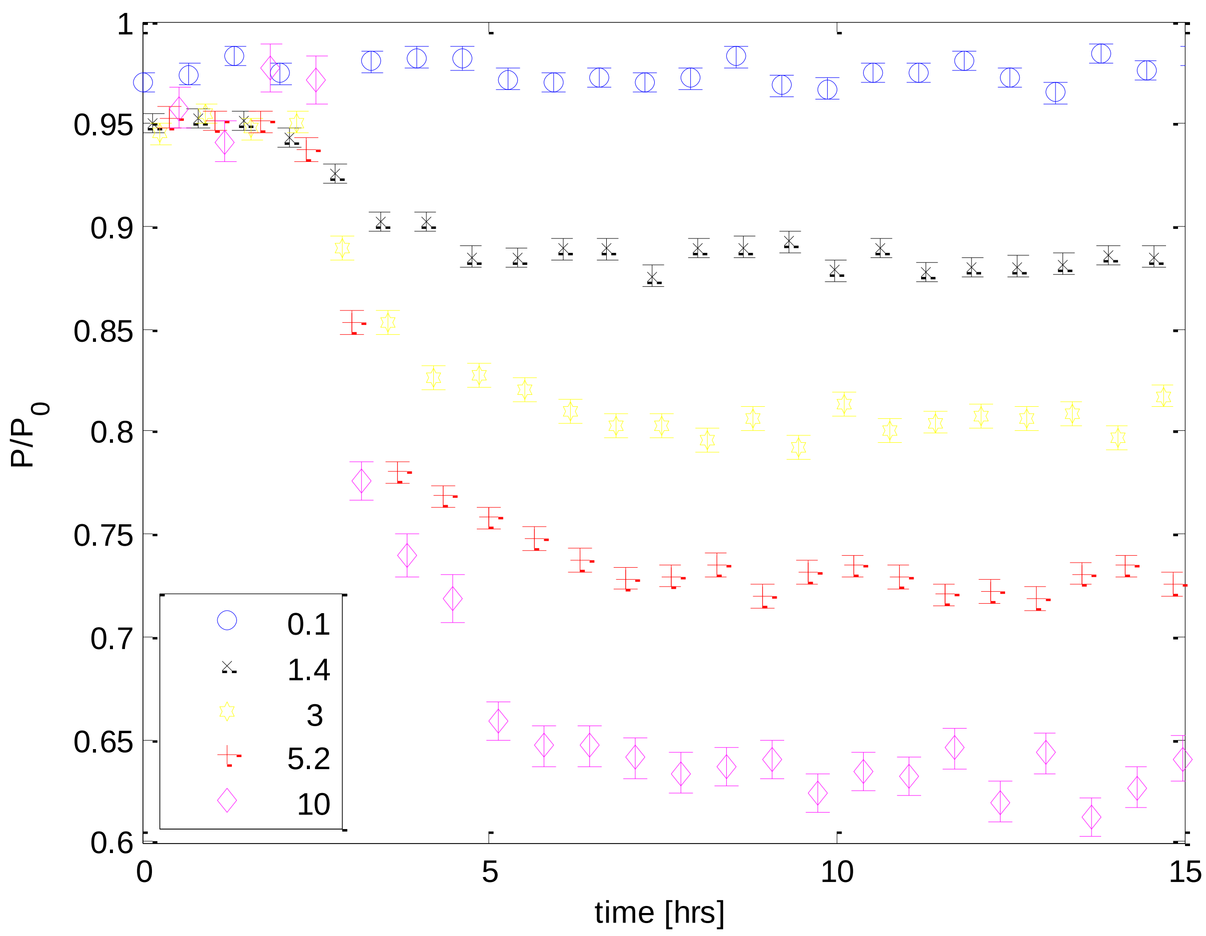
From milk to yogurt and curd



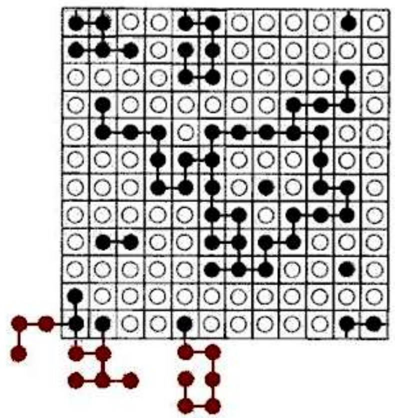


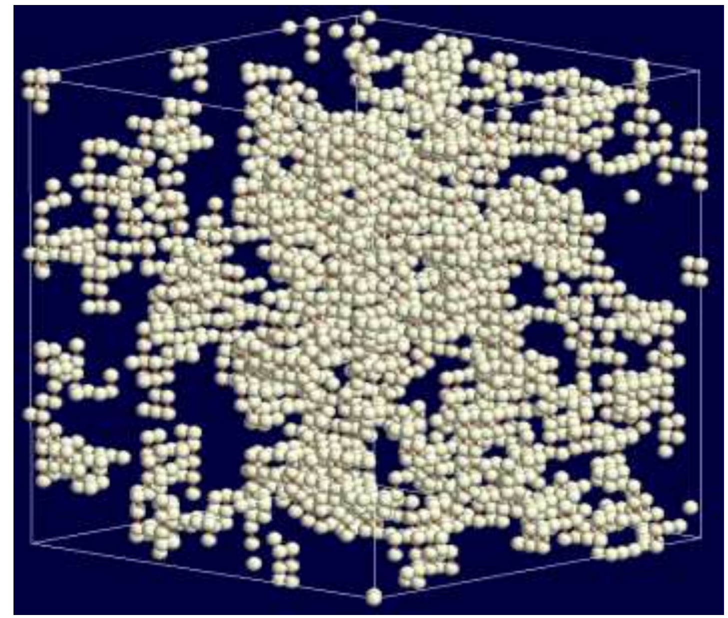
Tromp et al. Food Hydrocolloids **21**, 154-158 (2007)

Kinetic measurement casein aggregation



Simulation and conclusion





- Reaction limited cluster aggregation

Léon van Heijkamp et al.
J. Phys. Chem. A (2010)

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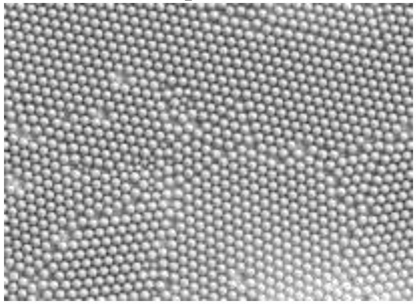
Granular matter

Robert Andersson

- To understand the bulk properties of assemblies of grains we better understand the microstructure of those assemblies.
- What is the distribution of density in an powder?
- How does all this change when we perturb the powder?



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SESANS experiments on SiO_2 powders
Exercise: interpret both measurements

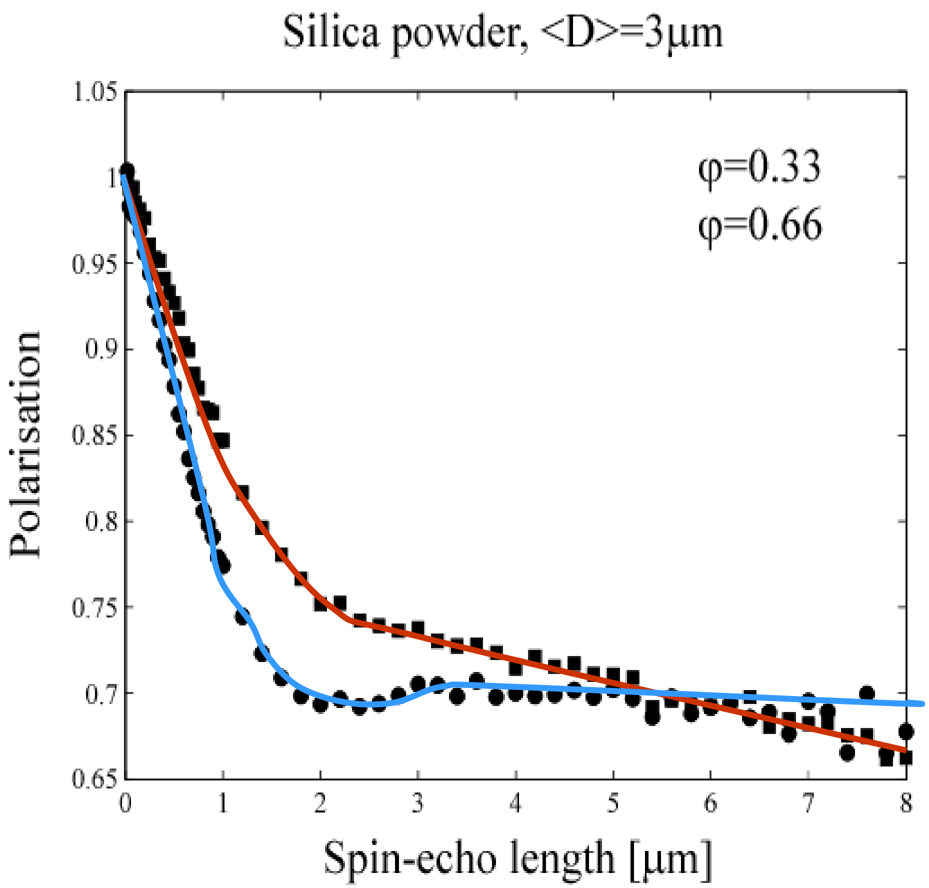
Two samples:

Compacted, Structure

Saturation at 3mm and a hard sphere repulsion peak

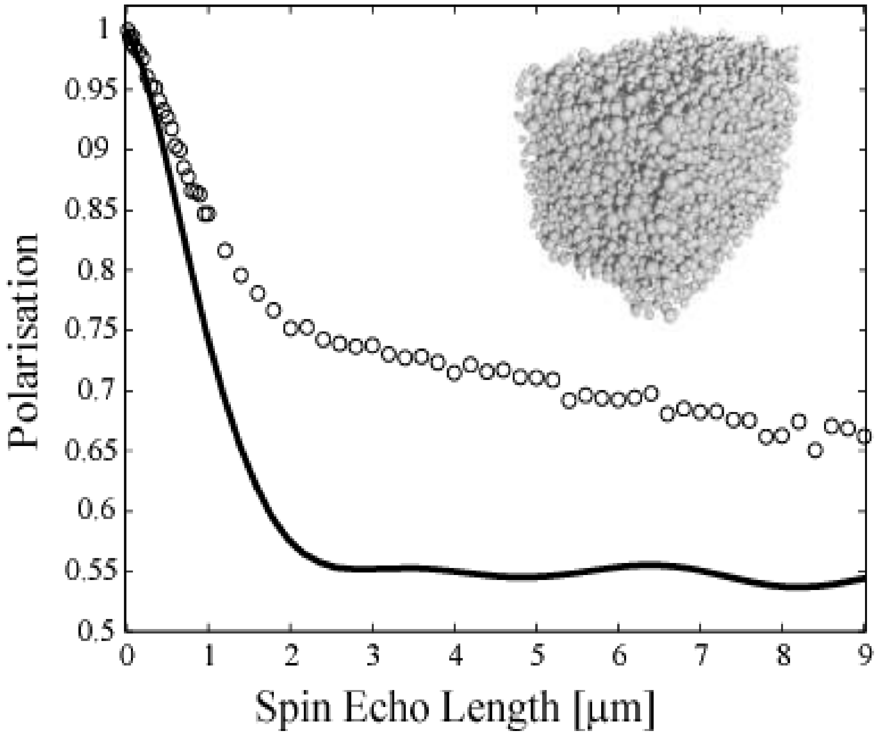
"Poured", Clustered

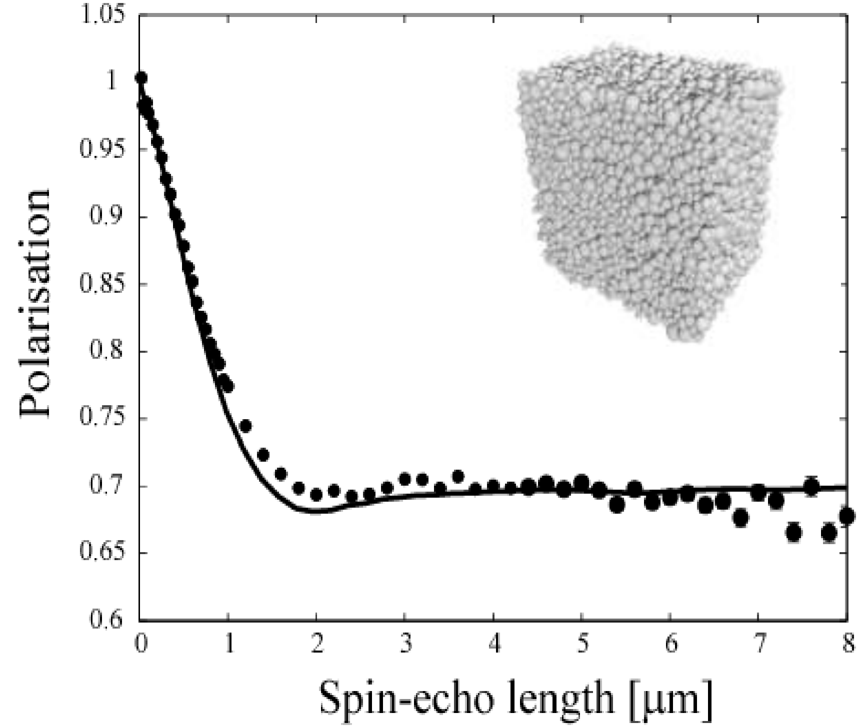
Correlations extends over measured range due to clusters



Molecular dynamics

Extract the SESANS correlation function from MD packings





Conclusion: simulations don't describe features of poured samples.
Big holes could explain measurements

R. Andersson *et al.* Granular Matter **10** 407-414 (2008)

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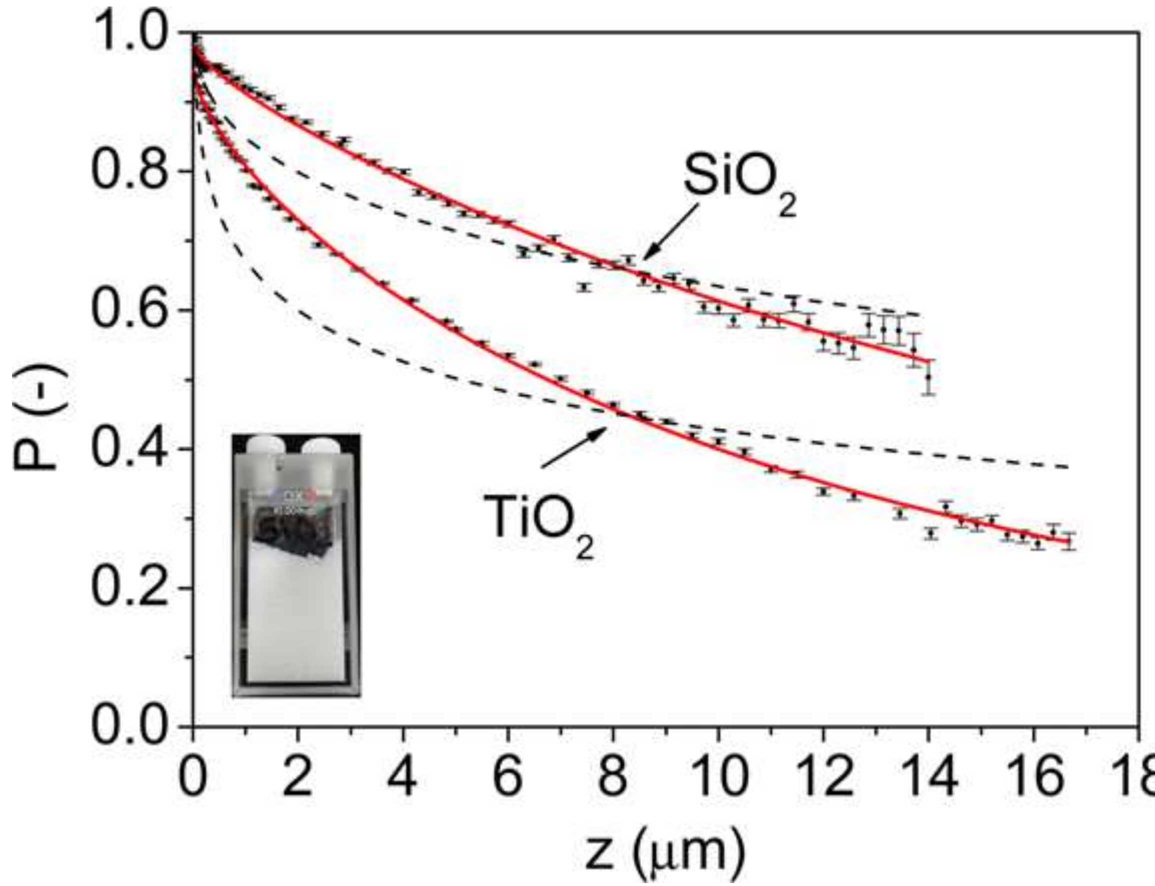
Fractal structure of nanoparticles in fluidised bed

Lilian de Martin

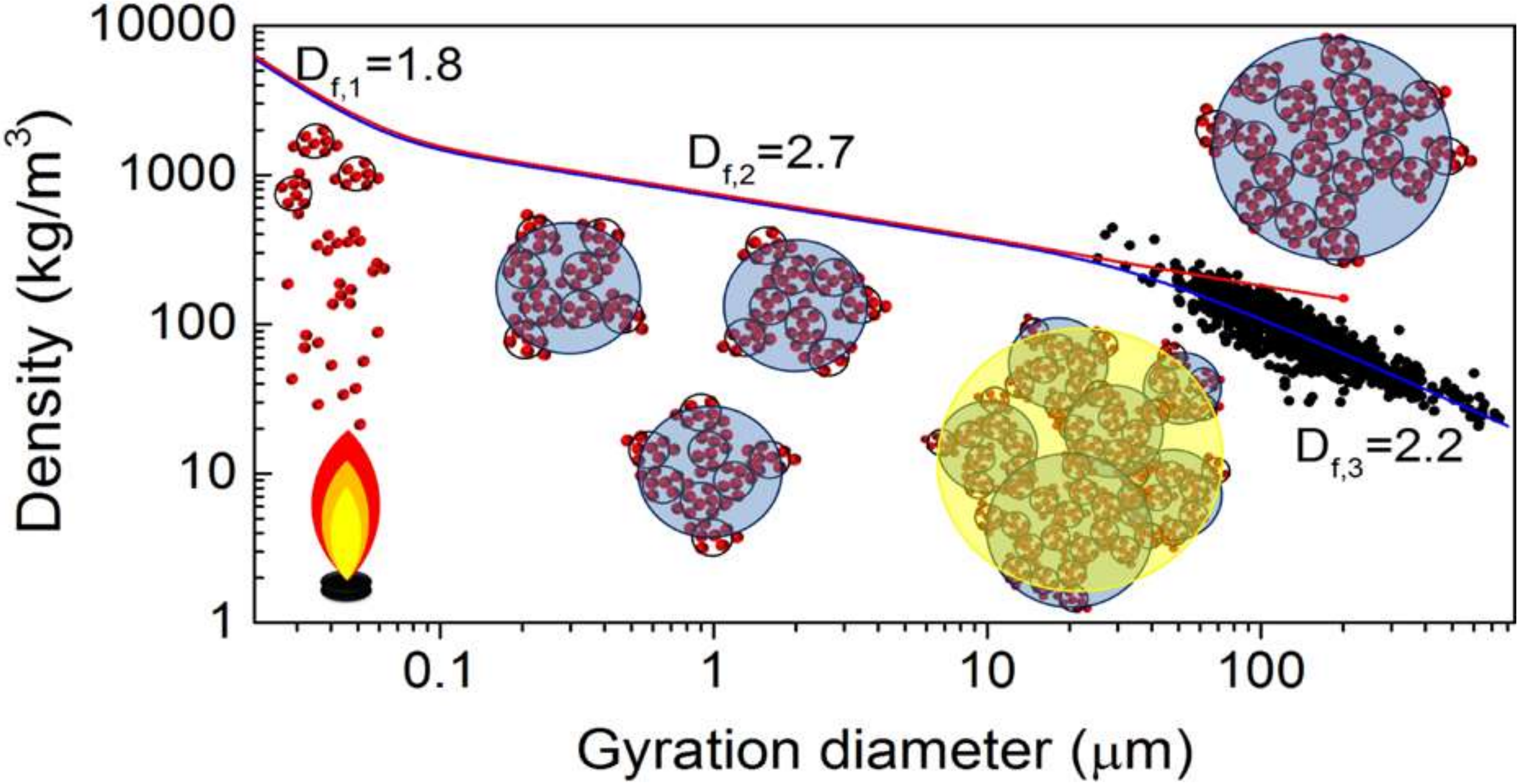


$$\gamma_1(r) = (r/r_p + 1)^{D_{f,1}-3} \quad \text{for } r \leq r_{c,1}$$

$$\gamma_2(r) = (r/a + 1)^{D_{f,2}-3} h(r, \xi_2) \quad \text{for } r > r_{c,1}$$

TU Delft

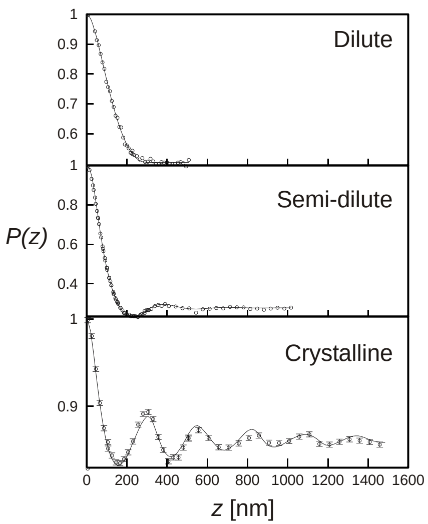
Nanopowder has three length regimes

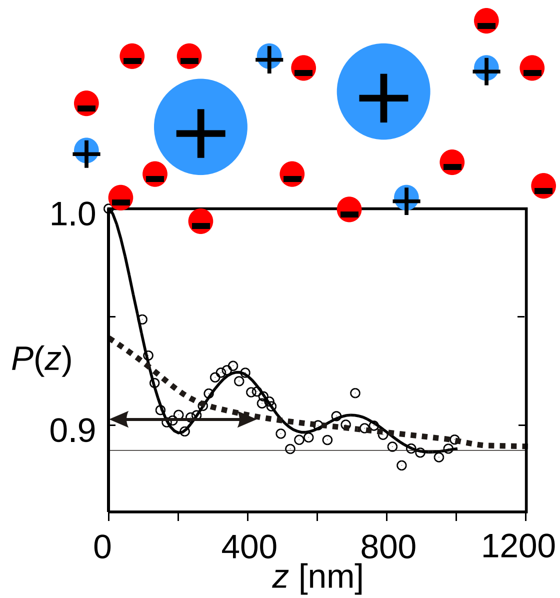


L. de Martin *et al.* Langmuir (2014) **30** 12696

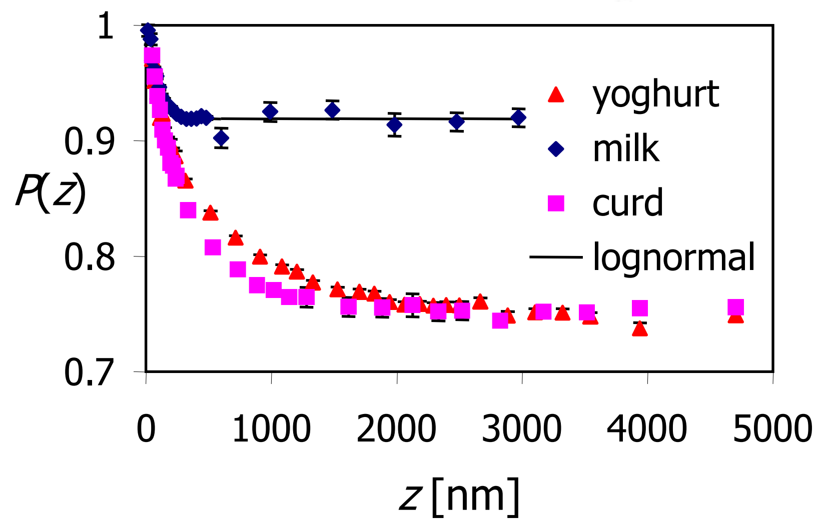
Applications of SESANS
real space, range 30 nm – 18 μm, no collimation

Colloidal interaction

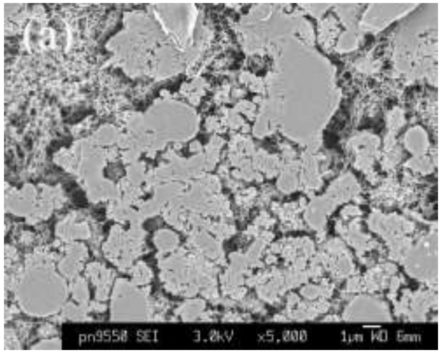


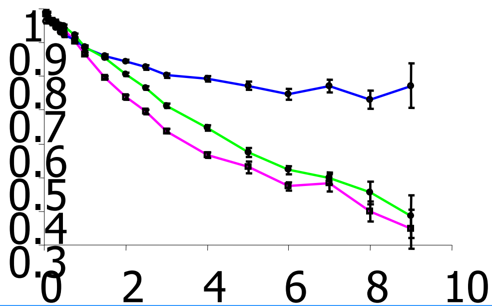


Dairy products



μ-emulsions





- Granular materials
- Drug delivery systems
- Enhanced oil recovery

TU Delft

Outline SESANS

- In 2 slides
- Instrument Delft
- Data analysis
- Examples
- **Where?**

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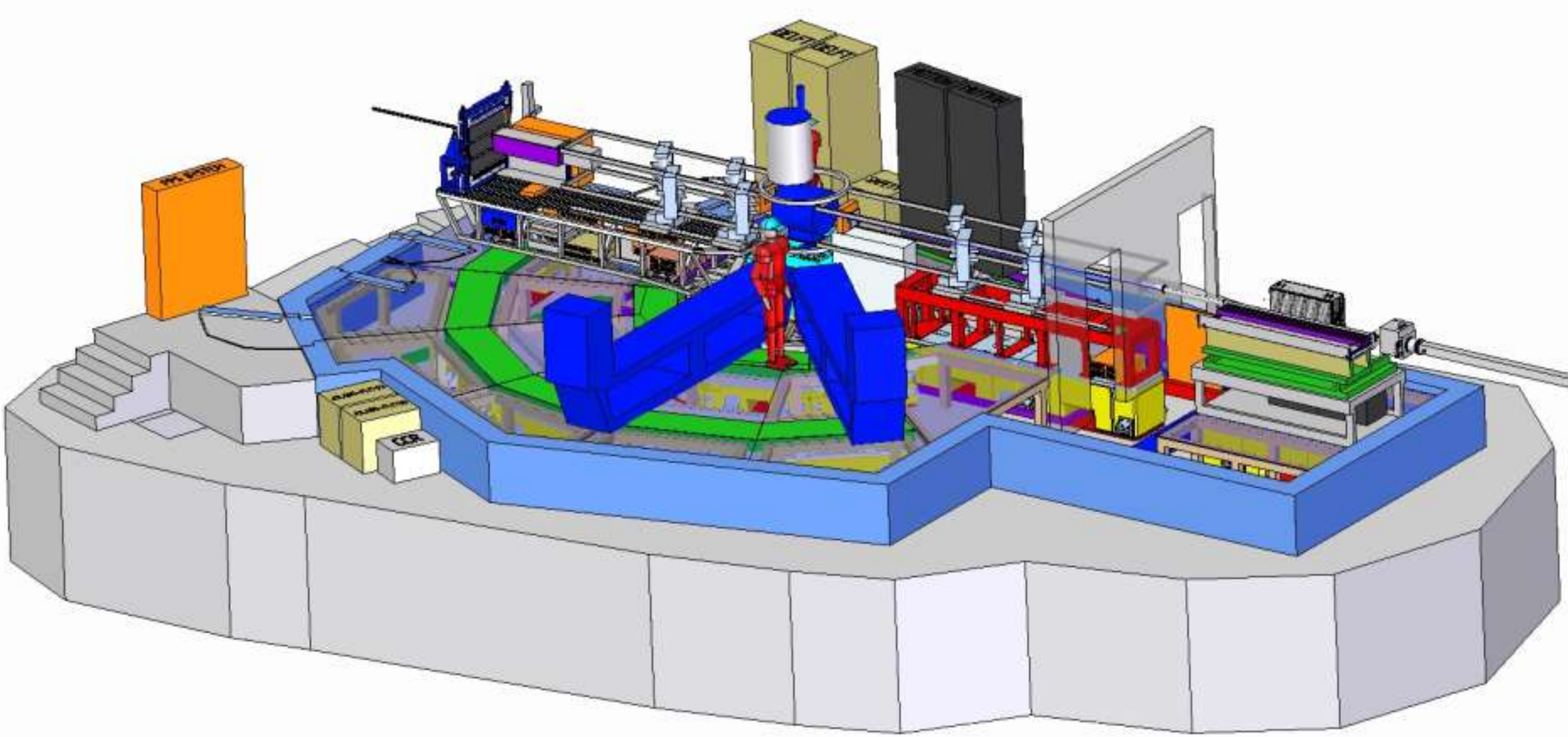
OFFSPEC @ 2nd target station at ISIS

Jeroen Plomp,
Victor de Haan,
Wicher Kraan,
Theo Rekveldt,
Wim Bouwman,
Robert Dalgliesh,
Sean Langridge,
Ad van Well

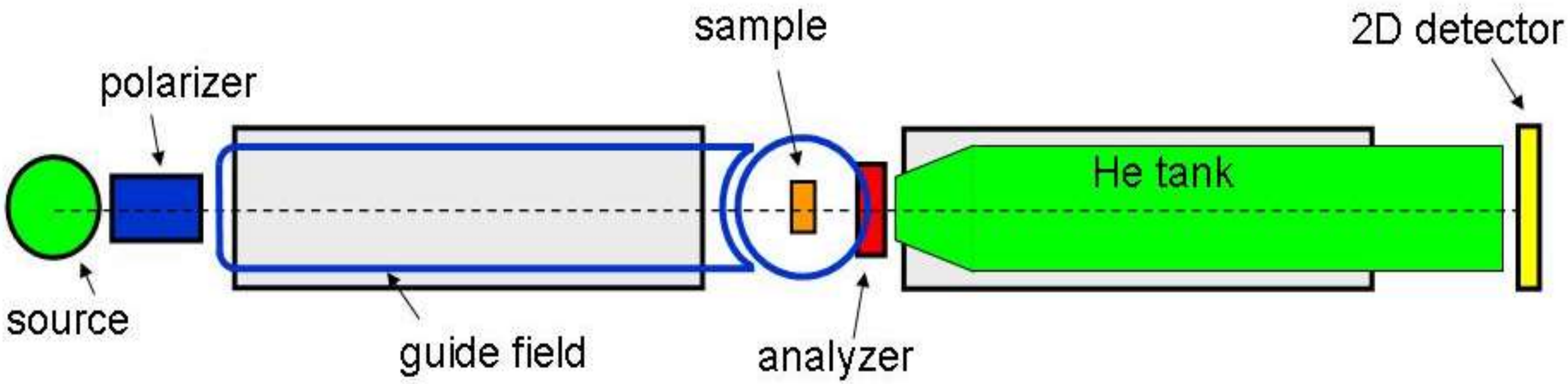
TUDelft

LARMOR: tool of Dutch Science and Industry

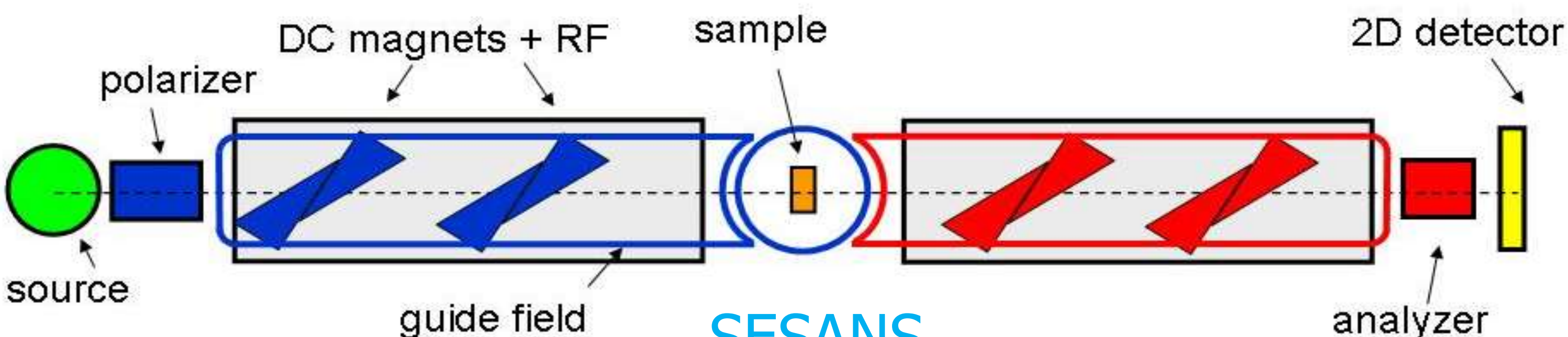


TU Delft

LARMOR @ ISIS



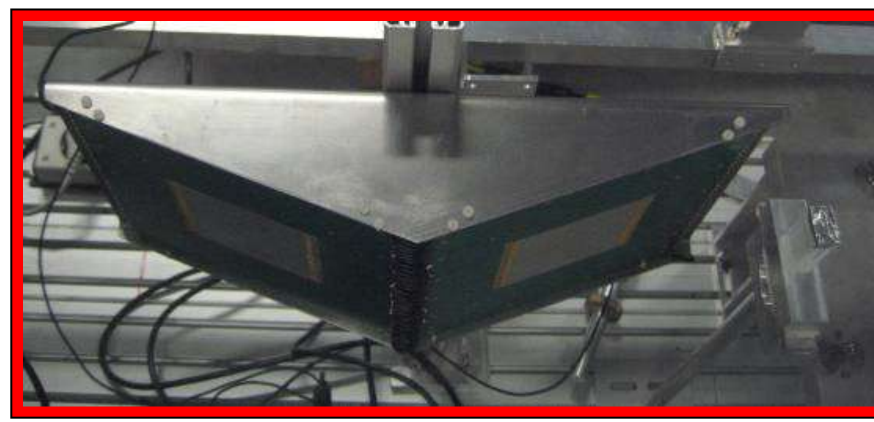
SANS with option for polarised neutrons



SESANS

Triangular solenoids

- Magnetic prisms as triangular solenoids
- Works also in time of flight
- Limited in spin-echo length
- Low tech, low weight, small volume



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SESANS instruments, outdated list when I made it ;-(

place	name	method	mono/ TOF	dedi- cated	max δ [μm]
Berlin	FLEX	bootstrap	M	no	0.7
Delft	SESANS	π-flip foils	M	yes	20
~~Delft~~	~~WESP~~	~~RF-flippers~~	~~TOF~~	~~no~~	~~1~~
ILL	EVA	bootstrap	M	refl	
FRM II	MIRA	bootstrap	M	no	1
FRM II	N-REX$^+$	BS + Δ	M	refl	
LENS	SESANS	triangle		yes	
SNS		triangle	TOF	refl	> 0.1
ISIS	OFFSPEC	RF-flippers	TOF	refl	15
PNPI	SESANS	RF-flippers	M	yes	
ISIS	LARMOR	RF-flippers	TOF	no	10-20

Outline SESANS

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TUDelft