Spin-Echo Small-Angle Neutron Scattering

Wim G. Bouwman

SESANS =

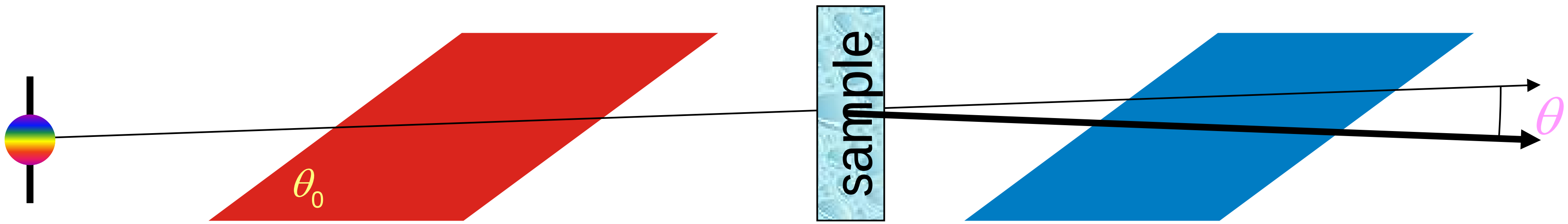
High resolution SANS

using a spin-echo technique

What to learn from this lecture?

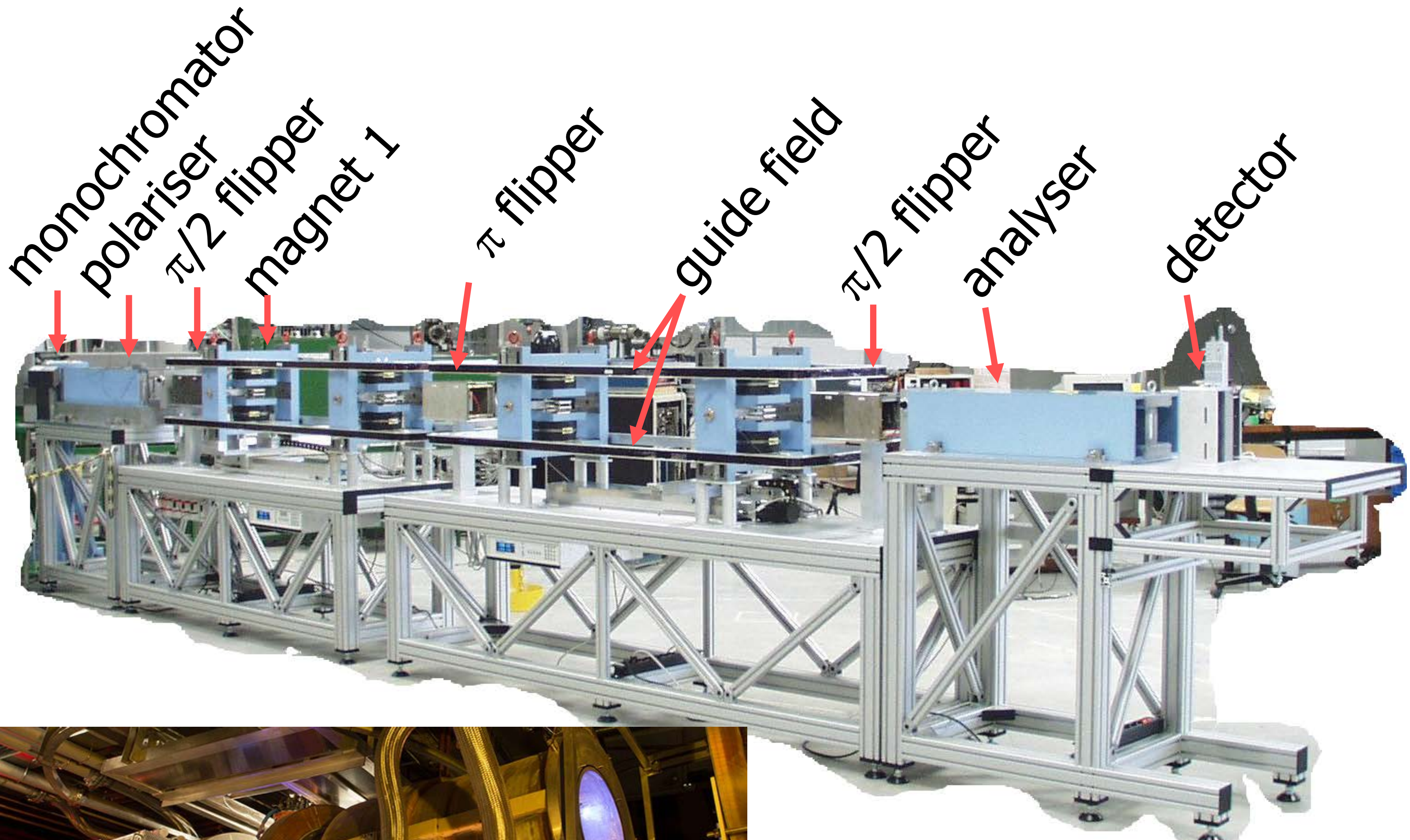
1. **Measurement principle**
2. Visual data interpretation
3. What kind of scientific problems

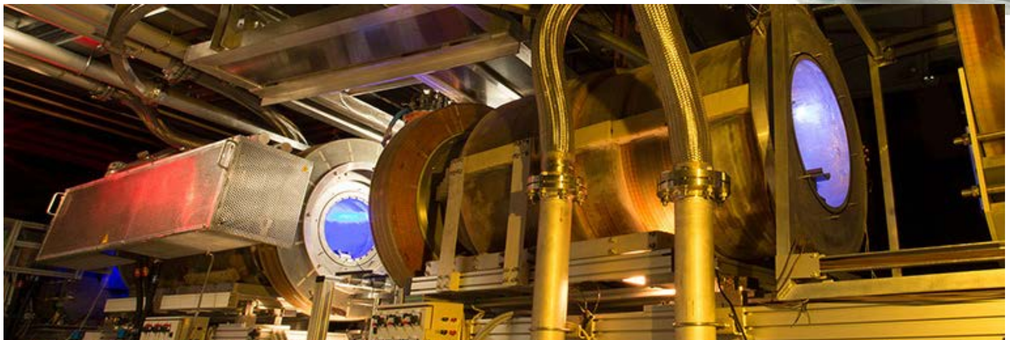
Larmor encoding of scattering angle spin-echo small angle neutron scattering



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

Realisation SESANS in Delft





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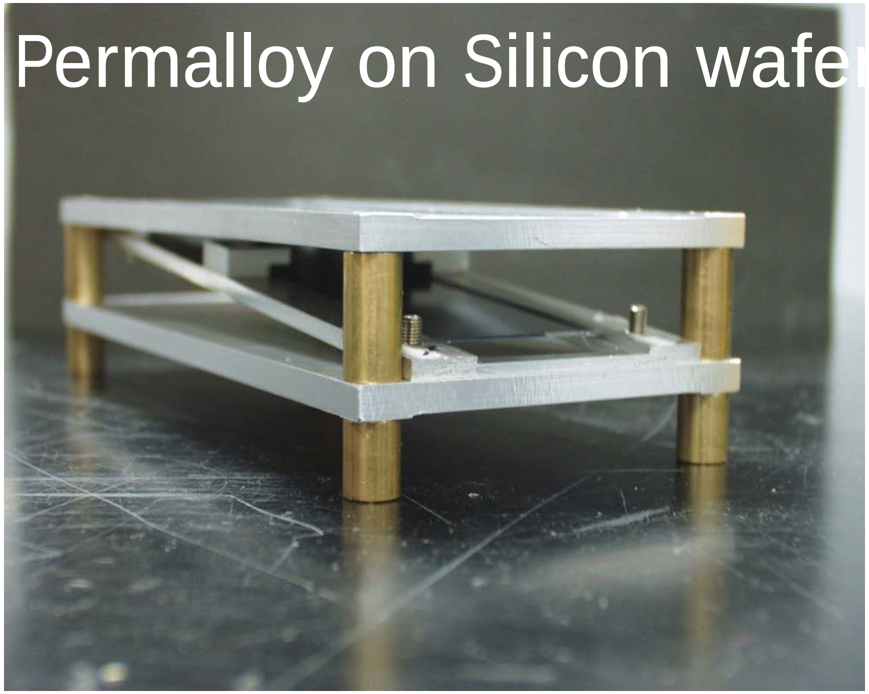
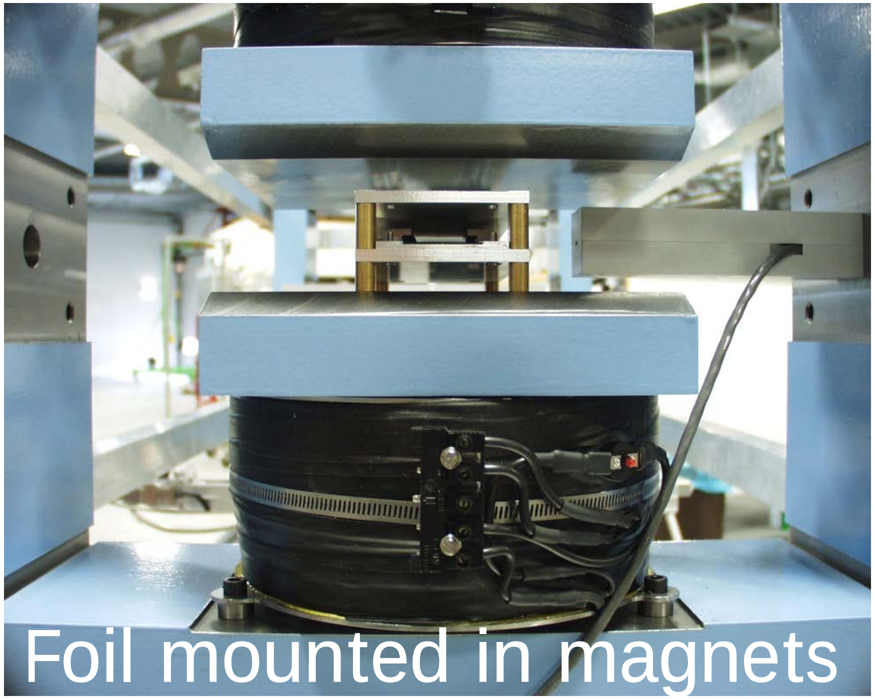
Magnetised foils tuned for π-flip: can be considered reversal field

3 μm permalloy film





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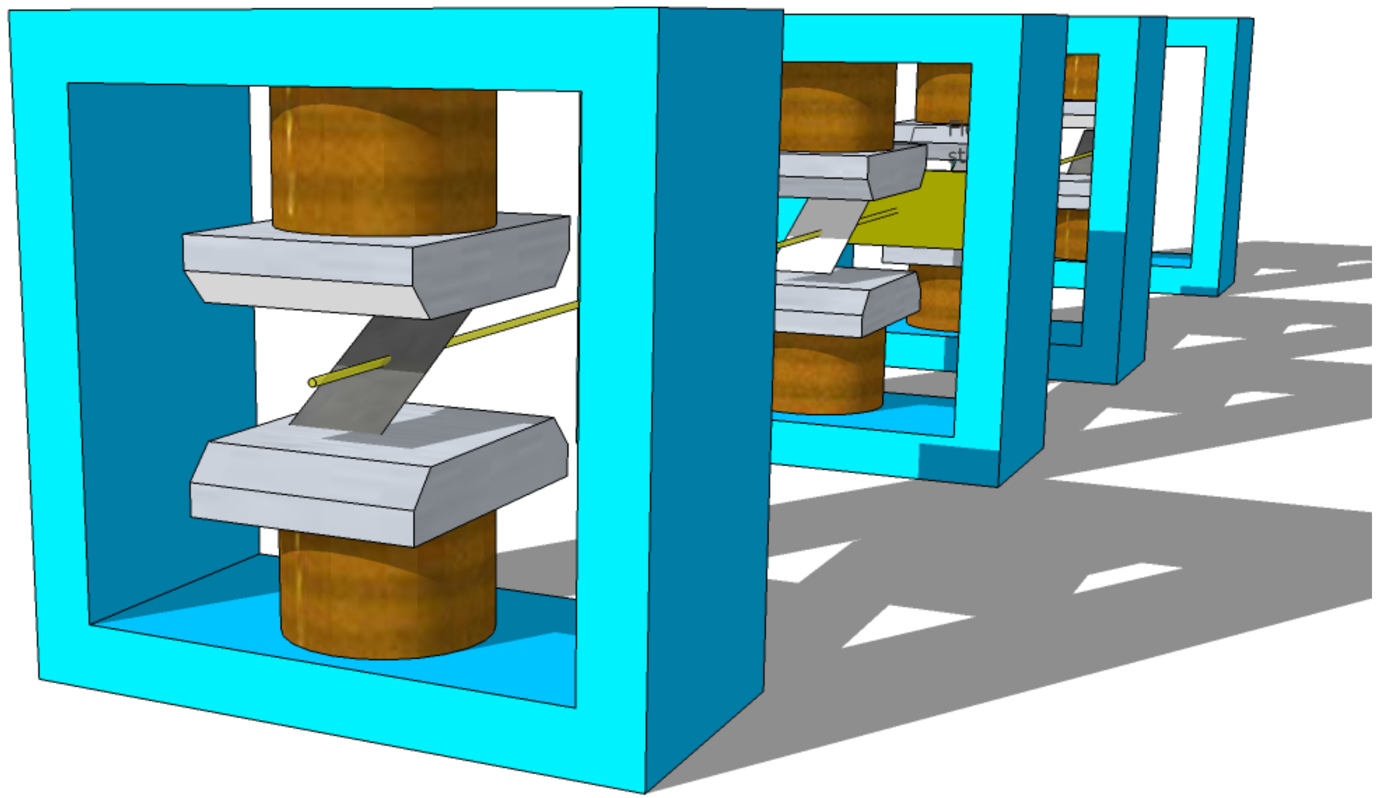
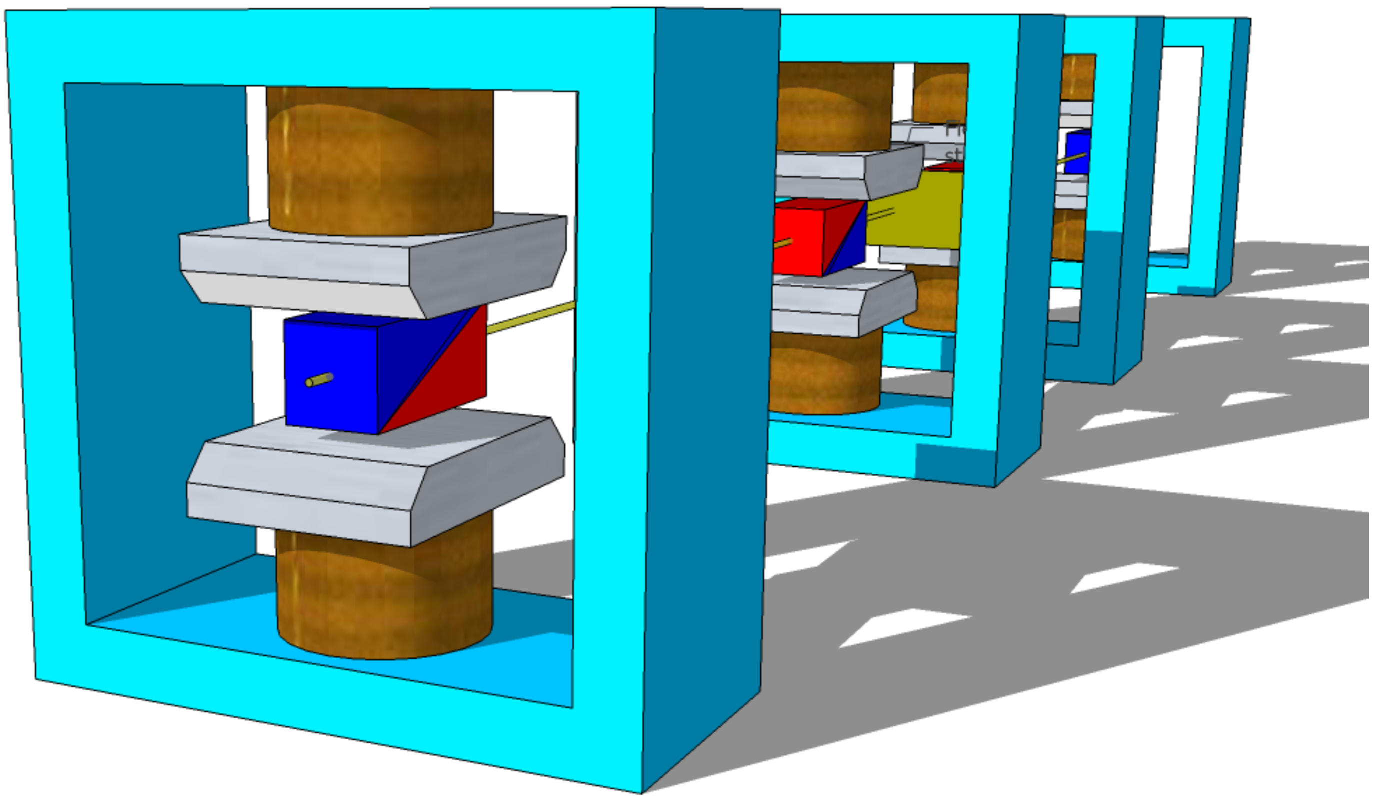
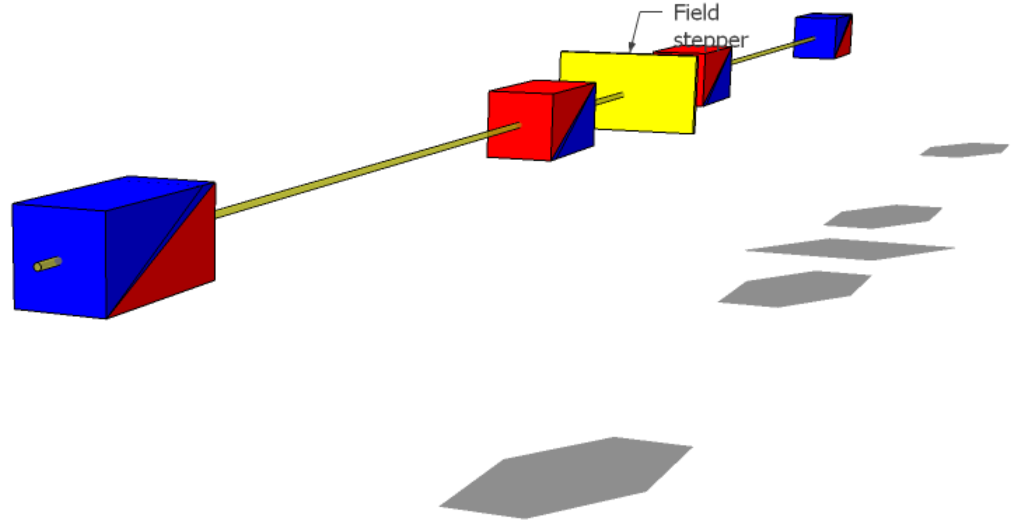
Precesion regions defined by foils and magnets (1)



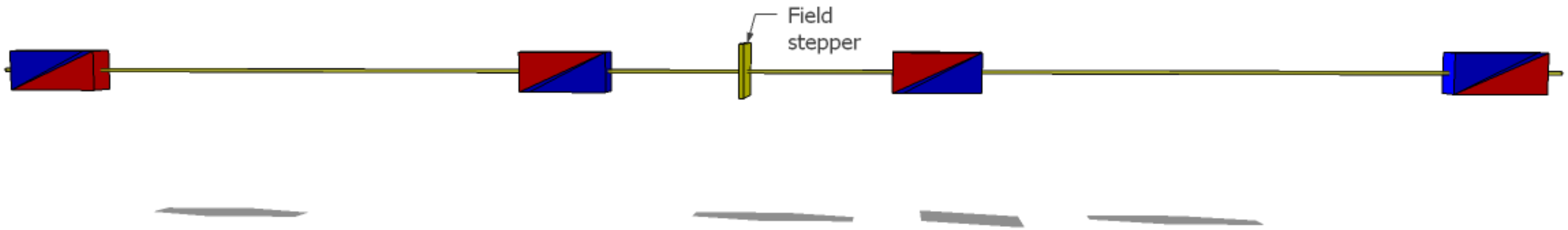
Precesion regions defined by foils and magnets (2)



Precesion regions defined by foils and magnets (3)

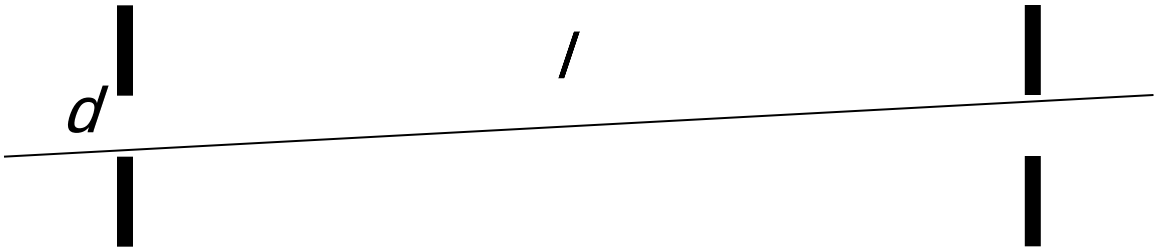


Precesion regions defined by foils and magnets (4)



Why is Delft SESANS resolution higher than SANS?

SANS

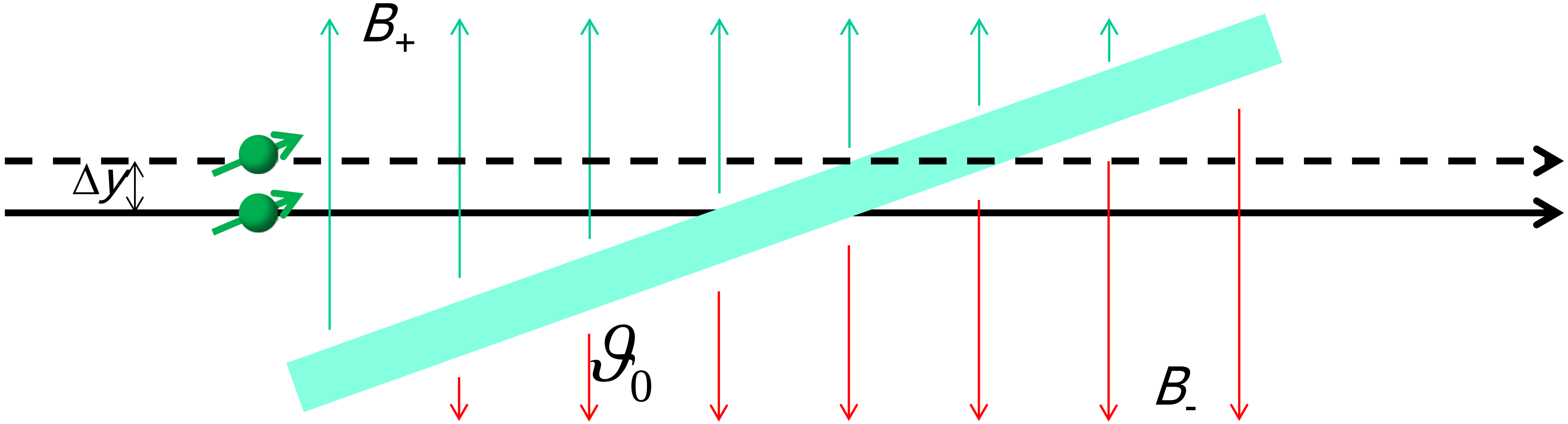


$$\delta\theta = d / l \quad = 10\text{mm}/10\text{m} = 1\text{mrad}$$

$$\varphi = cL\lambda B \qquad c = \frac{\gamma m}{h} \qquad \Delta\varphi = 2c\Delta y \cot(\vartheta_0)\lambda\Delta B$$

$$\Delta y = \frac{\Delta\varphi}{2c\cot(\vartheta_0)\lambda B} = \frac{1}{2\times(5\times10^{14}\,\mathrm{T^{-1}m^{-2}})(10)(2\times10^{-10}\,\mathrm{m})(0.2\,\mathrm{T})} \approx 3\mu\mathrm{m}$$

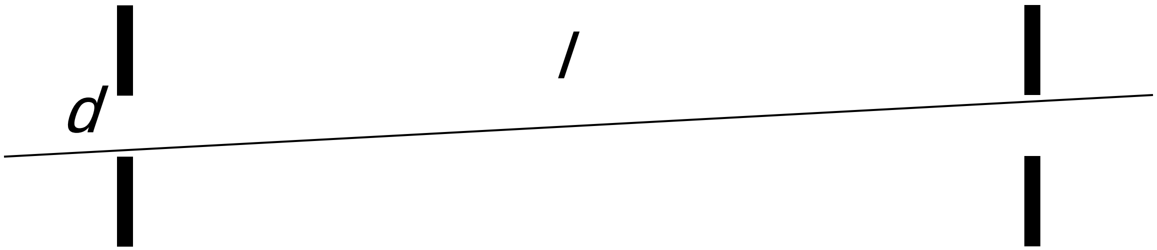
Effective slit width of foil flipper?



Delft

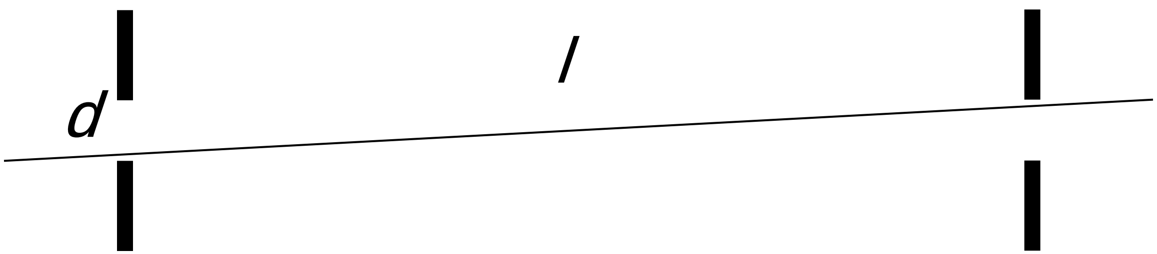
Why is Delft SESANS resolution 300 higher than SANS?

SANS



$$\delta\theta = d\,/\,l \quad =10\mathrm{mm}/10\mathrm{m}=1\mathrm{mrad}$$

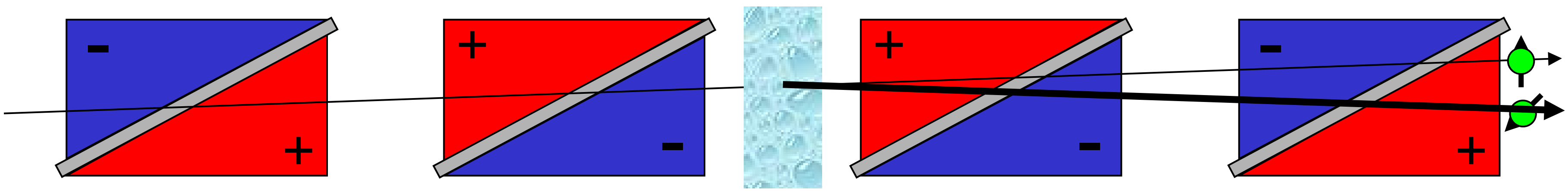
SESANS



$$\delta\theta = d\,/\,l \quad =3\mu\mathrm{m}/1\mathrm{m}=3\mu\mathrm{rad}$$

From SANS to SESANS

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



$\phi = Q_z \delta_z$ $\qquad$ $\delta_z = \dfrac{\gamma_n m \lambda^2 LB \cot\theta_0}{\pi h}$ spin-echo length

single neutron: $P = \cos(\phi) = \cos(Q_z \delta_z)$

single scattered neutron: $G(\delta_z) = \dfrac{1}{k_0^2} \int\int I(Q_y, Q_z) \cos(Q_z \delta_z) dQ_y dQ_z$

isotropic scattering: $G(\delta_z) = \dfrac{1}{k_0^2} \int I(Q) J_0(Q\delta_z) QdQ$

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

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Analogy to neutron spin-echo in classical description (Slides Peter Fouquet)

$$\varphi = t\omega$$

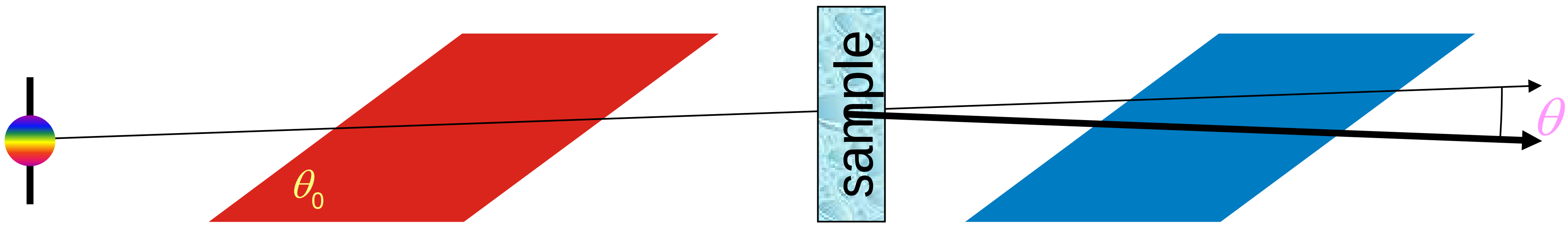
$$t = \frac{\varphi}{\omega} = \frac{\hbar}{m}\frac{\gamma_L \int \vec{B}\cdot d\vec{l}}{\bar{v}^3} = \frac{m^2\gamma_L \int \vec{B}\cdot d\vec{l}}{2\pi h^2}\lambda^3$$

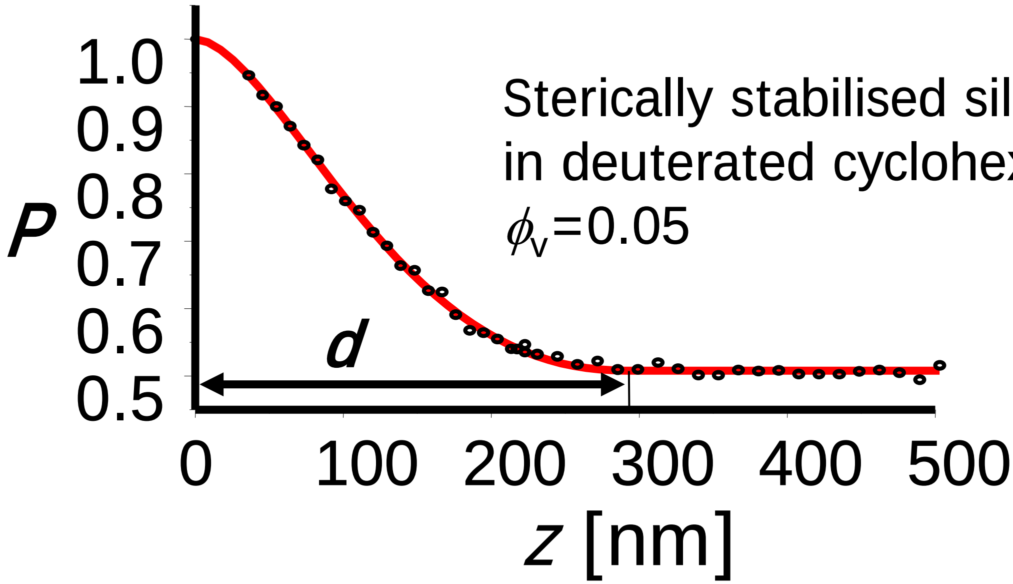
$$P_x(Q,t) = \frac{\int S(Q,\omega)\cos(\omega t)d\omega}{\int S(Q,\omega)d\omega}$$

What to learn from this lecture?

1. Measurement principle
2. **Visual data interpretation**
3. What kind of scientific problems

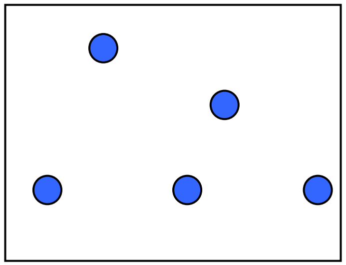
SESANS = Fourier transform scattering ⇒ projected density correlation function 20 nm – 20 μm





Sterically stabilised silica particles d=298 nm in deuterated cyclohexane

ϕ_V=0.05



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

Density, correlation, SANS, SESANS

$$I(Q) \propto \int \gamma(r)\frac{\sin(qr)}{qr} r^2 dr$$

$$G(\delta) = 2\int_0^\infty \gamma(x,0,\delta)\,dx = 2\int_\delta^\infty \frac{r\gamma(r)}{\sqrt{r^2-\delta^2}}\,dr$$

$$\begin{tikzcd}
 & \gamma(r) \arrow[dl] \arrow[dr] & \\
 & \rho(r) \arrow[u] & \\
I(Q) \arrow[rr] & & G(z)
\end{tikzcd}$$

$$G(\delta) \propto \int_0^\infty J_0(Q\delta)\, I(Q)\, Q\, dQ$$

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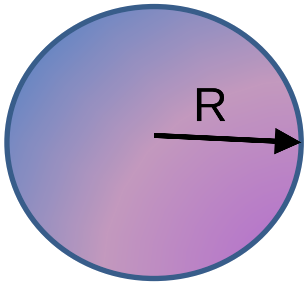
Spheres
(adapted from Karen Edler's lecture)

- 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:

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

Spheres in SESANS

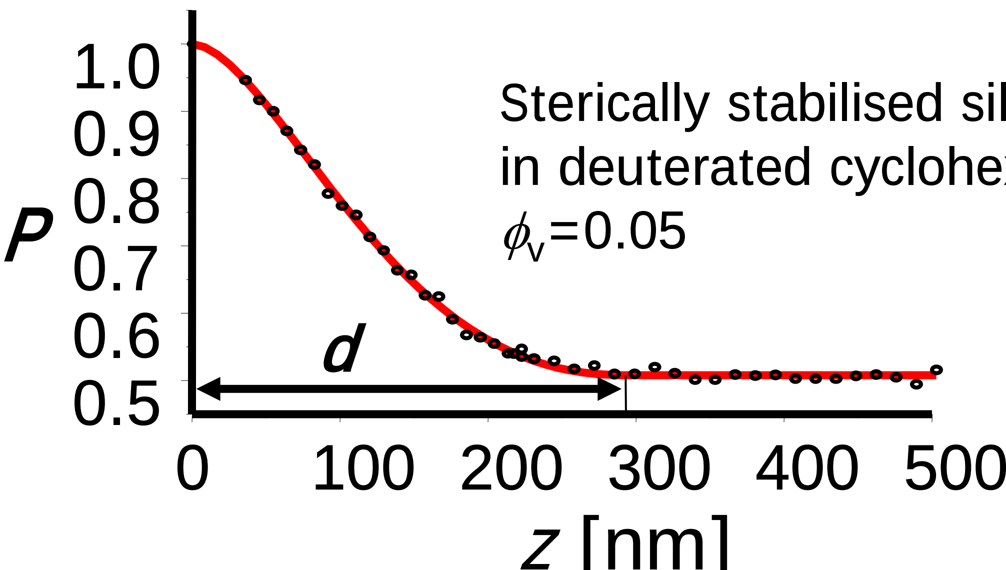
$$\gamma(r) = 1 - \frac{3}{4}\frac{r}{R} + \frac{1}{16}\left(\frac{r}{R}\right)^3$$

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

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

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

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



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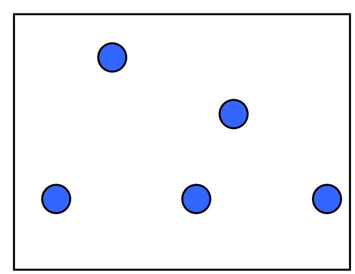
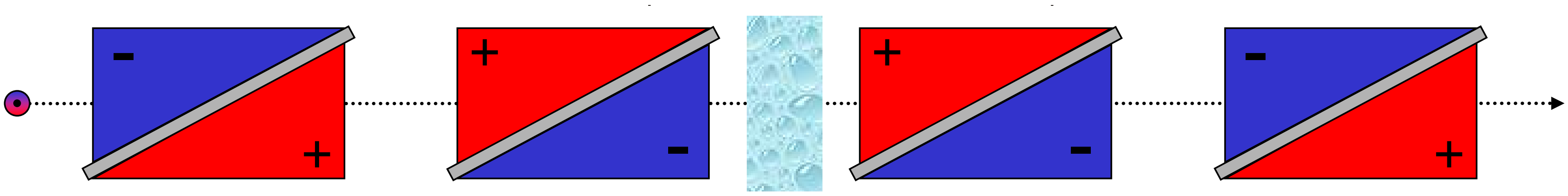


SESANS semi-quantum mechanically

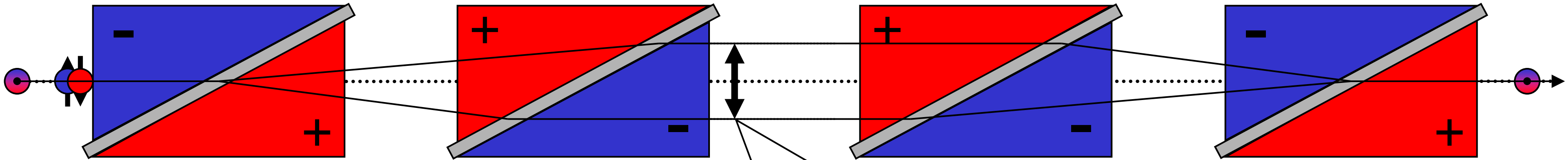
Wave function is superposition of eigen states:

$$\left|\Psi\right\rangle = \left|\Psi^{-}\right\rangle + \left|\Psi^{+}\right\rangle$$

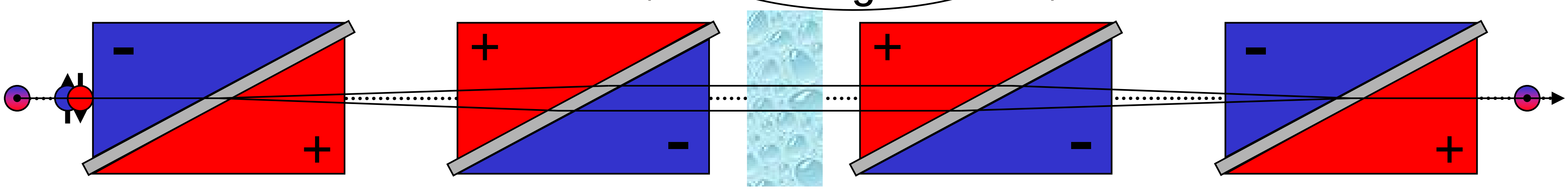


Shifting of eigen states

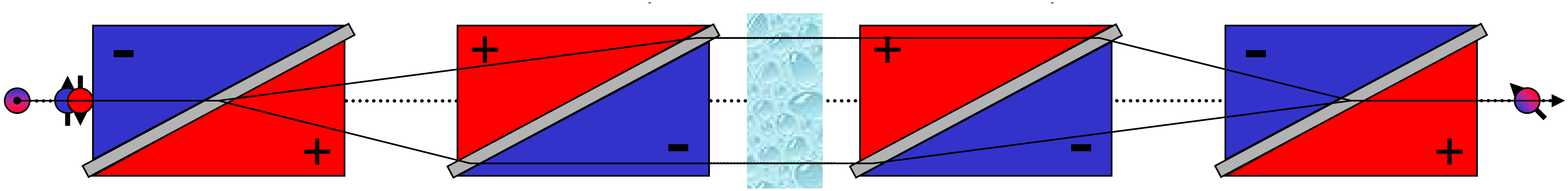
$|\Psi\rangle = |\Psi^-\rangle + |\Psi^+\rangle$ or = +



Focussing of eigen states



Low field: correlation short distance



High field: correlation long distance

Inhomogeneities -> phase shift -> depolarisation

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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

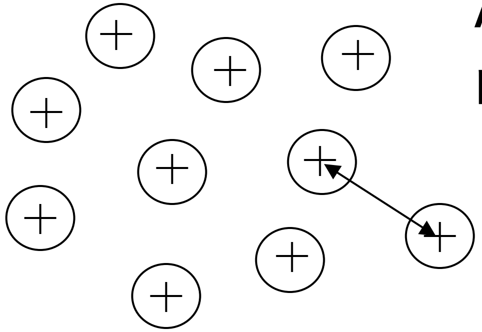
$\Rightarrow$ depends on particle shape

Structure Factor = scattering from different particles

$\Rightarrow$ depends on interactions between particles

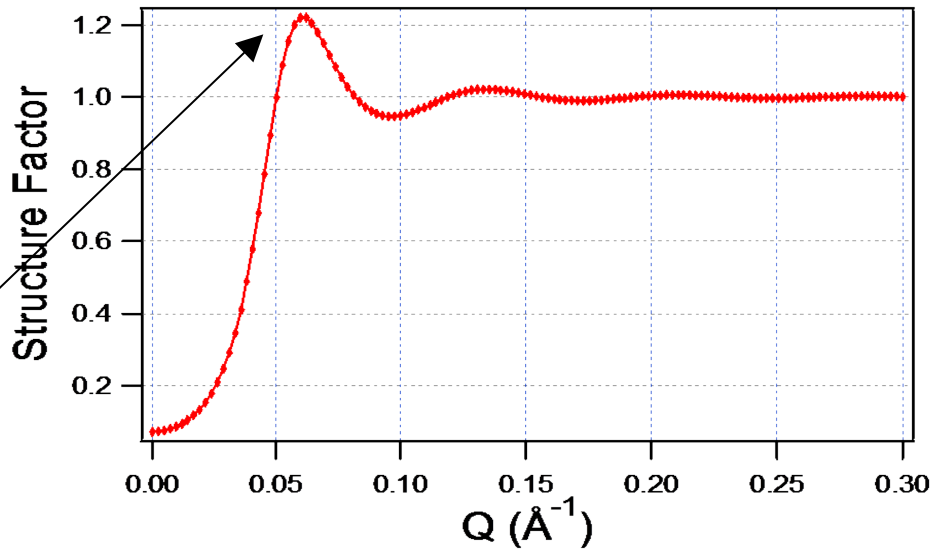
Structure Factors (Karen Edler)

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

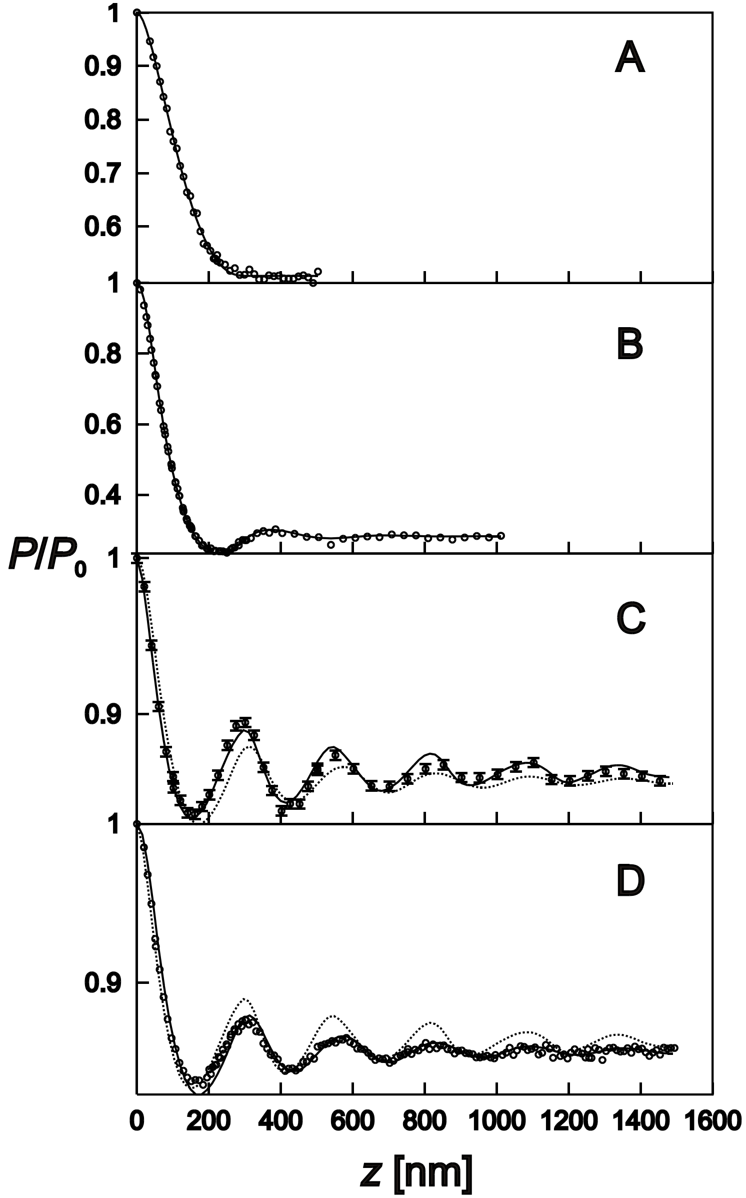


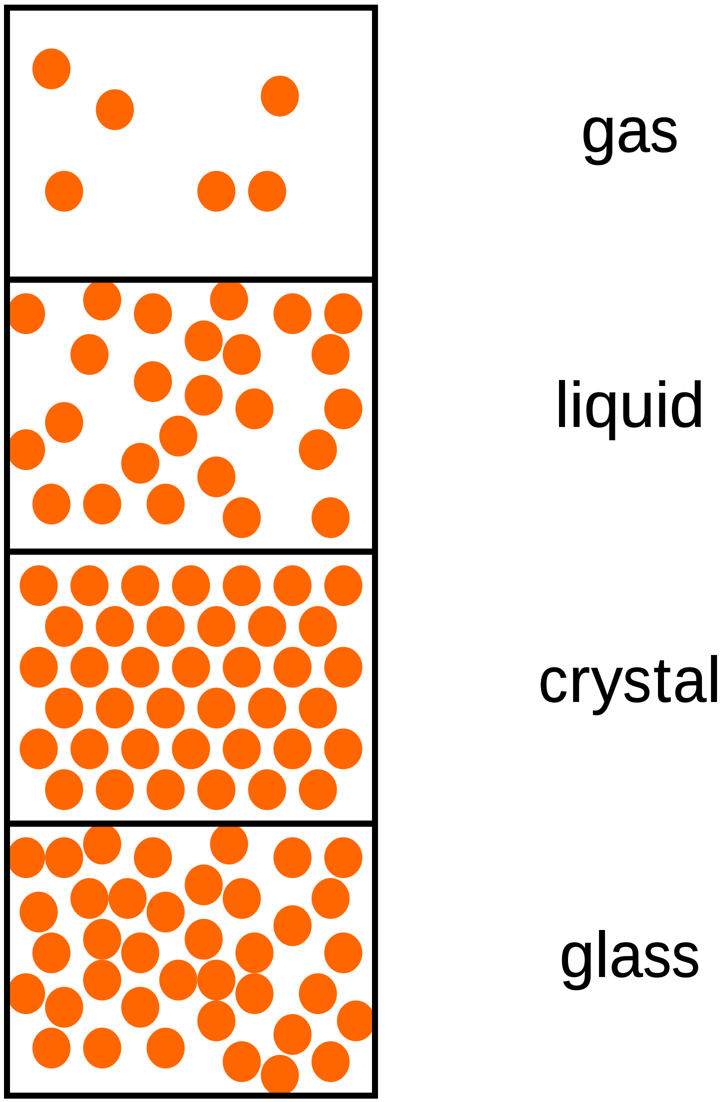
Average distance between nearest neighbours relatively constant
= “correlation distance”

Position of first maximum related to correlation distance



Structure factor in SESANS **convolution** product





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

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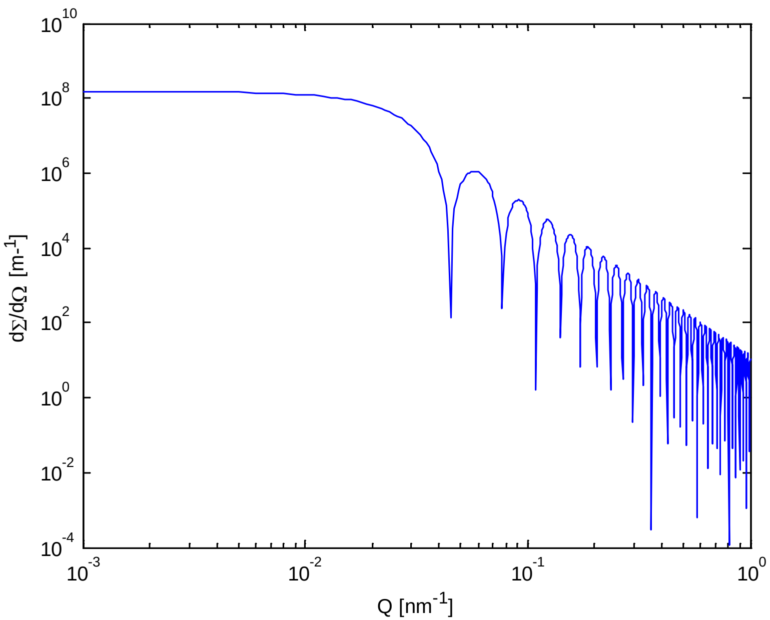
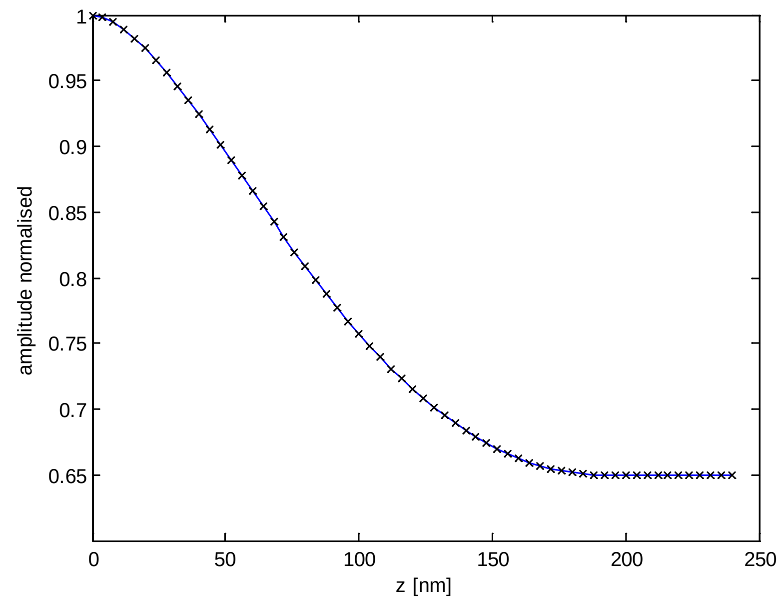
Present data analysis

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

User-friendly software for dissemination
Data-analysis: SANS into SESANS conversion





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

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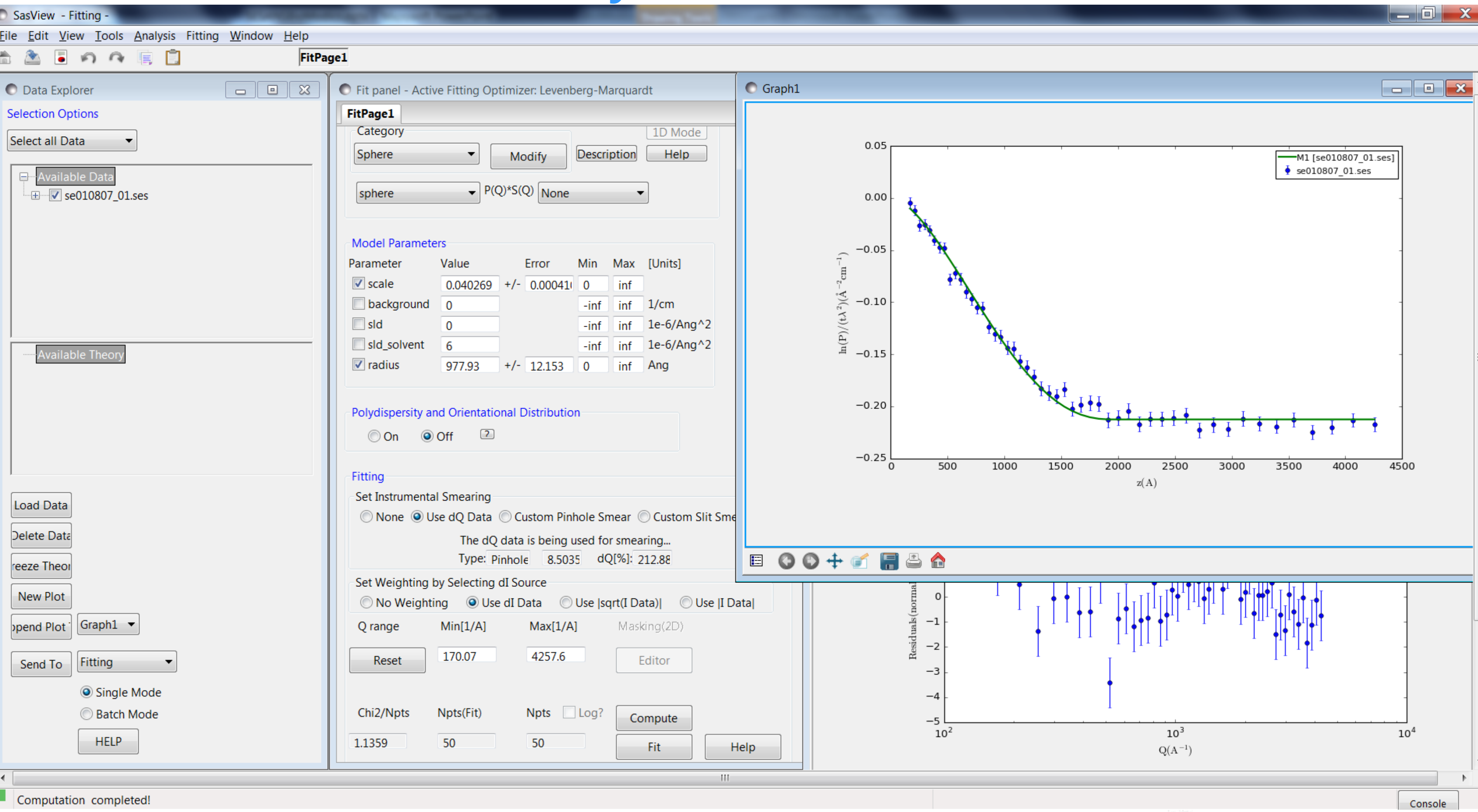
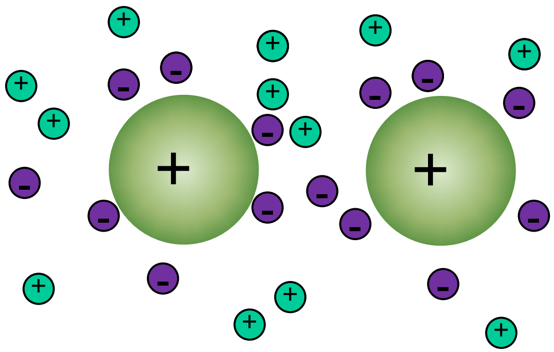
Data analysis with SasView 4.1
and Sasfit by Joachim Kohlbrecher



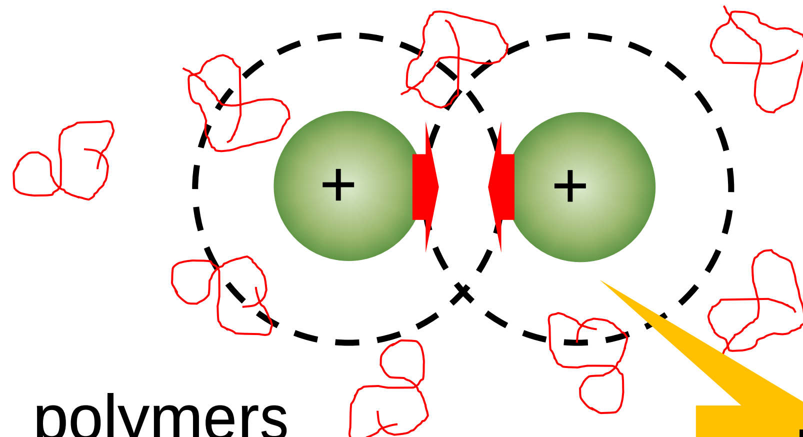
What to learn from this lecture?

1. Measurement principle
2. Visual data interpretation
3. **What kind of scientific problems**

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



salt
reduces
repulsion



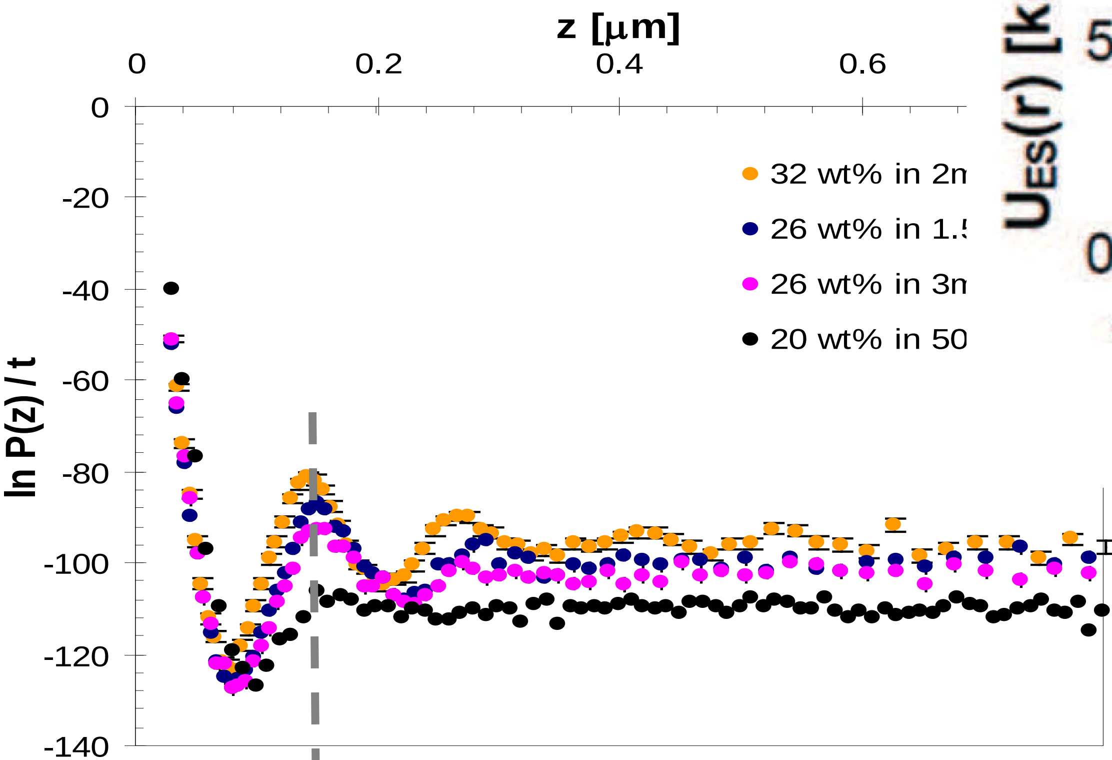
polymers
give
attraction

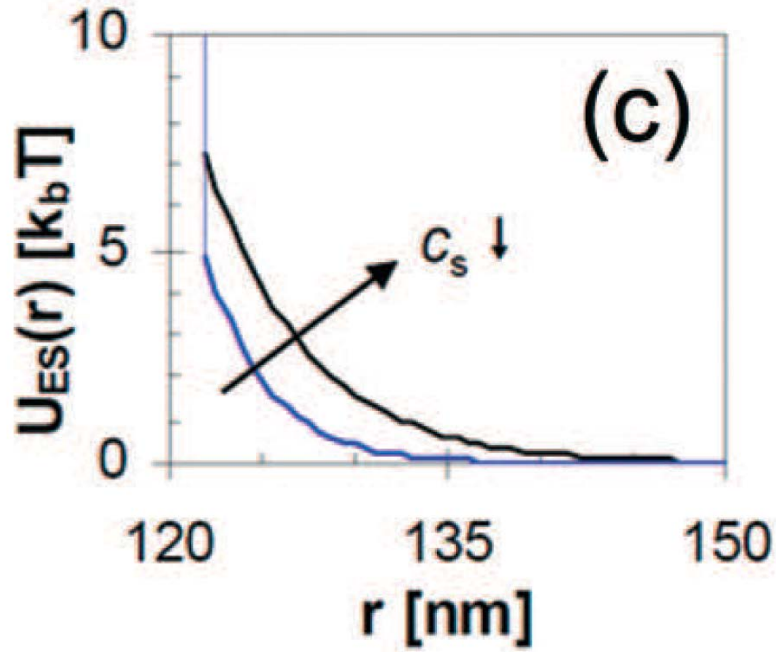
polymer
depletion
zone

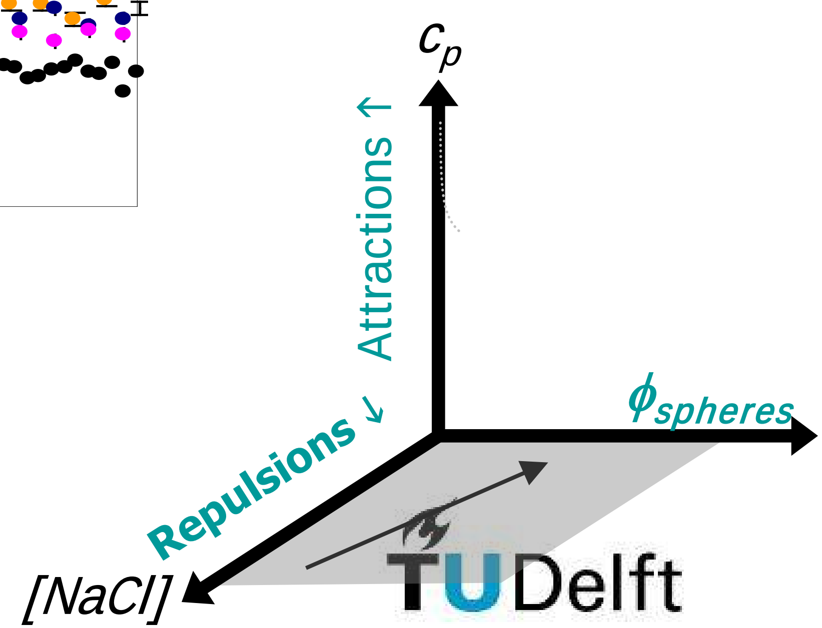
Kitty van Gruijthuijsen　　Peter Schurtenberger, Anna Stradner - Lund University

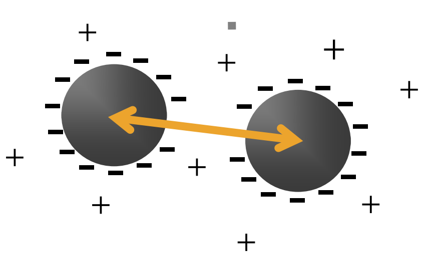
Adolphe Merkle Institute, Université de Fribourg

Colloids

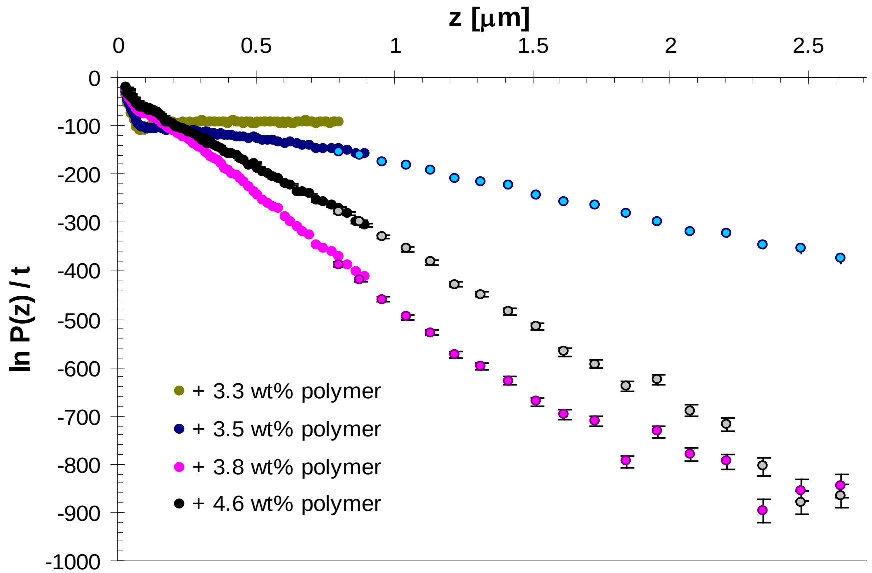

z [µm]
0
0.2
0.4
0.6
0
-20
-40
-60
-80
-100
-120
-140
ln P(z) / t
32 wt% in 2m
26 wt% in 1.!
26 wt% in 3m
20 wt% in 50

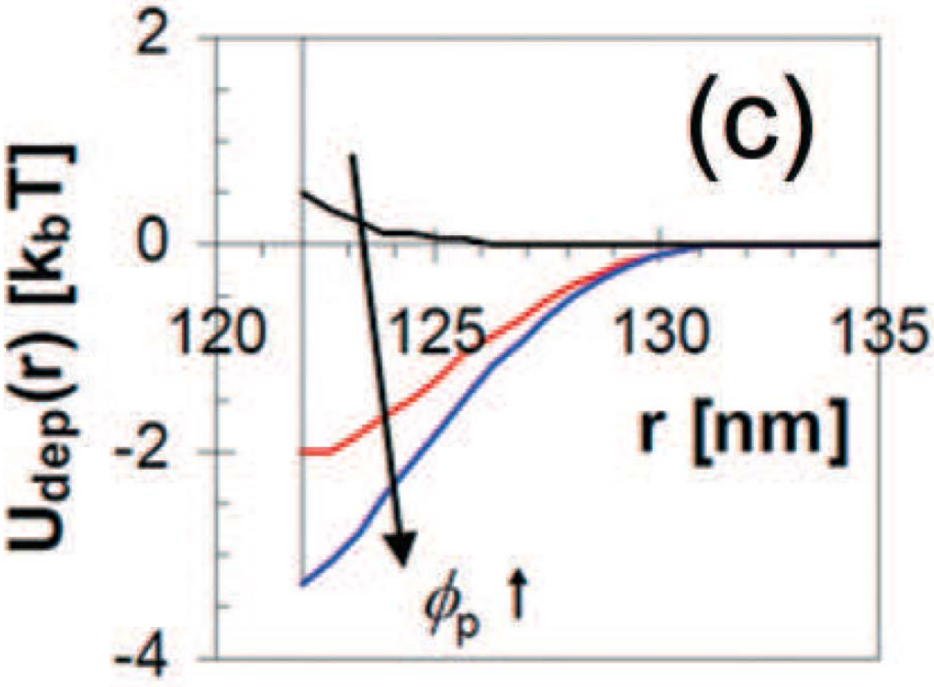

(c)
10
5
0
120
135
150
$U_{ES}(r)$ [k_bT]
r [nm]
c_s ↓

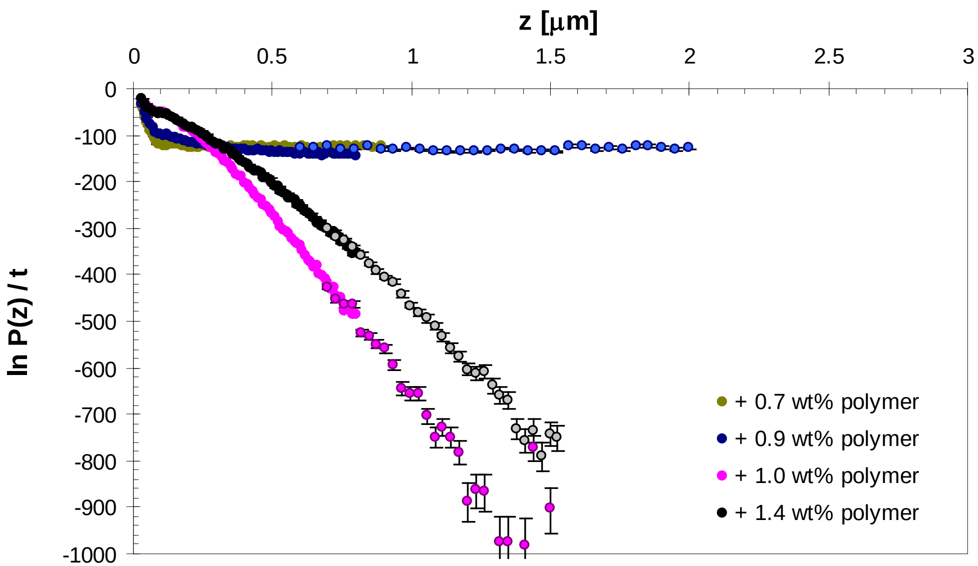

c_p
Attractions ↑
Repulsions ↓
$\phi_{spheres}$
[NaCl]



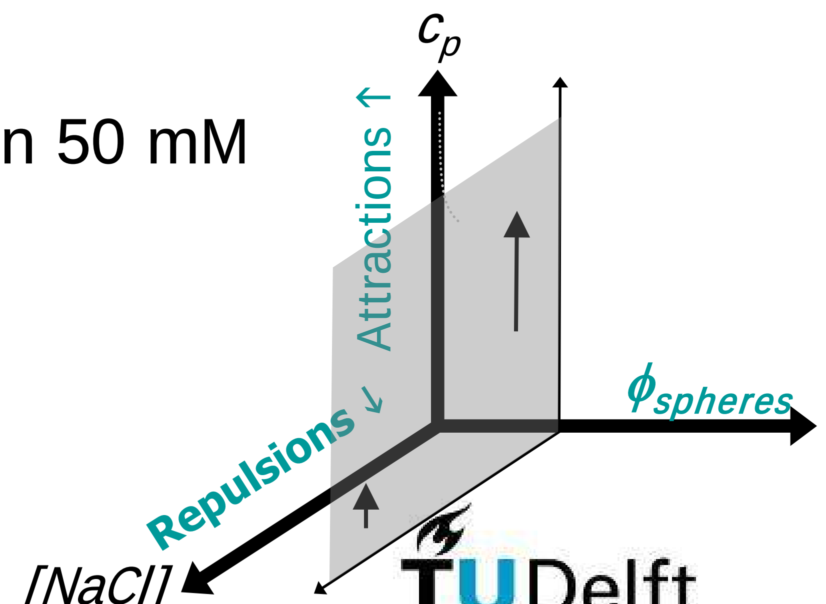
Gels







In 50 mM



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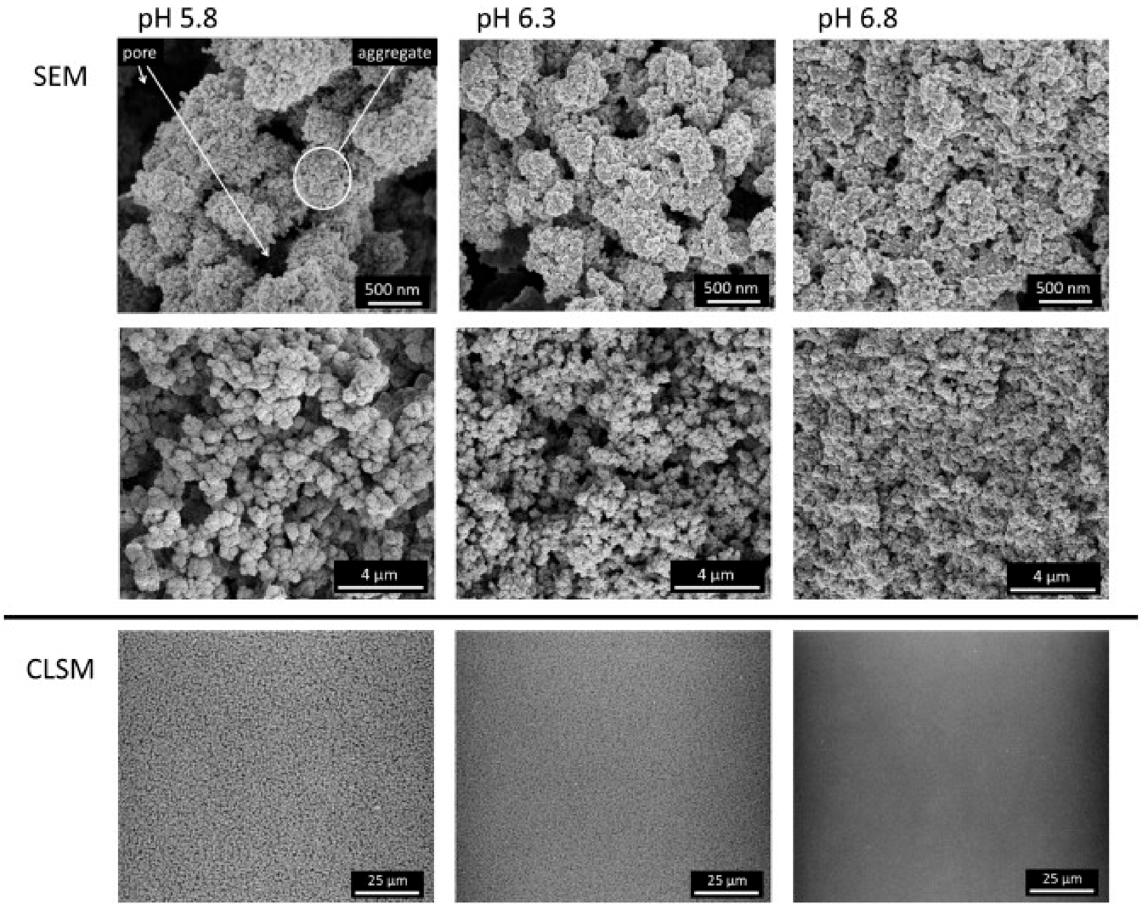
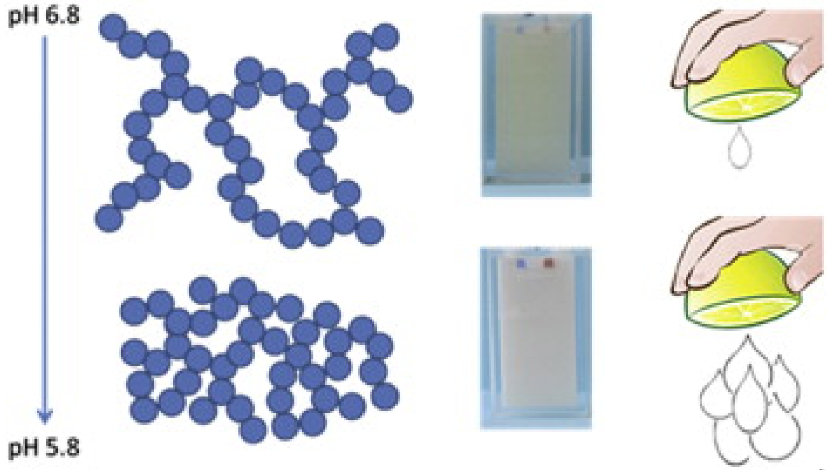
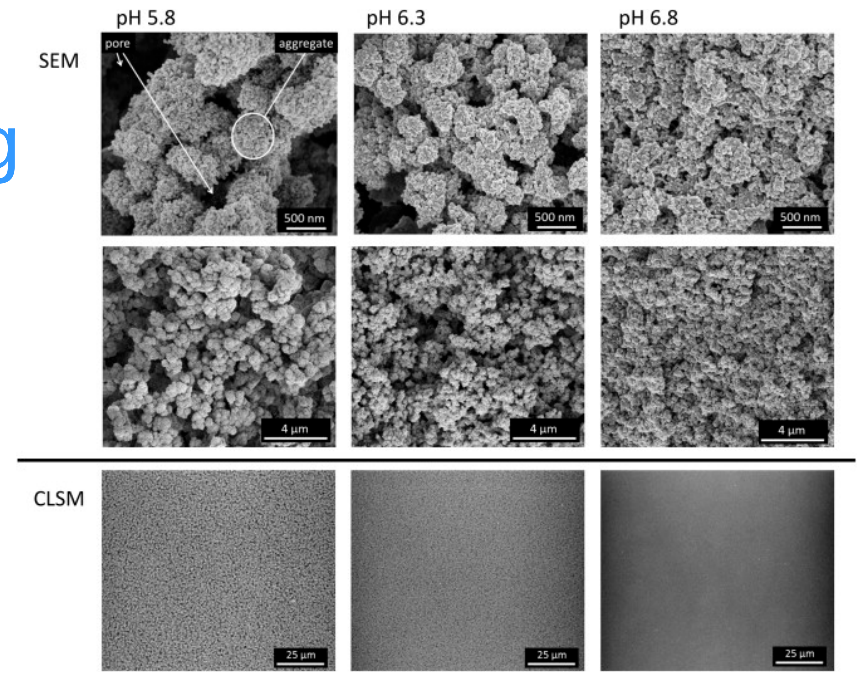
Water holding of ovalbumin gels
Juiciness, release tastants

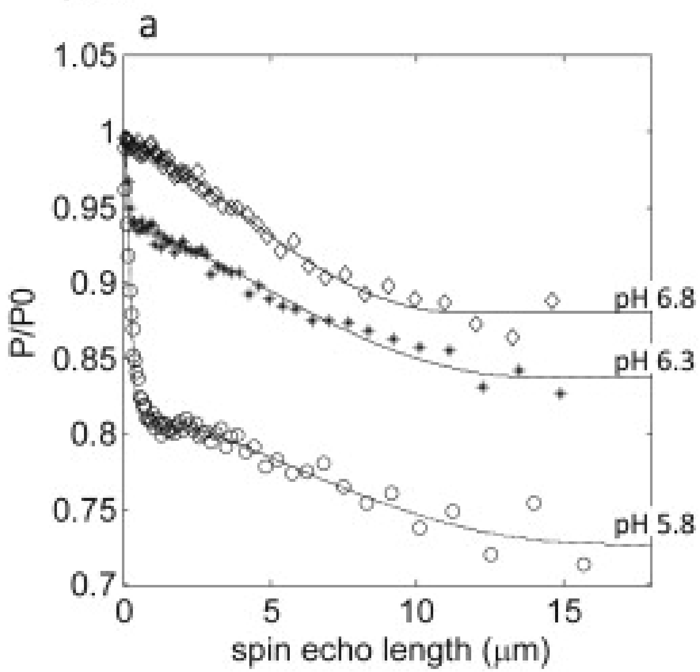


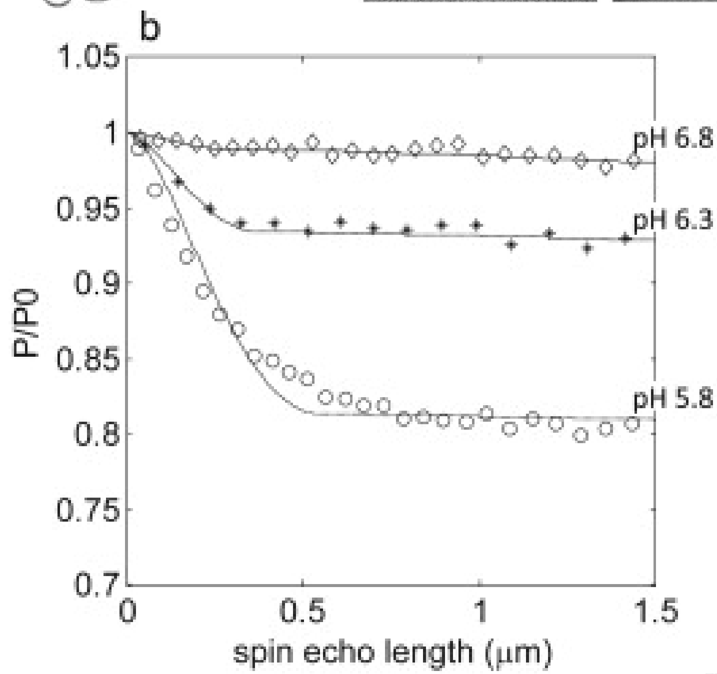
Maaike Nieuwland, TNO & TI Food and Nutrition

Acid reduces water holding





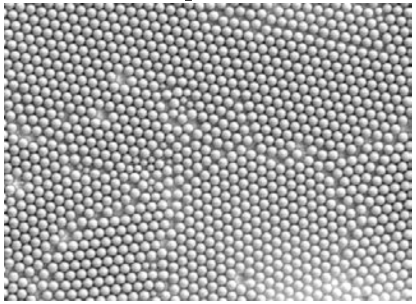




Granular matter

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

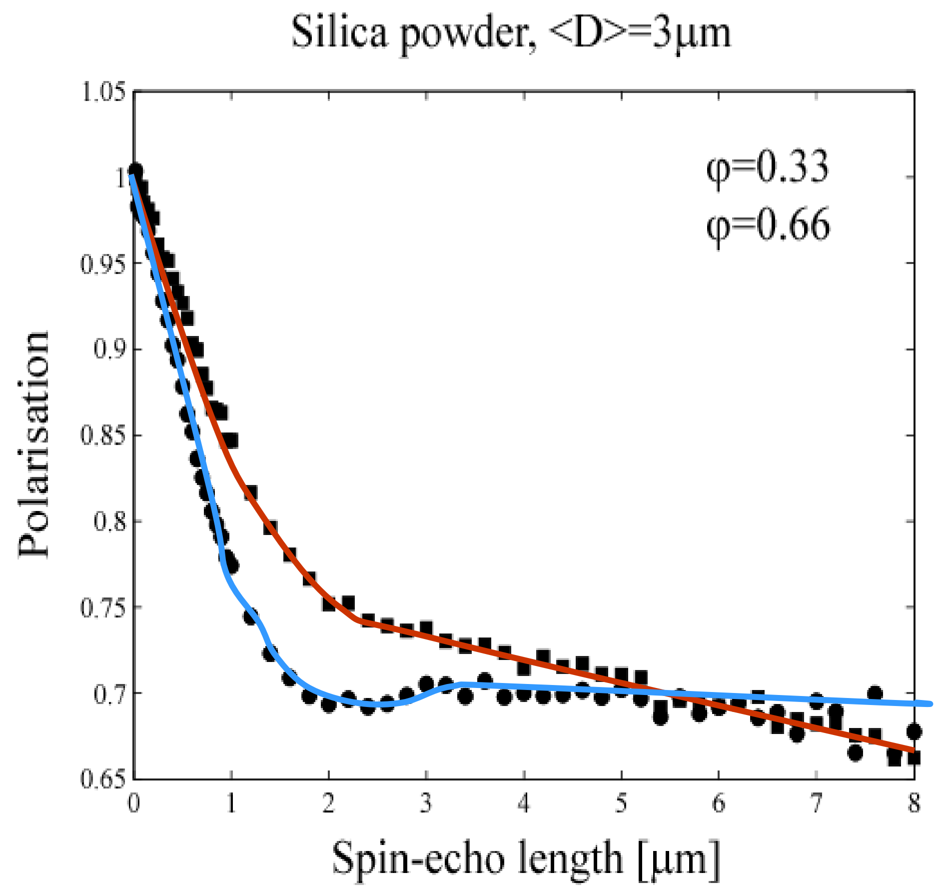
Two samples:

Compacted, Structure

Saturation at 3mm and a hard sphere repulsion peak

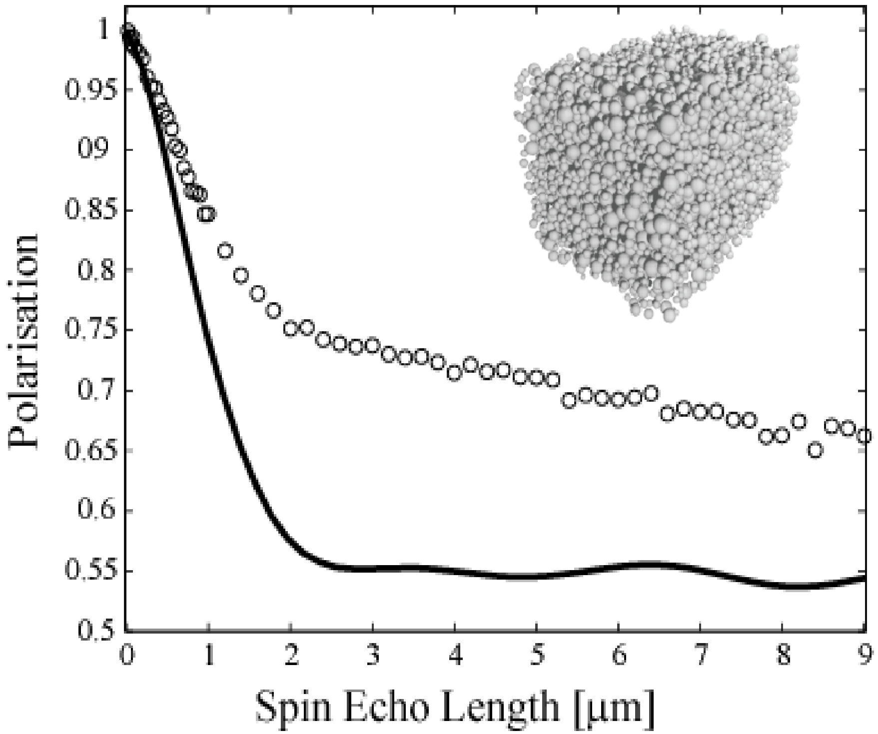
"Poured", Clustered

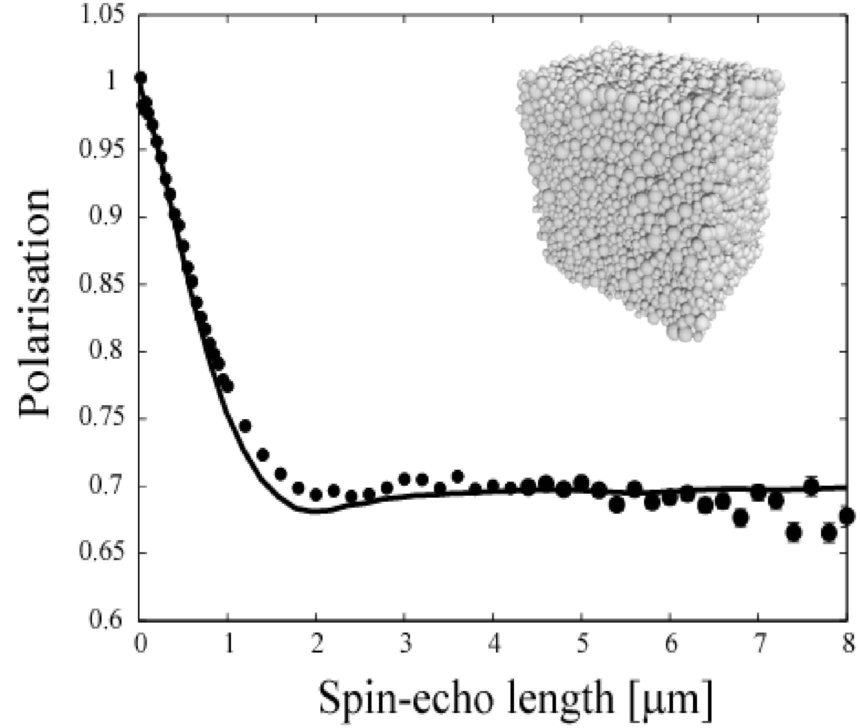
Correlations extends over measured range due to clusters



Molecular dynamics

Extract the SESANS correlation function from MD packings





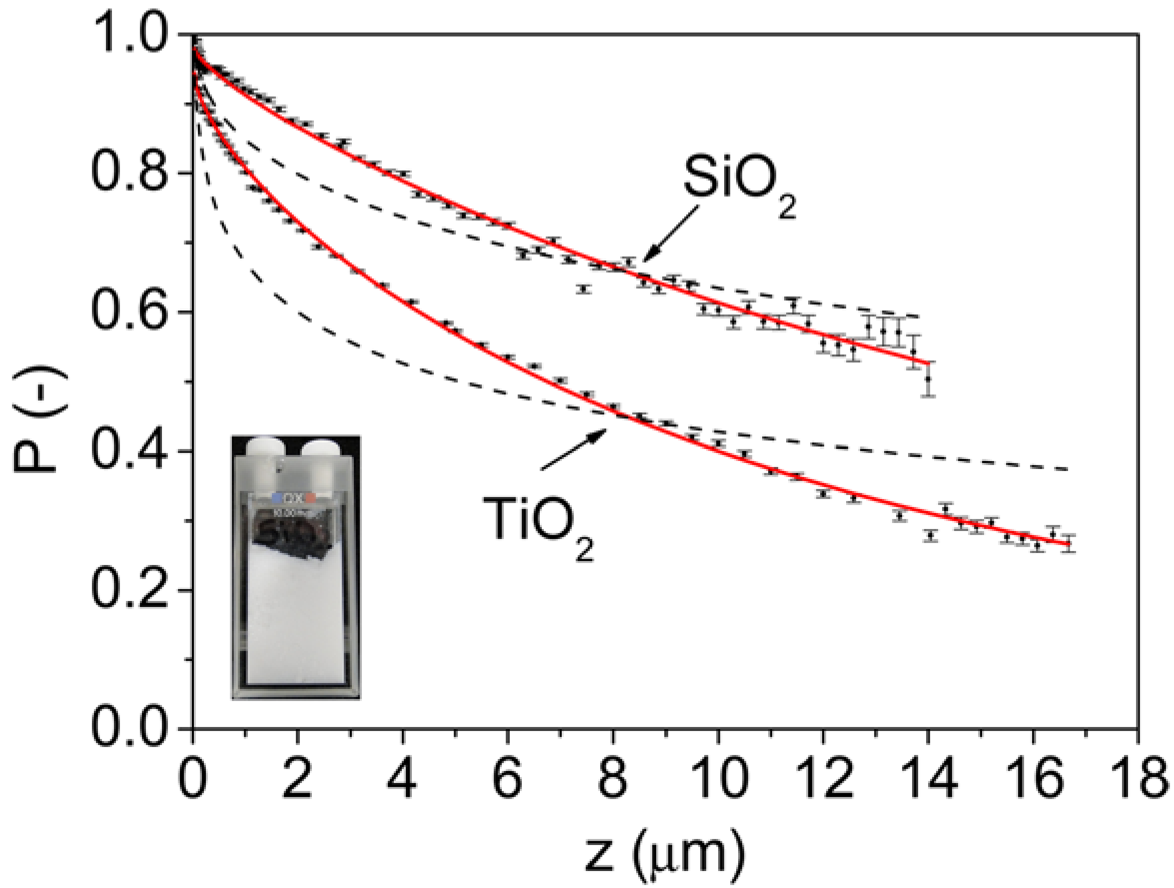
Conclusion: simulations don't describe features of poured samples.

Big holes could explain measurements

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

Fractal structure of nanoparticles in fluidised bed

Lilian de Martin

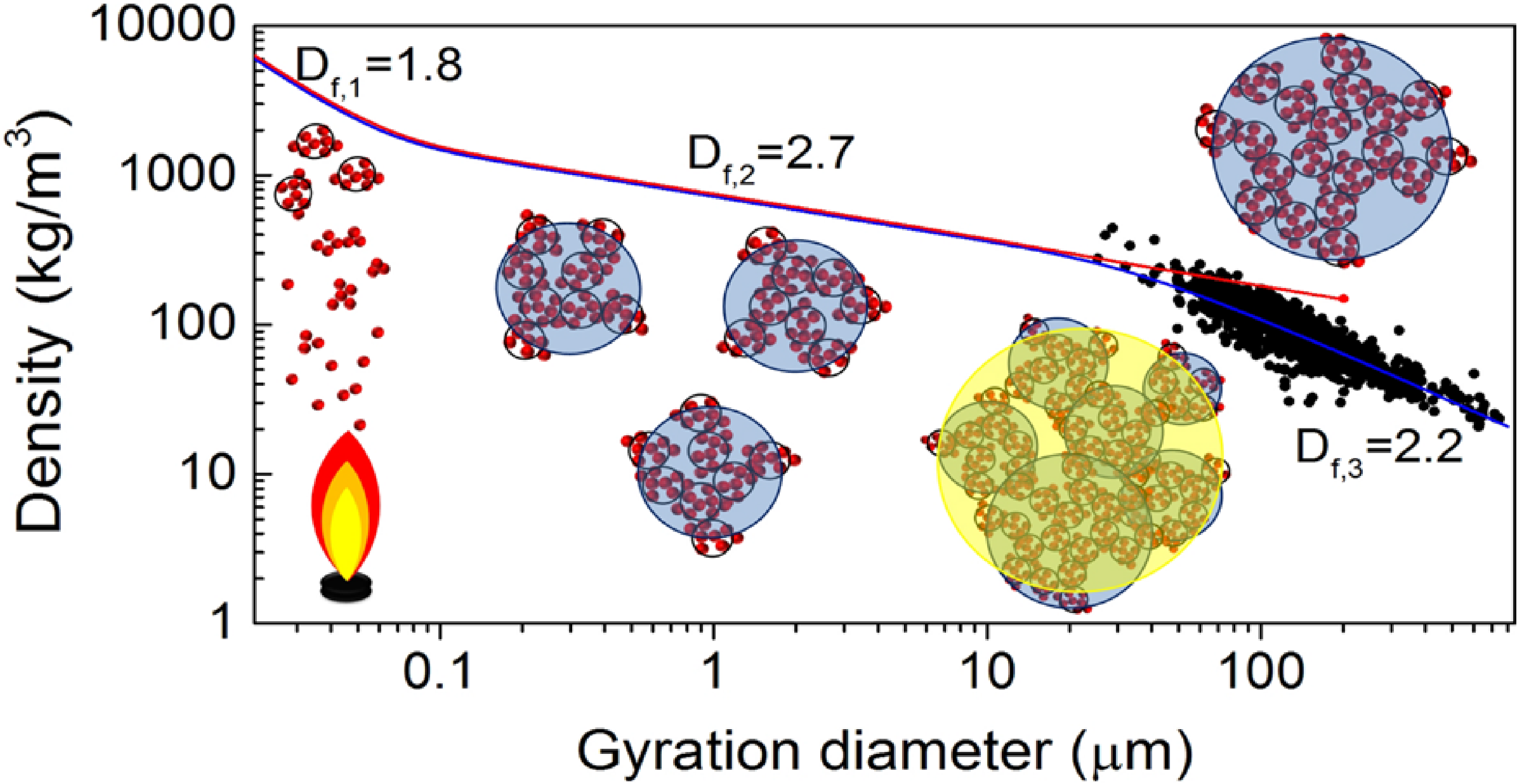


$$\gamma_1(r) = (r/r_p + 1)^{D_{f,1}-3} \quad \text{for } r \le r_{c,1}$$

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

TU Delft

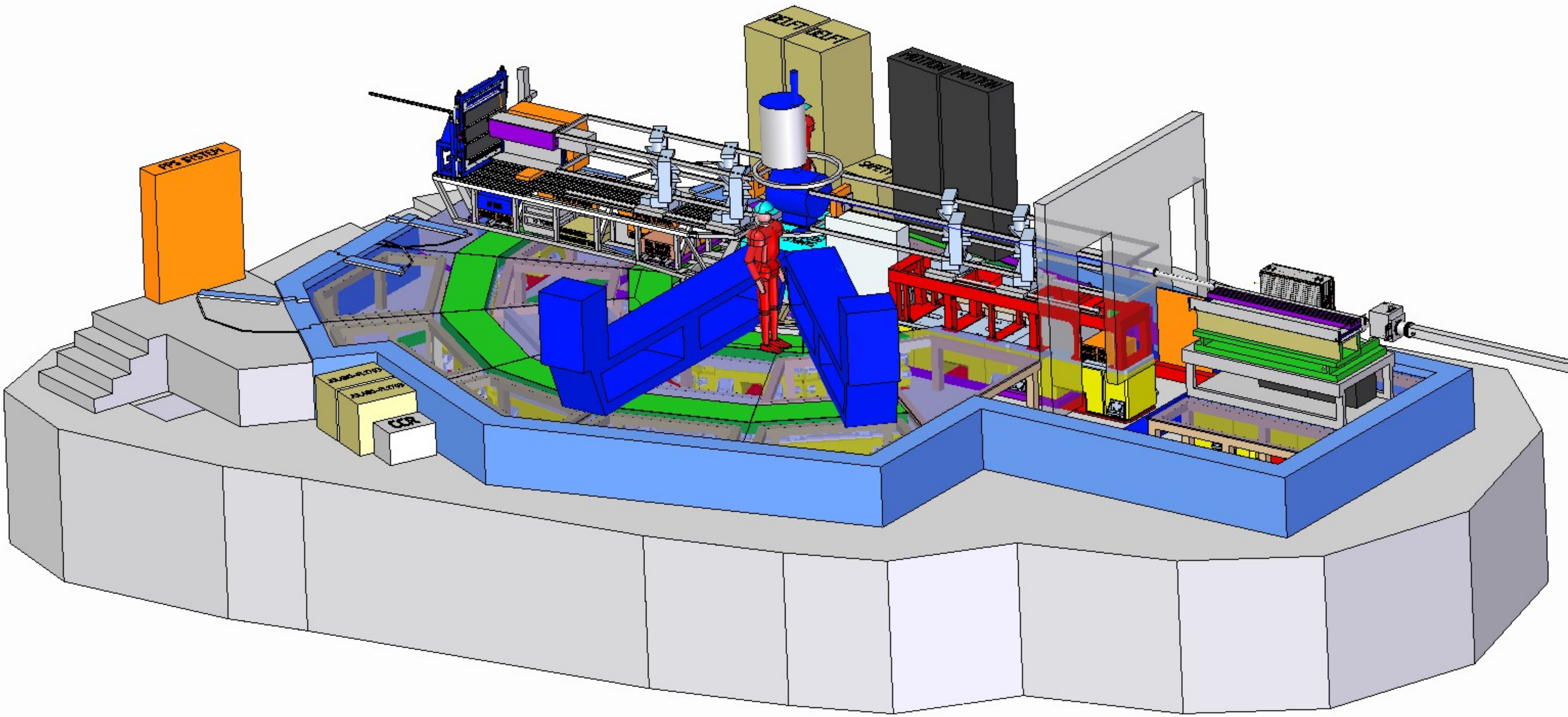
Nanopowder has three length regimes



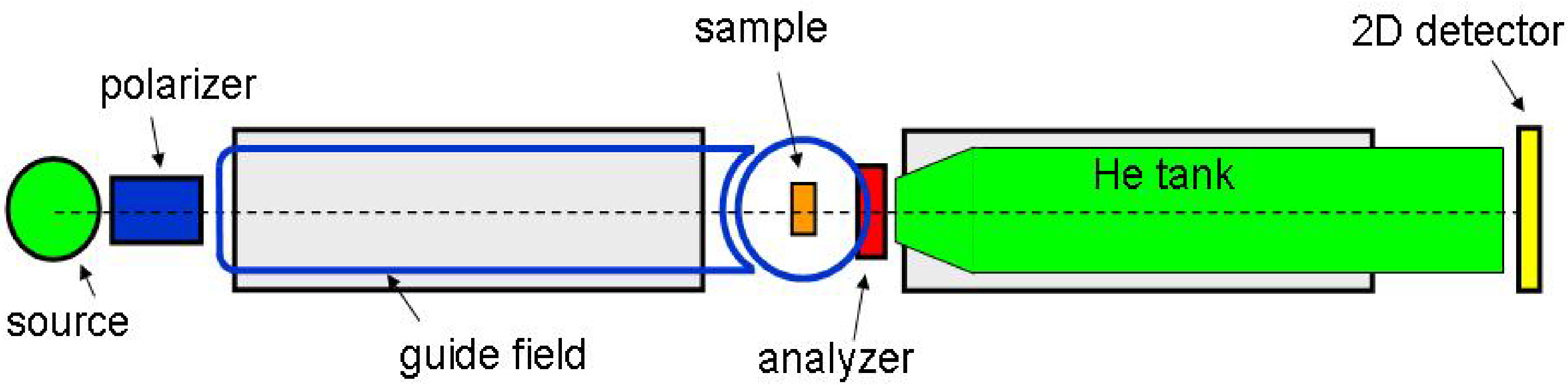
L. de Martin *et al.* Langmuir (2014) **30** 12696

TU Delft

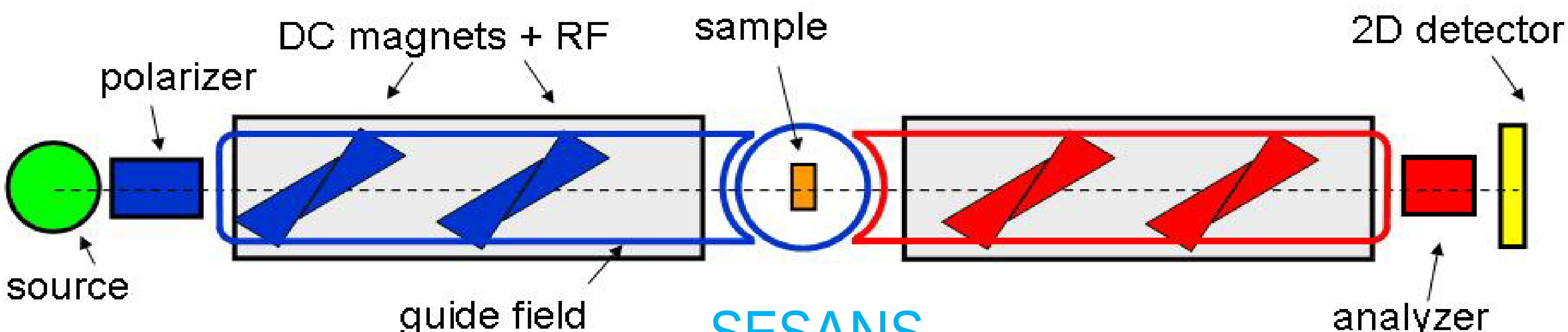
LARMOR: Delft coils for spin-echo



LARMOR @ ISIS



SANS with option for polarised neutrons



SESANS

SESANS real space scattering technique

Andersson, Robert, et al. "Analysis of spin-echo small-angle neutron scattering measurements." *Journal of Applied Crystallography* 41 (2008) 868

Rekveldt, M. Theo, et al. "Spin-echo small angle neutron scattering in Delft." *Review of Scientific Instruments* 76 (2005) 033901

Washington, A. L., et al. "Inter-particle correlations in a hard-sphere colloidal suspension with polymer additives investigated by Spin Echo Small Angle Neutron Scattering (SESANS)." *Soft Matter* 10 (2014) 3016

TUDelft