# SAS Data Analysis
# in Soft Matter Research

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SAS Workshop,  June 2, 2015, Utrecht University

- Dilute Colloids and Surfactant Systems
- Concentrated, Interacting Systems
- Liquid Crystalline Materials
- Transfer Kinetics of Lipids

# RDG: Spatially Averaged Intensity *I(q)*

The spatially averaged intensity *I(q)* is given by:

$$I(q) = <|E_1(\mathbf{q})|^2> = <\int_V \Delta\tilde{\rho}^2(\mathbf{r})\, e^{-i\mathbf{qr}} d\mathbf{r}>$$

$$= 4\pi \int_0^\infty \gamma(r)\, r^2 \frac{\sin qr}{qr} dr$$

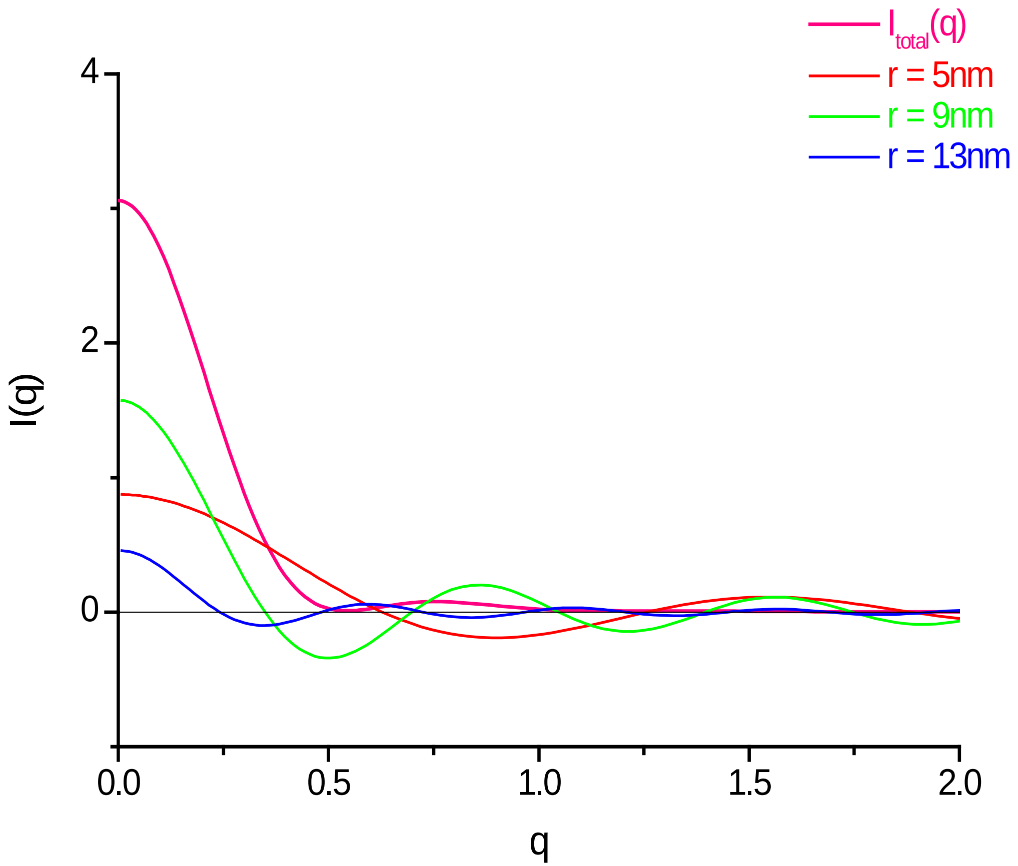
by introducing the *pair distance distribution function* (PDDF) *p(r)* with

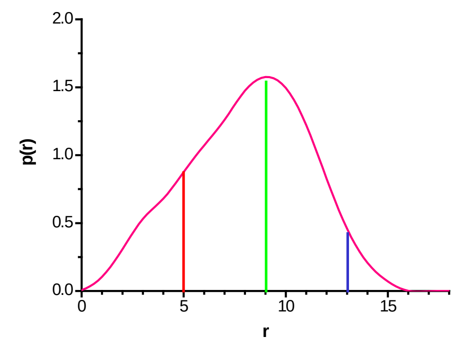
$$p(r) = \gamma(r)\cdot r^2 = \Delta\tilde{\rho}^2(r)\cdot r^2$$

we finally get

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr$$

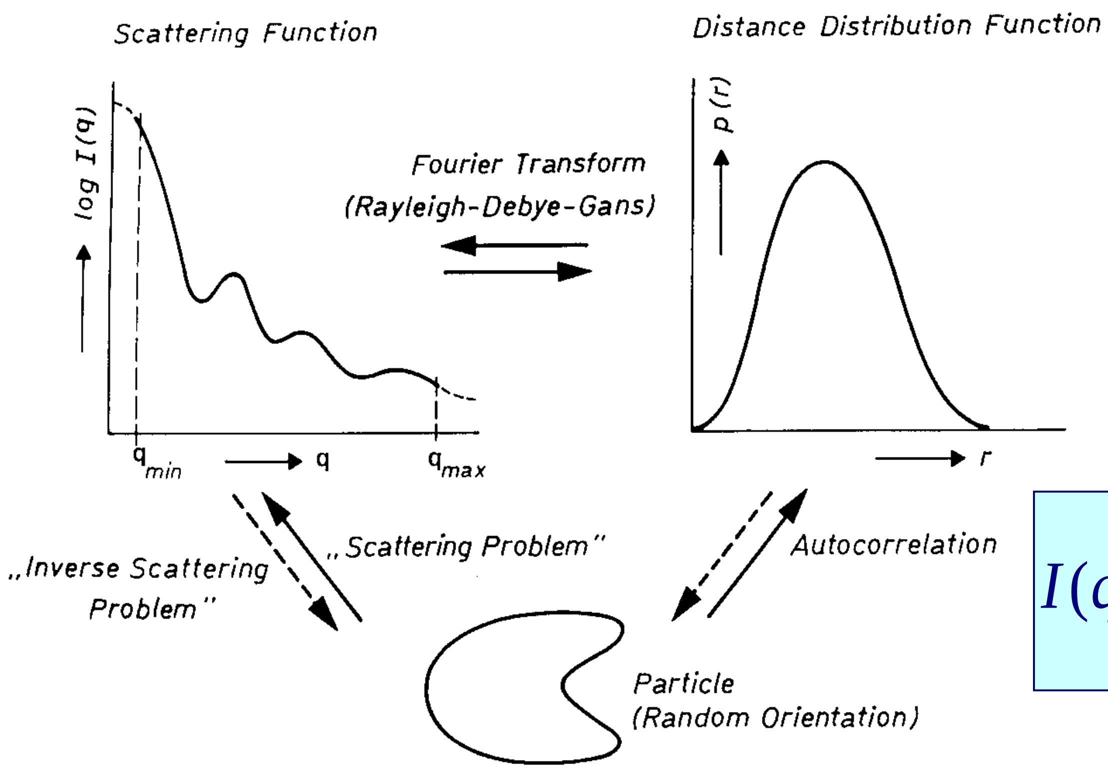
# Relation between $I(q)$ and $p(r)$




$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr$$

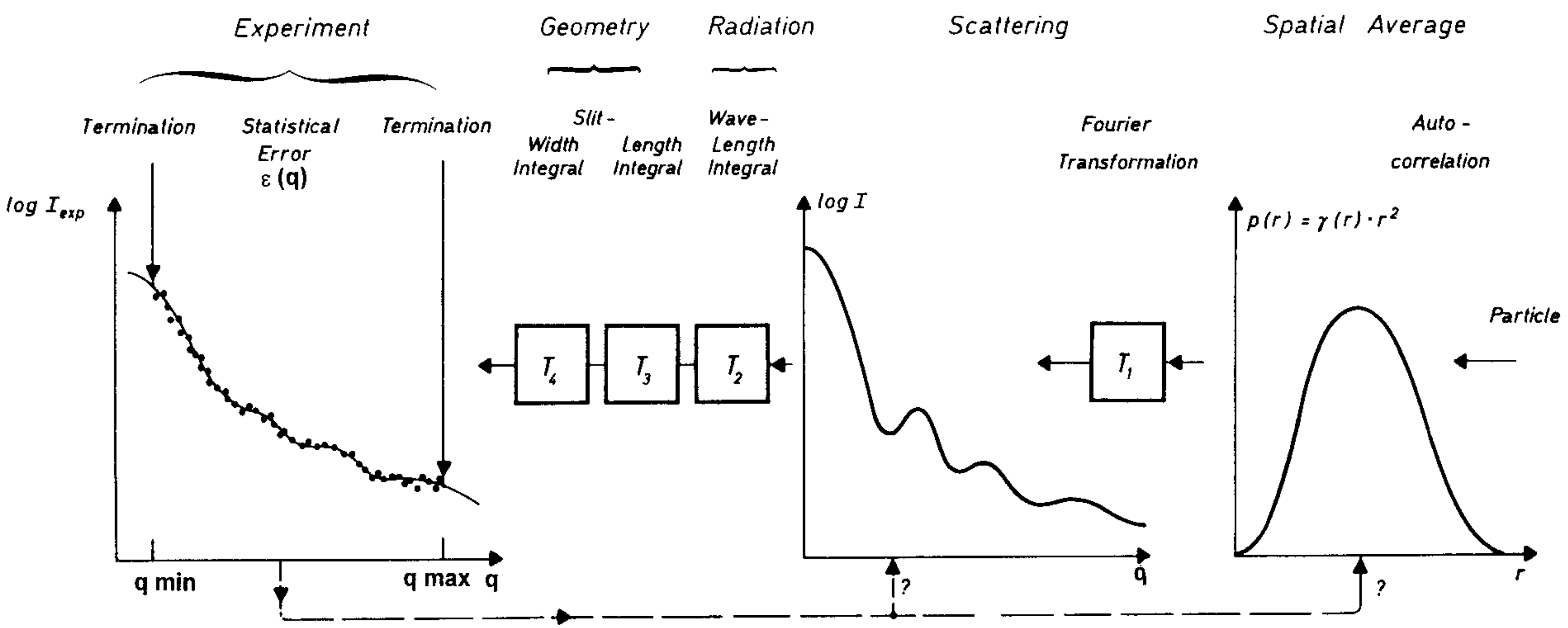
# The Scattering Problem and the Inverse Scattering Problem




$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr$$

For the solution of the inverse Problem it is essential to be able to calculate the PDDF form the experimental scattering curve with minimum termination effect without model assumptions.

# From experimental data to the PDDF - *IFT*



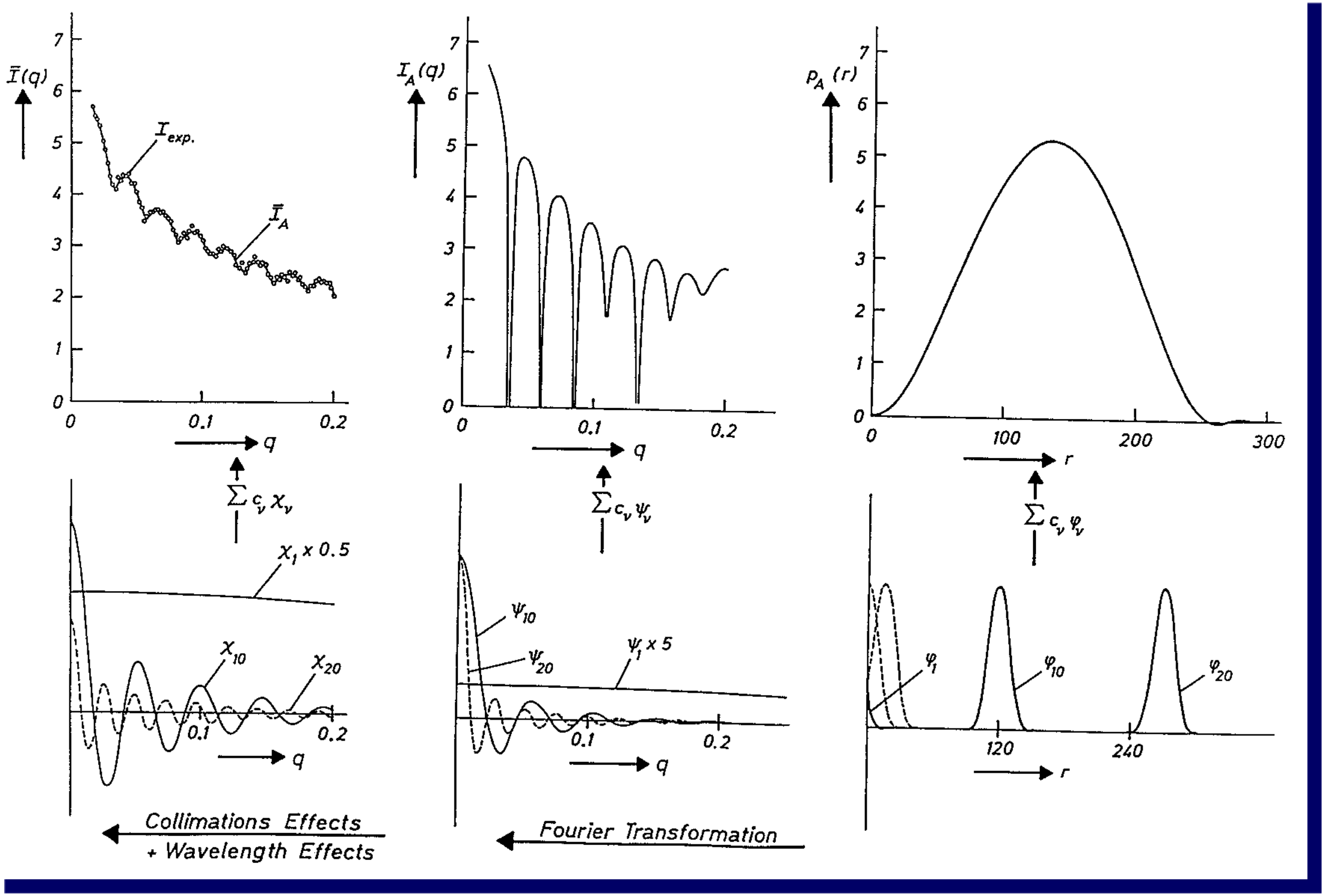

All transformations T1 to T4 are linear and are mathematically well defined,

this does not hold for their inverse transformations!

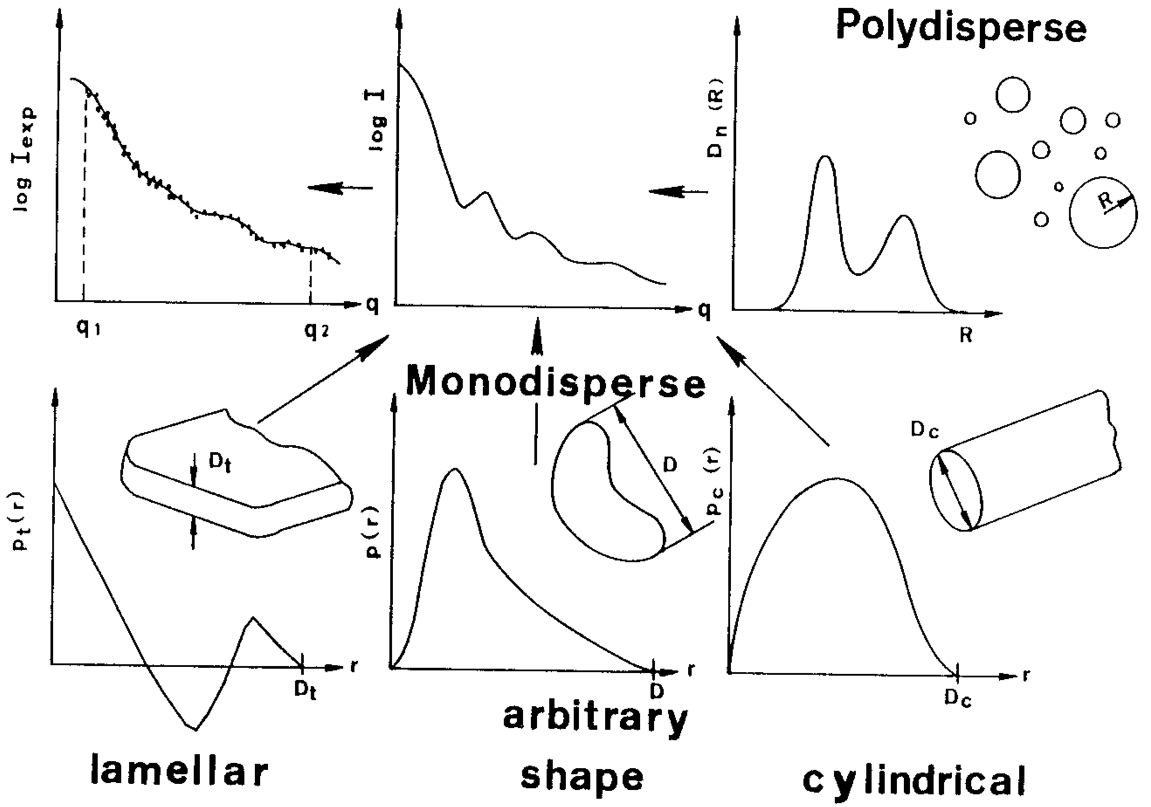
Solution: ***Indirect Fourier Transformation*** *IFT*

O. G. (1977). *J. Appl. Cryst.*, Vol. 10, 415-412.

# The Principles of the Indirect Fourier Transformation I

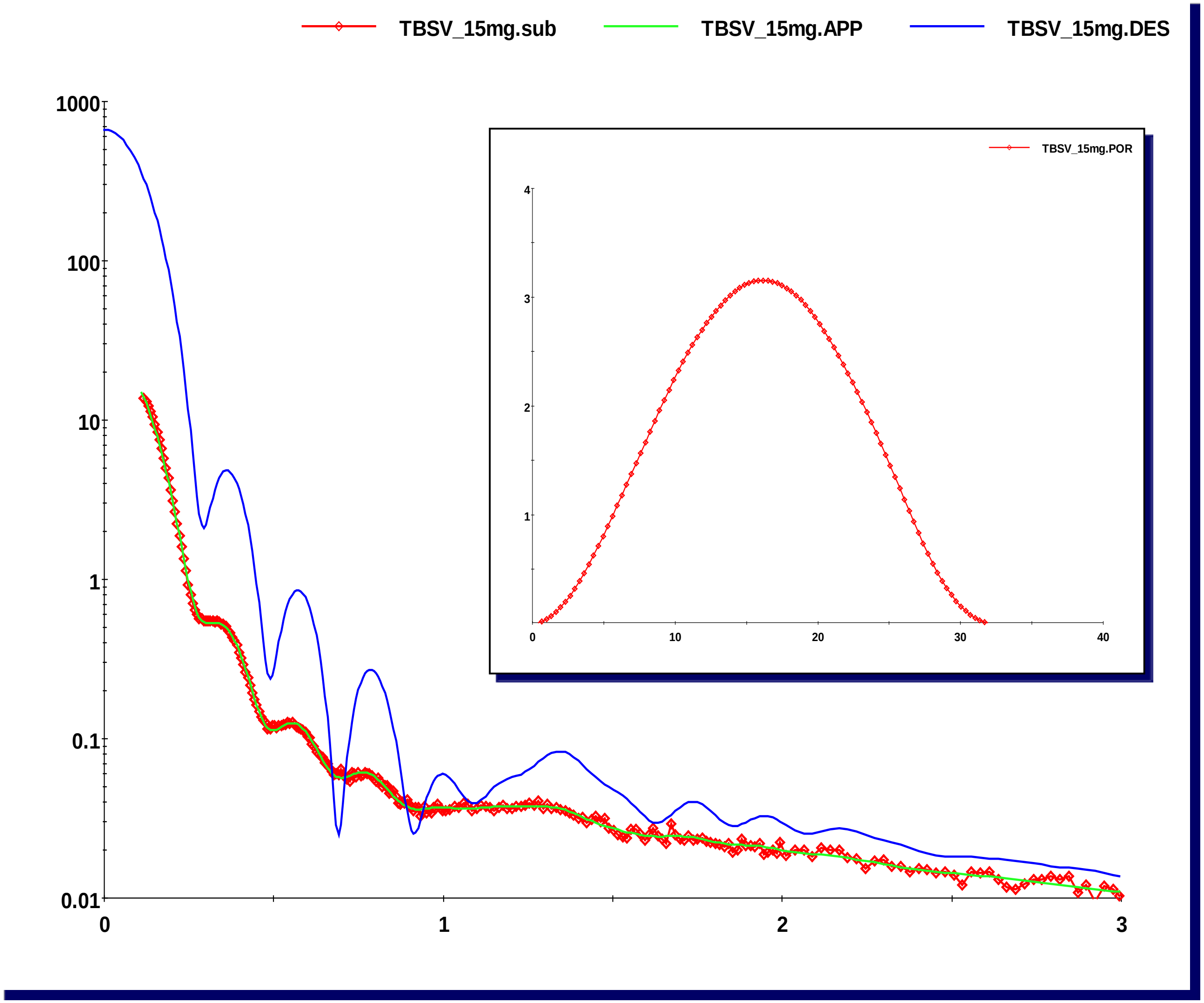


# Other IFT Applications - Overview

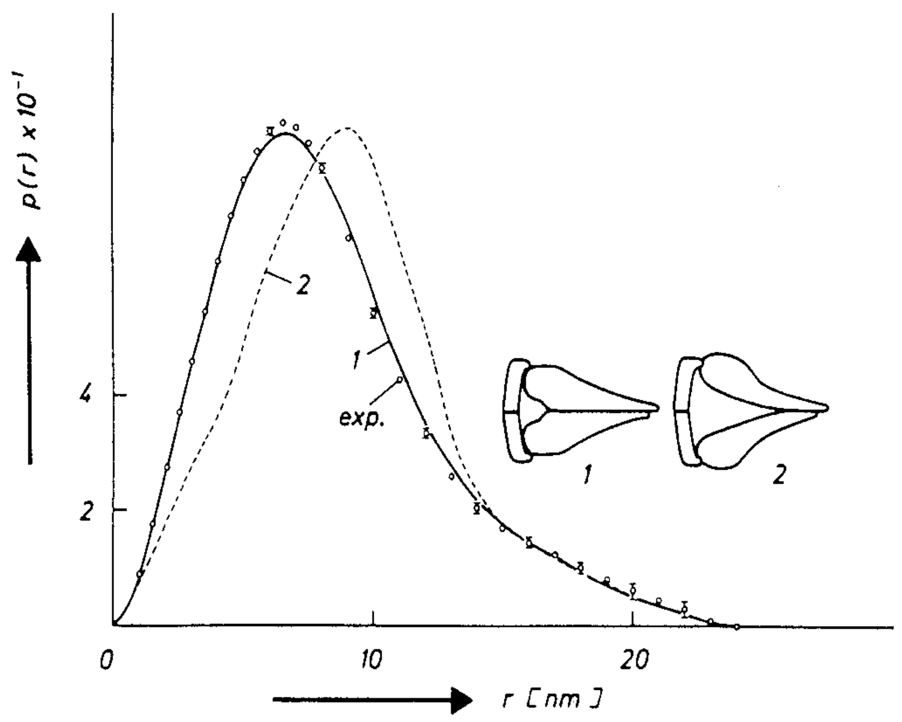



The IFT technique can also be applied to data from cylindrical or lamellar particles as well as to polydisperse systems

# Tomato Bushy Stunt Virus, 15mg/mL



# PDDF is very useful for model improvement!

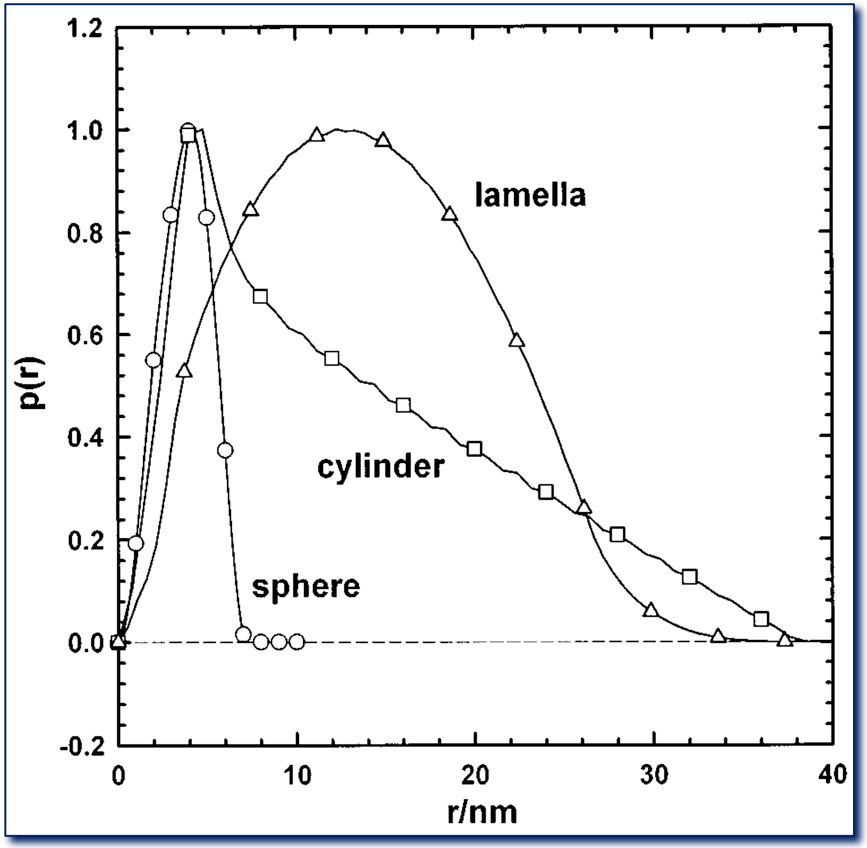


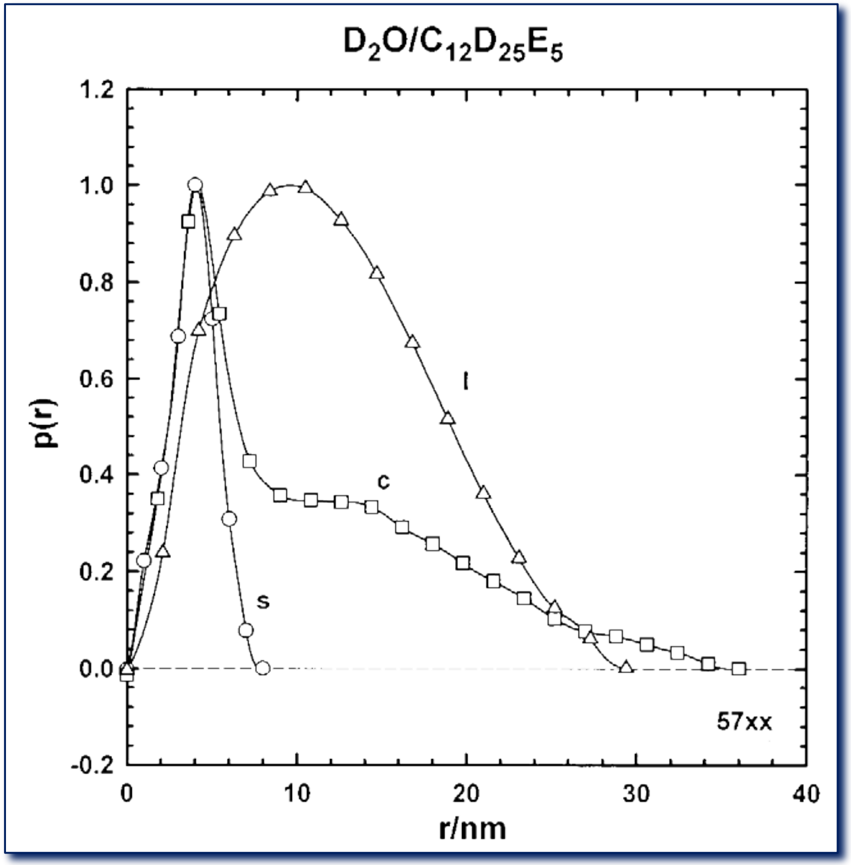

Comparison of the experimental PDDF of a core enzyme (points) with the theoretical PDDFs of two different models:

#2 suggested by literature data!   #1 best fit

O. Meisenberger et al., (1980). *FEBS Lett.*, Vol. 122, 117-120.

# Model Calculations vs. Surfactant Self-Assembly

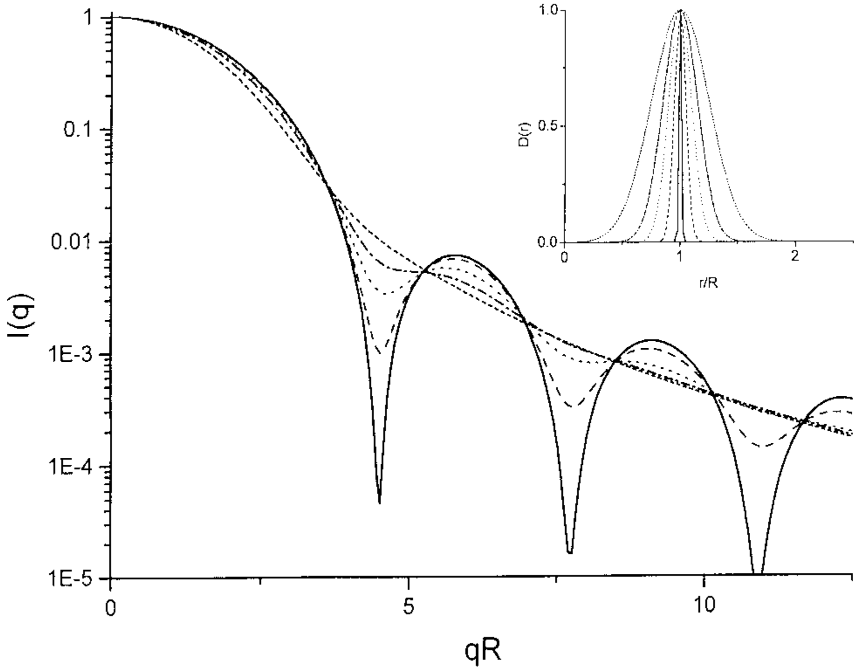



Pair distance distribution functions p(r) for the binary mixture $\mathbf{D_2O/C_{12}D_{25}E_5}$ at 5 °C (circles), 32 °C (squares), and 70 °C (triangles). These functions are obtained by indirect Fourier transformation of the SANS spectra.

R. Strey et al., *J. Chem. Phys*. (1996) Vol. 105, No. 3, 1175-1188.

# Polydisperse Systems




Intensity Distribution

$$I(q) = c_i \int_0^\infty D_i(R) \cdot P_0(q,R)\, dR$$

Volume or Mass Distribution

$$I(q) = c_v \int_0^\infty D_v(R) \cdot R^3 \cdot P_0(q,R)\, dR$$

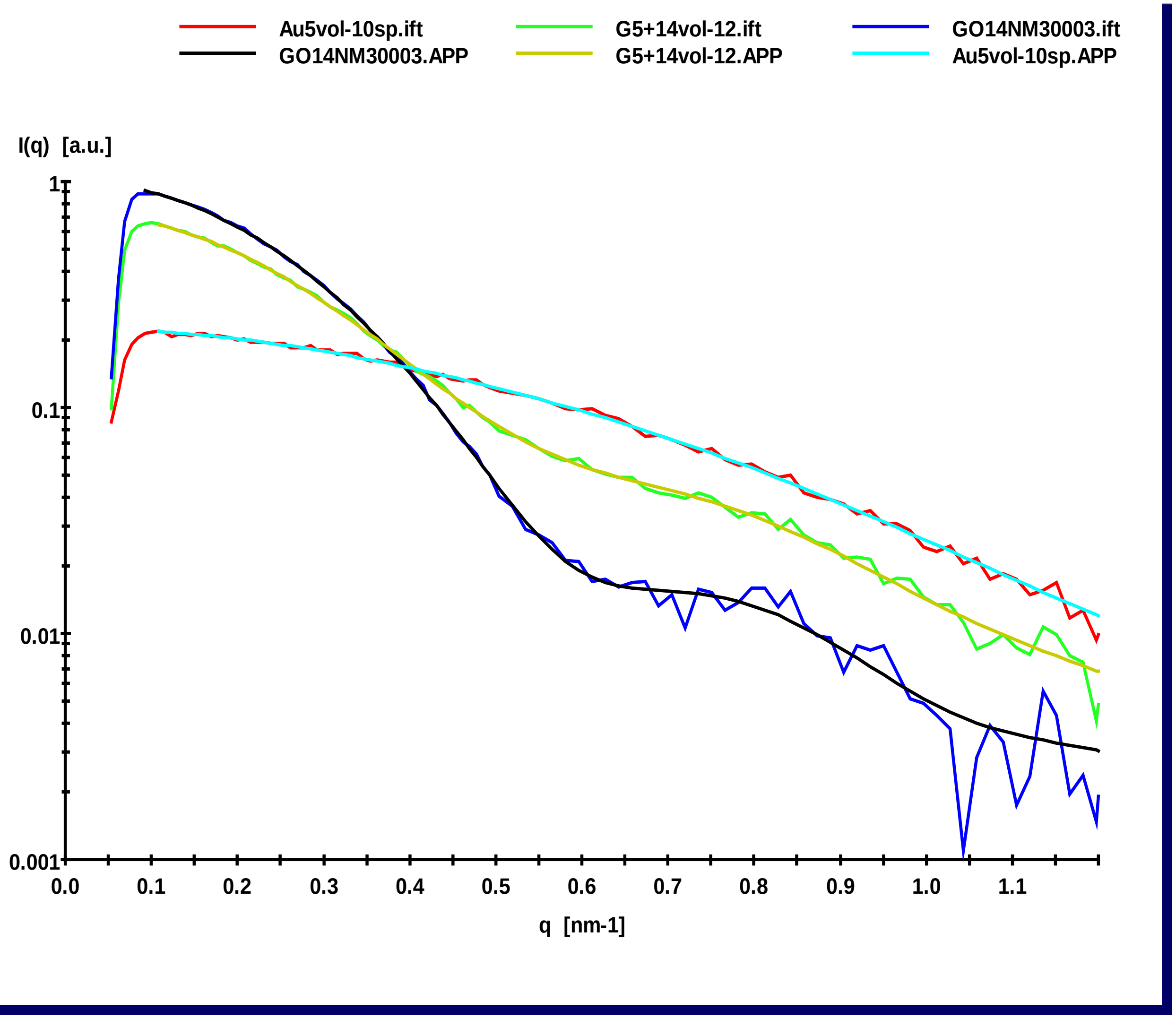
Number Distribution

$$I(q) = c_n \int_0^\infty D_n(R)\, R^6 \cdot P_0(q,R)\, dR$$

Scattering curves of Gaussian size distributions of spheres with varying width (see inset).

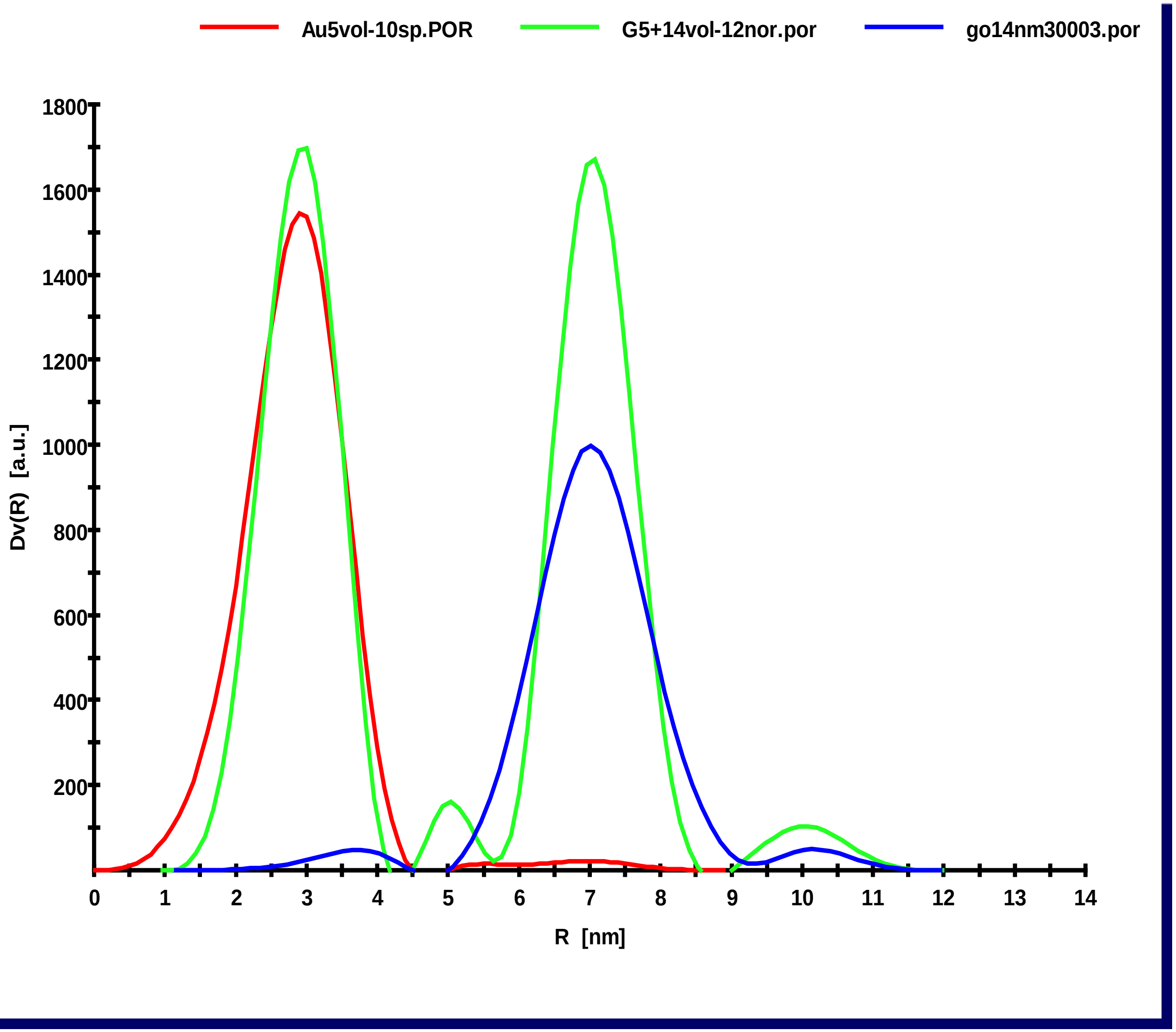
# Polydispersity Analysis

## Gold Nano – Colloids, $R_1$ » 3nm, $R_2$ » 7nm, Raw SAXS Data and Fit

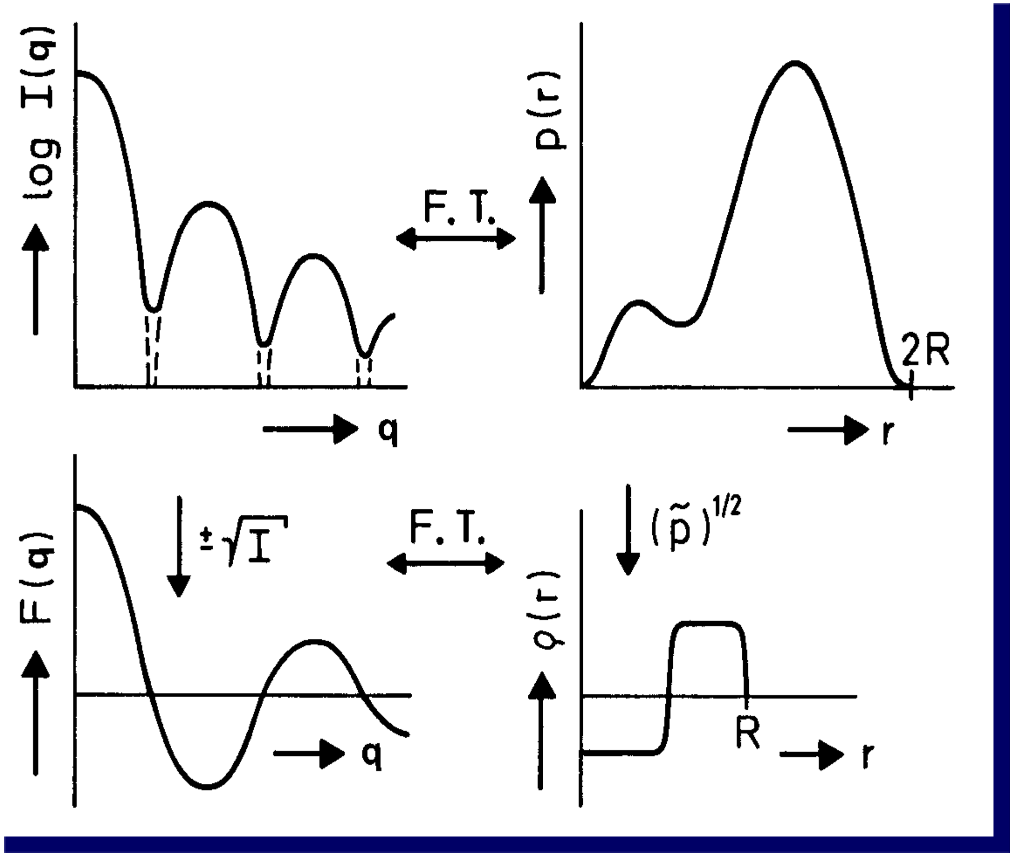


# Polydispersity Analysis – Volume Distribution

## Gold Nano – Colloids, $R_1$ » 3nm, $R_2$ » 7nm



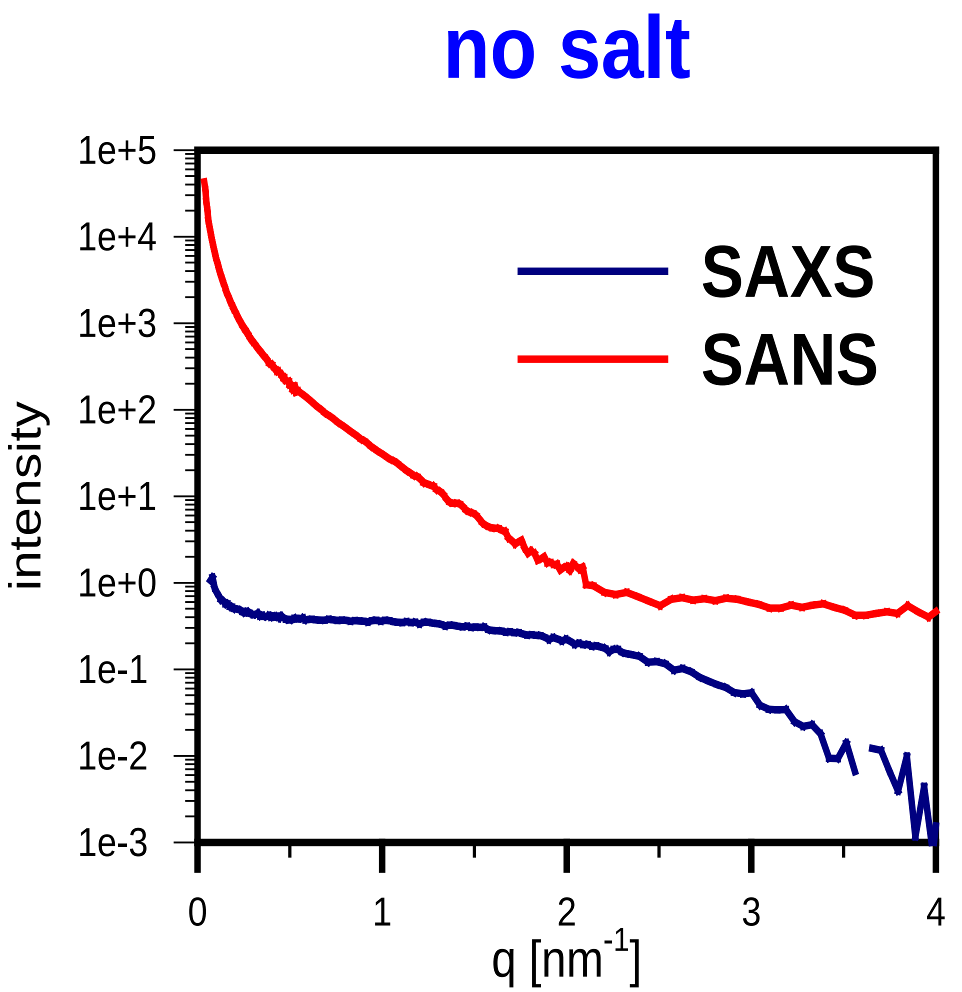
# Deconvolution of the PDDF – The *Magic Square*
# Direct Structure Analysis




Deconvolution of the PDDF *p(r) into* the radial density *Δρ(r)* is possible for:

- spherical symmetry
- circular cylinders with centro-symmetric radial density distributions
- centro-symmetric lamellae without in-plane inhomogeneities

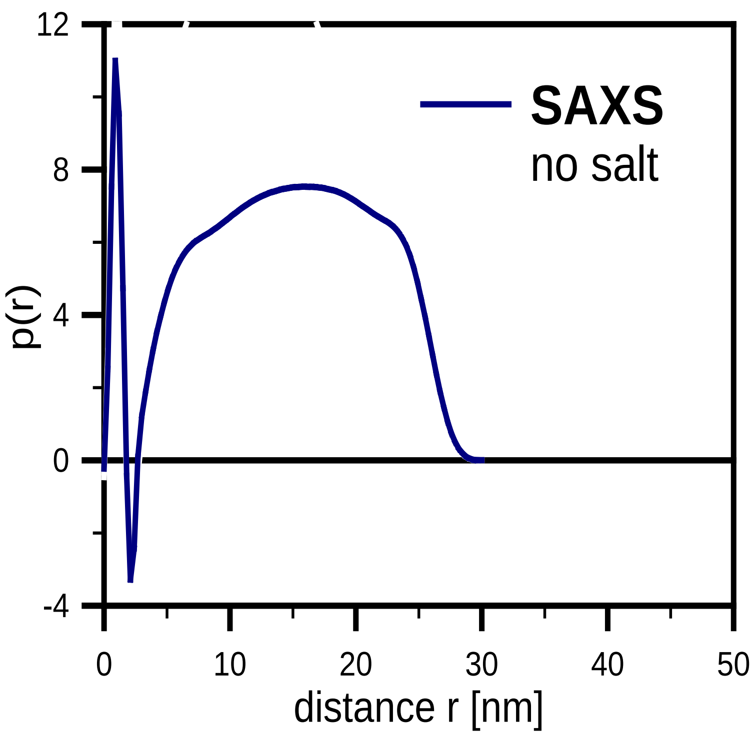
# Mixed Surfactant Systems – Vesicles

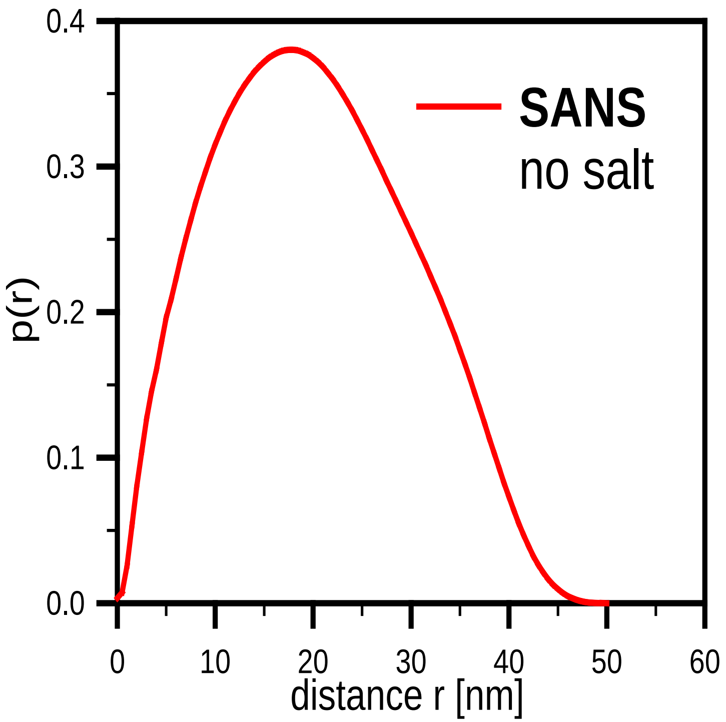



2wt% surfactant
(0.6% CTAB, 1.4% SOS)

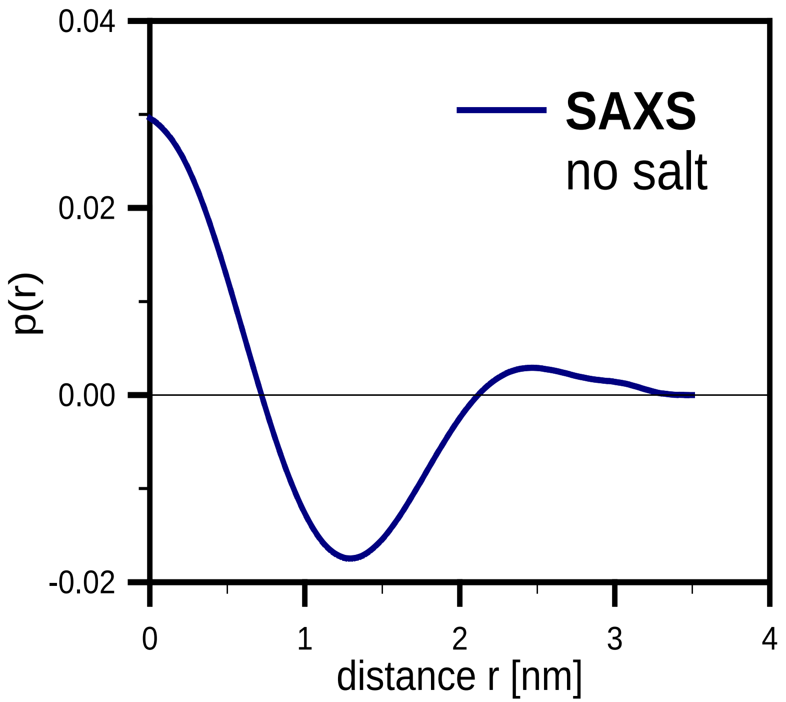
Co-operation with Eric Kaler, Delaware

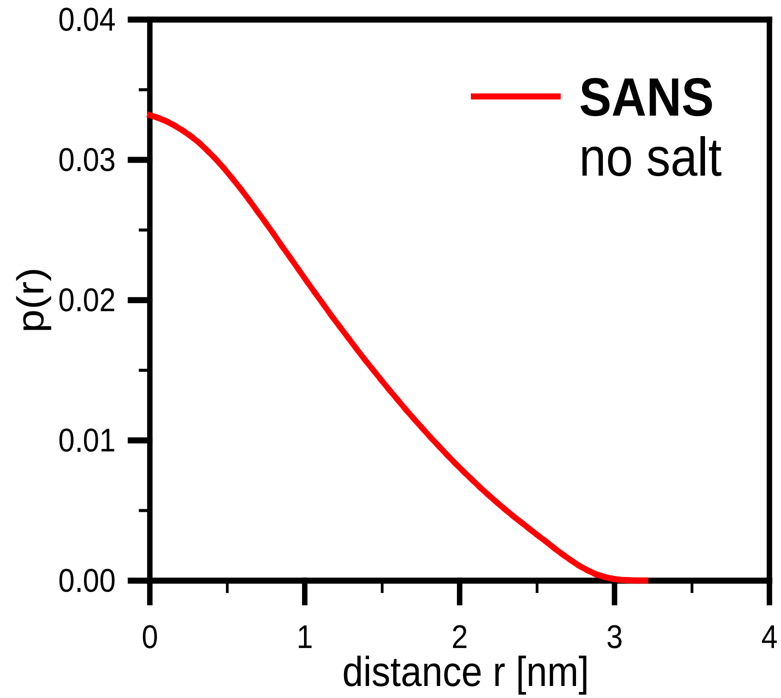
# Pair Distance Distribution Functions p(r)



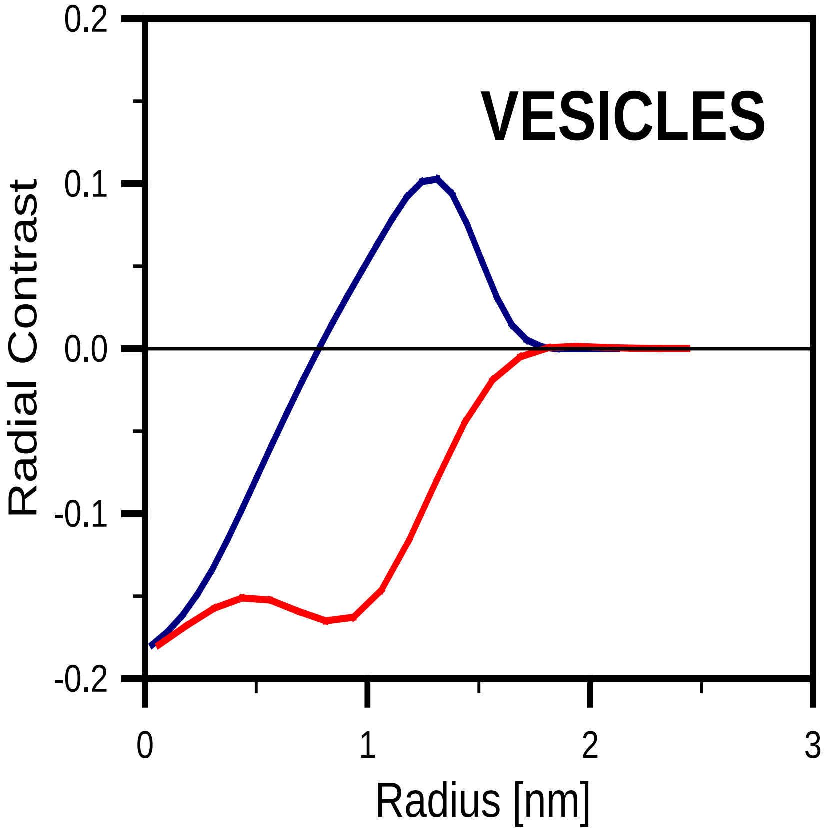



# Thickness Pair Distance Distribution Functions $p_t(r)$



# Scattering Contrast Profiles - no Salt

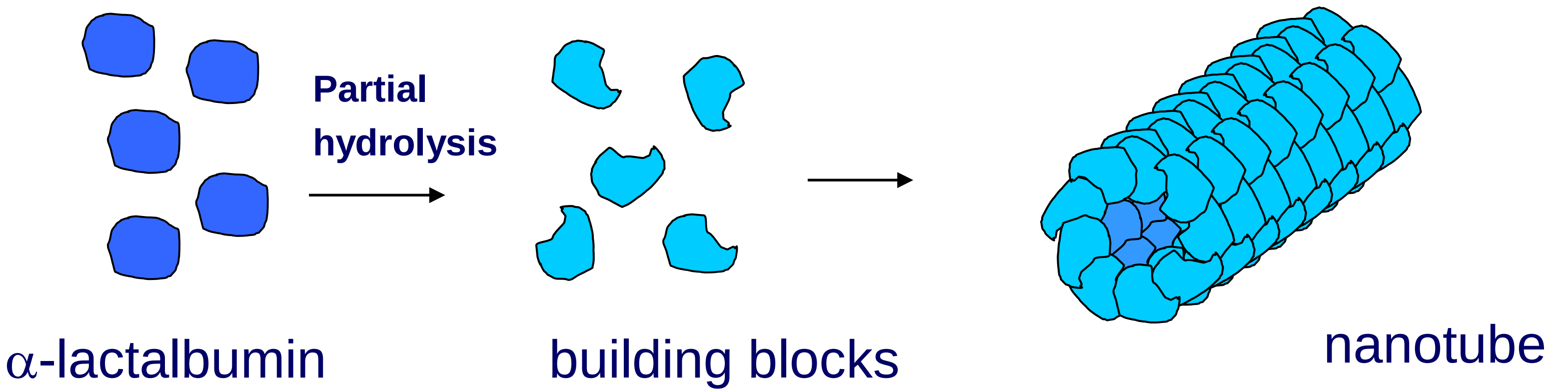



$r_c$: hydrocarbon core
$r_w$: maximum extent

SAXS: $r_c = 0.8 \pm 0.1$nm
$r_w = 1.8 \pm 0.1$nm
SANS: $r_w = 1.7 \pm 0.1$nm

D. I. Iampietro,, et al., *J. Phys. Chem. B* (1998), 102, 3105-3113.

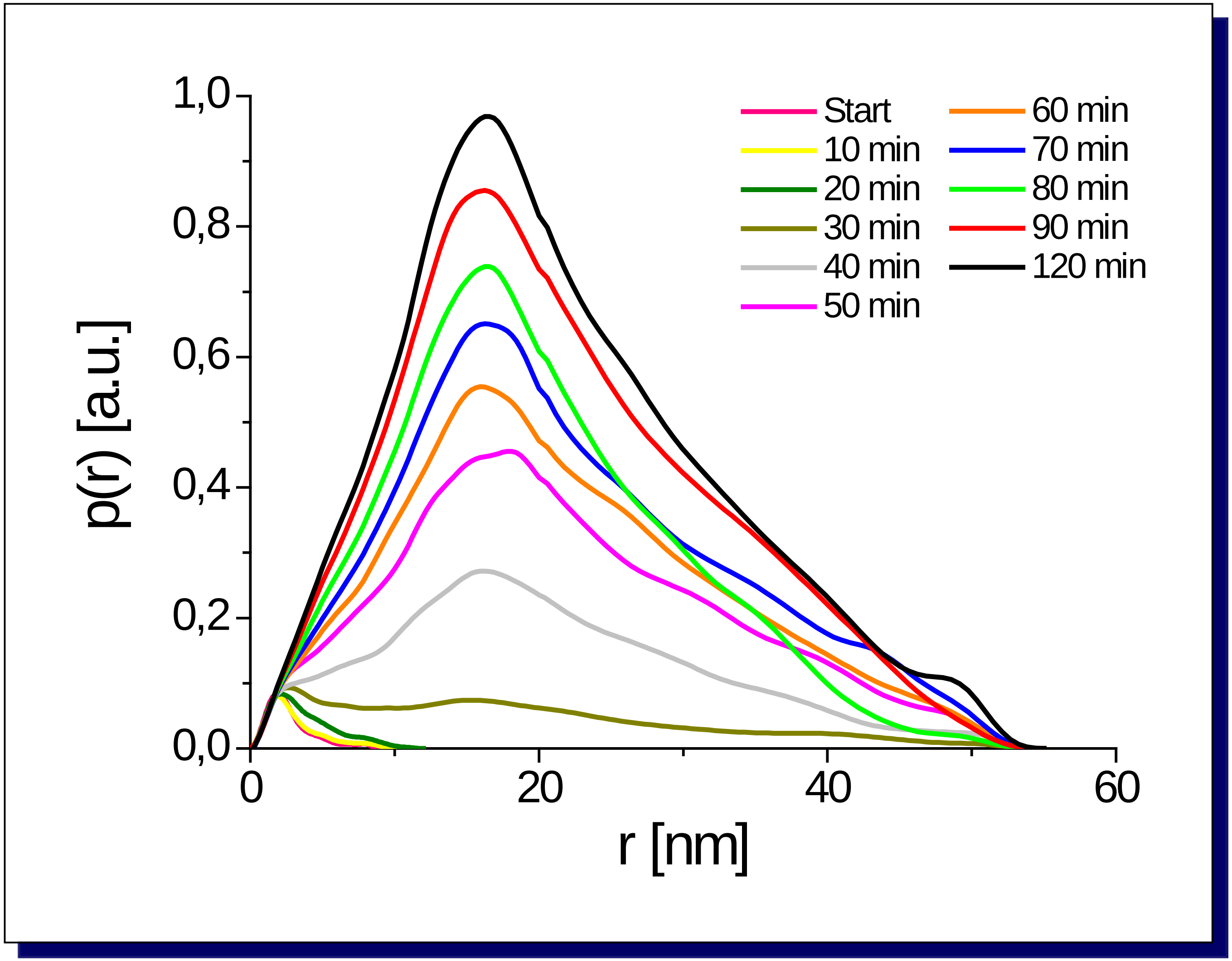
# Protein – Nano –Tubes (α-Lactalbumin)



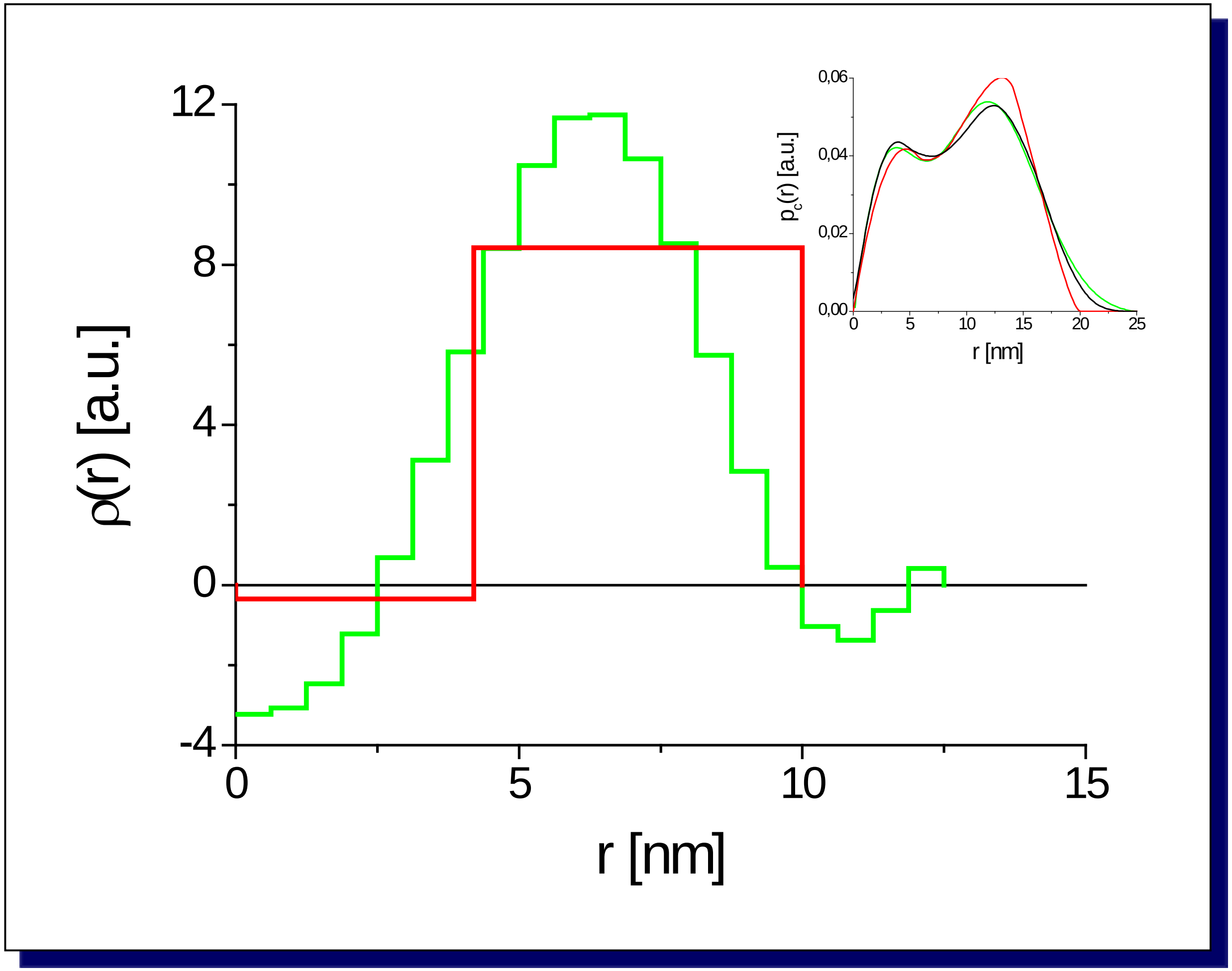

- 3% (2.1mM) α-lac in 75 mM Tris Buffer, pH 7.5
- Molar ratio (R) calcium/α-lac=3 (6.2mM)
- Serine Protease BLP – 1/250 (molar ratio)
- Optimum temperature T=50ºC
- Reaction monitored by Dynamic Light Scattering

Co-operation with Kees de Kruif, NIZO food research BV

# Growth of the Protein – Nano –Tubes with Time

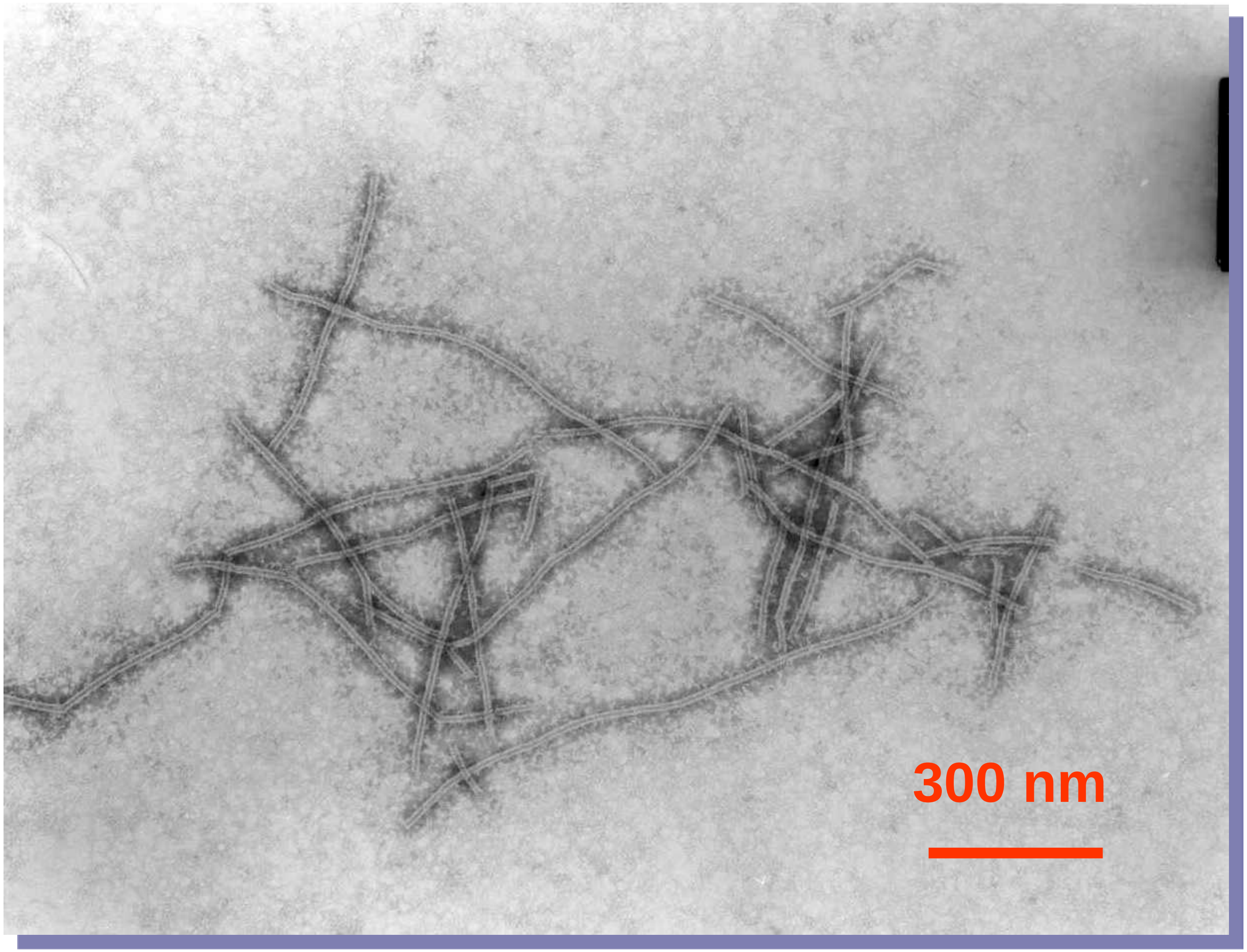


# Radial Electron Density Distribution in the Cross-Section




Free Monomer Content: 40% !

# TEM Picture of α-Lactalbumin Nano –Tubes




J. F. Graveland-Bikker et al., *J. Appl. Cryst.* (2006) 39, 180–184.

# Concentrated, Interacting Systems
## Theoretical Background

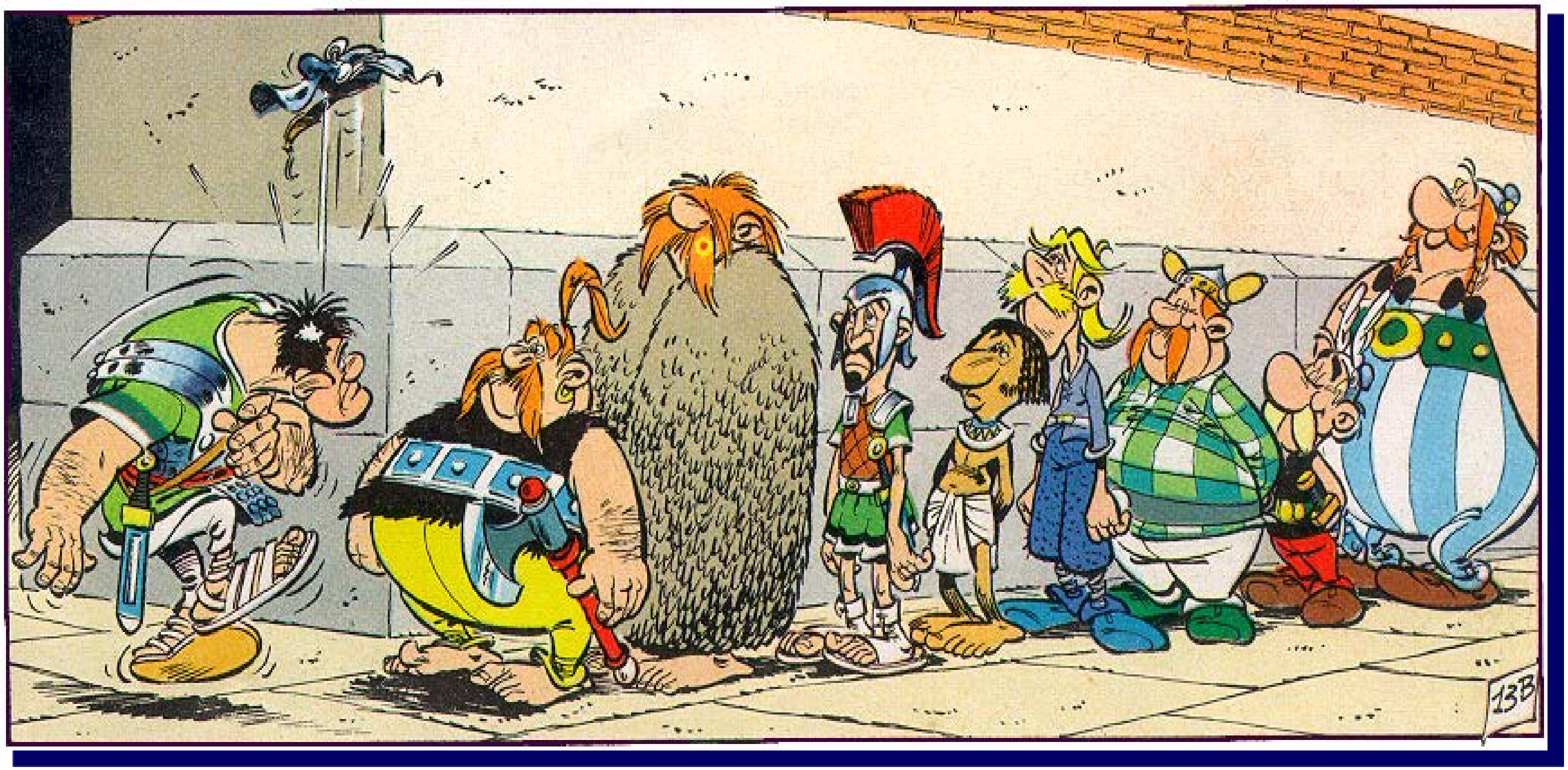
Assumption of monodisperse globular particles:

$$I(q) = n.P(q).S(q)$$

*n* ... Particle density
*q* ... Scattering vector
*I(q)* ... Scattering Intensity

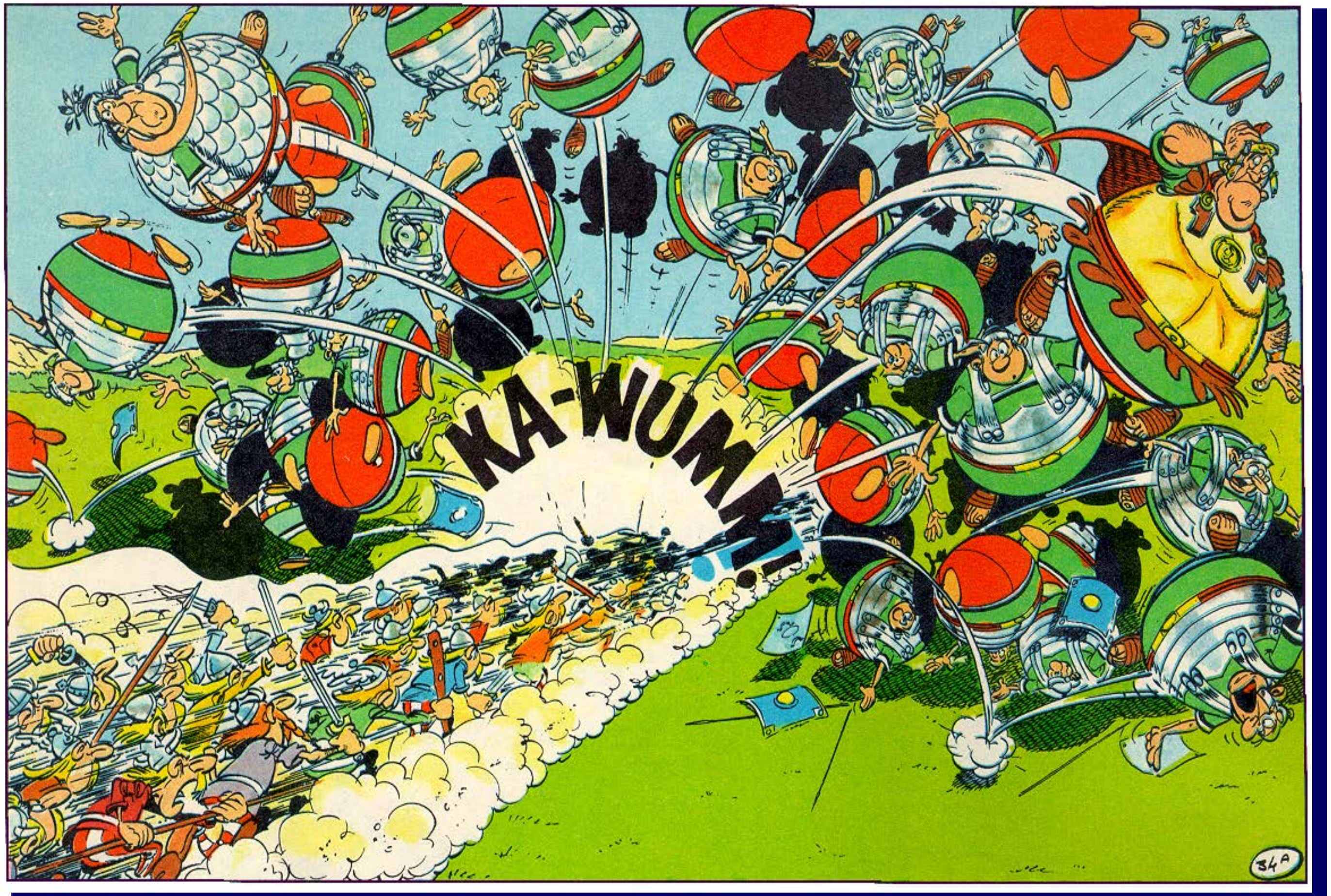
| | |
|---|---|
| *P(q)* ... Form Factor | $P(q) \leftrightarrow p(r)$ |
| *S(q)* ... Structure Factor | $[S(q) - 1] \leftrightarrow [g(r) - 1]$ |
| Interaction Potential: | Hard Spheres Potential |
| Closure relation: | Percus-Yevick-Approximation (analyt. Solution) |
| | Kinning & Thomas, *Macromolecules* (1984), **17** |

# Particle Form Factor P(q) - Artists View©




**©Asterix Legionnaire,** associated by Judith Brunner-Popela

# Structure factor S(q) - Artists View©




© **Le Grand Fossé** associated by Judith Brunner-Popela

# Fourier Transformation

$$I(q) = n.P(q).S(q)$$

Form Factor *P(q)* ↔ Pair Distance Distribution Function *p(r)*

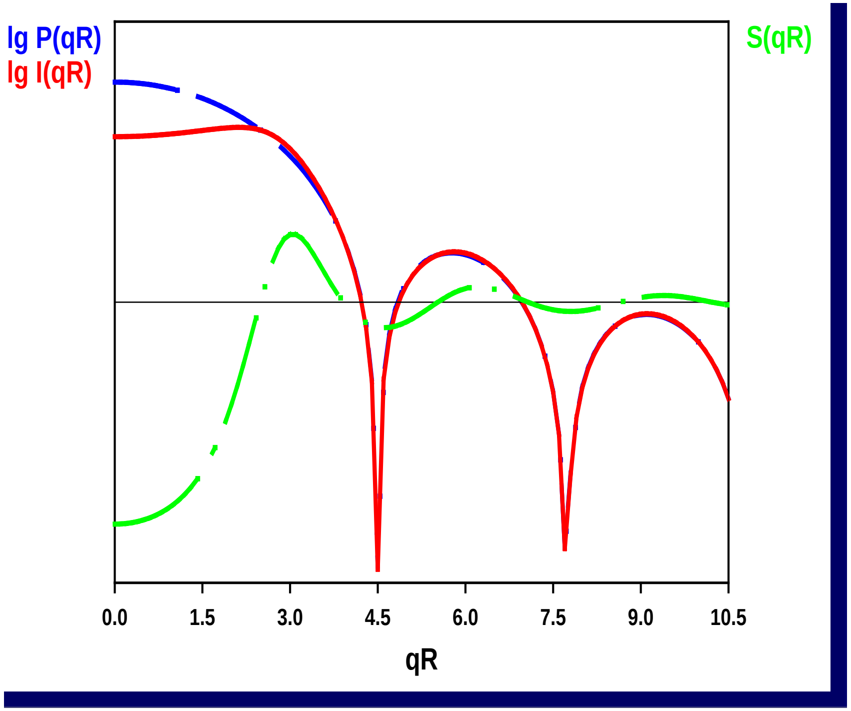
$$P(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr$$

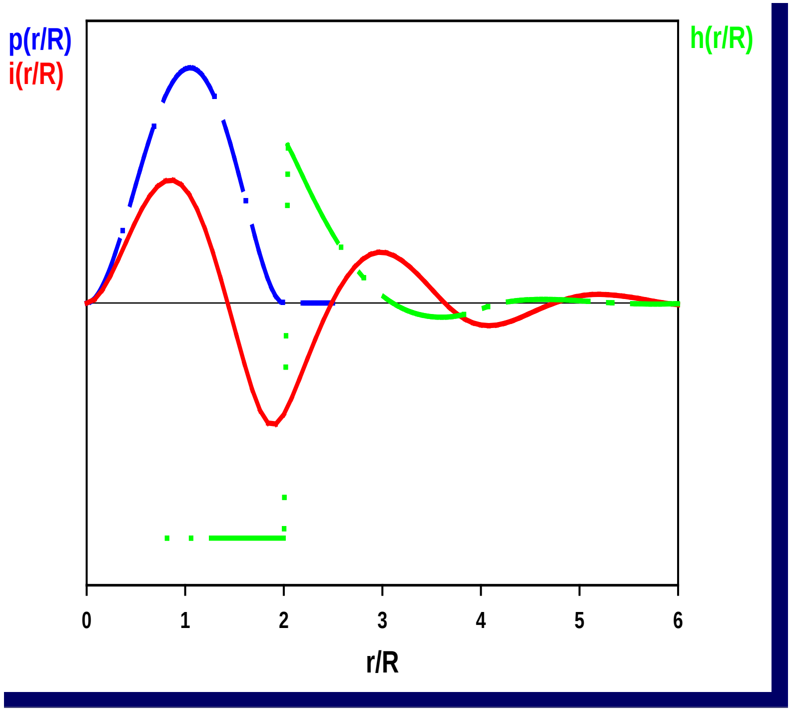
Structure Factor [*S(q)* - 1] ↔ Total Correlation Function [*g(r)* -1] $r^2$

$$S(q) - 1 = 4\pi n \int_0^\infty [g(r) - 1]\, r^2 \frac{\sin(qr)}{qr} dr$$

Due to the nearly identical structure of these equations it is obvious that it is not a trivial task to split the scattering intensity into these factors by mathematical means

# Schematic Presentation of the Influence of Interaction




Reziprocal space
(Measurement)

Real space
(Evaluation and interpretation)

# Basic Principles of the ***GIFT*** Method
# ***G**eneralized **I**ndirect **F**ourier **T**ransformation*

- Simultaneous determination of the form factor and the structure factor with a minimum of *a priori* information
- Model free determination of the form factor, only a maximum dimension has to be estimated
- Structure factor is determined with an adequate model (Percus-Yevick approximation)
- Polydispersity is taken into account by simple averaging ($S^{ave}(q)$) or by the correct hard spheres model ($S^{eff}(q)$, Vrij 1979)
- Determination of both terms by a specially designed coupled and stabilized Nonlinear Least Squares method (*Boltzmann Simplex Simulated Annealing*)

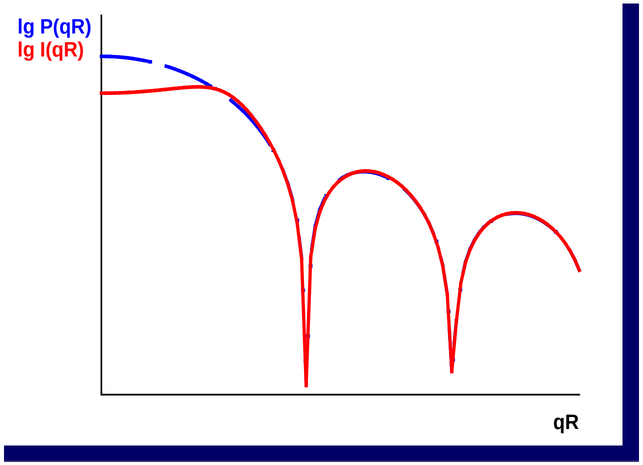

Brunner-Popela, J. et al. (1997) *J. Appl. Cryst.* 30, 431

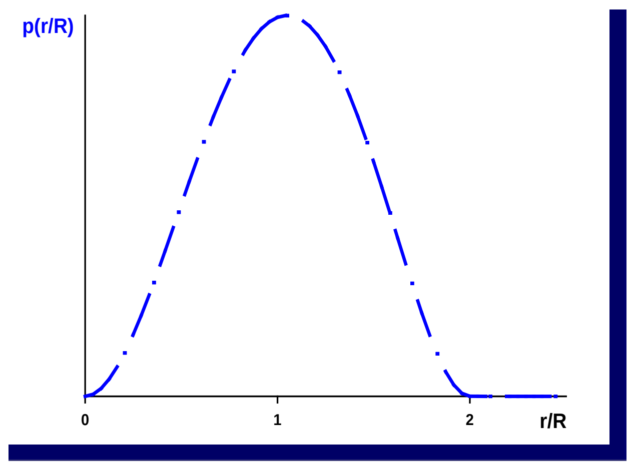
Bergmann, A., et al. (2000) *J. Appl. Cryst.* **33,** 1212 -1216.

Fritz, G., et al. *J. Chem. Phys.* (2000) 113, 9733-9740.

# Reciprocal Space ← FT → Real Space

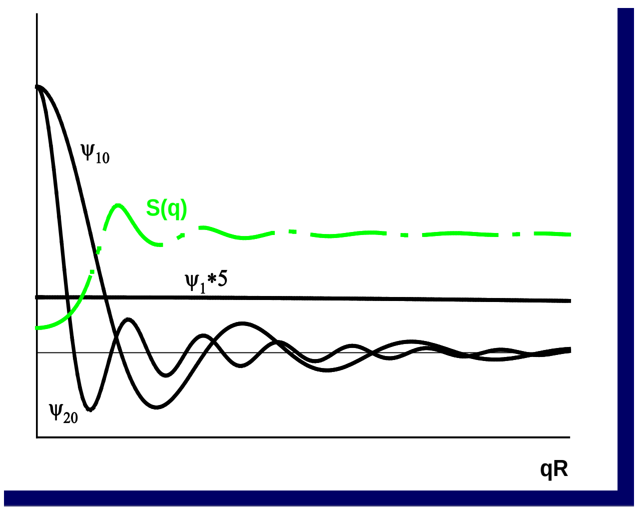
Brunner-Popela, J. and Glatter, O. (1997) *J. Appl. Cryst.* 30, 431

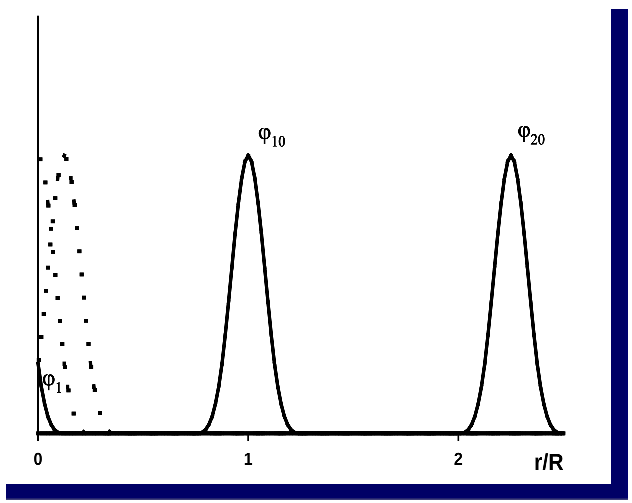


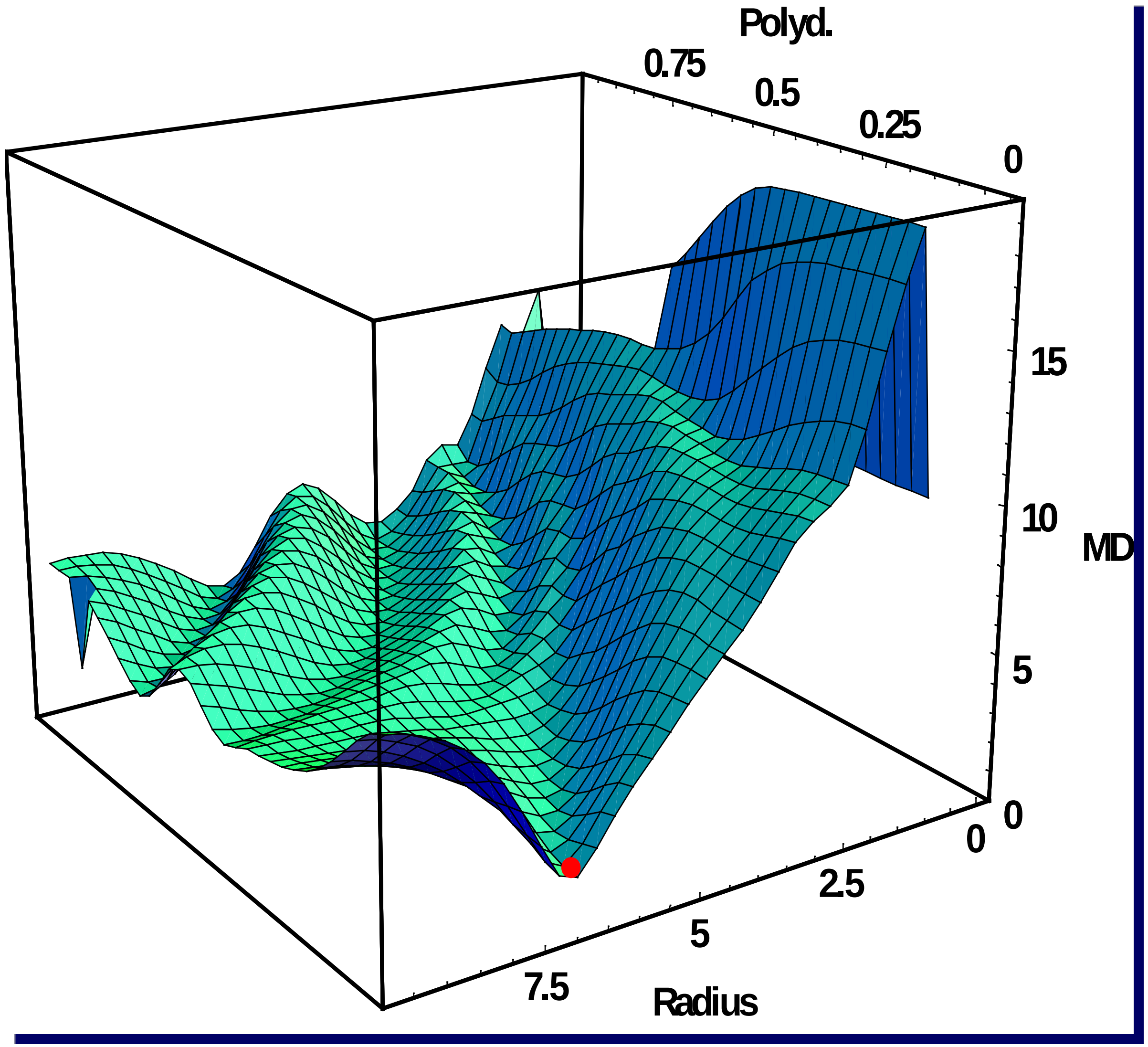

$$\sum c_\nu \psi_\nu \cdot S(q, d_k)$$

$$\sum c_\nu \varphi_\nu$$

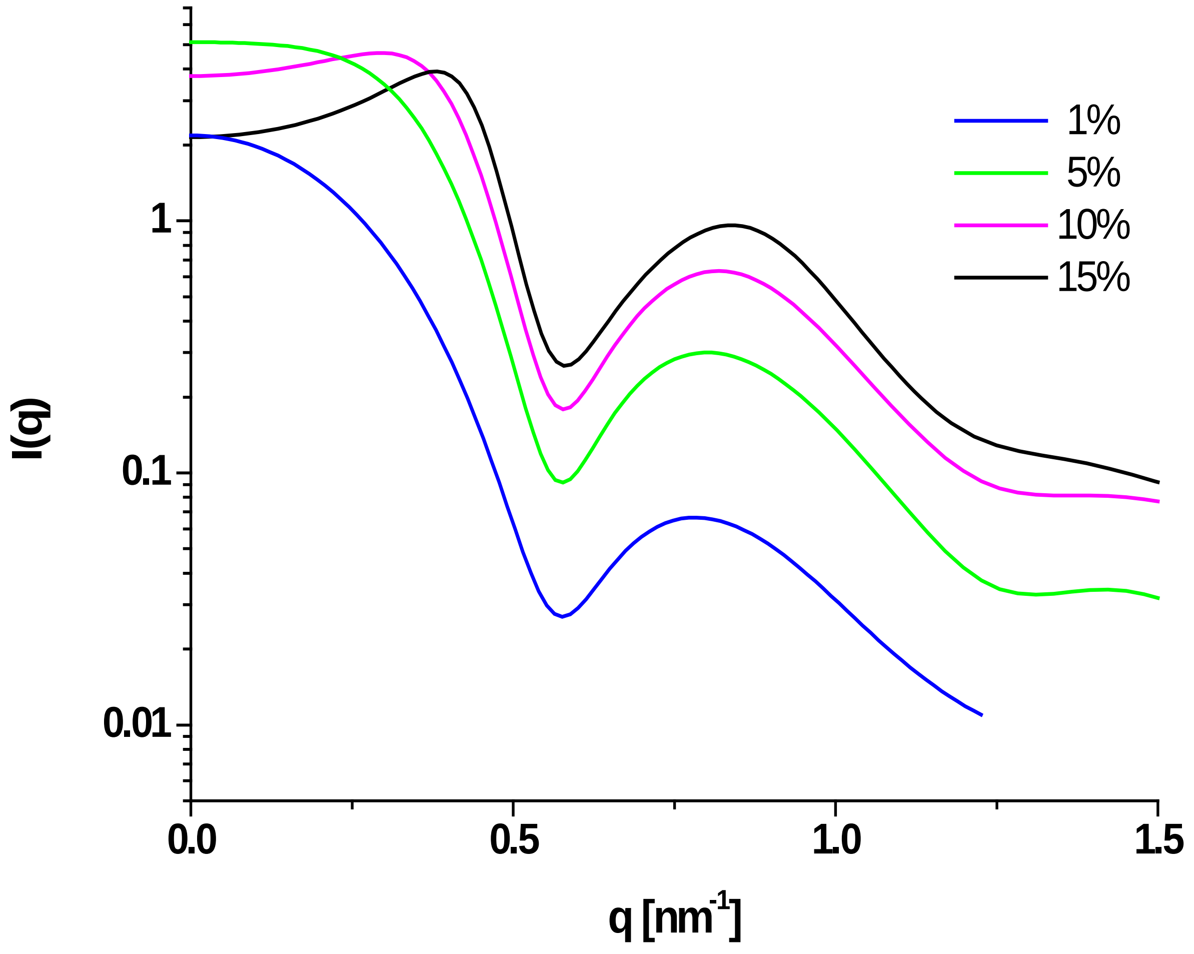


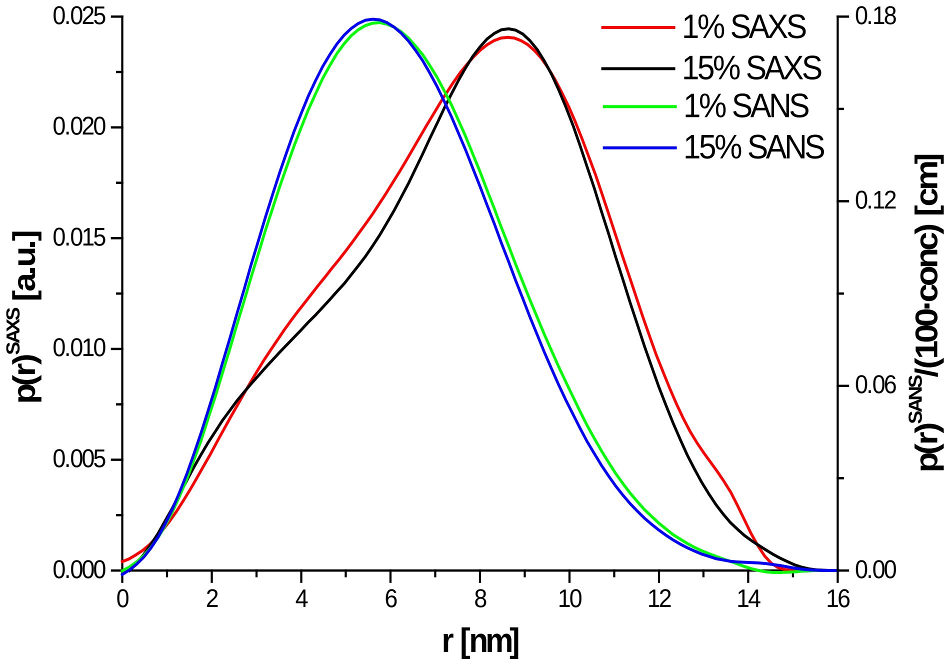
# Mean Deviation Hyper Surface, Solution: Boltzmann Simplex Simulated Annealing



# Pluronics P94,
# Desmeared SAXS Scattering Functions I(q)



# P94, Pair Distance Distribution Functions SAXS & SANS

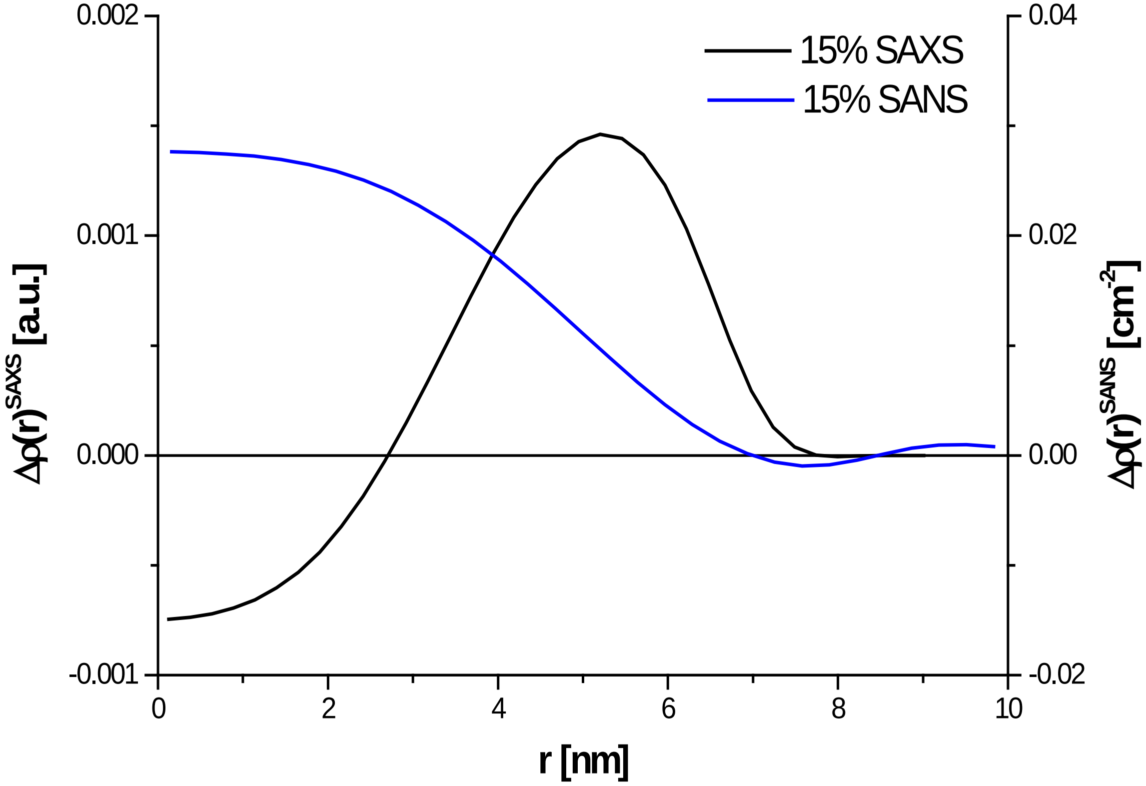



At higher concentration: just more of the same micelles!

BUT: Effective **volume fraction** about **twice** the polymer volume (hydration)!

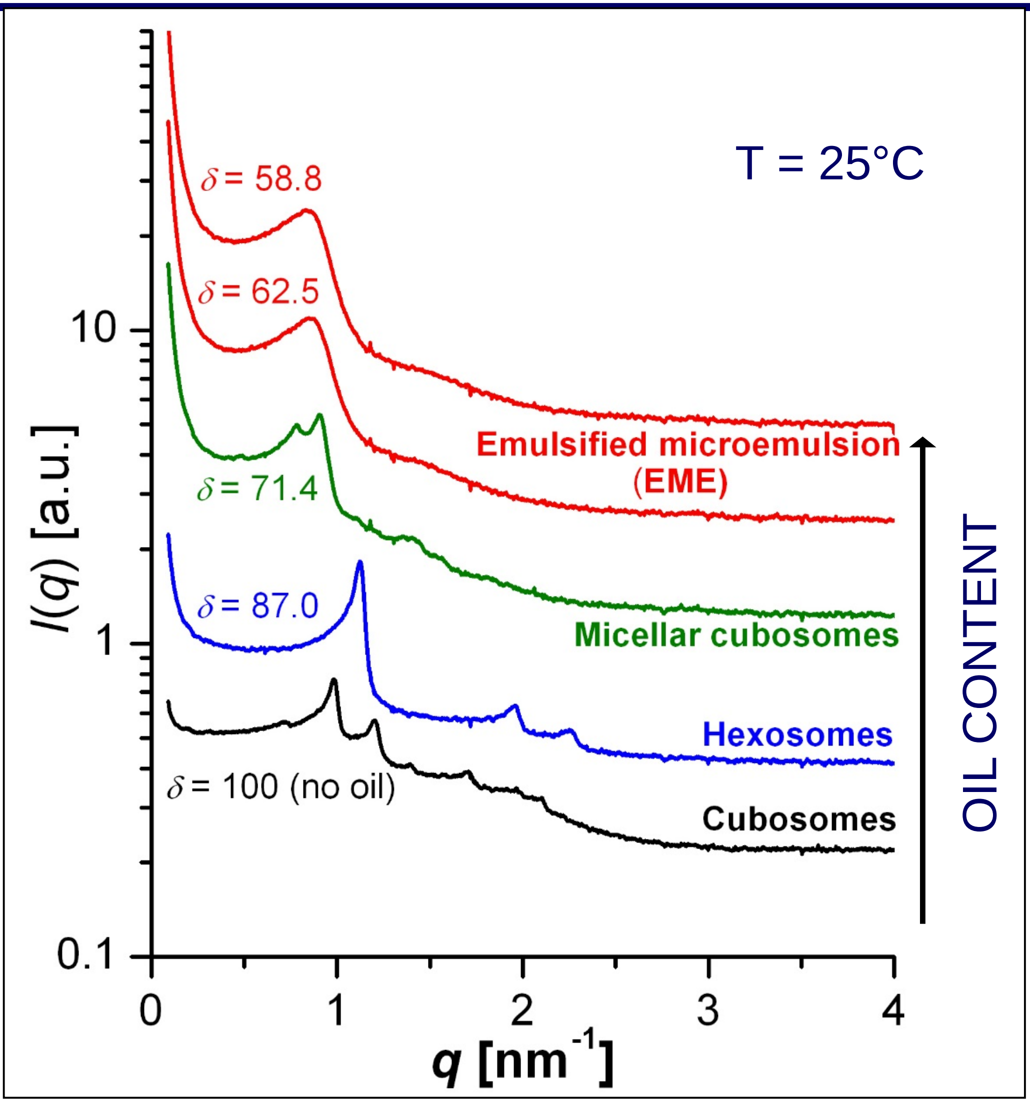
# P94, SAXS & SANS

## Radial Scattering Length Density Distribution

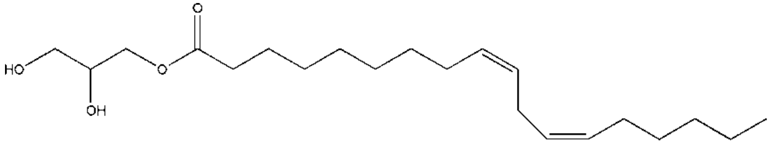



- Difference electron density in the core negative!
- Bulk PPO has a higher electron density than water!
- Core of the micelles is not equal to bulk phase!

# Controlling the Internal Nanostructure of MLO – ISAsomes Addition of Oil (Tetradecane, TC), Characterized by SAXS




MLO: Monolinolein




$$\delta = \frac{mass\ of\ \ MLO}{mass\ of\ \ (MLO + oil)} \times 100$$

Addition of oil changes the internal structure of the system!

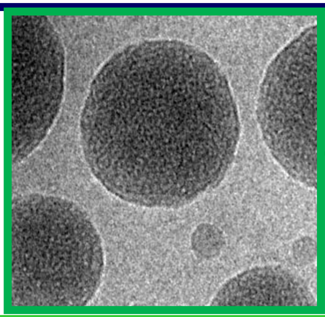
Different oils can be used!

Oleic Acid: pH sensitive!


Yaghmur, A.et.al. *Langmuir* (2005) 21, 569.
Salonen, A. et.al., *Langmuir* (2008) 24, 5306.
Yaghmur, A. et.al. *Langmuir* (2006), 22, 517.
Salentinig, S. et al. *Langmuir*, (2010), 26, 11670.

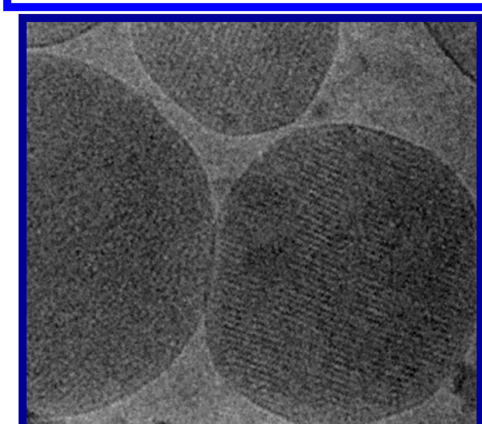
# Internal Structure of ISAsome Emulsions

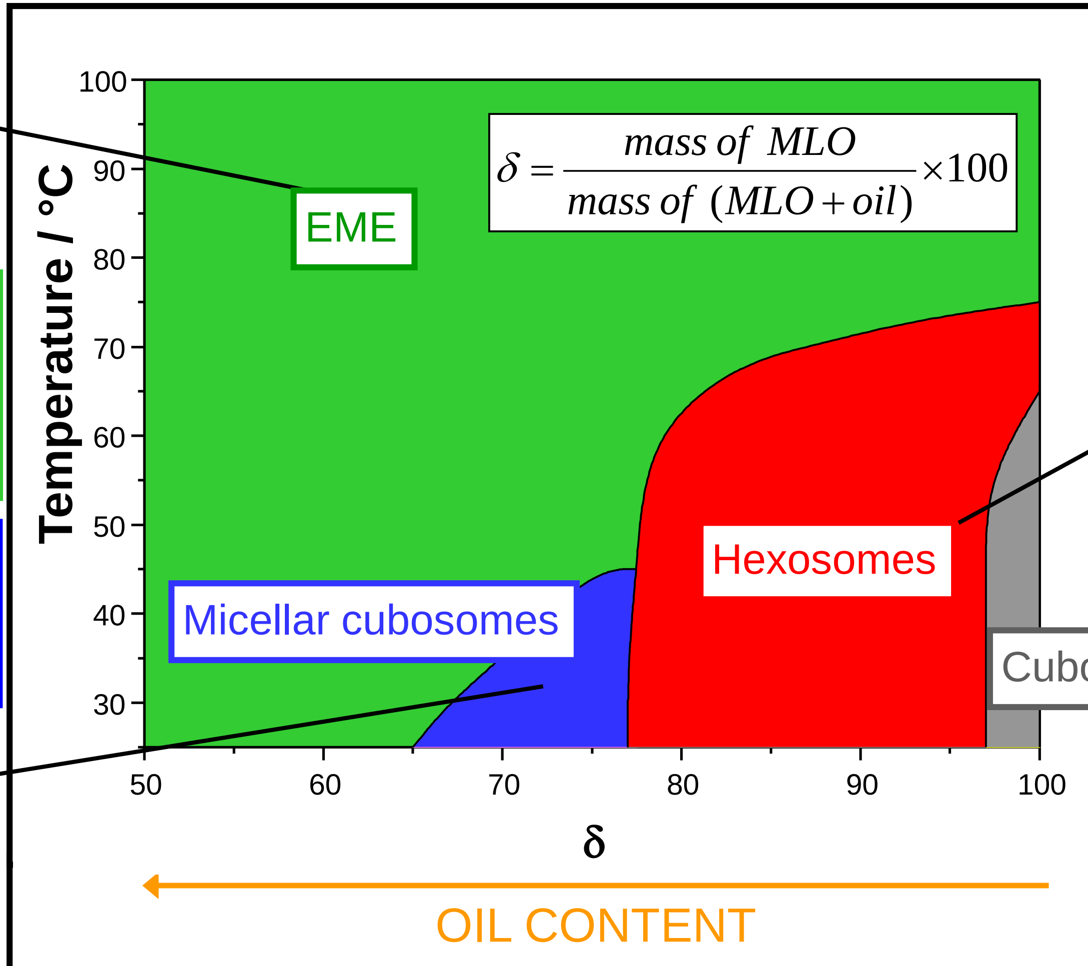
## $H_2O$ – MLO – TC. Stabilizer: Pluronic F127



***EME***
*Emulsified Microemulsion*
Water-in-oil microemulsion, emulsified in water

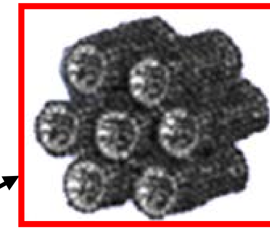
**Micellar Cubosomes:**
Discontinuous Micellar Cubic Phase ***Fd3m***



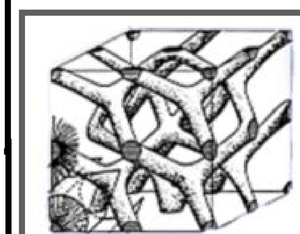



Guillot, S. et.al. (2006) *Colloids and Surfaces A* **291**, 78–84.

**Hexosomes**



Cubosomes

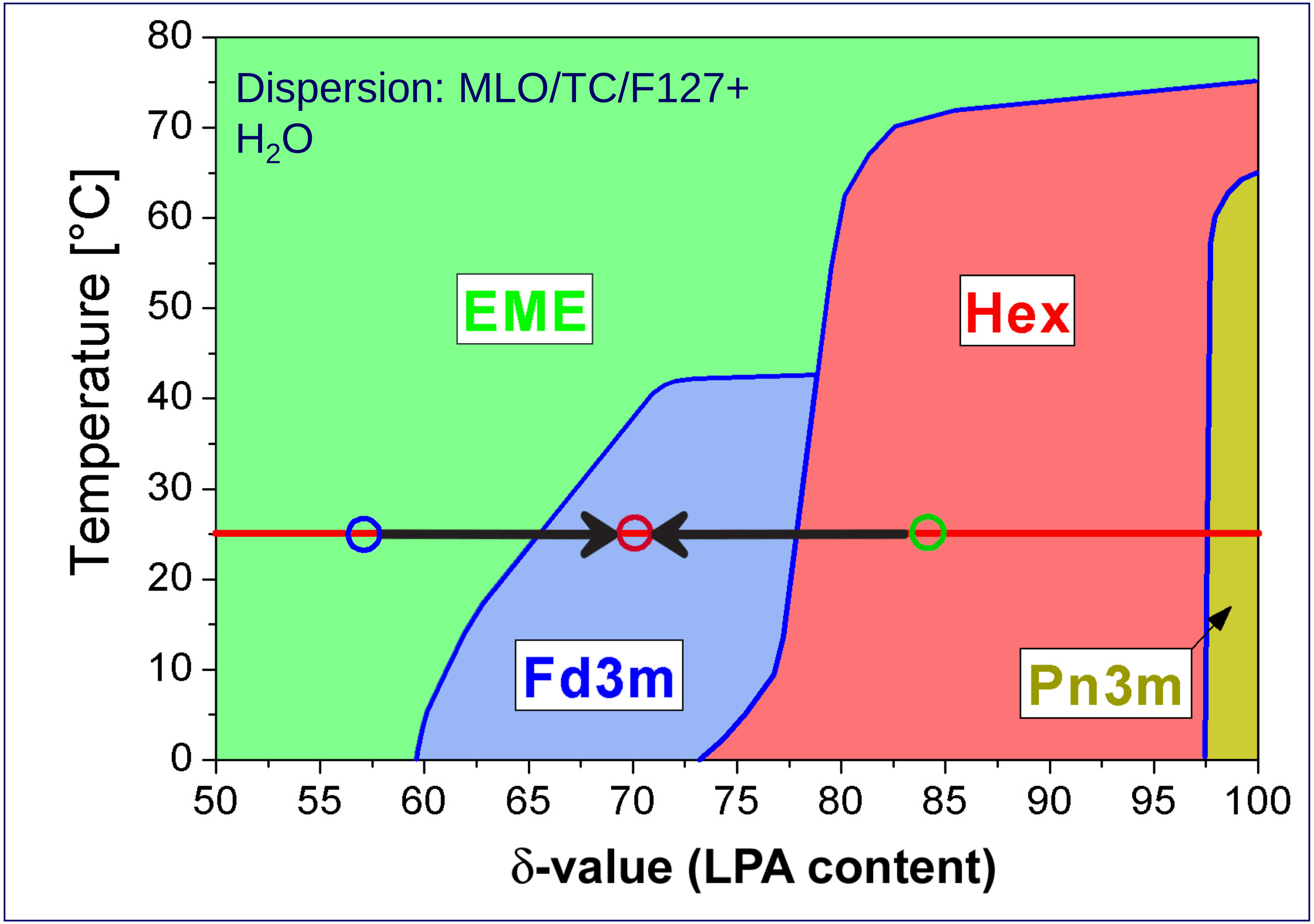


Bicontinuous Cubic Phase *Pn**3m***

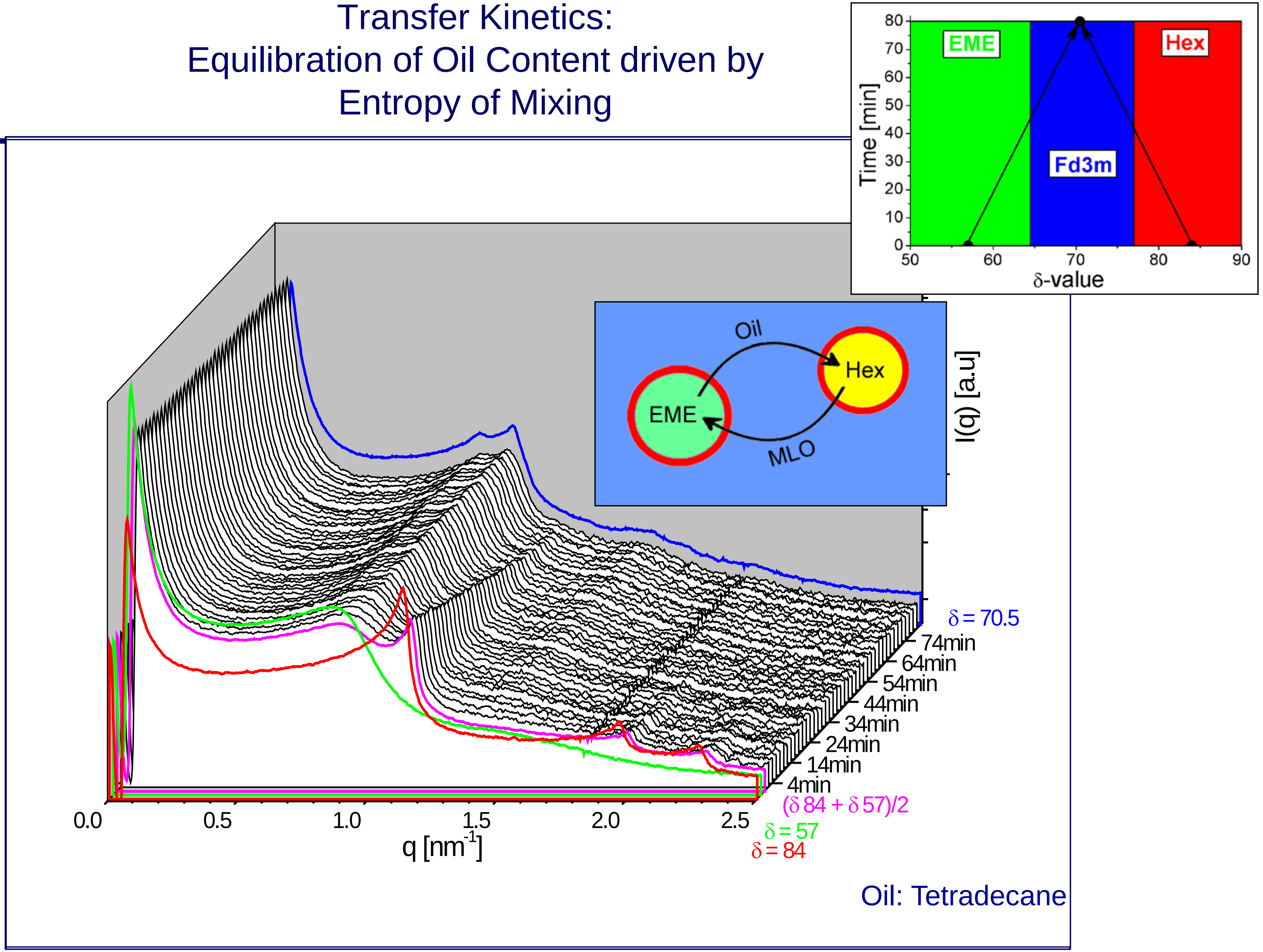
# Transfer Kinetics of Lipids

Moitzi, Ch. et al. *Advanced materials,* (2007) **19**, 1352-1358.

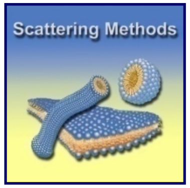
What happens if ISAsome emulsions with different compositions are mixed? Do they equilibrate? Why and How?

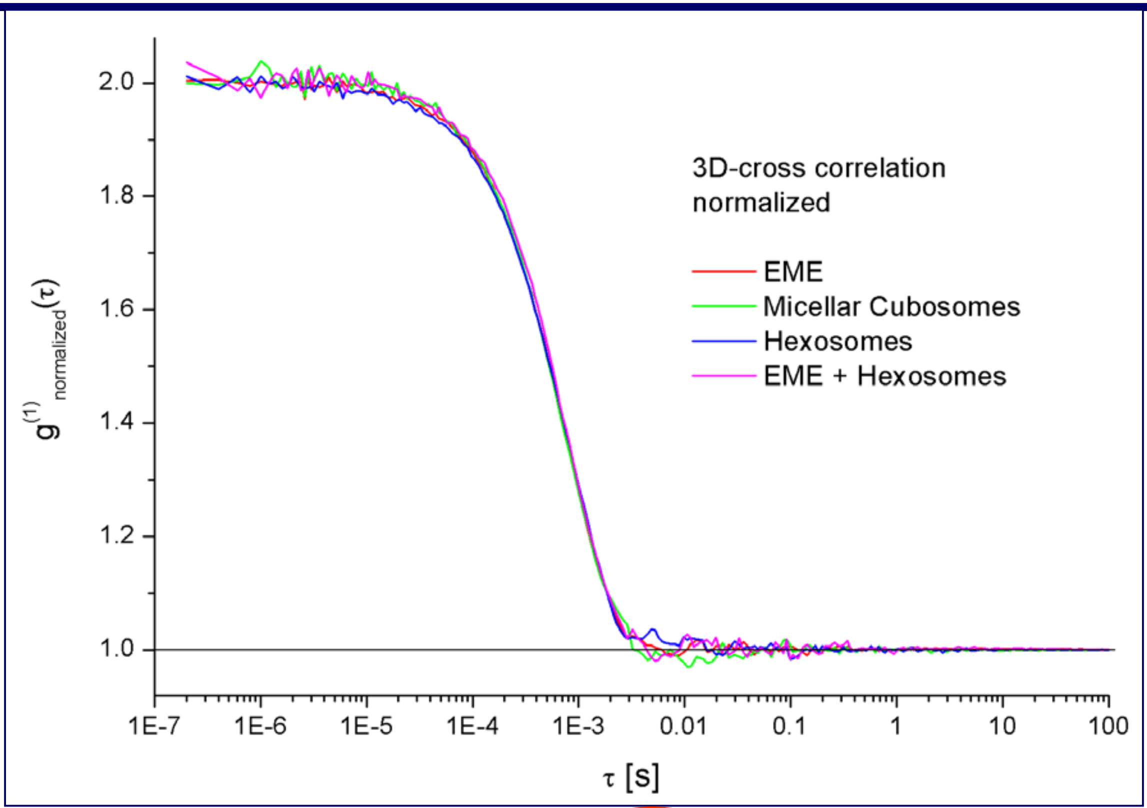


# Transfer Kinetics:
# Equilibration of Oil Content driven by Entropy of Mixing



# Is there a Particle Growth (Fusion)?
# → 3D-DLS (turbid system!)




No considerable change in particle sizes!

↓

Different driving force to Ostwald ripening! Compositional ripening!

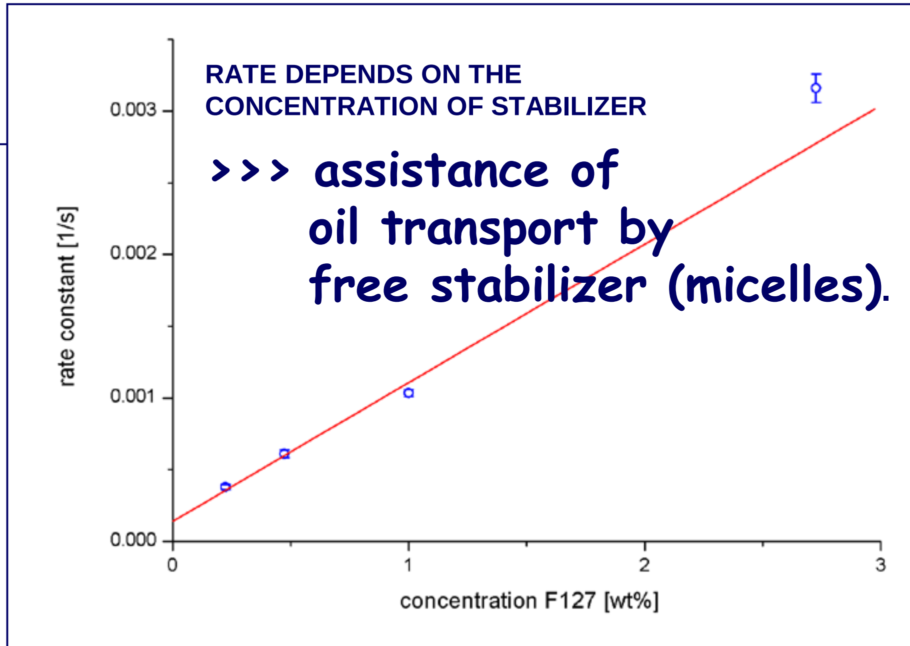
Entropy of mixing vs. Laplace pressure

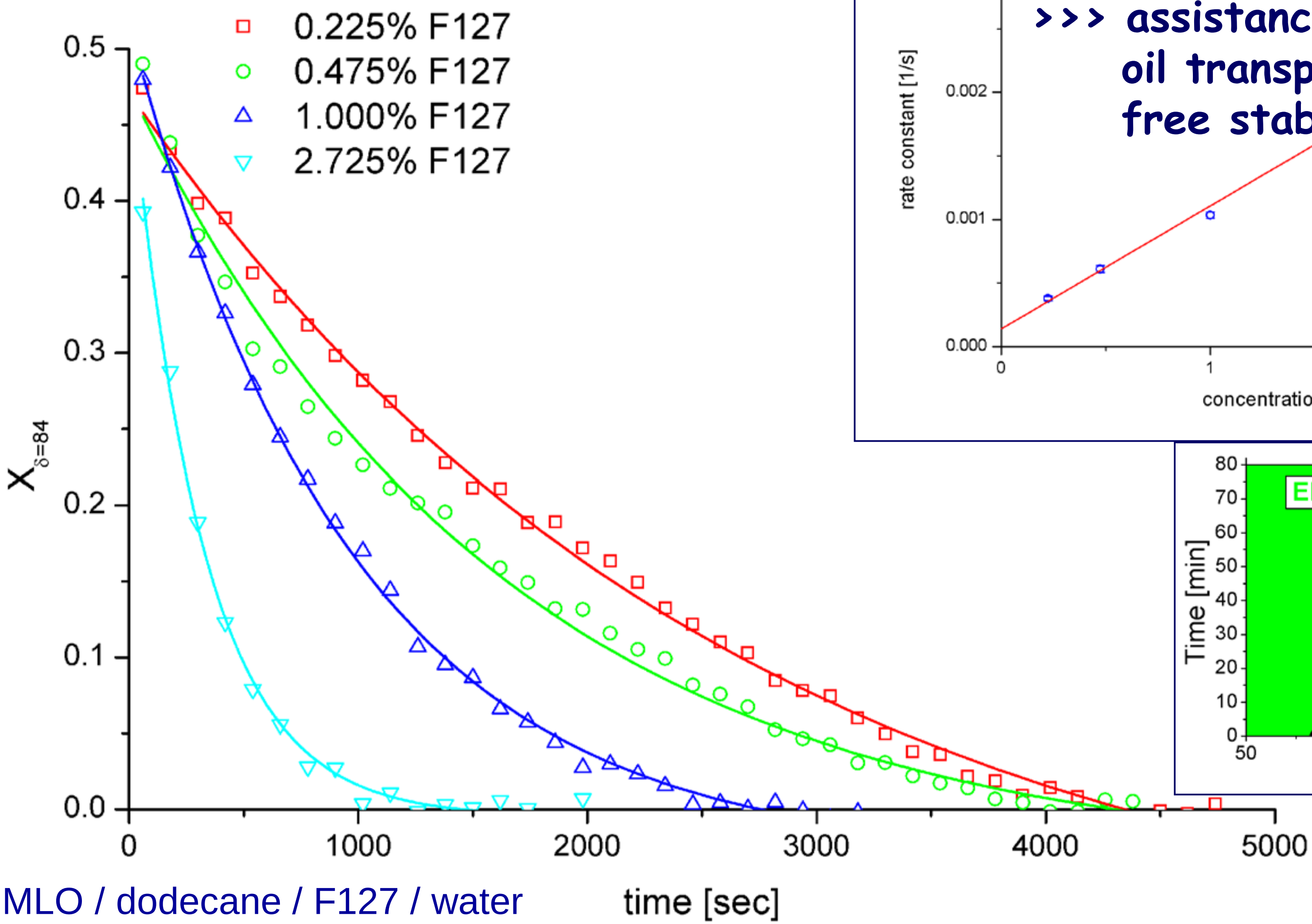
| δ-value | $R_H$ [nm] | Width [%] |
|---|---|---|
| 84 | 116.4 | 24.7 |
| 70.5 | 118.1 | 16.7 |
| 57 | 116.3 | 20.8 |
| 84 + 57 | 118.7 | 22.1 |

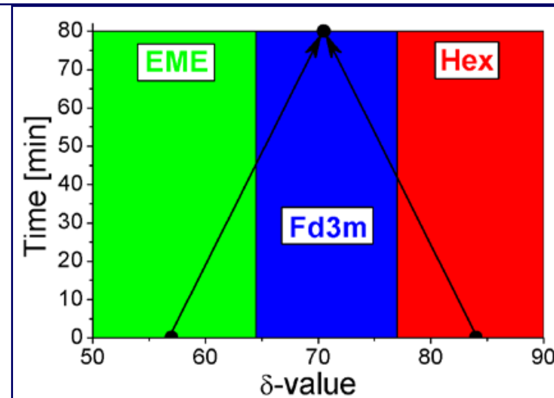
MLO/decane/F127

dispersed phase:1%

# Effect of Additional Stabilizer F127




MLO / dodecane / F127 / water

# Conclusions

- Scattering techniques work well for the characterization of soft matter
- Real space information is important
- Monodisperse systems (size, shape, internal structure)
- Polydisperse systems (size distribution)
- Concentrated interacting systems are challenging but give important information!
- Liquid crystalline systems can be characterized best by SAXS
- Lipid transfer kinetics can be studied in dispersed LC systems
- Complementary techniques (like DLS, like NMR or Cryo-TEM) are important

- **Main lesson: be open for unexpected results!**