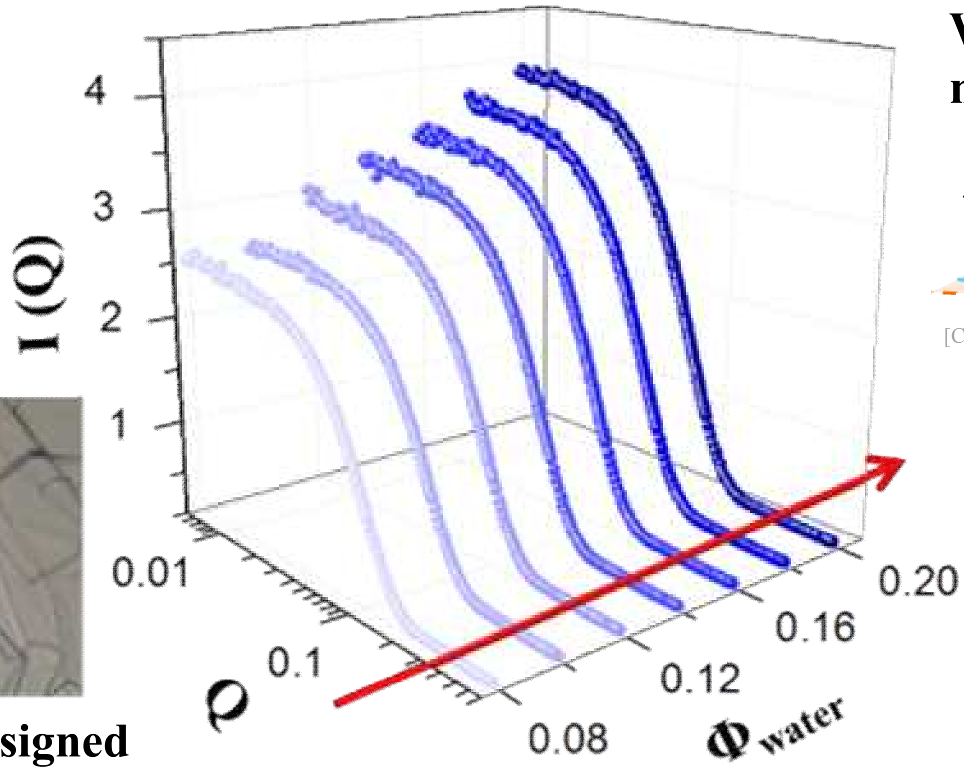
Journal club

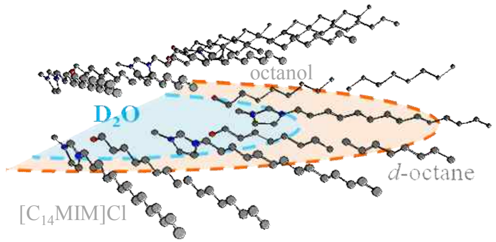
Droplet polydispersity and shape fluctuations in AOT [bis(2-ethylhexyl)sulfosuccinate sodium salt] microemulsions studied by contrast variation small -angle neutron scattering

L. Arleth and J. S. Pedersen, *Phys. Rev. E* **63**, 61406 (2001)

Yoonnam Jeon (2016. 01. 23)



Water in oil microemulsion



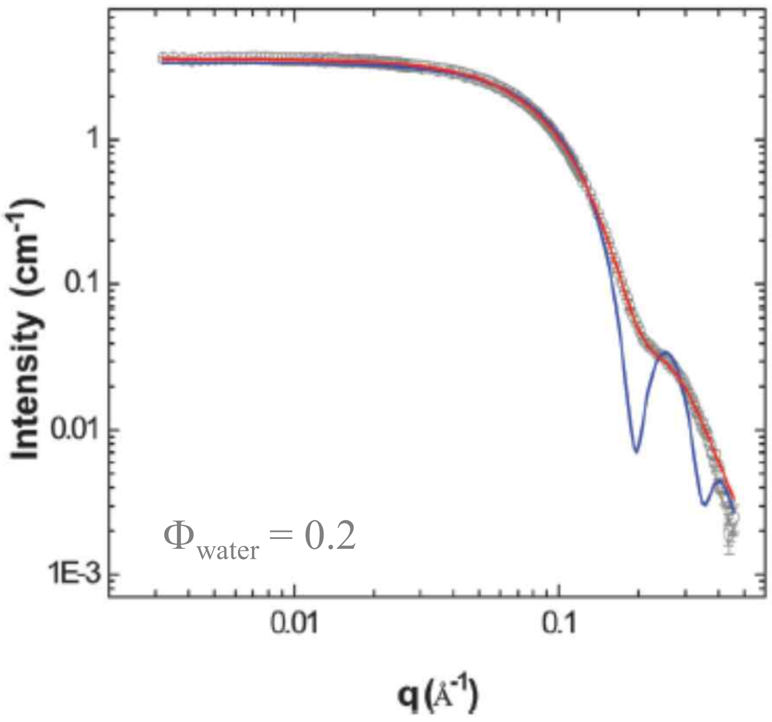
Kang et. al.,
Phys. Chem. Chem. Phys. **17**, 27833 (2015)

Molecular designed single crystal

Kang et. al.,
J. Phys. Chem. C **117**, 14332 (2013)

※ No direct evidence of ellipsoidal structure

→ Model fitting : sphere



Model	Volume density	Core radius (Å)	Shell thickness (Å)	Polydispersity
Mono	0.021	8	15	0
Poly-core	0.035	10	9	0.37

Kang et. al., *Phys. Chem. Chem. Phys.* **17**, 27833 (2015)

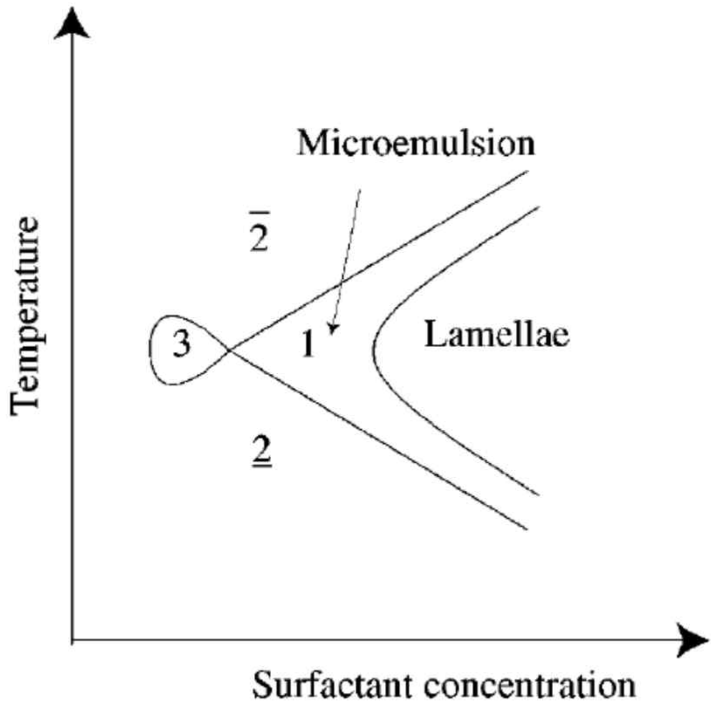
Question

0.37 polydispersity is quite high

SANS :
Ellipsoids is equivalent to that of a distribution of **poly disperse spheres**
Arleth and Pedersen,
Phys. Rev. E **63**, 061406 (2001)

INTRODUCTION

fish-diagram



Microstructure of microemulsions

Varies a lot depending upon
- actual system
- composition
- temperature
- additives

Simplest system

Water/alkane/C_iE_j (nonionic surfactant)

Water/alkane/AOT(ionic surfactant) – less simple in practice

Aim To get information about the polydispersity and shape fluctuations of the droplets

Polydispersity (σ / R_{av})

- AOT/water/hexane : 12% (Ricka et. al. 1991)

- AOT/water/iso-octane : 19% (Christ and Schurtenberger et. al. 1994)
- AOT/water/decane : 10% (Christ and Schurtenberger et. al. 1994)

- Theoritical prediction : 0.1 – 0.2
- Experimental reports : 10 – 45% (most often : 15 – 25%)

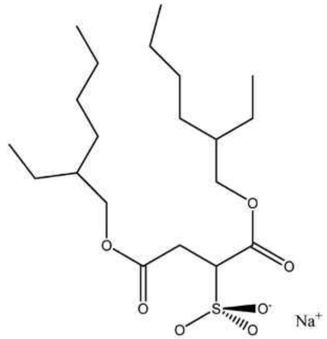
For nonionic surfactant (C_iE_j)

- polydispersity is independent of alkane type (Pedersen and cowokers, 1996)

Aim The polydispersity and shape fluctuations **using SANS**

SANS :
Ellipsoids is equivalent to that of a distribution of **poly disperse spheres**

EXPERIMENTS

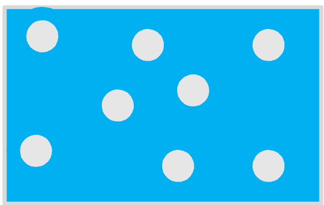


➢ Sample preparation

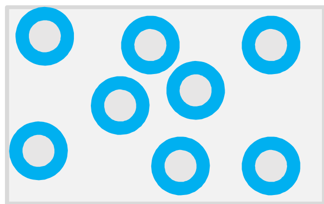
- AOT + water ~ 5% (water / AOT =38 molar ratio)
- Alkanes : decane & iso-octane

➢ Small Angle Neutron Scattering (SANS)

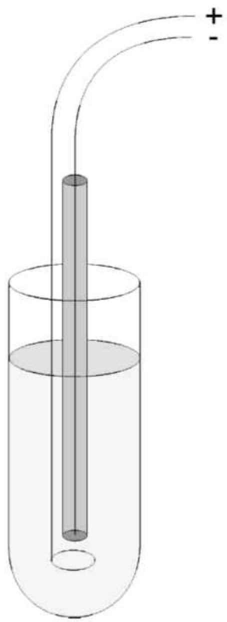
- Risø National Laboratory
- $0.004 < q < 0.26$ Å^{-1}
- Contrast matching exp. mixing with *h*- and *d*-alkanes



h-alkane



d-alkane

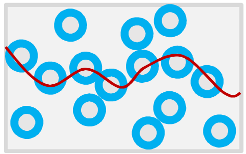


➢ Conductivity measurement

- CDM80 conductivity meter

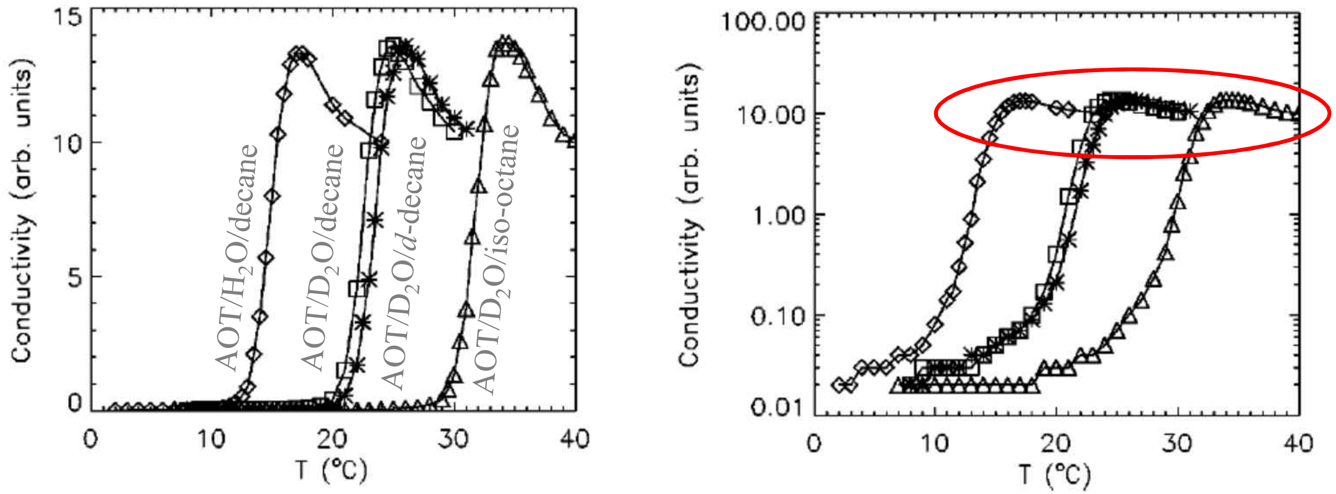
cathode and anode : Pt

- **Temperature dependent conductivity**



- Well known : AOT/water/alkane

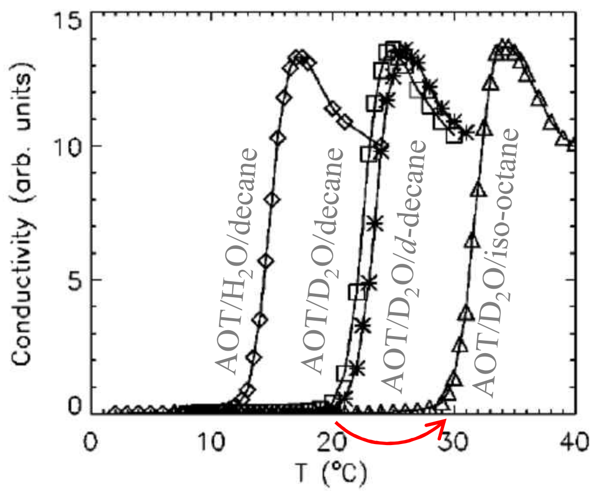
high T → - larger aggregates of droplets are formed
- allow the counterions of the AOT to move round



- **Slow decreased conductivity** Have not been able to find such an effect

- **Main interest : Position of transition**

- From w/o microemulsions to microemulsions with connected water domains



Sample	$T_{off\text{-}set}$ (°C)	T_{max} (°C)
AOT/H_2O/*h*-dec	12	17
AOT/D_2O/*h*-dec	19	25
AOT/D_2O/*d*-dec	20	26
AOT/D_2O/*h*-iso	28	34

jump : 9°C

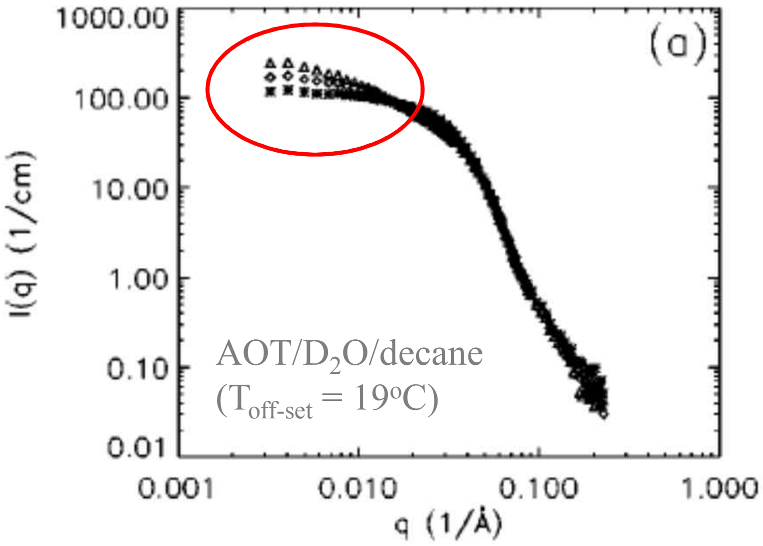
- **Conductivity jump by changing solvent** (decane → isooctane)

  - agreement with former measurement
  - connected to the **decreasing penetration of solvent** into the surfactant layer with **increasing molecular weight** ($m_{decane} > m_{isooctane}$)

- **Conductivity jump with heavy water**

  - suggest : water structure plays a very import role in the microemulsion phase behavior

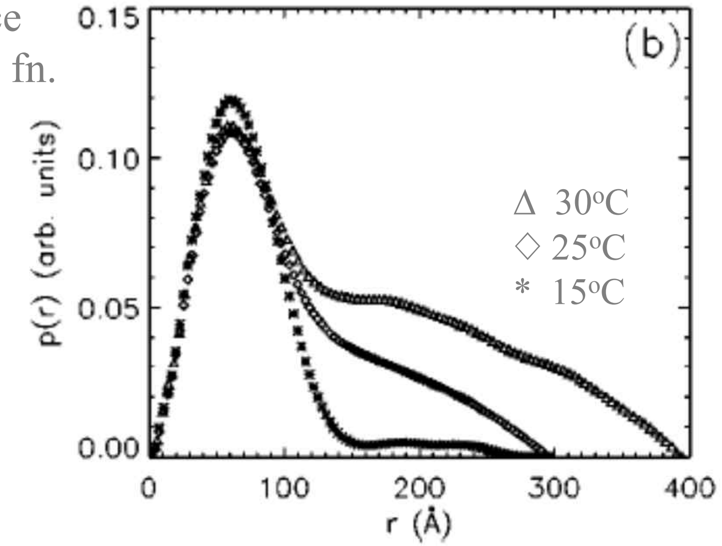
ANALYSIS OF SANS Temperature dependent pair distribution fn.



- **Increased scattering at low q with increasing temp.**

  - size of the droplets increases

pair-distance distribution fn.



- **For the same contrast**

  - spherical : give rise to a bell shaped curve
  - elongated (or polydisperse) :
    p(r) will have a tail and go to zero at higher r

➢ Form factor

- sphere

$$F_1(qR) = 3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}$$

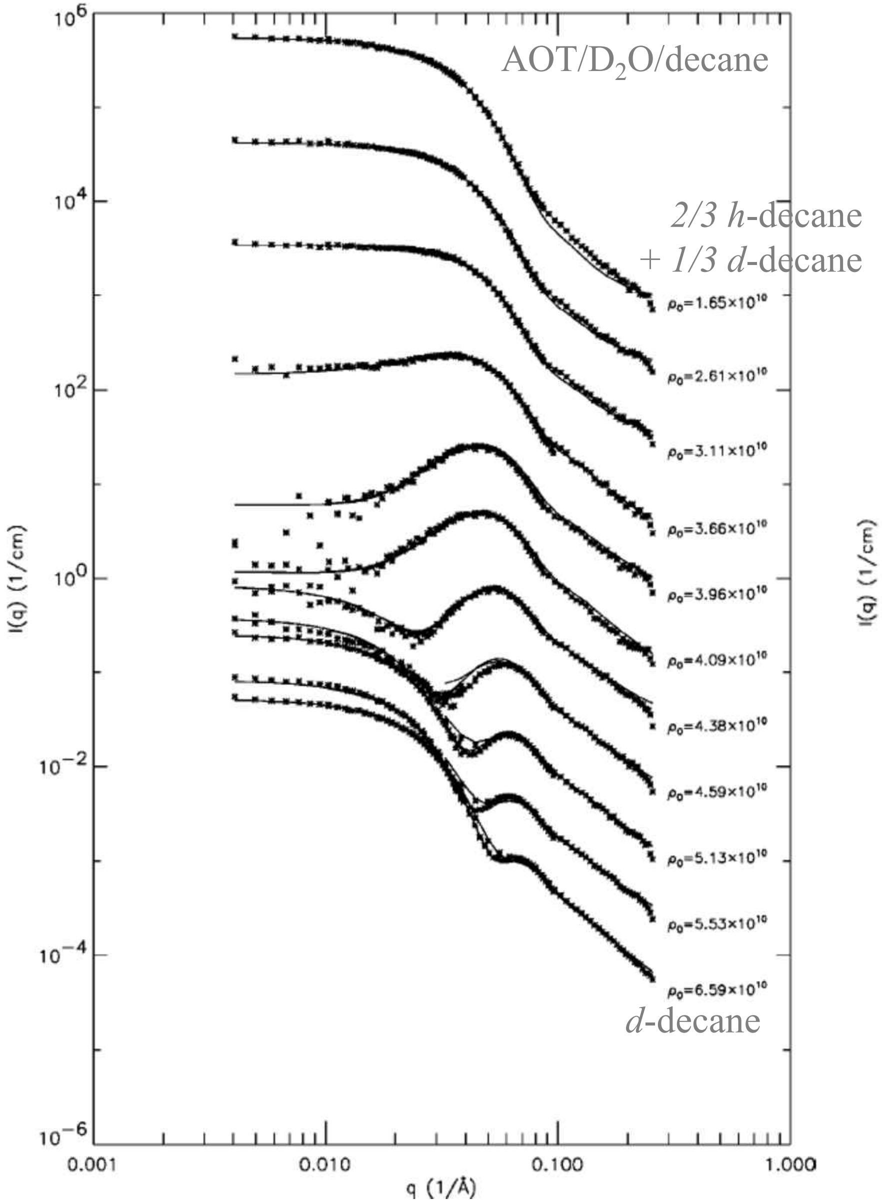
- ellipsoid

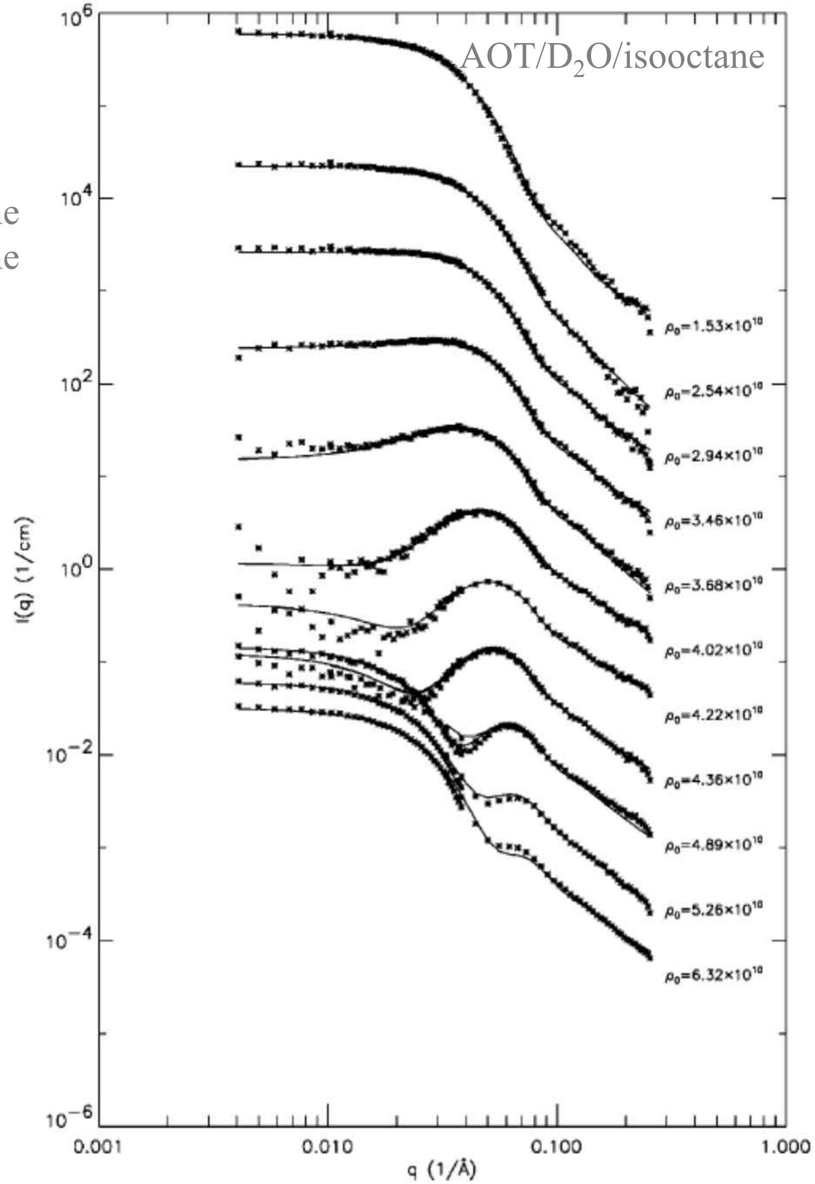
$$\langle F(q)^2 \rangle_0 = \int_0^{\pi/2} \left(\begin{array}{c} V_0(\rho_c - \rho_s)F_1(qR_c\sqrt{\sin^2\theta + \varepsilon_c{}^2\cos^2}(V_c+V_s)(\rho_s - \rho_{solvent}) \\ \times F_1(qR_s\sqrt{\sin^2\theta + \varepsilon_s{}^2\cos^2})^2 \end{array} \right) \sin\theta \, d\theta$$

➢ Structure factor

- Did not use the model that includes stickiness of the spheres
- Structure factor for a distribution of polydisperse hard spheres

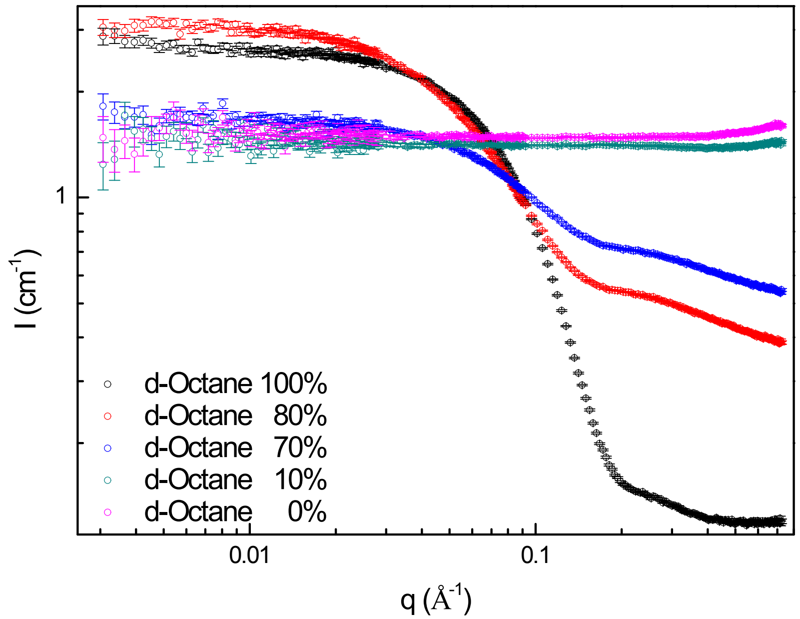
ANALYSIS OF SANS Contrast matching exp.

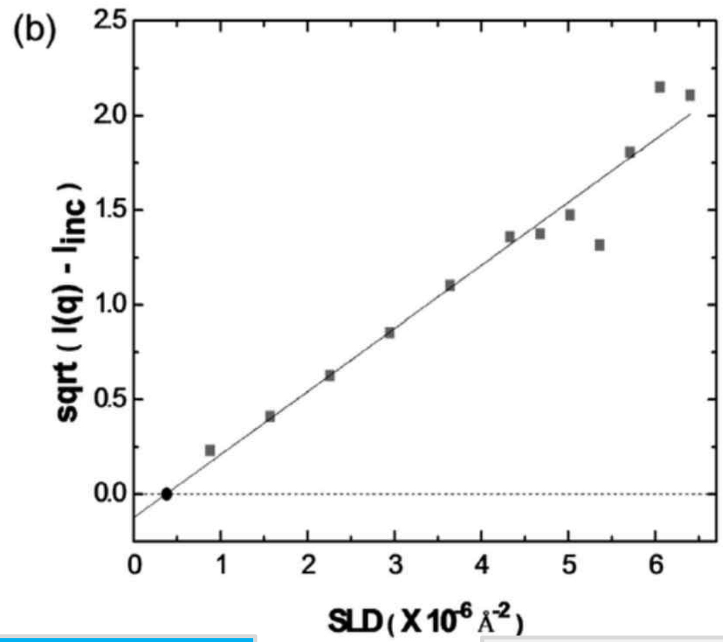


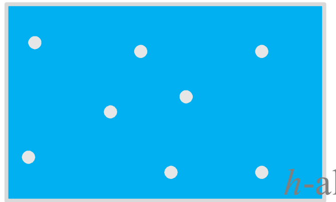


ANALYSIS OF SANS Contrast matching exp.

(IL : octanol : water = 1 : 4 : 2)

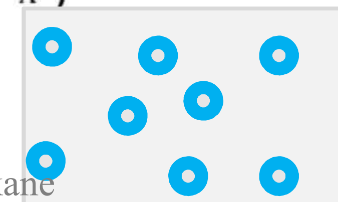






h-alkane

d-alkane

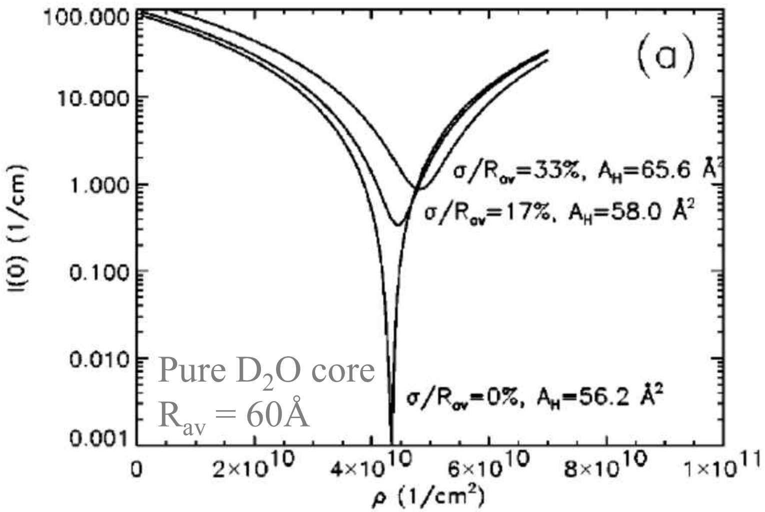


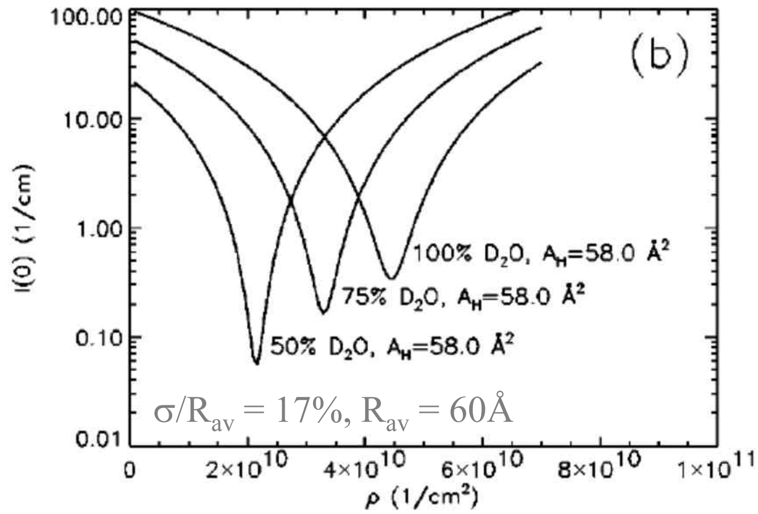
$\rho_{shell} \sim 0.7 \pm 0.1$ E-06 (Å^{-2})

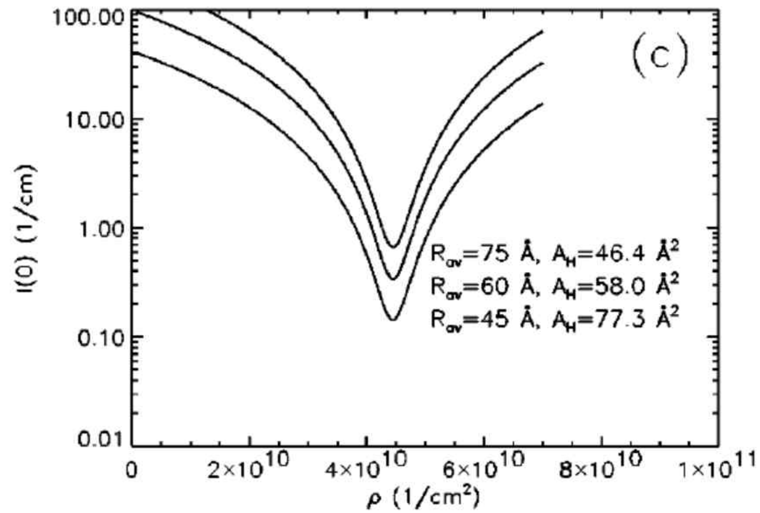
Kang et. al., *Phys. Chem. Chem. Phys.* **17**, 27833 (2015)

- **Model calculation of I(0)**

$$f(0) = V_c(\rho_c - \rho_s) + (V_c+V_s)(\rho_s - \rho_{solvent}) : form\ factor$$





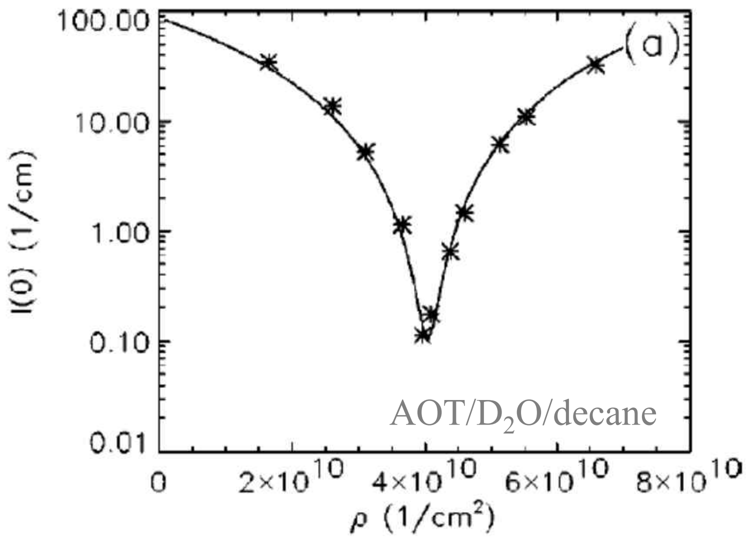


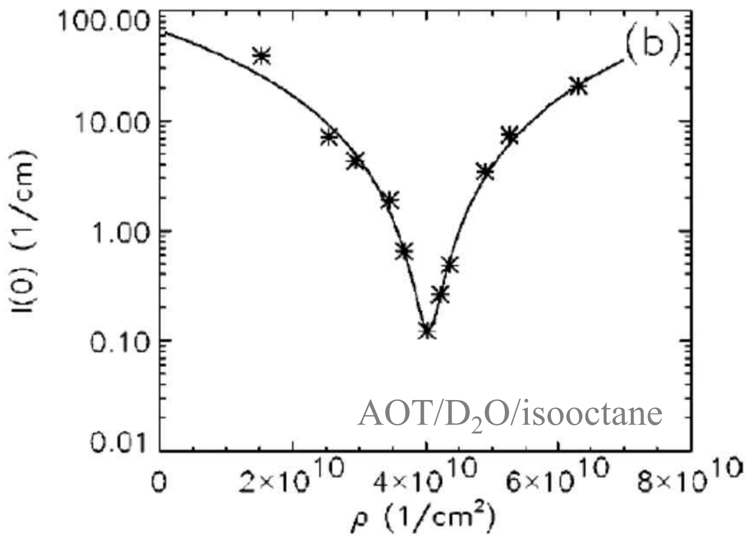
If the droplets are monodisperse (same composition and same ρ_c, ρ_s)

→ matched out at same $\rho_{solvent}$

Depth : Mainly determined by σ/R
Position : Mainly determined by composition of core
Absolute intensity : Mainly determined by mean radius

- **Experimental values of I(0)** with least-squares fit



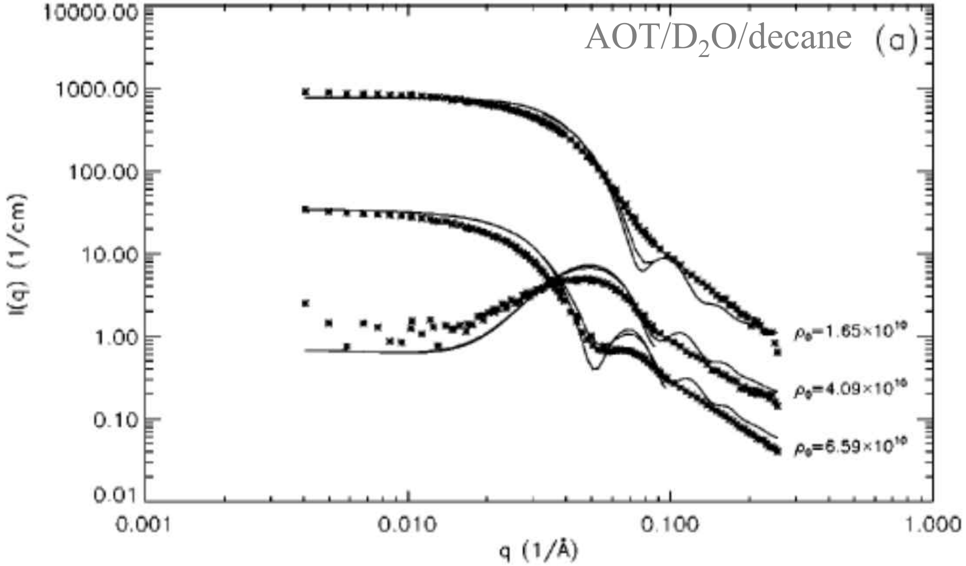


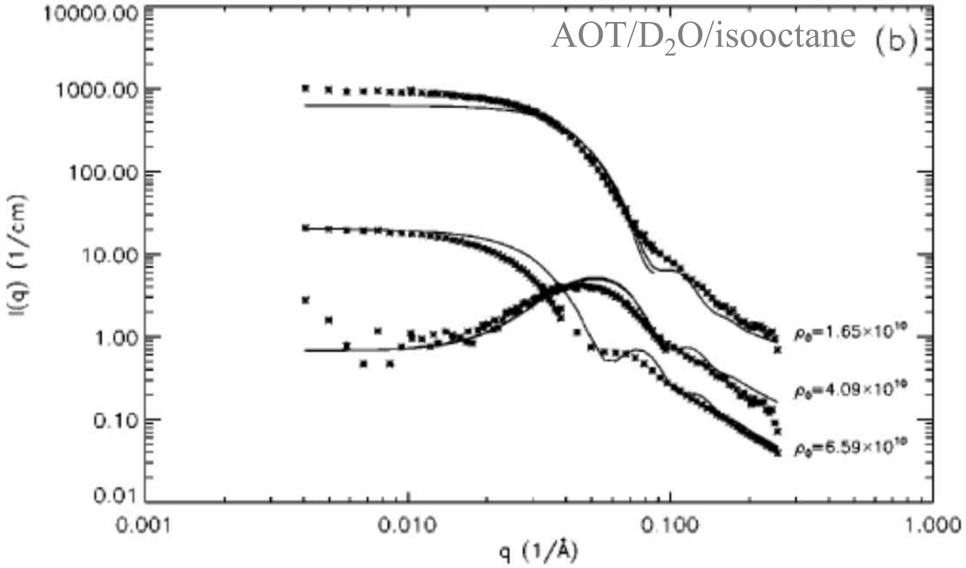
Parameter	AOT/D_2O/dec	AOT/D_2O/iso
R_{av} (Å)	61.91 ± 1.1	56.34 ± 1.0
σ / R_{av}	0.094 ± 0.009	0.120 ± 0.010
Purity_{D_2O}	0.928 ± 0.004	0.923 ± 0.004
A_{head} (Å^2)	54.9 ± 1.2	60.7 ± 1.2

Comparable with the value determined by contrast variation light scattering

- Hofmeier and cowokers, σ/R_{av} = 12% in the AOT/water/hexane
- Christ and Schurtenberger, σ/R_{av} = 10% in the AOT/water/decane

RESULTS & DISCUSSION SANS data fitting





data & model fitted to the I(0)

At higher q
modeled I(0) is much more oscillatory than the experimental I(q)

Suggest

The droplets are **more polydisperse** than indicated by the I(0) data
or
they are **nonspherical**

- **Angular dependent radius**

with, fluctuation amplitude u_{lm}, spherical harmonics Y_{lm}

$$R(\Omega) = R_{av} \left[1 + \underbrace{\Sigma\, u_{lm} Y_{lm}(\Omega)}_{\text{deviation from sphere}} \right]$$

- $u_{00} Y_{00}(\Omega)$: polydispersity term
- $u_{2m} Y_{2m}(\Omega)$: first order shape fluctuation term

$$\sigma / R_{av} \sim \sqrt{\frac{\langle |u_{00}|^2 \rangle}{4\pi}}$$

$$\varepsilon \text{ (axis ratio)} = \frac{R(0)}{R(\pi/2)} = \frac{1 + u_{00}/2\sqrt{\pi} + 10\sqrt{5/\pi}\, u_{20}/4}{1 + u_{00}/2\sqrt{\pi} - 5\sqrt{5/\pi}\, u_{20}/4}$$

Safran, *J. Chem. Phys.* **78**, 2073 (1983)

RESULTS & DISCUSSION Determination of the bending constant

$$\langle |u_{00}|^2 \rangle = \frac{k_B T}{12k \;\square\; 8(R/R_0)(k + k'/2) + 6k\square}$$

$$\langle |u_{20}|^2 \rangle = \frac{k_B T}{16(R/R_0)(k + k'/2) \;\square\; 12k\square}$$

Safran, *Phys. Rev. A* **43**, 2903 (1991)

where
k : bending elastic constant
k' : Gaussian bending elastic constant of the film
R_0 : droplet radius at the emulsification boundary

σ/R_{av}	ϵ	$\langle \lvert u_{00} \rvert^2 \rangle$	$\langle \lvert u_{20} \rvert^2 \rangle$	$\kappa\ (k_bT)$	$\bar{\kappa}\ (k_bT)$	System
0.157*	1.56*	0.310	0.0133	3.4±0.2	−5.9±0.4	Present measurements
0.156*	1.72*	0.306	0.0201	2.35±0.1	−3.8±0.2	AOT/D_2O/decane
						AOT/D_2O/iso-octane
0.22*	1.47	0.61	0.011*	3.9	-7.2	AOT/D_2O/decane
				(3.8)	(-7.5)	[14]
0.17	2.5	0.34	0.062	0.92*	−0.38*	$C_{10}E_5$/D_2O/octane
(0.20)						[57]
0.17	2.2	0.29	0.043	1.25*	−0.80*	$C_{10}E_5$/D_2O/*n*-dodecane
(0.15)						[15]

[14]Arleth and Pedersen, *Phys. Rev. E* **63**, 61406 (2001), [57]Safran and cowokers, *Phys. Rev. Lett.* **65**, 3348 (1990)
[15]Hellweg and Lagevin, *Phys. Rev. E* **57**, 6825 (1998)