Shape fluctuations of a spherical surfactant shell in a microemulsion

Antonio Faraone, Jason S. Gardner,
and Michihiro Nagao

Summer School on Methods and Applications of Neutron Spectroscopy

June 25-29, 2007

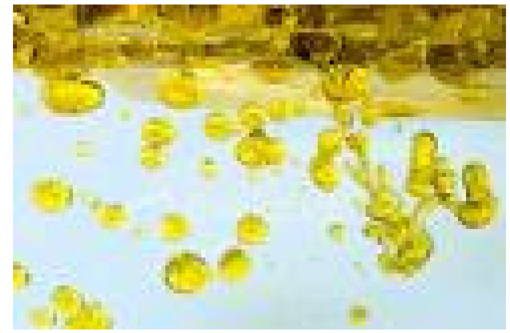
NIST Center for Neutron Research
Gaithersburg, MD 20899

Surfactant molecules

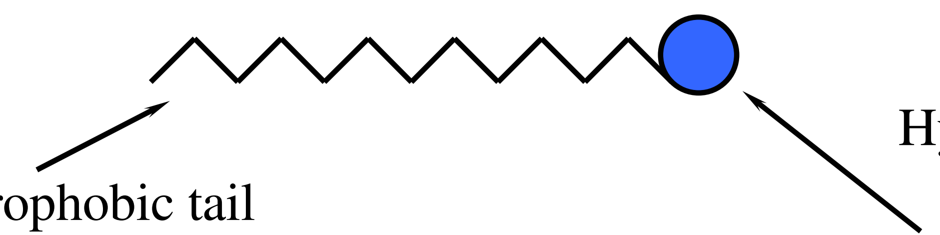
•Oils and water do not mix! Why?

Water is a polar liquid, $\varepsilon = 81$;

Oils are non polar, $\varepsilon \sim 2$



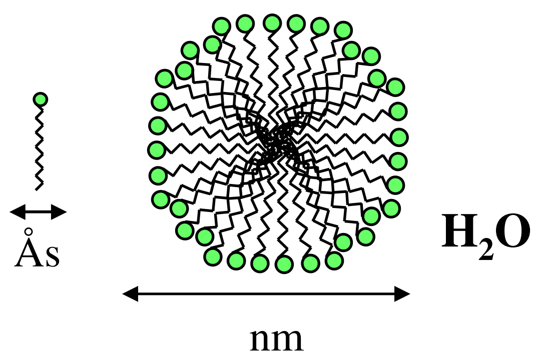
A surfactant ("Surface Active Agent") is soluble both in water and in organic liquids (oils)



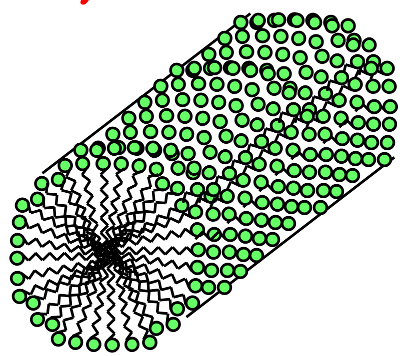
Surfactant aggregates in water

When surfactants are dissolved in water they:
- reduce the surface tension because they are adsorbed on the surfaces
- form variety of aggregates – micelles, lamellae, bicelles, vesicles, etc

Spherical micelles

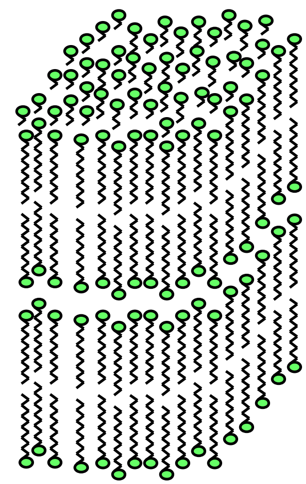


Cylindrical micelles

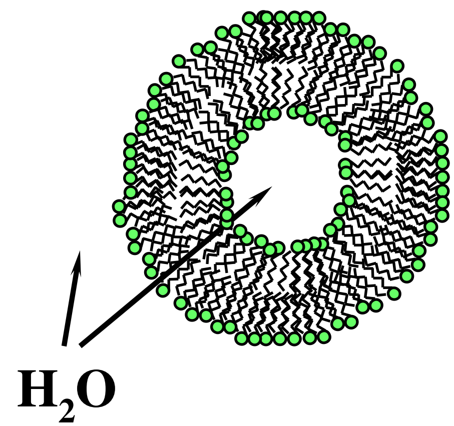


Wormlike micelles can be as long as few microns

Lamellae



Vesicles



Surfactants are everywhere

Surfactants are very useful to:

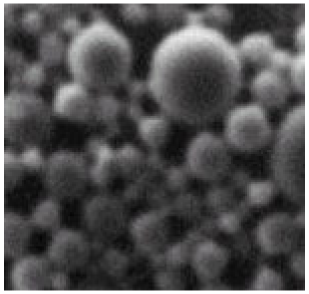
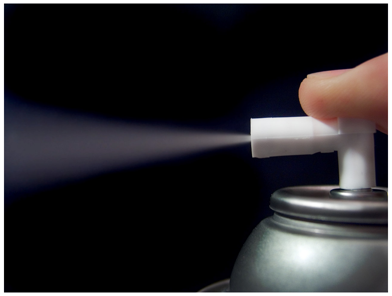
- Reduce the interfacial tension
- Solubilize oils in water
- Stabilize liquid films and foams
- Modify the interparticle interactions
- Stabilize dispersion
- Modify the contact angle and wetting
- …

Surfactants are everywhere II

Surfactants in our daily life:

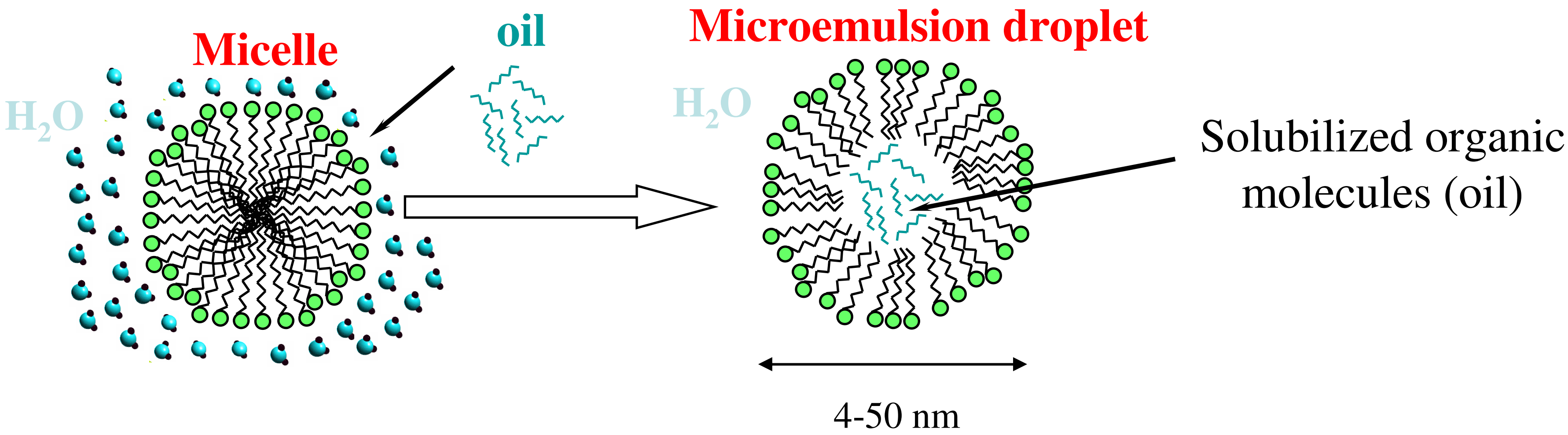
- Cosmetics – moisturizers, lotions, healthcare products, soap, …
- Food – mayonnaise, margarine, ice cream, milk, …
- Industry – lubricants, stabilizers, emulsifiers, detergents, …
- Medicine – drugs, bio applications, …
- Agriculture – aerosols, fertilizers, …
- …



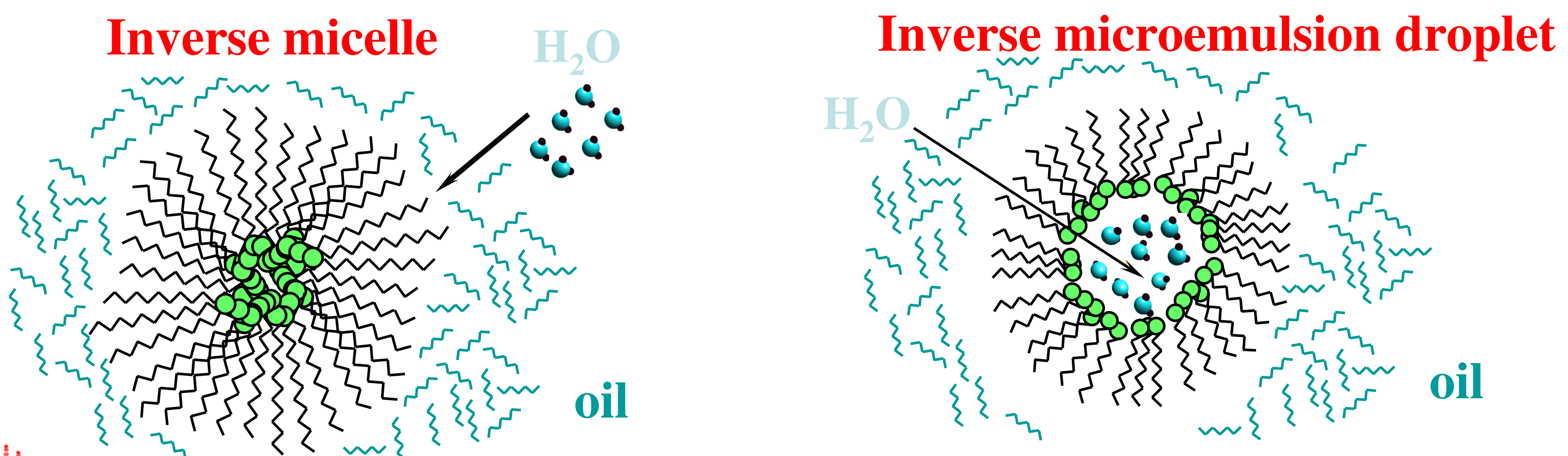




Micelles and Microemulsions

Oils and water do not mix?!? The surfactants help them mix.

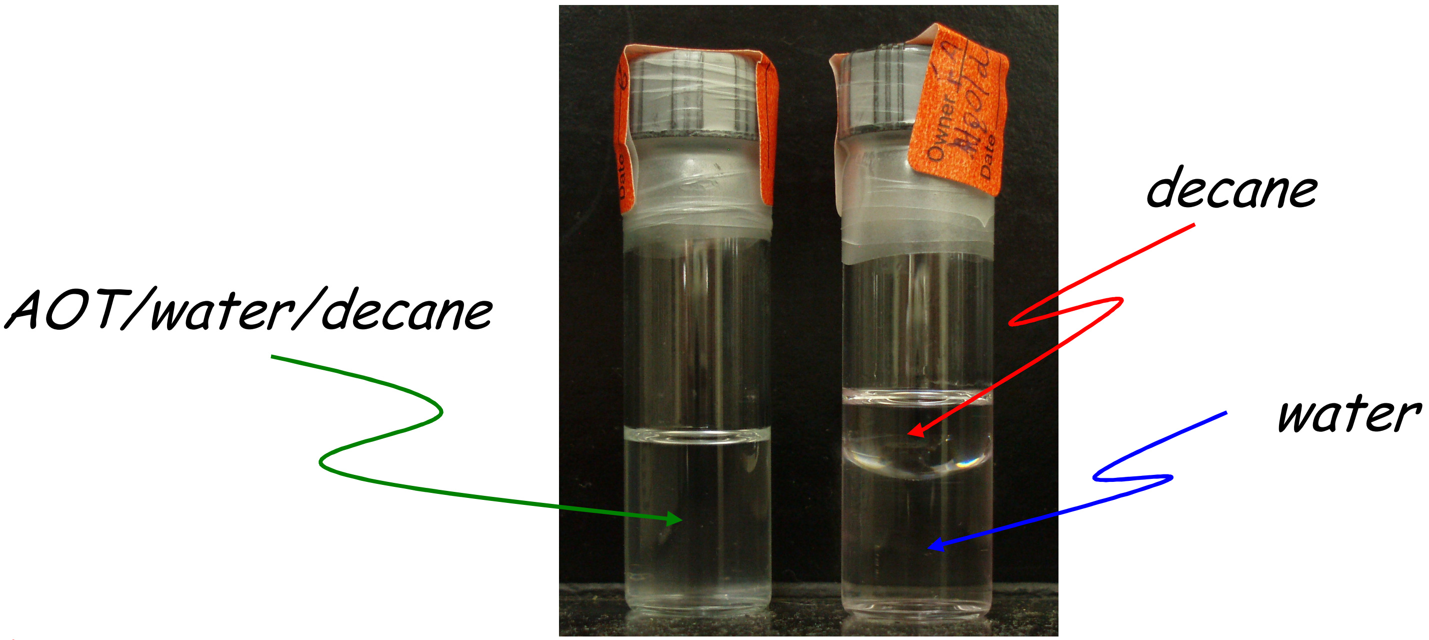


When surfactants are dissolved in oils they form “inverse” micelles, …



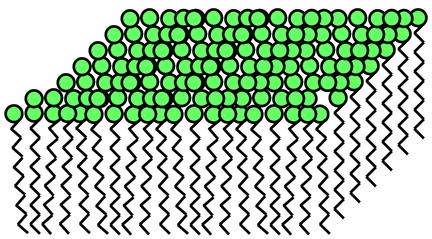
Microemulsion Properties

- Thermodynamically stable, isotropic, and optically transparent solutions
- The diameters range between 2 and 50 nm



Properties of the surfactant film

Surfactant film

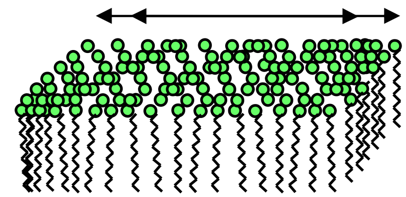


Properties of the surfactant film change with:

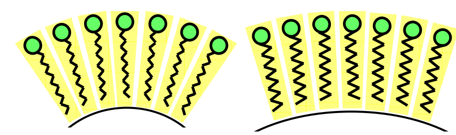
- Molecular structure
- Additives
- Ionic strength
- Co-surfactant
- Temperature, pressure etc.

Properties of the surfactant film:

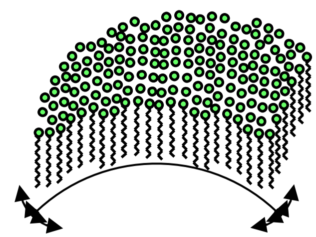
- Interfacial tension
- Lateral elasticity



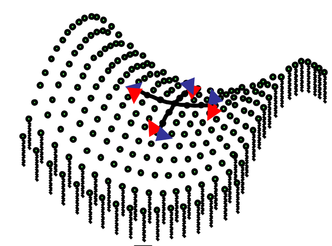
- Spontaneous curvature



- Bending elasticity



- Saddle splay elasticity



Helfrich Free Energy

$$E = \int \left[\gamma + \frac{k}{2}\left(\frac{1}{R_1} + \frac{1}{R_2} - \frac{2}{R_s} \right) + \frac{\bar{k}}{R_1 R_2} \right] dS$$

Microemulsion: How to study them

Structure

- Light Scattering
- Small Angle Scattering (Neutrons: SANS; x-rays: SAXS)
  - Large length scales (10 Å-1000 Å)
  - 'Low resolution diffraction technique'

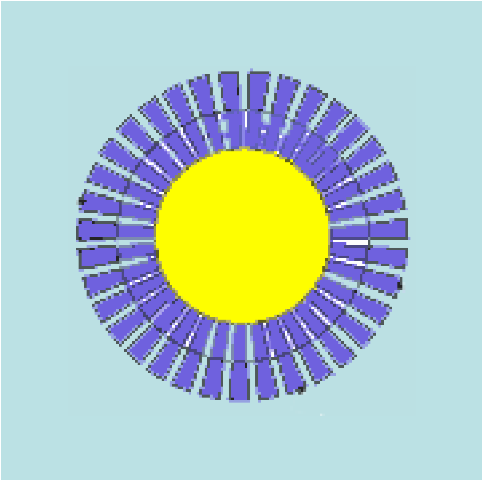
SANS:

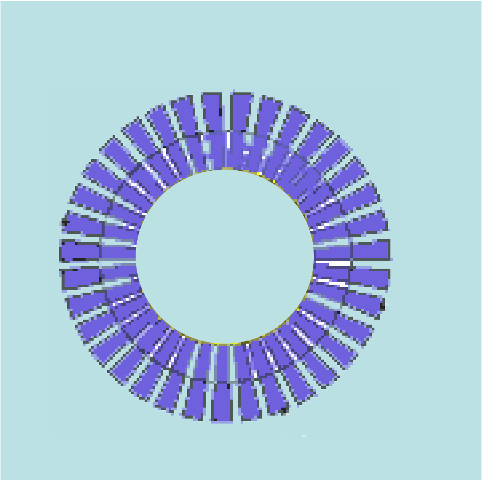
The intensity is the FT of the contrast distribution.

Contrast: Difference in Scattering Length Density

$$\rho = \frac{d}{M_w} N_A \sum_i b_i^{coh}$$

Contrast Matching Technique



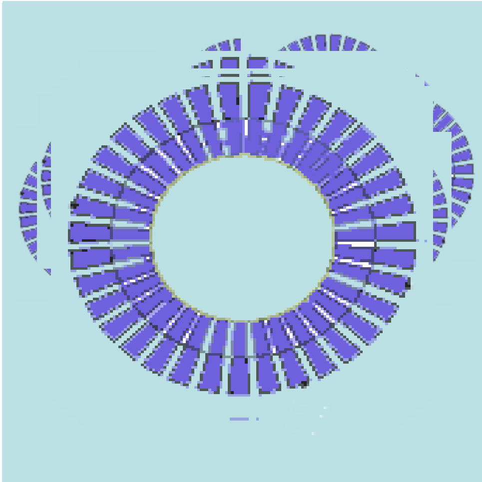


Microemulsion: How to study them

Dynamics

Microemulsions move in solution because of thermal energy.

- Diffusion
- Shape fluctuations



Experimental techniques:

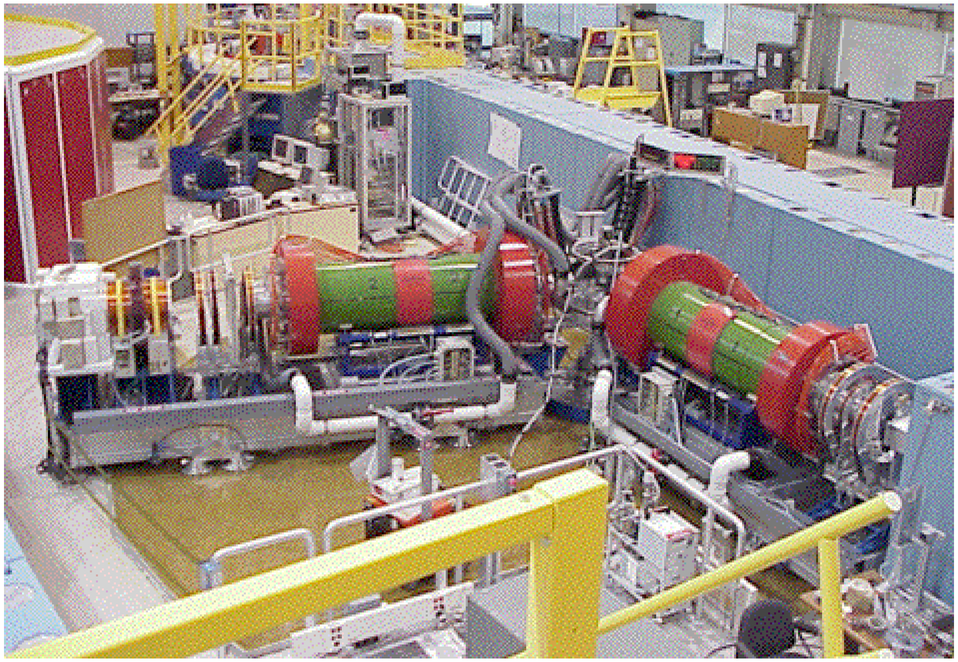
- Dynamic Light Scattering
- Nuclear magnetic resonance
- Neutron Spin-Echo (NSE)

NSE: T scale ~ 0.01 – 100 ns, L scale 1 – 100 Å

Neutron Spin-Echo Spectroscopy

- Achieves the highest energy resolution (100 ns ~ 0.02 μeV) among all neutron spectrometers by encoding neutron's individual velocity into their spins.
- NSE spectrometers work in the time domain.
- NSE measures the scattering length density fluctuations (corresponding to the SANS pattern).
- NG5-NSE is today the only NSE spectrometer operating in US.

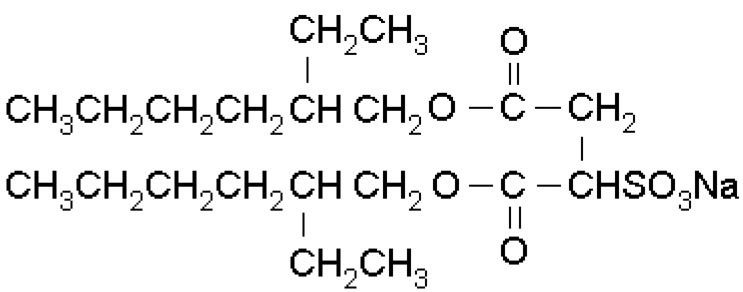
NCNR Neutron Spin-Echo Spectrometer:
NG5-NSE

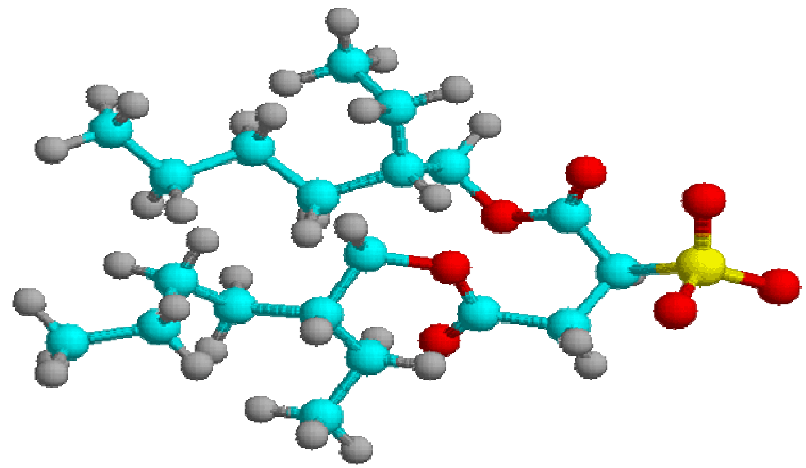


Experimental

Shape fluctuations in AOT/water/hexane microemulsion

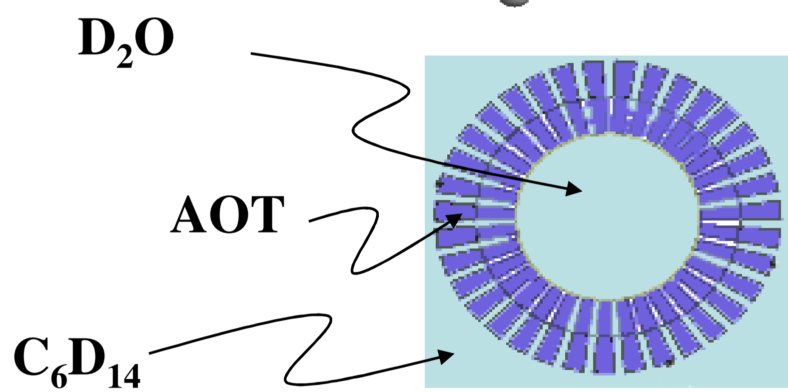
AOT



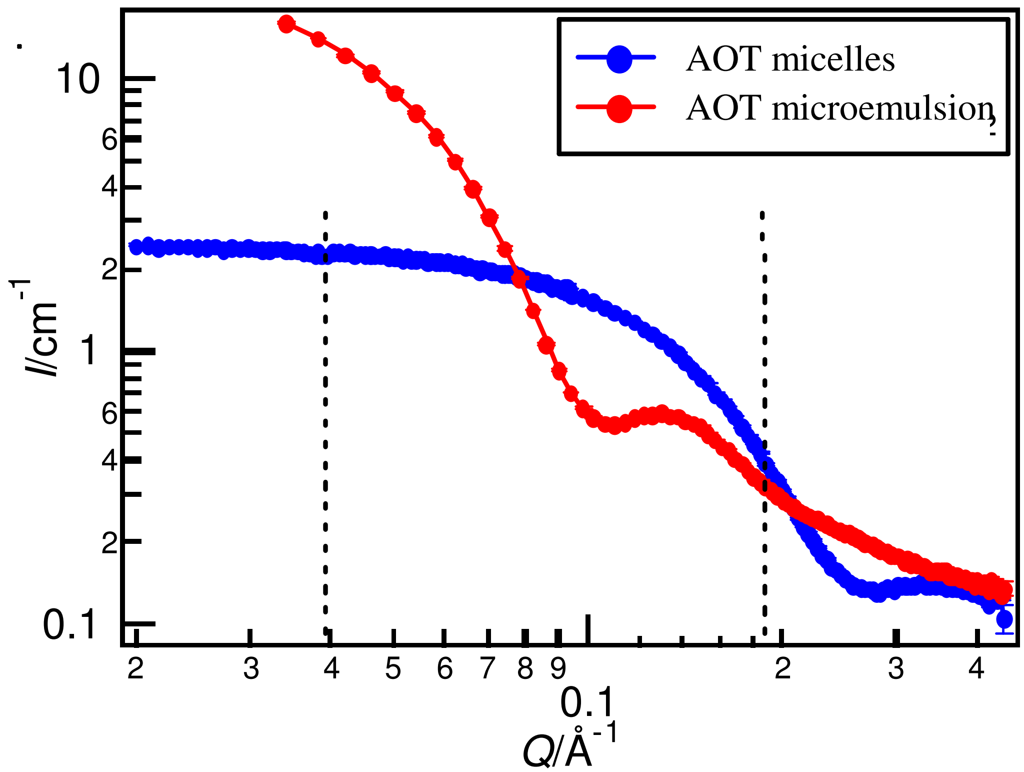


Inverse Microemulsion droplet

- Translational Diffusion
- Shape Fluctuations



SANS data



	σ_S (barn)	b^{coh} (fm)	b^{incoh} (fm)
H	82.03	-3.741	25.274
D	2.05	6.671	4.04

$AOT/D_2O/C_6D_{14}$

Vol. fraction	0.078
Avg. radius (Å)	~ 30
polydispersity	~ 0.2

SLD ($\times 10^{-6}$ Å^{-2})

n-hexane	-0.67
H_2O	-0.56
d-hexane	6.14
D_2O	6.35
AOT	0.10

Data Analysis: Diffusion

Fick's Law, Diffusion Equation

$$\frac{\partial \phi}{\partial t} = -D\nabla^2\phi$$

$$I(Q,t) = \exp\left[-DQ^2t\right]$$

NSE measures coherent dynamics.

- The diffusion coefficient measured is the collective diffusion coefficient.
- At finite concentration inter-particle interactions make the measured (effective) diffusion coefficient Φ and Q dependent: $D_c(\Phi,Q)$.
- In the limit of infinite dilution the diffusion coefficient coincides with the self diffusion coefficient.

Data Analysis: Shape Fluctuations

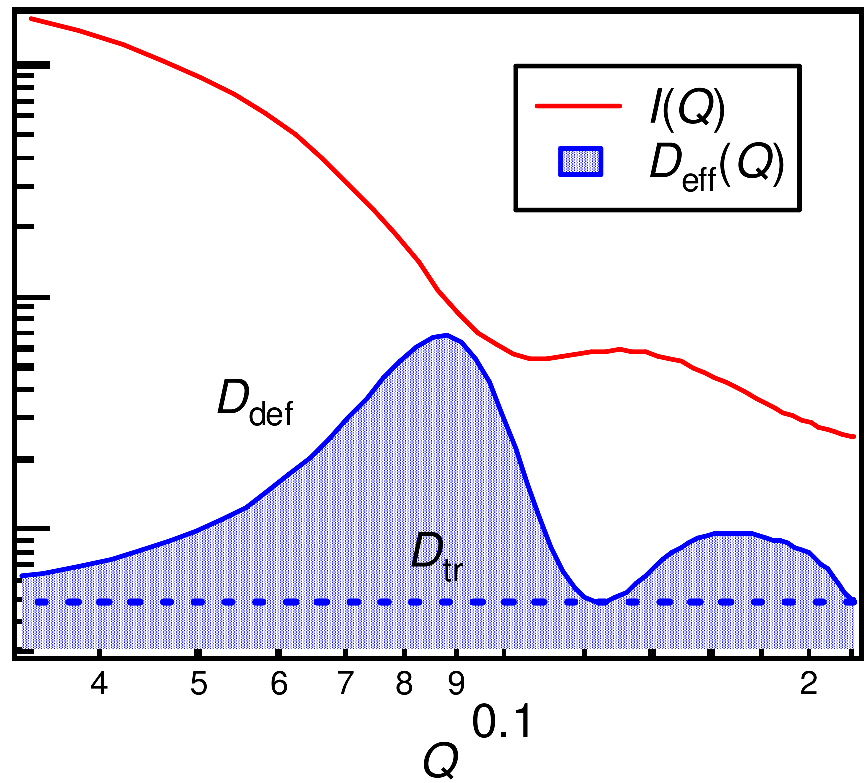
$$E_{bend} = \frac{k}{2}\int dS\left(\frac{1}{R_1}+\frac{1}{R_2}-\frac{2}{R_s}\right)+\bar{k}\int dS\,\frac{1}{R_1R_2}$$

Expansion of r in spherical harmonics with amplitude a:

$$r(\Omega) = r_0\left(1+\sum_{l,m} a_{lm}\mathrm{Y}_{lm}(\Omega)\right)$$

Frequency of oscillations of a droplet:

$$\lambda_2 = \frac{k}{\eta R_0^3}\left[4\frac{R_0}{R_s}-3\frac{\bar{k}}{k}-\frac{3k_BT}{4\pi k}f(\phi)\right]\frac{24\eta}{23\eta'+32\eta}$$



Data Analysis III

Translational Diffusion ⇒ $$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-DQ^2 t\right]$$

AOT/D_2O/C_6D_{14} Microemulsion
Translational Diffusion + shape fluctuations ⇒ $$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}(Q)Q^2 t\right]$$

The two dynamical processes are statistically independent.

$$D_{eff}(Q) = D_{tr} + D_{def}(Q)$$

$$D_{eff}(Q) = D_{tr} + \frac{5\lambda_2 f_2(QR_0)\langle |a_2|^2 \rangle}{Q^2\left[4\pi[j_0(QR_0)]^2 + 5 f_2(QR_0)\langle |a_2|^2 \rangle\right]}$$

$$f_2(QR_0) = [4 j_2(QR_0) - QR_0 j_3(QR_0)]^2$$

The goal is the bending modulus, k

$$D_{eff}(Q) = D_{tr} + \frac{5\lambda_2 f_2(QR_0)\left\langle |a_2|^2 \right\rangle}{Q^2\left[4\pi[j_0(QR_0)]^2 + 5 f_2(QR_0)\left\langle |a_2|^2 \right\rangle\right]}$$

$$\boxed{k = \frac{1}{48}\left[\frac{k_B T}{\pi p^2} + \lambda_2 \eta R_0^3 \frac{23\eta' + 32\eta}{3\eta}\right]}$$

λ_2 – the damping frequency – **frequency of deformation**

$\langle |a|^2 \rangle$ – mean square displacement of the 2-nd harmonic – **amplitude of deformation**

p^2 – size polydispersity, measurable by SANS or DLS

η and η' are the solvent and core viscosities