Diffusion of Surfactant Micelles and Shape Fluctuations of Microemulsions Studied by Neutron Spin Echo (NSE)

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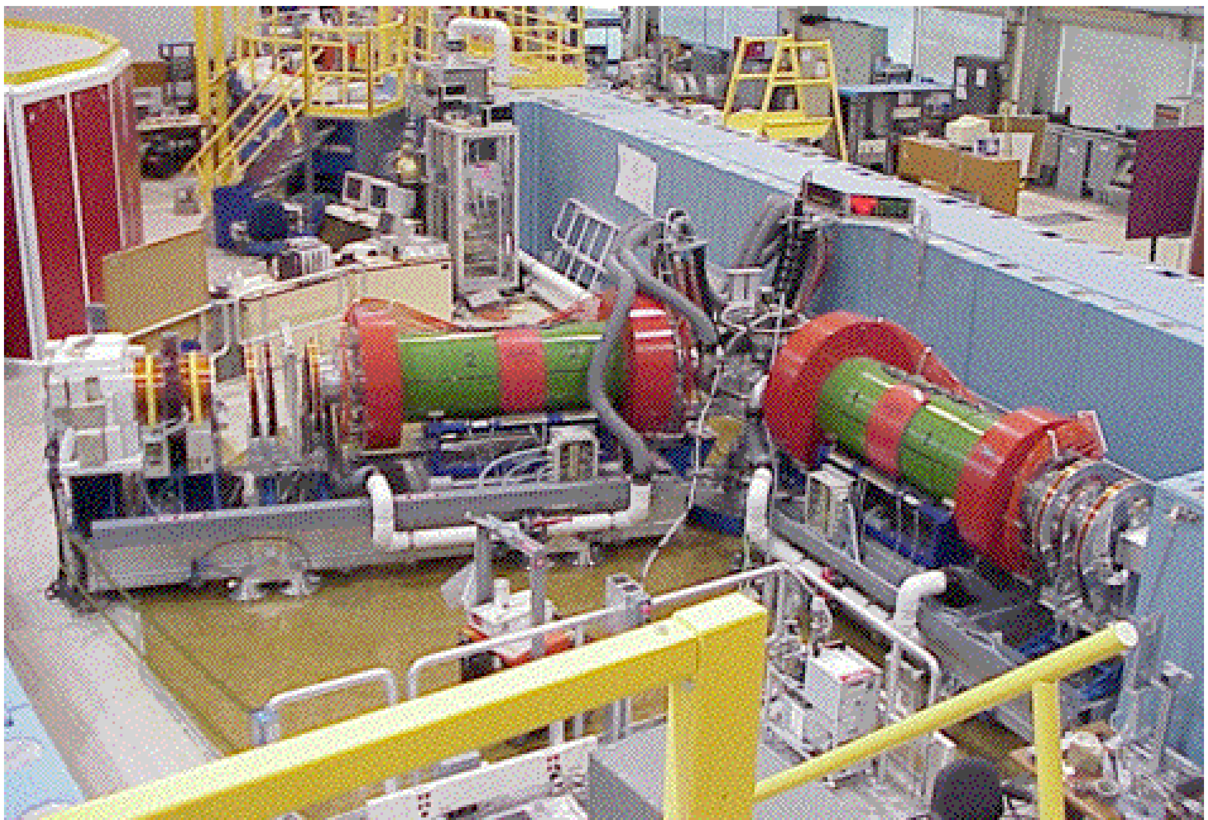

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NSE is a "dynamic" method

- NSE is a new method at NIST. The idea has come to Mezei in 1972 at a red traffic light at the corner of Alagút street in Budapest

- NSE is complementary to SANS. Using NSE we can measure the dynamics of the scattering system:

SANS ←→ static picture **NSE ←→ dynamic picture**

- NSE is a quasielastic method – small deviation from the elastic scattering

SANS ←→ elastic scattering **NSE ←→ quasielastic scattering**

- The NIST spectrometer is best used for measuring coherent diffusive or dispersionless excitations in the range of 0.01 to 200 nanoseconds. Bridges the gap in time scale between conventional inelastic neutron scattering and dynamic light scattering. Yields the intermediate scattering function *I*(*q*,*t*) as a result.

$$I(Q,t) = \int_{-\infty}^{\infty} S(Q,\omega)\cos(\omega t)\,d\omega$$

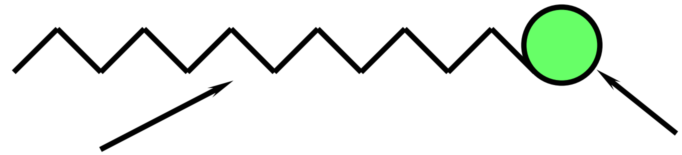
Content

- Surfactant aggregates in solution
- Why NSE?
- Experimental system
- NSE method
- Summary

Surfactant aggregates in solution

Oils and water do not mix!
Why?
Water is a polar liquid, $\varepsilon = 81$
Oils are non polar, $\varepsilon \sim 2$
(ε - dielectric const.)

Surfactant molecule



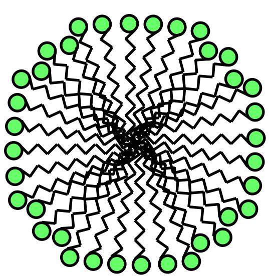
Hydrophobic tail
CH_3-CH_2-CH_2- …
CF_3-CF_2-CF_2- …

Hydrophilic head
$SO_3^-Na^+$
$NH_3^+Cl^-$
-$(OCH_2CH_2)_n$-

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

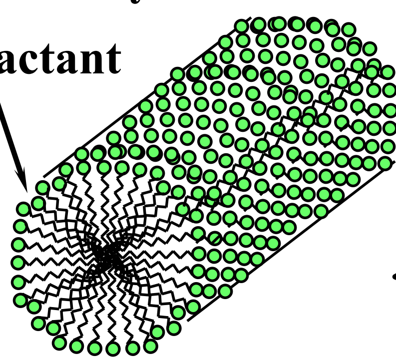
Spherical micelles



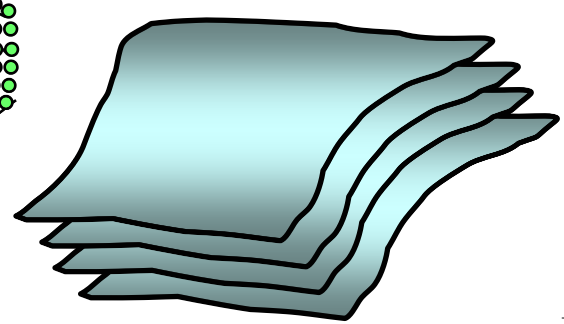
Surfactant

H_2O

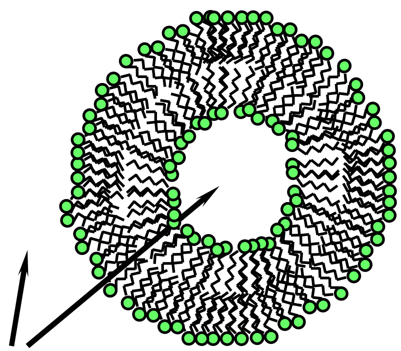
Cylindrical micelles



Lamellae



Vesicles

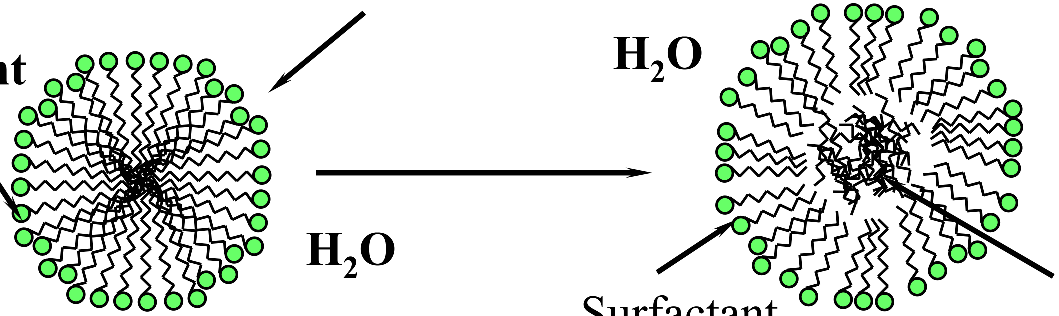


H_2O

micelles are small,
~ 4 nm in diameter

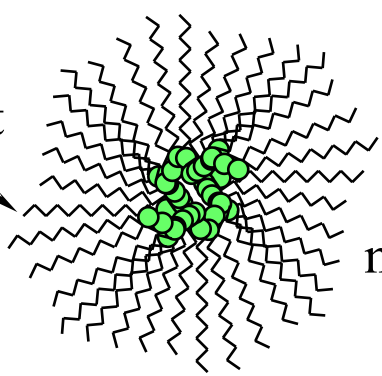
Micellar properties

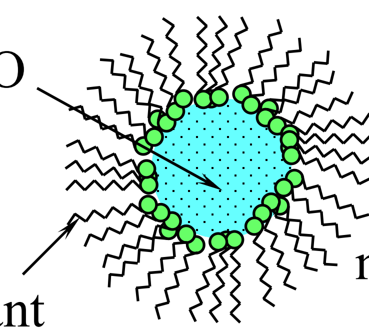
Oils and water do not mix?!? The surfactants help them mix.



microemulsion droplets are bigger, dia. 4 - 50 nm

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





Applications

Surfactants are very useful:

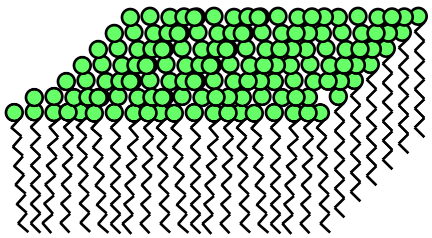
- To reduce the interfacial tension between oils and water
- To solubilize oils in water (and water in oils)
- To stabilize liquid films and to produce foams
- To stabilize emulsions
- To modify surfaces and interparticle interactions
- To facilitate spreading of liquids on surfaces (wetting)
- Other applications

Surfactants in our daily life:

- Food – mayonnaise, ice cream, milk, …
- Industry – lubricants, stabilizers, emulsifiers, foamers, detergents, soaps …
- Medicine – drugs, bio applications, …
- Cosmetics – healthcare products …
- Agriculture – aerosols, fertilizers …
- Many other …

Properties of the surfactant film

Surfactant film

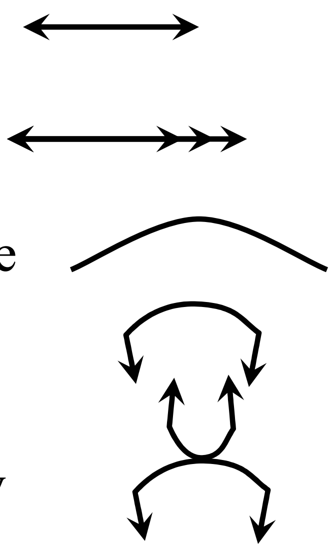


Properties of the surfactant film change with:

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

Properties of the surfactant film:

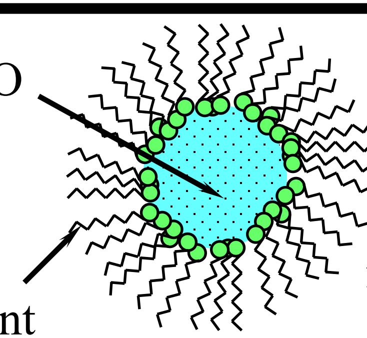
- Interfacial tension
- Lateral elasticity
- Spontaneous curvature
- Bending elasticity
- Saddle splay elasticity



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

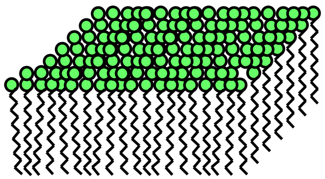
Why are the microemulsions so interesting:

- Thermodynamically stable, isotropic, and optically transparent solutions
- $R \sim 2 - 50$ nm (good scatterers)
- The curvature of the surfactant film can be controlled



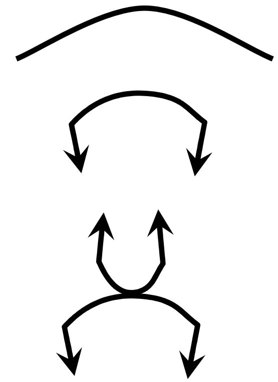
Why NSE?

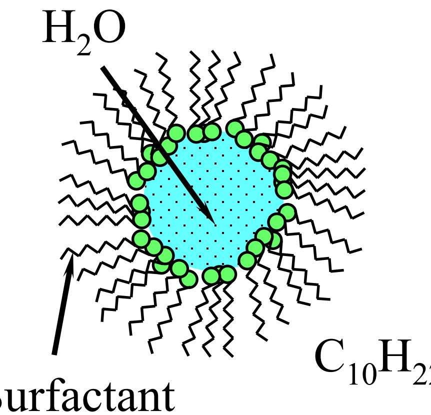
Surfactant film

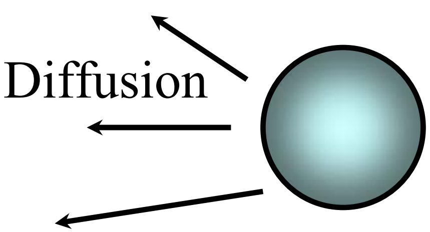


Goals:

- Spontaneous curvature
- Bending elasticity
- Saddle splay elasticity

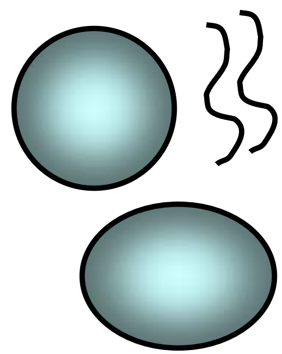






Diffusion:
- NMR
- Dynamic light scattering

(t scale > 100 ns)



Shape fluctuations are in very short time and length scales!

Spontaneous curvature, bending elasticity, saddle splay elasticity

↓

shape fluctuations

↓

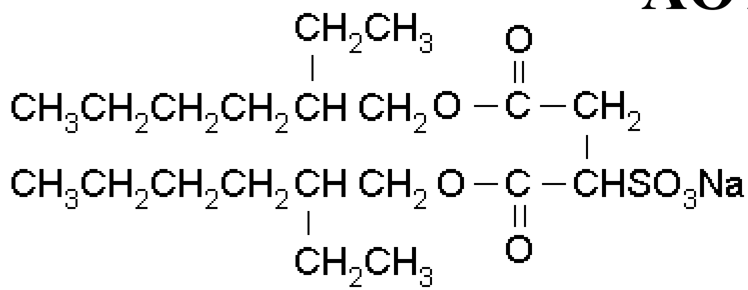
NSE

(t scale ~ 1 - 10 ns)

Experimental

Surfactant molecule

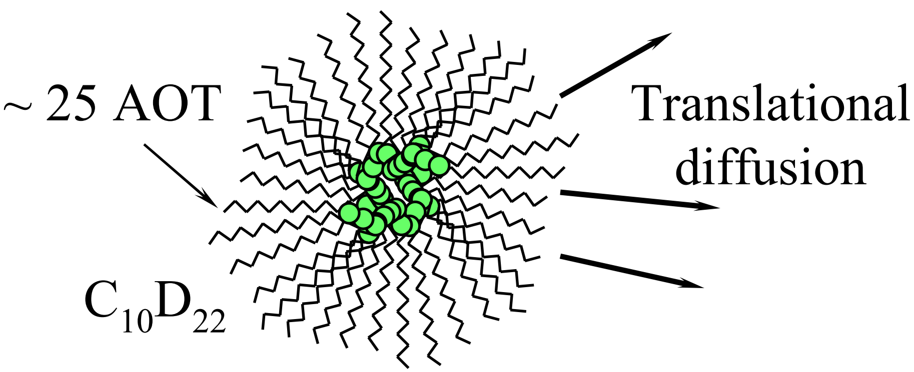
AOT



Experiment I

Diffusion of AOT micelles in $C_{10}D_{22}$
(5.4 % vol. fraction)

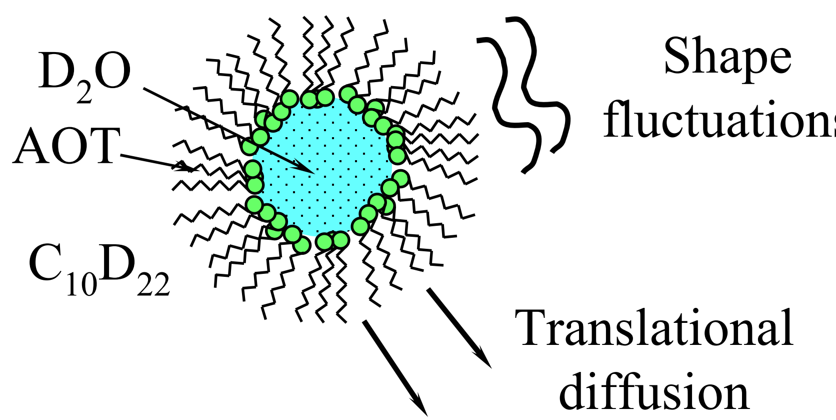
Inverse spherical micelle



Experiment II

Shape fluctuations in
$AOT/D_2O/C_{10}D_{22}$ microemulsion
(5.4/4.6/90 % vol. fraction)

Inverse microemulsion droplet

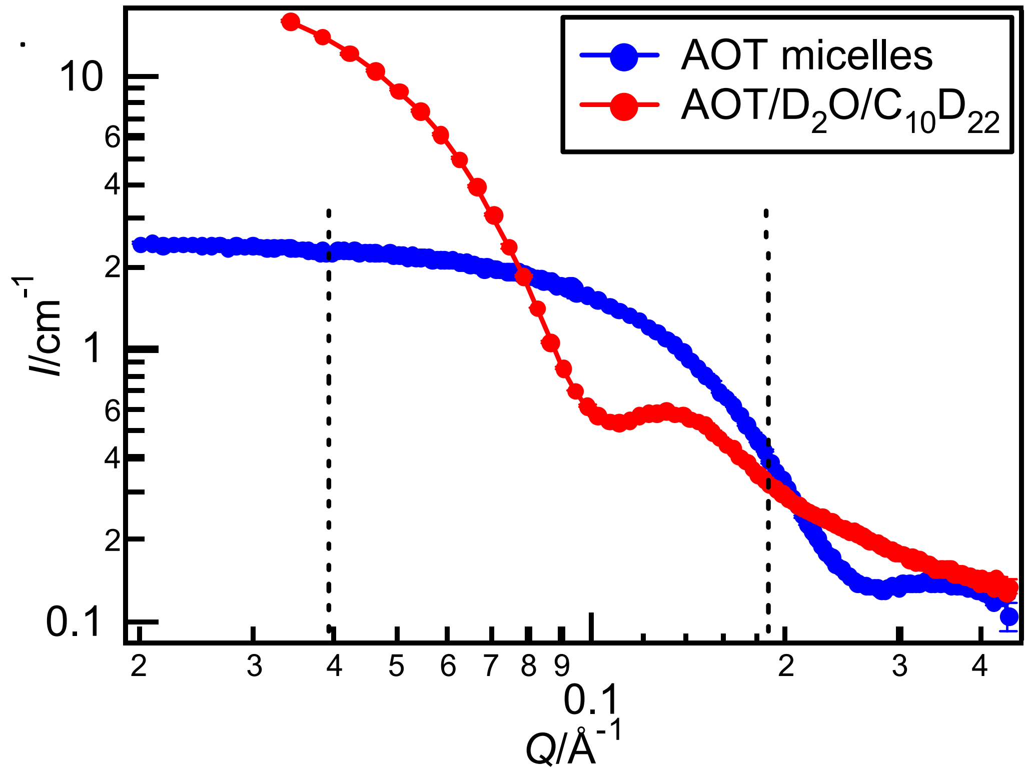


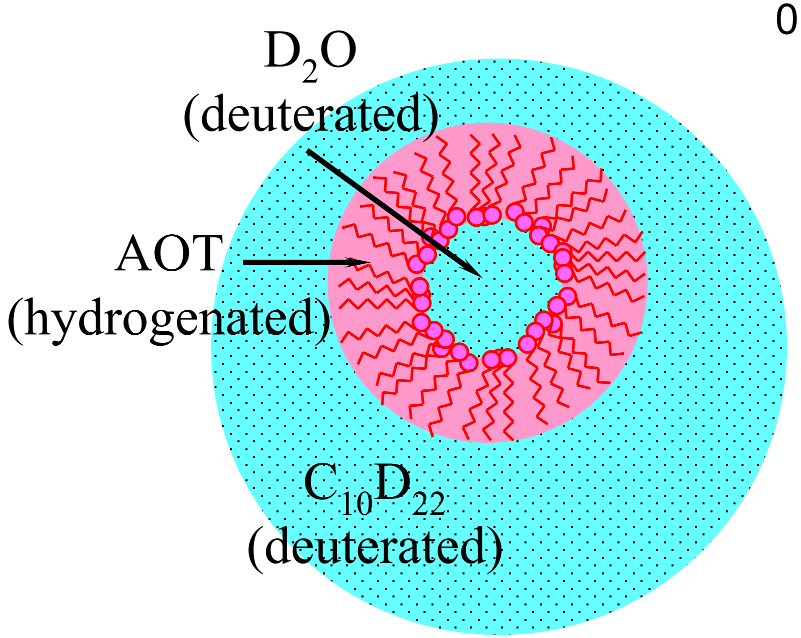
Shell contrast

cross section (barn)
H: 82.0 D: 7.6

SLD ($\times 10^{-6}$ Å^{-2})

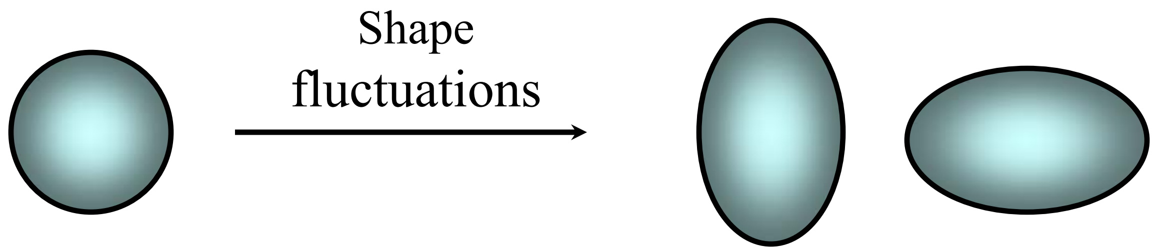
n-decane	-0.49
H_2O	-0.56
d-decane	6.5
D_2O	6.4



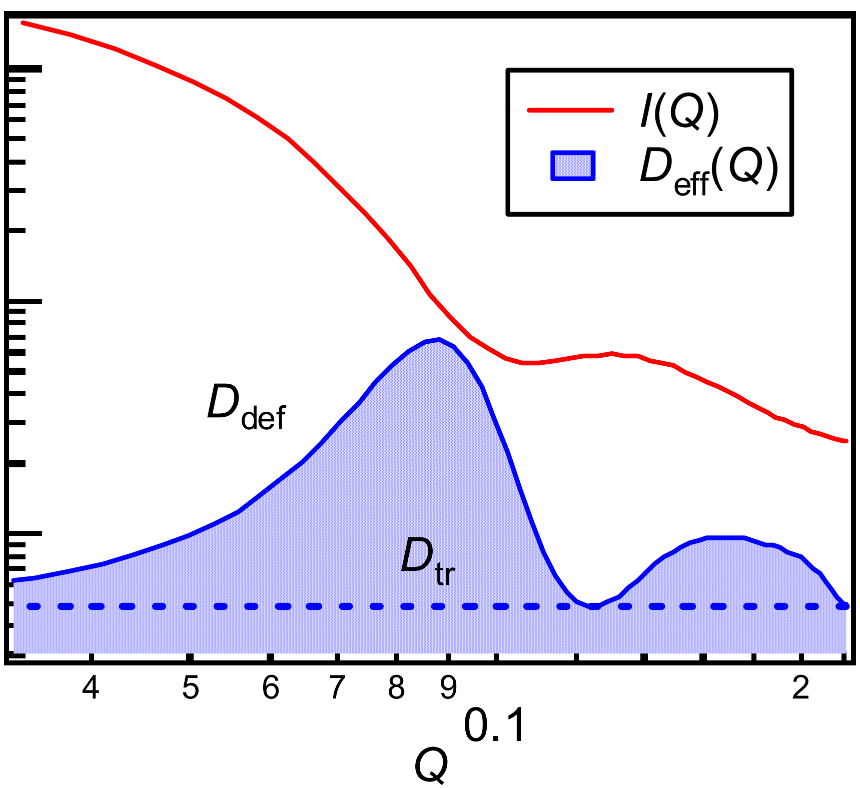


	Experiment I micelles	Experiment II microemulsion
Vol. fraction	0.054	0.1
Avg. radius (Å)	15.9	34
polydispersity	-	0.25
SLD core (Å^{-2})	-	6.4×10^{-6}
SLD shell (Å^{-2})	1×10^{-6}	1.6×10^{-6}
SLD solv. (Å^{-2})	6.5×10^{-6}	6.5×10^{-6}

Data analysis



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



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:

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

Summary of data analysis

Experiment I

AOT micelles in $C_{10}D_{22}$ $\longrightarrow$ $$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}Q^2t\right]$$

Experiment II

AOT/D_2O/$C_{10}D_{22}$ microemulsion $\longrightarrow$ $$\frac{I(Q,t)}{I(Q,0)} = \exp\left[-D_{eff}(Q)Q^2t\right]$$

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

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

$$f_2(QR_0) = 5[4j_2(QR_0) - QR_0 j_3(QR_0)]^2$$

Goal: Bending modulus of elasticity

$$k = \frac{1}{48}\left[\frac{k_BT}{\pi p^2} + \lambda_2 \eta R_0^3 \frac{23\eta' + 32\eta}{3\eta}\right]$$

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

Why is NSE so “exotic”?

- **Goals:** - Brownian diffusion in micellar systems
  - Shape fluctuations of lipid membranes and thin films
  - Intra-molecular and local segmental diffusion of proteins and polymers in solution
  - Intra- and inter- molecular dynamics of polymer melts and glasses
  - Other thermal fluctuations of soft matter

- The above phenomena produce energy transfer of **δE = 10^{-5} – 10^{-2} meV** (very small !!!)

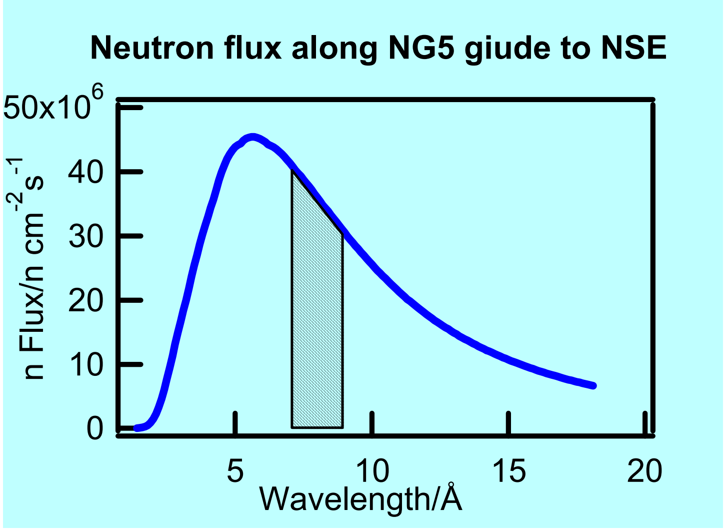
- We need low energy neutrons. Cold neutrons: λ = 5 – 12 Å, E = 0.5 – 3.3 meV

- **The problem:** neutron beam wavelength spread

$\Delta\lambda/\lambda$ = 5 – 20%, $\Delta E/E$ = 10 – 40%, **ΔE = 0.05 – 0.2 meV**

ΔE = 0.05 – 0.2 meV >> δE = 10^{-5} – 10^{-2} meV

- **The solution**: We need neutron precession in magnetic field. We are going to attach “internal” clock for each neutron. Thus, we can observe very small velocity changes of a neutron beam, regardless of the velocity spread

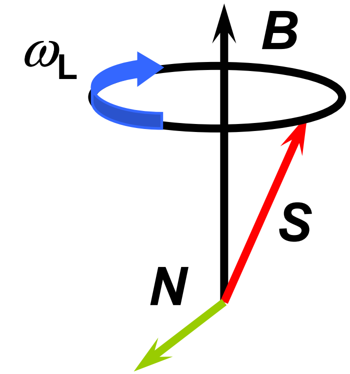


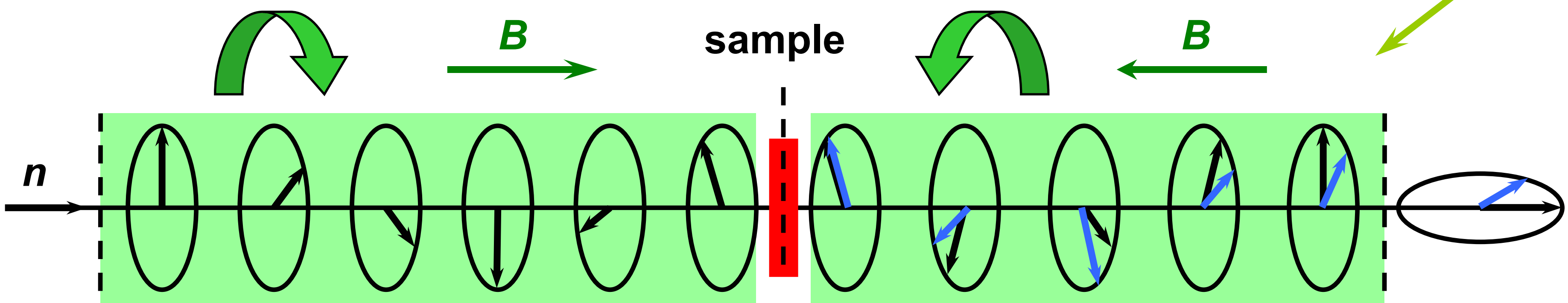
Principle of NSE

Neutrons posses spin and magnetic moment. They precess in magnetic fields with the Larmor frequency that depends on the strength of the magnetic field only. (g =1.83×10^{8} s^{-1}T^{-1})

$$N = S \times B$$

$$\omega_L = gB$$





Angle **0** φ

• elastic scattering φ **0**

• inelastic scattering φ **±**$\Delta\varphi$

<cos(±$\Delta\varphi$**)>**

$$\varphi = gB\frac{L}{v} \qquad \Delta\varphi = gBL\left(\frac{1}{v} - \frac{1}{v'}\right) = \frac{gBL\Delta v}{v^2}$$

$$\boxed{\frac{\Delta v}{v} \approx 10^{-5}\ !}$$

$$\langle P \rangle = \frac{\int_0^\infty I(\lambda) \int_{-\infty}^{\infty} S(\mathbf{Q},\omega)\cos(\Delta\varphi)\,d\omega\, d\lambda}{\int_0^\infty I(\lambda) \int_{-\infty}^{\infty} S(\mathbf{Q},\omega)\,d\omega\, d\lambda} = \left\langle \int_{-\infty}^{\infty} S(\mathbf{Q},\omega)\cos(\omega t)\,d\omega \right\rangle = \boxed{I(Q,t)}$$

Summary

• **NSE is a dynamic scattering method that yields the intermediate scattering function $I(q,t)$. NSE has the highest energy and time resolution among the neutron scattering methods, which is achieved by using the neutron precession in magnetic fields as an "internal" clock.**

• **NSE is suitable for studies on:**
- Brownian diffusion in micellar systems
- Shape fluctuations of lipid membranes and thin films
- Intra-molecular diffusion of proteins
- Local segmental diffusion of polymers in solution
- Intra- and inter- molecular dynamics of polymer melts and glasses
- Other thermal fluctuations of soft matter etc (time scale: 0.01 – 200 ns)

• **Some limitations**:
- The samples must produce strong scattering
- Hydrogenated samples in deuterated matrix are the best choice
- Samples must not be magnetic
- The scattering should be in appropriate Q-range ($0.02 < Q < 1.7$ Å^{-1})

Where to do NSE?

- NSE at NCNR, NIST, Gaithersburg is currently the only operating NSE in North America

- There are NSE spectrometers in France, Germany and Japan

- NCNR is a user facility. Beam time proposals are accepted twice a year. Information is posted at: http://www.ncnr.nist.gov/

- Further reading on NSE: http://www.mrl.ucsb.edu/~pynn/