Introduction to Neutron Spin Echo Spectroscopy

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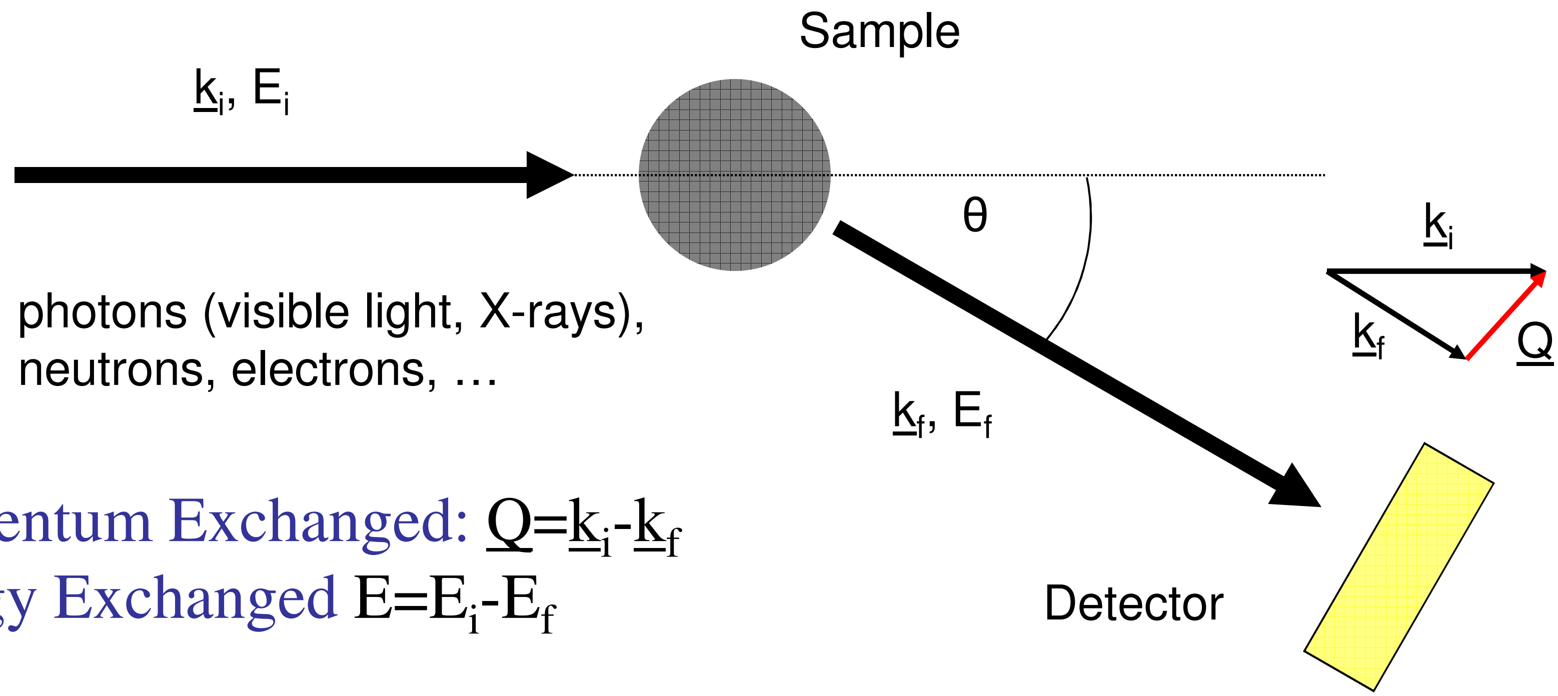
Outline

- Dynamic Neutron Scattering and NSE
  - Coherent and Incoherent Dynamics
- The principles of Neutron Spin Echo (NSE)
- NSE Spectrometers Around the World
- NSE Exercise
  - Collective Dynamics of Microemulsion Droplet.
- NSE History
- Conclusion

Dynamic Neutron Scattering

Static and Dynamic Scattering



Probe: photons (visible light, X-rays), neutrons, electrons, …

Momentum Exchanged: $\underline{Q}=\underline{k}_i-\underline{k}_f$

Energy Exchanged $E=E_i-E_f$

StaticScattering: $\dfrac{d\sigma}{d\Omega} \approx S(Q)$

Dynamic Scattering: $\dfrac{d^2\sigma}{d\Omega dE} \approx S(Q,E)$

$$S(Q) = FT\left\{\left\langle \exp[-i\underline{Q}(\underline{r}_i - \underline{r}_j)] \right\rangle\right\}$$

$$S(Q,E) = FT\left\{\left\langle \exp[-i\underline{Q}(\underline{r}(t) - \underline{r}(0))] \right\rangle\right\}$$

Fourier Transform of the Space Correlation Function

Fourier Transform of the Space-Time Correlation Function

Nuclear Interaction

Neutrons are scattered by the nuclei. Magnetic Scattering.

Scattering power varies "randomly" from <u>isotope</u> to <u>isotope</u>.

The scattering also depends on nuclear spin state of the atom.

- If the scattered neutron waves from the different nuclei have definite relative phases, they do interfere

Coherent Scattering

- If the scattered neutron waves from the different nuclei have RANDOM relative phases, they don't interfere

Incoherent Scattering

Scattering functions

$$S(Q,E) = S_{inc}(Q,E) + S_{coh}(Q,E)$$

$S_{coh}(Q,E)$ is the time and space Fourier transform of the ***PAIR*** correlation function

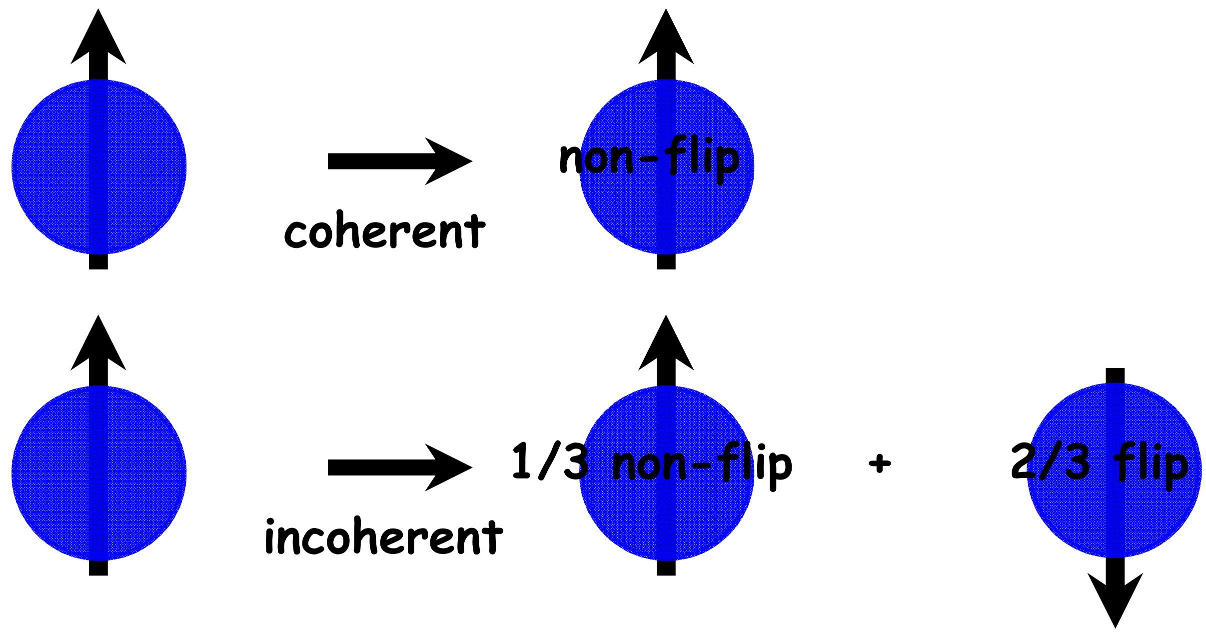
$$S_{coh}(Q,E) = FT\left\{\left\langle \exp\left[-iQ\left(\underline{r}_i(t) - \underline{r}_j(0)\right)\right]\right\rangle\right\}$$

$S_{inc}(Q,E)$ is the time and space Fourier transform of the ***SELF*** correlation function

$$S_{inc}(Q,E) = FT\left\{\left\langle \exp\left[-iQ\left(\underline{r}_i(t) - \underline{r}_i(0)\right)\right]\right\rangle\right\}$$

Hydrogen has a very high Incoherent Scattering Cross-Section

Scattering Event and Neutron Moment



2/3 of the polarization signal is lost during the incoherent scattering event

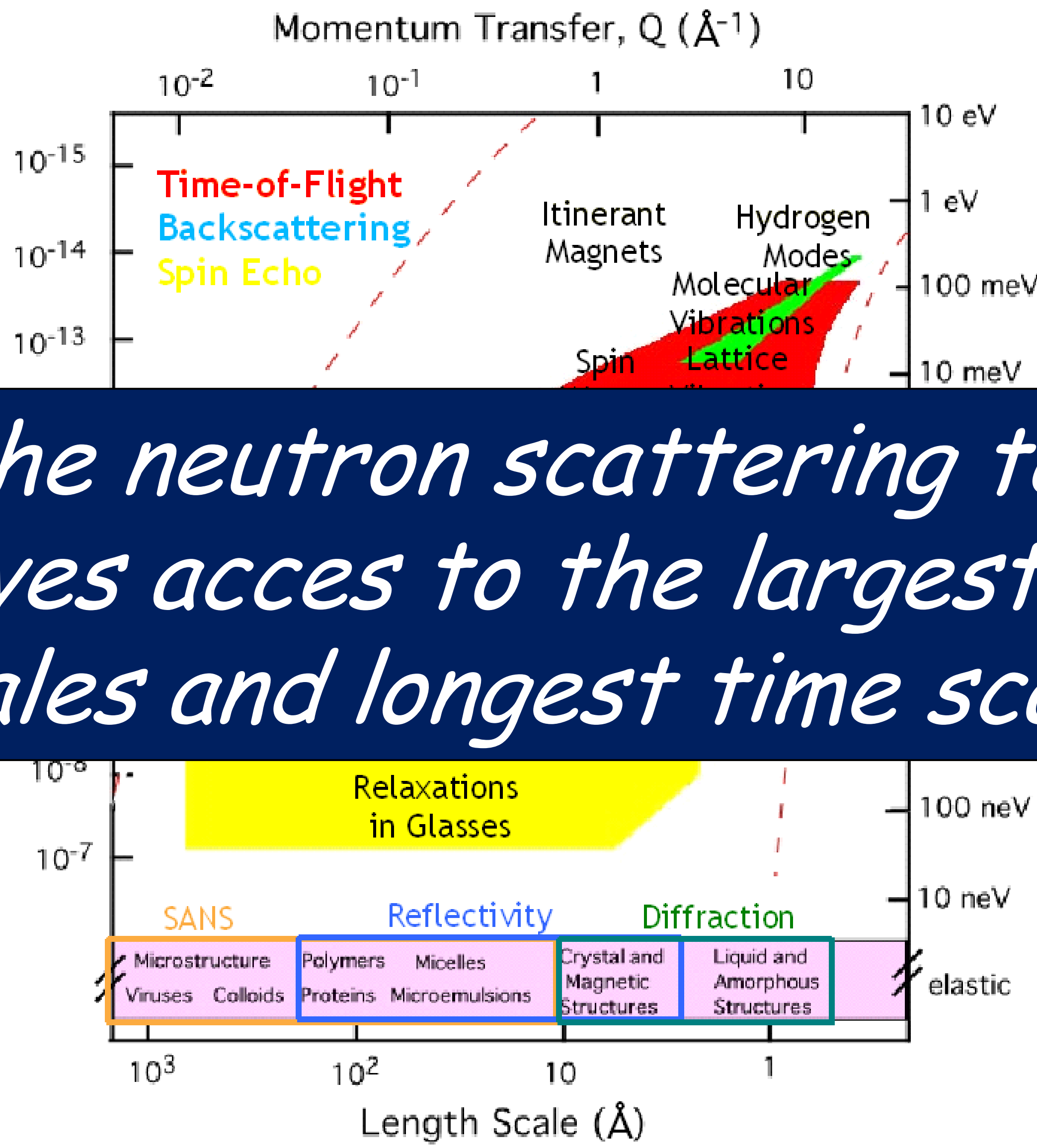
Coherent Scattering

- Static Scattering
  - Diffraction
  - Reflectometry
  - SANS
- Inelastic/Quasielastic Scattering
  - Collective dynamics
    - Phonons
    - Shape Fluctuations
    - Long Range coupled Domain Motions
    - …

Incoherent Scattering

- Inelastic/Quasielastic Scattering
  - Single Particle Dynamics
    - Diffusion
    - Rotation
    - Vibrations

Neutron Scattering Techniques



NSE is the neutron scattering techniques that gives acces to the largest length-scales and longest time scales

What Does NSE Study?

- Coherent Dynamics

  Density Fluctuations corresponding to some SANS pattern

  – Diffusion

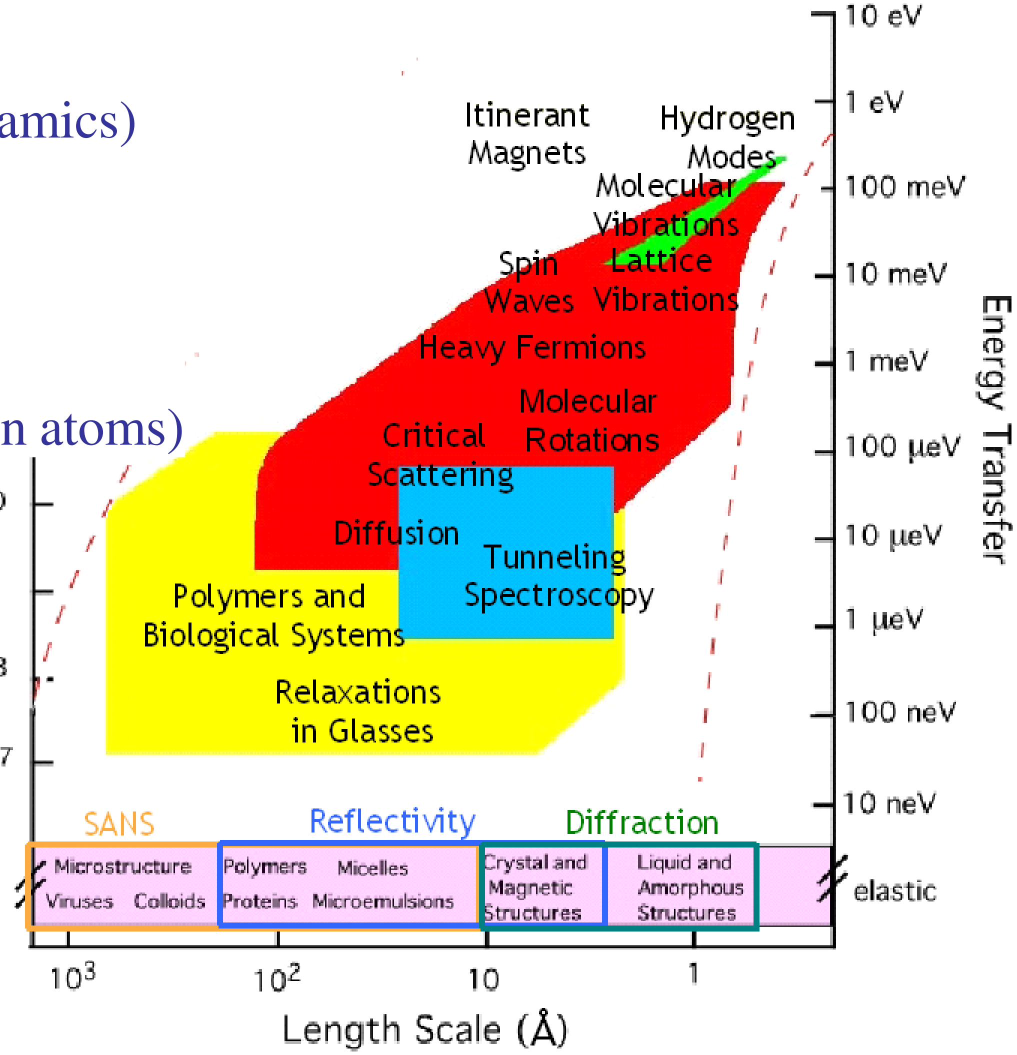
  – Shape Fluctuations (Internal Dynamics)

  – Polymer Dynamics

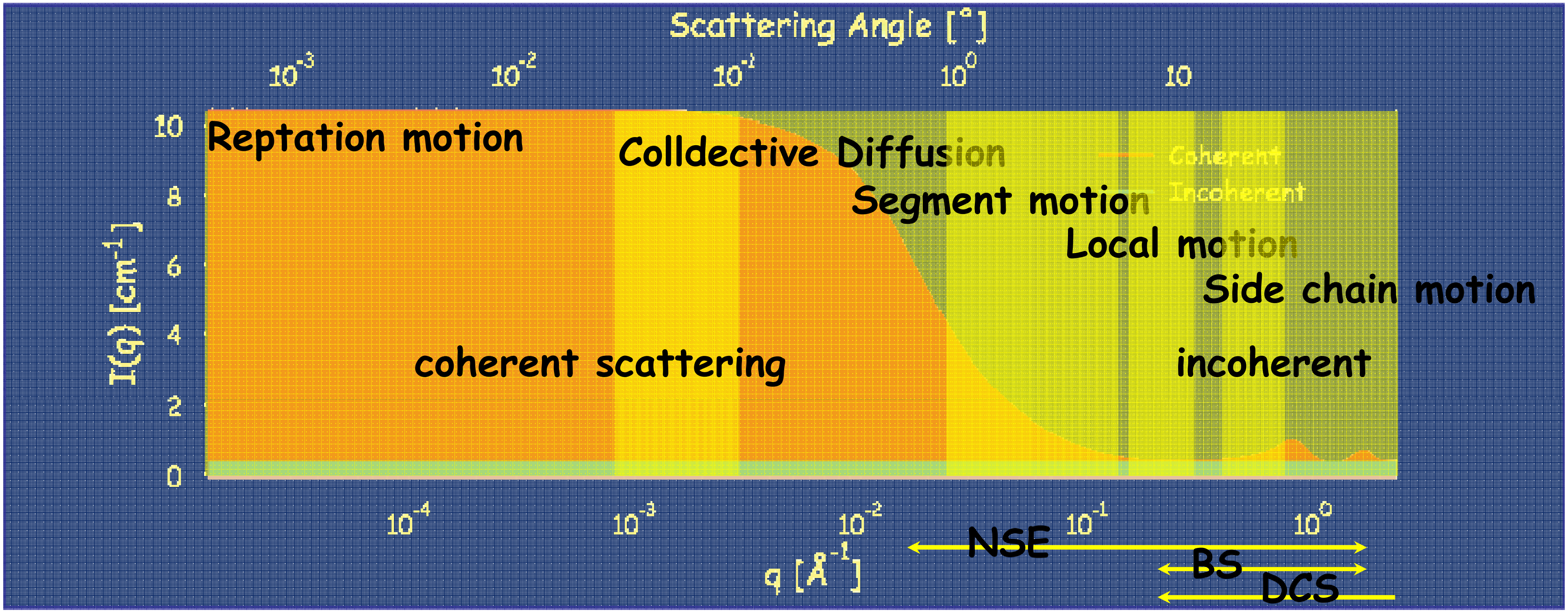
  – Glassy Systems
- Incoherent Dynamics

  Self-Dynamics (mostly of Hydrogen atoms)
- Magnetic Dynamics

  Spin Glasses



Dynamic Processes: Time and Length Scales
The Dynamics Landscape of Polymers



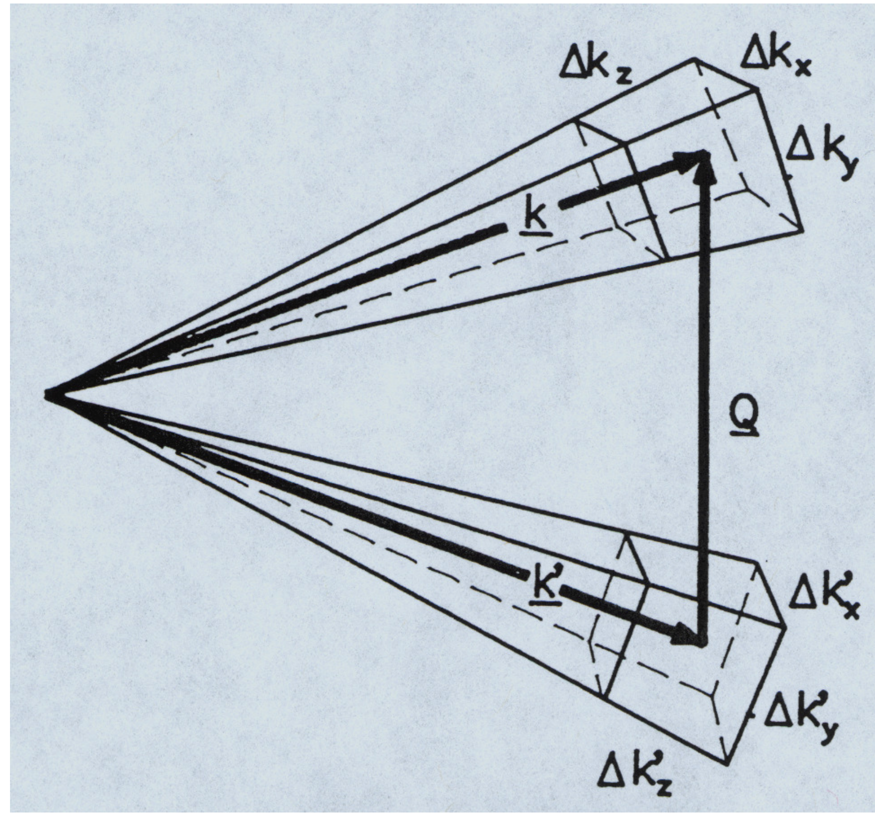
larger scale objects: slower dynamics

coherent dynamics at low q and at q corresponding to relevant length scales
incoherent dynamics at high q

Neutron Spin Echo

Instrumental Resolution

- Uncertainties in the neutron wavelength & direction of travel imply that Q and E can only be defined with a certain precision
- When the box-like resolution volumes in the figure are convolved, the overall resolution is Gaussian (central limit theorem) and has an elliptical shape in (Q,E) space
- The total signal in a scattering experiment is proportional to the phase space volume within the elliptical resolution volume



The better the resolution, the smaller the resolution volume and the lower the count rate

The Idea of Neutron Spin Echo

Neutron Spin Echo Breaks the Inverse Relationship between Intensity & Resolution

- Traditional – define *both* incident & scattered wavevectors in order to define E and **Q** accurately

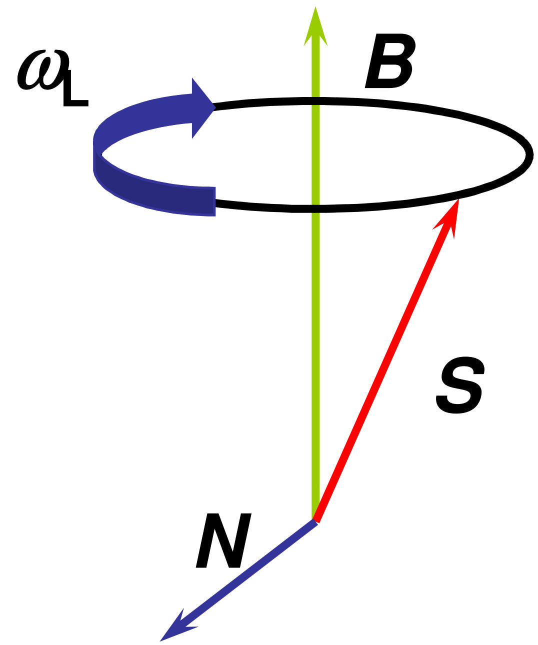
- Traditional – use collimators, monochromators, choppers etc to define both $\mathbf{k}_i$ and $\mathbf{k}_f$

- NSE – measure as a function of the *difference* between appropriate components of $\mathbf{k}_i$ and $\mathbf{k}_f$ (original use: measure $k_i - k_f$ i.e. energy change)

- NSE – use the neutron's spin polarization to encode the difference between components of $\mathbf{k}_i$ and $\mathbf{k}_f$

- NSE – can use large beam divergence &/or poor monochromatization to increase signal intensity, while maintaining very good resolution

Neutrons in magnetic fields: Precession



Neutron Properties

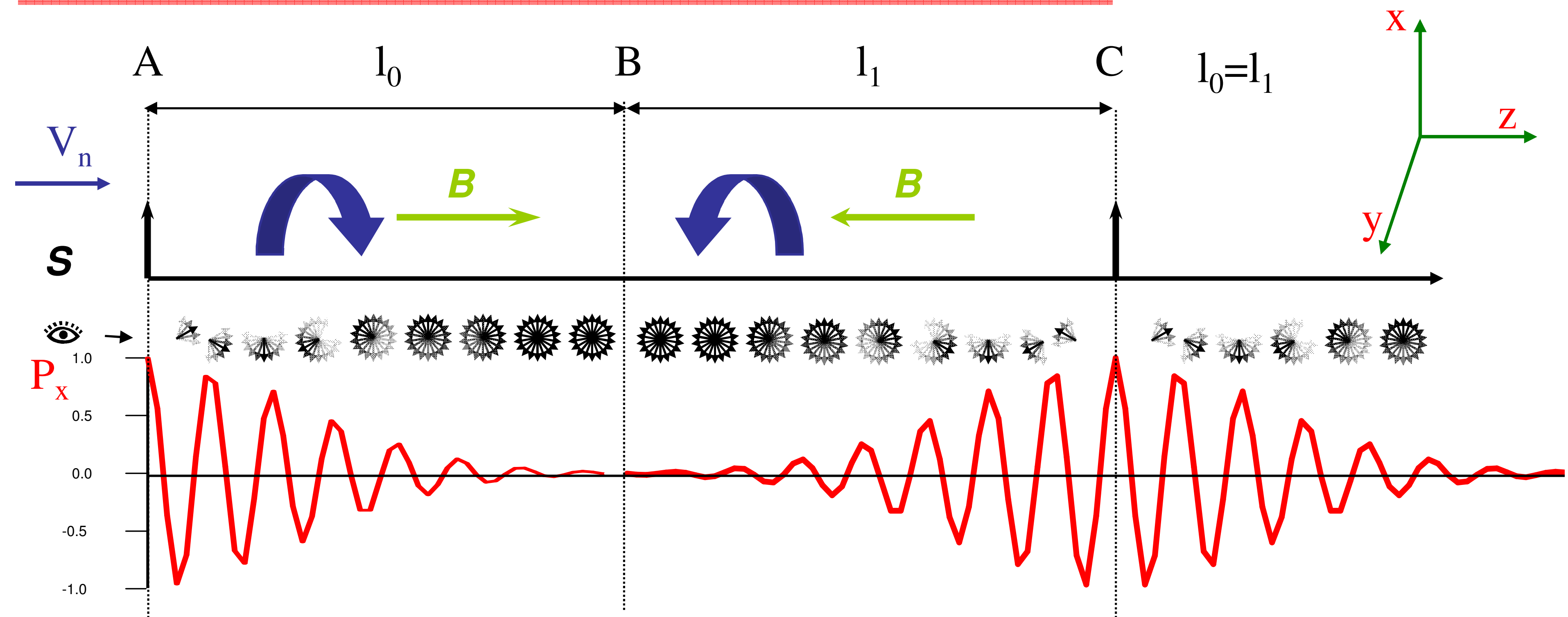
- Mass, $m_n = 1.675\times10^{-27}$ kg
- Spin, $S = 1/2$ [in units of $h/(2\pi)$]
- Gyromagnetic ratio $\gamma = \mu_n/[S\times h/(2\pi)] = 1.832\times10^{8}\ \mathrm{s^{-1}T^{-1}}$ (29.164 MHz $\mathrm{T^{-1}}$)

In a Magnetic Field

- The neutron experiences a torque from a magnetic field B perpendicular to its spin direction. ⇒ $N = S \times B$
- Precession with the Larmor frequency: ⇒ $\omega_L = \gamma B$
- The precession rate is predetermined by the strength of the field only. ⇒ $\dfrac{dS}{dt} = \gamma S \times B = S \times \omega_L$

Spin Echo effect

NSE measures the polarization: $P_x = \langle \cos\varphi \rangle$



$$\varphi = \gamma \frac{\int Bdl}{v}$$

$$P_x = \langle \cos\varphi \rangle = \int f(v) \cos\left[\frac{\gamma \int Bdl}{v} \right] dv$$

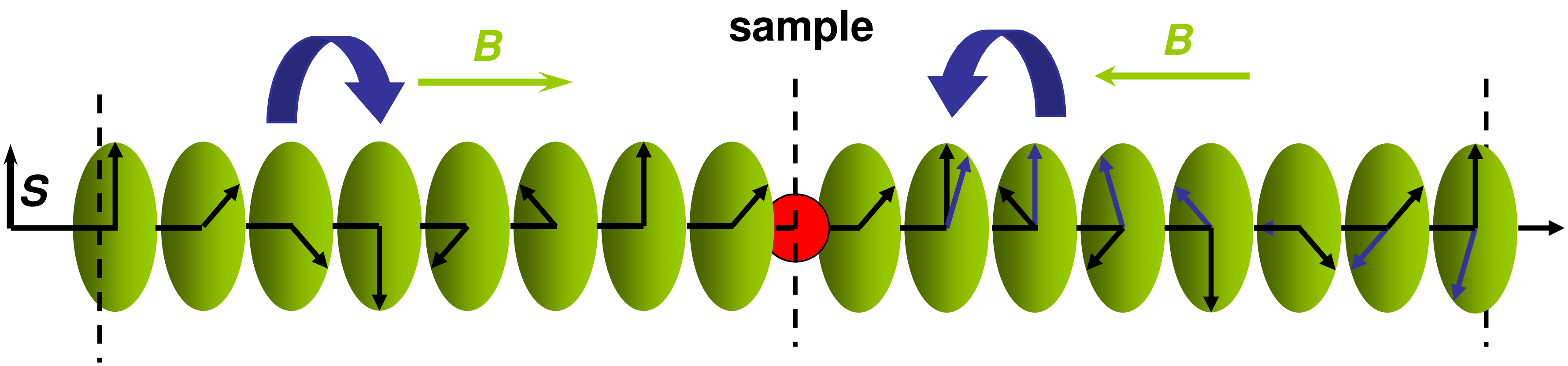
P_x is the Fourier transform of the wavelength distribution

$$P_x^C = \langle \cos\varphi \rangle = \int f(v) \cos\left[\left(\gamma \int_A^B Bdl + \int_B^C Bdl \right) \Big/ v \right] dv = 1$$

$$\boxed{P_x = \langle \cos\varphi \rangle = \int F(\lambda) \cos\left[\lambda \frac{m}{h} \gamma \int Bdl \right] d\lambda}$$

Scattering Event: Single Neutron

- elastic scattering
- inelastic scattering



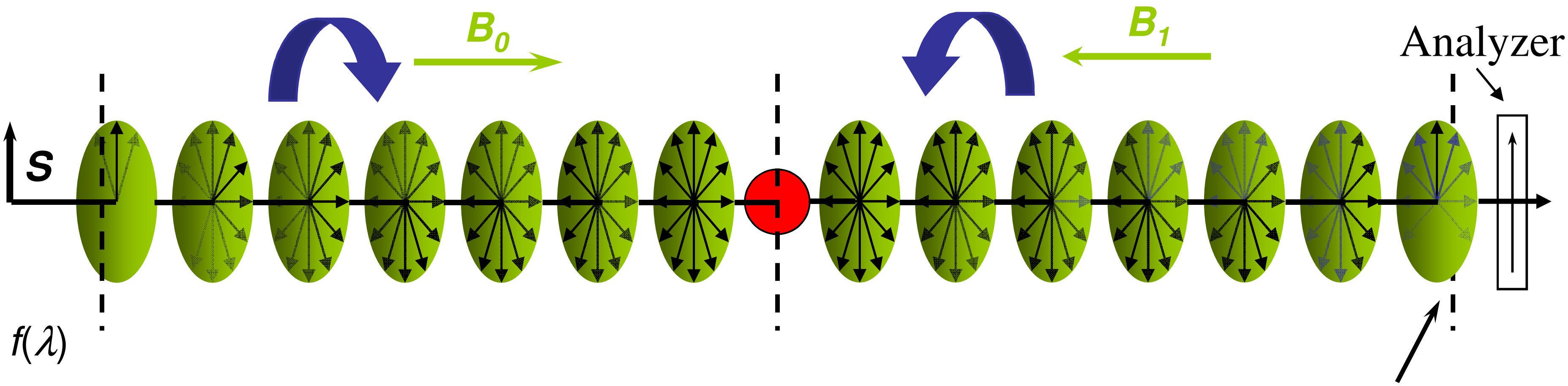
$$\varphi = \gamma \frac{\int B dl}{v} \qquad \Delta\varphi = \gamma\left(\frac{1}{v} - \frac{1}{v'}\right)\int B dl = \frac{\gamma \Delta v}{v^2}\int B dl = \frac{m\lambda}{h}\frac{\gamma \Delta v}{v}\int B dl$$

$$N(\lambda) = \frac{1}{2\pi}\int \frac{\gamma B m \lambda}{h} dl = \frac{\gamma m \lambda}{2\pi h}\int B dl = 7370 \times J[T \cdot m] \times \lambda[\mathring{A}]$$

$$J = \int B dl$$

J field integral. At NCNR: J_{max} = 0.5 T.m
N (λ=8Å) ≈ 3×10^5

Scattering Event: Neutron Beam



Again:
The measured quantity is the Polarization, i.e. the spin component along x: $P_x = \langle \cos\varphi(\lambda) \rangle$:

Elastic scattering

$$\overline{\varphi} = \left\langle \gamma \frac{\int B_0 dl}{v} - \gamma \frac{\int B_1 dl}{v} \right\rangle_{f(\lambda)}$$

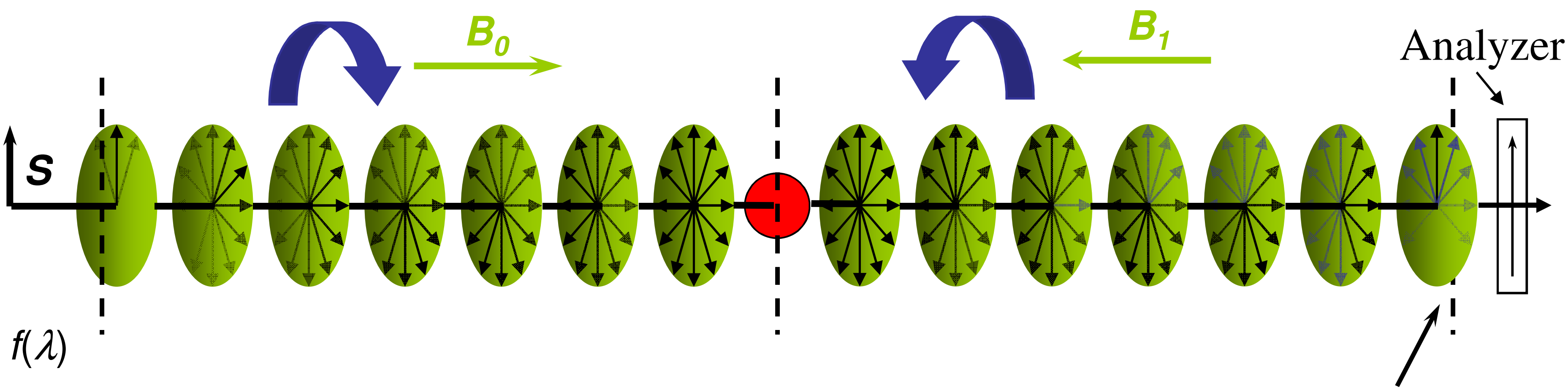
Echo Condition: $J_0 = J_1$

$$P_x = 1 \qquad \overline{\varphi} = 0$$

Note:

The requirement that $\varphi=0$ can be in some cases released. This treatment is valid for the most common case of Quasi-Elastic Scattering

Scattering Event: Neutron Beam



Again:
The measured quantity is the Polarization, i.e. the spin component along x: $P_x = \langle \cos\varphi(\lambda) \rangle$:

Quasi-Elastic scattering

$$\varphi = \left\langle \gamma \frac{\int B_0 dl}{v(\lambda)} - \gamma \frac{\int B_1 dl}{v(\lambda) + \delta v} \right\rangle$$

Series Expansion in δλ and δJ

$$\varphi \approx \gamma \frac{m}{h} J_0 \delta\lambda + \gamma \frac{m}{h} (J_0 - J_1)\lambda$$

$$\hbar\omega = \Delta E = \frac{h^2}{2m}\left[\frac{1}{\lambda^2} - \frac{1}{(\lambda+\delta\lambda)_2}\right] \approx \frac{h^2}{m}\frac{\delta\lambda}{\lambda^3}$$

$$\delta\lambda = \frac{\omega}{2\pi h} m\lambda^3$$

$$\varphi = \gamma \frac{m^2\lambda^3}{2\pi h^2} J_0 \omega + \cancel{\gamma \frac{m}{h} (J_0 - J_1)\lambda}$$

0 at the echo condition

The Basic Equations of NSE

$$P_x = \langle \cos(\varphi) \rangle = \iint f(\lambda) S(Q,\omega) \cos\left[\gamma \frac{m^2 \lambda^3}{2\pi h^2} J_0 \omega + \gamma \frac{m}{h} (J_0 - J_1) \lambda \right] d\lambda d\omega$$

Even Function

$$P_x = \langle \cos(\varphi) \rangle = \int f(\lambda) \cos\left[\gamma \frac{m}{h} (J_0 - J_1) \lambda \right] d\lambda \times \int S(Q,\omega) \cos\left[\gamma \frac{m^2 \lambda^3}{2\pi h^2} J_0 \omega \right] d\omega$$

FT of the wavelength distribution

FT of the Dynamic Structure Factor

Fourier time

$$t = \gamma \frac{m^2}{2\pi h^2} J_0 \lambda^3$$

$$P_x\left(\Delta J^{ph_i}, Q, t\right) = P_s\left(\Delta J^{ph_i}\right) \frac{\int S(Q,\omega) \cos[\omega t] d\omega}{\int S(Q,\omega) d\omega}$$

NSE measures the Fourier Transform of the Dynamic Structure Factor

How NSE works: summary

- If a spin rotates anticlockwise & then clockwise by the same amount it comes back to the same orientation

  - Need to reverse the direction of the applied field

  - Independent of neutron speed provided the speed is constant

- The same effect can be obtained by reversing the precession angle at the mid-point and continuing the precession in the same sense

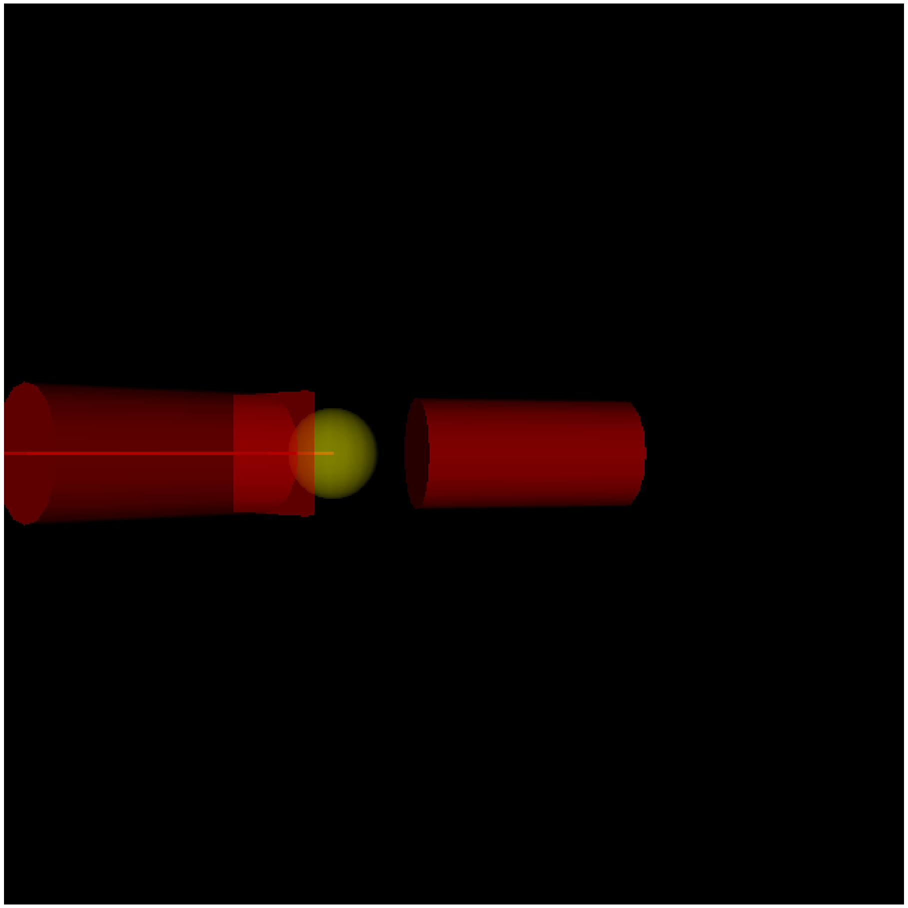
  - Use a π rotation

- If the neutron’s velocity is changed by the sample, its spin will not come back to the same orientation

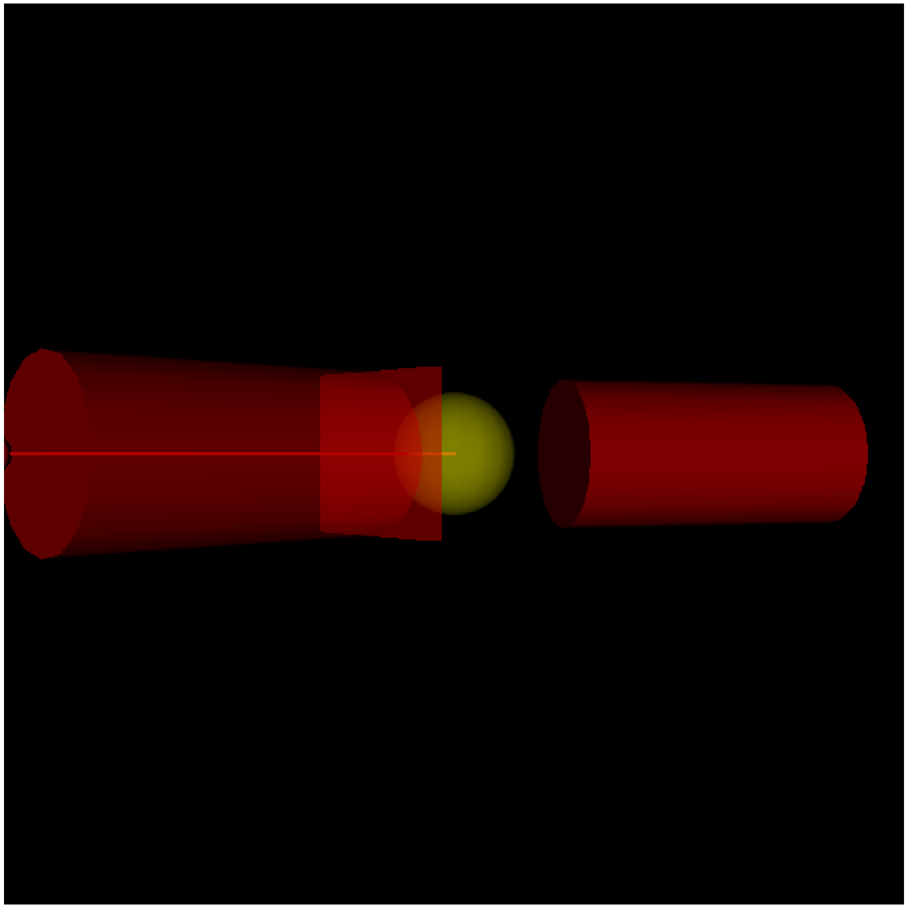
  - The difference will be a measure of the change in the neutron’s speed or energy.

NSE Effect

Elastic Scattering

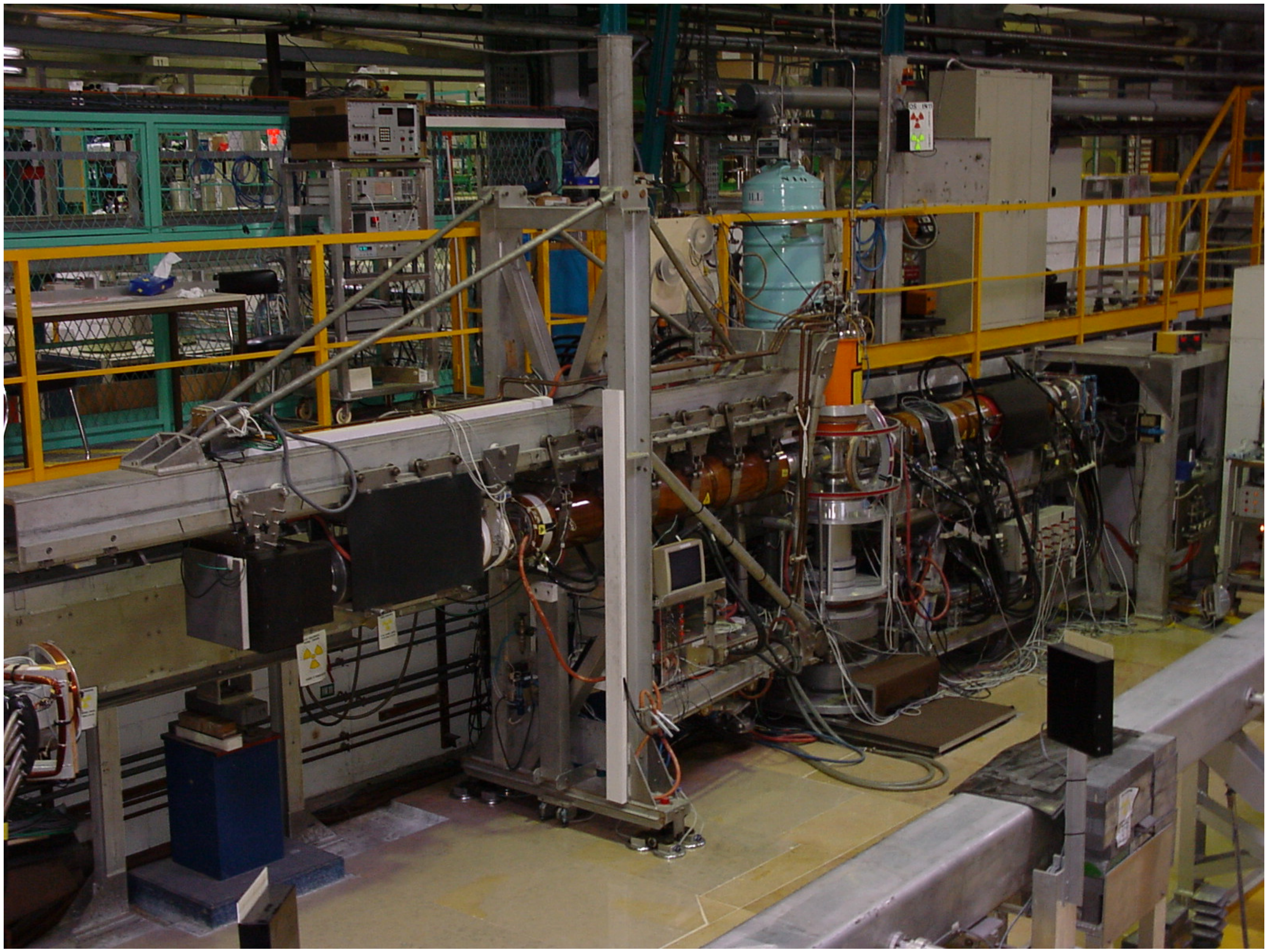


QuasiElastic Scattering



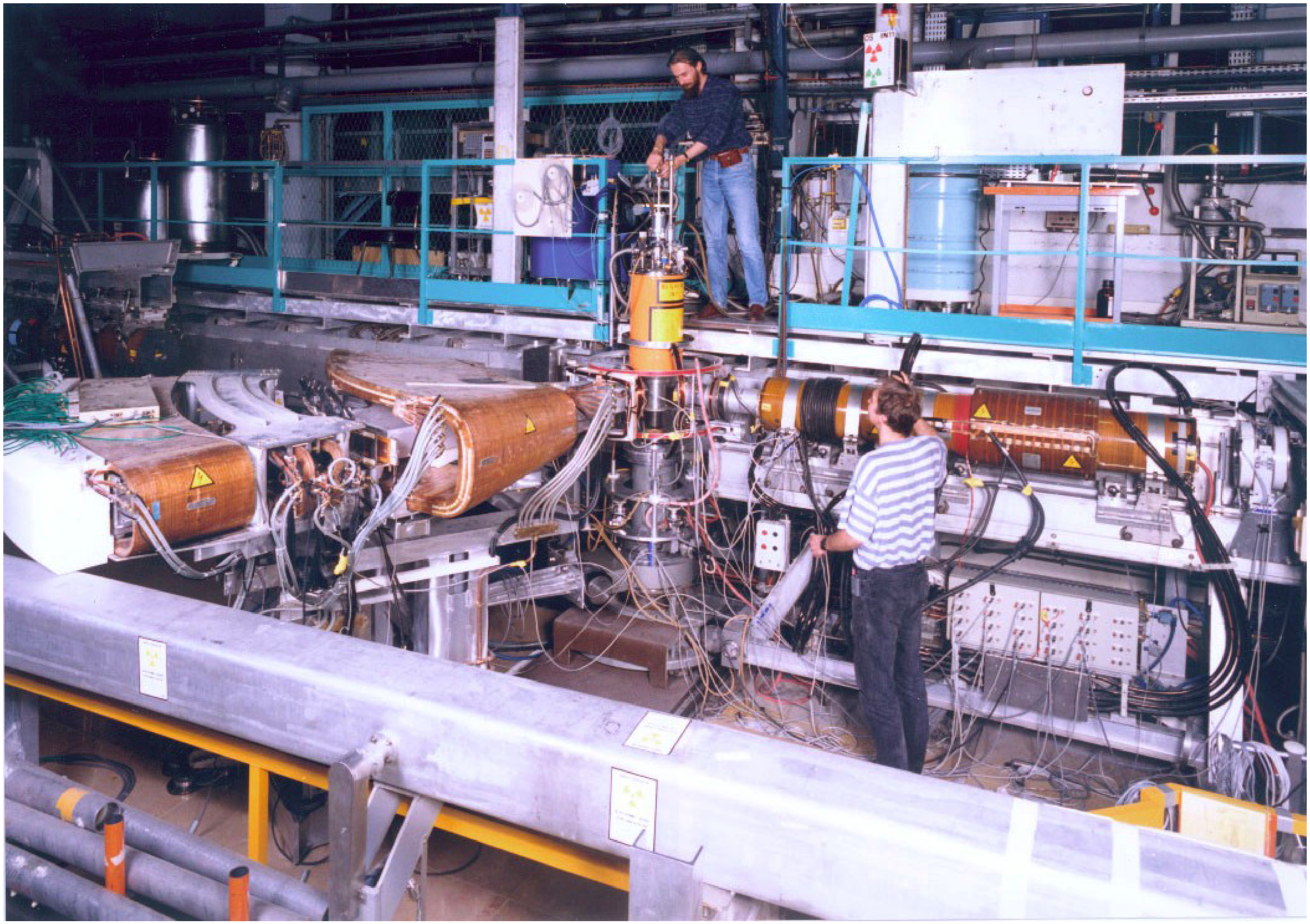
The Spectrometer

What does a NSE Spectrometer Look Like?



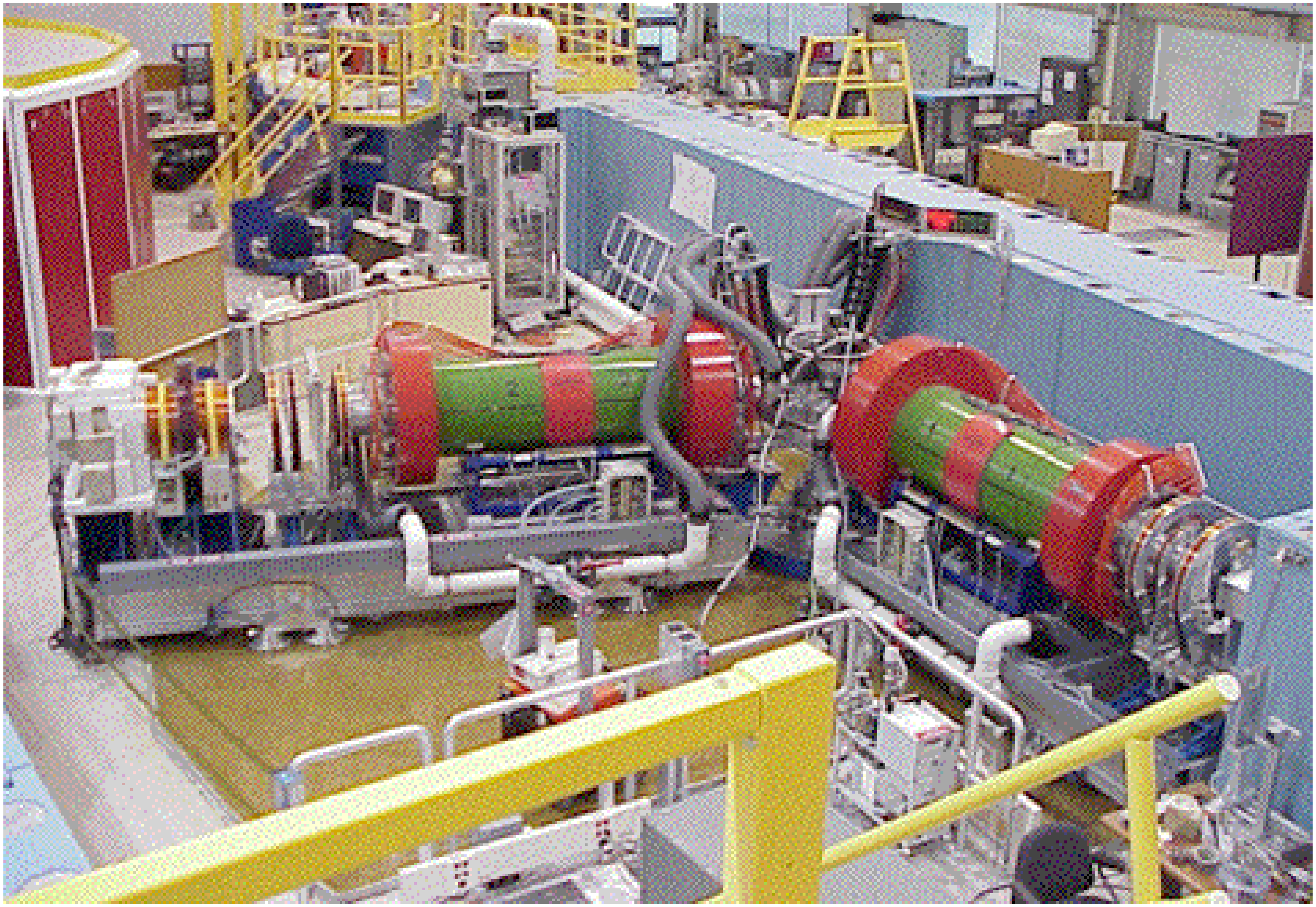
IN-11 @ ILL
The first

IN-11c @ ILL; Wide Detector Option



IN-15 @ ILL

NSE @ NCNR



NSE @ SNS

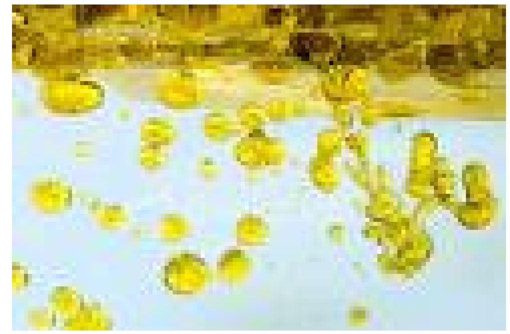
NSE Exercise

Surfactant molecules

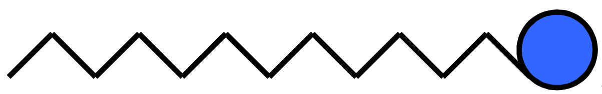
- Oils and water do not mix! Why?

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

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



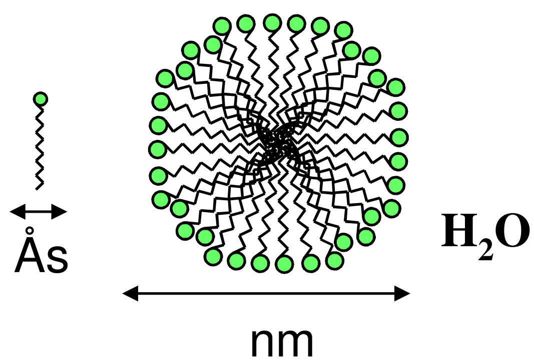
A surfactant ("Surface Active Agent") is soluble both in water and in organic liquids (oils)



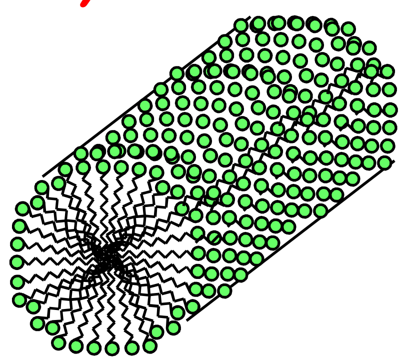
Surfactant aggregates in water

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

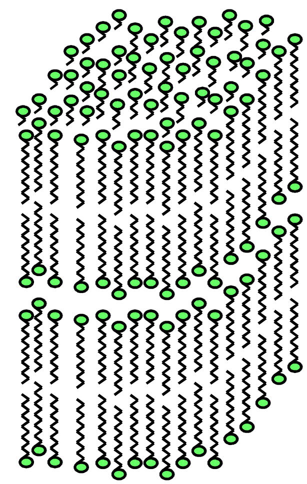


Cylindrical micelles

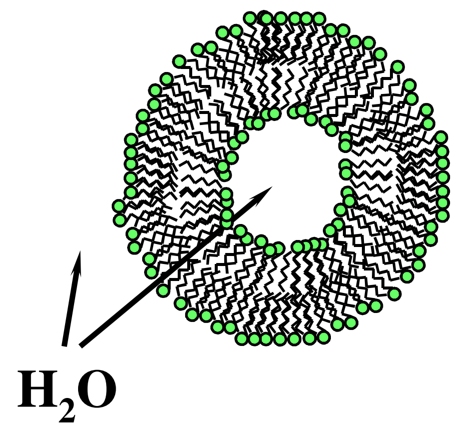


Wormlike micelles can be as long as few microns

Lamellae



Vesicles



Surfactants are everywhere

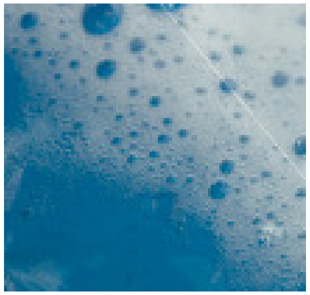
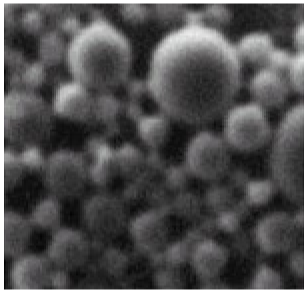
Surfactants are very useful to:

- 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

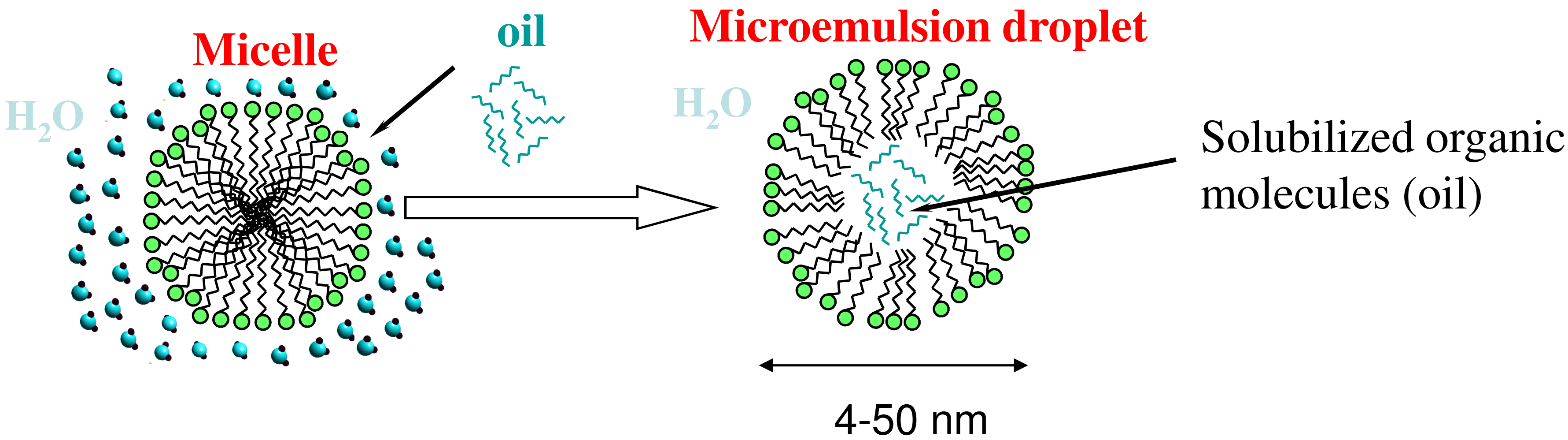
Surfactants in our daily life:

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

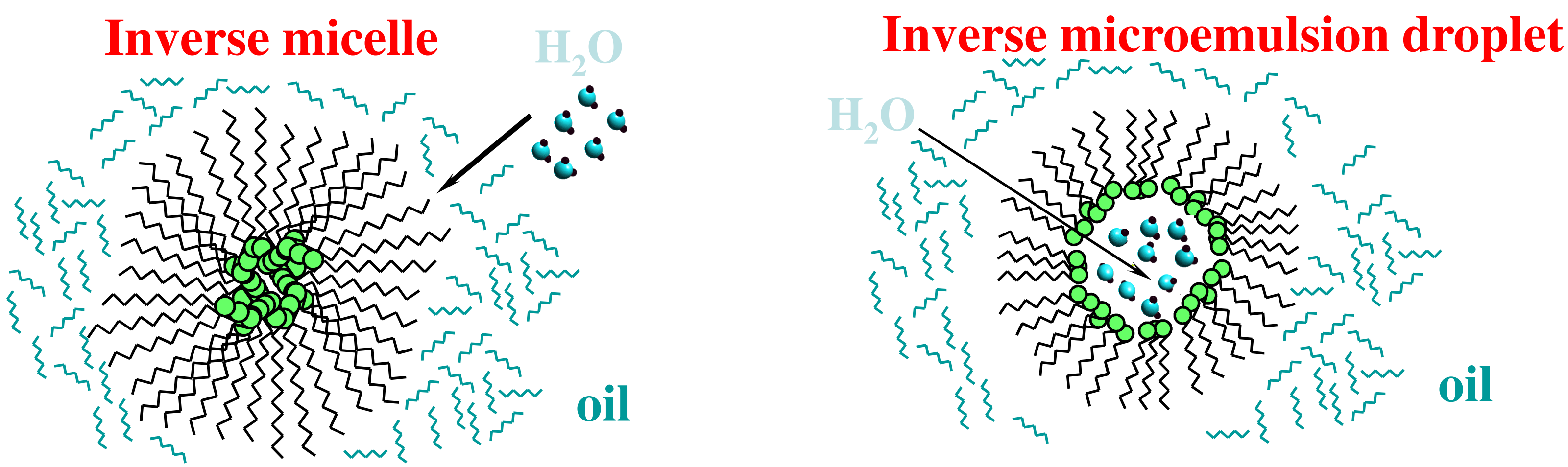
    

Micelles and Microemulsions

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

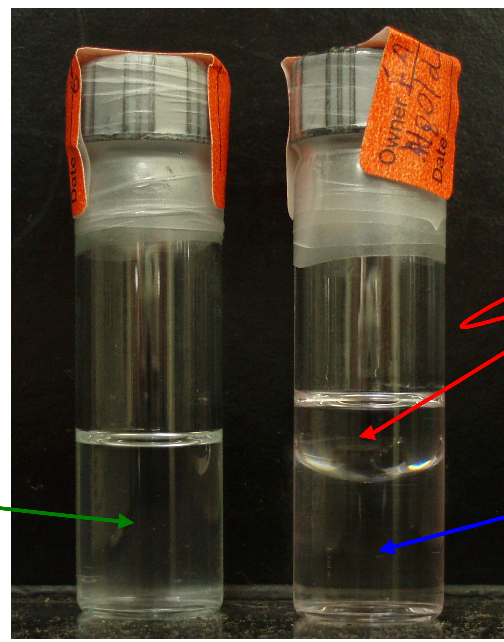


When surfactants are dissolved in oils they form "inverse" micelles, …



Microemulsion Properties

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



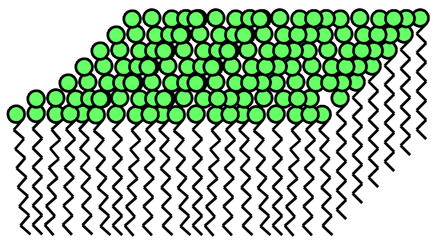
AOT/water/decane

decane

water

Properties of the surfactant film

Surfactant film

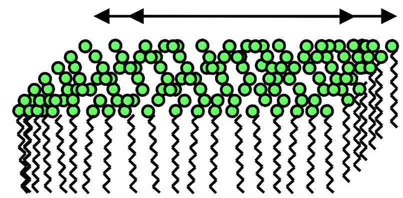


Properties of the surfactant film change with:

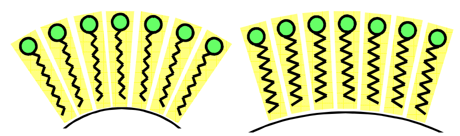
- Molecular structure
- Additives
- Ionic strength
- Co-surfactant
- Temperature, pressure etc.

Properties of the surfactant film:

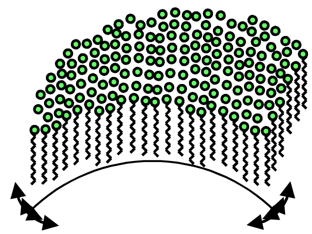
- Interfacial tension
- Lateral elasticity

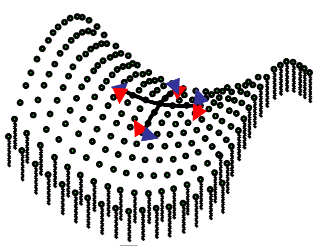


- Spontaneous curvature



- Bending elasticity





- Saddle splay elasticity

Helfrich Free Energy

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

An Example: Microemulsion

Structure

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

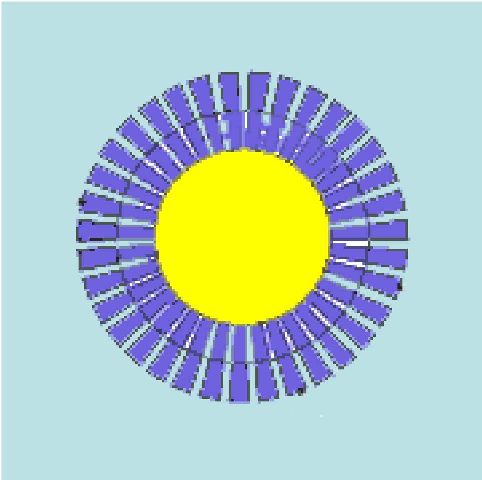
SANS:

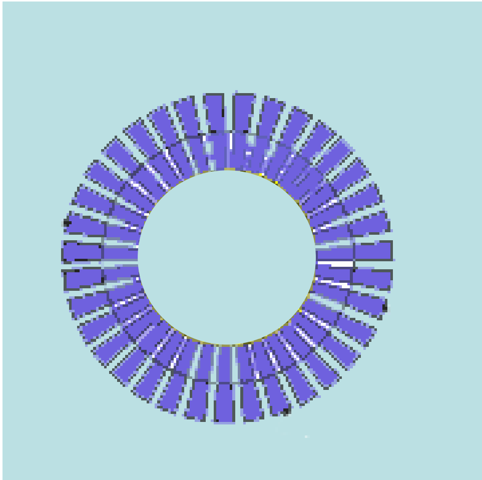
The intensity is the FT of the contrast distribution.

Contrast: Difference in Scattering Length Density

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

Contrast Matching Technique



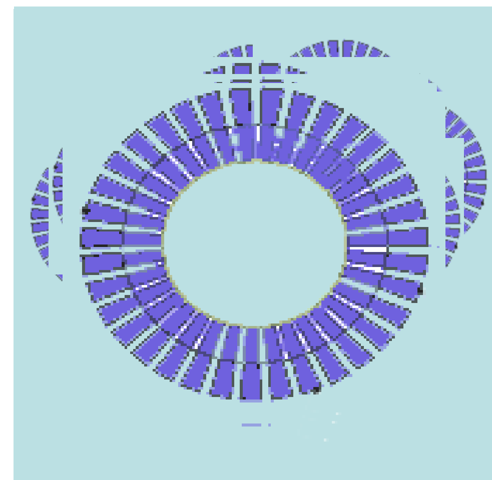


Microemulsion: How to study them

Dynamics

Microemulsions move in solution because of thermal energy.

- Diffusion
- Shape fluctuations



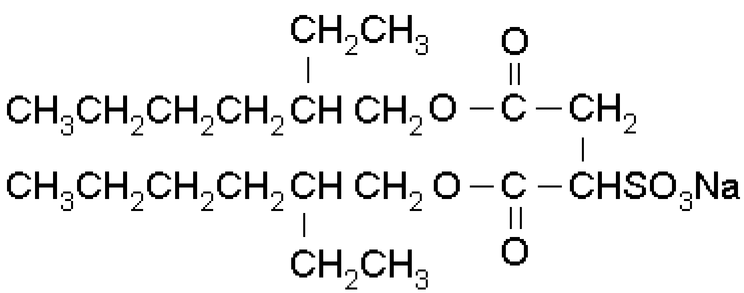
Experimental techniques:

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

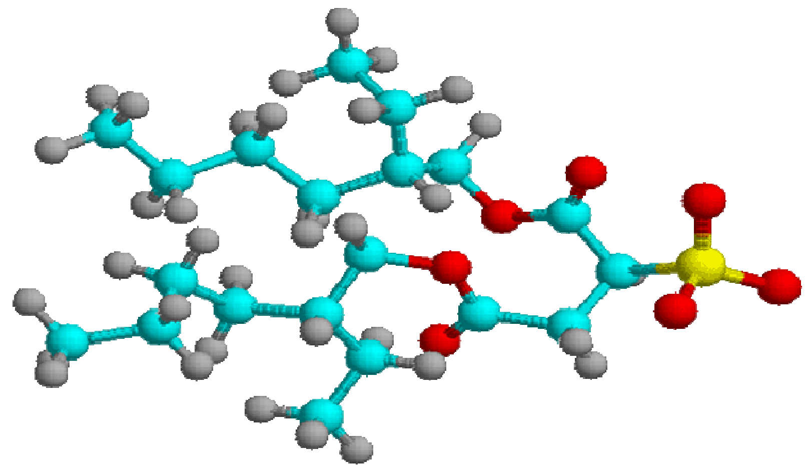
NSE: T scale from ≈0.01 to 100 ns, L scale from ≈1 to 100 Å

Experimental

Shape fluctuations in AOT/water/hexane microemulsion

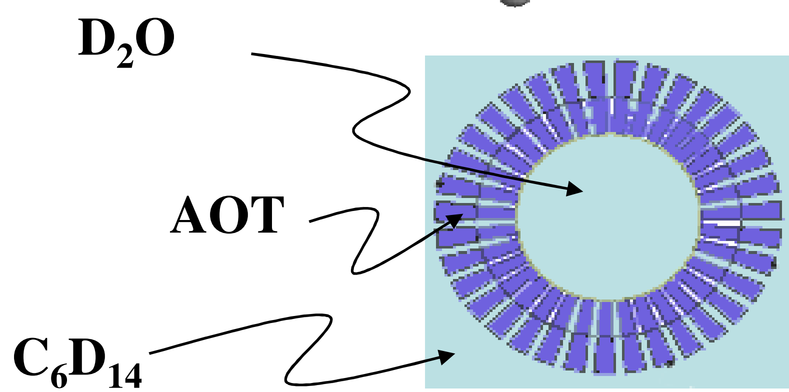


AOT

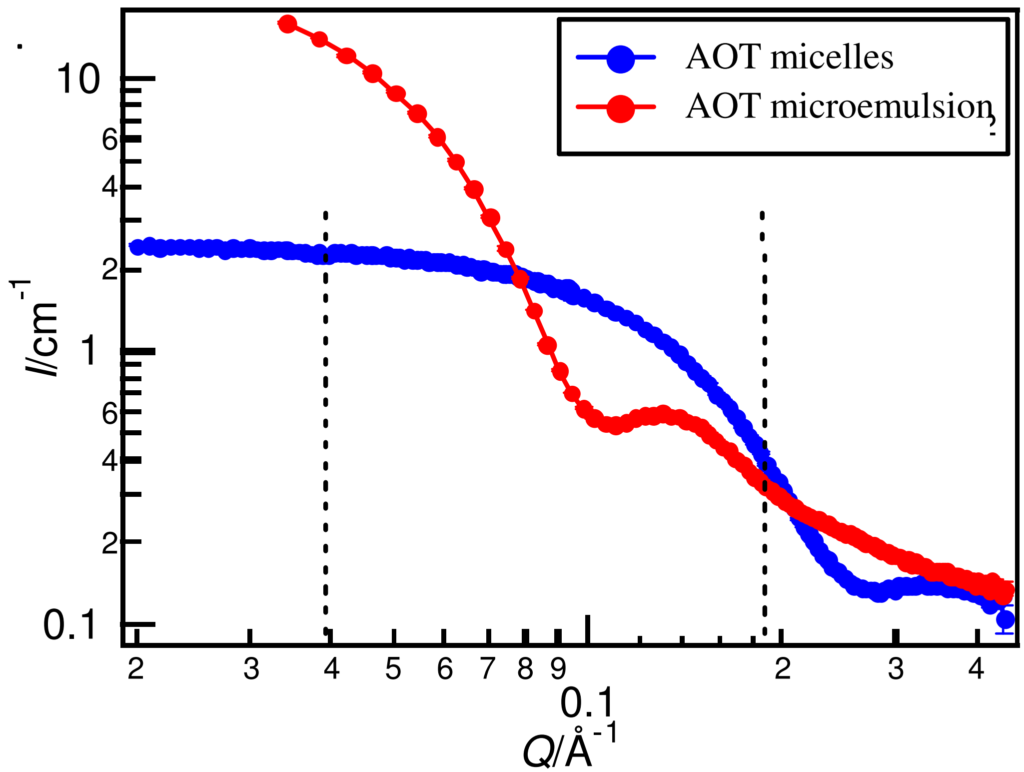


Inverse Microemulsion droplet

- 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 Law, Diffusion Equation

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

$$\frac{\partial I(Q,t)}{\partial t} = -D\nabla^2 I(Q,t)$$

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

NSE measures coherent dynamics.

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

Data Analysis: Shape Fluctuations

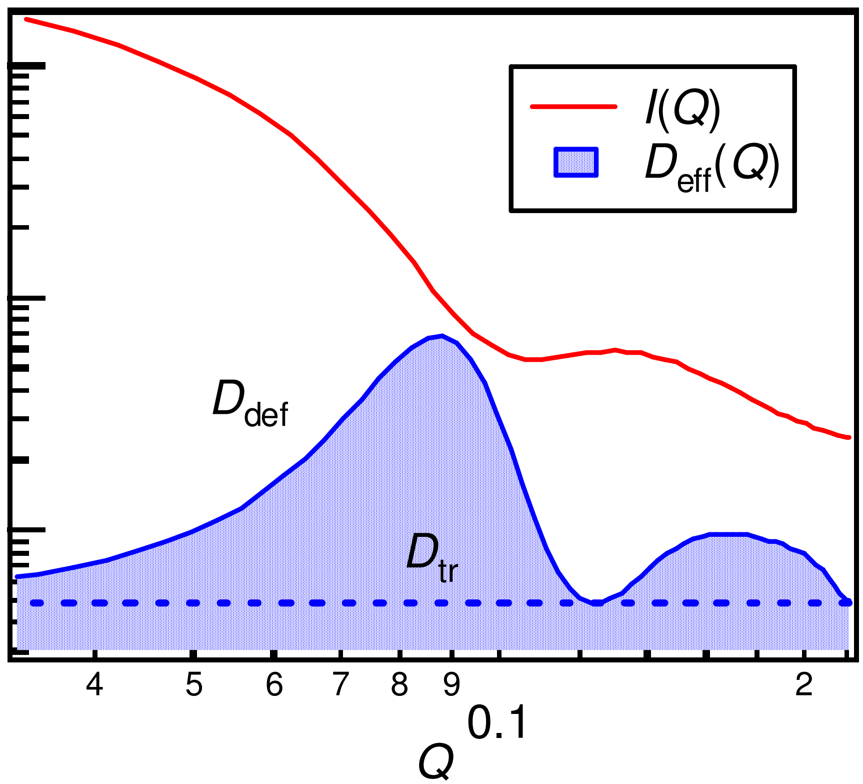
$$E_{bend} = \frac{k}{2}\int dS\left(\frac{1}{R_1}+\frac{1}{R_2}-\frac{2}{R_s}\right)+\bar{k}\int dS\,\frac{1}{R_1 R_2}$$

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:

$$\lambda_2 = \frac{k}{\eta R_0^3}\left[4\frac{R_0}{R_s}-3\frac{\bar{k}}{k}-\frac{3k_B T}{4\pi k}f(\phi)\right]\frac{24\eta}{23\eta'+32\eta}$$



Data Analysis III

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

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

The two dynamical processes are statistically independent.

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

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

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

The bending modulus, k

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

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

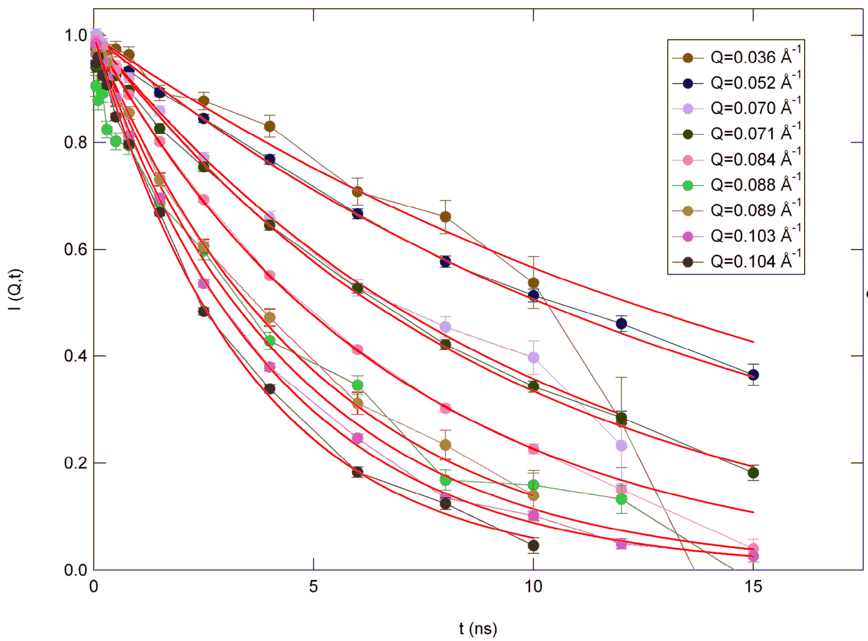
λ_2 – the damping frequency – **frequency of deformation**

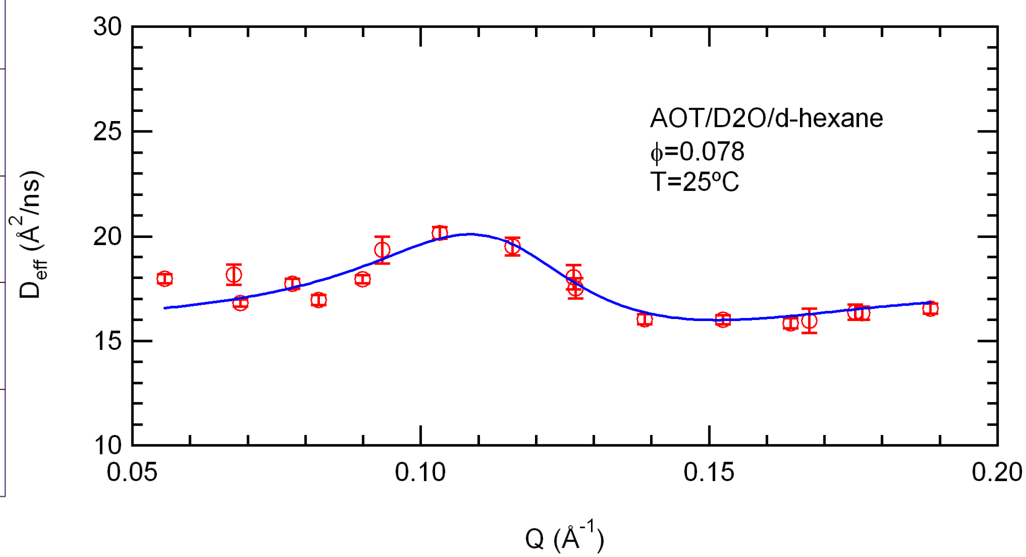
$<|a|^2>$ – mean square displacement of the 2-nd harmonic – **amplitude of deformation**

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

η and η' are the solvent and core viscosities

Results





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

NSE History

The beginning

Neutron Spin Echo: A New Concept in Polarized Thermal Neutron Techniques

F. Mezei

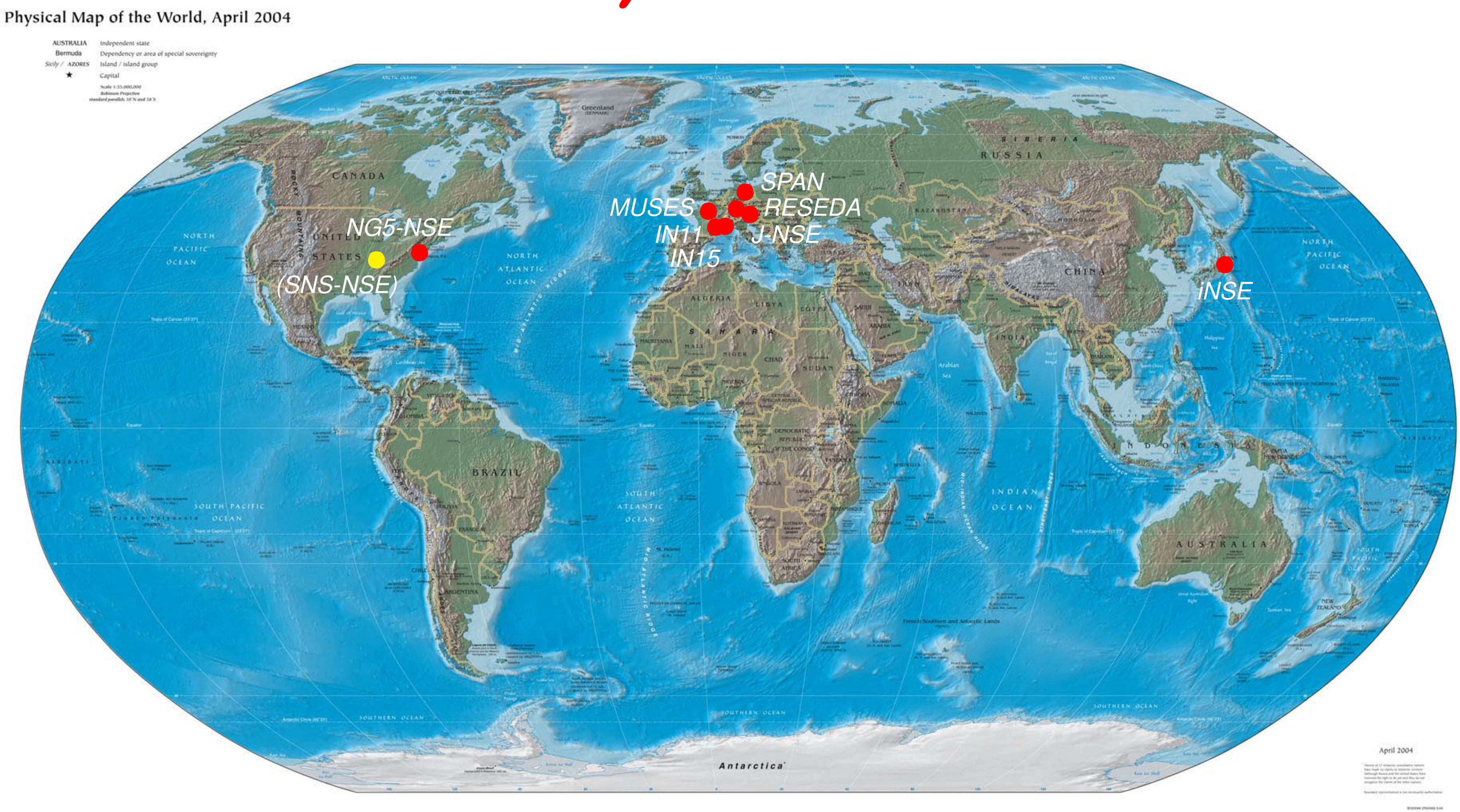
Institut Laue-Langevin, Grenoble, France* and
Central Research Institute for Physics, Budapest, Hungary

Received July 7, 1972

A simple method to change and keep track of neutron beam polarization non-parallel to the magnetic field is described. It makes possible the establishment of a new focusing effect we call neutron spin echo. The technique developed and tested experimentally can be applied in several novel ways, e.g. for neutron spin flipper of superior characteristics, for a very high resolution spectrometer for direct determination of the Fourier transform of the scattering function, for generalised polarization analysis and for the measurement of neutron particle properties with significantly improved precision.

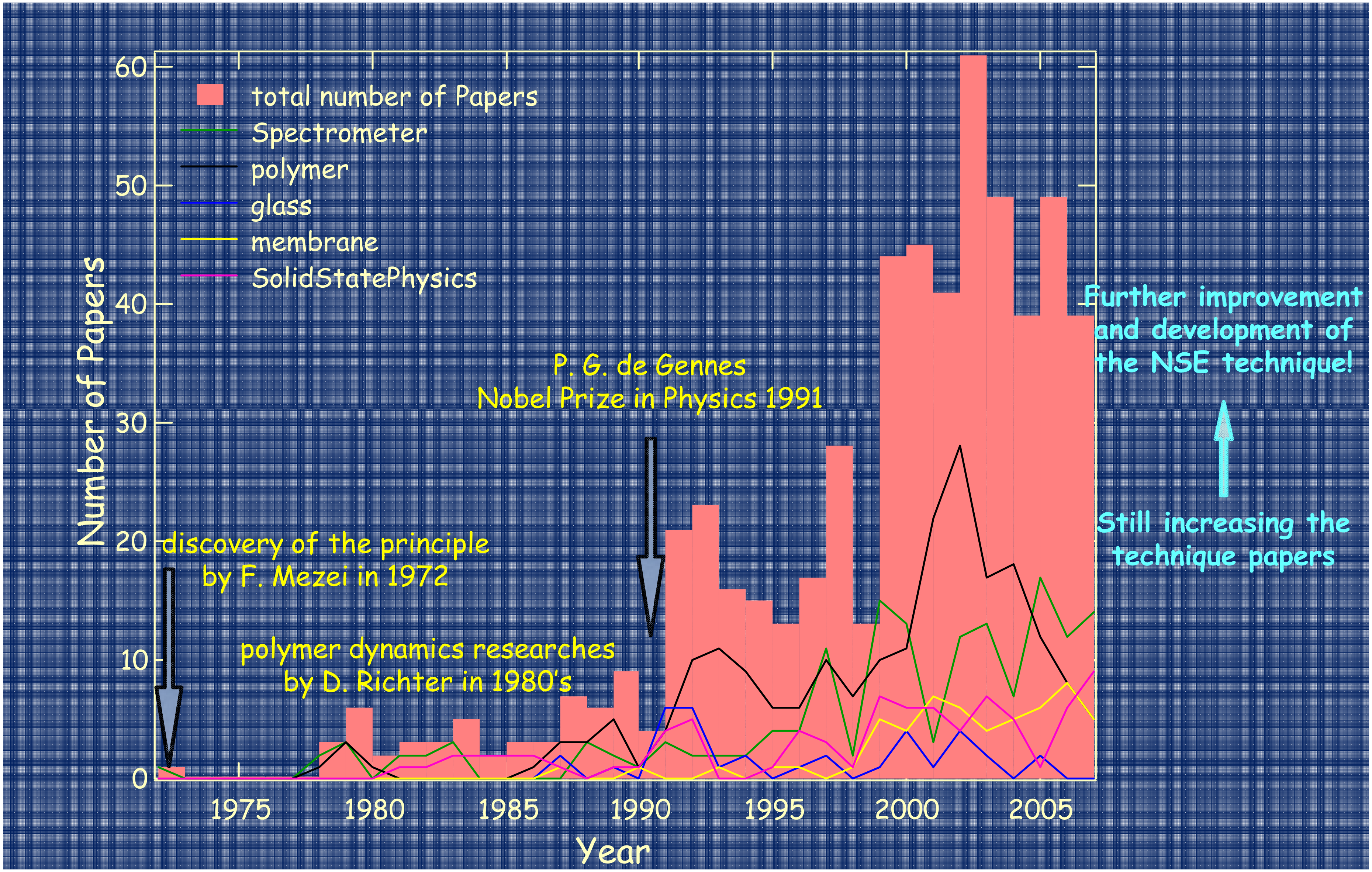
F. Mezei, *Z. Physik*. 255, 146 (1972).

NSE Today in the World



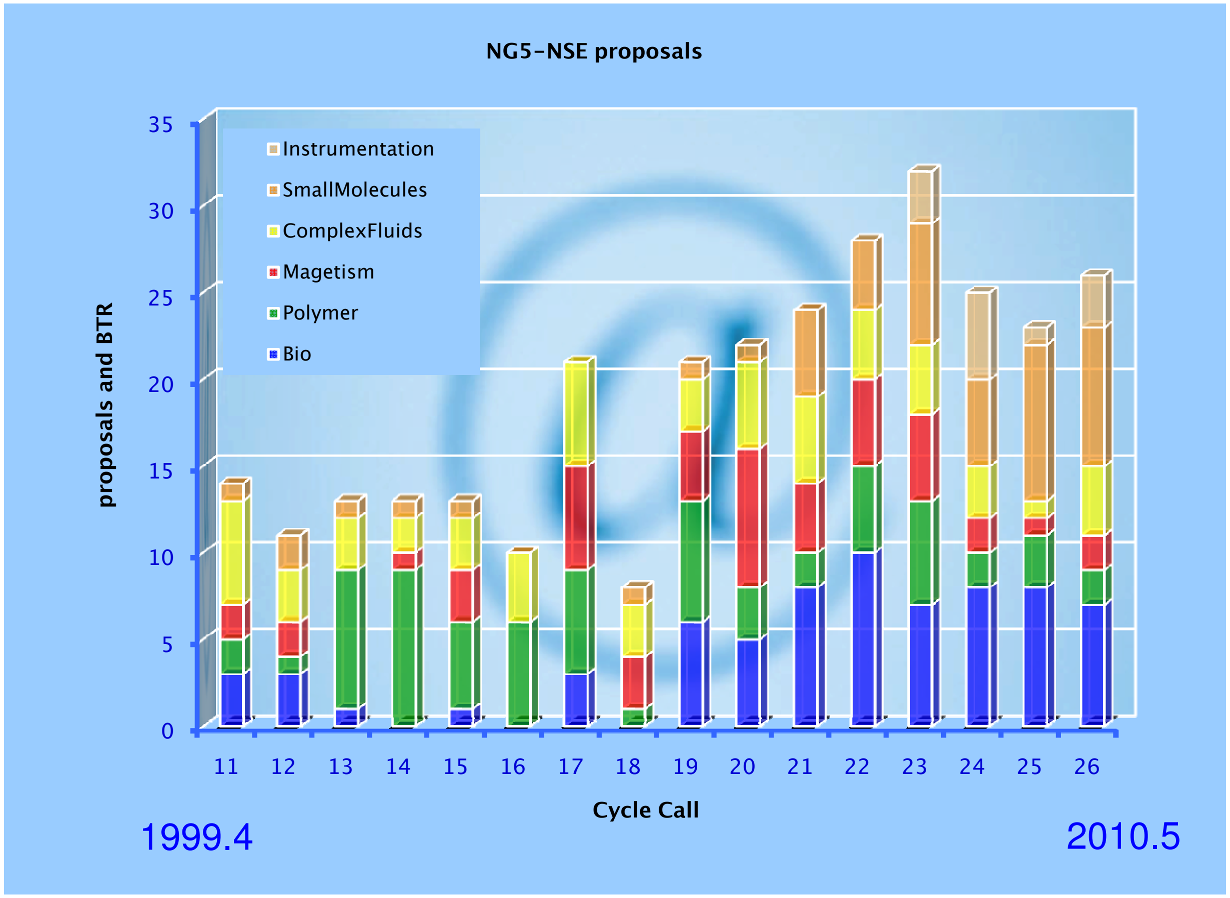
+ NSE option for triple-axis spectrometers
+ developing ones

NSE Publications



publication record; searched using web of science: keyword=neutron spin echo

NG5 NSE proposal statistics



Bio
- model bio-membrane
- protein motion

Polymer
- segment dynamics
- hydro gels
- polymer complex

Magnetism
- frustrated magnets
- spin glass

Complex Fluids
- microemulsions
- surfactant membranes
- cluster dynamics

Molecular Liquids
- confined water
- ionic liquids

Conclusions

Take Home Messages

- NSE gives you access to dynamics in the ps to ns time range (covering four orders of magnitude in time)
- NSE Resolution is independent of the beam resolution
- NSE data is measured as S(Q,t), i.e. in the time domain (the resolution can be simply divided out)

Caveat

Spin Echo is neutron intensive.

A successful experiment is due in large part to the sample selection (quality, amount, etc.). Make sure you:

- choose and characterize your sample well
- take advantage of the isotopic substitution technique

Further Readings

F. Mezei (ed.): Neutron Spin-Echo, *Lecture Notes in Physics*, **128**, Springer, Heidelberg, 1980

F. Mezei, C. Pappas, T. Gutberlet (Eds.): Neutron Spin-Echo Spectroscopy (2nd workshop), *Lecture Notes in Physics*, **601**, Springer, Heidelberg, 2003.

D. Richter, M. Monkenbusch, A. Arbe, and J. Colmenero, "Neutron spin echo in polymer systems" *Adv. in polym. Sci*, **174**, 1 (2005).