Measurements of self-diffusion coefficients by PGSE NMR

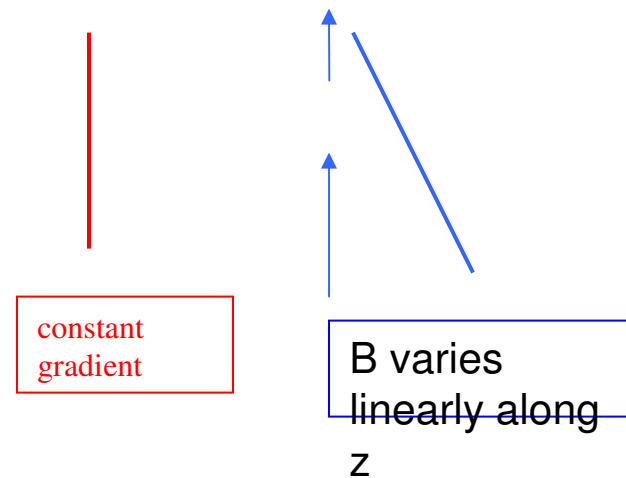## and microstructure of gels and microemulsions

Pulsed gradients

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

gradient operator

The most important is the gradient of the z component of B (because determines the Larmor frequency) Commonly, NMR spectrometers are equipped with gradients coil delivering pulsed gradients along the z axis, Gz

constant gradient

B varies linearly along z

Uniform gradients (G_z=cost) are the simplest

Simplest hardware: two coils in which current are flowing in opposite sense

The gradient strength is related to current intensity

rf coil center
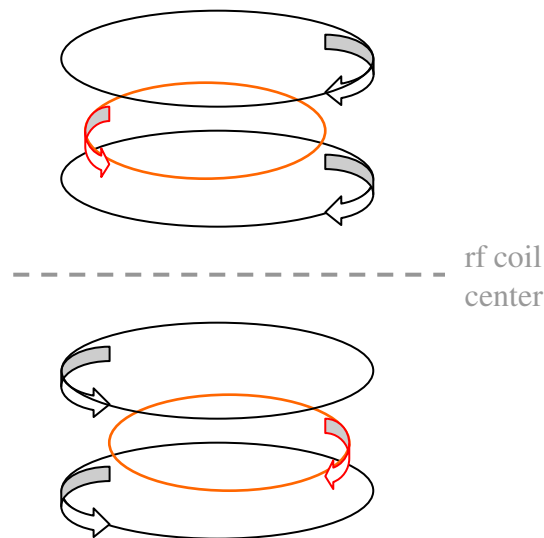
First application of PGSE to diffusion measurements: E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, 1965, **42**, 288-292.

Actual widespread use 20 years later

- **self-shielding coil**: overcomes the problem of eddy currents

Effects of a field gradient on the spin system

1. spatial labelling
2. defocussing

In the presence of a spatial field gradient the Larmor frequency depends on the spin position
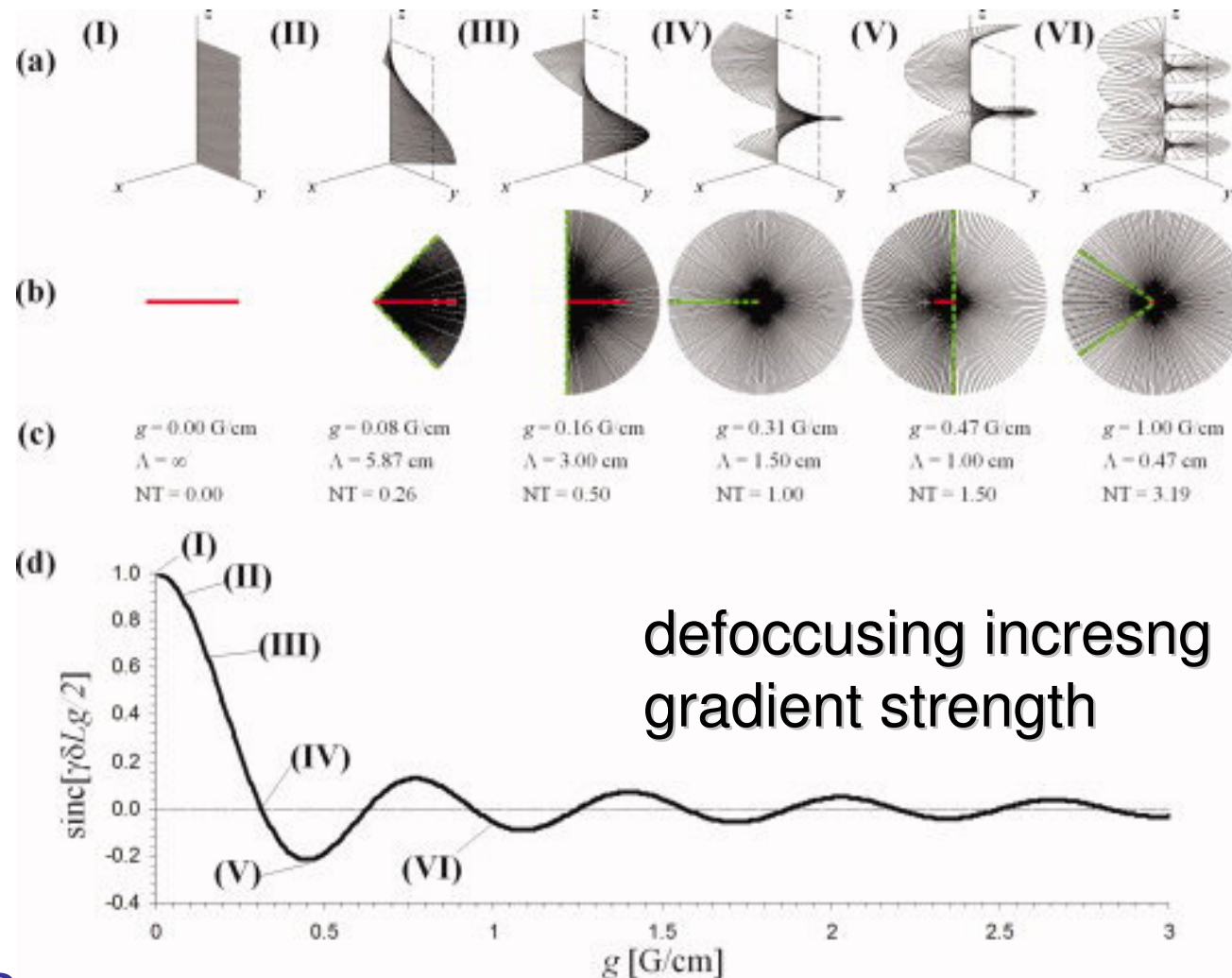
$$\omega_0(z) = -\gamma(B_0 + B_g) = -\gamma(B_0 + G_Z z)$$

as well as its phase angle after a time t ($\phi = \omega_0 t$)

$$\phi(z,t) = -\gamma(B_0 + G_Z z)t$$

In the presence of G_Z the phase angle depends on the z position of the considered spin.

Considering just the difference: $\phi(z,t) + \gamma B_0 t = -\gamma G_Z z t$

defoccusing incresng gradient strength

The Stejskal–Tanner equation generalized for any gradient shape— an overview of most pulse sequences measuring free diffusion

A gradient may be exploited to eliminate unwanted magnetisation by dephasing it.

defocussing in time

The resultant Mx is the sum of all M_X at the various heights (z) (taken as z=0 the center of the sample), which during the gradient are: $M_X(t,z)=MX(0)\cos(\gamma G_z zt)$.
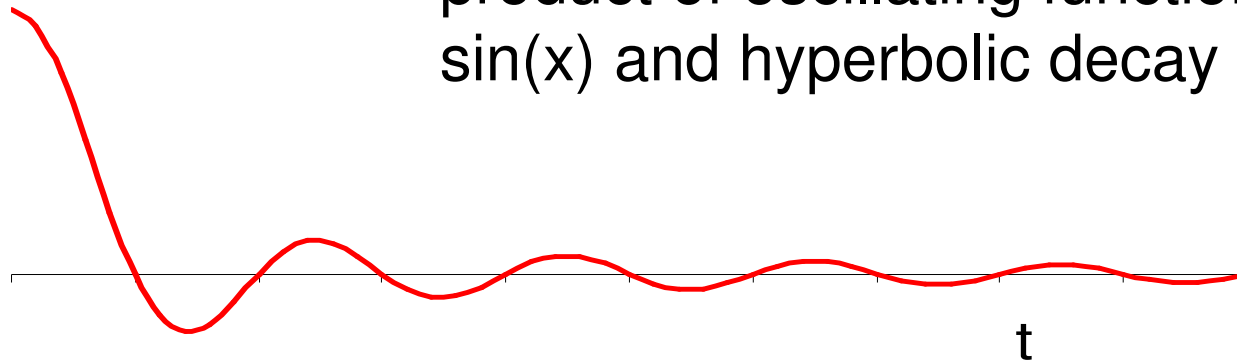
This is accomplished by integration:

$$M_{XTOT}(t) = M_{XTOT}(0)\frac{1}{r_{Max}}\int_{-\frac{1}{2}rMax}^{\frac{1}{2}rMax}\cos(\gamma G_z zt)dz$$

$$M_{XTOT}(t) = M_{XTOT}(0)\frac{2\sin\left(\frac{1}{2}\gamma G_z r_{Max}t\right)}{\gamma G_z r_{Max}t}$$

$$\frac{\sin x}{x}$$

$$x = 1/2\gamma G_z r_{Max}t$$

product of oscillating function
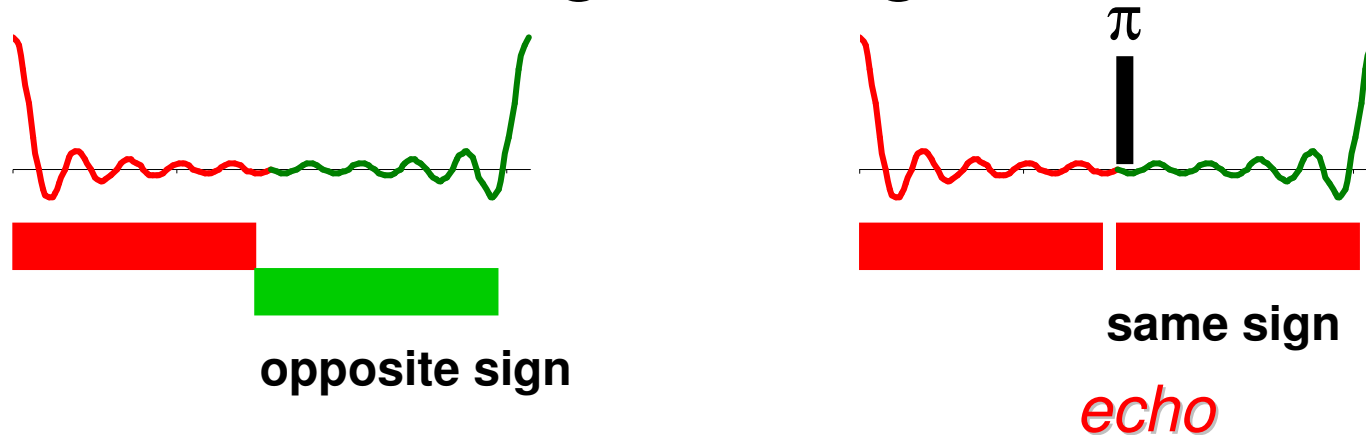sin(x) and hyperbolic decay

t

Magnetization disappears faster r
- the larger the nuclear γ
- the stronger the gradient

Unit of gradient strength: Gcm^{-1} (cgs) or Tm^{-1}

high resolution probe: up to 56 Gcm^{-1}= 0.56 Tm^{-1}

e.g. ^1H (γ= 26.75·10^7 rad $s^{-1}T-1$) r_{Max}= 1 cm, G_Z=
37 Gcm^{-1} (0.37 Tm^{-1}) t= 2 ms M_X will be reduced
by 10000 times

Refocussing of magnetisation

opposite sign

π

same sign

echo

- time interval Δ, between the gradients, during which the spin diffuse. The echo intensity will decrease with Δ (exponentially) due to diffusion, but also due to T_2

- δ gradient duration

G_Z π Δ G_Z
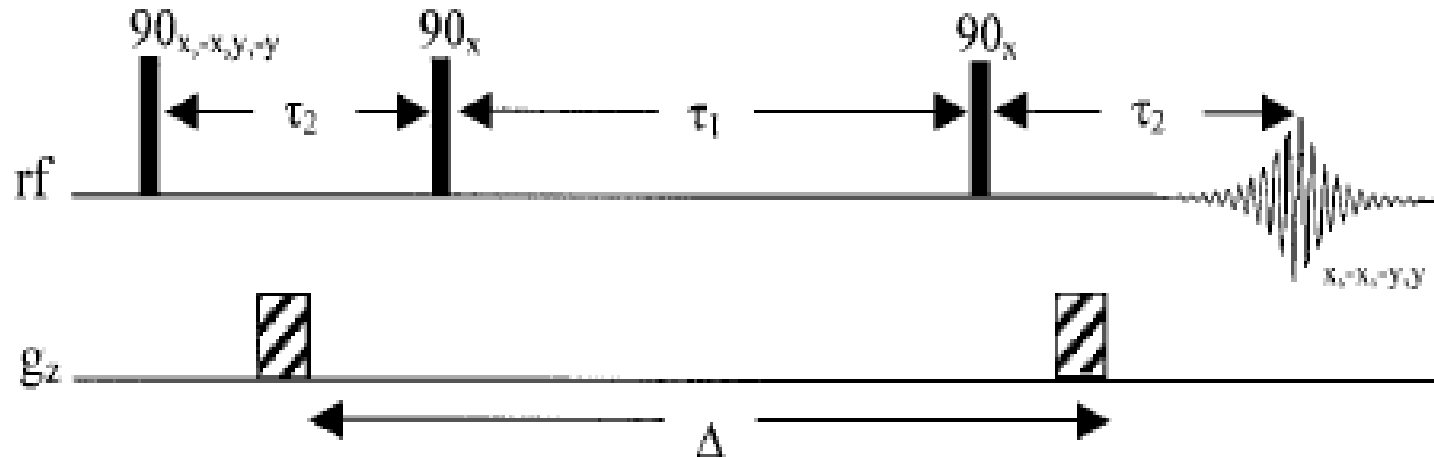
PGSE
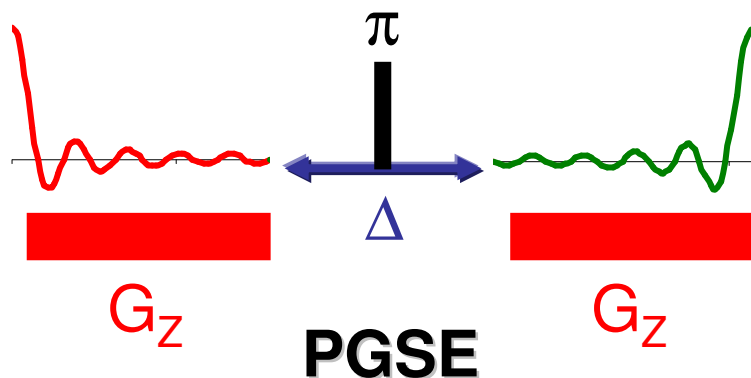
Stejskal-Tanner equation

$$E \equiv E_0 \exp\left[-D(\gamma G_Z \delta)^2 \left(\Delta - \frac{\delta}{3}\right) - \frac{2\Delta}{T_2}\right]$$
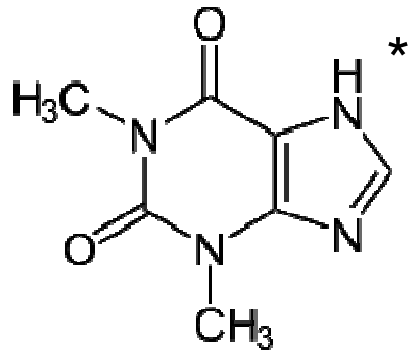
Pulse **G**radient **ST**imulated **E**cho

During τ_1 (most of Δ) the magnetization is longitudinal, thus avoiding modulation by scalar coupling and decaying with constant $1/T_1$.

$$E = \frac{1}{2}E(\Delta = 0)\exp\left[-D(\gamma G_z\delta)^2\left(\Delta - \frac{\delta}{3}\right) - R\right]$$
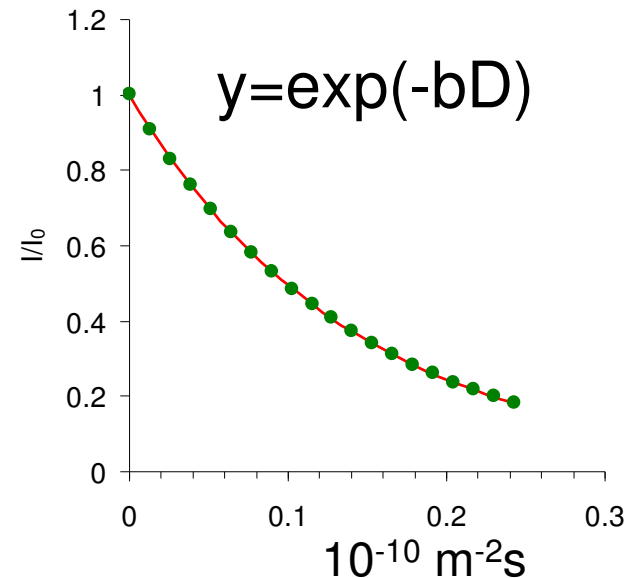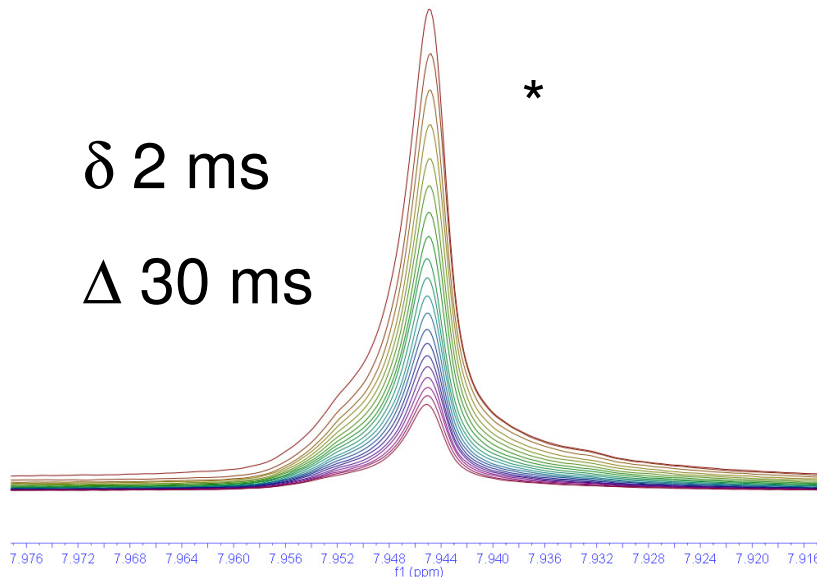
$R = 2\tau_2/T_2 + \tau_1/T_1$

Self-diffusion coefficient from echo decay fitting

Theophylline

D$_2$O 37 °C

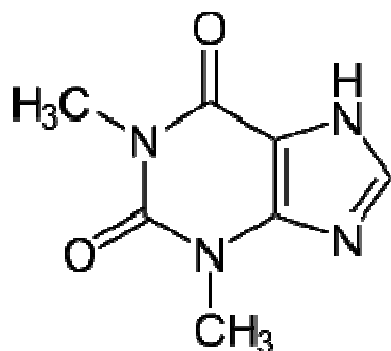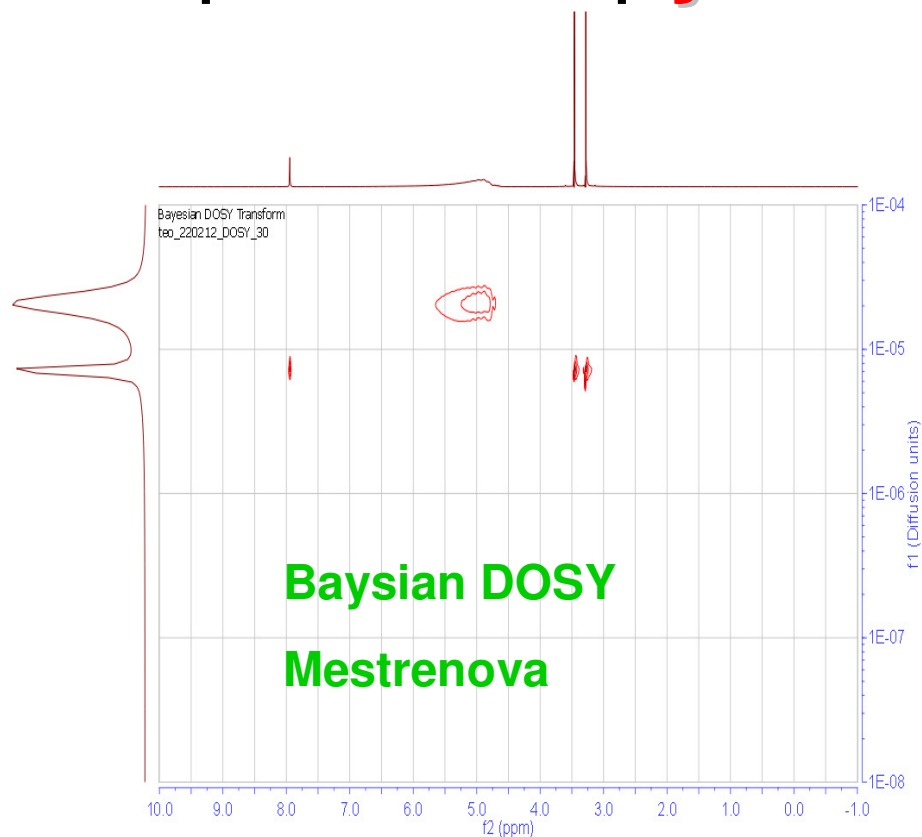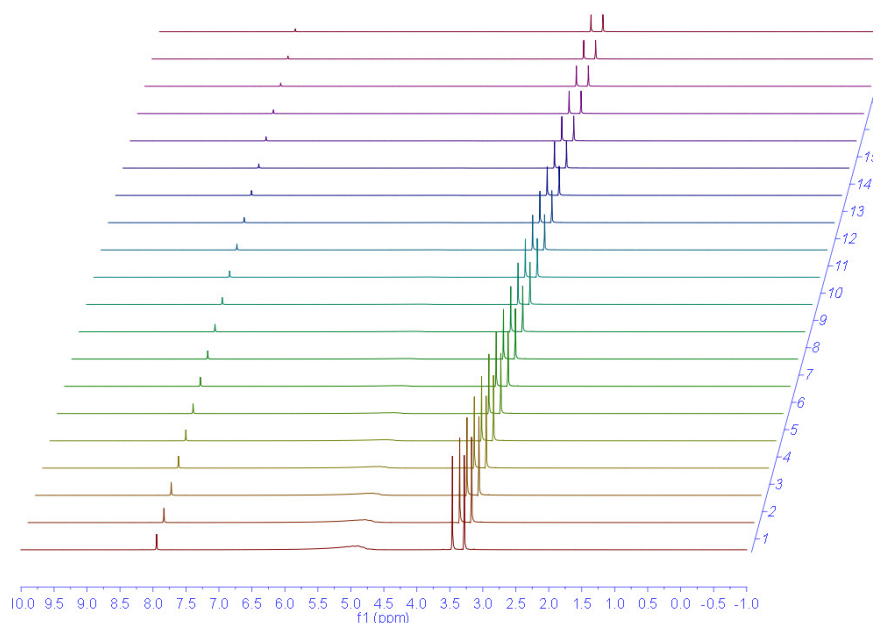Spectra acquired at constant Δ, and increasing G$_Z$, PGSTE experiment

y=exp(-bD)

δ 2 ms

Δ 30 ms

b= (γG$_Z$δ)^2(Δ-δ/3)

D= 7.1·10^{-10} m^{2}s^{-1}

independent of Δ

the experiment was repeated with Δ= 60 and 100 ms

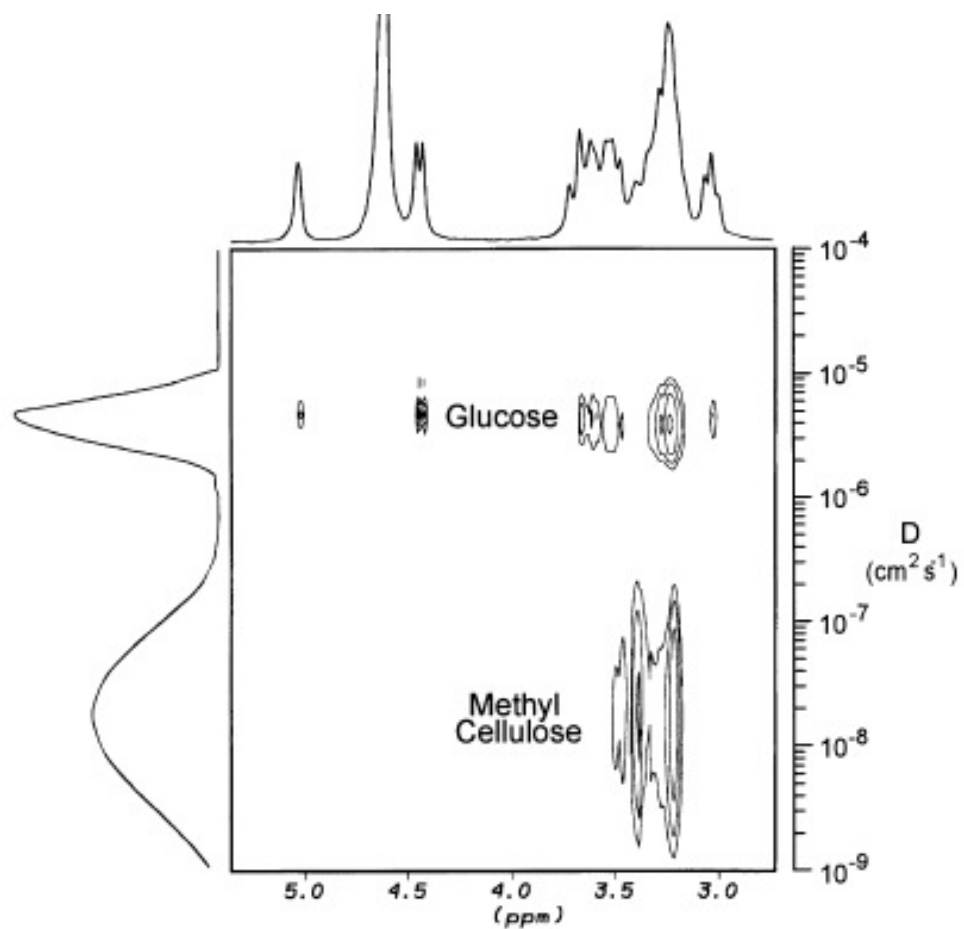# Diffusion Ordered Spectroscopy

Theophylline

D$_2$O 37 ℃

Baysian DOSY

Mestrenova

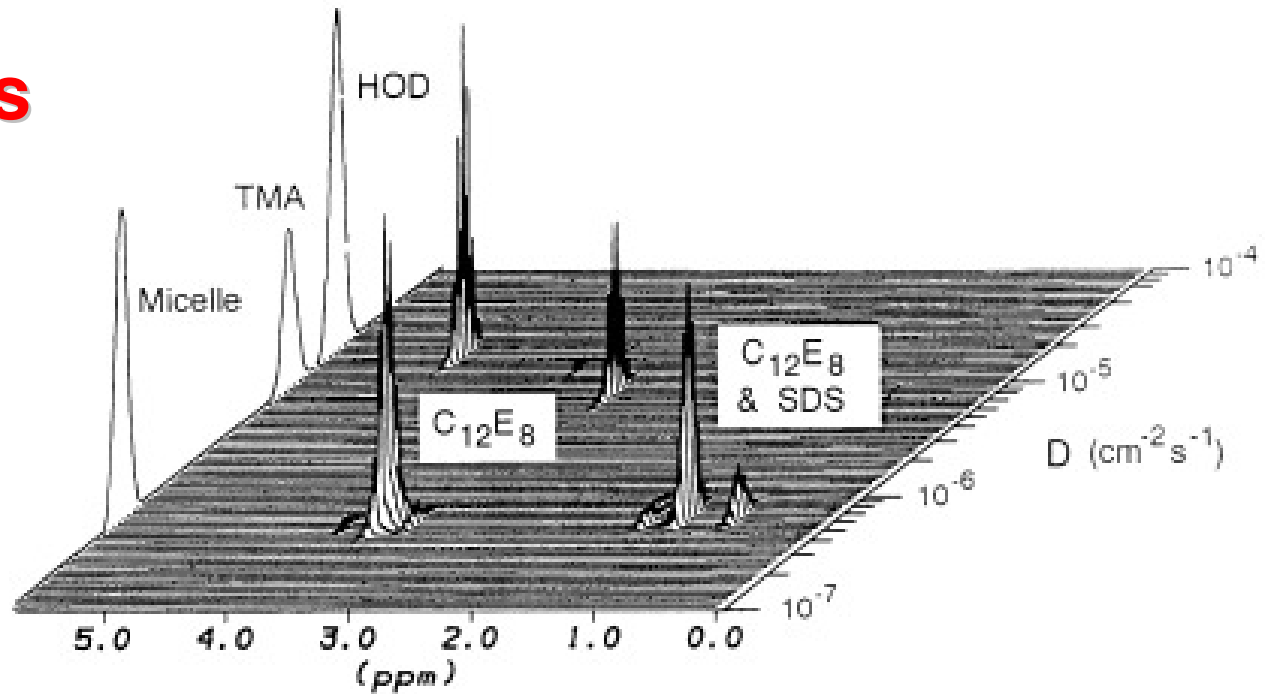2D spectrum with chemical shifts on dimension 1 and D on dimension 2
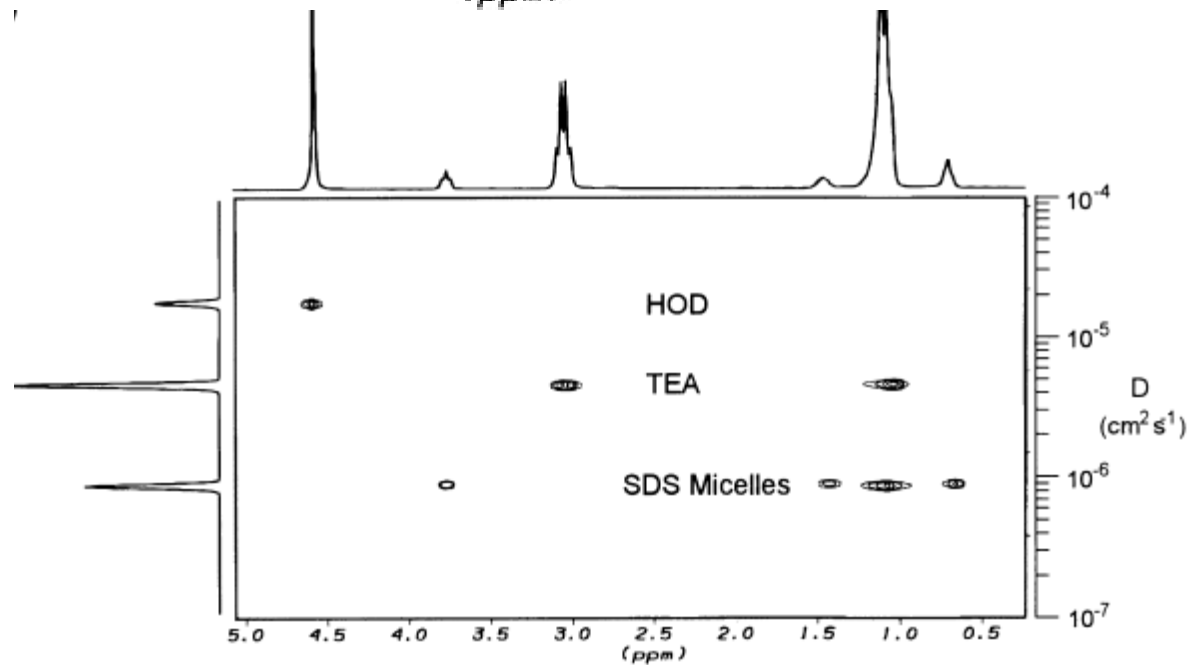
analysis of mixtures

C. S. Johnson Prog.
Magn. Reson. Spectrosc.
1999, 34, 203-256

micellar systems

TMA=
tetramethyl-
ammonium
chloride

TEA=
tetraethyl-
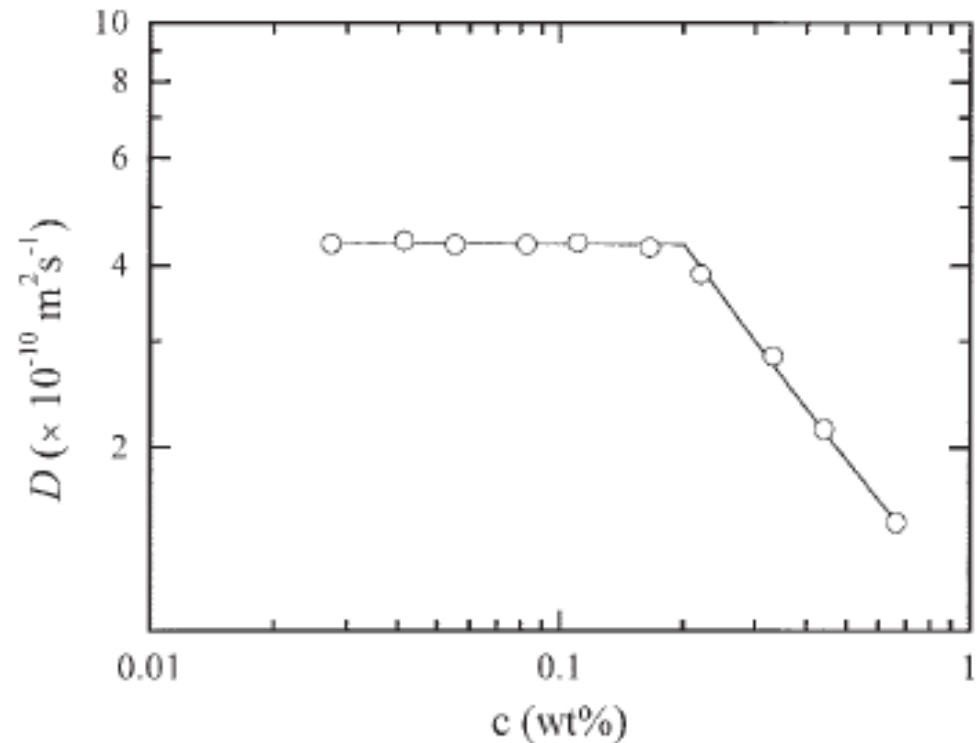ammonium
chloride

[Johnson1999]

cmc determination

SDS D_2O 25 °C

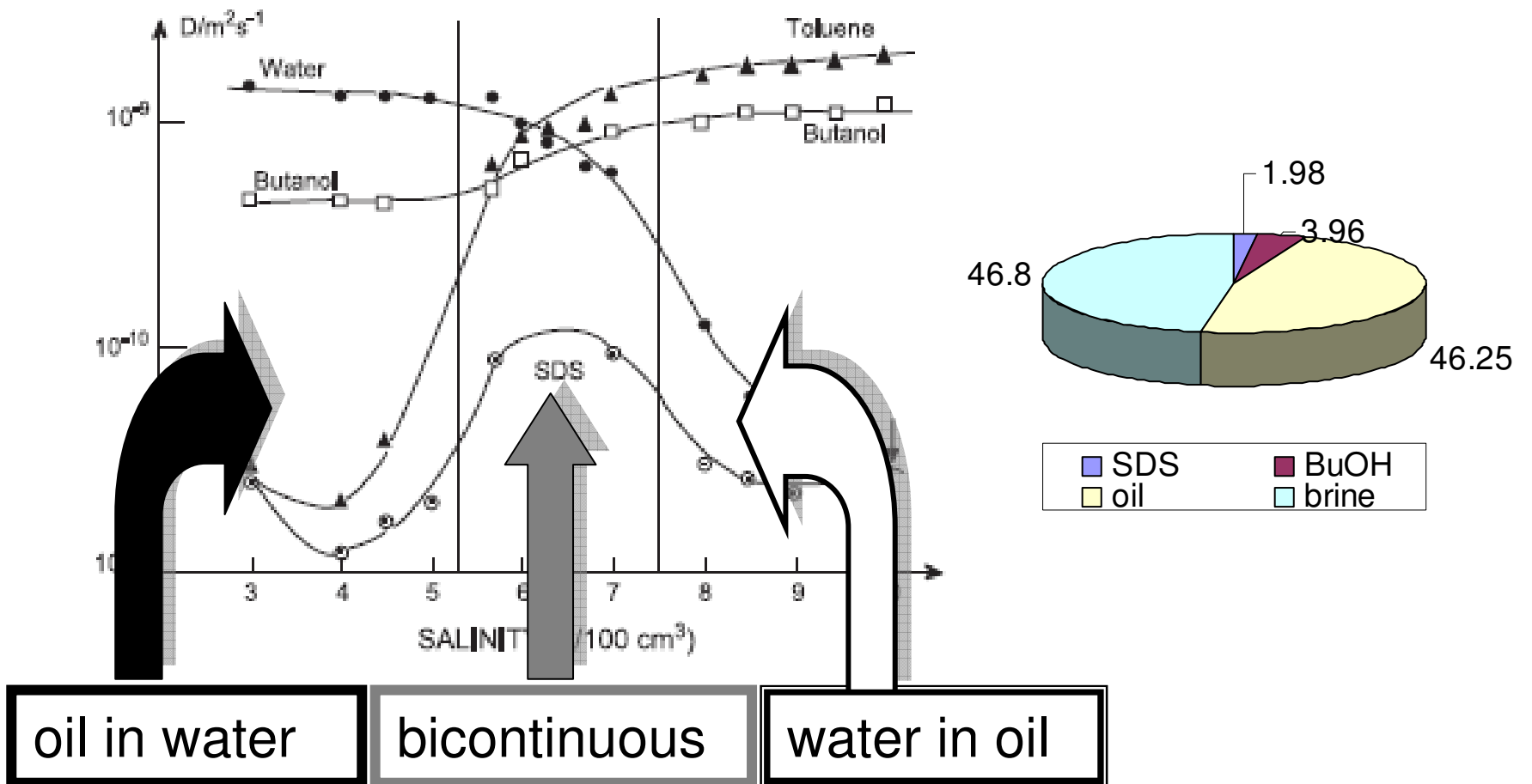$$D = D_f \frac{C_f}{C_t} + D_b \left(1 - \frac{C_f}{C_t} \right)$$

f: free

b: micellised

t: total surfactant

[O. Söderman et al. Concepts Magn. Reson. Spectr. 2004, 23A, 121-135]
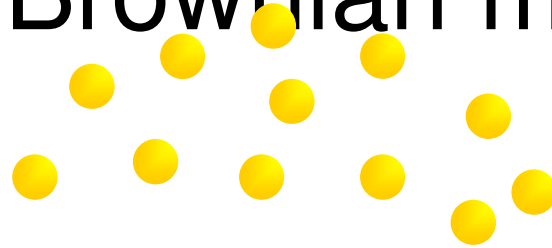
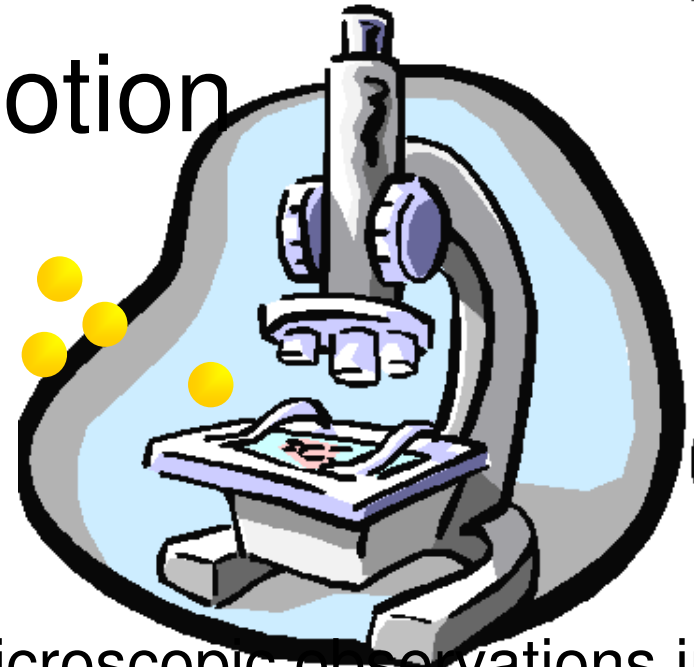# Transformation of a microemulsion structure

[P. Guering and B. Lindman Langmuir 1985, 1, 464-468]

Brownian motion

$$D = \frac{k_B T}{6\pi\eta R_H}$$

Robert Brown: A brief account of microscopic observations in the months of June, July and August, 1827, on the particles contained in pollen of plants; and on the general existence of active molecules in organic and inorganic bodies. Phil. Mag. 4, 16, 1829

Albert Einstein: Über die von der molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen" ("On the movement of small particles suspended in a stationary liquid demanded by the molecular-kinetic theory of heat") Annalen der Physik 1905

Diffusion in polyelectrolyte hydrogels
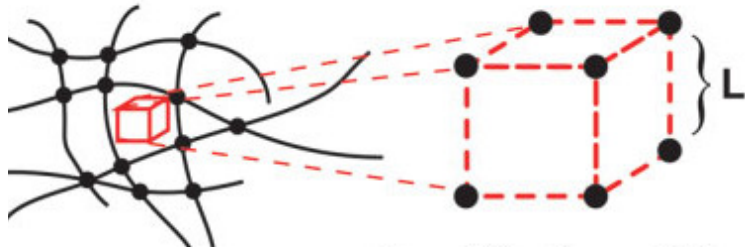
Hindered diffusion due to gel network

The main contribution come from steric hindrance

The steric hindrance is modeled in terms of obstruction effects

$$\frac{D_g}{D_0} = \exp\left[-\frac{\pi}{4}\left(\frac{r_s + r_f}{r + r_f}\right)^2\right]$$

with r_s: solute hydrodynamic radius, r_f: radius of the polymer chain, r: radius of the openings between the polymer chains

B. Amsden Macromolecules 2001, 34, 1430