The basics of NMR diffusometry

part 1
Introduction
(Kosma Szutkowski)

part 2
Motion encoded by NMR
(Janez Stepišnik)

Various aspects of diffusion NMR

- Free or unrestricted diffusion

- Restricted diffusion
  - isotropic diffusion; apparent diffusion and so-called effective diffusion coefficient
  - anisotropic diffusion

- Multi-component diffusion

Bruker Diff 25 (9.5 T/m G_z)

Bruker micro2.5 (1 T/m, G_x, G_y, G_z)

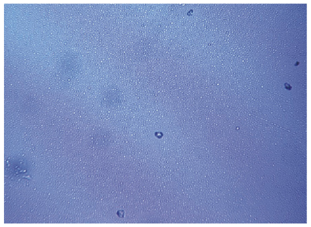
Gradient coils + amplifiers

- single direction
- orthogonal gradient system

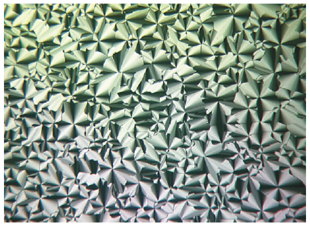
Some methods in diffusion NMR

- High magnetic constant field gradients
  - hole-burning diffusion
- Pulsed field gradient
  - PGSE (Stejskal-Tanner 1965)
- Multi-component diffusion
  - FT PGSE (Stilbs 1982)
- Fast diffusion methods (BURST, DUFIS, OUFIS)

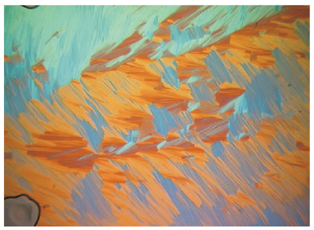
Applications: multicomponent diffusion in micellar solutions



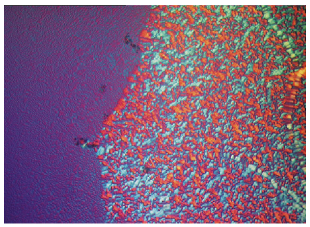
Isotropic phase
(x100)



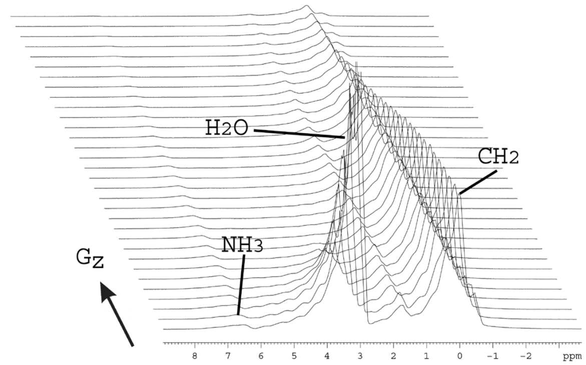
Hexagonal phase texture
(x100)



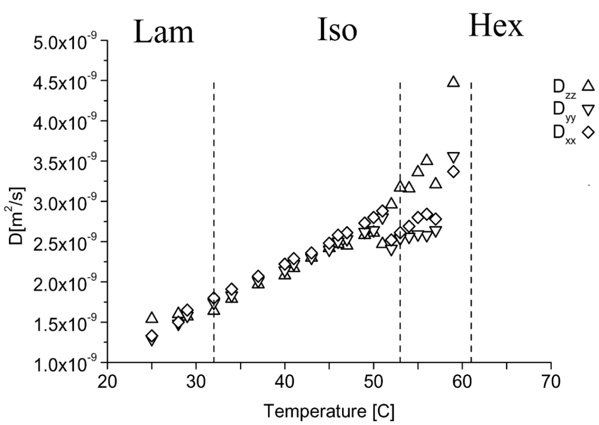
Lamellar phase texture
(x100)



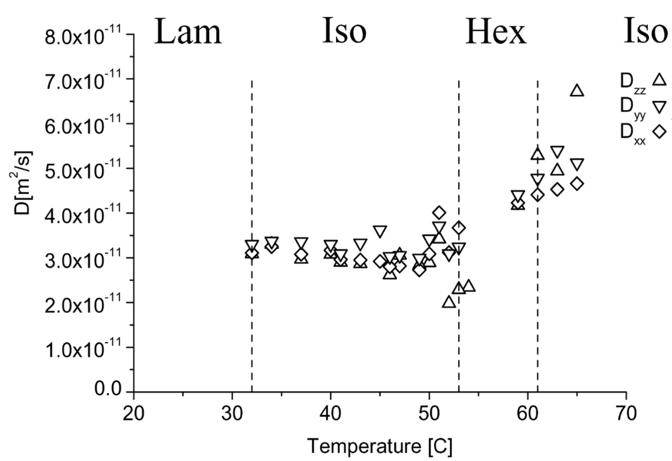
Hexagonal phase texture in the
transition state from isotropic
to hexagonal (x50)l

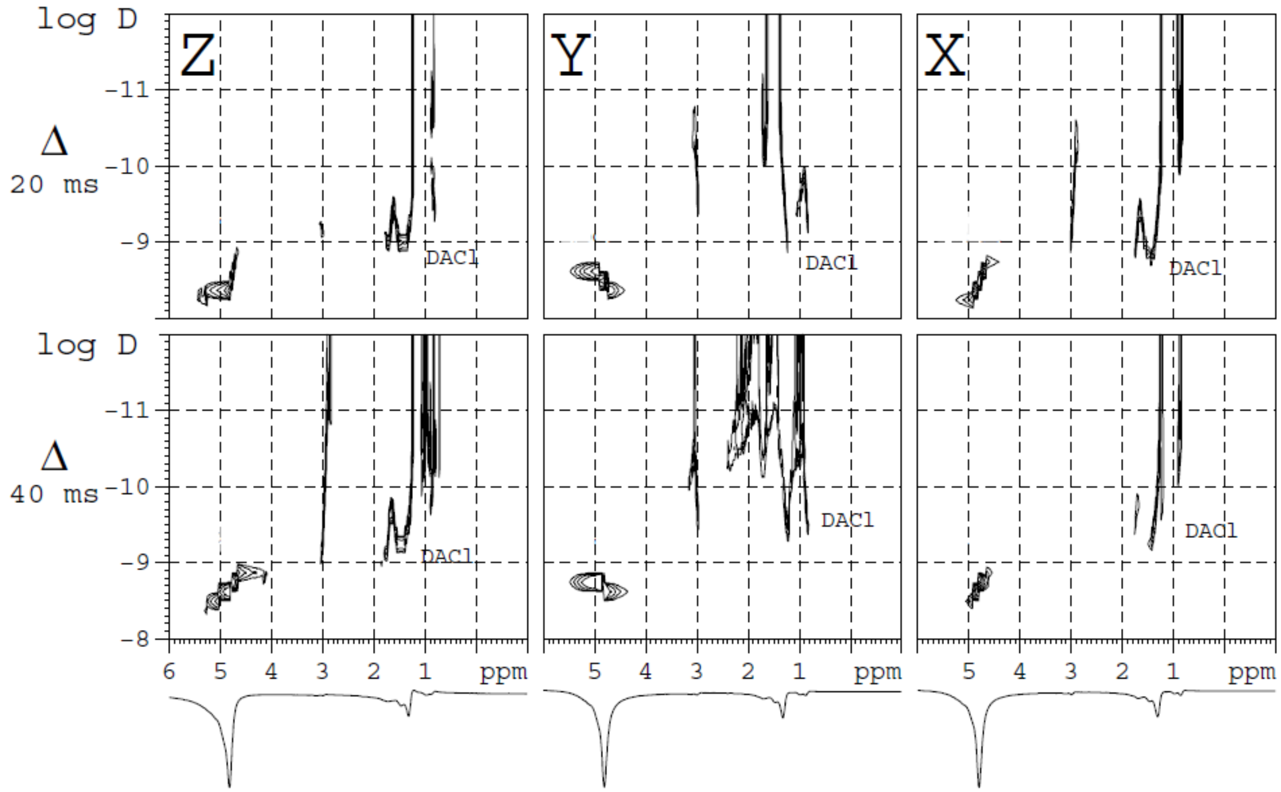


H_2O



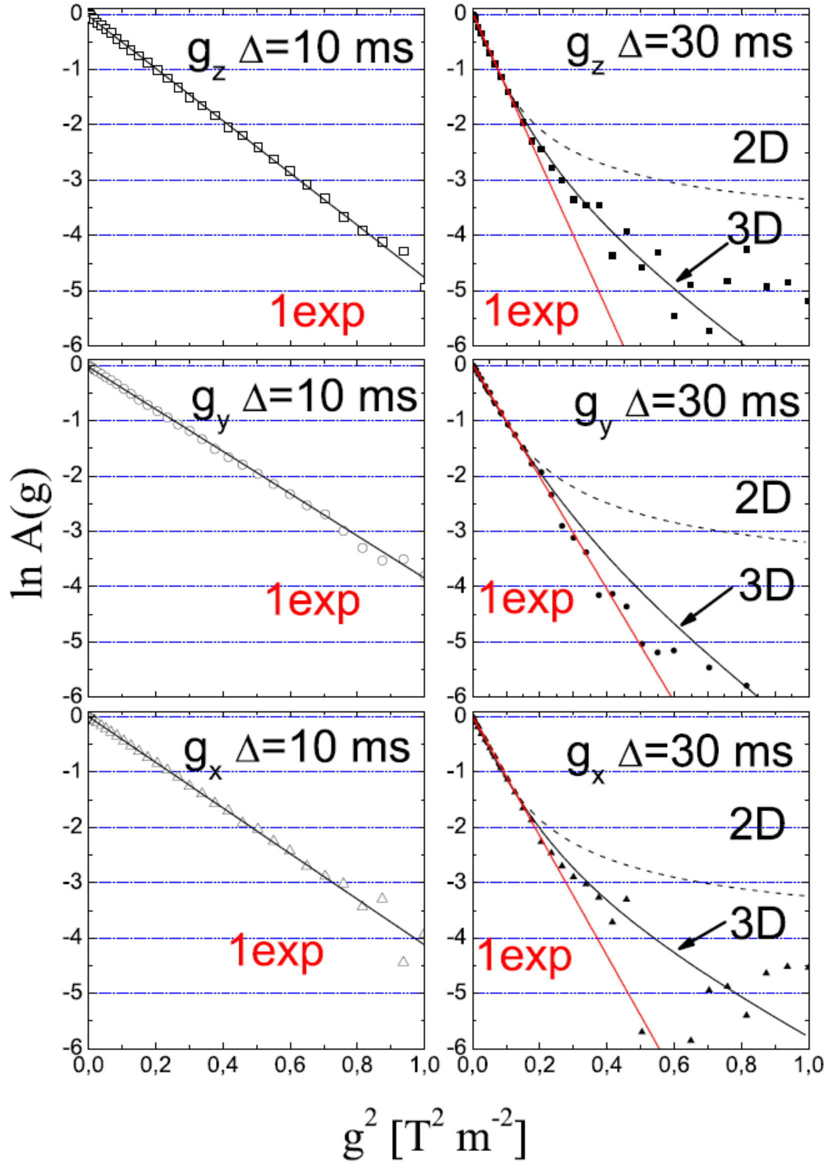
alkyl chain (-CH_2)





Diffusion Ordered SpectroscopY (DOSY)

Applications: information about morphology at microscale



1exp: E. O. Stejskal and J. E. Tanner, J. Chem. Phys. 42, 288 (1965). Gaussian diffusion propagator function

$$\ln A = -D\gamma^2\delta^2 g^2\left(\Delta - \frac{1}{3}\delta\right)$$

3D: P. T. Callaghan and O. Soderman, J. Phys. Chem **87**, 1737 (1983). Unoriented lamellar geometry:
$D_{||}$ diffusion parallel to the surface normal
$D_{\perp}$ diffusion perpendicular to the surface normal

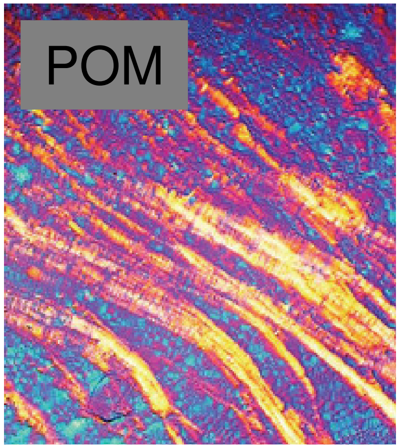
2D: $D_{\perp} >> D_{||}$ (non-permeable or non-perforated walls)

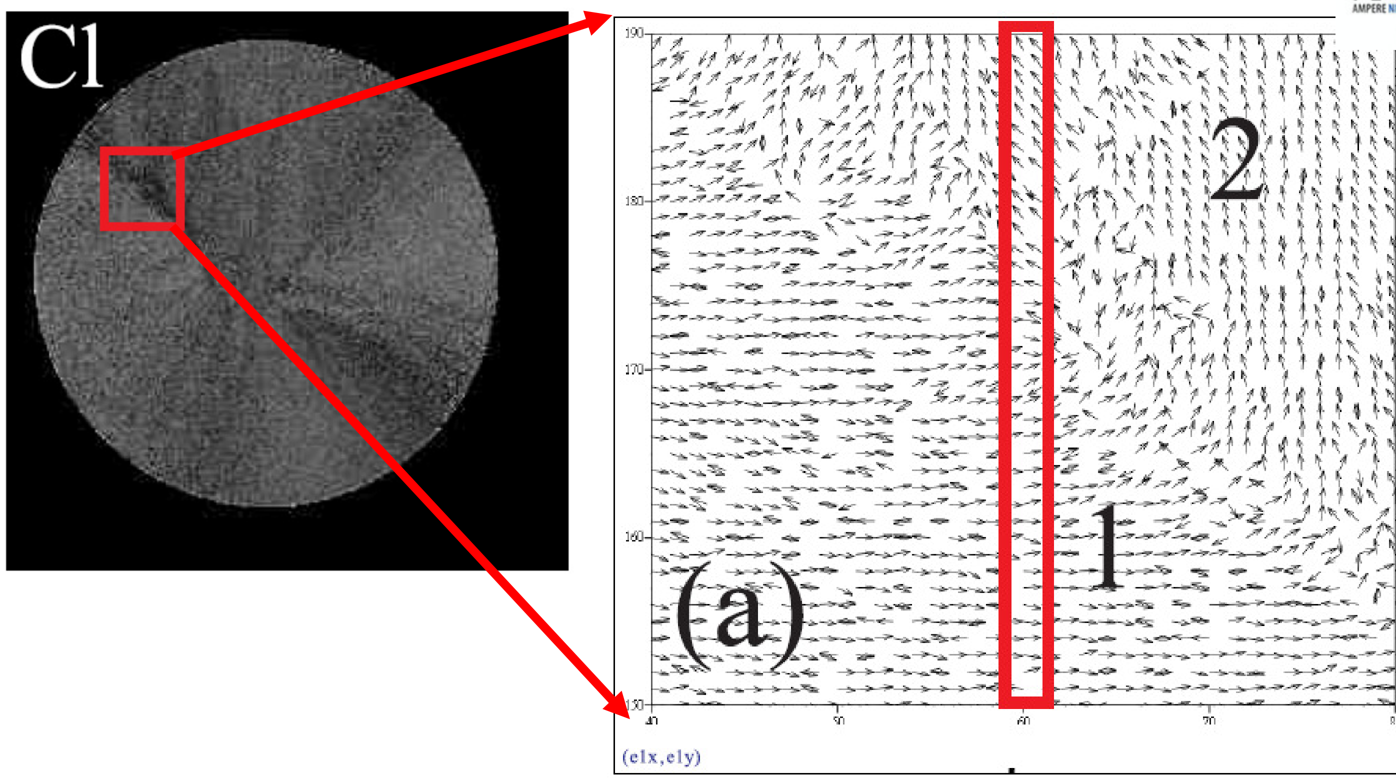
$$A_{3D} = \exp(-kD_{\perp})\int_0^1 \exp(-k(D_{||} - D_{\perp})x^2)\mathrm{d}x$$

$$\overline{z^2} = 2D_{||}(\Delta - \delta/3)\cos^2\theta + 2D_{\perp}(\Delta - \delta/3)\sin^2\theta$$

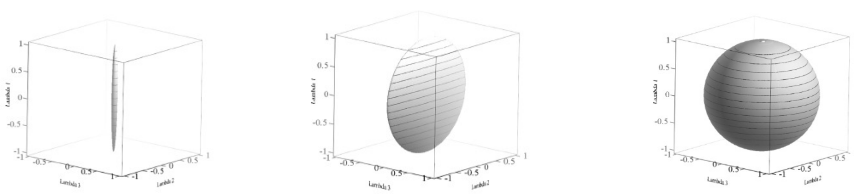
3D like diffusion – possible interspacings between micelles through which water diffuses

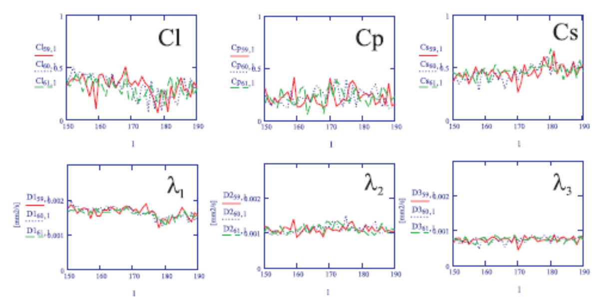
'Diffusion' combined with spin echo imaging



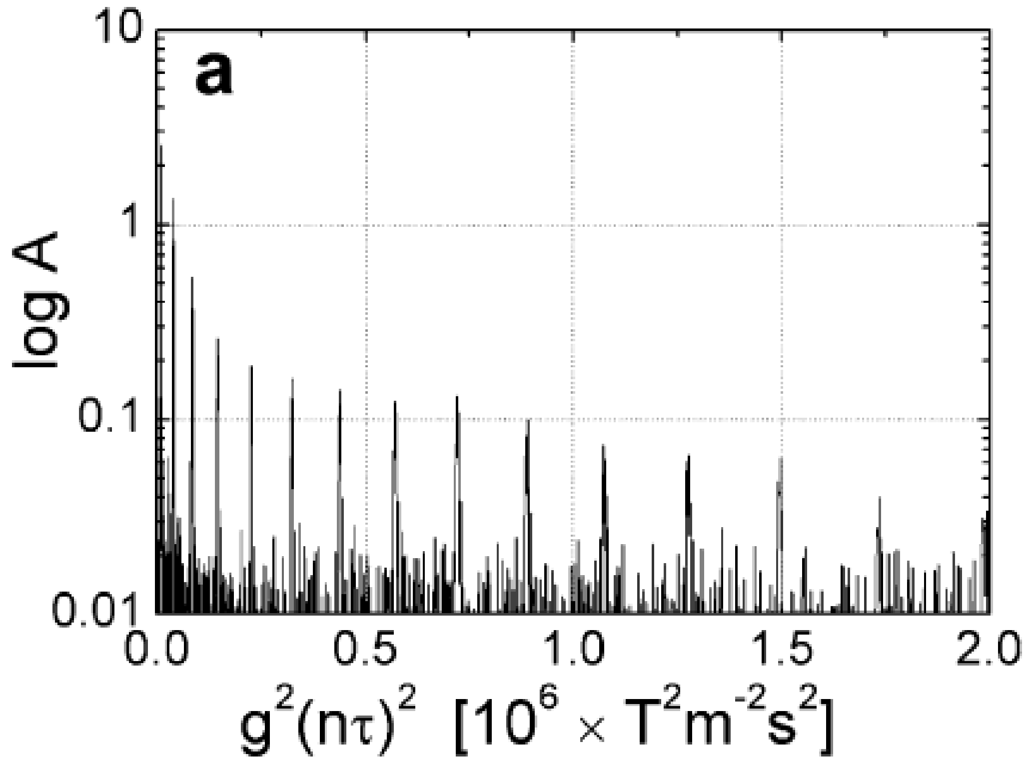


$$\mathbf{D} = \begin{vmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{vmatrix}$$



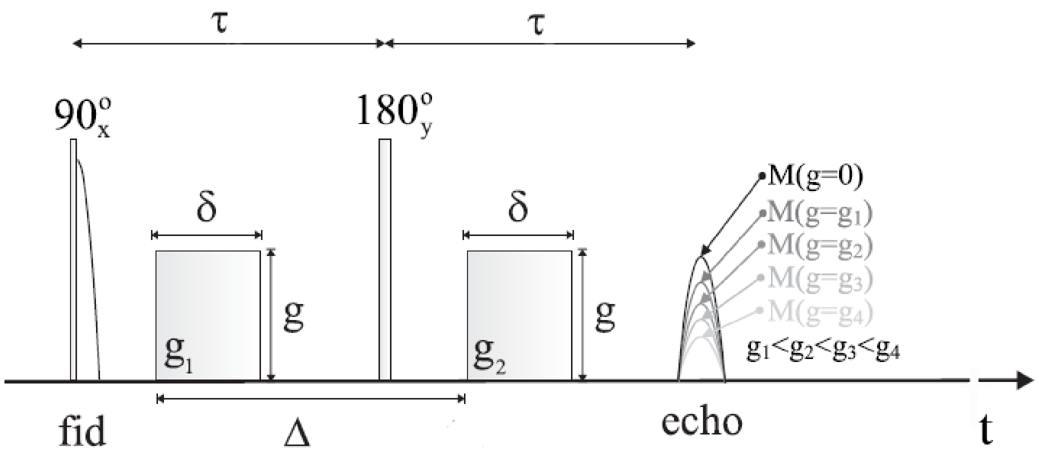


Applications: ultra fast diffusion experiments



Two component diffusion attenuation obtained for 3% wt. PEG_{6000} in water in less than 400 ms (single-shot OUFIS magnetization grating encoding)

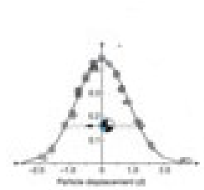
Pulsed Gradient Spin Echo (PGSE)



Stejkal-Tanner 1965

Bloch equations with diffusion terms
(Torrey, Phys. Rev. 1956, 104, 563)

Gaussian molecular displacement probability function during time Δ



$$A(g) = \exp[-D\gamma^2\delta^2 g^2(\Delta - \delta/3)]$$

How to relate diffusion with PGSE NMR?

Spins in motion

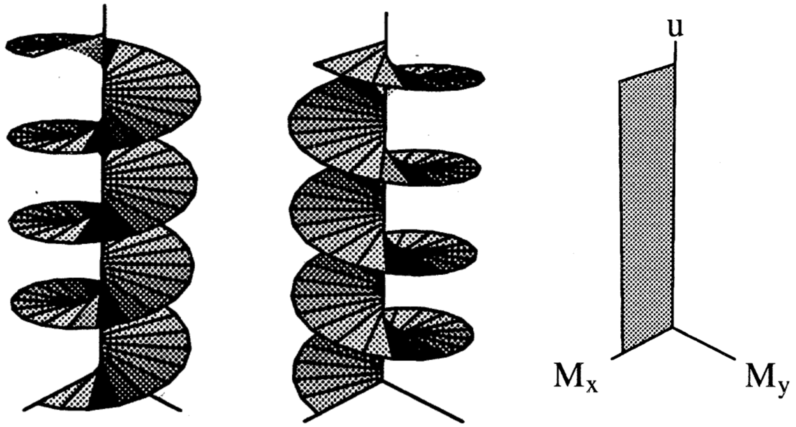
$$P(Z,t) = \left(2\pi\langle Z^2(t)\rangle\right)^{-\frac{1}{2}} \exp\left(\frac{-Z^2}{2\langle Z^2(t)\rangle}\right) \qquad \langle Z^2\rangle = \int_{-\infty}^{\infty} Z^2 P(Z,t)\,dZ = 2Dt \qquad Z^2 = 2Dt$$

Magnetic field gradient

$$G_z = \partial B_z / \partial z$$

Spins are tagged by
a spatial distribution of phase

Spin echo attenuation



The spins undergo several transformations during which a complete rephasing is expected assuming that no diffusion is present. Any translation in the direction of magnetic field gradient disturbs the closed cycle leading to smaller spin echo amplitude.

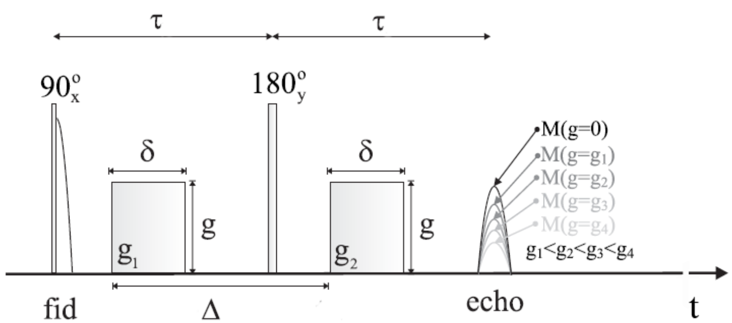
Starting point for calculations

The attenuation of spin echo induced by Gaussian diffusion factor

$$A = \exp[-D \int k^2(t) dt]$$

$$G_z = \frac{\partial B_z}{\partial z}$$ magnetic field gradient in *Z* direction

$$k = \gamma \int G dt$$ wave number in *k*-space, determines magnetization helix frequency

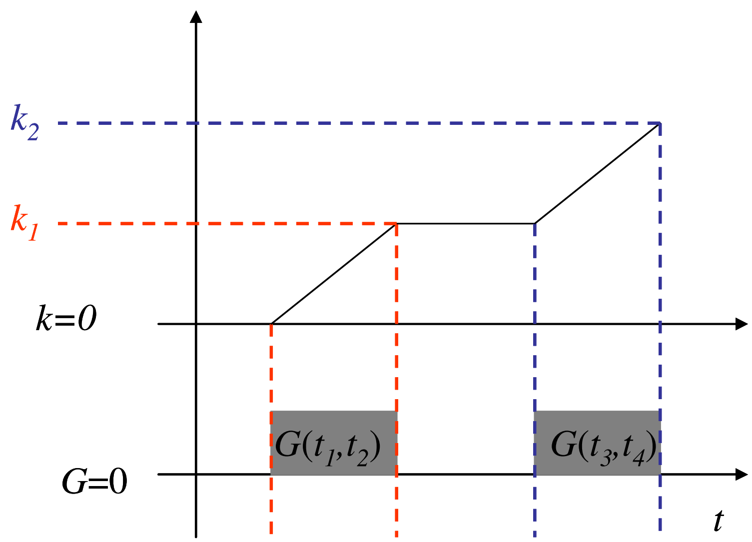


$$A(g) = \exp[-D\gamma^2\delta^2 g^2(\Delta - \delta/3)]$$

Coherence pathway: it is just an evolution of *k*-number in time in the absence of r.f. pulses

Once *k* is increasing, a magnetization helix is tightening

For a complete description of coherence pathways e.g. amplitude and phase calculations please refer to the paper:
A. Sodickson, D. G. Cory, Progress in Nuclear Magnetic Resonance Spectroscopy 33, 77-108, (1998)



$$k_1 = \gamma\int_{t_1}^{t_2} G dt = \gamma G(t_2 - t_1)$$

$$k_2 = \gamma\int_{t_3}^{t_4} G dt = \gamma G(t_4 - t_3)$$

$$G(t) = \begin{cases} G, t \in (t_1, t_2) \\ G, t \in (t_3, t_4) \\ 0, \text{elsewhere} \end{cases}$$

$$\Delta k_i^t = \gamma\int G_i dt = \gamma\int \frac{\partial B_i}{\partial i} dt$$

Δk_i^t is the transverse k value (transverse magnetization)

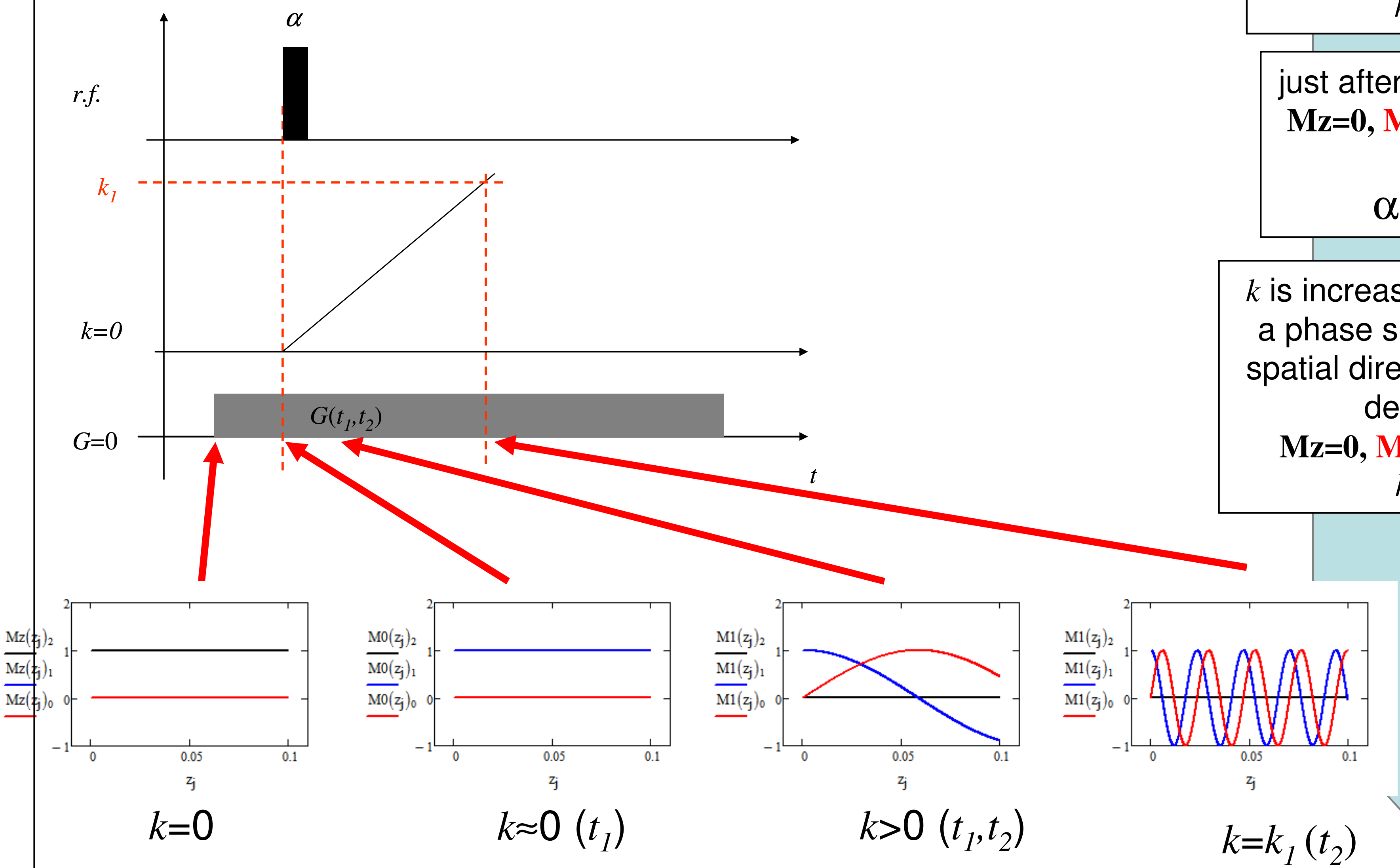
example: a simple one pulse sequence + gradient

r.f. pulse α (right-handed rectangular coordinate system)
-x phase, tip angle <90 º

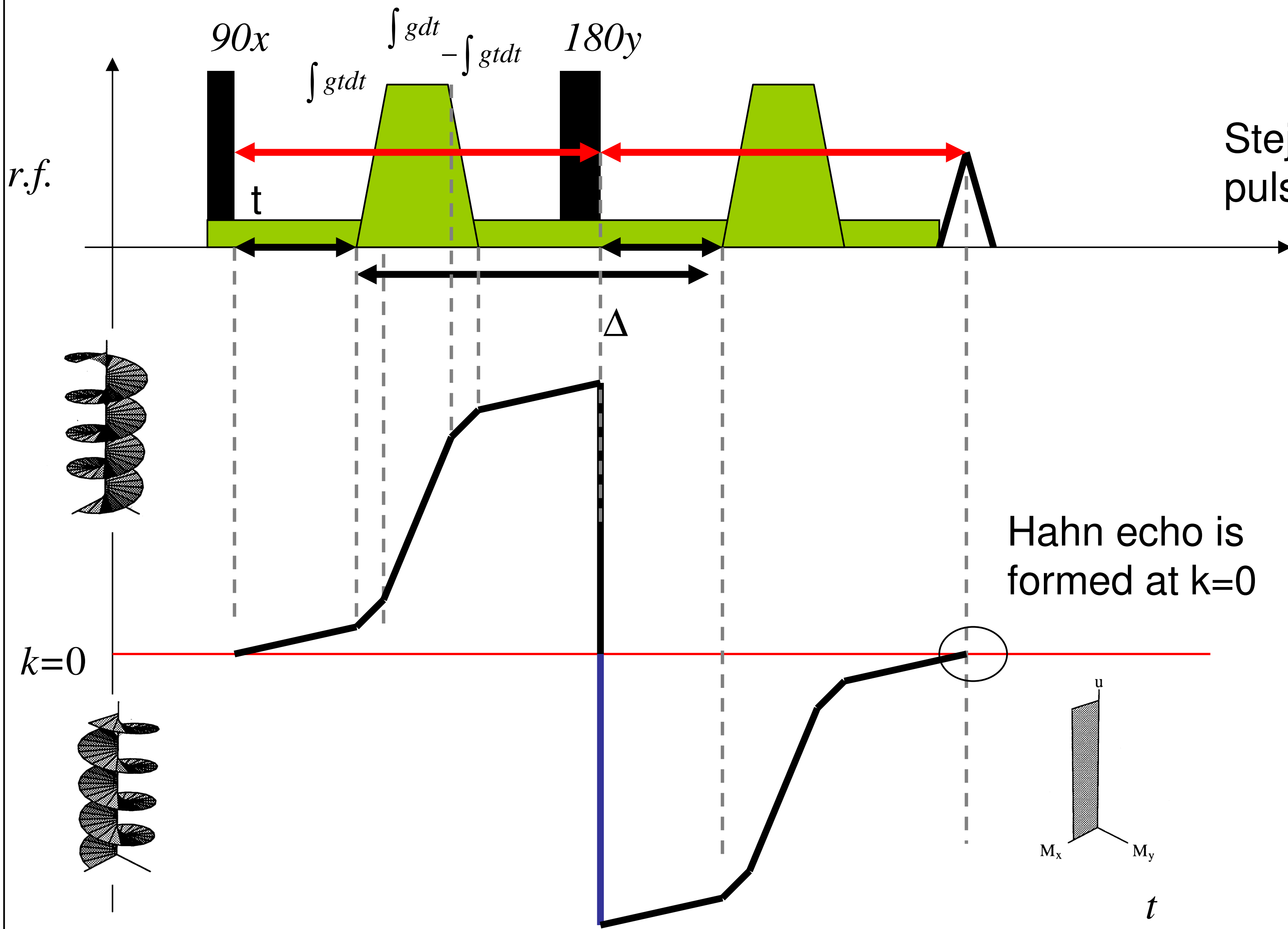
just before the pulse
Mz=1,Mx=0, My=0
k=0

just after the pulse α
Mz=0, Mx=0, My=1
k≈0
α=90 º$_{+x}$

k is increasing with time, a phase shift along the spatial direction starts to develop
Mz=0, Mx≠0, My ≠0
k>0



Coherence pathways: MS power point is you best friend

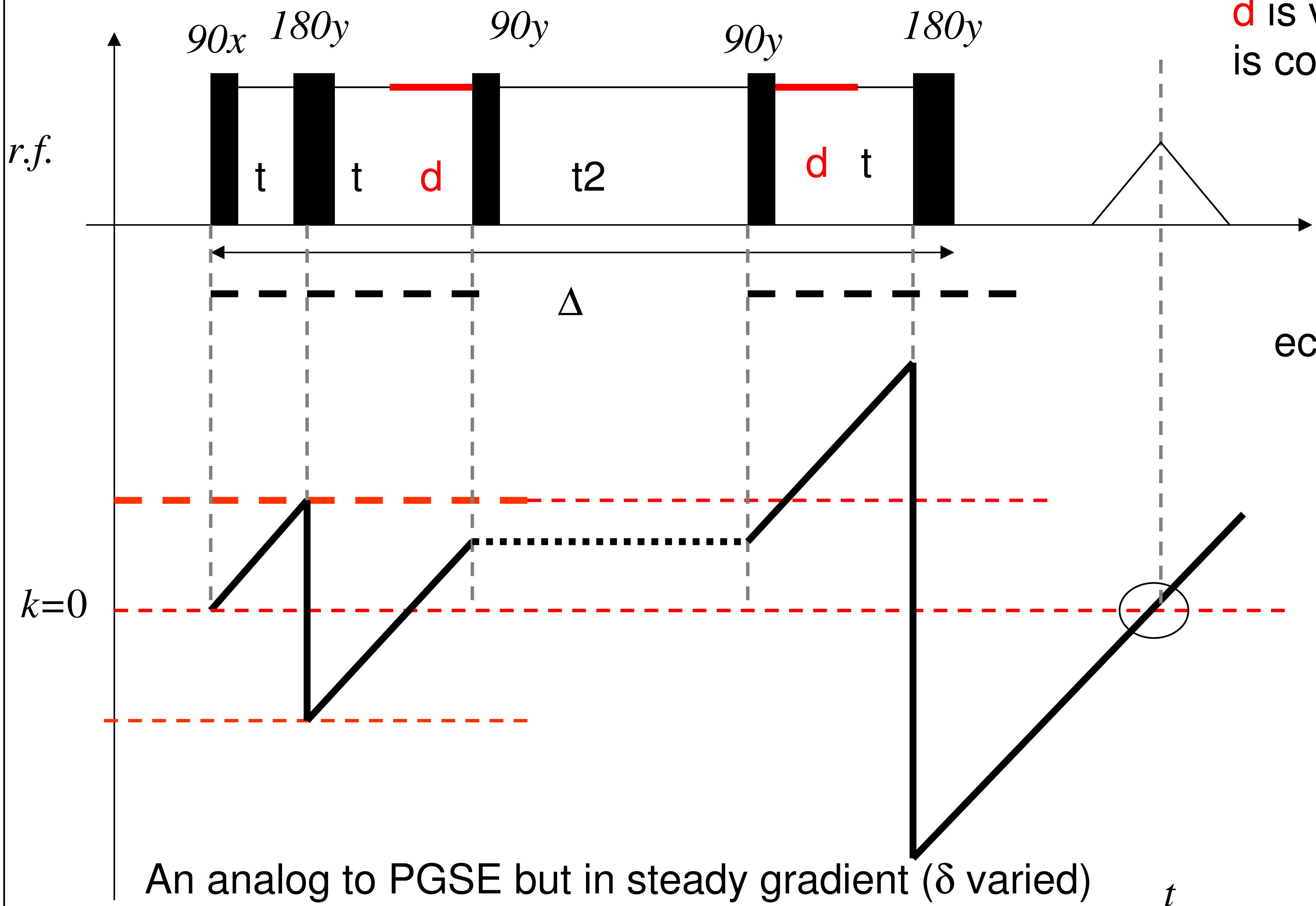


Stejskal-Tanner pulse sequence

Hahn echo is formed at k=0

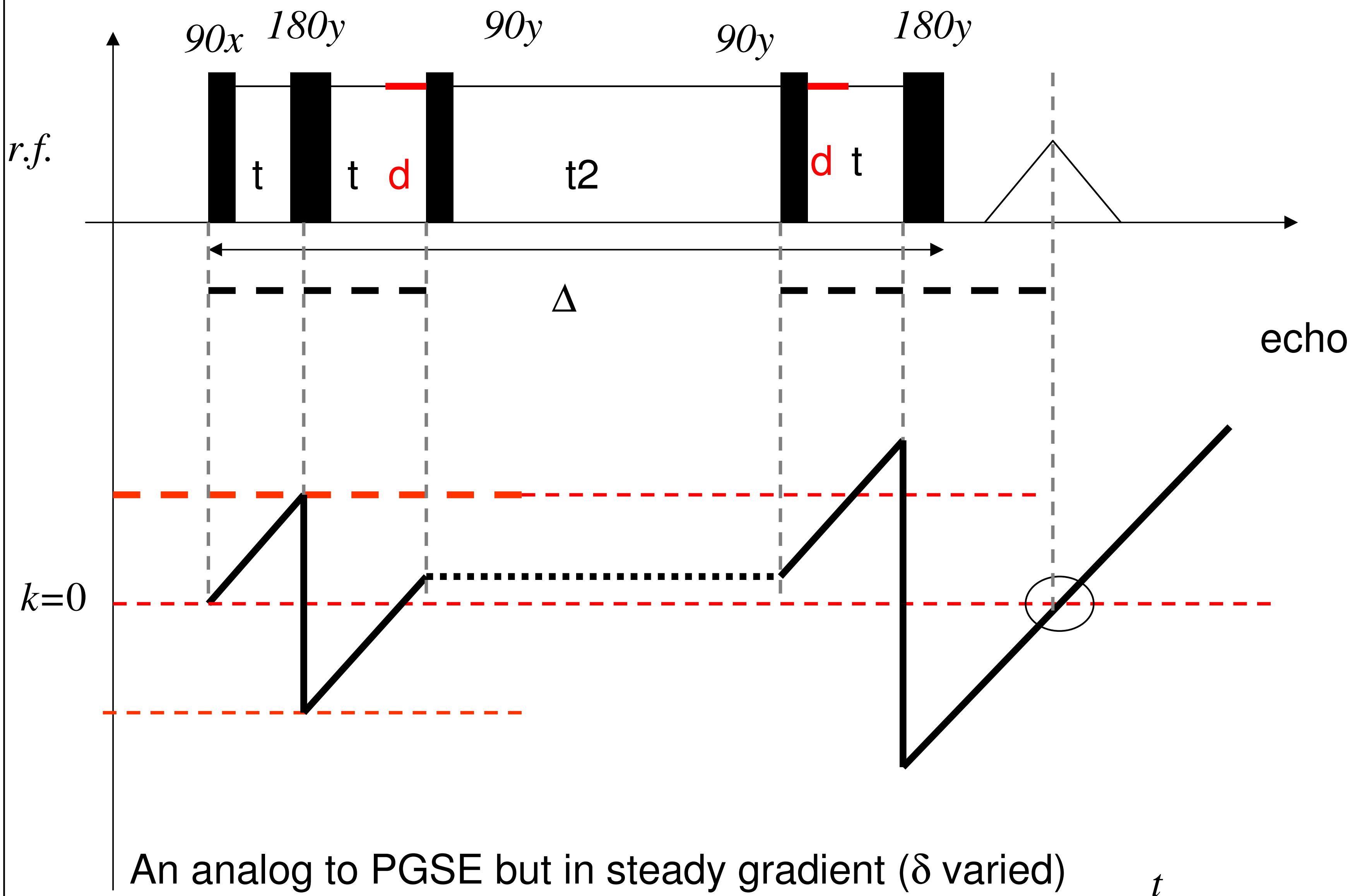
Relaxation compensated pulse sequence (steady gradient)

d is varied but Δ is constant



An analog to PGSE but in steady gradient (δ varied)

Relaxation compensated pulse sequence (steady gradient)



An analog to PGSE but in steady gradient (δ varied)

Please stay tuned and pay even more attention during next part!

Thank you!