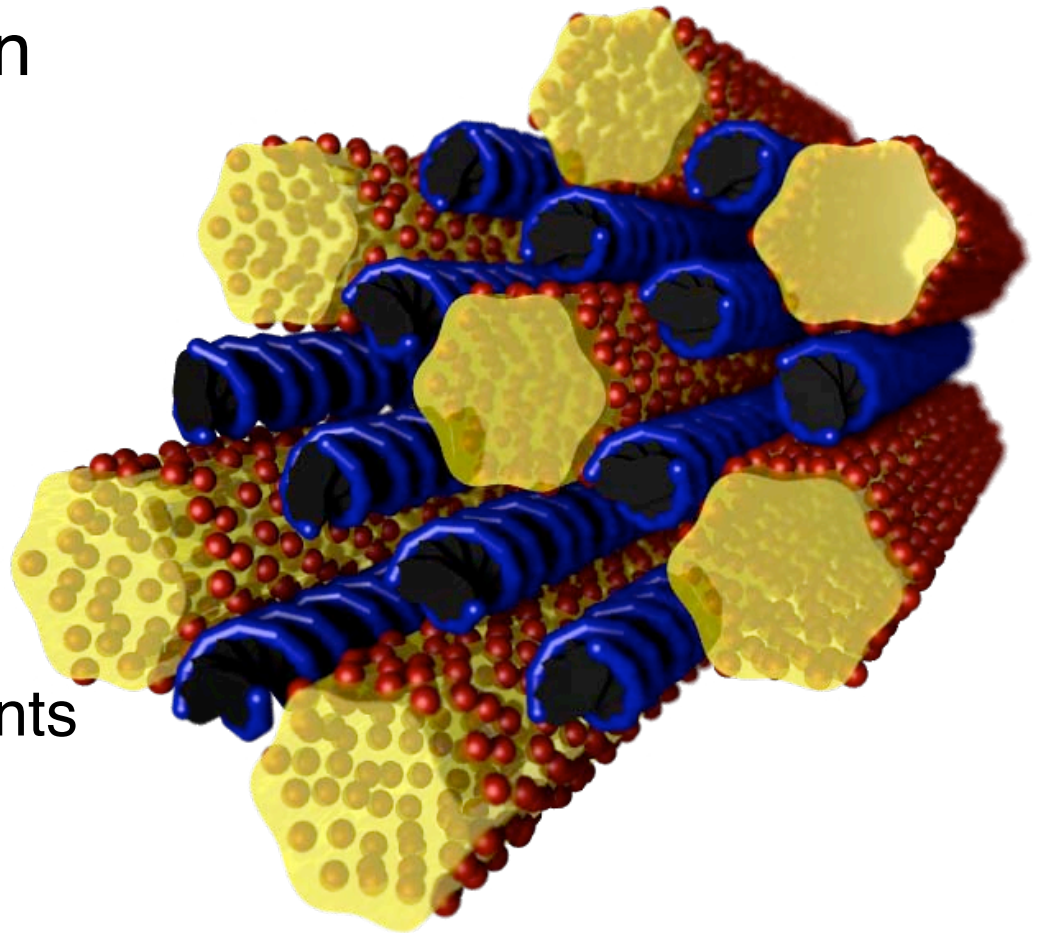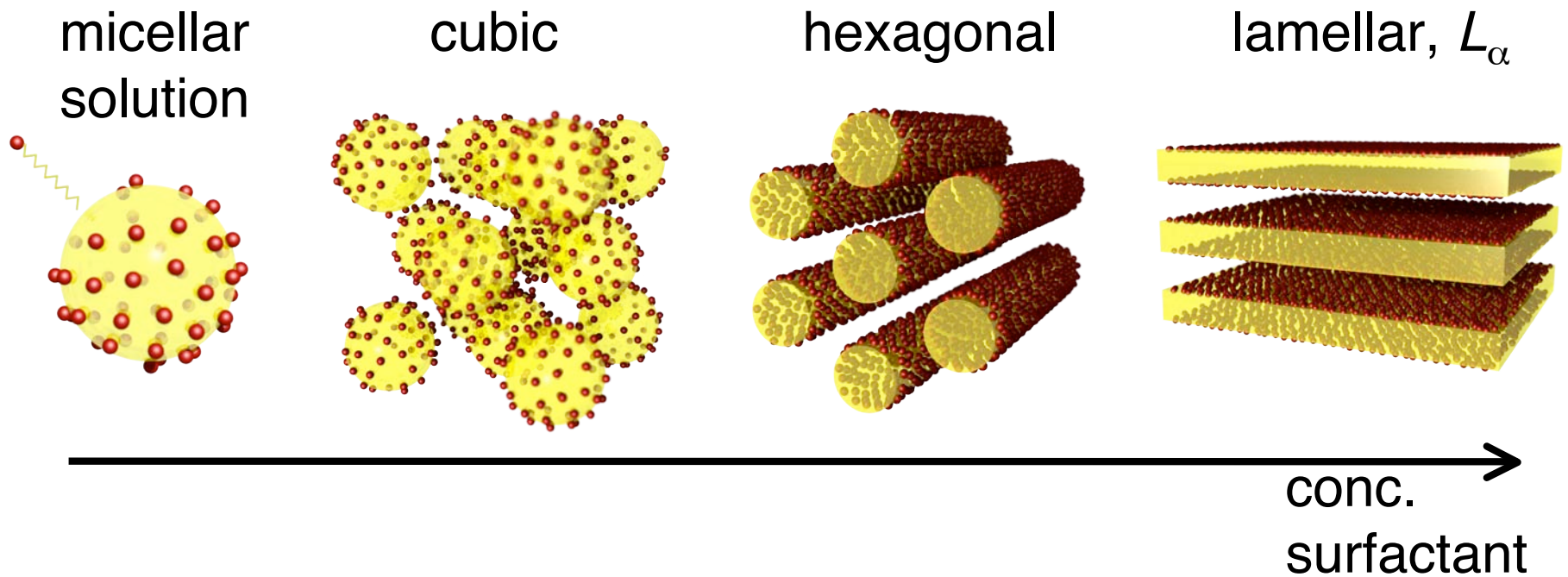# Liquid crystals

- Anisotropic motion
  - rotation
  - diffusion
- Effect on NMR measurables
  - CSA lineshapes
  - dipolar couplings
  - diffusion coefficients
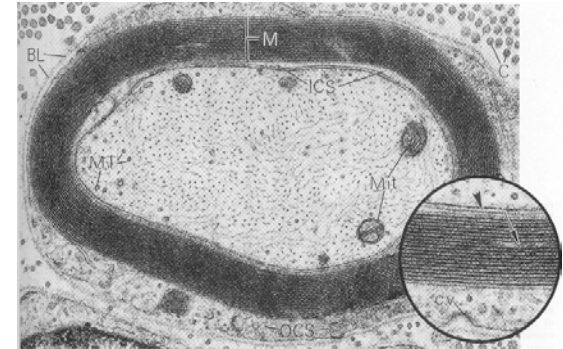
Surfactants and liquid crystals
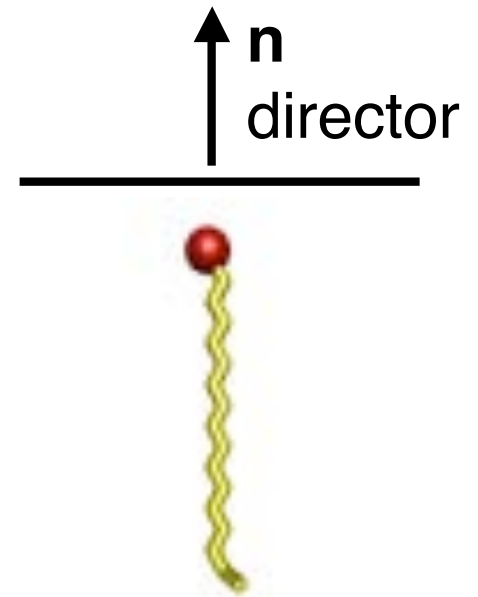
Self-assembly in water solution

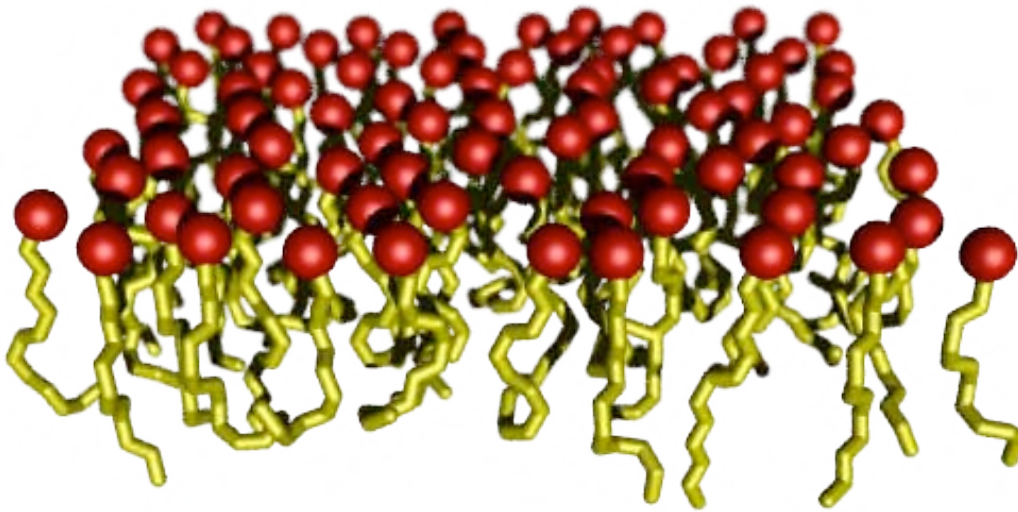| micellar solution	cubic	hexagonal	lamellar, L_α

→ conc. surfactant

Technical and biological systems
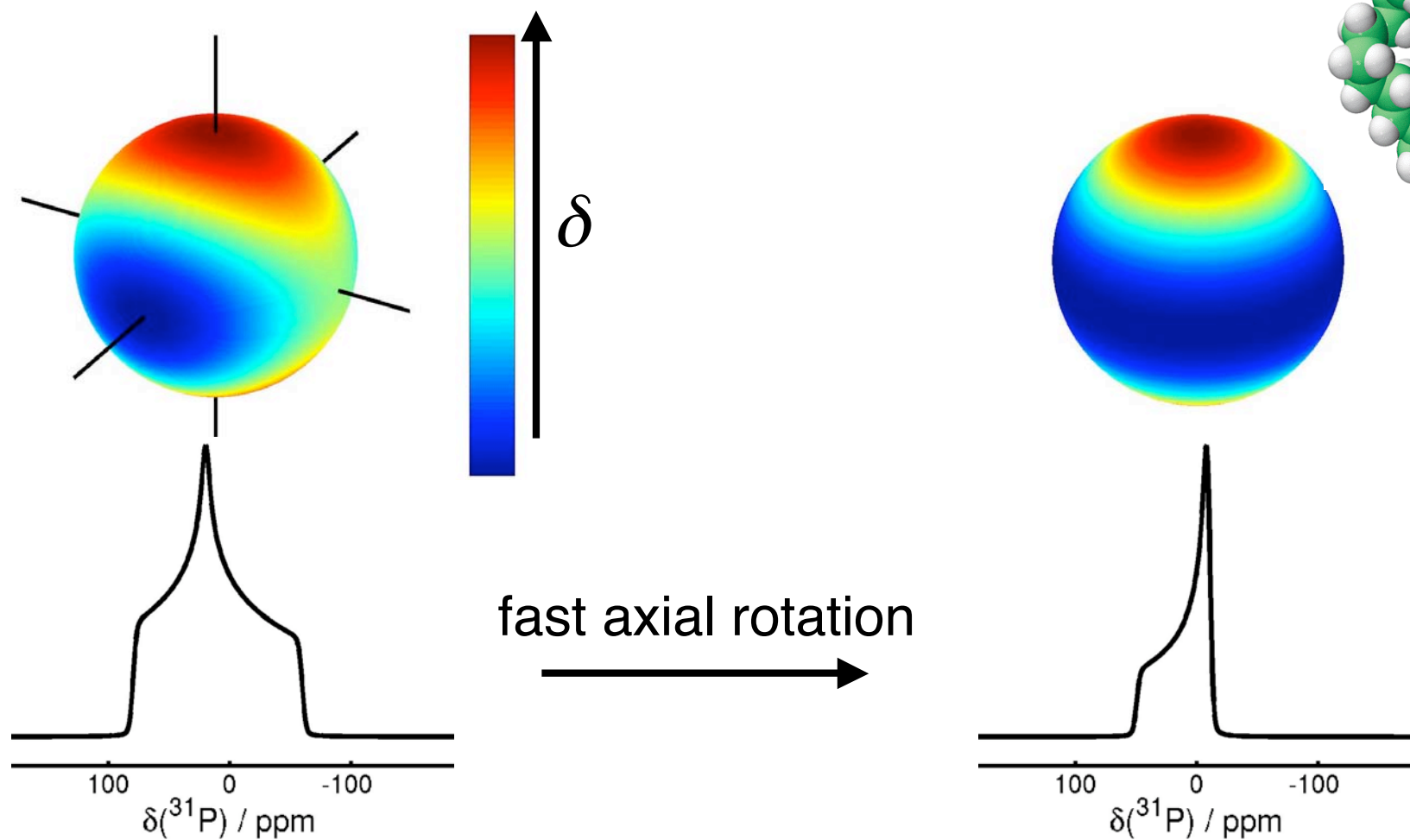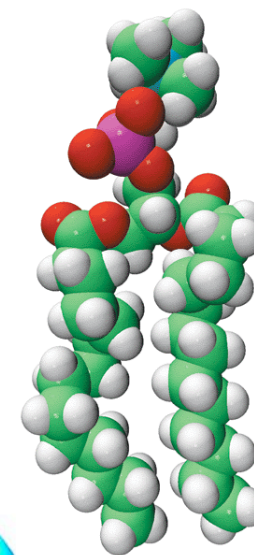
- Detergents, paints, food, …
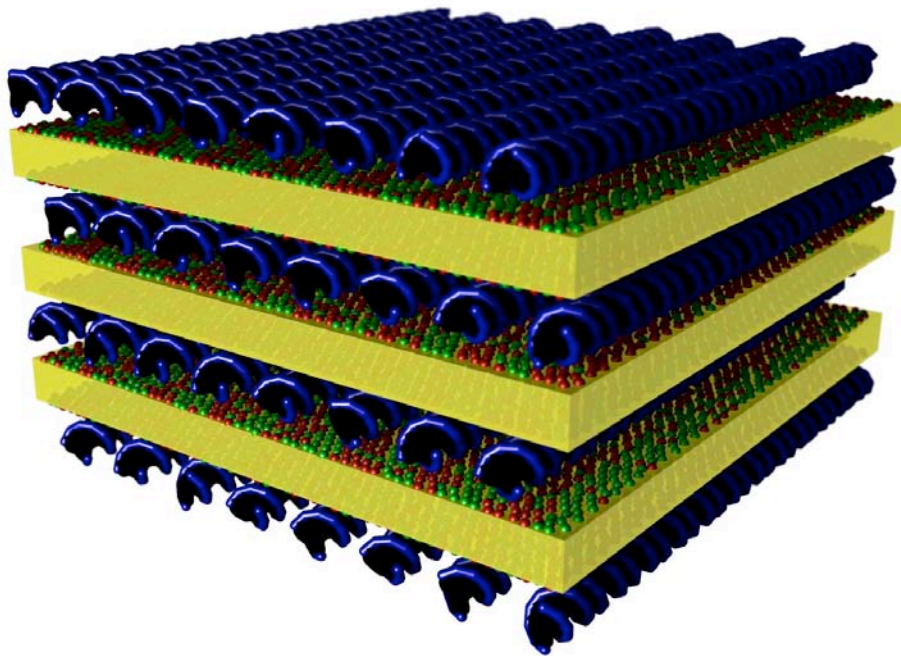- Biomembranes

Motion in a lamellar phase

- Rotation, translation, change of conformation
- Interactions $\perp$**n** averaged

n

director

^{31}P powder patterns

DMPC from Avanti website

δ

fast axial rotation

$\delta(^{31}P)$ / ppm

$\delta(^{31}P)$ / ppm

DNA and phospholipid

deconvolution
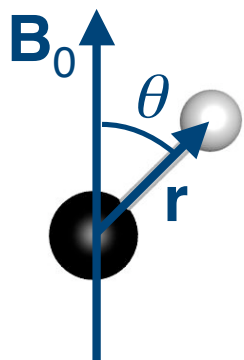
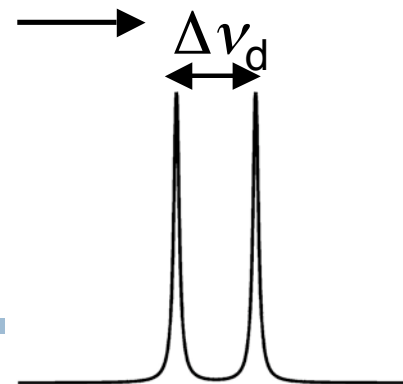Leal, Sandström, Nevsten, Topgaard, Biochim. Biophys. Acta (2008)
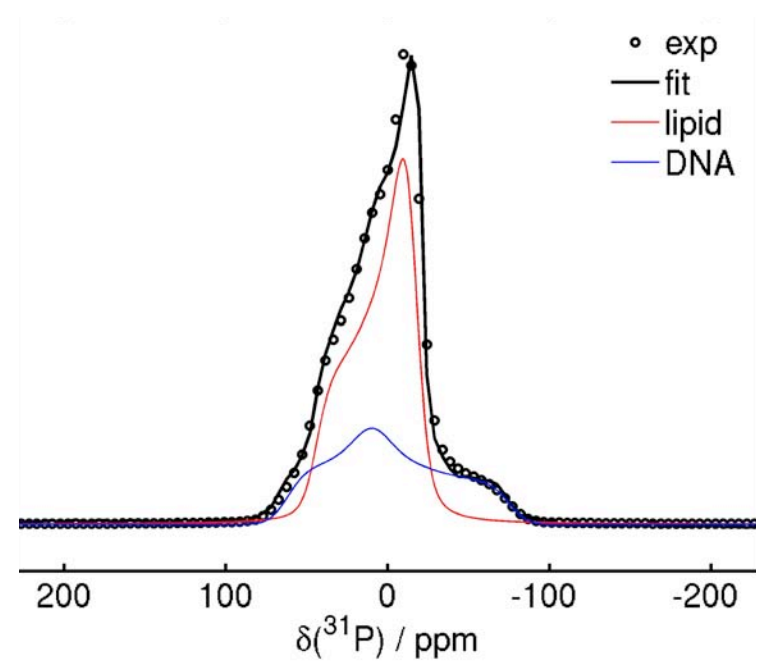
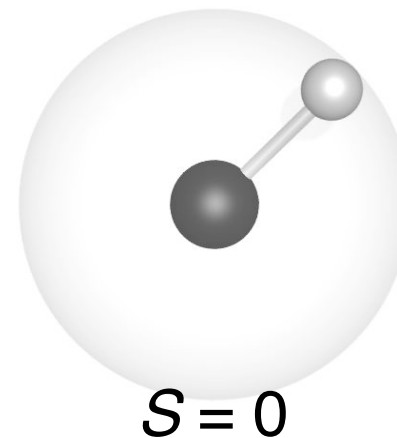# Fluctuating dipolar field, B_z
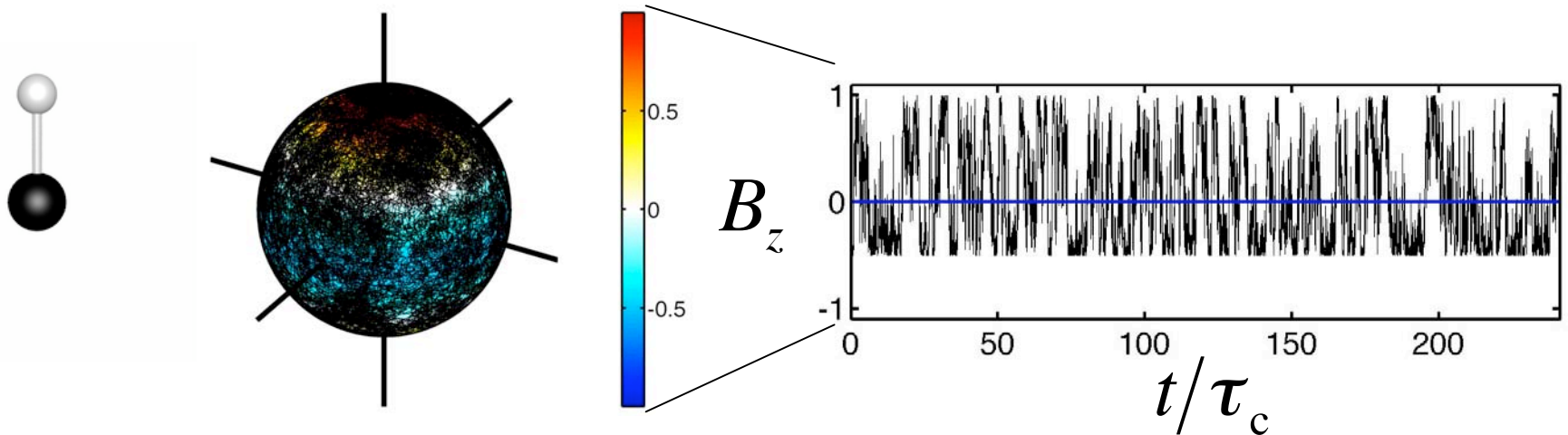
Average ≠ 0 if anisotropic

residual dipolar coupling, RDC $\longrightarrow$ Δv_{d}

Fast, anisotropic motion

$$\Delta v_{\mathrm{d}} = \frac{1}{2}\underbrace{\left\langle 3\cos^2\theta - 1\right\rangle}_{\text{order parameter, } S}\Delta v_{\mathrm{d,max}}$$

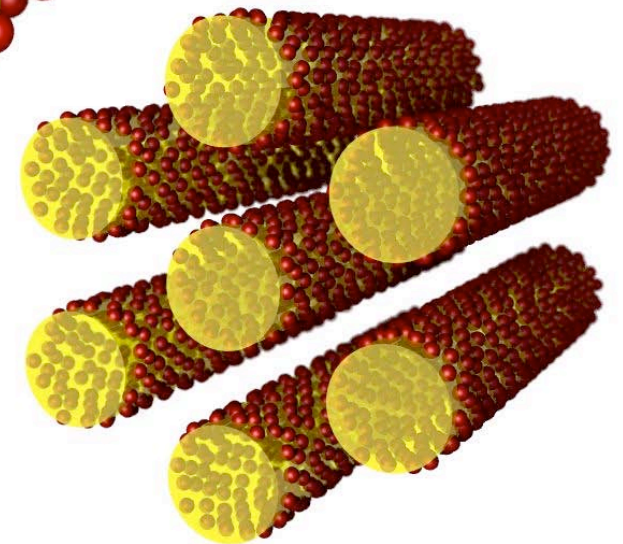$\longleftarrow$ average

B$_0$

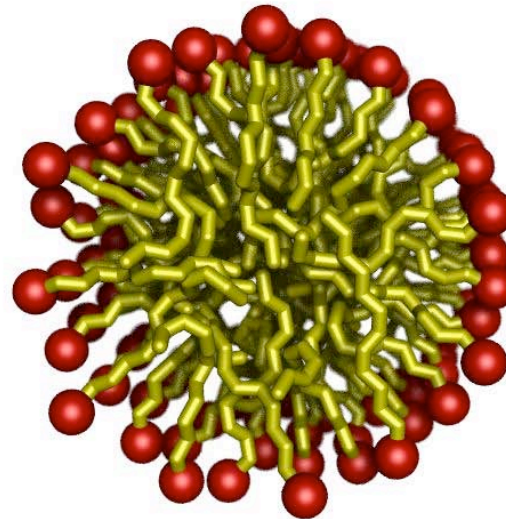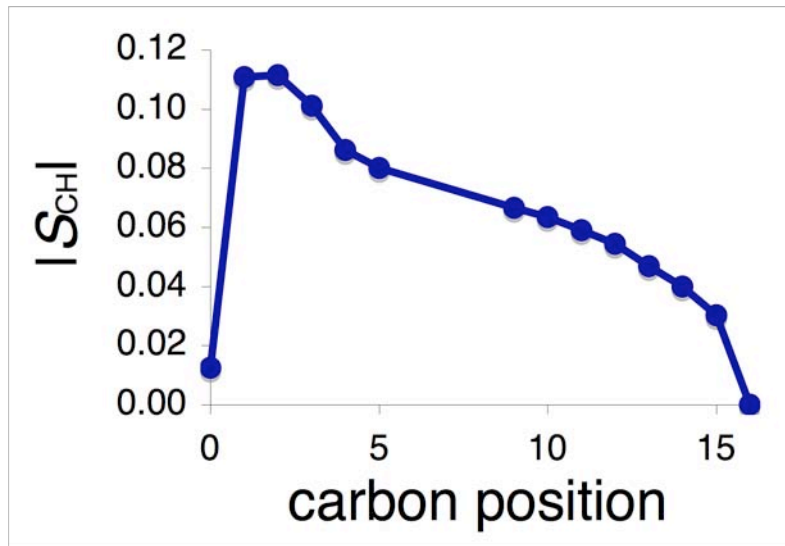θ

r
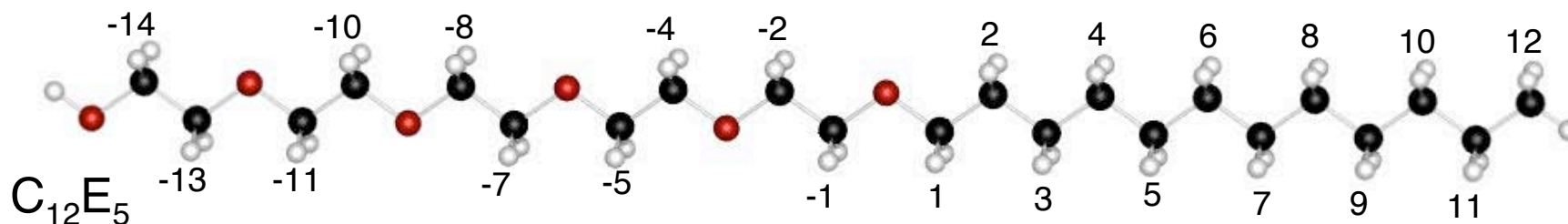
$S = 1/4$

$S = 0$

8
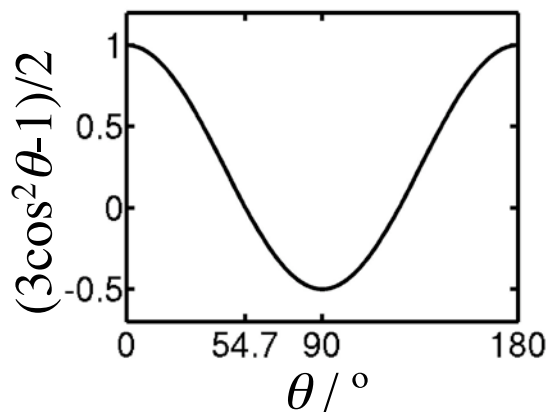
Separated local field
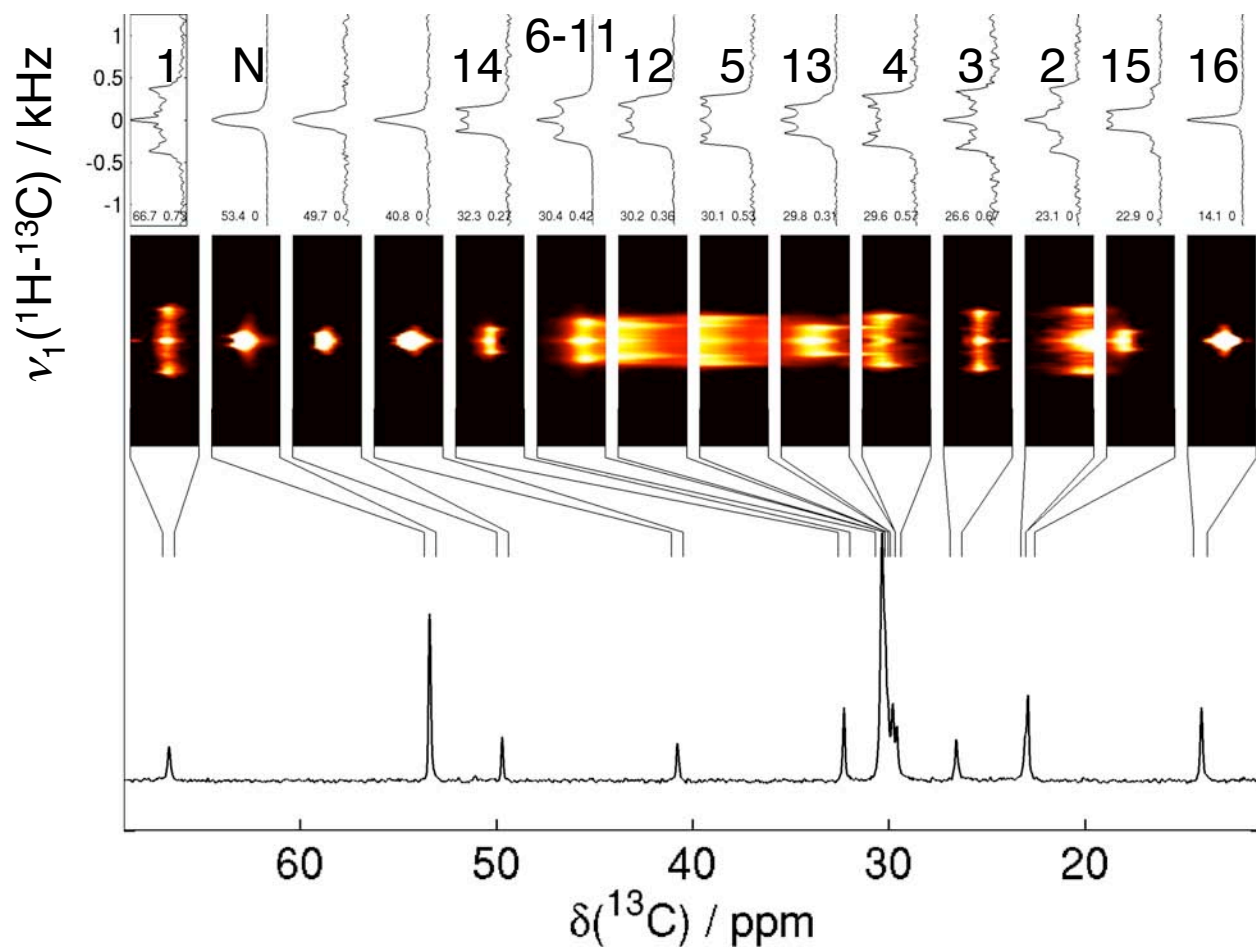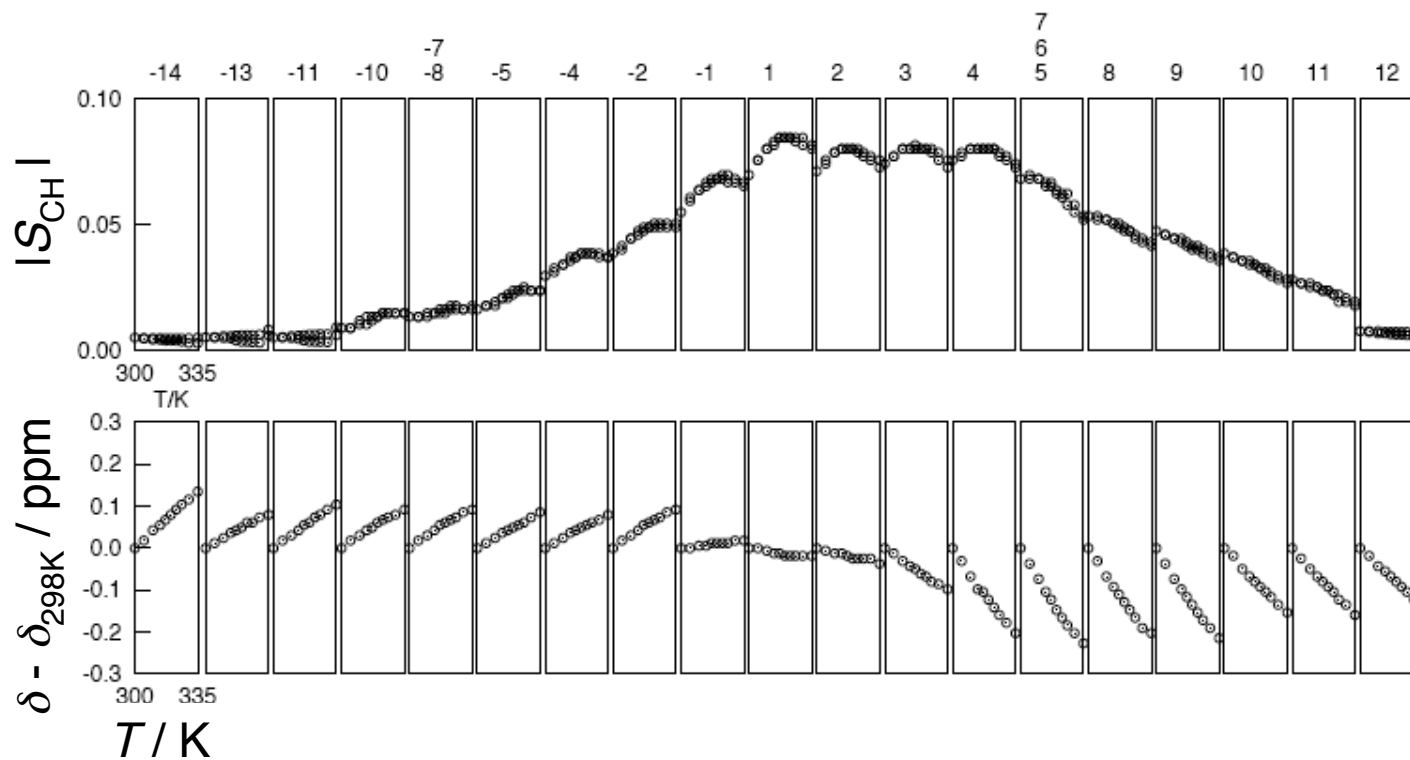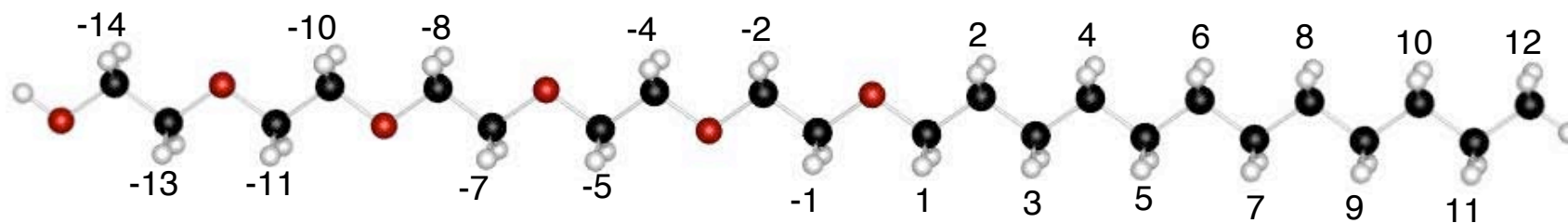

S_{CH} can be measured!
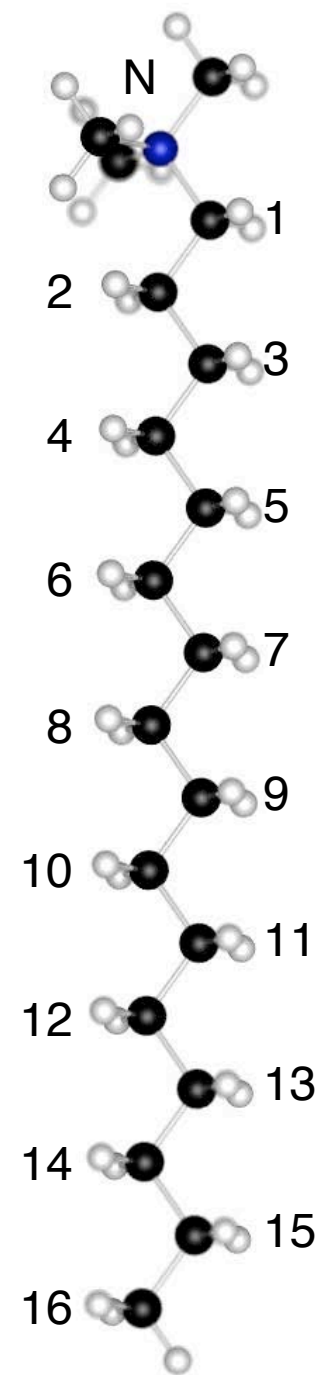
Order parameter, S_{CH}

Order parameter profile

L$_\alpha$, non-ionic surfactant

Ferreira, Medronho, Martin, Topgaard, Phys. Chem. Chem. Phys. (2008)
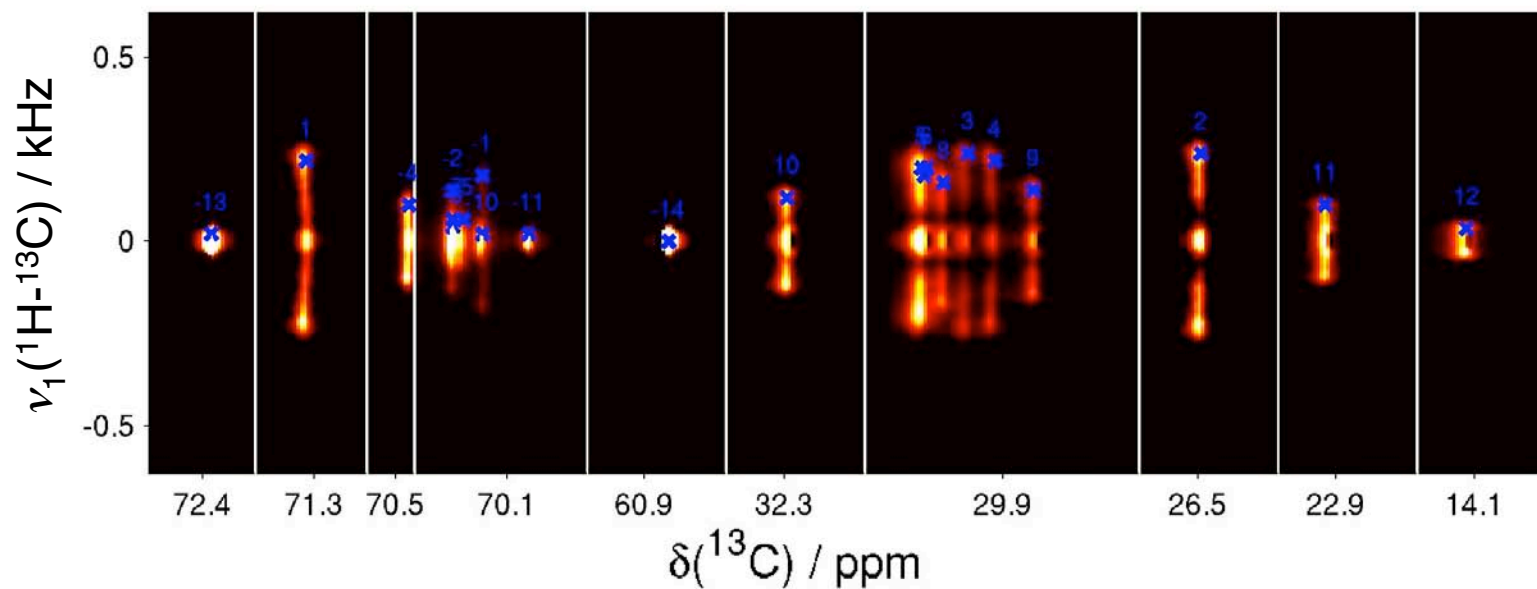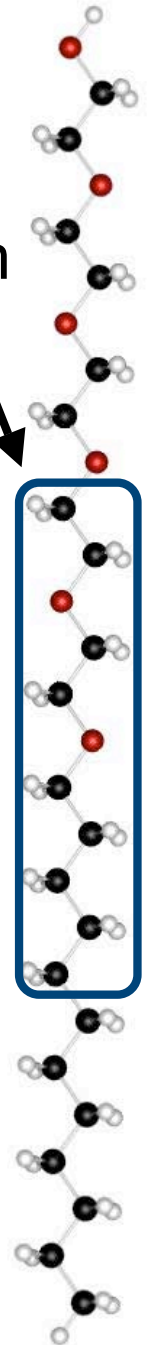
Effect of temperature

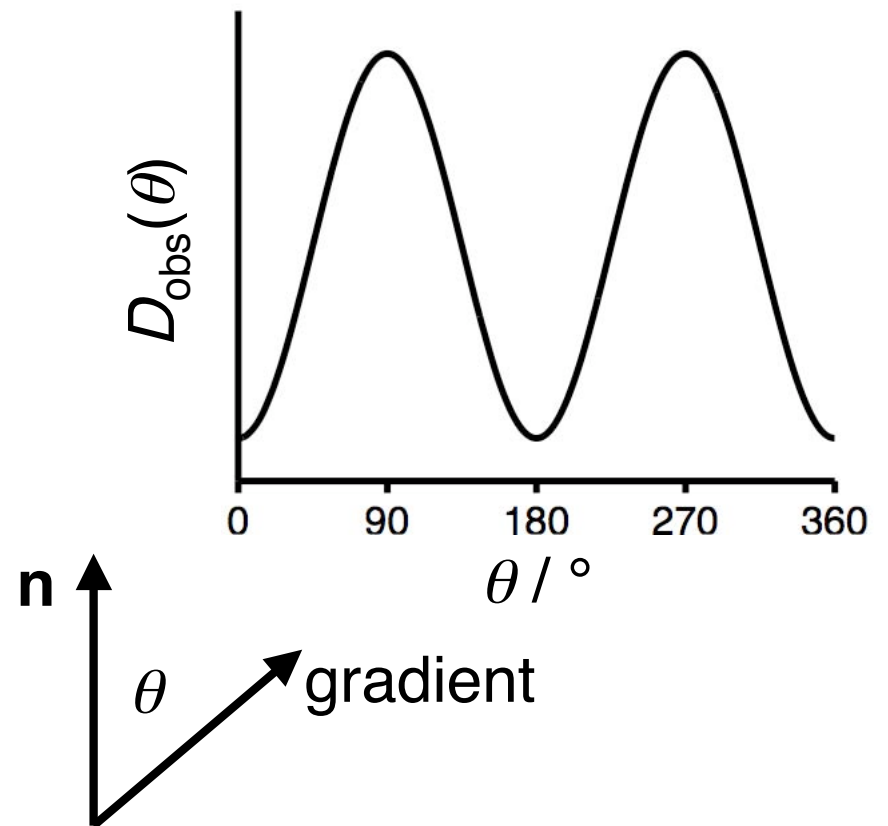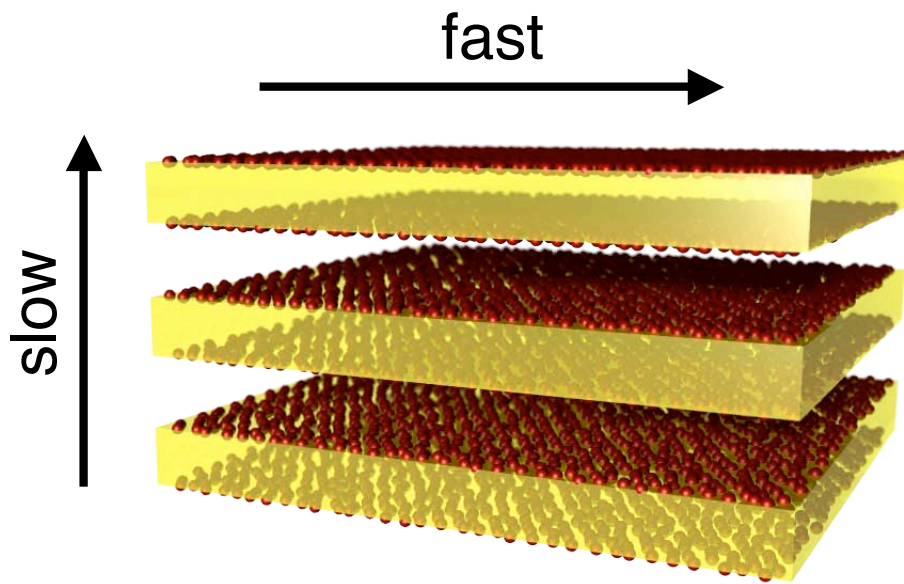# Conformation

- Lowest energy
  - alkyl: straight
  - ethylene oxide: gauche helix
- Increase *T:*
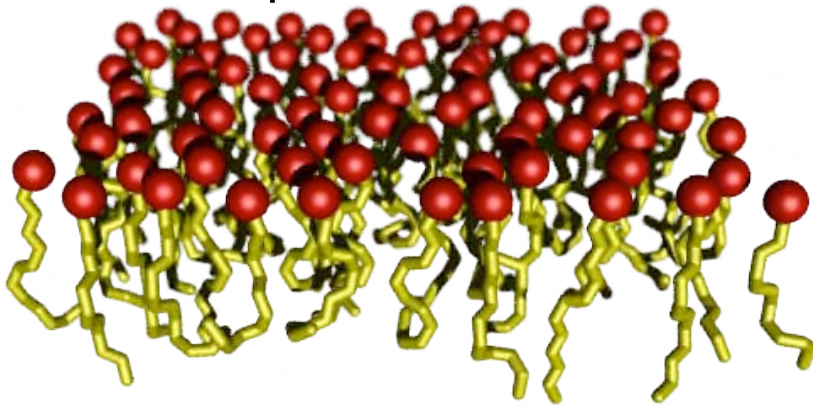 - alkyl: more *gauche*
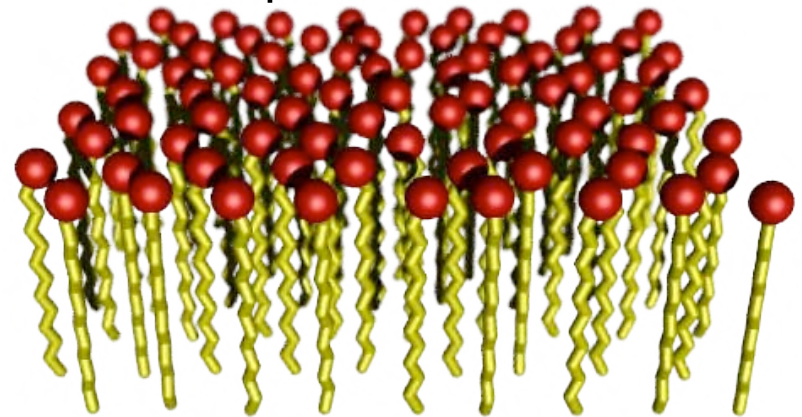 - ethylene oxide: more *trans*

Anisotropic diffusion

Liquid ordered phase
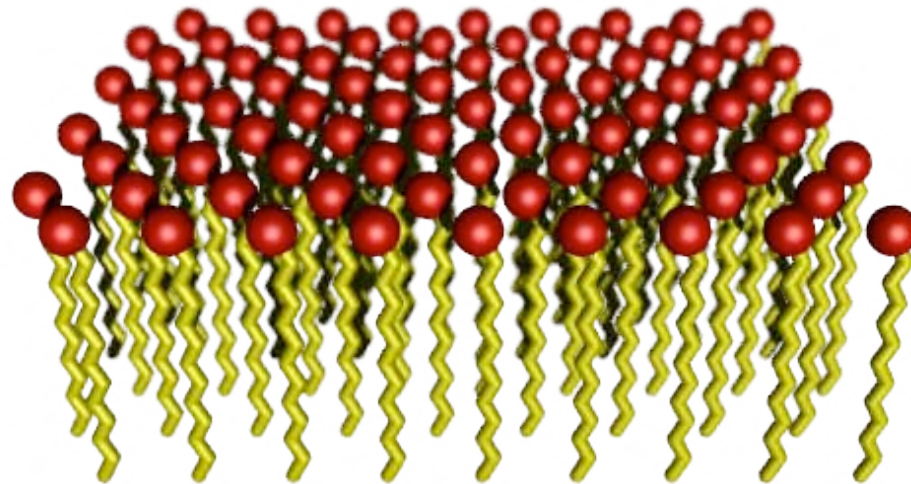
liquid disordered

liquid ordered

- Translational diffusion reduced factor 2-3
- Flat S_{CH} profile

Gel phase

- All-*trans* chains
- Molecularly ordered
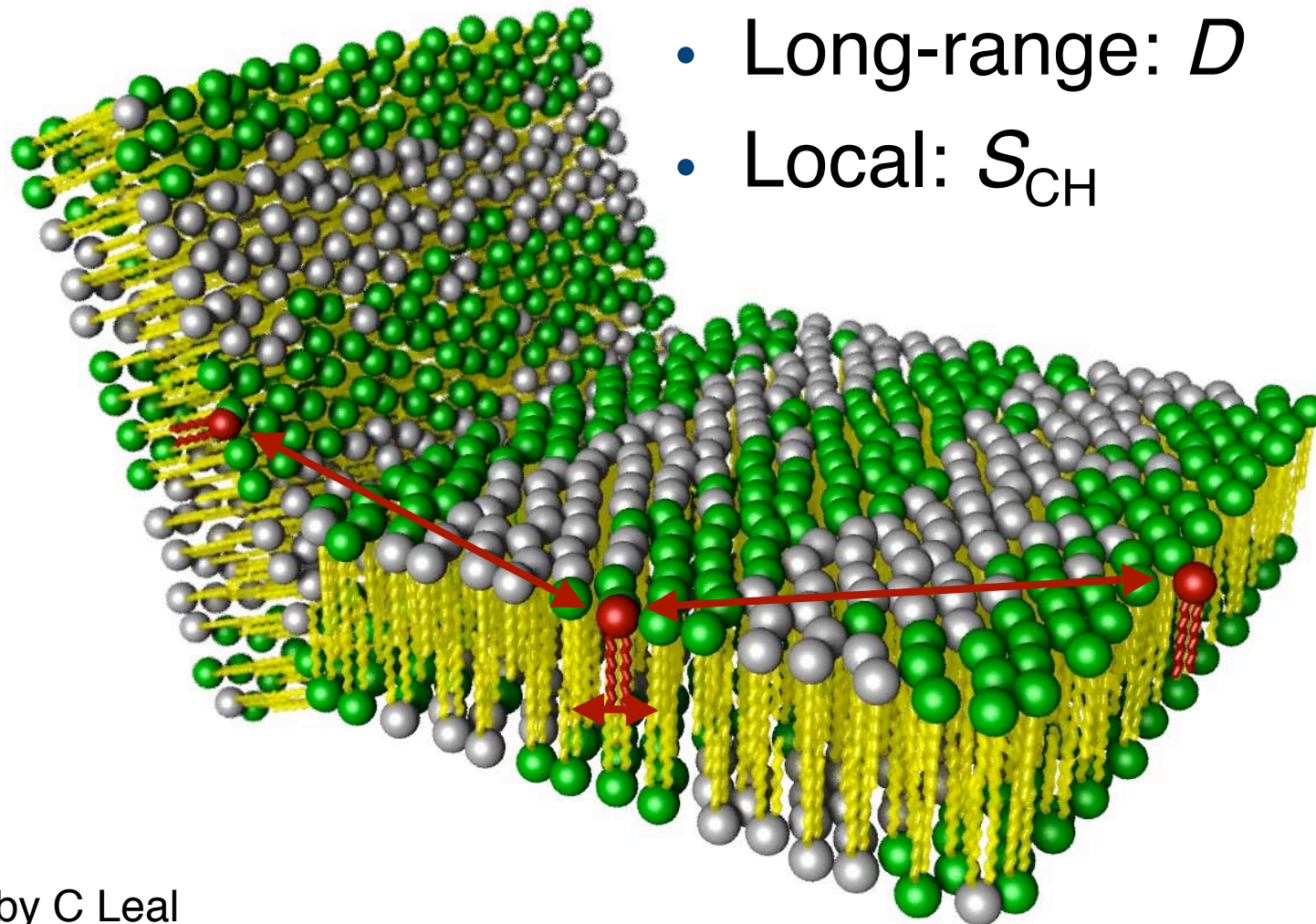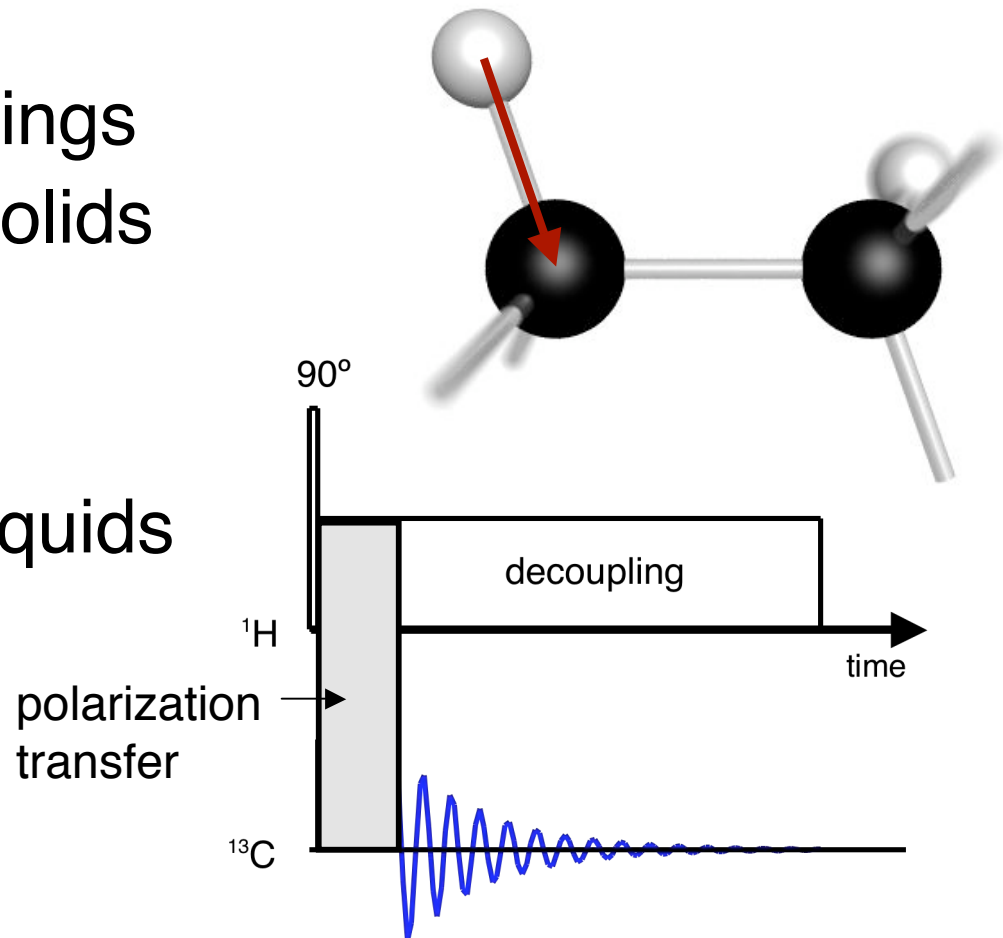- Slow diffusion

NMR useful info about membrane systems

- Long-range: D
- Local: S_{CH}

Figure by C Leal

$^1H \rightarrow ^{13}C$ polarization transfer

- CP
  - dipolar couplings
  - efficient for solids
- INEPT
  - *J*-couplings
  - efficient for liquids

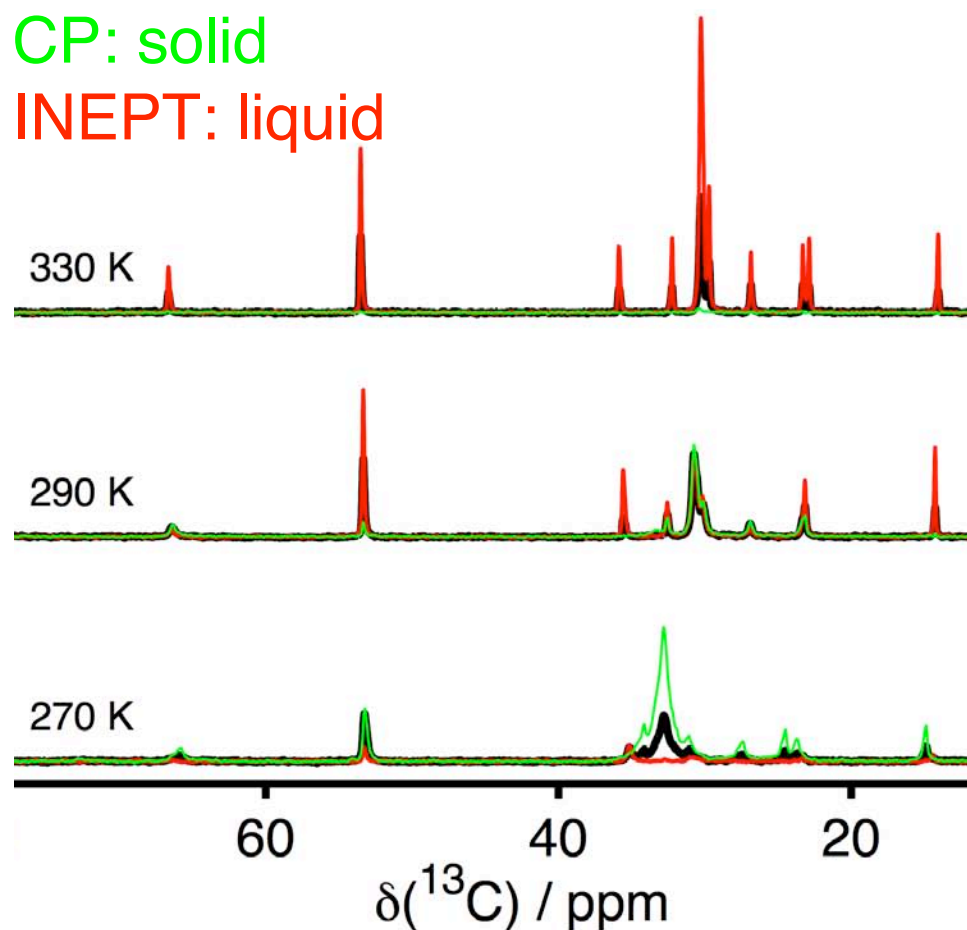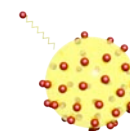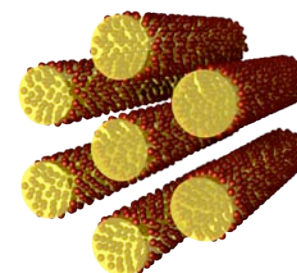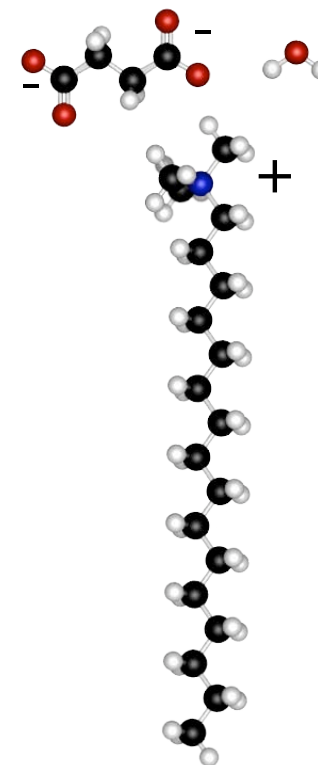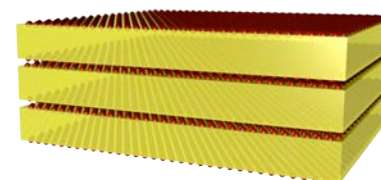# Solid or liquid?

DP: quantitative
CP: solid
INEPT: liquid

330 K — micellar solution
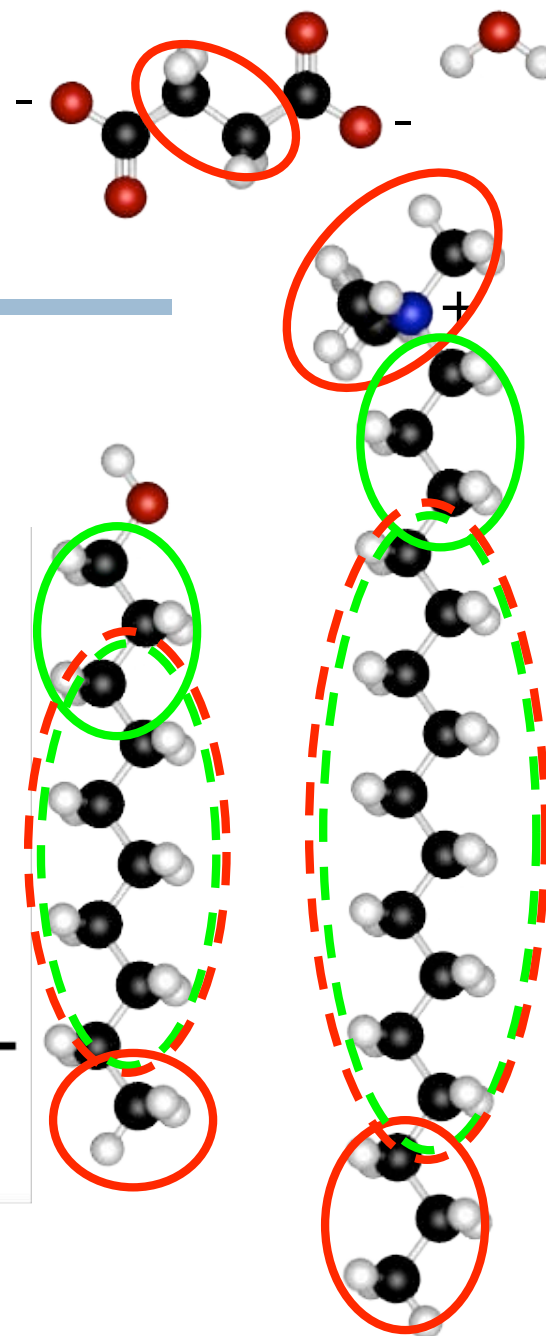
290 K — liquid crystal
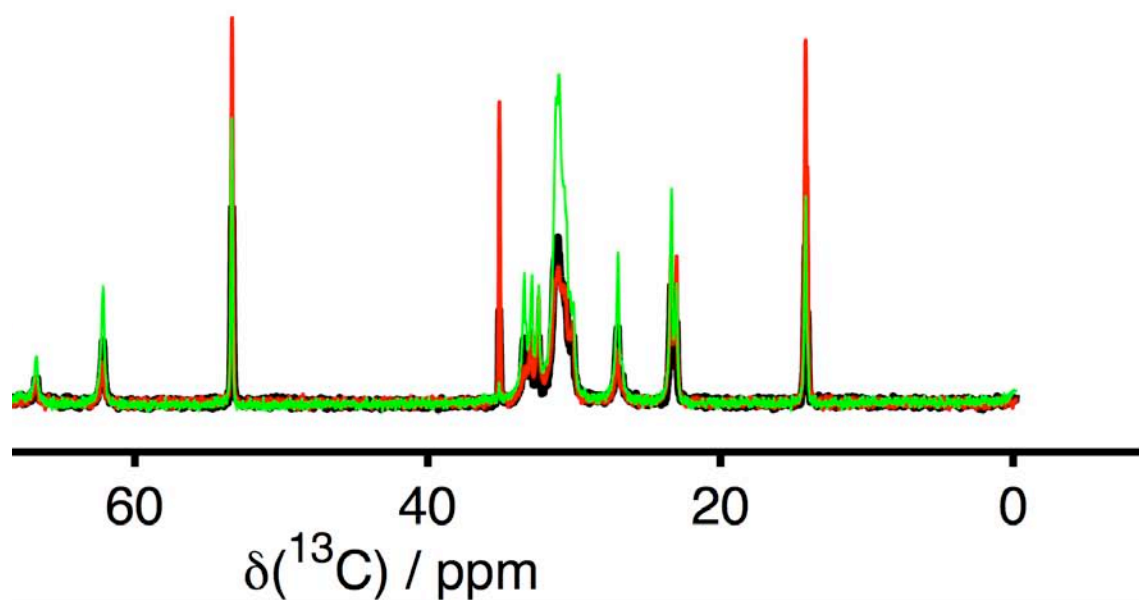
270 K — solid

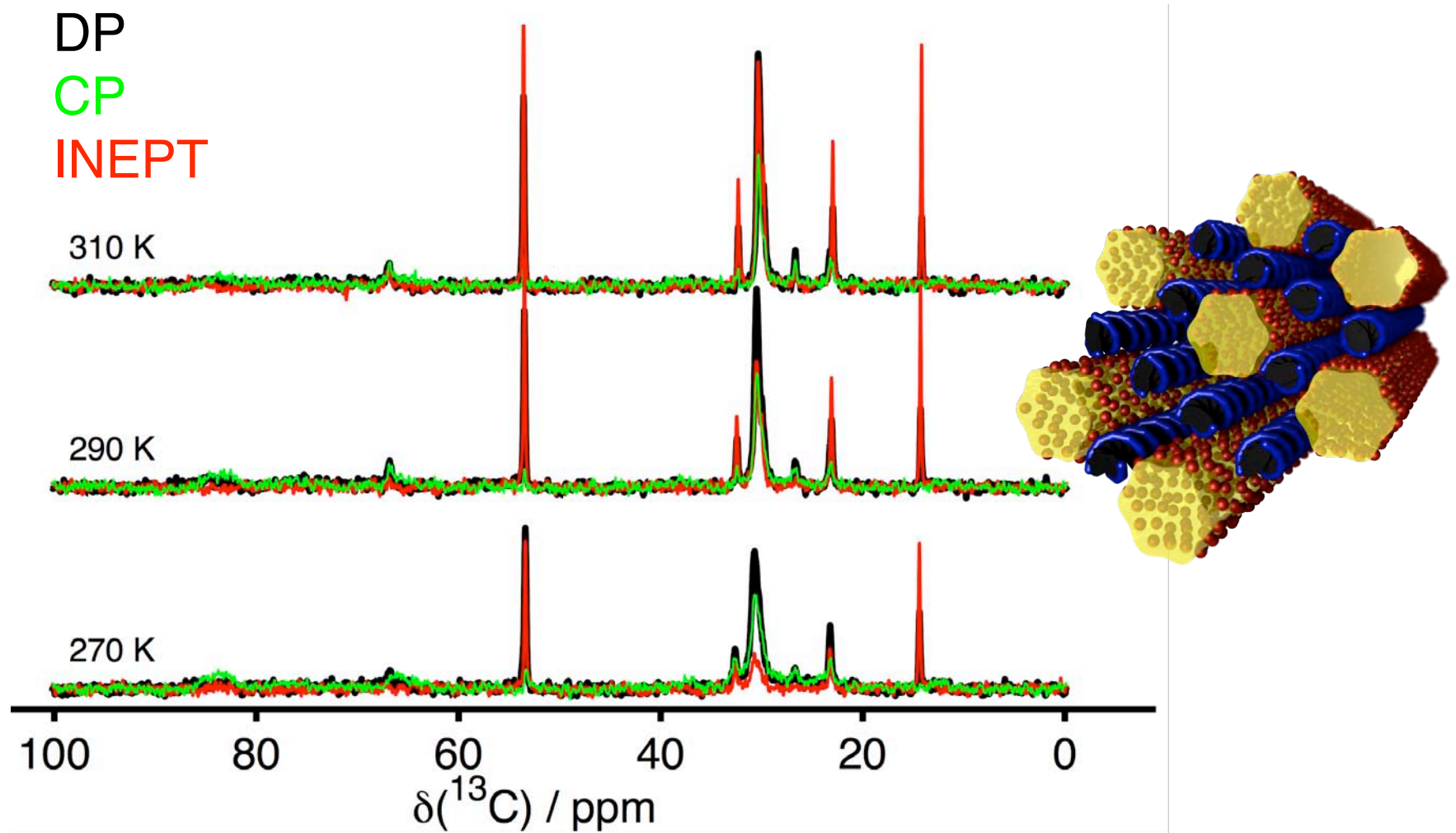$\delta(^{13}C)$ / ppm
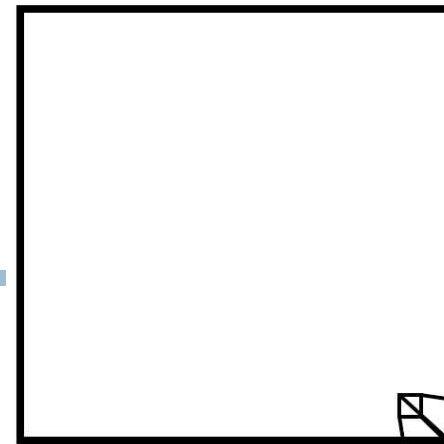
60   40   20
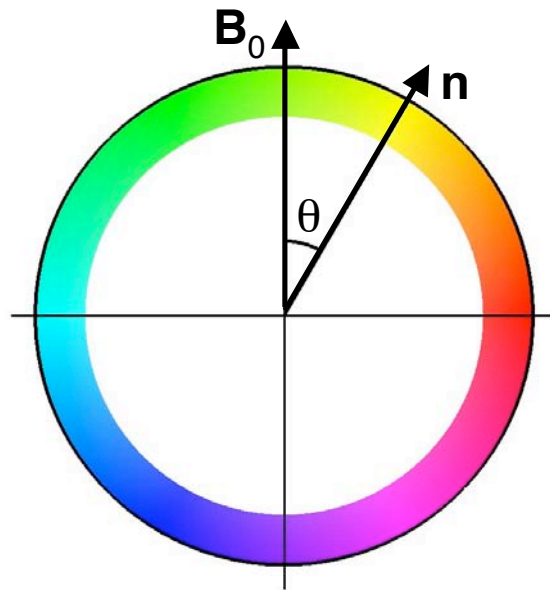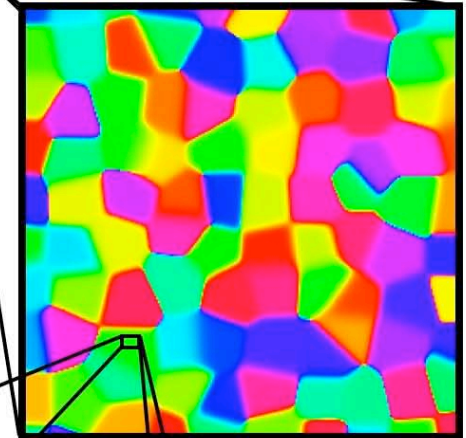
Segment resolution

DP
CP
INEPT

CTA-DNA: no solid crystals

Domain size
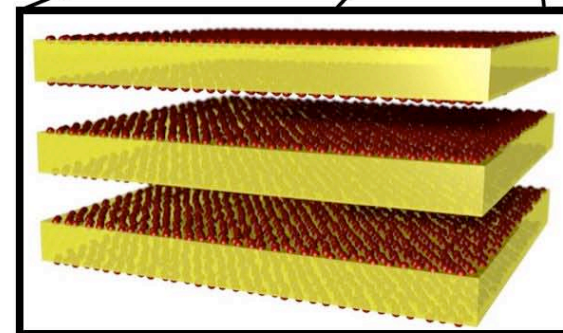
Influence on NMR measurables?

CSA, RDC, D

mm-scale: isotropic

μm-scale: anisotropic domains

nm-scale: lamellae

Trends in D and S_{CH}?

hexagonal LC

liquid disordered

lamellar LC

liquid ordered

gel