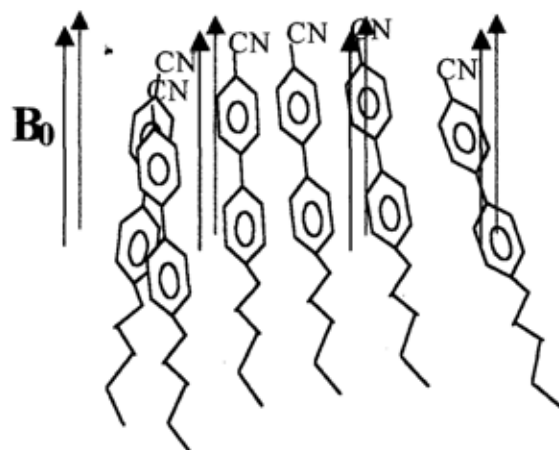


1. APPENDIX 0: RMN AND SPIN DYNAMICS

[SLI92,HAR87]

Let 's consider a probe of crystal or liquid crystal in a static magnetic field $\mathbf{B}_0 = B_0 \mathbf{e}_z$.

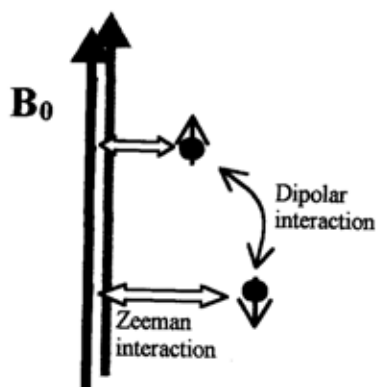


A nematic liquid crystal (here the 5CB) in a static magnetic field

The ^1H and ^{13}C present in the probe, having magnetic properties, via their spin $1/2$,

- interactuate with the field \mathbf{B}_0 (Zeeman interaction)
- interactuate between them (dipolar interaction)

the NMR(in semi-ordered to ordered phases) is dedicated to the study of these interactions.



Representation of the dominant interactions in a NMR sample

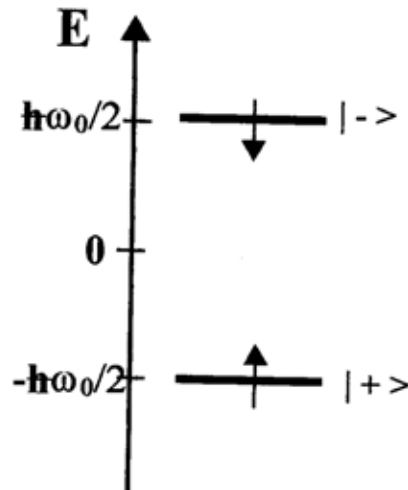
1.1. The Zeeman interaction

The Zeeman interaction hamiltonian of a 1H with the field B_0 is:

$$\mathcal{H}_z = -\mu_H B_0 = -\gamma_I \hbar B_0 I^z = -\hbar \omega_0 I^z$$

(γ_I is the gyromagnetic ratio of the 1H , ω_0 its Zeeman frequency)

The energies and wave functions solutions of the Schrödinger's time-independent equation are represented as follows:



Schematic representation of the two possible spin configurations (parallel ($| + >$) and antiparallel ($| - >$) to B_0), and their respective energies.

1.2. Inducing transitions between energy levels: the magnetic resonance.

1.2.1. Perturbated hamiltonian

In order to induce transitions between the states of the Zeeman hamiltonian, we need a perturbation:

- of resonant frequency = corresponding to the natural transition frequency between the Zeeman levels of the system,

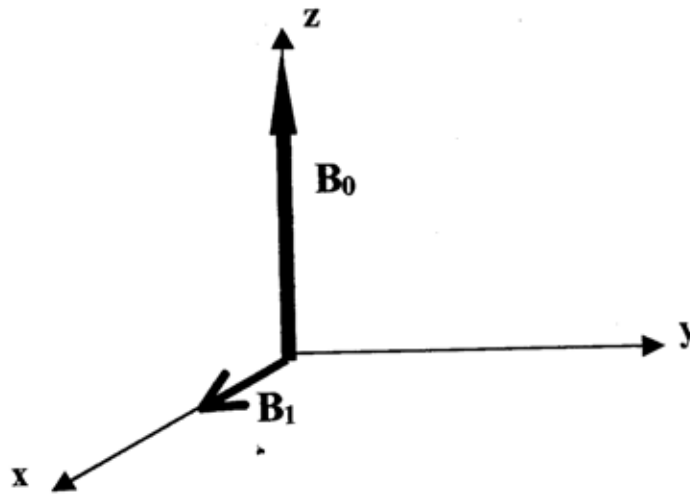
- that adds non-diagonal terms in the hamiltonian = coupling terms, between states.

We can achieve it with a perturbative magnetic field $B_1(t) \perp B_0$:

$$B_1(t) = 2B_1 \cos(\omega t) \mathbf{e}_x$$

$$\omega \simeq \omega_0 \quad (\text{resonance condition})$$

$$B_1 \ll B_0 \quad (\text{perturbation condition})$$



The static (B_0) and oscillating perturbing (B_1) magnetic fields.

The perturbed hamiltonian, in the laboratory frame, is:

$$\mathcal{H} = -\hbar\omega_0 I^z - 2\hbar\omega_1 \cos(\omega t) I^x, \quad \omega_1 = \gamma_I B_1$$

1.2.2. Rotating frame

Let's consider the change of function:

$$|\psi'\rangle = e^{-i\omega t I^z} |\psi\rangle$$

(physically, $|\psi'\rangle$ is the rotated of $|\psi\rangle$ of an angle ωt around e_z , from here the expression: rotating frame.)

$|\psi'\rangle$ is solution of the new Schrödinger's equation:

$$\frac{\partial |\psi'\rangle}{\partial t} = \frac{1}{i\hbar} \mathcal{H}' |\psi'\rangle$$

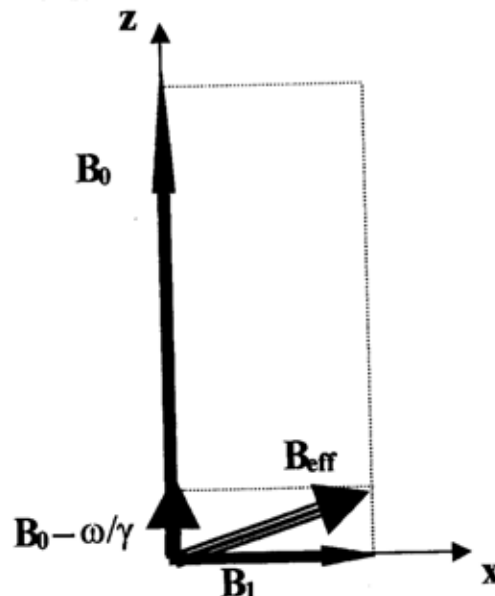
with

$$\mathcal{H}' = -\hbar(\omega_0 - \omega) I^z - \hbar\omega_1 I^x$$

which is the hamiltonian of one spin in an effective field:

$$\mathbf{B}_{eff} = \left(B_0 - \frac{\omega}{\gamma_I}\right) \mathbf{e}_z + B_1 \mathbf{e}_x$$

On resonance ($\omega = \omega_0 = \gamma_I B_0$), $\mathbf{B}_{eff} = B_1 \mathbf{e}_x$.



The effective fields as seen from the rotating frame.

The spin wave functions defined in this frame will have the same behaviour as spin functions in an immobile frame, in presence of a field B_{eff}

1.2.3. Effect of a resonant pulse

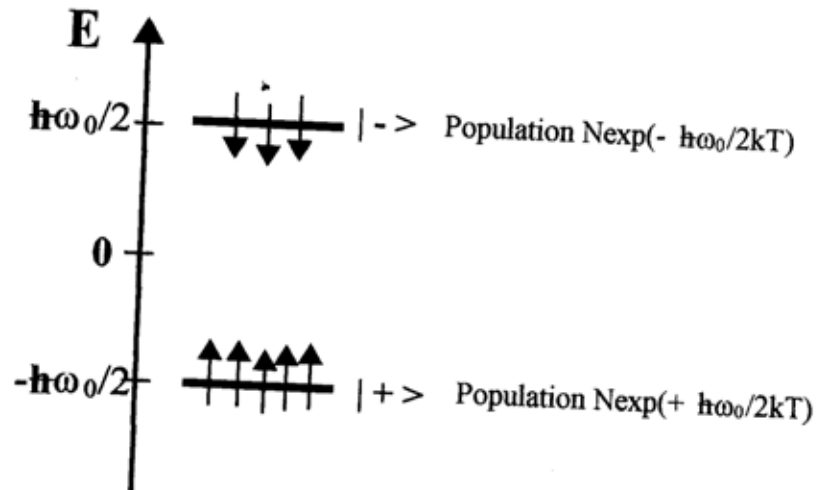
Effect on one spin

Let's consider $|\psi'(0)\rangle = |\psi(0)\rangle = |+\rangle_z$

We have $|\psi'(t)\rangle = e^{-\frac{iH't}{\hbar}} |\psi'(0)\rangle = e^{-i\omega_{1f}t} |+\rangle_z = \cos(\omega_{1f}t) |+\rangle_z - \sin(\omega_{1f}t) |-\rangle_z$

Interpretation in terms of energy-level populations:

Let's consider an ensemble of N non-interacting 1H spins, in presence of B_0 . The partition Boltzmann law gives us the following populations for the energy levels:

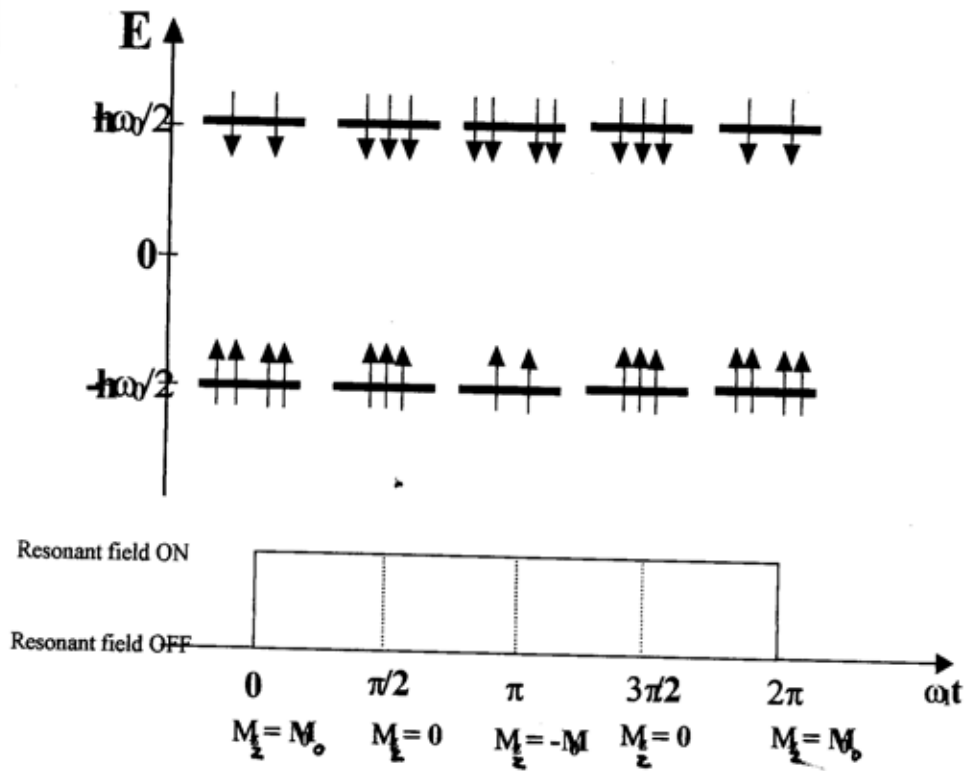


Schematic representation of the populations of the two respective energy levels. There is a thermodynamical excess of spins « parallel » to B_0 , that leads to the macroscopic detectable magnetization.

Having an excess of spins parallel to B_0 than antiparallels, the probe presents a macroscopic magnetization:

$$M_0 = \frac{1}{4} \gamma_I \hbar \frac{\hbar\omega_{0I}}{kT} e_z = M_{0I} e_z$$

When we apply the resonant pulse, we induce transitions between the two energy levels, changing the relative populations.



Schematic representation of the populations of the two respective energy levels, as is applied the resonant field. The resonant field, inducing transitions between the levels, also modifies the macroscopic magnetization.

Interpretation in terms of density matrix; effect on the macroscopic magnetization.

In thermal equilibrium, without resonant perturbation, the density matrix of the system is:

$$\rho(0) = \rho_0 = \frac{1}{2N} \exp\left(-\frac{H}{kT}\right) = \frac{1}{2N} \exp\left(\frac{\hbar\omega_0 I^z}{kT}\right) \simeq \frac{1}{2N} \left(1 + \frac{\hbar\omega_0 I^z}{kT}\right)$$

Following a pulse $\theta = \omega_0 t$ of resonant field $2B_1 \cos(\omega_0 t) e_x$ (X_θ pulse) we have:

$$\rho(t) = \exp\left(-it\frac{H}{\hbar}\right) \rho(0) \exp\left(it\frac{H}{\hbar}\right)$$

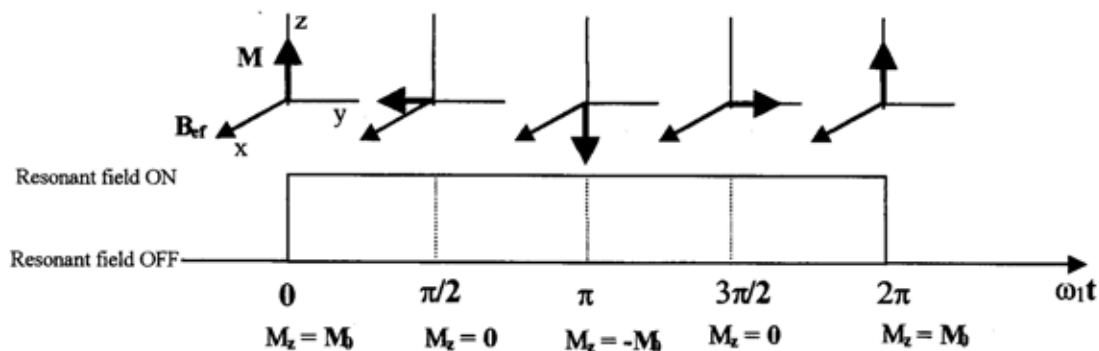
say, in the rotating frame

$$\begin{aligned} \rho(t) &= \exp(-i\omega_0 t I^z) \rho(0) \exp(i\omega_0 t I^z) \\ &= \frac{1}{2N} \left(1 + \frac{\hbar\omega_0}{kT} (\cos(\omega_0 t) I^z - \sin(\omega_0 t) I^y)\right) \end{aligned}$$

And the macroscopic magnetization of the probe is:

$$M(t) = \text{Tr}(\rho(t)M) = M_0 (\cos(\omega_0 t) e_z - \sin(\omega_0 t) e_y)$$

say, the magnetization precesses around the effective field with angular velocity ω_0 .



*Schematic representation of precession of the macroscopic magnetization, first aligned with B_0 , as applied the resonant field.
The magnetization, in the rotating frame, precesses around the effective field.*

1.3. Detection of the NMR signal

1.3.1. Ideal case

We've seen that following a $X_{\pi/2}$ pulse, the macroscopic magnetization is launched to the xy plane:

When we turn off the radiofrequency, we let the macroscopic magnetization in presence of the static magnetic field B_0

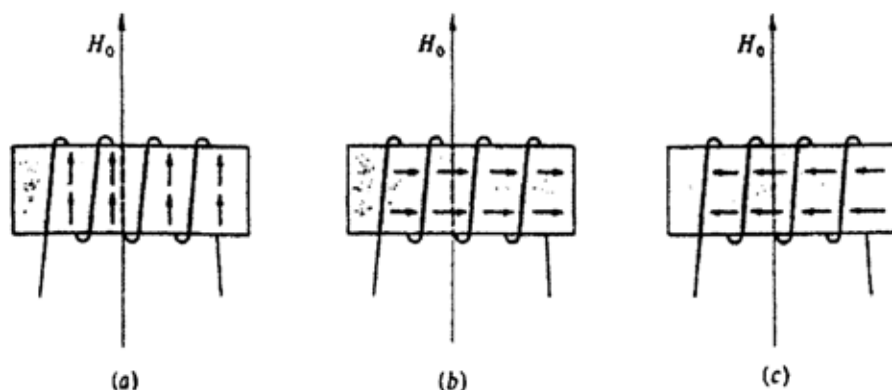
$$\begin{aligned} \rho(t > t_{\pi/2}) &= \exp(-i\omega_{0I}(t - t_{\pi/2})) \rho(t_{\pi/2}) \exp(i\omega_{0I}(t - t_{\pi/2})) \\ &= \frac{1}{2N} \left(1 - \frac{\hbar\omega_{0I}}{kT} (\cos(\omega_{0I}(t - t_{\pi/2}))I^y - \sin(\omega_{0I}(t - t_{\pi/2}))I^x) \right) \end{aligned}$$

And the macroscopic magnetization is:

$$M(t) = \text{Tr}(\rho(t)M) = M_0 (-\cos(\omega_{0I}(t - t_{\pi/2}))e_y + \sin(\omega_{0I}(t - t_{\pi/2}))e_x)$$

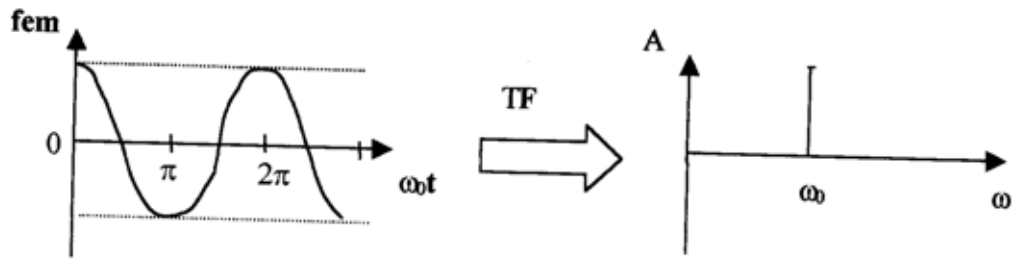
say, the macroscopic magnetization precesses around B_0 with angular velocity ω_{0I} .

This modulation of the precessing transversal magnetization produces, by induction, a f.e.m in a coil, proportional to the magnetization in the axis of the coil



(a) Coil containing sample. In thermal equilibrium an excess of moments is parallel to H_0 . (b) and (c) Following a 90-degree pulse, the excess moments precess perpendicular to H_0

The Fourier transform of this f.e.m is the NMR spectra of the studied sample.

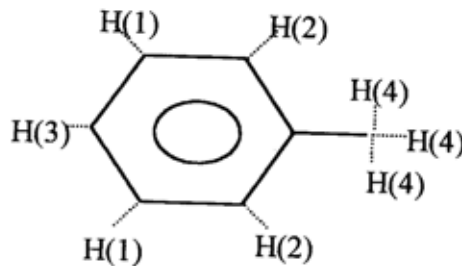


The ideal (no relaxation, only one frequency) fem and its fourier transform.

1.3.2. Real case

A real probe:

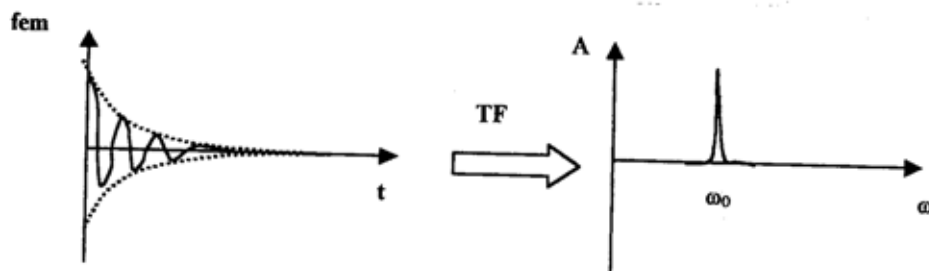
-Can contain atoms of the same specie, but non-equivalent = their surroundings differ, from here the local magnetic field, from here the resonant frequency.



Equivalent and non-equivalent atoms :

Because of their identic surroundings, the ¹H labelled with the same number are magnetically equivalent. Groups with different numbers are non-equivalent.

- Presents a transversal magnetization that, for various reasons, decays in time.



More realistic fem and the corresponding spectra

-an oscillation at the frequency ω_0 in the fem gives a line at ω_0 in the spectra;

-an attenuation of characteristic time T in the fem gives a line of width $1/T$ in the spectra

1.3.3. Informations available via the spectra

- the characteristic resonance frequencies of each atom or group of equivalent atoms ($\omega_{0I_1}, \omega_{0I_2}, \omega_{0I_3} \dots$),
- the characteristic times in which decay the corresponding magnetizations ($T_{2_1}, T_{2_2}, T_{2_3} \dots$), via the line width,
- the natural abundancy of each groups of atoms, via the area of the line.

From all these characteristics, we can deduce physical structural properties of the probe. With more advanced puls sequences than the single $X_{\frac{\pi}{2}}$ we will be able to study more "profound" properties.

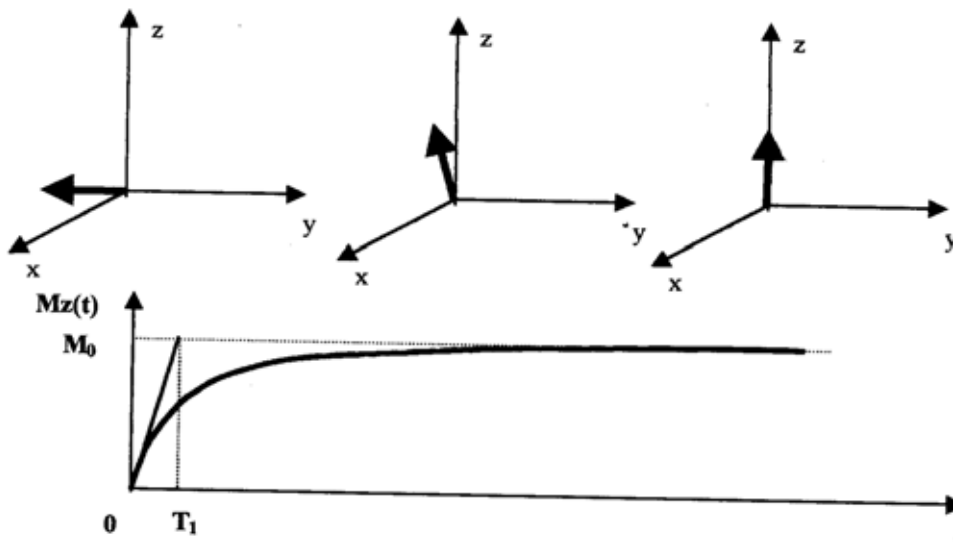
1.4. Relaxation Processes and FID attenuation.

Two mechanisms are contributing to the decay of the FID:

- The coming back to the thermal equilibrium of the magnetization, of characteristic time T_1 ,
- The loss of coherence between all the spins that contribute to the magnetization, of characteristic time T_2

1.4.1. The spin-red relaxation: T_1

The magnetization, in the xy plane, out of equilibrium, exchanges energy with the red (=with the degrees of freedom of translation, rotation, vibration of the molecules of the crystal) and comes back to thermal equilibrium ($M = M_0 e_z$) in a characteristic time T_1

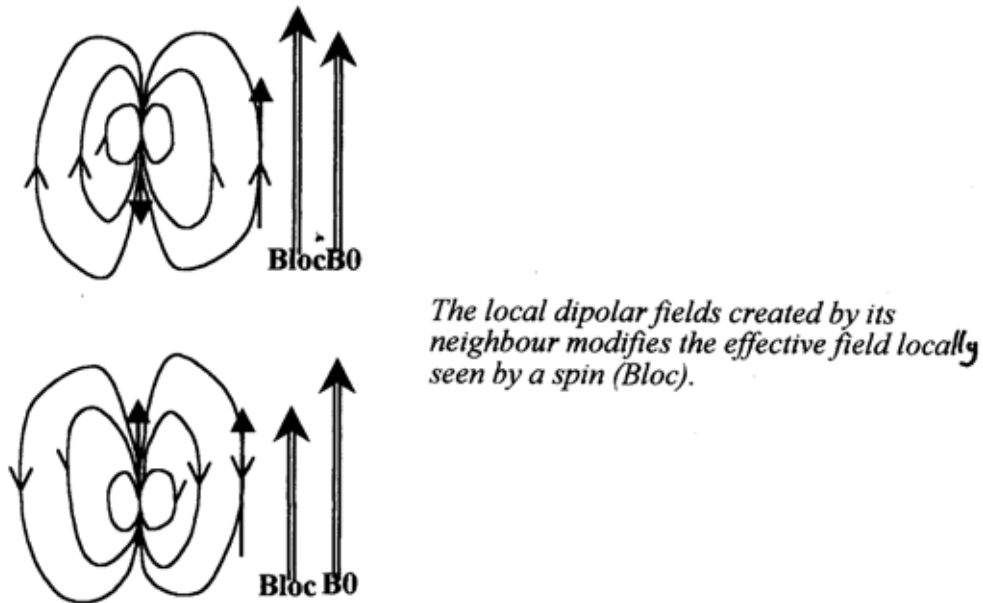


Thermodynamical relaxation of the magnetization

In a time T_1 , the interactions of the spins with the external degrees of freedom of the molecule lead the relaxation of the ~~parallel~~ magnetization, that goes back to the equilibrium value

1.4.2. The spin-spin relaxation: T_2

In a probe of crystal or liquid crystal, where the relative moves between neighbour molecules are small, the spins interactuate between them via the dipolar interaction: the local field, seen by each one of the spins is modified by the smaller fields created by the magnetic dipoles that are his neighbours.

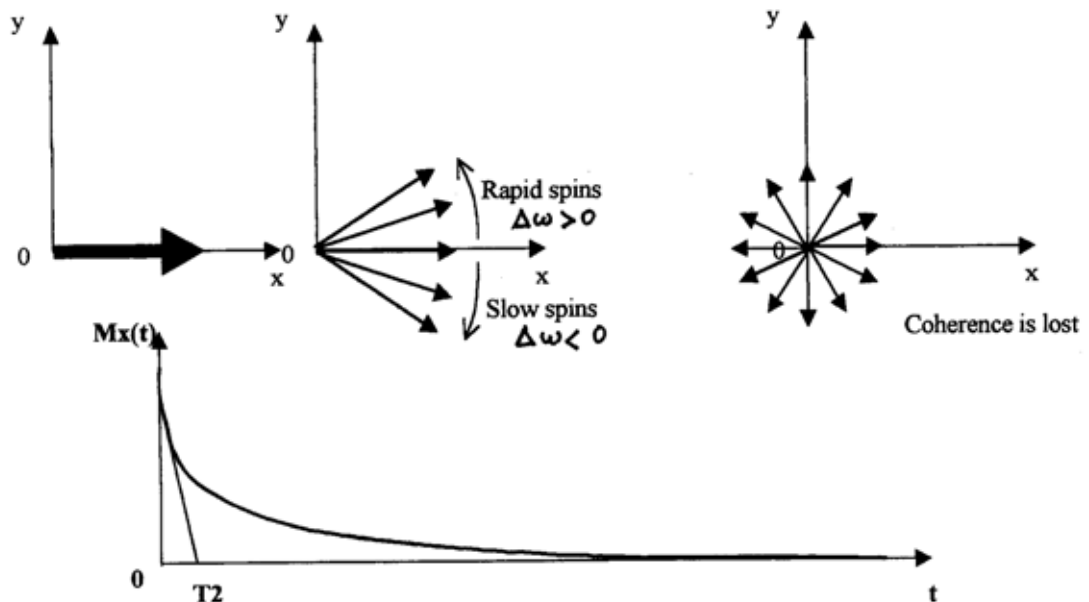


Hence, each one has a precession-frequency, around e_z :

$$\omega_i = \gamma B_{local} = \gamma(B_0 + B_{dipolar\ interaction}) = \omega_0 + \Delta\omega_i$$

We can represent the loss of coherence of the magnetization in the rotating frame:

The magnetization loses coherence, because of the dipolar interactions, in a characteristic time T_2 ($T_2 \ll T_1$ in solids)



The spin decoherence in the rotating frame : because of local fields created by the neighboring spins, all the spins don't precess at the same speed around the field B_0 . In a characteristic time T_2 coherence is lost and the macroscopic transversal magnetization decays to 0.

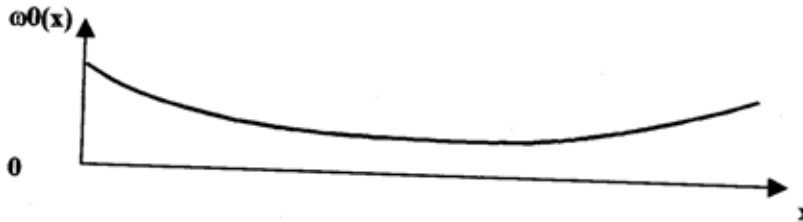
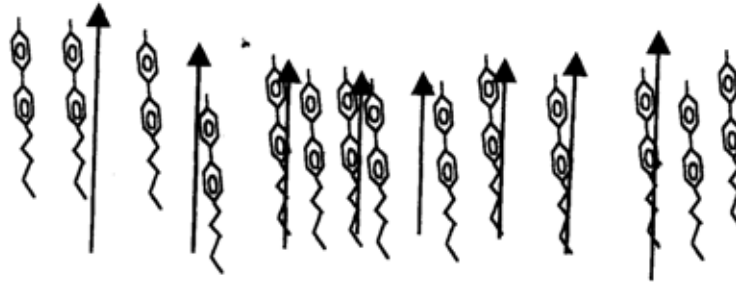
1.4.3. The effect of the inhomogeneities of the static B_0 field

The instrumentation does not allow us to apply to the probe a perfectly homogeneous field. Each area of the probe, even without dipolar interaction, sees a local field:

$$B_{local} = B_0 + B_{inhomogeneity}$$

The precession frequency of the spins around e_z changes around the probe:

$$\omega_{local} = \gamma B_{local} = \gamma(B_0 + B_{inhomogeneity}) = \omega_0 + \Delta\omega_{local}$$



The static field B_0 for instrumental imperfections, is inhomogeneous in the sample. Distinct zones in the sample will be associated with different spin precession frequencies, because of the different B_0 they see. This leads to a decoherence phenomenon analogous to the spin decoherence due to the spin dipolar local fields.