

2. STUDIES OF THE SPIN DIFFUSION PROCESSES IN THREE DIFFERENT CRISTALLINE SAMPLES.

2.1. Introduction:

Nuclear spin dynamics, or "spin-diffusion", is a powerful tool of analysis for the local and long range structure in ordered phases: since the diffusion rate depends on the internuclear interactions, it contains information on the spatial disposition of the nuclei.

In this study, we will invert the spin diffusion process, inverting the secular part of the dipolar hamiltonian, cause of the diffusion; allowing the polarization of a system of spins to resuscitate after coherence loss ! (the polarization echo PE)[EMTP92].

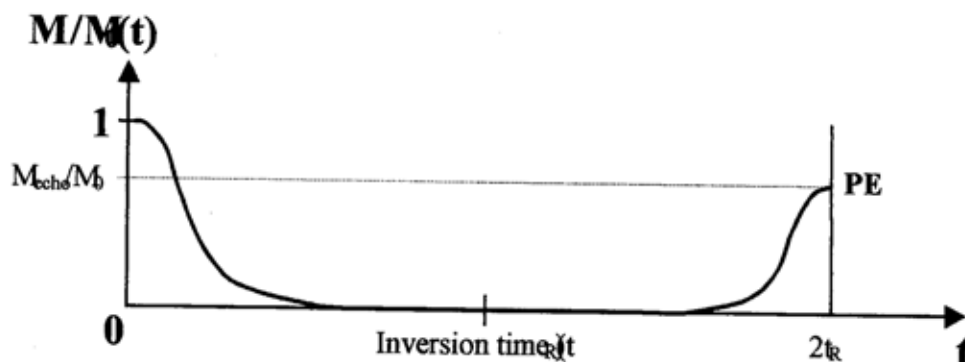


Illustration of the polarization echo : at the time t_R the dipolar hamiltonian is reversed. So is the diffusion of the magnetization, leading to a polarization echo (PE) at a time $2t_R$.

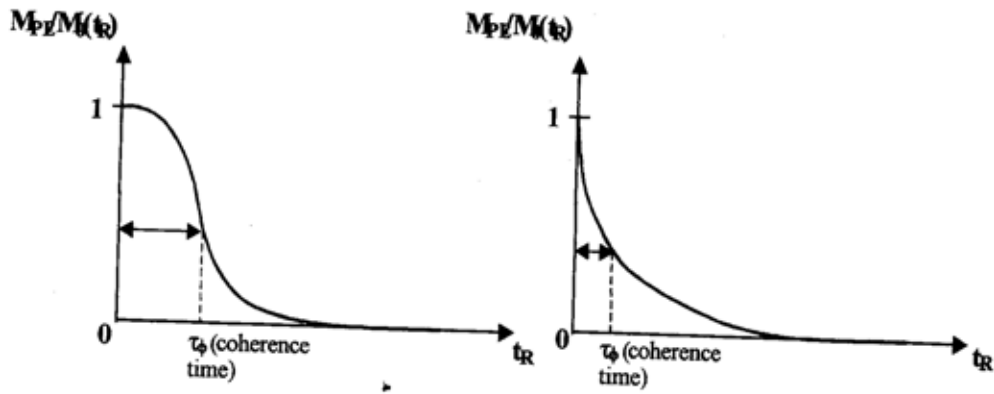
However, the amplitude of the PE decreases as the evolution time before inverting the hamiltonian increases. A study of the attenuation of the echo in function of the evolution-involution time ($PE = f(t_R)$)

- could provide us with a new observation tool for the molecular structure and motion (in case of liquid crystals), which so far has not been exploited;

- could give us additional information on the underlying stochastic processes that govern the spin diffusion, destroying the magnetization coherence.

The questions we will try to answer to are:

- What is the functional dependence of the curve $PE = f(t_R)$?
- What information can be obtained from the functional form and the decay rate of that curve ?
- What is the mechanism that leads to the decay of that curve ? Does the reversal of the spin dynamics show any *instability* with respect to natural fluctuations due to interactions of the spin system with the environment ?



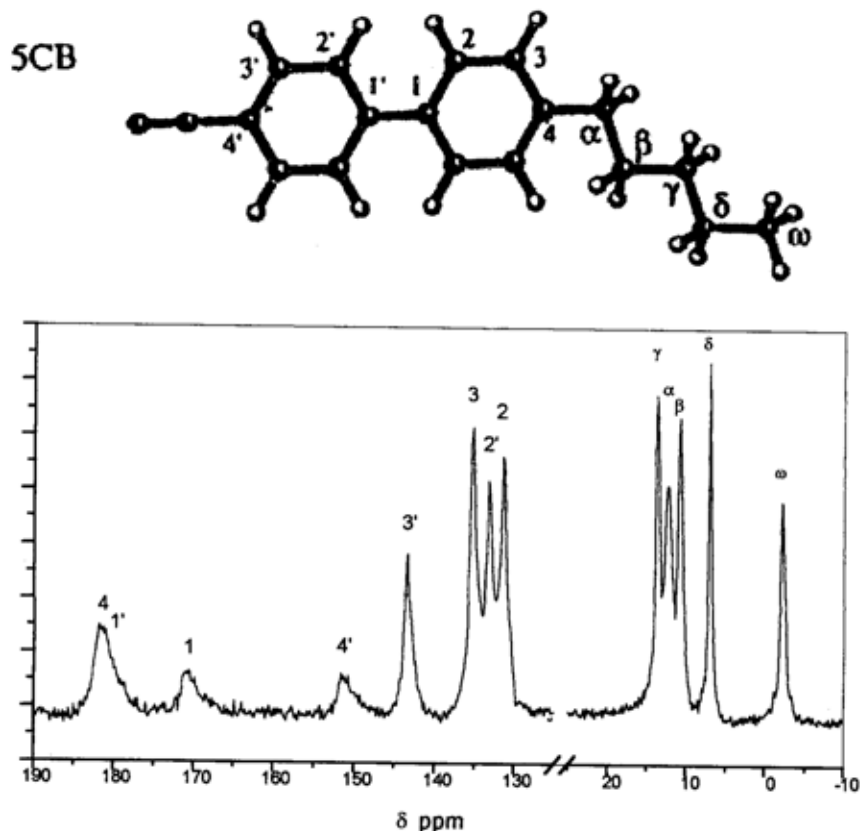
Two characteristic functional forms of decay for the polarization echo ($PE=f(t_R)$).
 The gaussian one is rather characteristic of solid systems. It evolves towards the exponential
 when motion appears (in liquid crystals for instance).
 In case of a solid, the coherence time decreases as the number of interacting bodies increase.

Other studies [Usa98] have already proved that the decay of the echo has its origin in the stochastic nature of the dipolar interaction. We will try to understand the physical underlyings of the decay of the echo, and study this echo in different samples of crystals and liquid crystals to see how the structural and dynamical characteristics of the samples appear in the form of the decay curve.

2.2. The studied samples

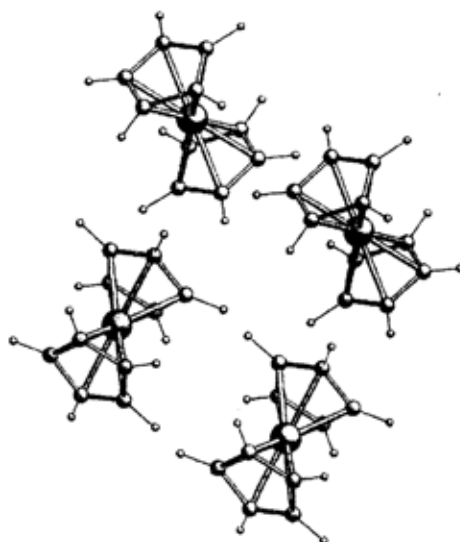
We will applicate the same pulse sequence (ZME sequence [ZME92]) to three different samples:

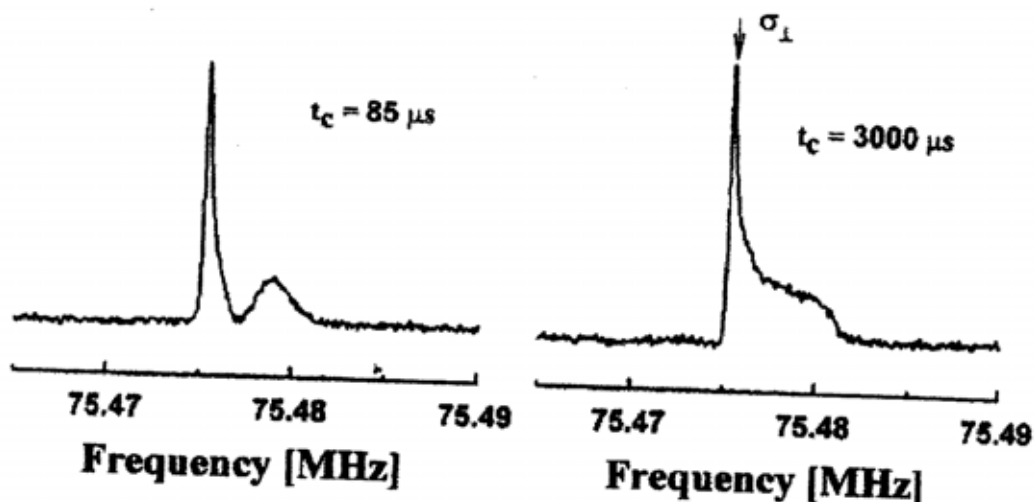
- A liquid crystal, the 5CB [Aug97] (p-pentyl-p'-cyanobiphenyl, $CN(C_6H_4)_2(CH_2)_3CH_3$), in order to study the possible resources of the ZME sequence as a structure characterization tool. This crystal presents its nematic phase at room temperature ($295.5K < T < 308K$);



The 5CB molecular structure, and its ^{13}C spectra, as obtained by cross-polarization at room temperature.

- A highly ordered crystal, the ferrocene ($(C_5H_5)Fe(C_5H_5)$) [SD78], in order to go further in the fundamental physical concepts involved in the ZME sequence;





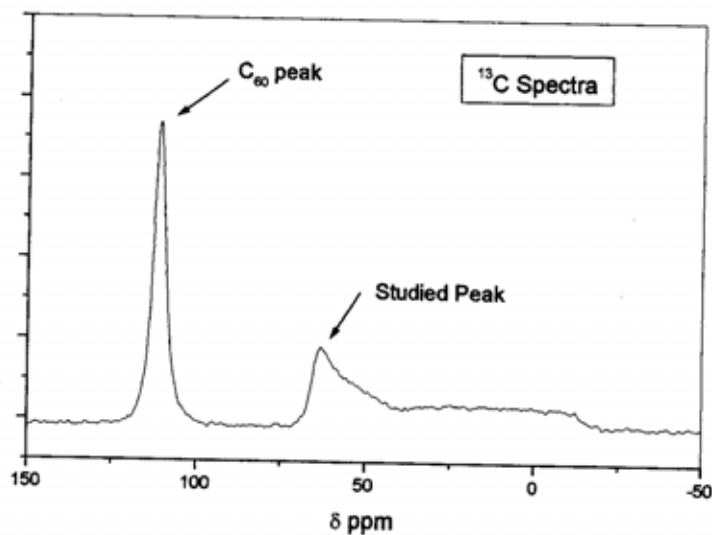
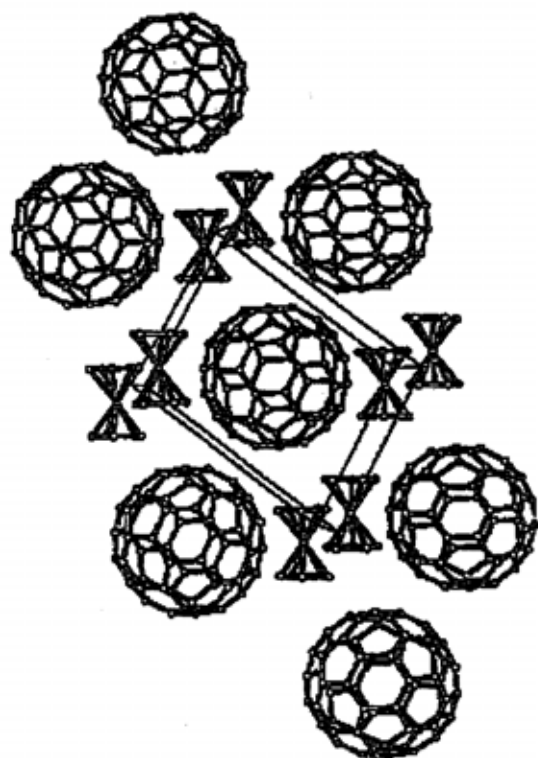
The ferrocene crystal structure in its room-temperature monoclinic form., as obtained by short (85 μs) and long (3000 μs) cross-polarization.

The chemical shift is determined by the orientation of the molecules relative to the static magnetic field B_0 .

It is seen that the quickness of the polarization transfer depends strongly on the orientation.

The highest peak, on the left, represents the signal of the molecules perpendicular to B_0 .

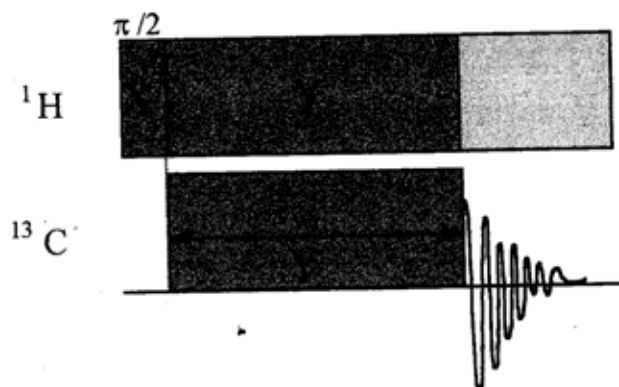
- The same crystal with the molecules of ferrocene well isolated between them by molecules of fullerene; in order to compete the studies made on ferrocene, reducing the number of the interacting 1H spins: the $C_{60}(\text{ferrocene})_2$ crystal [KTW99].



The $C_{60}(\text{ferrocene})_2$ crystal structure and its ^{13}C spectra, as obtained by long (2000 μs) cross-polarization.

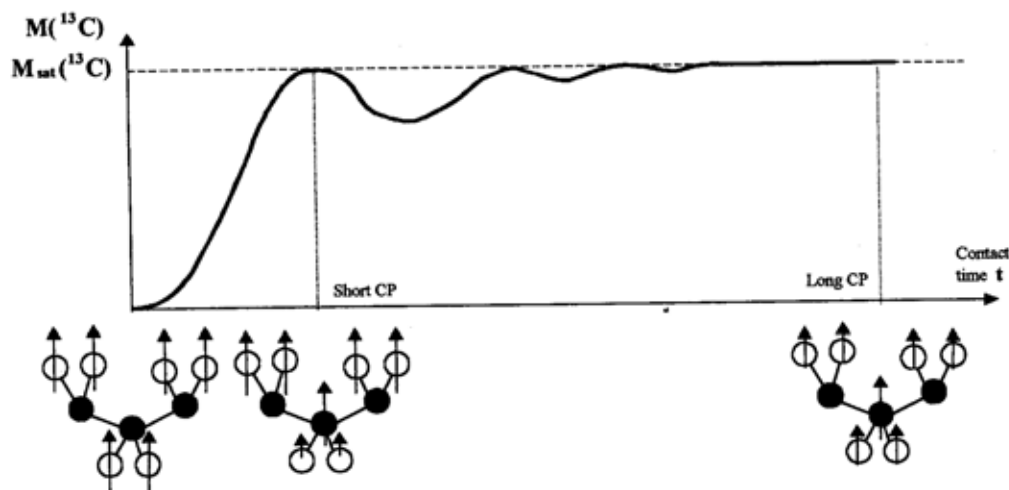
The C_{60} balls intercalated between the ferrocenes attenuate strongly the intermolecular interactions.

2.3. A previous indispensable experiment: The cross-polarization [MKBE74].



The cross-polarization pulse sequence. We measure the signal amplitude of the ^{13}C as a function of the cross-polarisation « contact » time τ_{var}

We need to perform the cross-polarisation sequence with our samples, to determine the short and long cross-polarization time, that permits a site to exchange polarisation with its nearest neighbours only or with all the sample respectively.

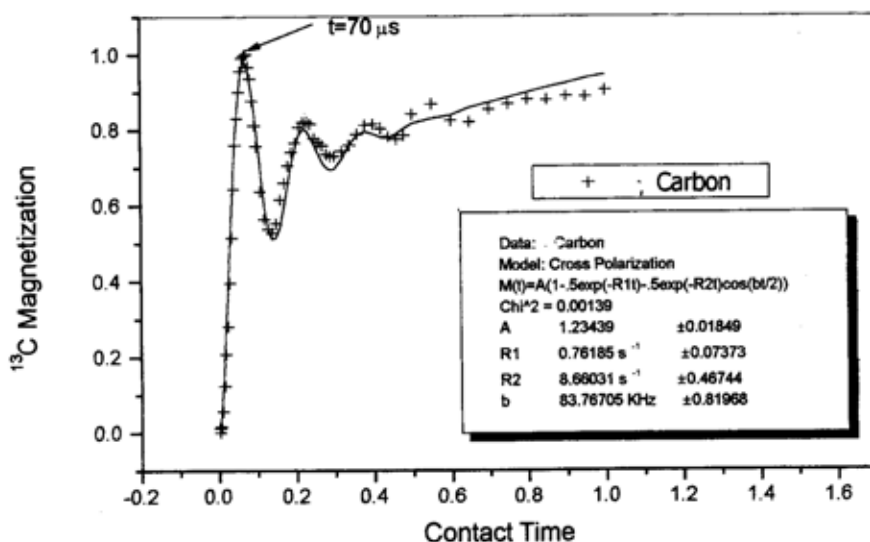


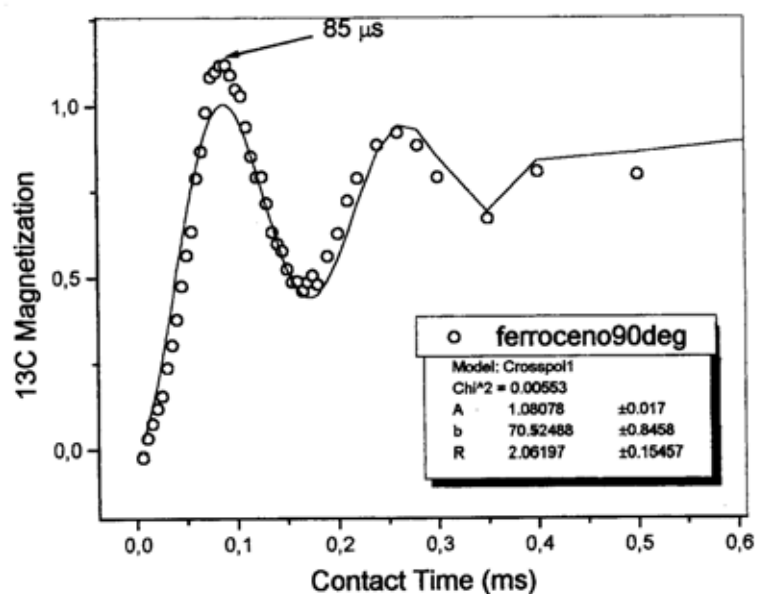
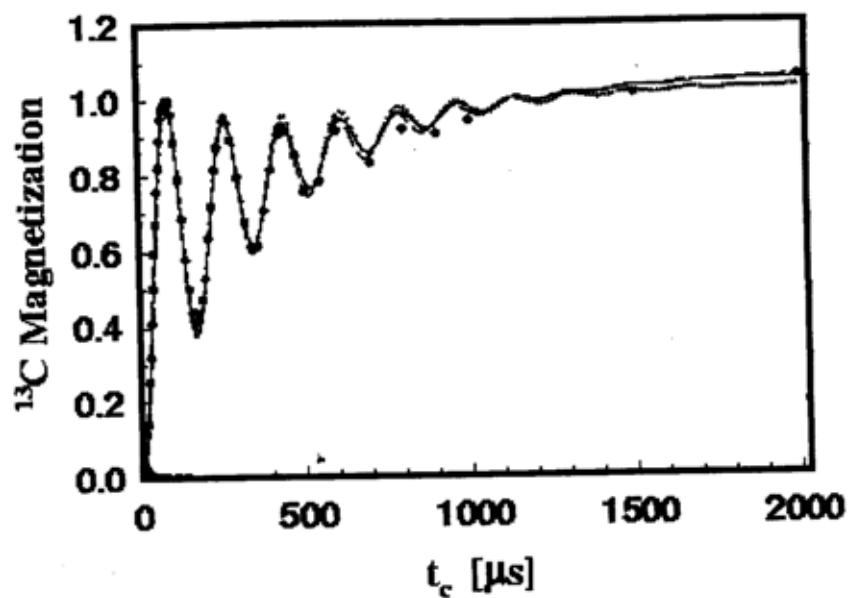
The short and long cross-polarisation
Here a black circle is a C, a white one an H. The C in the middle is a the considered sites in all the sample.
At short times, (the first maximum of the polarization) all the magnetisation of the ^{13}C comes from his nearest neighbours.
At long times, this magnetisation comes from contributions from all the H sites, that have had time enough to communicate part of their magnetization to the ^{13}C

^{13}C . The arrows represent the macroscopic magnetization of ^{13}C . The arrows represent the macroscopic magnetization of ^{13}C . The arrows represent the macroscopic magnetization of ^{13}C .

2.3.1. Results:

- in 5CB, we measure the response to the cross-polarisation of the α carbon.
- in ferrocene and in $\text{C}_{60}(\text{ferrocene})_2$ we measure the response to the cross-polarisation of the carbons in the molecules perpendicular to B_0 .





Cross-polarization curves for the 5CB, ferrocene and C₆₀(ferrocene)₂. The oscillations awaited fit very well the theory.

That allows us to determine the following parameters for the experiments to come :

Sample	Short CP time	Long CP time
5CB	70 μ s	2000 μ s
Ferrocene	85 μ s	3000 μ s
C ₆₀ (ferrocene) ₂	85 μ s	3000 μ s

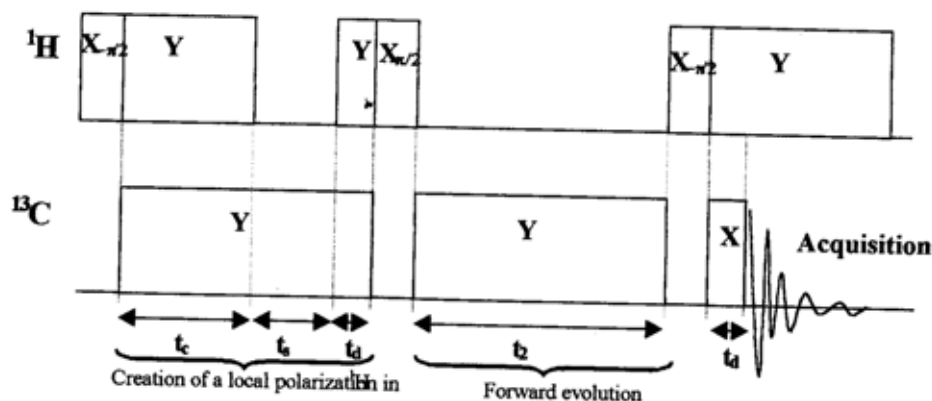
2.4. Study of the spin dynamics

2.4.1. Study of the "forward-dynamics" [Pas95],[Pas96]:

Before studying the evolution-involution of the magnetization, let's first study the evolution only ("forward dynamics"):

We will study the decay of a local polarization in the ^1H , as a function of the evolution time in the dipolar Hamiltonian H_d .

This is achieved by using the ZME sequence with a 0 or fixed involution time t_1 but with variable evolution time t_2 .

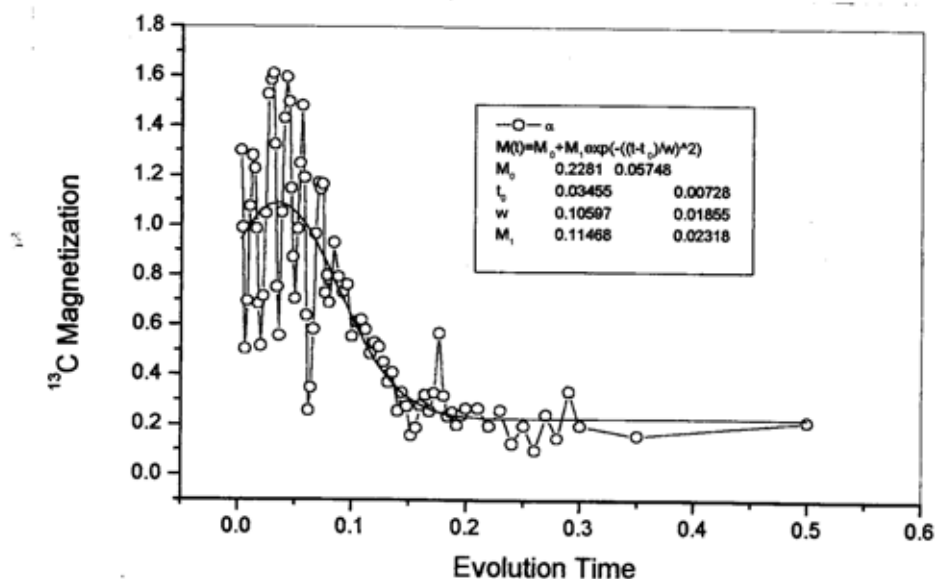


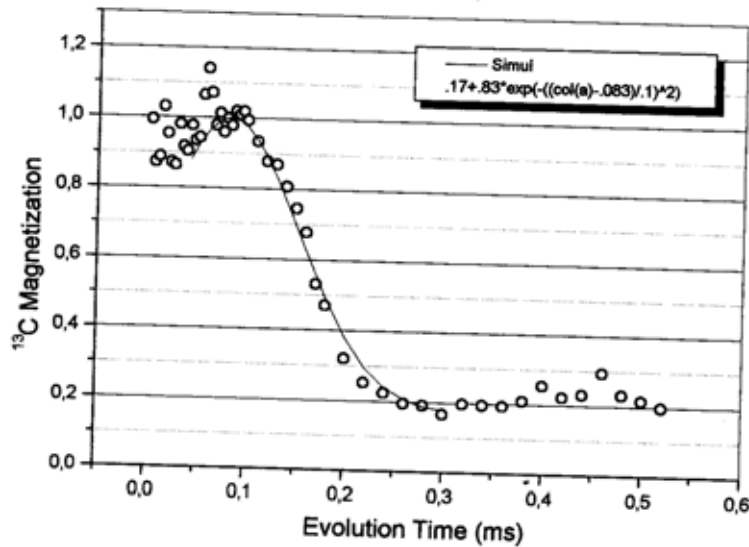
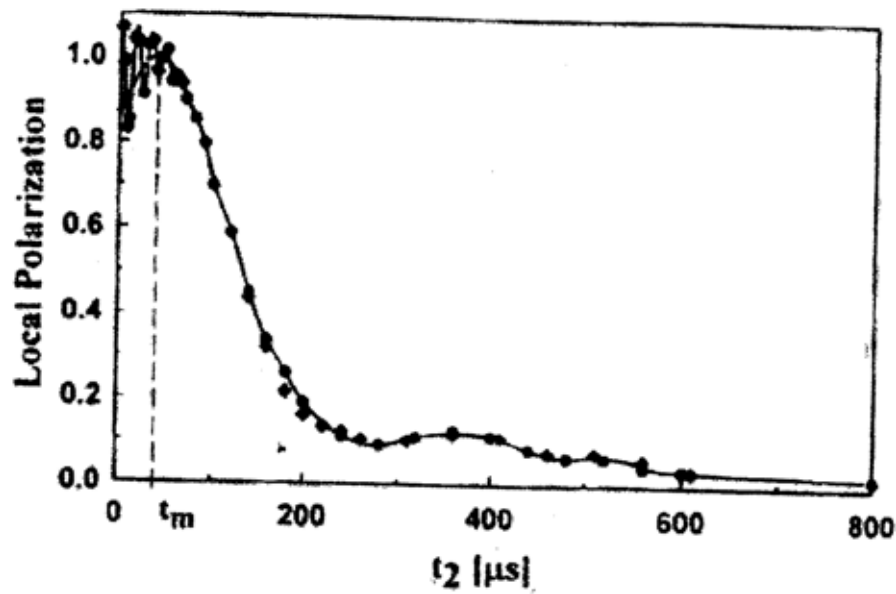
Pulse sequence for the study of forward dynamics of a local polarization :

- 1) Creation of a local polarization : first ^{13}C spin polarization is prepared by long cross-polarization (t_c). Then it is kept spin-locked while the ^1H polarization loses coherence (t_d). Then polarization is locally injected from ^{13}C to its ^1H neighbour with a short cross-polarization (t_d).
- 2) Evolution of the ^1H polarization in the dipolar hamiltonian (t_2).
- 3) The remaining ^1H polarization is locally injected to its ^{13}C neighbour with a short cross-polarization (t_d).
- 4) We thus measure the remaining ^1H polarization, after evolution, using its ^{13}C neighbour as a local probe.

The results (remaining local polarization versus evolution time) are shown below for our three samples.

- in 5CB, we measure the response to the cross-polarisation of the α carbon.
- in ferrocene and in $\text{C}_{60}(\text{ferrocene})_2$ we measure the response to the cross-polarisation of the carbons in the molecules perpendicular to B_0 .





The forward dynamics : in all cases, the local magnetization decays : it is because it begins diffusing, transferred from site to site thanks to the flip-flop term of the dipolar Hamiltonian.

2.4.2. Observations

1) In all cases, it appears clearly that the magnetization begins increasing, when, in this experiment, the evolution time t_1 is 0 !

In reality, it is because there is a small *involution* during the $\pi/2$ pulses on 1H , and during the cross-polarization periods. This involution begins by being reverted, hence the increase of the echo at short times.

2) A measure of the characteristic decay times (the time for the local magnetization to decrease to one half of its initial value leads us to:

5CB	$88 \pm 15 \mu s$
Ferrocene	$83 \mu s$
$C_{60}(\text{ferrocene})_2$	$83 \mu s$

This is a measure of the efficiency of the dipolar interactions, as it is a measure of the rapidity of the spin-diffusion process.

From these results we see that around the studied sites, the dipolar interactions in our three samples are quite equivalent.

The fact that the *ferrocene* and $C_{60}(\text{ferrocene})_2$ crystals show the same characteristic decay time is a proof that *intramolecular* interactions govern the spin diffusion process. The local magnetization, in the observed time scale, do not diffuse further than the molecule boundaries.

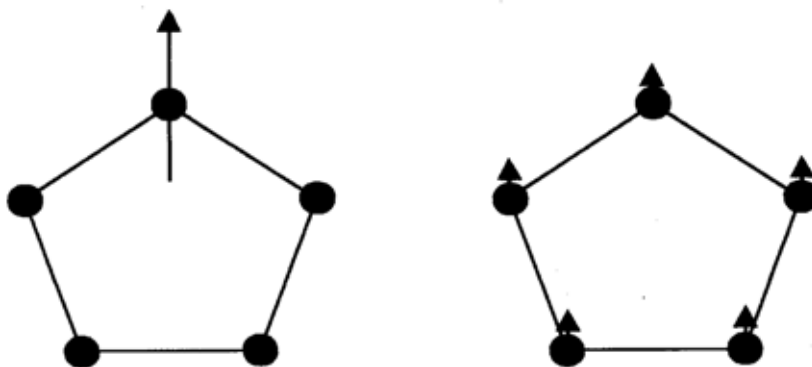
It is consequent with the observation of a *quantum beat* : a little rebound of the magnetization echo at around $350\mu s$ after the top of the echo.

This *quantum beat* [Pas95][Pas96] is due to constructive interference phenomenae in the local polarization, and reveals the *intrinsic quantic nature of the spin diffusion*.

Classically speaking, it can be seen as the *rebound* of the local magnetization on the neighbour sites (it resambles the sound echoes).

3) We can see quick additional oscillations in the refocalized magnetization near the top of the echo. These oscillations, of pulsation measured to be ω_1 , have a *quantic interference* nature. They can be eliminated, modifying slightly the pulse sequence, as it has been done for the studies in $C_{60}(\text{ferrocene})_2$ (the oscillations are no more visible). Their physical origin is explained in appendix 3.

4) In $C_{60}(\text{ferrocene})_2$, the asymptotic value of the magnetization, within the experimental time scale, is equal to $0.2 = 1/5$. It can be explained assuming that the initially localized polarization is now shared by the five spin sites in the ring.



The distribution of the polarization in a five- 1H spins ring :

The initially polarized 1H distributes its polarization to all his neighbours in the ring. In the end only remains $1/5$ of the initially localized polarization in each site.

We observe this asymptotic value in $C_{60}(\text{ferrocene})_2$ and not in ferrocene (where the magnetization decays to 0); because of the weaker *intermolecular* interactions: the molecules of ferrocene are well isolated by the balls of C_{60} .

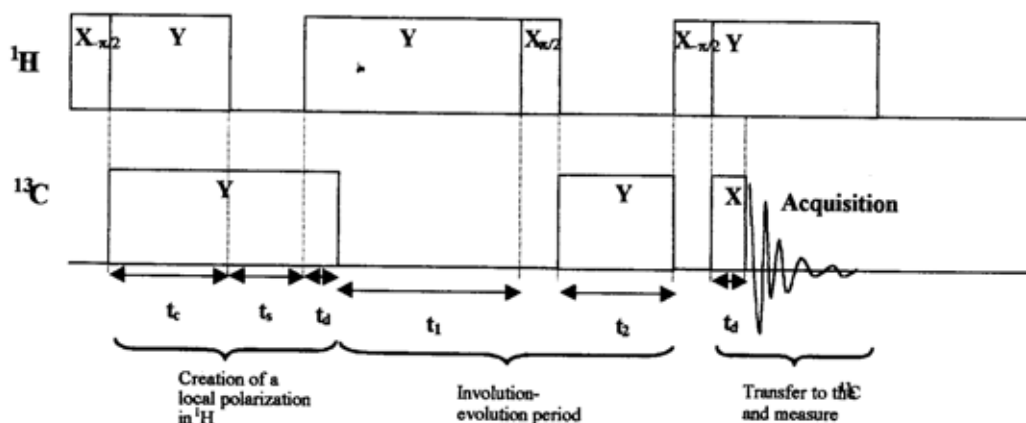
This is correlated with a bigger quantum echo in $350\mu s$ after the top of the echo in $C_{60}(\text{ferrocene})_2$ than in ferrocene. (Amplitude 0.3 in $C_{60}(\text{ferrocene})_2$ and only 0.12 in ferrocene), although it is not very well visible because hidden in the remaining polarization.

2.5. Study of the decay of the echo: at last the ZME sequence [Usa98],[Lev98].

Let's study now the evolution-involution sequence, by use of the ZME sequence [ZME92].

The ^1H spin system first *involutionates* in the hamiltonian $-\frac{1}{2}H_d$ during a time t_1 and then *evolucionates* in H_d during $t_2 \simeq 2t_1$ (modulo the involution during the $\pi/2$ pulses), in order to create the polarization echo.

We use the ZME sequence, with variable t_1 and t_2 .



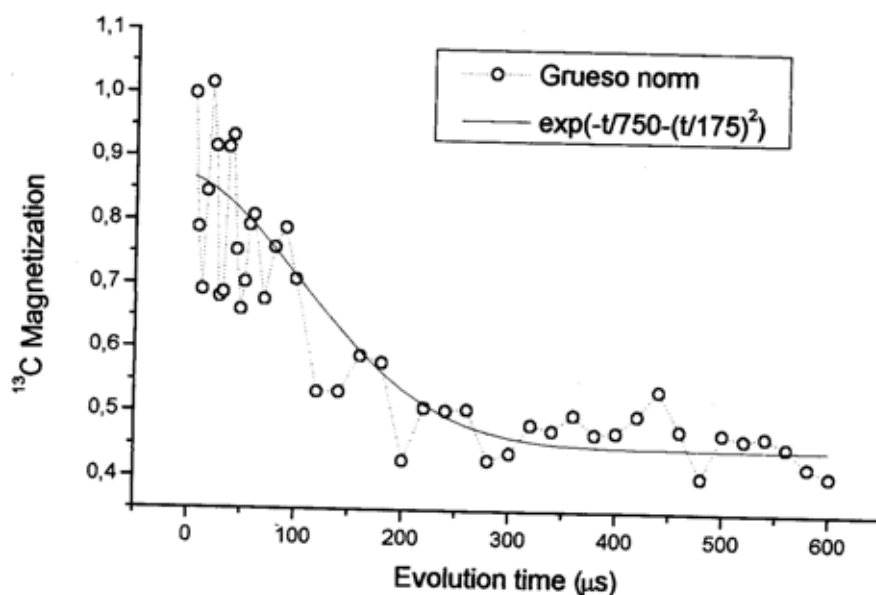
The ZME sequence for the polarization echo

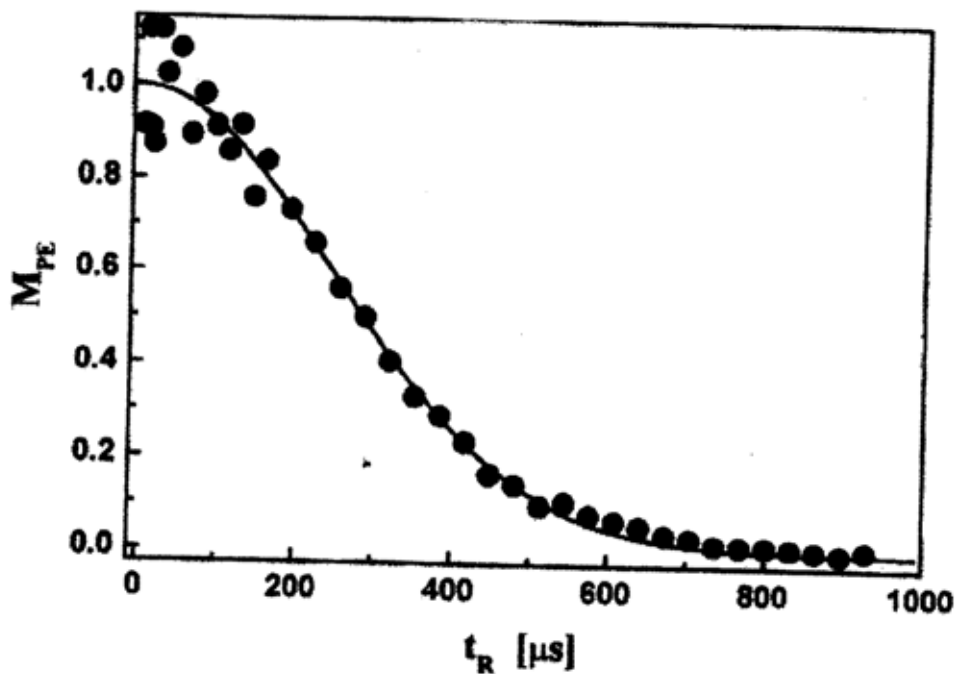
- 1) A local polarization is created in the ^1H ;
- 2) This polarization involutes in $-H_d/2$ during t_1 , then evolves in H_d during $t=t_1/2$
- 3) The refocalized polarization is locally measured, by means of the ^{13}C .

This sequence should allow us to study the decay of the echo as a function of the evolution-involution time

2.5.1. Results

We obtain the following experimental curves for the studied samples:





Attenuation of the polarization echo in 5CB and in the ferrocene single crystal (results on $C_{60}(\text{ferrocene})_2$ are not disponible yet.) The solid lines represent:

- a *Gaussian-exponential* fitting in the case of the 5CB liquid crystal, with the characteristic mid-height time $t_{\frac{1}{2}} = 125 \pm 13 \mu\text{s}$
- a *Gaussian* fitting in the case of the ferrocene crystal, with the characteristic mid-height time $t_{\frac{1}{2}} = 245 \pm 5 \mu\text{s}$.

2.5.2. Observations:

- 1) A measure of the characteristic decay times (the time for the local refocalized magnetization to decrease to one half of its initial value) can be compared with the characteristic spin-diffusion times:

	spin diffusion time	refocalization decay time
5CB	$88 \pm 15 \mu\text{s}$	$125 \pm 13 \mu\text{s}$
ferrocene	$83 \mu\text{s}$	$245 \pm 5 \mu\text{s}$
$C_{60}(\text{ferrocene})_2$	$83 \mu\text{s}$	-

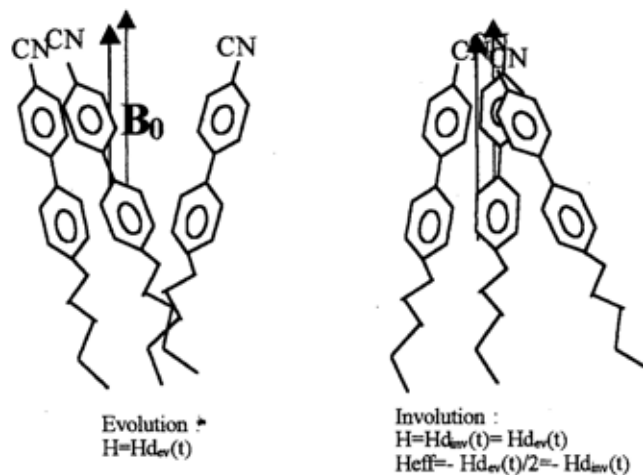
We see that, though the spin diffusion times in the three samples are nearly equivalent, the spin refocalisation decay times are quite different from 5CB to ferrocene. It may be due, as we will see, to interactions of the environment stronger with the liquid crystal than with the crystal.

- 2) The partially exponential decay in the 5CB curve can be considered as a manifestation of the presence of a strong irreversible process.

This might be explained as follows:

The crystal liquid molecules present a little motion in their nematic phase []: translational motion along their axis and rotational motion, especially in the more mobile alkyl queue.

It might be that in the evolution phase, the molecule is not in the same position as in the involution phase. The dipolar hamiltonian, which is written in terms of the relative positions of the interacting atoms, thus changes (we have a time-dependent hamiltonian). Thus it can't be perfectly inverted, and the polarization can't be perfectly refocalized.

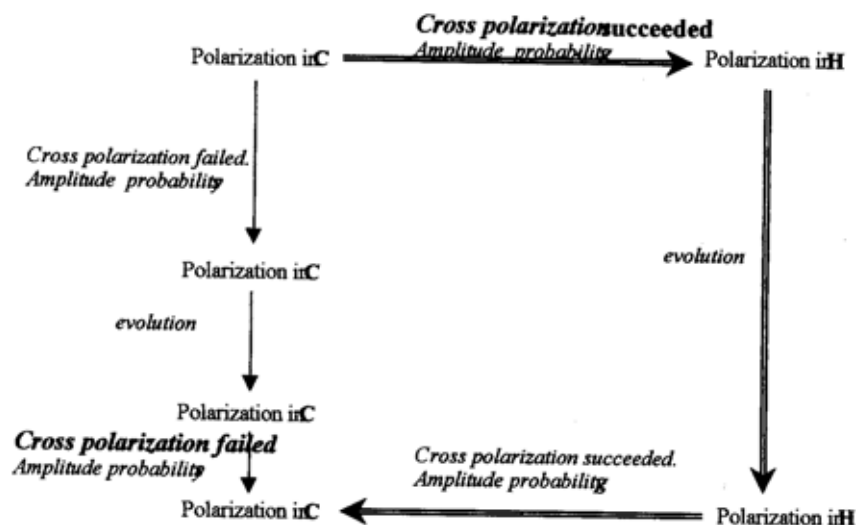


In the evolution-involution sequence, the molecules of 5CB have time to move : the dipolar hamiltonian changes irreversibly and cannot be inverted.

The characteristic time for this exponential attenuation, as taken out from the fitting, is $750\mu s$. It should correspond to one of the motional characteristic times.

3) We see that in 5CB, the ^{13}C polarization does not decay to 0 in the experimental time scale, but remains at an asymptotic value of 0,43.

This is only an experimental imperfection and traduces the fact that the cross-polarizations are not 100% efficient: the remaining polarization at large times is the polarization that stayed in ^{13}C from the beginning to the end, and has never been transferred to 1H .



The two possible paths for the polarization in the forward dynamics and ZME sequences.

A significant part of the measured polarization in ^{13}C comes from a polarization that never left the ^{13}C , and had no time to decay because of the spin-lock.

The only relevant information comes from the polarization that explored the 1H system.

It is consequent with the fact that we observe so big oscillations around the top of the echo (cf appendix 3: the measure of the relative amplitude of the oscillations is a measure of the transfer amplitude probabilities s and g)

4) The gaussian decay is characteristic of an attenuation that is controlled by the dipolar interaction [Usa98]. In the ferrocene-containing samples, it is clearly dipolar interaction that governs the attenuation of the decay. In 5CB, it is part of the decay mechanism.

2.5.3. Tentative of explanation:

It might be that between the evolution and involution period, the situation of the spins (i.e the spins wave function) evolves just a little bit, by interaction with the environment. This uncontrollable evolution may be the phenomenon that leads to the practical impossibility, so good might be our refocalization experiment, to recover 100% of the initial magnetization in the echo.

Quantically speaking, we have to understand that the little changes in the wave function between evolution and involution are due to an unpredictable *perturbation hamiltonian* of interaction with the environment, hamiltonian that no experimental processing could invert.

When the involution occurs in the total hamiltonian:

$$H = H_d + \Sigma(t)$$

the involution occurs in

$$H = -H_d + \Sigma(t)$$

with Σ being the unreversible, maybe time-varying, hamiltonian of interaction of the spin system with the environment.

The refocalized magnetization in an initially locally polarized $|i\rangle$ state would be proportional to (in the case of a non-time-varying Σ hamiltonian):

$$M_{echo} = \left[\langle i | \exp \left(-\frac{it}{\hbar} \Sigma \right) | i \rangle \right]^2$$

(t is here the total time of the evolution-involution period).

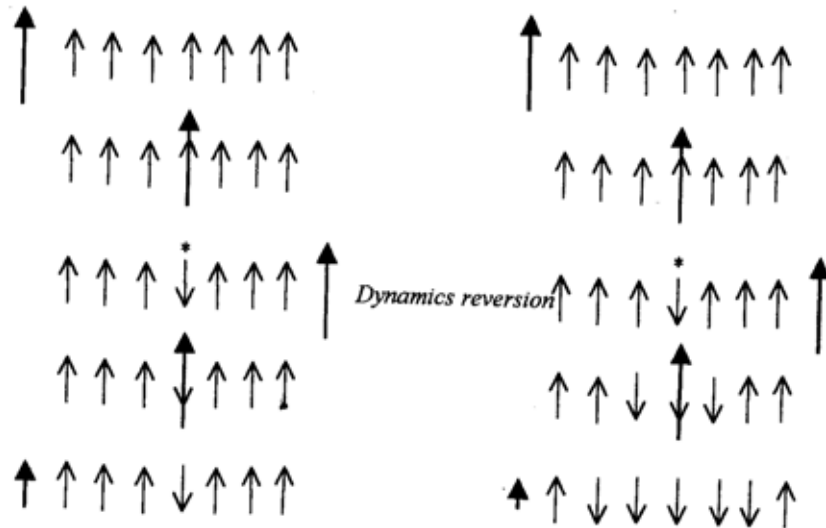
Thus the measure of the decay of the echo could give us information about Σ and the interaction of our quantic system with his macroscopic classical environment.

In classical systems, such little changes ("errors") in the spins configuration (this can be an accidental *flip-flop* of one spin, for instance) between evolution and involution phases can lead to exponentially growing errors. This is the signature of *many-body classical chaos*. The classical equivalent of our spin system would exhibit a refocalized magnetization that decays exponentially with time.

However, it has been numerically shown that, in simple quantum systems, such errors *do not increase exponentially with time* []. Basically, it is due to the fact that quantum theory is unitarian.

- If our system is not chaotic (no exponential increase of little configuration errors), we should observe a refocalized magnetization that decreases proportionally with the number of "errors" in the spins configuration, appearing between evolution and involution phases. If it is the case, the decay curve provides us with a measure of the interactions of the spin system with the environment.

- It might be that this *many-body* quantum system is chaotic (little configuration errors grow with time !). If it is the case, it is certainly due to the dipolar interactions that allow the configuration error to "diffuse" in the spin system, contaminating it like an epidemic. It has to be veriflicated by a more advanced theory, or at least with numerical calculations. But numerical calculations in many-body interacting spin systems are difficult to perform.



The one-body and many-body diffusing processes :

The magnetization in one site (bold arrow) evolves within the spin system (thin arrows).

During the evolution-involution time occurs an « error » (*) in the spins configuration.

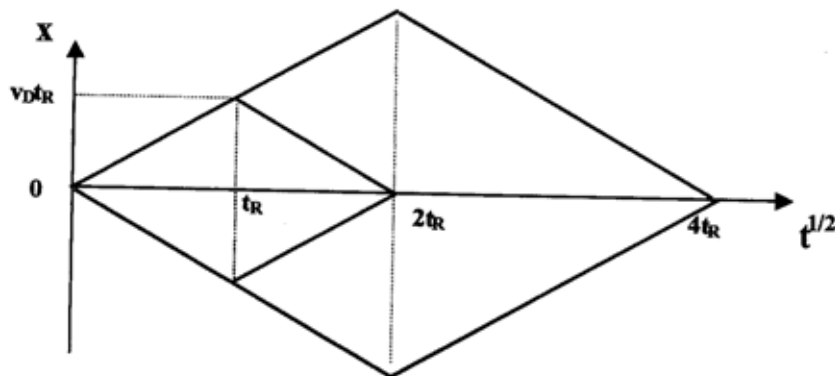
-in a one-body quantum model, the error does not increase with time. The refocalized magnetization only suffer punctual change due to the error.

in a many-body system, the error is allowed to propagate through the spin system, because of the dipolar interactions. The refocalized magnetization suffers an extended change due to the spatial extension of the propagated error.

The ferrocene-like gaussian decay of the echo reminds us of diffusion processes:

The further the initial local polarization "diffuses" around the spin system, the more "errors" can appear in the evolution-involution way, the number of errors appearing to be increasing with the length of the explored way.

As, in a diffusion process, the mean length of the explored way as a function of the diffusion time is gaussian, so is the number of errors appearing in the spin system. These errors also increase with a gaussian-like spin diffusion phenomenon. Hence gaussian is the mismatch of the refocalized polarization with the initial one.



The diffusion of the local polarization :

If the reversion time is t_R , the polarization has time to explore a zone of length $v_d t_R$ in the evolution period (v_d is the diffusion speed).

In all the explored zone can occur changes between evolution and evolution, that contributes to the mismatch between initial and refocalized polarization.

The mismatch increases with the number of changes, i.e with the length of the explored zone, i.e with the evolution time t_R .

2.5.4. Conclusion:

The gaussian shape observed is characteristic of the spin-diffusion process.

The irreversibility appears because the way to go forward is never the same as to go backwards, because of slight modifications due to the interactions of the spins with the environment. The longer the way, the more differences in the forward and backward ways.

The characteristic decay time could give us:

- a measure of the diffusion speed, if we know about the interaction of the spin system with the environment;
- a better understanding of the interaction of the spin system with the environment, if we know the diffusion speed.

But these measures are not obvious and require a more advanced treatment.