The evolution of local spin polarization in finite systems involves interference phenomena that give rise to quantum dynamical echoes and non-ergodic behavior. We predict the conditions to observe these echoes by exploiting the NMR sequences devised by Zhang et al. [Phys. Rev. Lett. 69, 2149 (1992)], which uses a rare $^{13}$C as local probe for a dipolar coupled $^{1}$H spin system. The non-ideality of this probe when testing mesoscopic systems is carefully analyzed revealing the origin of various striking experimental features.

In recent years interest has aroused on transport properties of mesoscopic systems [69]. Examples range from photons propagating through a colloidal solution to electrons in nanostructures. In most of the systems the quantum phenomena manifest as transport properties which are not linear with the size of the system. Since the Boltzmann equation does not retain interferences after collisions, it is necessary the use of the Schrödinger equation (e.g. in Liouville [1] or Keldysh’s form [3]). Thus, a localized excitation, after diffusing away and reaching the boundaries, might return as quantum dynamical echoes [8] resembling the familiar sound echoes. A trivial case occurs when a particle is placed in one side of a symmetrical double well potential and oscillates among them. While in these examples the high group velocities of the excitations restrict the observation of interference phenomena in the time domain, the local excitations in a system of nuclear spins with magnetic dipolar interactions evolve with characteristic times on the hundreds of micro-seconds and can be tested by using an NMR technique devised recently by Zhang, Meier and Ernst [7] (ZME). While they addressed a realization of the Lochsmidt daemon [8], they showed that, by applying an appropriate radio-frequency pulse sequence involving cross-polarization, the spin $S$ of a rare $^{13}$C (1.1% abundance) bonded to a $^{1}$H with spin $I_1$ can be used as a local probe that injects magnetization in the proton and captures it at a later time. The set of magnetic dipolar coupled $^{1}$H within a molecule constitutes the mesoscopic system where the spin dynamics can be monitored. The rest of the crystal constitutes a weakly interacting thermal bath.

The experimental time evolution of the polarization of a proton spin in a crystal of ferrocene, $(C_5H_5)_2Fe$, shows a nearly exponential decay of the local magnetization toward an asymptotic value of 0.2 of the initial polarization. This was interpreted as an "unhindered" spin diffusion among the five protons of a single ring. This is based on the assumption that the $^{13}$C is an ideal local probe, i.e. the polarization transfer between the $^{1}$H and $^{13}$C is complete and it takes a short time as compared with the characteristic time of the $^{1}$H-$^{1}$H interactions [13]. However, there are two aspects in the results of this ingenious experiment which do not fit with our current understanding of mesoscopic quantum dynamics: One is the linear decay of the magnetization observed for short times which is obviously inconsistent with the expected quadratic decay. The other is the monothonic decay which does not reveal any of the interference features characteristic of quantum evolution in systems with few degrees of freedom. The search for the conditions to actually observe quantum dynamical echo and answer to these questions lead us to solve the Schrödinger equation for the model system proposed by ZME.

Let us consider an ideal situation in which there is a perfect local probe which is able to inject magnetization in a single $^{1}$H nucleus and to measure it later. The system consists of $N$ $I$-spins governed by the magnetic dipolar ($\alpha = 1$) Hamiltonian truncated with respect to the dominant Zeeman interaction:

$$\mathcal{H}_{1f} = \sum_{j>k} d_{jk} \left[ \alpha 2I^+_j I^-_k - \frac{1}{2} (I^+_j + I^-_j) \right]. \tag{1}$$

Site $j$ spin operators $I_j$ are dimensionless. Subscripts start sequentially from $j = 1$. The interaction parameters are

$$d_{jk} = -\frac{\mu_0 \gamma_I^2 \hbar^2}{4\pi r_{jk}^3} \left( \frac{1}{2} (3\cos^2 \theta_{jk} - 1) \right), \tag{2}$$

where $\gamma_I$ is the gyromagnetic factor of the $I$-spins, $r_{jk}$ are internuclear distances and $\theta_{jk}$ their angles with the static magnetic field. A simplifying fact about ferrocene is that the ring performs fast rotations around its fivefold symmetry axis with a very short correlation time ($10^{-12}$s) and therefore the interaction parameter is time averaged. The new constants depend only on the angle $\theta$ between the molecular axis and the magnetic field and the angles $\gamma_{j,k}$ between the internuclear vectors and the rotating axis. The factor in brackets in Eq. (2) becomes $\langle \frac{1}{2} (3\cos^2 \theta - 1)(3\cos^2 \gamma_{j,k} - 1) \rangle = 1/2$ for a magnetic field normal to the axis. All sites in a molecule are then equivalent and the five fold symmetry is recovered, giving $d_1 = 1576Hz \times 2\pi \hbar$ for nearest neighbors. A locally polarized initial state $|i\rangle$ evolves toward a final state $|f\rangle$ with probability:

$$P_{f,i}(t_1) = \left| \langle f | \exp\left[ -\frac{1}{\hbar}\mathcal{H}_{1f} t_1 \right] | i \rangle \right|^2. \tag{3}$$
In the high temperature limit all the $N_i = N_f$ configurations compatible with an up projection of the spin $I_1$ are equally probable. Then the magnetization will be:

$$M(t) = 2 \left[ \sum_{f} \sum_{j} \frac{1}{N_i} P_{ji}(t_1) - \frac{1}{2} \right]. \quad (4)$$

For an *ideal* system of five spins arranged in a ring configuration, there is 1 configuration with total projection $5/2$, and there are 5, 10, 10, 5 and 1 configurations with projections $3/2$, $1/2$, $-1/2$, $-3/2$ and $-5/2$ respectively. On each of these subspaces there are 1, 4, 6, 4, 1 and 0 possible initial and final states with spin $I_1$ polarized summing up $N_i = 16$. The evolution under Hamiltonian (6) is called ‘diffusion’ in the laboratory frame. For the results of local polarization presented in Fig. 1 we multiply by $-\frac{1}{2}$ the above interaction constants, which correspond to the experimental case of ‘diffusion’ in the rotating frame. The dashed line represents the evolution when only nearest neighbor interactions are taken into account, while the full line considers all the interactions. At intermediate times, the first shows a clear quantum dynamical echo at around $1400 \mu s \approx 5 \times \sqrt{2} \times \hbar/(\frac{1}{2}d_1)$, which can be interpreted as the time the excitation needs to wind around a ring of length $L = 5a$ at an average speed $v_M / \sqrt{2}$, with maximum group velocity $v_M = a(\frac{1}{2})d_1 / \hbar$. This is confirmed by the study of correlation functions at different sites: the polarization at site 2 and 5 has the first maximum at $280 \mu s$ and at sites 3 and 4 around $560 \mu s$. Including second neighbors interactions, maxima are split and weakened, this can be assigned to the effect of short-cutting the path around. Although dynamical echoes are still visible, one may conclude that they are weaker when more degrees of freedom become effectively mixed. In the long time regime a striking effect is noticeable in the inset of Fig. 1: local polarization does not distribute around the value $1/5$ but rather oscillates around $M = \lim_{t \to \infty} t^{-1} \int_0^t M(t')dt' \approx 0.32$. This non-ergodic behavior is a consequence of the degeneracy of opposite quasi-momenta in perfect rings. We have observed this for single rings as well as for pairs of coaxial rings with $N \leq 10$ spins interacting according to dipolar ($\alpha = 1$), Ising like ($\alpha \gg 1$), Heisenberg ($\alpha = -\frac{1}{2}$) and XY ($\alpha = 0$) interactions by studying $M$. In the last situation we obtained the analytical high temperature solution of Eq. (6), which for odd rings gives: $\overline{M}_I = 1/N + (N-1)/N^2$, where the second term accounts for the degenerate quasi-momentum states. The complete ferrocene molecule gives $\overline{M}_I \approx 0.2$. Here we distinguish rings rotating independently or as a whole, keeping an eclipsed or staggered conformation. While the first present a weaker version of the dynamical echoes of the single ring, in the other two the echoes and valleys merge in a sort of plateau for intermediate times. For very short times the magnetization decreases quadratically with $t_1$. The coefficient is the configuration average of the sum of squares of the coupling constants effective to the flip-flop process in each configuration.

These results clearly do not represent the experimental data in ZME [6]. Although quantum dynamical echoes are indeed attenuated by including the interactions with other rings and molecules, the linear decay of the magnetization suggests that some quantum evolution has already occurred for the experimental time $t_1 = 0$. Therefore, it is important to consider that magnetization is injected and monitored using the spin $S$, which constitutes a non-ideal probe. The complete pulse sequence is schematized in Fig. 2. The most relevant part is as follows: A) The magnetization from an initially $y$ polarized $S$ spin is transferred to the $y$-axis of the $I_1$ spin (and in lesser degree to its neighbors) through a cross polarization pulse of duration $t_d$, when both the abundant and rare spins are irradiated at their respective resonant frequencies with field strengths fulfilling the Hartmann-Hahn [8] condition $\gamma_I B_{1y}^I = \gamma_S B_{1y}^S$. The time $t_d$ is the shortest of those that maximize the polarization transfer [9]. B) The $I$-spins evolve in presence of $B_{1y}^I$ during a time $t_1$. Thus, the relevant evolution of the spin-diffusion sequence occurs in a rotating frame. C) Another cross-polarization pulse of length $t_p = t_d$ is applied to transfer back the polarization to the $x$-axis of $S$. D) The $S$ polarization is detected while the $I$-system is kept irradiated (high-resolution condition). Therefore a better simulation of the experiment includes the $I$’s spins system, the non ideal probe $S$ and their interaction. The $I$-$S$ dipolar interaction extends the sum in (6) to the $S$ spin. The interaction coefficient is $b_k$ defined as (6) with a $\gamma_I$ replaced by a $\gamma_S$ and distances and angles modified accordingly. Given the difference in gyromagnetic factors the dipolar $I$-$S$ interaction is truncated dropping terms that mix different Zeeman subspaces, hence:

$$H_{IS} = \sum_k b_k 2I^z_k S^z, \quad (5)$$

When two r.f. fields are applied to both $I$ and $S$ spins, these are quantized in their corresponding rotating frames and the total Hamiltonian is:

$$H^{(z)} = H_{II} + H_I + H_S^{(z)} + H_{IS} \quad (6)$$

the superscript indicates the direction of $B_{1S}$.

The isolated $I$-spins system is described by the first two terms, where $H_I = -\omega_{11} \sum_k I^y_k$ is the effect of the r.f.. In the case of strong irradiation, $|\omega_{11}| \gg |d_jk|$, we can approximate (6) in a frame tilted to the rotating $y$ axis by

$$H'_{II} = \left[-\frac{1}{2}\sum_{j>k} d_{jk} \left[ 2I^y_j I^y_k - \frac{1}{2} (I^+_j I^-_k + I^-_j I^+_k) \right] \right]. \quad (7)$$

As usual, we neglected non-secular terms of the form $(I^+_j I^-_k - I^-_j I^+_k)$. It is the factor $-\frac{1}{2}$ relating (6) and
what allows the realization of the Lochsmidt daemon [6] by experimentally switching the evolution from one situation to the other which leads to a polarization echo [7], not to be confused with the quantum dynamical echoes described above. The isolated probe in the presence of a r.f. field along y (x) direction is described by \( H_S^{(x)} = -\hbar \omega_{1S} S^x \) with \( \hbar \omega_{1S} = \gamma_S B_1^{(x)} \). The system-probe interaction with an additional truncation in the doubly rotating frame is:

\[
H_{IS} \approx \sum_k b_k \frac{(i)}{2} [I_k^+ S^- + (-1) I_k^- S^+],
\]

where factors in parenthesis correspond to \( B_1^{(y)} \). In Fig. 2, the evolution starting with the polarized \( S \) spin involves two Hamiltonians, during the times \( t_d \) and \( t_p \) the evolution is given by the total Hamiltonian \( H^{(y)} \), but during \( t_1 \) as well as during the acquisition, the irradiation makes the action of \( H_{IS} \) negligible (high resolution condition) and evolves with \( H_{II} + H_I \). The probability of having an initial state \( |ib\rangle \) with the probe polarized along \( y \) direction and a final state \( |fx\rangle \) with the probe polarized along \( x \) is:

\[
P_{f,x}(t_1) = |\langle fx | \exp[-\frac{i}{\hbar} H^x t_p] \exp[-\frac{i}{\hbar} (H_I + H_{II}) t_1] \exp[-\frac{i}{\hbar} H_{IS} t_d] |ib\rangle|^2.
\]

The resulting magnetization is shown in Fig. 3 with open circles. For short \( t_1 \) the evolution is linear with time and the dynamical echoes are still noticeable but appear shifted to shorter times. Both effects are consequence of the evolution of the magnetization in the I-I system during the two cross polarization periods: by comparing with Fig.1, it is clear that the overall effect of them is to shift the curve in a time shorter than their sum. This is verified by superposing the ideal evolution from Fig. 1, shifted in \( t_{shift} = 126 \mu s < (t_d + t_p) \) and renormalized with a factor of \( a = 1.22 \) obtained from the short time behavior. This explains why the asymptotic value of the magnetization in the complete sequence has been raised to \( M_{n,i} = aM_1 \approx 0.4 \) from the \( M_1 \approx 0.32 \) around which the ideal polarization of Fig.1 oscillates. Then \( M_{n,i} \) overestimates the fraction of magnetization remaining in the proton. The fact that Figs. 1 and 3 can be superposed indicates that \( S-I \) interactions do not break the five-fold symmetry appreciably within the relevant experimental times, this is a consequence of the high resolution condition.

These results indicate that the experimental [6] asymptotic value \( M_{exp} = 0.2 = M_{n,i} \) originates on the evolution that has already occurred at \( t_1 = 0 \), when polarization starts to be recorded and is normalized. A more proper normalization would give an ideal asymptotic value \( M_1 \approx M_{exp}/a = 0.16 \), lower than \( M_1 \) for the complete molecule (two coupled rings). Since, as discussed above, the quantum evolution does not give an equi-distribution of polarization, to achieve the experimental 0.2, the evolution must involve a system with \( N \gg 10 \). With the important number of spins other than those belonging to one molecule, the boundary of the system becomes fuzzy, weakening the interferences that originate the quantum dynamical echoes. Then, it becomes clear why these do not show up in the reported experiments.

An interesting phenomenon shown up by the non-ideal evolution in Fig 3 is the small high frequency \( \approx \omega_{11} \) oscillation around the superposed ideal curve. This effect is due to an incomplete \( S-I \) transfer which allows interference of phases accumulated during evolution \( t_1 \) by sub-spaces with different total spin \( \sum I_k^y \) projection; i.e. the interference of the dashed and dotted paths of polarization amplitudes in Fig. 2. They may originate the small ’dispersion’ observed in the top of the polarization echo in the experimental curve.

In summary, we have solved the relevant part of a non-ideal spin ‘diffusion’ experiment for a simple five-spins system resorting to the usual assumptions to generate the system, probe and system-probe Hamiltonians: truncation of the dipolar Hamiltonian and total decoupling under high resolution conditions (during the time \( t_1 \)). We have shown that while \( ^{13}\text{C} \) behaves as a non-ideal local probe, its effect can be reasonably quantified. As occurs in all mesoscopic physics the probes are actually part of the system [12] and therefore have a relevant role in the interpretation of the results. This undesired effect can be experimentally overcome in part, by studying the diffusion in the laboratory frame which tends to compensate the non-ideality of the probe and shrinks in a factor \( \frac{1}{2} \) the time scale, ’cleaning’ the evolution from interactions different than the secular dipolar one. We predict that a spin ‘diffusion’ experiment in molecular crystals containing few interacting spins per molecule should present quantum dynamical echoes. Possible candidates are molecules with single rings of the form \( \text{C}_n\text{H}_n \). Molecules with linear topology in the interaction network present less important second neighbors interaction, making the interference effects even stronger.

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Figure 1: Ideal evolution of a $^1$H-spin polarization as a function of $t_1$ for a system of 5 spins in a ring. Dashed line considers only nearest neighbor interaction $d_1$. Full line is the exact dipolar evolution. The inset shows fluctuations around the value $\overline{M}_i = 0.32$.

Figure 2: Pulse sequence for measurement of proton spin ‘diffusion’ in the rotating frame. A $\pi/2$ pulse on the abundant $^1$H spins system creates a polarization that is transferred during $t_C$ to a rare $^{13}$C. After the decay of the proton spin coherence during $t_S$: (A) the $^{13}$C polarization is locally injected to the bonded proton, (B) ‘diffusion’ in the protons system is allowed and (C) it is captured again in the $^{13}$C where (D) it is recorded.

Figure 3: Non-ideal evolution of a $^1$H spin polarization in a ring of ferrocene (open circles) as detected in a strongly coupled $^{13}$C spin. Calculation uses the pulse sequence in Fig. 2 with $t_d = t_p = 85 \mu s$ with the molecular symmetry axis at an angle of $\pi/2$ with the external magnetic field. Full line is the ideal evolution in Fig.1, shifted in $126 \mu s$ and normalized accordingly.