Some Ergodic Problems in Spin Dynamics

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A revolution in nonequilibrium statistical mechanics took place in 1970. But discussions indicate, that it passed unnoticed by workers, who are not related with spin dynamics and magnetic resonance directly.

The revolution consisted in theoretical invention and experimental realization of evolution inversion in many-particle system, which was considered and proved as real thermodynamic object in many fine preceding studies.

The system: nuclear spins, isolated from lattice = nuclei ^{19}F in single crystal CaF_2 (simple cubic lattice for the spins) for example.

The best of these preceding studies:

1) development of dynamical nuclear polarization [see for example V.A.Atsarkin. Dynamical nuclear polarization. Moscow: Nauka 1980].

2) observation of magnetic phase transitions [A.Abragam & M.Goldman. Nuclear Magnetism: Order & Disorder. Clarendon, 1982].

All achievements here were founded on microscopic description of quasiequilibrium states as Gibbs distributions with corresponding thermodynamic properties and on application of calculated transition rates – standard method for description of irreversible processes.

Inversion of evolution was fulfilled by W.-K.Rim, A.Pines, and J.Waugh (PRL 25, 218, 1970) in the same spin system, but they had very important precursor – Erwin Hahn with more simple one-particle spin echo.

Hahn's spin echo (Phys. Rev. 80, 580 1954). The Hamiltonian

$$H_Z = H_{Z0} + H_{Z1}, \quad H_{Z0} = \omega_0 I_z, \quad H_{Z1} = \sum_j \Delta_j I_j^z \qquad \Delta_j \ll \omega_0$$

Initial state

$$\rho_0 = \frac{\exp(-\beta H_Z)}{Tr(\exp(-\beta H_Z)} \to \frac{1}{Tr(1)}(1 - \beta H_Z) \approx \frac{1}{Tr(1)}(1 - \beta \omega_0 I_z)$$

After applying a rf-pulse, rotating on angle $\pi/2$ around the y-axis

$$\rho_0 \to (\tfrac{\pi}{2} y) \to \rho_1 = \frac{1}{Tr(1)}(1 - \beta \omega_0 I_x).$$

Observable value is FID = free induction decay $F(t)$

$$\langle I_x \rangle = Tr(I_x e^{-iH_Z t} \rho_1 e^{iH_Z t}) \sim \cos(\omega_0 t) F(t),$$

$$F(t) = \langle I_x I_x(t) \rangle_0 / \langle I_x^2 \rangle_0 = \langle I_x e^{iH_{Z1} t} I_x e^{-iH_{Z1} t} \rangle_0 / \langle I_x^2 \rangle_0 = \langle e^{i\Delta t} \rangle_\Delta$$

$$\langle Q \rangle_0 = Tr(Q)/Tr(1)$$

Here $<\cdots>_\Delta$ is averaging on random symmetric distribution of shifts Δ_j within the sample. Gauss or Lorentz distributions are considered as realistic producing $F(t)=\exp(-t^2/(2T_2^2))$ or $F(t)=\exp(-|t|/T_2)$ correspondingly.

Superoperators are used for short notations:

$$H_{Z1}^{\times} I_x = [H_{Z1}, I_x], \quad e^{iH_{Z1}t} I_x e_0^{-iH_{Z1}t} = e^{iH_{Z1}^{\times}t} I_x, \quad F(t) = \langle I_x e^{iH_{Z1}^{\times}t} I_x \rangle_0 / \langle I_x^2 \rangle_0$$

Main constructive idea consists in looking for a method to invert the Hamiltonian sign. Then we can organize the evolution in such a way that up to time t_1 the system evolves by usual way, and later during the time τ it evolves with inverted Hamiltonian:

$$F(t = t_1 + \tau) = \langle I_x e^{-iH_{Z1}^{\times}\tau} e^{iH_{Z1}^{\times}t_1} I_x \rangle_0 / \langle I_x^2 \rangle_0.$$

At the time $\tau = t_1$ the observable comes to its initial value $F(t=0)=1$ producing the echo. The Hamiltonian inversion is realized by application of two pulses, producing rotation of spins on the angle π around the x-axis*. As a result:*

$$F(t = t_1 + \tau) = \langle I_x V_{-\pi x}^{\times} e^{iH_{Z1}^{\times}\tau} V_{\pi x}^{\times} e^{iH_{Z1}^{\times}t_1} I_x \rangle_0 / \langle I_x^2 \rangle_0.$$

Very impressive effect, but system is very simple, like ideal gas.

Magic echo of Waugh

Hahn's method solves the problem of evolution inversion for one particle evolution of spin system in external field.

Magic echo of Waugh (1970) solves the problem for **many particle evolution of the system**. This evolution belongs to irreversible processes in all other properties.

This phenomenon is **first processes**, wherefrom we know exactly for the first time that our time-reversible equations of motion describe irreversible evolution. For example, we see here, that additional unknown small multi-particle interactions are not necessary to create irreversibility.

Explanation of the magic echo requires some preliminary notations and calculations.

Secular dipole-dipole interaction

Nuclear spin system in static external field is described by the Hamiltonian

$$H = H_{Z0} + H_{d0},$$

$$H_{Z0} = \omega_0 I_z, \quad H_{d0} = \frac{1}{2}\sum_{\mathbf{r}\neq\mathbf{q}} \frac{\gamma^2\hbar}{|\mathbf{r}-\mathbf{q}|^3}\left(\mathbf{I}_\mathbf{r}\mathbf{I}_\mathbf{q} - 3(\mathbf{n}_{\mathbf{rq}}\mathbf{I}_\mathbf{r})(\mathbf{n}_{\mathbf{rq}}\mathbf{I}_\mathbf{q})\right), \quad \mathbf{n}_{\mathbf{rq}} = \frac{\mathbf{r}-\mathbf{q}}{|\mathbf{r}-\mathbf{q}|}.$$

For strong external field $\omega_0 \gtrsim 10^4\omega_{loc}$. Here ω_{loc} is typical speed of rotation of a spin in the field, produced at its position by other spins. Applying the interaction representation

$$\frac{d}{dt}\rho = -i[H,\rho], \quad \rho = e^{-iH_{Z0}t}\rho_1 e^{iH_{Z0}t},$$

$$\frac{d}{dt}\rho_1 = -i[H_{d0}(t),\rho_1], \quad H_{d0}(t) = e^{iH_{Z0}t}H_{d0}e^{-iH_{Z0}t}.$$

we can average last equation over fast oscillations (with frequencies ω_0 and $2\omega_0$), and obtain that

$$\frac{d}{dt}\rho_1 = -i[H_{dz},\rho_1], \quad H_{dz} = \frac{1}{2}\sum_{\mathbf{rq}} b_{\mathbf{rq}}(3I_\mathbf{r}^z I_\mathbf{q}^z - \mathbf{I}_\mathbf{r}\mathbf{I}_\mathbf{q}),$$

$$b_{\mathbf{rq}} = \frac{\gamma^2\hbar}{2|\mathbf{r}-\mathbf{q}|^3}(1-3\cos^2\vartheta_{\mathbf{r}-\mathbf{q}}), \quad b_{\mathbf{rr}} = 0.$$

Last Hamiltonian is known as secular part of dipole-dipole interactions.

Observable is again free induction decay

$$F(t) = \langle I_x I_x(t) \rangle_0 / \langle I_x^2 \rangle_0 = \langle I_x e^{iH_{dz}t} I_x e^{-iH_{dz}t} \rangle_0 / \langle I_x^2 \rangle_0.$$

It is very important that big Hamiltonian H_Z produces simple evolution – pure rotation around the z-axis. To find a way for inversion of the secular Hamiltonian H_{dz} we can took into account that if additional rotating alternating field is applied at resonance frequency, then after separating of total rotation at Larmor frequency the system evolves according to equation

$$\frac{d}{dt}\rho_1 = -i[\omega_1 I_x + H_{dz}, \rho_1],$$

Here magnitude of rotating field $\omega_1 << \omega_0$. If $\omega_1 >> \omega_{loc}$, then we can apply interaction representation again using $\omega_1 I_x$ as large Hamiltonian. Than

$$\rho_1 = e^{-i\omega_1 I_x t} \rho_2 e^{i\omega_1 I_x t}$$

$$\frac{d}{dt}\rho_2 = -i[e^{i\omega_1 I_x t} H_{dz} e^{-i\omega_1 I_x t}, \rho_2]$$

The Hamiltonian here has static part and oscillations with frequencies ω_1 and $2\omega_1$. Averaging over the oscillations we have

$$\langle e^{i\omega_1 I_x t} H_{dz} e^{-i\omega_1 I_x t} \rangle_t = -\frac{1}{2} H_{dx} = -\frac{1}{2} V_{\frac{\pi}{2}y} H_{dz} V^{+}_{\frac{\pi}{2}y}.$$

$$H_{dx} = \frac{1}{2} \sum_{\mathbf{rq}} b_{\mathbf{rq}} (3 I^x_{\mathbf{r}} I^x_{\mathbf{q}} - \mathbf{I_r I_q}).$$

Abstracting from simple total rotations around static ang alternating fields we can switch on alternating field at time $t=t_1$ and switch it out at $t=t_1+\tau$, and apply pulses, rotating on angles $\pi/2$ and $-\pi/2$ around y-axis just before and after applying of alternating field. As a result

$$F(t = t_1 + \tau + t_2) = \left\langle I_x e^{iH^{\times}_{dz} t_2} V^{\times}_{-\frac{\pi}{2}y} e^{-\frac{i}{2} H^{\times}_{dx} \tau} V^{\times}_{\frac{\pi}{2}y} e^{iH^{\times}_{dz} t_1} I_x \right\rangle_0 / \langle I_x^2 \rangle_0 =$$

$$= \langle I_x \exp(iH^{\times}_{dz}(t_1 - \frac{\tau}{2} + t_2)) I_x \rangle_0 / \langle I_x^2 \rangle_0.$$

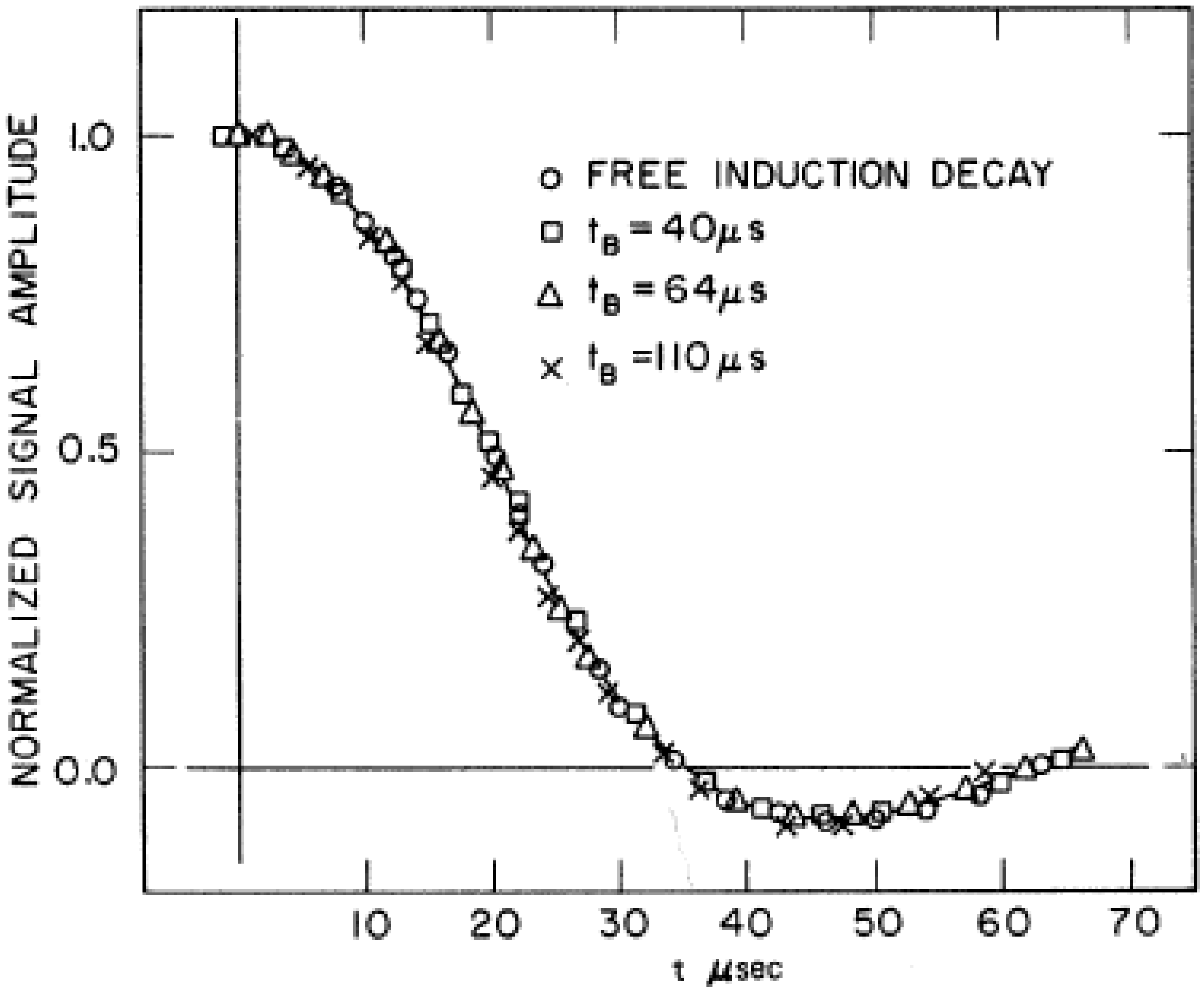
The echo take place at $t_{eff} = t_1 - \tau/2 + t_2 = 0$.

The procedure can be repeated many (thousands!) times up to the moment, when accumulation of errors can not be considered as negligible.

Inversion of spin diffusion is possible as well: Ernst et al. PRL 69, 2149, 1992.

Checking of coincidence of the echo signals for different delay times $\tau = t_B$

Waugh et al. PRB 3, 684, 1971.



Conclusions of the study

1. "Irreversible" evolution of the spin system is defined by known dipole-dipole interaction. In absence of ergodic theorem it was not evident at all.

2. Irreversibility of the evolution reflects specifics of experiments, where small assortment of initial conditions is available, and only simplest correlation in the system are observable.

3. We received strong indication that, in accordance with T-invariance of known interaction, all laboratory processes should be classified as experimentally reversible and not yet reverted.

Remark.

All discussion was carried out for isolated spin system. Typical time of spin lattice relaxation $T_1 \sim 10^3$ sec, while duration of free induction decay $T_2 \sim 10^{-3}$ sec. Therefore the approximation is expected as justified for $t \leq 10$ sec at least.

Hierarchy of interactions as a cause of irreversibility in quasi-isolated systems

Isolated systems are absent. As a rule we expect, that the system is isolated good enough, if isolation is satisfactory relative interactions, which can disturb the evolution of directly observable values. They are connected with “visible” part of the density matrix. But reversibility is defined by invisible (unmeasured) part of the density matrix as well. If it will be destroyed by external influence, then inversion of evolution will be impossible.

Invisible part of density matrix contains multi-particle correlation, while observables are described by one- and two-particle operators as a rule (moment, energy, or their densities, and so on). Speed of reaction of N-body operator on external perturbation is proportional, roughly speaking, to N^{α} with $\alpha=0.5 \div 1$. Therefore the system can became irreversible due to small external influence at time, when it produces negligible effect on observables. Examples of estimation of many-spin correlation, sustaining this statement, can be found in the article: T.Charpentier, D.Sakellariou, J.Virlet, F.Dzheparov, J.-F.Jacquinot J. Chem. Phys. 127, 224506, 2007.

Ergodic theorem for an impurity spin subsystem in a paramagnet

Mathematical model forming the basis for description of polarization transfer in impurity spin system is of the form

$$H = H_0 + H_1, \quad H_0 = \sum_j \omega_j(t) I_j^z, \quad H_1 = \frac{1}{2} \sum_{jk} a_{jk} I_j^+ I_k^-,$$

Here $$I_j^+ = I_j^x + i I_j^y, \quad I_j^- = (I_j^+)^+,$$

$$a_{i \neq j} = a_0 r_0^3 (1 - 3\cos^2 \vartheta_{ij}) / r_{ij}^3, \quad a_{jj} = 0.$$

H_1 represents so called flip-flop term producing spin transitions, and local field $\omega_j(t)$ is induced by surrounding thermostat spins at the j-th impurity spin.
It is a δ-correlated normal stationary random process:

$$\langle \omega_j(t) \omega_k(\tau) \rangle_n = \frac{2}{T_2} \delta(t - \tau) \delta_{jk},$$ and for reasonable functions α_j (t)

$$U(t, t_0, [\alpha]) = \left\langle \exp\left(i \sum_{j=1}^{N} \int_{t_0}^{t} d\tau \, \alpha_j(\tau) \omega_j(\tau) \right) \right\rangle_n = \exp\left[-\sum_{j=1}^{N} \left| \int_{t_0}^{t} \frac{d\tau}{T_2} \alpha_j^2(\tau) \right| \right].$$

The system is open, but it has additive integral of motion $I_z = \sum_{k=1}^{N} I_k^z$.

It is simple enough to admit to study the evolution of the system to equilibruim state [Dzheparov, JETP 89, 753 (1999).

Basic property: it follows from the δ-correlated nature of the process $\omega_j(t)$ that

$$U(t,t_0,[\alpha]) = U(t,t_1,[\alpha])\,U(t_1,t_0,[\alpha]), \quad \text{if } t \geqslant t_1 \geqslant t_0 .$$

The Liouville equation can be written n integral form

$$\rho(t) = V(t,0)\rho_0 - i\int_0^t d\tau\, V(t,\tau) L_1 \rho(\tau), \quad V(t,t_0) = \exp\left(-i\int_{t_0}^t d\tau\, L_0(\tau)\right).$$

$$L_0(t)\rho = [H_0(t),\rho], \qquad L_1\rho = [H_1,\rho]$$

The averaging over the process $\omega_i(t)$ can be fulfilled using exact relations

$$\langle V(t,\tau)\rangle_n = \exp\left(-\frac{|t-\tau|}{T_2}\sum_{j=1}^{N} S_j\right), \qquad S_j f = [I_j^z,[I_j^z,f]],$$

$$\langle V(t,t_0)\rangle_n = \langle V(t,\tau)\rangle_n \langle V(\tau,t_0)\rangle_n ,$$

where f is an arbitrary operator and $t \geqslant \tau \geqslant t_0$.

As a consequence

$$\langle V(t,\tau)L_1\rho(\tau)\rangle_n=\langle V(t,\tau)\rangle_n L_1\langle\rho(\tau)\rangle_n .$$

$$\langle\rho(t)\rangle_n=\langle V(t,0)\rangle_n\rho_0-i\int_0^t d\tau\langle V(t,\tau)\rangle_n L_1\langle\rho(\tau)\rangle_n ,$$

or, in differential form,

$$\langle\dot{\rho}\rangle_n=-(R+iL_1)\langle\rho\rangle_n , \quad R=\frac{1}{T_2}\sum_{j=1}^{N} S_j , \quad t\geqslant 0.$$

All the stationary solutions ρ_{DS} are described by the general formula

$$\rho_{DS}=F(I_z),$$

where $F(x)$ is a fairly arbitrary function, which is constrained only by the conditions that ρ_{DS} be nonnegative, Hermitian, and normalized.

It is important here, that interaction is long-ranged.

Analysis indicates, that Gibbs equilibrium can be achieved for special class of initial conditions only. Indeed, the Gibbs distribution $\rho_G=\exp(\Phi-\beta I_z)$ has special relations between fluctuations $D_n=\mathrm{Tr}((\Delta I_z)^n\rho_G)$, where $\Delta I_z=I_z-\mathrm{Tr}(I_z\rho_G)$, and they do not depend on time together with I_z. Therefore, if these relations are not fulfilled in initial state, then final state is not Gibbs one.

Conclusion.

I hope that the report will help to include the spin dynamics into field of your activity, and you will remember about spin systems during your studies in ergodic theory.

Thank you for attention!