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NONERGODIC NUCLEAR DEPOLARIZATION IN NANO-CAVITIES

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Recently, it has been observed that the effective dipolar interactions between nuclear spins of spin-carrying molecules of gas in a closed nano-cavities are independent of the spacing between all the spins. We derive exact time-dependent polarization for all spins in the spin-$1/2$ ensemble with spatially independent effective dipolar interactions. If the initial polarization is on a single (first) spin, $P_1(0) = 1$, then the exact spin dynamics of the model is shown to exhibit periodic short pulses of the polarization of the first spin, the effect being typical of systems having a large number N of spins. If $N \gg 1$, then within the period $4\pi/g$ ($2\pi/g$) for odd (even) N-spin clusters, with g standing for the spin coupling, the polarization of spin 1 switches quickly from unity to the time-independent value $1/3$ over the time interval about $(g\sqrt{N})^{-1}$. Thus, spin 1 spends almost all the time in the time-independent condition $P_1(t) = 1/3$. The period and the width of the pulses determine the volume and the form factor of the ellipsoidal cavity. The formalism is adapted to the case of time-varying nano-fluctuations of the volume $V(t)$ of cavitation nano-bubbles. If the coupling $g(V(t))$ is varied by the Gaussian-in-time random noise due to the variation of the volume $V(t)$, then the envelope of the polarization peaks goes irreversibly to $1/3$. The polarization dynamics of a single spin exhibits the Gaussian (exponential) time dependence when the correlation time of fluctuations of the nano-volume is larger (smaller) than $\langle(\delta g)^2\rangle^{-1/2}$, where $\langle(\delta g)^2\rangle$ is the variance of the $g(V(t))$ coupling. Finally, we report exact calculations of the NMR line shape for the N-spin gaseous aggregate.

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1. INTRODUCTION

The nature of ergodicity as a fundamentally important element of the consonant description of statistical mechanics is currently being discussed in the NMR context [1]. Spin dynamics is ergodic if the initial polarization prepared at a single (first) spin is spread over the system, leading, as time proceeds, to the spatially uniform distribution of the polarization, as expected on the basis of a simple physical intuition. On the other hand, nonergodic behavior that was recently observed numerically in the nuclear spin-$1/2$ $1D$ chains with the general XYZ spin Hamiltonian [2] enters such that the time-averaged polarization of the first spin turns out to be several times larger than the time average polarization of any other spin in the chain. This observation of nonergodicity has been extended to $1D$ chains and rings with the XY Hamiltonian [3], showing analytically that the time-averaged polarization of the first spin differs by the factor 1.5–2 from the time-averaged polarization of all the other spins in the chain. These considerations in $1D$ spin clusters address the problem of the nature of ergodicity for different spin Hamiltonians. Motivated by the study of nonergodic spin dynamics and because an exact solution is a lucky exception in statistical mechanics, we assume in this paper that spin interactions can be considered independent of the spacing between the spins rather than having an r^{-3} dependence.

Recently, a spin Hamiltonian with space-independent spin couplings has been applied for exploring the NMR spectra of the gas of spin-carrying molecules undergoing fast thermal motion within nonspherical cavities [4]. In that report, the authors have arrived at the space-independent effective spin couplings by motionally averaging the exact dipolar Hamiltonian over uniformly distributed spatial coordinates of the spins in nanometer-size cavities. This technique is expected to have a promising application for determining the pore

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shapes and sizes [5] by the NMR spectra.

With regard to the effective nuclear spin Hamiltonian with infinite-range couplings, it is noteworthy that this type of interactions has also been proposed in the theory of nano-electrodes [6, 7]. There, the infinite-range dipolar nuclear interactions are induced indirectly due to the fast energy transfer between the electron and nuclear spins. On the coarse-grain time scale of the fast electron spin dynamics, the slow effective nuclear spin dynamics is governed by an effective nuclear spin Hamiltonian with an infinite-range interaction. Quite apart from its importance as a physical model in the NMR experiments for the many-spin aggregate in a confined volume [4, 6, 7] and few proton molecules [8], the model with infinite-range spin interactions is of a fundamental interest in its own right because it allows treating the 3-dimensional case exactly, without any reference to a $1D$ spin ordering. It represents the quantum nonequilibrium version of the exactly solvable equilibrium spin model [9], has a mapping to the BCS pairing Hamiltonian of superconductivity [10], and has long been considered as a test for many-body problems in higher spatial dimensions, $D \gg 1$. The objective of this paper is to present the exact solution of nonergodic dynamics with an infinite-range spin Hamiltonian in the N-spin ensemble.

To our knowledge, the only result reported on this model is that of Waugh [11], who announced (without proof) that the time-averaged polarization of the first spin is exactly equal to $(N+2)/3N$ and the polarization of any other spin is exactly $2/3N$ for odd numbered, N, spin cluster. To clarify the problem of spin dynamics, the present paper reports a detailed analytic theory of the average polarization for both odd and even numbered spin clusters; it also gives the theory of spin dynamics that is entirely missing in [11]. A condensed form of this paper has been published in [12]. A brief overview of the present paper is as follows. In Sec. 2, we construct the effective nuclear spin Hamiltonian of spin-carrying molecules in a nano-cavity. Section 3 gives the formalism required to obtain the exact time-dependent polarization. This is followed by Sec. 4 that discusses three issues of the polarization dynamics that are amenable to the techniques of the Sec. 2: the nonergodicity of the polarization dynamics of a single spin in the nano-cavity, the polarization dynamics of a single spin within a fluctuating nano-bubbles, and the spectral line shape of the nuclear spin ensemble. Finally, Sec. 5 summarizes the results of the calculations and confronts the results obtained with the known analytic results for the XY Hamiltonian.

2. EFFECTIVE NUCLEAR SPIN HAMILTONIAN IN A NANO-CAVITY

The purpose of this section is to construct the effective spin Hamiltonian $\overline{H}$ that governs spin dynamics of spin-carrying molecules in a nano-size cavity on the coarse-grain temporary scale of the order 10 ps. At these space-time scales, the effective spin Hamiltonian differs from the exact dipolar Hamiltonian; in particular, the many-body spin Hamiltonian $\overline{H}$ has a high symmetry that permits the exact solution for the spectrum and, as a result, the exact derivation of the polarization dynamics of the gas within the nano-cavity. In this section, we summarize the main ideas of [4]; however, in deriving the effective spin Hamiltonian $\overline{H}$ by averaging over spin spatial coordinates, we generalize the effective spin coupling to the case of a nonperfect gas in the nano-cavity.

The starting point of the derivation of the operator $\overline{H}$ is the expression

$$\begin{aligned}\rho(t, \{\mathbf{I}_n, \mathbf{r}_n(t), \mathbf{p}_n(t)\}_{n=1}^N) = \\ = U(t)\rho(0, \{\mathbf{I}_n, \mathbf{r}_n(0), \mathbf{p}_n(0)\}_{n=1}^N)U^{-1}(t),\end{aligned} \quad (1)$$

for the density matrix with completely specified coordinates $\{\mathbf{r}_n(t)\}_{n=1}^N$ and momenta $\{\mathbf{p}_n(t)\}_{n=1}^N$ of N spin-carrying molecules. The propagator $U(t)$ is associated with the time-dependent exact dipolar Hamiltonian (in frequency units)

$$\begin{aligned}H(t) = \sum_{1\le i<j}^{N} h_{i,j}(t), \\ h_{i,j}(t) = \gamma^2\hbar P_2(\cos\theta_{ij}(t)) r_{ij}^{-3}(t)(\mathbf{I}_i\mathbf{I}_j - 3I_{iz}I_{jz}),\end{aligned} \quad (2)$$

where γ stands for the gyromagnetic ratio, $I_{n\alpha}$ $(\alpha = x, y, z)$ specify the spin-1/2 operators, and $\theta_{ij}(t)$ is the instant polar angle between the vector $r_{ij}(t)$ from $r_i(t)$ to $r_j(t)$ and the external magnetic field B.

A cornerstone fact for the construction of the effective spin Hamiltonian is the essential difference between the time scale of the relaxation in the phase space $r^N - p^N$ and the time scale of the spin dynamics under the Hamiltonian in Eq. (2). Actually, for the hydrogen gas at room temperature and atmospheric pressure, the following estimations hold. The average concentration

$$\bar{n} \approx 2.7 \cdot 10^{19}\ \text{molecules/cm}^3,$$

the mean free path

$$\lambda = (\bar{n}\pi a^2)^{-1} \approx 10^{-4}\ \text{cm}$$

for the radius of a molecule $a \approx 10^{-8}$ cm and the thermal velocity $\bar{v} \approx 10^5$ cm/s. Then, a simple order-of-magnitude calculation leads us to expect that for the gas in the cavity of the size $\ell \approx 10$ nm, the Knudsen diffusion coefficient is

$$\mathcal{D} \approx \bar{v}\ell \approx 10^{-1}\ \mathrm{cm}^2/\mathrm{s},$$

the characteristic time scale of the spatial relaxation of the gas (due to the diffusive reflection from the wall of the pore) to the spatially homogeneous distribution is

$$t_{dif} \approx \ell^2/\mathcal{D} \approx 10^{-11}\ \mathrm{s},$$

and the characteristic time scale of the velocity relaxation towards the Maxwell distribution is

$$t_v \approx \ell/\bar{v} \approx 10^{-11}\ \mathrm{s}.$$

These time scales t_v and t_{dif} are well separated from the NMR time scale $t_{nmr} = 10^{-4}$–10^{-3} s associated with the dipolar interaction in Eq. (2). The smallness of the parameter

$$\varepsilon = \frac{t_{rel}}{t_{nmr}} = 10^{-7} \ll 1, \qquad (3)$$

where

$$t_{rel} = \max(t_v, t_{dif}),$$

allows determining the average nuclear spin Hamiltonian governing the behavior of the nuclear spins over a coarse-grain time intervals Δt obeying

$$t_{rel} \ll \Delta t \ll t_{nmr}. \qquad (4)$$

Averaging the exact Hamiltonian over time Δt is performed to the zeroth order in the perturbation expansion in powers of the parameter ε, yielding the average (or effective) Hamiltonian [13]

$$\overline{h_{i,j}} = \frac{1}{\Delta t}\int\limits_0^{\Delta t} h_{i,j}(r_i(t'), r_j(t'))\, dt', \qquad (5)$$

with the corrections being of the order $\mathcal{O}(\varepsilon^1)$.

The decisive point of the following treatment is the replacement of time integration in Eq. (5) with integration over spatial coordinates within the confined region. Equating the temporal averaging with the spatial averaging makes sense under the ergodic hypotheses [14],

$$\frac{\delta t(dr^N, dp^N)}{t} = Z^{-1}\exp\left(-\frac{E}{kT}\right) dr^N dp^N, \qquad (6)$$

where the notation implies that a representative point living in the whole phase space $r^N - p^N$, while moving over the time t, $t_{rel} \ll t \ll t_{nmr}$, spends only a fraction

$$Z^{-1}\exp\left(-\frac{E}{kT}\right) dr^N dp^N$$

of the whole time t within the volume $dr^N dp^N$, with E being the total energy. Relation (6) incorporates the Gibbs stochastic level of description into the dynamical treatment of molecular collisions. The phase space degrees of freedom are assumed to relax to their equilibrium distribution at a given temperature T.

We introduce the equilibrium pair distribution function for molecules 1 and 2,

$$D_2(r_1, r_2) = \\ = \frac{\int\limits_V d^3r_3 \ldots \int\limits_V d^3r_N \exp\left(-\frac{U(r^N)}{kT}\right)}{\int\limits_V d^3r_1 \ldots \int\limits_V d^3r_N \exp\left(-\frac{U(r^N)}{kT}\right)}, \qquad (7)$$

where $U(r^N)$ denotes inter-molecular electrostatic interactions (we recall that $\|U\|/\|H\| \approx 10^7$ [15]). Then, taking ergodicity (6) for granted, the evolution of the spin degrees of freedom on the coarse-grain time scale Δt in Eq. (4) is governed by the static (time-independent) effective Hamiltonian

$$\overline{H} = \sum_{1\le i<j}^{N} \overline{h_{i,j}}, \quad \overline{h_{i,j}} = g\sum_{1\le i<j}^{N} (\mathbf{I}_i\mathbf{I}_j - 3I_{iz}I_{jz}) \qquad (8)$$

with spacing-independent pair couplings g for any pair of spins i and j,

$$g = \gamma^2\hbar \int\limits_V\int\limits_V d^3r_i\, d^3r_j D_2(r_i, r_j) P_2(\cos\theta_{ij}) r_{ij}^{-3}. \qquad (9)$$

The effective operator $\overline{H}$ involves only the (slow) spin operators, whereas the (fast) spatial coordinates of the nucleus (labeled by indices i and j) are integrated out. On the coarse-grain scale Δt, any nuclear spin «feels» the field that is independent of the spatial coordinates of all the other spins flying within the nano-cavity but depends on the quantum states of those spins.

The effective spin coupling g encodes the information about the shape and size of the nano-cavity. The primary objective of the preceding discussion is to present the expression for the coupling g in Eq. (9) for an ellipsoidal nano-cavity.

For perfect hard-sphere molecules within the nano-cavity, the pair distribution function is given by

$$D_2(r_i, r_j) = V^{-2}$$

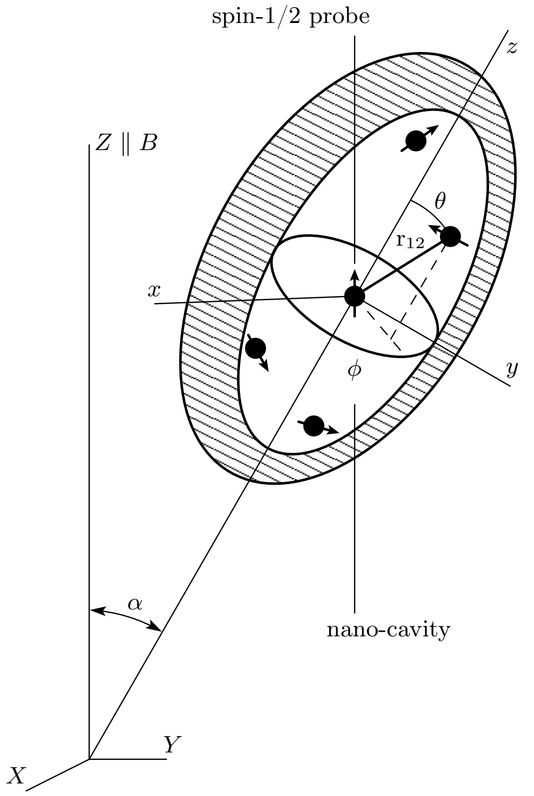

Fig. 1. Schematic representation of a nano-cavity partially occupied with spin-carrying molecules undergoing rapid thermal motion

for the molecules i and j in the cavity. Hence, the averaging in Eq. (9) gives

$$g = \frac{\gamma^2 \hbar F}{V},$$
$$F = \frac{1}{V} \times \tag{10}$$
$$\times \int\limits_V \int\limits_V d^3r_1\, d^3r_2 \theta(|r_1 - r_2| - \sigma) P_2(\cos\theta_{12}) r_{12}^{-3},$$

where the function $\theta(x)$ $(= 1(0)$ for $x > 0(< 0))$ excludes the intersection of two hard spheres having the diameter σ. In this paper, we use the remarkable fact [4] that the volume V of the nano-cavity enters the expression for the effective coupling g in Eq. (10), which itself enters the polarization (defined below in Sec. 3), giving rise to the dependence of the polarization on the volume of the nano-cavity by no means as trivial as merely proportional to the volume.

The transformation of the coordinates r_1 and r_2 to the relative coordinate $r_{12} = r_1 - r_2$ and the coordinate of the center of gravity $r = (r_1 + r_2)/2$, see Fig. 1, reduces the form factor F in Eq. (10) to the form

$$F = \int\limits_V \theta(|r_1 - r_2| - \sigma) d^3r_{12}\, P_2(\cos\theta_{12}) r_{12}^{-3}. \tag{11}$$

It is convenient to assume that the initial point of the vector $r_{12} = r_1 - r_2$ starts at the origin of the frame of reference xyz connected with the ellipsoid, see Fig. 1. Straightforward integration over r_{12} in Eq. (11), see, e.g., [16], yields the sought form factor

$$F = I\pi P_2(\cos\alpha),$$
$$I = \begin{cases} \dfrac{2}{3} + 2\left(\dfrac{1}{\varepsilon^2} - 1\right)\left(1 - \dfrac{1}{\varepsilon}\mathrm{Arcth}\varepsilon\right), \\ \qquad\qquad a \ge b \\ \dfrac{2}{3} - 2\left(\dfrac{1}{|\varepsilon|^2} + 1\right)\left(1 - \dfrac{1}{|\varepsilon|}\mathrm{Arctg}|\varepsilon|\right), \\ \qquad\qquad a \le b. \end{cases} \tag{12}$$

Here, ε is the excentricitet of the ellipsoid with the principal axes $a, b = c$. Equation (12) shows that the dependence of the form factor on the angle α between the z axis of the reference frame of the ellipsoid and the Z axis of the laboratory reference frame is factored out. For $a \gg b$, we have $\varepsilon = 1$ and $I = 2/3$. For $a = b$, we have $\varepsilon \to 0$ and Eq. (12) gives $I = 0$. For $a \ll b$, $|\varepsilon| \to \infty$ and $I = 2/3 - 2 = -4/3$. These limiting cases confirm the result reported in [4].

3. POLARIZATION DYNAMICS

We consider the spin Hamiltonian $\overline{H}$ of an N-spin cluster in a uniform external magnetic field B parallel to the Z axis of a fixed reference frame XYZ and the spatially independent spin couplings g in Eq. (10),

$$\overline{H} = \omega \sum_{n=1}^{N} I_{nz} +$$
$$+ \frac{g}{2} \sum_{m \ne n}^{N} \{\zeta I_{mz} I_{nz} - I_{mx} I_{nx} - I_{my} I_{ny}\}, \tag{13}$$

where $\omega = \gamma B$ denotes the Zeeman frequency and ζ is an arbitrary factor.

The standard way of approaching the N-spin aggregate is to find the polarization at the n-th spin at a time instant t given the initial polarization at the 1-st spin,

$$P_n(t) = \frac{\mathrm{tr}\,\{\exp(i\overline{H}t) I_{1z} \exp(-i\overline{H}t) I_{nz}\}}{\mathrm{tr}\,\{I_{1z}^2\}}. \tag{14}$$

The Hamiltonian in Eq. (13) can be rewritten as (up to the constant $gN(1 - \zeta/2)/4$)

$$\overline{H} = \omega I_z + \frac{g}{2}(\zeta + 1) I_z^2 - \frac{g}{2} I^2, \tag{15}$$

where

$$I = \sum\nolimits_{n=1}^{N} I_n$$

is the total spin and

$$I_z = \sum_{n=1}^{N} I_{nz}$$

is its projection on the z axis. The polarization $P_n(t)$ in Eq. (14) is unchanged if we modify the Hamiltonian $\overline{H}$ in Eq. (15) to the effective one

$$H' = -\frac{g}{2} I^2. \tag{16}$$

In addition, the equivalence of polarizations $P_n(t)$ of all spins except the first, as well as time conservation of the total polarization $\sum_{n=1}^{N} P_n(t)$ allow us to focus on the first spin only,

$$P_1(\tau) = \frac{\operatorname{tr}\left\{\exp(i\tau I^2) I_{1z} \exp(-i\tau I^2) I_{1z}\right\}}{\operatorname{tr}\left\{I_{1z}^2\right\}}, \tag{17}$$

where the dimensionless time scale is defined as $\tau = gt/2$.

A powerful tool for investigating the problem in Eq. (17) is the theory of coupling of angular momenta [17, 18]. To describe it, we consider the total spin cluster composed of two subsystems A and B. The subsystem A has only the spin $I_1 = I_A$ and the remaining fragment B of the spin cluster has the spin I_B, with the total spin $I = I_A + I_B$. The states of the two subsystems A and B are coupled together within the state of the whole system $A \otimes B$ through the Clebsch–Gordan (CG) coefficients

$$|I_A, I_B, I, m\rangle = \sum_{\substack{m_A = \pm 1/2 \\ m_B = m - m_A}} C^{I,m}_{I_A, m_A; I_B, m_B} |I_A m_A\rangle |I_B m_B\rangle, \tag{18}$$

where $I_A = 1/2$ and $m_A = \pm 1/2$ are the spin and its magnetic quantum numbers for the 1-st spin respectively, and I_B and $m_B = m - m_A$ are the spin and its magnetic quantum numbers of the fragment B. For $I_B = 0$, only $I = 1/2$ and $m = \pm 1/2$ are allowed. For $I_B \geq 1/2$, the allowed I and m are $I = I_B \pm 1/2$, $-I \leq m \leq I$. The CG coefficients are given by (see, e.g., [19])

$$\begin{aligned} C^{I_B+1/2,m}_{1/2,1/2;I_B,m-1/2} &= C^{I_B-1/2,m}_{1/2,-1/2;I_B,m+1/2} = \left(\frac{I_B + 1/2 + m}{2I_B + 1}\right)^{1/2}, \\ C^{I_B+1/2,m}_{1/2,-1/2;I_B,m+1/2} &= -C^{I_B-1/2,m}_{1/2,1/2;I_B,m-1/2} = \left(\frac{I_B + 1/2 - m}{2I_B + 1}\right)^{1/2}. \end{aligned} \tag{19}$$

The two pairs of independent variables (I_B, m_B) and $(I_A = 1/2,\ m_A = \pm 1/2)$ are used for determining the trace in Eq. (17) for the whole N-spin system $A \otimes B$,

$$\operatorname{tr}\{\dots\} = \sum_{I_B = I_B^{min}}^{N_B/2} w(I_B) \times \sum_{I=|I_B - 1/2|}^{I_B + 1/2} \sum_{m=-I}^{I} \langle I_A, I_B, I, m| \dots |I_A, I_B, I, m\rangle, \tag{20}$$

where $N_B = N - 1$ is the number of spins in the fragment B; the minimal value of I_B is $I_B^{min} = 0$ for even N_B and $I_B^{min} = 1/2$ for odd N_B. The factor

$$w(I_B) = \frac{2I_B + 1}{N_B + 1} \binom{N_B + 1}{\frac{1}{2} N_B + I_B + 1} \tag{21}$$

is the number of ways of grouping N_B individual spins 1/2 into the total spin I_B. The factor $w(I_B)$ satisfies the relation [17, 18, 20]

$$\sum_{I_B \geq |m_B|}^{N_B/2} w(I_B) = \binom{N_B}{\frac{1}{2} N_B + m_B}. \tag{22}$$

The right-hand side of Eq. (22) is the number of states for each allowed eigenvalue m_B of the fragment B.

To deal with the diagonal evolution matrices in Eq. (17), we introduce additional bases of the bra, $\langle I_A, I_B, I', m'|$, and ket, $|I_A, I_B, I', m'\rangle$, vectors in the Hilbert space $\mathcal{H}(I_A) \otimes \mathcal{H}(I_B)$ for fixed values $I_A = 1/2$ and I_B; we then use the completeness of the $2(2I_B + 1)$ orthonormal basis vectors belonging to the space $\mathcal{H}(I_A) \otimes \mathcal{H}(I_B)$,

$$1_{\mathcal{H}(I_A) \otimes \mathcal{H}(I_B)} = \sum_{I' = |I_B - 1/2|}^{I_B + 1/2} \sum_{m'=-I}^{I} |I_A, I_B, I', m'\rangle \langle I_A, I_B, I', m'|, \tag{23}$$

and, finally, insert the representation of unity in Eq. (23) in front of the rightmost operator I_{1z} in Eq. (17), whose matrix elements are given by

$$\langle I_A, I_B, I', m'| I_{1z} |I_A, I_B, I, m\rangle = \delta_{m,m'} \times \sum_{m_A = \pm 1/2} m_A C^{I',m'}_{1/2, m_A; I_B, m' - m_A} \times C^{I,m}_{1/2, m_A; I_B, m - m_A}. \tag{24}$$

With these algebraic steps, we immediately obtain the polarization $P_1(\tau)$ in terms of the CG coefficients as

$$\begin{aligned}P_1(\tau) = 2^{-(N_B-1)} \sum_{I_B=I_B^{min}}^{N_B/2} w(I_B) \sum_{\substack{|I_B-1/2|\le I\le I_B+1/2\\ |I_B-1/2|\le I'\le I_B+1/2}} \; \sum_{\substack{-I\le m\le I\\ -I'\le m'\le I'}} \delta_{m,m'} \exp\left(i\tau\{I(I+1)-I'(I'+1)\}\right) \times \\ \times \left(\sum_{m_A=\pm 1/2} m_A C^{I',m'}_{1/2,m_A;I_B,m'-m_A} C^{I,m}_{1/2,m_A;I_B,m-m_A}\right)^2 .\end{aligned} \tag{25}$$

For the term $I_B = 0$, only a single pair ($I = 1/2$, $I' = 1/2$) is allowed in the sum in Eq. (25), and for $I_B \ge 1/2$, the four pairs of (I, I') must be distinguished in this sum depending on the sign (+) or (−) in the expressions

$$(I, I') = \left(I = I_B \pm \frac{1}{2},\; I' = I_B \pm \frac{1}{2}\right). \tag{26}$$

Armed with the polarization $P_1(\tau)$ in Eq. (25), we now decompose it into the time-independent part $\overline{P_1}$ and the oscillating part $P_1^{osc}(\tau)$,

$$P_1(\tau) = \overline{P_1} + P_1^{osc}(\tau). \tag{27}$$

The time-independent contribution $\overline{P_1}$ to the function $P_1(\tau)$ is provided by the quantum numbers m, m' belonging to the states $I = I' = I_B \pm 1/2$ if $I_B \ge 1/2$, and by the quantum numbers m, m' belonging to the states $I = I' = 1/2$ if $I_B = 0$,

$$\overline{P_1} = 2^{-(N_B-1)} \sum_{I_B=I_B^{min}}^{N_B/2} w(I_B) \sum_{I=|I_B-1/2|}^{I_B+1/2} \sum_{m=-I}^{I} \left(\sum_{m_A=\pm 1/2} m_A \left(C^{I,m}_{1/2,m_A;I_B,m-m_A}\right)^2\right)^2 . \tag{28}$$

Our aim is now to sum over the indices m and I for a fixed value of I_B in Eq. (28). For this, we start with the state $I_B = 0$ that arises for even N_B (see the comments to Eq. (20)). For $I_B = 0$, only $I = 1/2$ is allowed, and the partial polarization $\overline{P_1}(I_B)$ in Eq. (28) is given by

$$\overline{P_1}(I_B = 0) = 2^{-(N_B-1)} w(0) \sum_{m=-1/2}^{1/2} m^2. \tag{29}$$

Next, we consider the contribution to $\overline{P_1}$ in Eq. (28) from the spin $I_B \ge 1/2$. In this situation, $I = I_B \pm 1/2$ are allowed and invoking the CG coefficients in Eq. (19), the contributions $\overline{P_1}(I_B)$ to $\overline{P_1}$ can be conveniently written as

$$\overline{P_1}(I_B) = 2^{-N_B} w(I_B) \sum_{\mu=-I_B}^{I_B} \frac{2\mu+1}{2I_B+1}. \tag{30}$$

Combining $\overline{P_1}(I_B = 0)$ in Eq. (29) and $\overline{P_1}(I_B)$ in Eq. (30) results in

$$\overline{P_1} = 2^{-N_B} \sum_{I_B=I_B^{min}}^{N_B/2} w(I_B) \sum_{\mu=-I_B}^{I_B} \frac{2\mu+1}{2I_B+1}. \tag{31}$$

The sum over μ in Eq. (31) easily yields

$$\sum_{\mu=-I_B}^{I_B} (2\mu+1)^2 = (2I_B+1)\left(1+\frac{4}{3}I_B(I_B+1)\right), \tag{32}$$

and substituting $w(I_B)$ from Eq. (21), we arrive at the sought result

$$\begin{aligned}\overline{P_1} = \frac{2^{-N_B}}{N_B+1} \sum_{I_B=I_B^{min}}^{N_B/2} \binom{N_B+1}{\frac{1}{2}N_B + I_B + 1} \times \\ \times \left(1 + \frac{4}{3} I_B(I_B+1)\right).\end{aligned} \tag{33}$$

The remaining sum over I_B in Eq. (33) depends on whether N_B is an even or odd number. If N_B is even, then $I_B^{min} = 0$ and straightforward summation over I_B in Eq. (33), with the known sums involving the binomial coefficients

$$\begin{aligned}\sum_{I_B=0}^{N_B/2} \binom{N_B+1}{\frac{1}{2}N_B + I_B + 1} = 2^{N_B}, \\ \sum_{I_B=0}^{N_B/2} I_B(I_B+1)\binom{N_B+1}{\frac{1}{2}N_B + I_B + 1} = N_B 2^{N_B-2},\end{aligned} \tag{34}$$

yields the polarization

$$\overline{P_1} = \frac{N+2}{3N} \tag{35}$$

for an odd $N = N_B + 1$ spin cluster [11]. If N_B is odd, then $I_B^{min} = 1/2$ and some simple algebra gives the polarization

$$\overline{P_1} = \frac{N+2-2^{1-N}\binom{N}{N/2}}{3N} \tag{36}$$

for an even $N = N_B + 1$ spin cluster.

When $N \gg 1$, the polarization $\overline{P_1}$ in Eq. (36) behaves as

$$\frac{N+2-2(\pi N/2)^{-1/2}}{3N}.$$

Equations (35) and (36) give the sought time-independent contributions $\overline{P_1}$ to the total polarization $P_1(\tau)$ in Eq. (27) for odd and even numbered spin clusters, respectively.

It remains to find the time-dependent contribution $P_1^{osc}(\tau)$ to the total polarization $P_1(\tau)$ in Eq. (25). Among the four pairs (I, I') in Eq. (26), only the pairs (I, I') with $I \neq I'$ contribute to the time-dependent part of the function $P_1(\tau)$ in Eq. (25). This occurs for $I_B \geq 1/2$ only, because otherwise, i.e., for $I_B = 0$, the allowed values $I = I' = 1/2$ are already encountered in the time-independent polarization $\overline{P_1}$. Thus, among the four pairs (I, I') in Eq. (26) only the two pairs $(I = I_B + 1/2, I' = I_B - 1/2)$ and $(I = I_B - 1/2, I' = I_B + 1/2)$ are allowed and provide complex conjugate contributions to the real-valued function $P_1^{osc}(\tau)$. It suffices to deal with the first pair, $(I = I_B + 1/2, I' = I_B - 1/2)$. The polarization becomes

$$P_1^{osc}(\tau) = 2^{-(N_B-1)} \sum_{I_B=1/2}^{N_B/2} w(I_B) \sum_{m=-(I_B+1/2)}^{I_B+1/2} \sum_{m'=-(I_B-1/2)}^{I_B-1/2} \delta_{m,m'} 2\cos\left(2\tau(I_B+1/2)\right) \times \\ \times \left(\sum_{m_A=\pm 1/2} m_A C^{I_B-1/2,m'}_{1/2,m_A;I_B,m'-m_A} C^{I_B+1/2,m}_{1/2,m_A;I_B,m-m_A} \right)^2 . \tag{37}$$

To complete the derivation of the function $P_1^{osc}(\tau)$, we use the expression for the factor $w(I_B)$ in Eq. (21), the CG coefficients in Eq. (19), and sum over m and m' in Eq. (37) for a fixed value of I_B. This gives

$$P_1^{osc}(\tau) = \frac{2^{-N_B+3}}{3(N_B+1)} \sum_{I_B=1/2}^{N_B/2} \binom{N_B+1}{\frac{1}{2}N_B + I_B + 1} \times \\ \times I_B(I_B+1)\cos(2\tau(I_B+1/2)). \tag{38}$$

Finally, by gathering the expressions for $\overline{P_1}$ in Eqs. (35) and (36) and the expression for $P_1^{osc}(\tau)$ in Eq. (38), we go over (with the substitution $k = I_B - 1/2$ for even N and $k = I_B$ for odd N) to the total polarization at the first spin,

$$P_1(\tau) = \frac{N+2-2^{1-N}\binom{N}{N/2}}{3N} + \frac{2^{4-N}}{3N} \times \\ \times \sum_{k=0}^{N/2-1} A_k(N)\cos(\tau(N-2k)) \tag{39}$$

for an even N-cluster, and

$$P_1(\tau) = \frac{N+2}{3N} + \frac{2^{4-N}}{3N} \times \\ \times \sum_{k=0}^{(N-1)/2} A_k(N)\cos(\tau(N-2k)) \tag{40}$$

for an odd N-cluster, with the coefficient

$$A_k(N) = \left(\frac{N+1}{2} - k\right)\left(\frac{N-1}{2} - k\right)\binom{N}{k}$$

arising in both cases. Formulas (39) and (40) are the central result of the paper. They are used to describe a variety of systems in the next section.

4. DISCUSSION

4.1. Nonergodic spin dynamics

As Eq. (40) states, for large odd-N clusters, the time-averaged polarization $\langle P_1(\tau)\rangle$ of spin 1 tends to 1/3, while the time-averaged polarization $2/3N$ of any other spin tends to 0, i.e., polarization of spin 1 does not spread uniformly over an N-spin cluster. We call this behavior the nonergodic spin dynamics, to confront it with the ergodic spin dynamics providing the $1/N$ polarization for all spins in an N-spin ensemble. Figure $2a$ shows the behavior of the polarization $P_1(\tau)$ for a series of odd-N clusters. The principle features of the periodic pulses of the polarization are determined by two factors: first, time reversibility of the dynamics affects the exact reentrance of the polarization to the prepared value $P_1(0) = 1$ after each period $4\pi/g$, and, second, gives rise to the time interval with the time-independent polarization of spin 1, see the Appendix for details. For large-N clusters, the total period $4\pi/g$ can be partitioned into the switching time

$$t^{sw} = 4\pi \frac{\mathcal{O}(1)}{g\sqrt{N}}$$

and the stopping time

$$t^{st} = \frac{4\pi}{g}\left(1 - \frac{\mathcal{O}(1)}{\sqrt{N}}\right);$$

we recall that $\tau = gt/2$. As shown in the Appendix, the polarization $P_1(\tau)$ is peaked at the instants $t = 0, 2\pi/g, 4\pi/g, \ldots$. The profile of the function $P_1(\tau)$, e.g., around $\tau = 0$, is

$$P_1(\tau) = \frac{1}{3} + \frac{2}{3}\left(1 - \tau^2 N\right)\exp\left(-\frac{\tau^2 N}{2}\right). \qquad (41)$$

The function $P_1(\tau)$ has the same profile around all the instants $\tau = m\pi$, for all integer m. The interval between the successive peaks and their width are

$$T = \frac{2\pi}{g}, \quad \Delta_T = 4\pi\frac{\mathcal{O}(1)}{g\sqrt{N}}, \qquad (42)$$

respectively. In other words, for large-N clusters, the polarization of spin 1 stays at the fixed value $\overline{P_1} = 1/3$ almost all the time. The oscillating part of $P_1(\tau)$ is an odd function of time with respect to the instants $\tau = \pi/2, 3\pi/2, \ldots$, as is apparent from Eq. (40).

Figure $2b$ shows the profiles of the polarization for N-spin clusters with even N. For large even values of N, the polarization at spin 1 stays fixed over the long time interval

$$t^{st} = \frac{2\pi}{g}\left(1 - \frac{\mathcal{O}(1)}{\sqrt{N}}\right)$$

within each period $2\pi/g$. Unlike odd-N clusters, the profiles of $P_1(\tau)$ for even-N clusters are even functions of time with respect to time instants $\tau = \pi/2, 3\pi/2, \ldots$.

Using the experimental values of the time interval T and the width of the pulses Δ_T in Eq. (42) together with the expressions for the coupling g in Eqs. (10) and (12), we find that the volume and form factor are given by

$$\begin{gathered} V = \frac{4}{c}\left(\frac{T}{\Delta_T}\right)^2, \\ F\left(\frac{a}{b}\right) P_2(\cos\alpha) = \frac{8}{c}\,\frac{T}{\gamma^2\hbar\Delta_T^2}, \end{gathered} \qquad (43)$$

where $c = N/V$ denotes the concentration of the molecules carrying spin 1/2 and the angle α is assumed to be known.

4.2. Polarization dynamics in fluctuating nano-bubbles

Equations (39) and (40) can be adapted to account for the time dependence of the volume of the nano-cavity, thereby providing a means to explore NMR imaging of cavitation bubbles in water [21], blood [22], etc., along with the conventional high-speed photography. Dynamics of the surface of a typical bubbling behavior occurs at a millisecond time scale [21], i.e., at the same time scale that is relevant for the nuclear spin dynamics. It is therefore legitimate to ask how the dynamics of a nano-size volume affects the nuclear spin dynamics. Our intention in this section is to show that fluctuations of the nano-volume (governed either by external inputs or by inherently thermal noise) drive the polarization to the nonergodic value 1/3 irreversibly, and therefore time-periodic pulsating of the polarization breaks down as time proceeds.

The formulation in Sec. 3 is easily extended to the case of a time-varying volume V because the coupling $g(V(t))$ enters Hamiltonian (13) as a common factor in front of the operator part. The functional form of the polarization $P_1^{osc}(\tau)$ in Eq. (38), which has been derived for time-independent coupling g, is generalized to the case of a function $g(t)$ provided that the time $\tau = gt/2$ in Eq. (38) is replaced with a new time,

$$\tau = \frac{1}{2}gt \to \frac{1}{2}\int_0^t g(t')dt'. \qquad (44)$$

We are interested in transformation (44),

$$g(t) = \langle g\rangle + \delta g(t), \qquad (45)$$

where $\delta g(t)$ is the Gaussian random noise characterized by the first two moments

$$\begin{gathered} \langle \delta g(t)\rangle = 0, \\ \langle \delta g(t_1)\delta g(t_2)\rangle = \langle(\delta g)^2\rangle\gamma(|t_1 - t_2|), \end{gathered} \qquad (46)$$

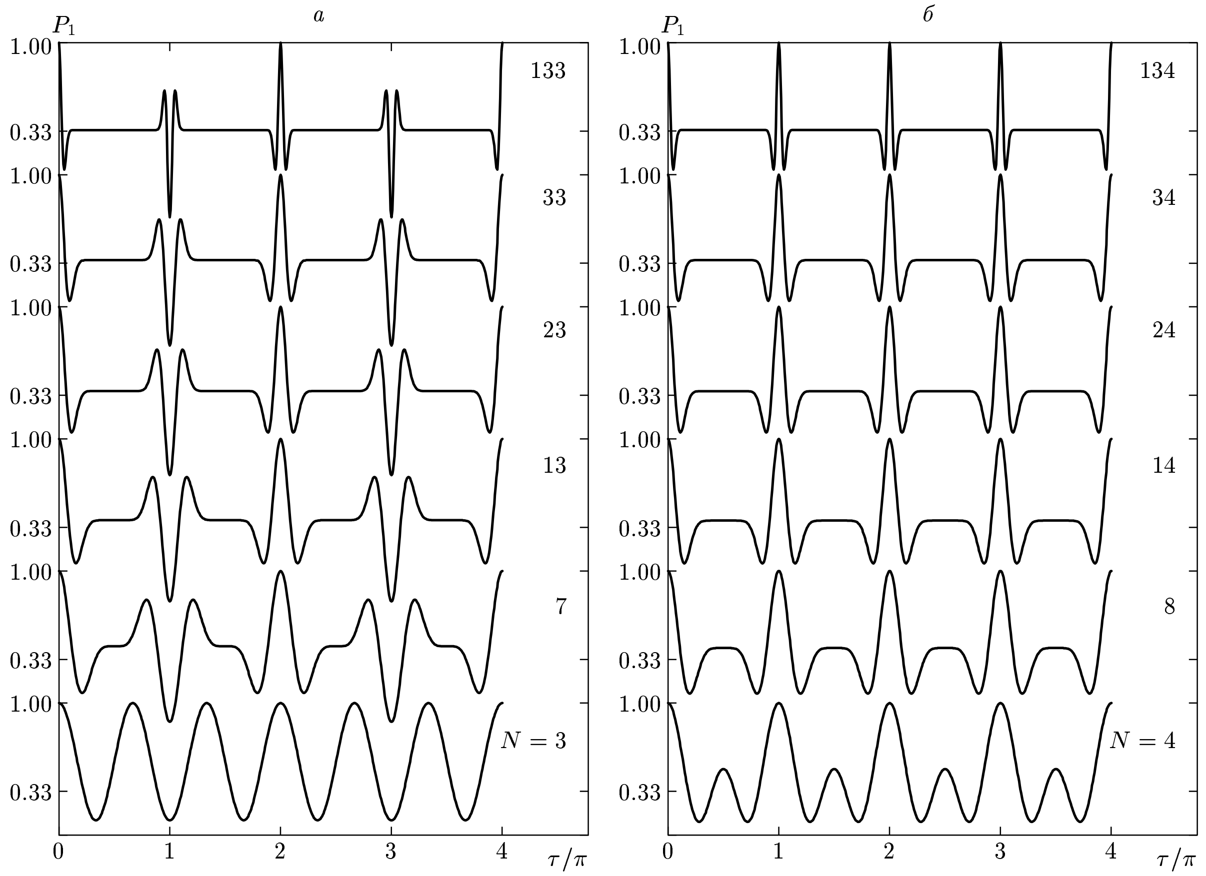

Fig. 2. a — Polarization $P_1(\tau)$ in Eq. (40) of the first spin is varied with the dimensionless time $\tau = gt/2$ for the series of an odd total number N of spins. b — Polarization $P_1(\tau)$ in Eq. (39) for the series of even N

where $\langle(\delta g)^2\rangle$ is the variance and $\gamma(t)$ denotes the correlation function, for example, $\gamma(t) = \exp(-t/t_c)$, with t_c being the correlation time. In accordance with the comment before Eq. (44), we replace the factor

$$\cos\left(2\tau(I_B + 1/2)\right)$$

in Eq. (38) with

$$\cos\left[(I_B + 1/2)\left(\langle g\rangle t + \int_0^t \delta g(t')\,dt'\right)\right].$$

Gaussian averaging of this factor over the random function $\delta g(t)$ is performed as (see, e.g., [15])

$$\left\langle \exp\left(i(I_B + 1/2)\int_0^t \delta g(t')dt'\right)\right\rangle_{\delta g} = \\ = \exp\Big(-(I_B + 1/2)^2\langle(\delta g)^2\rangle T^2\Big), \quad (47)$$

with

$$T^2 = \int_0^t (t - t')\,\gamma(t')\,dt'. \quad (48)$$

We first confine our attention to the polarization for even N, with $N \gg 1$, and then close the section with the final result for odd N, $N \gg 1$. We write the polarization in Eq. (38) with averaging (47) as

$$P_1(t) = \overline{P_1} + \frac{2^{-N_B+3}}{3(N_B + 1)} \times \\ \times \sum_{I_B=1/2}^{N_B/2} \binom{N_B + 1}{\frac{1}{2}N_B + I_B + 1} I_B(I_B + 1)\Phi(t), \quad (49)$$
$$\Phi(t) = \exp\left(-(I_B + 1/2)^2\langle(\delta g)^2\rangle T^2\right) \times \\ \times \cos\left(\langle g\rangle t(I_B + 1/2)\right).$$

The exponent in Eq. (49) tell us that the successive peaks of the time-dependent part of $P_1(t)$ reduce to

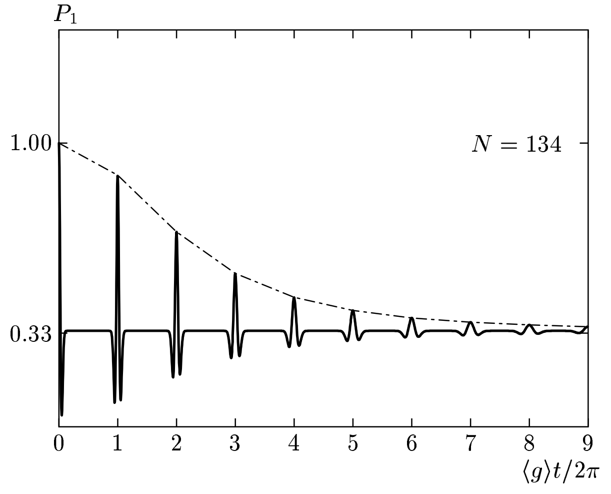

Fig. 3. Polarization dynamics of a single spin, $P_1(t)$, within the $N = 134$ spin aggregate when the volume of the nano-cavity fluctuates providing the relative variance of the g coupling equal to $\langle(\delta g)^2\rangle/\langle g\rangle^2 = 10^{-4}$, see Eqs. (51) and (52)

zero as $t \to \infty$, and therefore only the time-independent part of $P_1(t)$, i.e., $\overline{P_1} = 1/3$ in Eq. (33), survives as $t \to \infty$ after the Gaussian averaging over the function $\delta g(t)$. The integral over t' in the constant T^2 in Eq. (48) can be evaluated in the two asymptotic cases, for the large and the small correlation time [15],

$$T^2 = \begin{cases} t^2/2 & \text{if} \quad t_c^2\,\langle(\delta g)^2\rangle \gg 1, \\ t_c t & \text{if} \quad t_c^2\,\langle(\delta g)^2\rangle \ll 1. \end{cases} \tag{50}$$

To find the function $P_1(t)$ in Eq. (49) for $N \gg 1$, we can replace the sum in Eq. (49) with the Gaussian averaging, as in Eq. (A.3) in the Appendix, which gives

$$P_1(t) = \frac{1}{3} + \frac{16}{3N^{3/2}\sqrt{\pi/2}} \times \\ \times \sum_{n=1}^{N/2} \cos\left(\langle g\rangle tn\right)\left(n^2 - \frac{1}{4}\right)\exp(-an^2), \tag{51}$$

where

$$a = \frac{2}{N} + \langle(\delta g)^2\rangle T^2. \tag{52}$$

Figure 3 shows the polarization dynamics of a single spin within the $N = 134$ spin aggregate for

$$\frac{\langle(\delta g)^2\rangle}{\langle g\rangle^2} = 10^{-4}.$$

Based on the formulas in the Appendix, we simplify the sum over n in Eq. (51) via the Poisson resummation formula. Defining the partial sums entering Eq. (51) by

$$S_1(t) = \sum_{n=1}^{N/2} \cos\left(\langle g\rangle tn\right)\exp(-an^2) = \\ = -\frac{1}{2} + \frac{1}{2}\sqrt{\frac{\pi}{a}}\sum_{q=-\infty}^{\infty} \exp\left(-\pi^2\left(q + \frac{\langle g\rangle t}{2\pi}\right)^2/a\right), \tag{53}$$

and

$$S_2(t) = \sum_{n=1}^{N/2} \cos\left(\langle g\rangle tn\right) n^2 e^{-an^2} = -\frac{\partial S_1(t)}{\partial a} = \\ = \frac{\sqrt{\pi}}{4a^{3/2}}\sum_{q=-\infty}^{\infty}\left(1 - \frac{2\pi^2}{a}\left(q + \frac{\langle g\rangle t}{2\pi}\right)^2\right) \times \\ \times \exp\left(-\frac{\pi^2}{a}\left(q + \frac{\langle g\rangle t}{2\pi}\right)^2\right), \tag{54}$$

we obtain

$$P_1(t) = \frac{1}{3} + \frac{16}{3N^{3/2}\sqrt{\pi/2}}\left(S_2(t) - \frac{1}{4}S_1(t)\right). \tag{55}$$

To find the envelope of the successive peaks of the function $P_1(t)$ in Eq. (55), we substitute the time $t = 2\pi m/\langle g\rangle$ in Eqs. (53)–(55), with m running over integer numbers. This gives the polarization at the discrete values m,

$$S_1(m) = \sum_{n=1}^{N/2} \exp(-an^2) = \\ = -\frac{1}{2} + \frac{1}{2}\sqrt{\frac{\pi}{a}}\sum_{k=-\infty}^{\infty}\exp\left(-\frac{\pi^2 k^2}{a}\right), \tag{56}$$

$$S_2(m) = \sum_{n=1}^{N/2} n^2\exp(-an^2) = \\ = \frac{\sqrt{\pi}}{4a^{3/2}}\sum_{k=-\infty}^{\infty}\left(1 - \frac{2}{a}\pi^2 k^2\right)\exp\left(-\frac{\pi^2 k^2}{a}\right). \tag{57}$$

The functions $S_1(m)$ and $S_2(m)$ inherit their dependence on the «time» m through the constant a in Eqs. (52) and (50),

$$a = \\ = \begin{cases} \dfrac{2}{N} + 2\pi^2 m^2 \dfrac{\langle(\delta g)^2\rangle}{\langle g\rangle^2} & \text{if} \quad t_c^2\langle(\delta g)^2\rangle \gg 1, \\ \dfrac{2}{N} + 2\pi m t_c \dfrac{\langle(\delta g)^2\rangle}{\langle g\rangle} & \text{if} \quad t_c^2\langle(\delta g)^2\rangle \ll 1, \end{cases} \tag{58}$$

where we substitute $t = 2\pi m/\langle g\rangle$ in Eqs. (52) and (50). For $N \gg 1$ and $m \gg 1$, we drop the summand $2/N$ in Eq. (58) assuming that $a \gg 1$,

$$a \approx \begin{cases} 2\pi^2 m^2 \dfrac{\langle(\delta g)^2\rangle}{\langle g\rangle^2} & \text{if} \quad t_c^2\langle(\delta g)^2\rangle \gg 1, \\ 2\pi m t_c \dfrac{\langle(\delta g)^2\rangle}{\langle g\rangle} & \text{if} \quad t_c^2\langle(\delta g)^2\rangle \ll 1. \end{cases} \tag{59}$$

For $a \gg 1$, we find the sums over k in Eqs. (56) and (57) by again using the Poisson resummation formula, Eq. (A.5), which accelerates convergence of the sums for $a \gg 1$. Reading Eq. (A.4) backwards, from the right-hand side to the left-hand side, we obtain

$$I(a) = \sqrt{\frac{\pi}{a}} \sum_{k=-\infty}^{\infty} \exp\left(-\frac{\pi^2 k^2}{a}\right) = \\ = \sum_{\ell=-\infty}^{\infty} \exp(-a\ell^2) = 1 + 2e^{-a} + \mathcal{O}(e^{-4a}). \tag{60}$$

Thus, Eqs. (53) and (54) become

$$S_1(m) = -\frac{1}{2} + \frac{1}{2} I(a) = e^{-a}, \tag{61}$$

$$S_2(m) = -\frac{1}{2}\frac{\partial I(a)}{\partial a} = e^{-a}, \tag{62}$$

and Eq. (55) therefore gives the polarization of the first spin

$$P_1(m) = \frac{1}{3} + \frac{4\sqrt{2}}{N^{3/2}\sqrt{\pi}} e^{-a} \tag{63}$$

with a in Eq. (59).

We conclude this section with the result for the total polarization for an odd total number N of spins. Due to alternating peaks of the polarization $P_1(t)$ in Eq. (40) (see also Fig. 2*a*), we obtain

$$P_1(m) = \\ = \begin{cases} \dfrac{1}{3} - \dfrac{4\sqrt{2}}{N^{3/2}\sqrt{\pi}} e^{-a} & \text{for large odd } m, \\ \dfrac{1}{3} + \dfrac{4\sqrt{2}}{N^{3/2}\sqrt{\pi}} e^{-a} & \text{for large even } m. \end{cases} \tag{64}$$

Equation (64), with a in Eq. (59), shows that the polarization peaks $P_1(m)$ of a spin-carrying gas have a Gaussian and an exponential time dependence for large and small correlation times of the fluctuations of the nano-bubbles, respectively.

4.3. NMR line shape

To calculate the NMR line shape exactly, we use the same effective Hamiltonian (13) as described in Sec. 3. The NMR line shape is the Fourier transform of the free induction decay (FID), $F(t)$, of an N-spin ensemble [15]. The NMR line shape on the protons in hydrogenated thin silicon films provided the first experimental evidence for the validity of effective Hamiltonian (13) in nano-cavities [4]. We are interested in the FID signal

$$F(t) = \frac{\mathrm{tr}\left\{e^{iHt} I_+ e^{-iHt} I_-\right\}}{\mathrm{tr}\left\{I_+ I_-\right\}} \tag{65}$$

with

$$I_\alpha = \sum_{n=1}^{N} I_{n\alpha}, \quad I_\pm = I_x \pm i I_y, \quad \alpha = x, y, z.$$

The reason for an exact solution for the FID in Eq. (65) is that the total Hamiltonian in Eq. (13) can be expressed in terms of the three collective spin operators I_α just as in Eq. (15). Because $[\mathbf{I}^2, I_\alpha] = 0$, we can rewrite Eq. (65) as

$$F(t) = \frac{\mathrm{tr}\left\{e^{iGtI_z^2} I_+ e^{-iGtI_z^2} I_-\right\}}{\mathrm{tr}\left\{I_+ I_-\right\}}, \tag{66}$$

with $G = 3g/2$ for dipolar interactions in the effective Hamiltonian (13) with $\zeta = 2$. The Heisenberg equation of motion for the operator

$$I_+(t) = \exp(iGtI_z^2) I_+ \exp(-iGtI_z^2)$$

is solved exactly as

$$I_+(t) = \exp(iGt(2I_z - 1)) I_+(0), \quad I_+(0) = I_+.$$

The averaging in Eq. (65) is performed in the $N!/(N_\uparrow! N_\downarrow!)$-fold degenerate basis of the states $(N_\uparrow, N_\downarrow)$ with $N_\uparrow$ ($N_\downarrow$) spins up (down), such that $N_\uparrow + N_\downarrow = N$ and $I_z = (N_\uparrow - N_\downarrow)/2$. The averaging gives the FID

$$F(t) = \left[\cos\left(\frac{3}{2} g t\right)\right]^{N-1}. \tag{67}$$

The effect of dephasing of proton spins within the nano-cavity due to the interactions with the protons at the surface of the nano-cavity is introduced phenomenologically as

$$F(t) = \left[\cos\left(\frac{3}{2} g t\right)\right]^{N-1} \exp\left(-\frac{t}{T_2}\right). \tag{68}$$

where the time T_2 relevant for the experiments [4] is $T_2 \approx$ 1–3 ms. The moments of the line shape are

$$M_n = \int_{-\infty}^{\infty} d\omega \omega^n \Im(\omega) = \left[\frac{d^n F(t)}{d(it)^n} \right] \bigg|_{t=0}, \qquad (69)$$

where $\Im(\omega)$ enters through the Fourier transformation of the FID,

$$F(t) = \int_{-\infty}^{\infty} d\omega \, \Im(\omega) e^{i\omega t}. \qquad (70)$$

The function $\Im(\omega)$ is meaningful for the frequencies $0 < \omega < \gamma^2 \hbar / \sigma^3$, with σ standing for the diameter of hard-sphere spin-carrying molecules. The upper cutoff of the frequency provides finite second and fourth moments for $gT_2 \gg 1$,

$$\begin{aligned} M_2 &= (N-1)\,(3g/2)^2\,, \\ M_4 &= (N-1)(3N-5)\,(3g/2)^4\,. \end{aligned} \qquad (71)$$

The moment M_2 derived in [4] by the Van Vleck formula coincides with M_2 in Eq. (70), as it should. The line shape in the nano-cavity volume appears to be volume-dependent (through the coupling g in Eq. (10)), allowing one to determine the volume of the nano-pores in hydrogenated silicon film [4].

5. CONCLUSION

We have presented the exact time-dependent description of spin-1/2 dynamics with infinite-range spin interactions and the initial polarization prepared on a single spin 1, i.e., $P_1(0) = 1$. Spin dynamics for odd and even numbered clusters demonstrates periodic pulses of the polarization $P_1(\tau)$ on spin 1. For large-N clusters with odd N, the polarization on spin 1 has pulses over the time interval

$$t^{sw} = 4\pi \frac{\mathcal{O}(1)}{g\sqrt{N}},$$

from $P_1(0) = 1$ to the time-independent polarization, which therefore lasts

$$t^{st} = \frac{4\pi}{g} \left(1 - \frac{\mathcal{O}(1)}{\sqrt{N}} \right)$$

within any period $4\pi/g$. For large-N clusters with even N, the switching time is

$$t^{sw} = 2\pi \frac{\mathcal{O}(1)}{g\sqrt{N}}$$

and the period equals $2\pi/g$. The stationary polarization on spin 1 is nonergodic, because its value tends to 1/3 (instead of tending to the ergodic value $1/N$) as N tends to infinity. The profiles of the polarizations within the series of odd (even) large clusters are remarkably similar.

The specific polarization profile in clusters with infinite-range spin interactions is in sharp contrast with the polarization profiles in $1D$ clusters with the nearest-neighbor XY Hamiltonian [3]. Two differences can be drawn from the presented results.

1. The overall behavior of the polarization $P_1(t)$ in the system with an infinite-range interaction is strictly reversible, periodic with the period $4\pi/g$ for any N, whereas on large $1D$ chains ($N \gg 1$) with the XY Hamiltonian, the polarization $P_1(t)$ on spin 1 moves in irregular fashion.

2. For N-spin clusters with $N \gg 1$, the polarization $P_1(t)$ of spin 1 exhibits a plateau region at the nonergodic value $\overline{P_1} = 1/3$; the pulses of the polarization $P_1(t)$ have a short time span about $4\pi\mathcal{O}(1)/(g\sqrt{N})$. This is in contrast to the behavior of the polarization $P_1(t)$ in $1D$ spin chains with the XY Hamiltonian, where polarization on spin 1 depends on time in irregular fashion with $t^{st} = 0$.

Finally, this paper demonstrates the sensitivity of the polarization dynamics (reversibility and ergodicity in many-spin systems) to the radius of the interaction. Incorporation of the real dipolar interactions into the theory is the most challenging task of dynamical theory and the accurate answer is not settled yet, although the general picture of the spin dynamics is known to be diffusional [23].

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APPENDIX

Derivation of Eq. (41)

We want to prove that the function $P_1^{osc}(\tau)$ in Eq. (38) for $N \gg 1$ has the form of periodic pulses, each of the width

$$\Delta_T = 4\pi \frac{\mathcal{O}(1)}{g\sqrt{N}}$$

at equidistant time instants $\tau = 0, 2\pi, 4\pi, \ldots$, such that the profile of $P_1^{osc}(\tau)$, e.g., at the time instant $\tau = 0$ is

$$P_1^{osc}(\tau) = \\ = \frac{2}{3}\left(1-\tau^2 N\right)\exp\left(-\tau^2 N/2\right), \quad \text{for } N \gg 1. \tag{A.1}$$

To prove Eq. (A.1), we introduce the new variable

$$n = I_B + \frac{1}{2}$$

in Eq. (38), such that the function $P_1^{osc}(\tau)$ takes the form (we recall that the total number of spins is equal to $N = N_B + 1$)

$$P_1^{osc}(\tau) = \frac{16}{3N}\sum_{n=1}^{N/2} 2^{-N}\binom{N}{N/2+n} \times \\ \times \left(n^2 - \frac{1}{4}\right)\cos(2\tau n). \tag{A.2}$$

Next, we use the asymptotic formula for the binomial distribution,

$$2^{-N}\binom{N}{N/2+n} = \frac{1}{\sqrt{\pi N/2}} \times \\ \times \exp\left(-\frac{n^2}{N/2}\right)\left(1 + n^3\frac{\mathcal{O}(1)}{\sqrt{N}}\right). \tag{A.3}$$

Equation (A.3) allows us to consider summation in Eq. (A.2) as averaging over the Gaussian distribution function. To simplify the calculation of Eq. (A.2) further, we apply the Poisson identity [24]

$$\sum_{\ell=-\infty}^{\infty}\cos(2\pi\epsilon\ell)\exp(-a\ell^2) = \\ = \sqrt{\frac{\pi}{a}}\sum_{k=-\infty}^{\infty}\exp\left(-\frac{\pi^2(k+\epsilon)^2}{a}\right). \tag{A.4}$$

In many circumstances, including the present ones, the resulting sum over k in the right-hand side of Eq. (A.4) converges much faster than the original sum over ℓ in the left-hand side of Eq. (A.4). To apply Eqs. (A.4) to Eq. (A.2), we can expand the sum in Eq. (A.2) up to $n = \infty$ because the terms in the sum in Eq. (A.2) practically vanish for $n > N/2$ and $N \gg 1$. Thus, by Poisson identity (A.4), we introduce the sum (a partial contribution to the sum in Eq. (A.2))

$$S_1(\tau) = \sum_{n=1}^{N/2}\cos(2\tau n)\exp\left(-\frac{n^2}{N/2}\right) = -\frac{1}{2} + \\ + \frac{1}{2}\sqrt{\frac{\pi N}{2}}\sum_{k=-\infty}^{\infty}\exp\left(-\pi^2\left(k+\frac{\tau}{\pi}\right)^2\frac{N}{2}\right). \tag{A.5}$$

To show that the function $S_1(\tau)$ has the form of Gaussian peaks at the equidistant instants $\tau = 0, \pm\pi, \pm 2\pi, \ldots$, it suffices to analyze the function $S_1(\tau)$ around the point $\tau = 0$. The leading contribution to the sum in Eq. (A.5) is then provided by the term $k = 0$. We note that if we analyze the peak around $\tau = m\pi$, where m is an integer, then the leading contribution to $S_1(\tau)$ comes from the term $k = -m$. Thus, in considering $N \gg 1$, we can drop all the terms in Eq. (A.5) except the leading term $k = 0$, which yields

$$S_1(\tau) = -\frac{1}{2} + \frac{1}{2}\sqrt{\frac{\pi N}{2}}\exp\left(-\frac{\tau^2 N}{2}\right). \tag{A.6}$$

Analogously, we determine the partial sum

$$S_2(\tau) = \sum_{n=1}^{N/2}\cos(2\tau n)\, n^2\exp\left(-\frac{n^2}{N/2}\right) = \\ = -\frac{\partial}{\partial(2/N)}S_1(\tau) = \frac{N^{3/2}\sqrt{\pi}}{8\sqrt{2}}\left(1-\tau^2 N\right) \times \\ \times \exp\left(-\frac{\tau^2 N}{2}\right). \tag{A.7}$$

At $N \gg 1$, the function $S_1(\tau)$ in Eq. (A.6) has a negligible contribution to the function

$$P_1^{osc}(\tau) = \frac{16}{3N^{3/2}\sqrt{\pi/2}}\left(S_2(\tau) - \frac{1}{4}S_1(\tau)\right)$$

in comparison with the contribution of the function $S_2(\tau)$ in Eq. (A.7), yielding the sought result in Eq. (A.1).

In general, the function $P_1^{osc}(\tau)$ for an arbitrary τ has pulses at the moments $\tau = k\pi$ with integer k,

$$P_1^{osc}(\tau) = \sum_{k=-\infty}^{\infty}\frac{2}{3}\left(1-\pi^2\left(k+\frac{\tau}{\pi}\right)^2 N\right) \times \\ \times \exp\left(-\pi^2\left(k+\frac{\tau}{\pi}\right)^2\frac{N}{2}\right). \tag{A.8}$$

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