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THE MULTIPLE QUANTUM NMR DYNAMICS IN SYSTEMS OF EQUIVALENT SPINS WITH A DIPOLAR ORDERED INITIAL STATE

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The multiple quantum (MQ) NMR dynamics in the system of equivalent spins with the dipolar ordered initial state is considered. The high symmetry of the Hamiltonian responsible for the MQ NMR dynamics (the MQ Hamiltonian) is used to develop analytic and numerical methods for the investigation of the MQ NMR dynamics in systems consisting of hundreds of spins from the "first principles". We obtain the dependence of the intensities of the MQ NMR coherences on their orders (profiles of the MQ NMR coherences) for systems of 200–600 spins. It is shown that these profiles may be well approximated by exponential distribution functions. We also compare the MQ NMR dynamics in the systems of equivalent spins having two different initial states, the dipolar ordered state and the thermal equilibrium state in a strong external magnetic field.

1. INTRODUCTION

The multiple quantum (MQ) NMR dynamics in solids [1] is extremely useful for investigating solid structures and dynamical processes therein, for counting the number of spins in impurity clusters [2, 3], and for simplifying the standard NMR spectra [4]. The MQ NMR experiments typically deal with samples where the nuclear spin system is initially prepared in the thermal equilibrium in a strong external magnetic field [1]. But the MQ NMR experiments can be carried out with samples prepared in different initial states [5]. In particular, a spin system can be prepared in the dipolar ordered state [6] using either the adiabatic demagnetization method in a rotating reference frame [6, 7] or the two-pulse Broekaert–Jeener sequence [6, 8]. The MQ NMR dynamics with this initial state in small spin systems have been simulated in Refs. [9, 10]. Using the dipolar ordered initial state in the MQ NMR experiment, we should expect an earlier appearance of multiple spin clusters and correlations in comparison with the MQ NMR experiment with the thermal equilibrium initial state in a strong external magnetic field. In fact, the analysis of MQ NMR experiments with six–eight spin systems [9, 10] demonstrates that the six–eight order MQ coherences appear earlier in the experiment with the dipolar ordered initial state.

One of the basic problems in the theoretical description of the MQ NMR experiments is an exponential increase in the density matrix size with the number of spins. Therefore, modern numerical methods have been developed for simulation of the MQ NMR dynamics based on either the Chebyshev polynomial expansion [11] or quantum parallelism [12]. However, these methods allow studying the MQ NMR dynamics in systems of no more than several dozen of spins. A significant progress in this direction has been achieved in simulation of the MQ NMR dynamics in the system of equivalent spins [13–15], which can be prepared, for instance, by filling a closed nanopore with the gas of spin-carring molecules (or atoms). Because of the special symmetry of the Hamiltonian governing the dynamics in such a spin system, it becomes possible to study the MQ NMR dynamics in systems of hundreds of spins and even more [15, 16]. The nature of the above-mentioned symmetry can be clarified as follows. As long as the characteristic time between two successive collisions with the nanopore walls is several orders less than the time of mutual flip-flops of any two nuclear spins (which is defined by their dipole–dipole interaction (DDI)) [13, 14], it seems reasonable to use the averaged DDI, which can be obtained by averaging over the spin positions in a nanopore [13]. This means that the constant of the averaged DDI remains the same for any pair of spins in the nanopore [13], and hence the nuclear spins become equivalent. For this reason,

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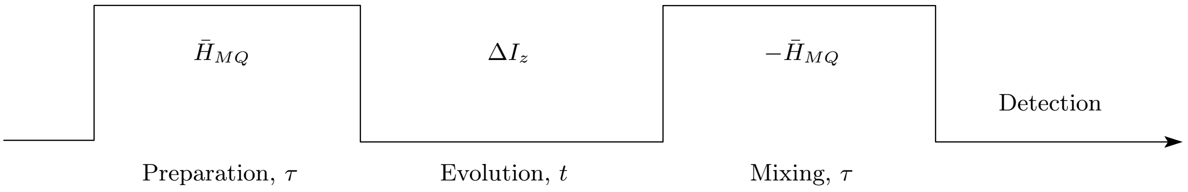

Fig. 1. The basic scheme of the four-period MQ NMR experiment

the Hamiltonian of the nuclear spin DDI in a nanopore commutes with the operator of the squared total spin angular momentum I^2 [15, 16]. It then becomes possible to use the basis of common eigenfunctions for the operator of the squared total spin momentum I^2 and of its projection I_z on the direction of the external magnetic field instead of the standard multiplicative basis of the eigenfunctions of I_z, which yields an exponential increase in the Hilbert space dimensionality with the number of spins [15, 16]. As a result, we simplify the calculations and hence succeed in both the investigation of the MQ NMR dynamics in systems of 200–600 spin-$1/2$ particles [15] and the study of the dependence of the coherence relaxation time on the MQ NMR coherence order and the number of spins [17]. We emphasize that the nuclear spin system with the thermodynamic equilibrium initial state in a strong external magnetic field was used in Refs. [15–17].

The MQ NMR dynamics in a large system of equivalent spins with the dipolar ordered initial state is studied in the present paper. The theory of MQ NMR dynamics of equivalent spins with this initial state is given in Sec. 2. The dependence of the MQ NMR coherence intensities on the coherence orders (the profiles of MQ NMR coherence intensities) for systems of 200–600 spins is studied in Sec. 3. The MQ NMR dynamics in systems with the dipolar ordered initial state is compared with the dynamics in systems with the thermal equilibrium initial state in a strong external magnetic field in Sec. 4. The basic results are collected in Sec. 5.

2. THE MQ NMR COHERENCE INTENSITIES IN SYSTEMS OF EQUIVALENT SPINS PREPARED IN THE DIPOLAR ORDERED INITIAL STATE

We consider the system of equivalent spin-$1/2$ particles with the DDI in a strong external magnetic field. The secular part of the DDI Hamiltonian [6] is

$$H_{dz} = \sum_{j<k} D_{jk}(2I_{jz}I_{kz} - I_{jx}I_{kx} - I_{jy}I_{ky}), \qquad (1)$$

where

$$D_{jk} = \frac{\gamma^2\hbar}{2r_{jk}^3}(1 - 3\cos^2\theta_{jk})$$

is the DDI constant, γ is the gyromagnetic ratio, r_{jk} is the distance between the jth and kth spins, θ_{jk} is the angle between the internuclear vector $\mathbf{r}_{jk}$ and the external magnetic field $\mathbf{B}_0$, and $I_{j\alpha}$ ($\alpha = x, y, z$) is the jth spin projection operator on the axis α. Using either the adiabatic demagnetization in a rotating reference frame [6, 7] or the Broekaert–Jeener two-pulse sequence [6, 8], the spin system can be prepared in the dipolar ordered initial state with the density matrix

$$\rho(0) = \frac{1}{Z}\exp(-\beta H_{dz}) \approx \frac{1}{2^N}(1 - \beta H_{dz}), \qquad (2)$$

where $\beta = \hbar/kT$ is the inverse spin temperature, $Z = \operatorname{Tr}\exp(-\beta H_{dz})$ is the partition function, and N is the number of spins.

If the system under consideration consists of spin-carring molecules (atoms) in a closed nanopore, then the DDI is averaged (incompletely) by the fast molecular diffusion such that the DDI constants for any spin pair become equal to each other, $D_{jk} \equiv D$ [13, 14]. As a result, Hamiltonian (1) can be written as [14]

$$\bar{H}_{dz} = \frac{D}{2}(3I_z^2 - I^2), \qquad (3)$$

where $I_\alpha = \sum_{i=1}^N I_{i\alpha}$ and $I^2 = I_x^2 + I_y^2 + I_z^2$ is the square of the spin angular momentum. It is important to justify that the high-temperature approximation in (2) is applicable to the system of equivalent spins. The simple analysis [18] demonstrates that approximation (2) for the system with Hamiltonian (3) is valid if

$$\beta DN \ll 1. \qquad (4)$$

The systems considered in our work have $N = 200$–600, and hence condition (4) is satisfied.

The MQ NMR experiment consists of four basic periods shown in Fig. 1: the preparation period τ, the evolution period t, the mixing period τ, and the detection. The MQ NMR coherences are generated in the preparation period due to irradiation of the sample by a multiple eight-pulse sequence of resonance pulses [1]. We express the MQ NMR coherences in terms of the density matrix of the preparation period. For this, we note that the averaged Hamiltonian $\bar{H}_{MQ}$ (nonsecular two-spin/two-quantum Hamiltonian [1]) describing the MQ dynamics in the system of equivalent spins during the preparation period in a rotating reference frame can be written as [15, 16]

$$\bar{H}_{MQ} = -\frac{D}{4}\{(I^+)^2 + (I^-)^2\}, \tag{5}$$

where I^+ and I^- are the raising and lowering operators ($I^\pm = I_x \pm iI_y$). To investigate the MQ NMR dynamics, we have to find the density matrix $\rho(\tau)$ for the spin system by solving the Liouville equation [6]

$$i\frac{d\rho}{d\tau} = [\bar{H}_{MQ}, \rho(\tau)], \tag{6}$$

with the initial condition $\rho(0) = \bar{H}_{dz}$. This initial condition is obtained from Eqs. (2) and (3) by dropping both the unit operator and the factor $-\beta/2^N$, which are not significant for the MQ NMR dynamics. With the Hamiltonians for the different periods of the MQ NMR experiment (which are shown in Fig. 1), we can write the expression for the dipolar energy $\langle \bar{H}_{dz}\rangle(\tau, t)$ after the mixing period of the MQ NMR experiment (Fig. 1) as

$$\begin{aligned}\langle \bar{H}_{dz}\rangle(\tau, t) &= \\ &= \frac{\mathrm{Tr}\{U^+(\tau)e^{-i\Delta t I_z}U(\tau)\bar{H}_{dz}U^+(\tau)e^{i\Delta t I_z}U(\tau)\bar{H}_{dz}\}}{\mathrm{Tr}\{\bar{H}_{dz}^2\}} = \\ &= \frac{\mathrm{Tr}\{e^{-i\Delta t I_z}\rho(\tau)e^{i\Delta t I_z}\rho(\tau)\}}{\mathrm{Tr}\{\bar{H}_{dz}^2\}},\end{aligned} \tag{7}$$

where $\rho(\tau) = U(\tau)\bar{H}_{dz}U^+(\tau)$ is the solution of Eq. (6) and $U(\tau) = \exp(-i\bar{H}_{MQ}\tau)$. It is convenient to represent the solution of Eq. (6) as the series [19]

$$\rho(\tau) = \sum_k \rho_k(\tau), \tag{8}$$

where $\rho_k(\tau)$ obeys the relation $[I_z, \rho_k(\tau)] = k\rho_k(\tau)$, which can be considered the definition of $\rho_k(\tau)$ (in other words, $\rho_k(\tau)$ collects those entries of the density matrix $\rho(\tau)$ that are responsible for the kth order MQ NMR coherence). Then Eq. (7) becomes

$$\begin{aligned}\langle \bar{H}_{dz}\rangle(\tau) &= \sum_k e^{-ik\Delta t}\frac{\mathrm{Tr}\{\rho_k(\tau)\rho_{-k}(\tau)\}}{\mathrm{Tr}\{\bar{H}_{dz}^2\}} = \\ &= \sum_k e^{-ik\Delta t}J_k(\tau),\end{aligned} \tag{9}$$

where the kth-order MQ NMR coherence intensity J_k is defined as [19]

$$J_k(\tau) = \frac{\mathrm{Tr}\{\rho_k(\tau)\rho_{-k}(\tau)\}}{\mathrm{Tr}\{\bar{H}_{dz}^2\}}. \tag{10}$$

This formula is used in the numerical analysis of the MQ NMR coherences in Sec. 3.

It is easy to write the explicit expression for $\mathrm{Tr}\{\bar{H}_{dz}^2\}$. First, using Eq. (3), we can write

$$\begin{aligned}\mathrm{Tr}\{\bar{H}_{dz}^2\} &= \frac{D^2}{4}\mathrm{Tr}(3I_z^2 - I^2)^2 = \\ &= \frac{D^2}{4}\mathrm{Tr}\{9I_z^4 - 3I_z^2I^2 + I^2(I^2 - 3I_z^2)\} = \\ &= \frac{3D^2}{4}\mathrm{Tr}\{3I_z^4 - I_z^2I^2\} = \frac{3D^2}{2}\mathrm{Tr}\{I_z^4 - I_x^2I_z^2\}.\end{aligned} \tag{11}$$

Here, we use that

$$\mathrm{Tr}\{I^2(I^2 - 3I_z^2)\} = 0, \quad \mathrm{Tr}\{I_x^2I_z^2\} = \mathrm{Tr}\{I_y^2I_z^2\}. \tag{12}$$

Next, it is simple to obtain explicit expressions for $\mathrm{Tr}\{I_z^4\}$ and $\mathrm{Tr}\{I_x^2I_z^2\}$:

$$\begin{aligned}\mathrm{Tr}\{I_z^4\} &= 2^{N-4}N(3N-2), \\ \mathrm{Tr}\{I_x^2I_z^2\} &= 2^{N-4}N^2.\end{aligned} \tag{13}$$

Finally, Eqs. (11)–(13) yield the result

$$\mathrm{Tr}\{\bar{H}_{dz}^2\} = 3N(N-1)2^{N-4}D^2. \tag{14}$$

Taking the structure of the MQ Hamiltonian $\bar{H}_{MQ}$ into account, it can be readily shown that only even-order MQ NMR coherences appear in our numerical experiment and the coherence order cannot exceed the number of spins N [1, 19].

It is obvious that MQ Hamiltonian (5) commutes with the square of the total spin momentum operator I^2 [15–17]. Because $[I^2, I_z] = 0$, it is possible to use the basis of common eigenfunctions of the operators I^2 and I_z for the description of the MQ NMR dynamics. Just this fact allows avoiding the problem of the exponential increase in the matrix size with the number of spins, which occurs in the traditional multiplicative basis [1] of the eigenfunctions of I_z. In the new basis, the MQ Hamiltonian $\bar{H}_{MQ}$ consists of blocks $\bar{H}_{MQ}^S$ corresponding to the different values of the total spin momentum S ($\hat{S}^2 = S(S+1)$, $S = N/2, N/2-1, N/2-2, \ldots, N/2-[N/2]$, where $[i]$ is the integer part of i):

$$\bar{H}_{MQ} = \mathrm{diag}\left\{\bar{H}_{MQ}^{N/2}, \bar{H}_{MQ}^{N/2-1}, \ldots, \bar{H}_{MQ}^{N/2-[N/2]}\right\}. \tag{15}$$

Since the Hamiltonian $\bar{H}_{dz}$ in (3) is diagonal in the basis of common eigenfunctions of I^2 and I_z, the density matrix $\rho(0)$ can also be split into diagonal blocks $\rho^S(0)$ with

$$S = \frac{N}{2}, \frac{N}{2}-1, \frac{N}{2}-2, \ldots, \frac{N}{2} - \left[\frac{N}{2}\right].$$

Consequently, the matrix $\rho(\tau)$ also has the diagonal block structure with blocks $\rho^S(\tau)$. The problem is thus separated into a set of independent problems for each $(2S+1)\times(2S+1)$-dimensional block $\rho^S(\tau)$, which is a solution of Liouville equation (6) with the Hamiltonian $\bar{H}^S_{MQ}$. Of course, expansion (8) can be applied to each block ρ^S. The contribution $J_{k,S}$ from the block ρ^S to the intensity J_k of the kth-order coherence is defined by the obvious formula [15]

$$J_{k,S}(\tau) = \frac{\mathrm{Tr}\{\rho^S_k(\tau)\rho^S_{-k}(\tau)\}}{\mathrm{Tr}\{\bar{H}^2_{dz}\}}, \qquad (16)$$

where $\rho^S_k(\tau)$ is the contribution from the matrix ρ^S to the kth-order coherence. We must take into account that each block $\rho^S(\tau)$ is degenerated with the multiplicity $n_N(S)$ [15, 20]:

$$n_N(S) = \frac{N!(2S+1)}{\left(\frac{N}{2}+S+1\right)!\left(\frac{N}{2}-S\right)!}, \qquad 0 \le S \le \frac{N}{2}. \qquad (17)$$

As a result, the observable intensities $J_k(\tau)$ $(-N \le k \le \le N)$ are given by [15, 16]

$$J_k(\tau) = \sum_S n_N(S) J_{k,S}(\tau). \qquad (18)$$

We recall that the size of each block $\bar{H}^S_{MQ}$ of the MQ NMR Hamiltonian $\bar{H}_{MQ}$ is $2S+1$. Taking the block degeneration into account, we obtain the correct value for the matrix dimensionality of both the Hamiltonian $\bar{H}_{MQ}$ and the density matrix ρ [15]:

$$\sum_S n_N(S)(2S+1) = 2^N, \qquad (19)$$

which is valid for the system of N interacting spin-1/2 particles.

Numerical algorithms describing the MQ NMR dynamics in the systems of equivalent spins with a thermal equilibrium initial state in the strong external magnetic field have been developed in [15–17]. With minor corrections, these algorithms can be used for simulating the dynamics of the MQ NMR coherences in the spin system with the dipolar ordered initial state. In particular, the integral of motion related to the MQ NMR Hamiltonian invariance under the rotation through the angle π around the z axis [21] is also present. Therefore, for odd N, it suffices to solve the problem for the MQ NMR Hamiltonians with the matrix size two times lower and then double the resulting intensities [21]. We use spin systems with odd N in all numerical calculations in the next section.

3. NUMERICAL ANALYSIS OF THE MQ NMR PROFILES

Using the method developed in the preceding section, we investigate the profiles of MQ NMR coherences. Because all spins are "nearest neighbors" in the system of equivalent spins, an N-spin cluster appears already after the time interval $\tau \sim 1/D$. However, some rearrangement of this cluster is required for the MQ coherence formation [15]. The analysis of the MQ NMR coherence dynamics demonstrates that the quasistationary profile of the MQ NMR coherences is created during $\bar{\tau} \approx 2$ ($\bar{\tau} = D\tau$ is the dimensionless time hereafter) and remains fast oscillating for $\bar{\tau} > 2$. Because of these oscillations, it is convenient to use the averaged intensities $\bar{J}_k$ [15] instead of the intensities J_k themselves. We estimate the dimensionless averaging time interval as $T \sim 2\pi/|\lambda^{min}_{3/2}| \approx 7.255$, where $\lambda^{min}_{3/2} = \sqrt{3}/2$ is the minimal eigenvalue of the Hamiltonian [15, 16]. For convenience, we take $T = 8$, and hence

$$\bar{J}_k = \frac{1}{T}\int\limits_2^{2+T} J_k(\bar{\tau})\, d\bar{\tau}. \qquad (20)$$

It can be observed that the $\bar{J}_k$ do not significantly vary with an increase in T, and hence the definition of the averaged intensities in Eq. (20) is valid. Although the dynamics of all coherences has been found in numerical simulations, the intensities of the higher-order coherences are negligible, and we therefore represent the intensities of the MQ NMR coherences up to the 50th order in the figures below. The profiles of MQ NMR coherence intensities for systems of 201, 401, and 601 spins with a dipolar ordered initial state are shown in Fig. 2. These profiles are similar to those that have been found for the systems with a thermal equilibrium initial state in a strong external magnetic field [15, 16]. Similarly to Refs. [15, 16], the averaged intensities of MQ NMR coherences are separated into two families:

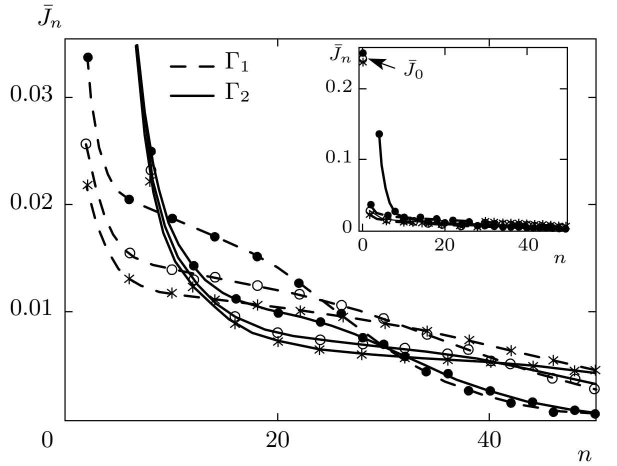

Fig. 2. Profiles of the coherence intensities $\bar{J}_n$ for spin systems with $N = 201$ (•), 401 (○), 601 (∗). The inset demonstrates that the zeroth-order coherence belongs to neither Γ_1 nor Γ_2. Only intensities of positive-order coherences are presented

$$\begin{aligned} \Gamma_1 &= \{\bar{J}_{4k-2},\ \ k = 0, \pm 1, \pm 2, \ldots\}, \\ \Gamma_2 &= \{\bar{J}_{4k},\ \ k = \pm 1, \pm 2, \ldots\}, \end{aligned} \tag{21}$$

with the zeroth-order coherence intensity $\bar{J}_0$ not corresponding to any of these families. Each family can be approximated by a smooth distribution function as

$$\bar{J}_{2k} \approx \begin{cases} A_1 \left(1 + \sum\limits_{i=1}^{4} (-1)^i a_{1i} (2|k|)^i \right) e^{-2\alpha_1 |k|}, \\ \qquad\qquad k = \pm 1, \pm 3, \ldots, \\ A_2 \left(1 + \sum\limits_{i=1}^{6} (-1)^i a_{2i} (2|k|)^i \right) e^{-2\alpha_2 |k|}, \\ \qquad\qquad k = \pm 2, \pm 4, \ldots, \end{cases} \tag{22}$$

where the parameters A_i, a_{ij}, and α_i for spin systems with $N = 201$, 401, and 601 are collected in the Table. The algorithm to determine the approximation parameters is similar to that suggested in Ref. [15].

Similarly to the profiles of the MQ NMR coherence intensities obtained for systems of equivalent spin-1/2 particles with a thermal equilibrium initial state in a strong external magnetic field [15], the profiles for the systems with the dipolar ordered initial state seem to be exponential. This conclusion agrees with results obtained during an elaboration of numerous MQ NMR spectra [22] and contradicts the phenomenological theory [1] that predicts the Gaussian profiles of the MQ NMR coherence intensities.

Liouville equation (6) and formulas (10) for the MQ NMR coherence intensities yield the conservation law for the sum of the coherence intensities [23]:

$$\sum_k \bar{J}_k(\tau) = 1. \tag{23}$$

This law and approximating formula (22) allow finding a good approximation to the zeroth-order coherence intensity. We compare the calculated values of $\bar{J}_0$ (see Eq. (10)) with the values

$$\bar{J}_0^{appr} = 1 - 2 \sum_{k=1}^{\infty} J_{2k}$$

found using the above conservation law and distribution function (22):

$$\begin{aligned} \bar{J}_0 &= \begin{cases} 2.519 \cdot 10^{-1}, & N = 201, \\ 2.417 \cdot 10^{-1}, & N = 401, \\ 2.361 \cdot 10^{-1}, & N = 601, \end{cases} \\ \bar{J}_0^{appr} &= \begin{cases} 2.501 \cdot 10^{-1}, & N = 201, \\ 2.381 \cdot 10^{-1}, & N = 401, \\ 2.387 \cdot 10^{-1}, & N = 601. \end{cases} \end{aligned} \tag{24}$$

Some discrepancy between $\bar{J}_0$ and $\bar{J}_0^{appr}$ appears because we take only coherences up to the 50th order into account in constructing distribution function (22), while contributions from the higher-order coherences are missing.

4. COMPARISON OF THE MQ NMR DYNAMICS IN SPIN SYSTEMS WITH TWO DIFFERENT INITIAL STATES

The preparation of the system in a dipolar ordered initial state means that the two-spin correlations appear already at the initial time, unlike in the standard MQ NMR experiment, where the thermal equilibrium initial state is determined by the one-spin Zeemann interaction with the external magnetic field [9, 10]. This statement is justified by Fig. 3, where the formation times $\bar{\tau}_f(n)$ of different-order coherences for both initial states are represented. Here, by the formation time $\bar{\tau}_f(n)$ of the nth coherence, we mean the instant when the nth coherence intensity $J_n(\bar{\tau})$ reaches the value $\bar{J}_n$ for the first time. We see that the MQ NMR coherences in the system with the dipolar ordered initial state (the

Table. The parameters A_i, a_{ij}, and α_i of the distribution function given by Eq. (22) for $N = 201$, 401, and 601

N	A_1	a_{11}	a_{12}	a_{13}	a_{14}	α_1
201	$8.498 \cdot 10^{-2}$	$3.133 \cdot 10^{-1}$	$8.025 \cdot 10^{-2}$	$6.109 \cdot 10^{-3}$	$2.739 \cdot 10^{-4}$	$2.437 \cdot 10^{-1}$
401	$4.546 \cdot 10^{-2}$	$1.694 \cdot 10^{-1}$	$3.357 \cdot 10^{-2}$	$1.649 \cdot 10^{-3}$	$5.739 \cdot 10^{-5}$	$1.638 \cdot 10^{-1}$
601	$3.546 \cdot 10^{-2}$	$1.456 \cdot 10^{-1}$	$2.471 \cdot 10^{-2}$	$1.028 \cdot 10^{-3}$	$2.855 \cdot 10^{-5}$	$1.342 \cdot 10^{-1}$
N	A_2	a_{21}	a_{22}	a_{23}	a_{24}	a_{25}
201	2.217	$4.029 \cdot 10^{-1}$	$7.522 \cdot 10^{-2}$	$7.638 \cdot 10^{-3}$	$4.624 \cdot 10^{-4}$	$1.562 \cdot 10^{-5}$
401	1.411	$3.587 \cdot 10^{-1}$	$5.648 \cdot 10^{-2}$	$4.616 \cdot 10^{-3}$	$2.116 \cdot 10^{-4}$	$5.136 \cdot 10^{-6}$
601	1.210	$3.441 \cdot 10^{-1}$	$5.123 \cdot 10^{-2}$	$3.924 \cdot 10^{-3}$	$1.664 \cdot 10^{-4}$	$3.686 \cdot 10^{-6}$
N	a_{26}	α_2				
201	$2.510 \cdot 10^{-7}$	$3.039 \cdot 10^{-1}$				
401	$5.533 \cdot 10^{-8}$	$2.183 \cdot 10^{-1}$				
601	$3.512 \cdot 10^{-8}$	$1.940 \cdot 10^{-1}$				

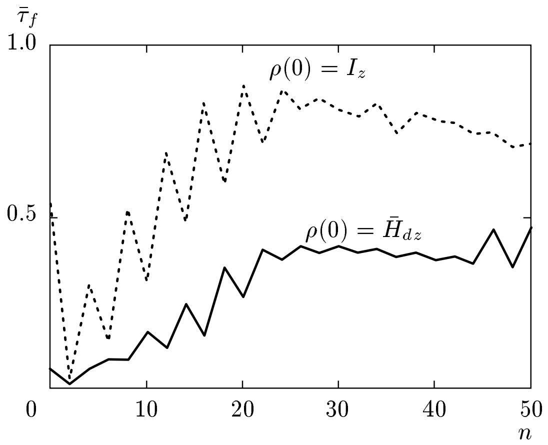

Fig. 3. Coherence formation time $\bar{\tau}_f$ versus the coherence number for the dynamics of equivalent spins with the dipolar ordered and the thermal equilibrium in the strong external field initial states

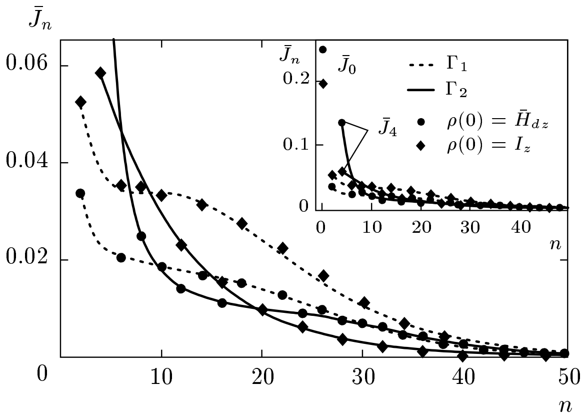

Fig. 4. The MQ NMR profiles for the systems of equivalent spins with the dipolar ordered and thermal equilibrium in the strong external magnetic field initial states, $N = 201$; the inset demonstrates that $\bar{J}_0$ and $\bar{J}_4$ are essentially larger in the case of the dipolar ordered initial state

lower solid line) appear much earlier. This result agrees with that obtained in [9] for the MQ NMR in systems with a small number of spin-1/2 particles.

The profiles of the MQ NMR coherence intensities for the system of $N = 201$ spins with both the dipolar ordered and the thermal equilibrium in a strong magnetic field initial states are compared in Fig. 4. This figure demonstrates that the discrepancy between the two families of MQ NMR coherences, Γ_1 and Γ_2, is larger for $n < 10$ and smaller for $n > 10$ in the case of the dipolar ordered initial state. The inset shows that $\bar{J}_0$ and $\bar{J}_4$ are essentially larger in the case of the dipolar ordered initial state.

Thus, similarly to the usual NMR experiments in solids [6], the MQ NMR experiment in the systems of equivalent spins with the dipolar ordered initial state can be useful in supplementing the MQ NMR experiment with the thermal equilibrium initial state in a strong external magnetic field.

5. CONCLUSIONS

We have studied the MQ NMR dynamics in systems of equivalent spin-$1/2$ particles with the dipolar ordered initial state. For this, we modified the method developed in Ref. [15] for the system of equivalent spin-$1/2$ particles with the thermal equilibrium initial state in a strong external magnetic field. Similarly to Ref. [15], the high symmetry of such systems allows investigating the dynamics in large spin systems containing hundreds of interacting spins. We obtain the dependence of the MQ NMR coherence intensities on their order (the profiles of the MQ NMR coherence intensities) in systems of 200–600 spins and demonstrate that these profiles can be well approximated by exponential distribution functions. Because similar results have been obtained in Refs. [15, 16] for systems with the thermal equilibrium initial state in a strong external magnetic field, we may suppose that the exponential profiles of the MQ NMR coherence intensities are a fundamental fact in the MQ NMR dynamics. The theoretical results obtained in Refs. [24, 25] confirm this conclusion.

We demonstrate that the MQ NMR coherences appear faster in the spin systems with the dipolar ordered initial state. The MQ NMR experiments with the dipolar ordered initial states extend the possibilities of MQ NMR spectroscopy in the study of the structures of solids and the dynamical processes therein.

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REFERENCES

1. J. Baum, M. Munovitz, A. N. Garroway, and A. Pines, J. Chem. Phys. **83**, 2015 (1985).
2. J. Baum, K. K. Gleason, A. Pines, A. N. Garroway, and J. A. Reimer, Phys. Rev. Lett. **56**, 1377 (1986).
3. C. E. Hughes, Progr. Nucl. Magn. Reson. Spectrosc. **45**, 301 (2004).
4. W. S. Warren, D. P. Weitekamp, and A. Pines, J. Chem. Phys. **73**, 2084 (1980).
5. G. B. Furman and S. D. Goren, J. Phys.: Condens. Matter **17**, 4501 (2005).
6. M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids*, Clarendon, Oxford (1970).
7. C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).
8. J. Jeener and P. Broekaert, Phys. Rev. **157**, 232 (1967).
9. S. I. Doronin, E. B. Fel'dman, E. I. Kuznetsova, G. B. Furman, and S. D. Goren, Phys. Rev. B **76**, 144405 (2007).
10. S. I. Doronin, E. B. Fel'dman, E. I. Kuznetsova, G. B. Furman, and S. D. Goren, Pis'ma v Zh. Eksp. Teor. Fiz. **86**, 26 (2007).
11. V. V. Dobrovitski, H. A. De Raedt, M. I. Katsnelson, and B. N. Harmon, Phys. Rev. Lett. **90**, 210401 (2003).
12. W. X. Zhang, P. Cappellaro, N. Amtler, B. Pepper, D. G. Cory, V. V. Dobrovitski, C. Ramanathan, and L. Viola, Phys. Rev. A **80**, 052323 (2009).
13. J. Baugh, A. Kleinhammes, D. Han, Q. Wang, and Y. Wu, Science **294**, 1505 (2001).
14. E. B. Fel'dman and M. G. Rudavets, Zh. Eksp. Teor. Fiz. **125**, 233 (2004).
15. S. I. Doronin, A. V. Fedorova, E. B. Fel'dman, and A. I. Zenchuk, J. Chem. Phys. **131**, 104109 (2009).
16. S. I. Doronin, A. V. Fedorova, E. B. Fel'dman, and A. I. Zenchuk, Phys. Chem. Chem. Phys. **12**, 13273 (2010).
17. S. I. Doronin, E. B. Fel'dman, and A. I. Zenchuk, J. Chem. Phys. **134**, 034102 (2011).
18. F. S. Dzheparov, Preprint ITEP, No. 7–10 (2010).
19. E. B. Fel'dman and S. Lacelle, J. Chem. Phys. **107**, 7067 (1997).
20. L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, Vol. 3: Quantum Mechanics: Non-Relativistic Theory*, Nauka, Moscow (1974); Pergamon, New York (1977).
21. S. I. Doronin, E. B. Fel'dman, I. Ya. Guinzbourg, and I. I. Maximov, Chem. Phys. Lett. **341**, 144 (2001).
22. S. Lacelle, S.-J. Hwang, and B. C. Gerstein, J. Chem. Phys. **99**, 8407 (1993).
23. D. A. Lathrop, E. S. Handy, and K. K. Gleason, J. Magn. Reson. Ser. A **111**, 161 (1994).
24. V. E. Zobov and A. A. Lundin, Zh. Eksp. Teor. Fiz. **130**, 1047 (2006).
25. V. E. Zobov and A. A. Lundin, Zh. Eksp. Teor. Fiz. **139**, 519 (2011).