Dipolar Order and Spin-Lattice Relaxation in a Liquid Entrapped into Nanosize Cavities

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It was shown that by means of the two-pulse sequence, the spin system of a liquid entrapped into nanosize cavities can be prepared in quasi-equilibrium states of high dipolar order, which relax to thermal equilibrium with the molecular environment with a relaxation time $T_{1\mathrm{d}}$. Measurements of the inverse dipolar temperature and spin-lattice relaxation time in the local fields provide an important information about the cavity size V, its shape F, and orientation θ (with respect to the external magnetic field) of the nanopores.

Key words: Dipolar Ordered State; Liquid; Nanosize Cavities.
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1. Introduction

Detection and study of molecular motions and spin-lattice relaxation, in wide temperature and frequency ranges, is one of the major challenges of magnetic resonance. The study of the spin-lattice relaxation in local fields gives an important information about atomic and molecular motions, which can not be obtain in strong fields.

There are two basic nuclear magnetic resonance (NMR) methods to detect and analyze slow molecular motions. One of which is based on the adiabatic demagnetization in a rotating frame (ADRF) [1, 2]. Another method is based on pairs of phase-shifted radiofrequency (RF) pulses (the JB method) [3]. Application of ADRF or JB methods to the nuclear spin system results in a transfer of the Zeeman order, which is established under the effect of the external magnetic field, into spin-spin order, where nuclear spins are oriented along the internal local field caused by dipole–dipole interactions (DDI). This state is characterized by the nuclear dipolar energy and nuclear dipolar temperature [1].

However, all studies deal with the relaxation of the nuclear dipolar energy in bulk solids [4 – 11] and do not consider the spin-lattice relaxation in substances confined within nanosized areas such as nanopores, nanocavities or existing specific nanometric objects like nanotubes, nanodiamond, nanoonions, and nanograins. At the same time, all aforementioned nanoobjects possess unique physical and chemical properties that differ from properties of bulk materials of the same chemical content and structure. Examples include various physical and chemical properties [12]. One of these unique phenomena is manifested in the fact that in nanosized confined gas or liquids intermolecular DDI between nuclear spins are not averaged to zero, as usually happens in bulk materials [13]. The averaged dipolar coupling constant depends on the volume and shape of the nanopore and its orientation relatively to the external magnetic field [13 – 16]. As a result, this effect may be applied to obtain useful information from the nuclear magnetic resonance experiments [17].

Here we consider the phenomena of spin-lattice relaxation of dipolar energy of the nuclear spins in a liquid entrapped into nanosize cavities. As example we will consider of nuclear spin-$\frac{1}{2}$ carrying molecules in aqueous solution [18].

2. Effective Hamiltonian

Let us consider a system of nuclei, each carrying a nuclear spin $I = 1/2$, in a strong external magnetic field $\vec{H}$ in an aqueous solution entrapped into nanosize cavities. The dynamics of the spin system under consideration and its relaxation can be described by a solution of the equation for the state operator $\rho(t)$,

$$\mathrm{i}\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = [H(t), \rho(t)], \tag{1}$$

with Hamiltonian

$$H = H_0 + H_{\mathrm{dd}} + H_{\mathrm{SL}}(t), \tag{2}$$

where H_0 is the Zeeman interaction Hamiltonian,

$$H_0 = \omega_0 \sum_{\mu} I_{z\mu}, \tag{3}$$

$\omega_0 = \gamma|\vec{H}|$ is the Zeeman frequency of the nuclei, the operator I_μ^z is the projection of the angular spin momentum operator of a spin μ on the z-axis. H_{dd} is the secular part of the nuclear DDI Hamiltonian,

$$H_{\mathrm{dd}} = \sum_{\mu\neq\eta} G_{\mu\eta}\left[I_{z\mu}I_{z\eta} - \frac{1}{4}\left(I_{+\mu}I_{-\eta} + I_{-\mu}I_{+\eta}\right)\right], \tag{4}$$

where

$$G_{\mu\eta} = \frac{\gamma^2\hbar}{r_{\mu\eta}^3} P_2\left(\cos\theta_{\mu\eta}\right), \tag{5}$$

$r_{\mu\eta}$ and $\theta_{\mu\eta}$ are the spherical coordinates of the vector $\vec{r}_{\mu\eta}$ connecting the μth and ηth nuclei in a coordinate system with the z-axis along the external magnetic field, $P_2\left(\cos\theta_{\mu\eta}\right) = \frac{1}{2}\left(1 - 3\cos^2\theta_{\mu\eta}\right)$, $I_{+\mu}$ and $I_{-\mu}$ are the raising and lowering operators of a spin μ. The term $H_{\mathrm{SL}}(t)$ represents the spin-lattice coupling, responsible for relaxation of the spin system toward thermal equilibrium with the lattice and can be presented as a sum of the terms [1, 19]

$$H_{\mathrm{SL}}(t) = \sum_{k=-2}^{2}\sum_{\mu\neq\eta} A_{\mu\eta}^{(k)} \Phi_{\mu\eta}^{(-k)}(t), \tag{6}$$

where $A_{\mu\eta}^k$ is a spin operator and $\Phi_{\mu\eta}^{(-k)}(t)$ is a random function of time.

The Hamiltonian (6) represents a time dependent perturbation of small amplitude [19]. The spin-lattice coupling is supposed to be a random function of time, an approach that corresponds to considering the lattice classically.

For a bulk liquid or gas sample, molecular diffusion [19, 20] will cause the dipole–dipole interaction Hamiltonian to effectively vanish because the intensity of interaction depends on the angle $\theta_{\mu\eta}$ as $P_2\left(\cos\theta_{\mu\eta}\right)$, see (5). The average value of this quantity over the sphere is zero. In a nanosized cavity, molecules of the gas or liquid system will subject to restricted diffusion. Then the motional time throughout the whole cavity is much shorter than the NMR time scale, $t_{\mathrm{mov}} \ll t_{\mathrm{NMR}}$ [13–16]. Let us estimate the characteristic size of the nanocavity, where each spin in the liquid sample will experience the nonzero average dipolar interaction. The diffusion coefficient of the molecules of water can be estimate by using the Einstein–Stokes equation for diffusion of spherical particles through liquids with low Reynolds number, $D = \frac{k_{\mathrm{B}}T}{6\pi\sigma a}$, where k_{B} is the Boltzmann constant, T is the absolute temperature of the lattice, $\sigma = 8.94\cdot 10^{-4}\,\frac{\mathrm{Ns}}{\mathrm{m}^2}$ is the dynamic viscosity of the solvent, and $a = 2\cdot 10^{-10}$ m is the molecular van der Waals radii of a soluble in aqueous solution [21]. Within this hydrodynamic model, with the assumption of a complete contact between the solute surface and the solvent, the so-called stick limit, for the soluble molecules in aqueous solution, we have the diffusion coefficient $D \approx 2\cdot 10^{-9}\,\frac{\mathrm{m}^2}{\mathrm{s}}$.

The typical NMR time scale, that characterizes the flip–flop transition, is $t_{\mathrm{NMR}} = \frac{a^3}{\gamma^2\hbar} \simeq 10^{-5}$ s. Estimation of the size of nanocavity, where the DDIs are not averaged to zero, gives $l \ll \sqrt{D\cdot t_{\mathrm{NMR}}} \simeq 100$ nm. Therefore for porous materials the typical length of the cavity filled by a liquid must be much smaller than 100 nm where the DDIs can not be averaged to zero. Another limitation is the shape of the cavity, which should not be a sphere [13, 16]. Then, taking into account the ergodic theorem [13–15], the evolution in a nanosize cavity can be described by the averaged DDI Hamiltonian,

$$\bar{H}_{\mathrm{d}} = G\sum_{\mu\neq\eta}\left[I_{z\mu}I_{z\eta} - \frac{1}{4}\left(I_{+\mu}I_{-\eta} + I_{-\mu}I_{+\eta}\right)\right], \tag{7}$$

with space-independent pair couplings G for any pair of spins μ and η [14, 15],

$$G = \frac{\gamma^2\hbar}{V} P_2(\cos\theta) F, \tag{8}$$

where V is the volume of the cavity and F is the form factor depending on the geometric shape and dimensions of the cavity. θ denotes the orientation of the cavity with respect to the external magnetic field (Fig. 1). The averaged DDI Hamiltonian (7) can be rewritten in

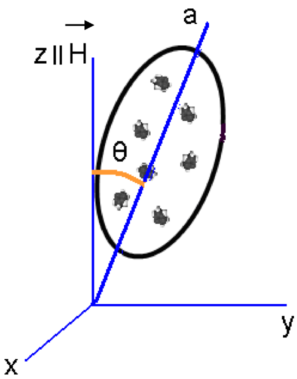

Fig. 1 (colour online). Soluble molecules in an aqueous solution in a nanocavity in an external magnetic field directed along the z-axis. θ is the angle between the external magnetic field $\vec{H}$ (parallel to z-axis) and the principal axis a of the nanovoid.

the form [15]

$$\bar{H}_\mathrm{d} = \frac{G}{2}\left[3I_z^2 - \vec{I}^2\right], \tag{9}$$

where $\vec{I}^2 = I_x^2 + I_y^2 + I_z^2$ is the square of the total nuclear spin operator.

3. Pulse Transfer Zeeman Order into Dipolar Order

Since in a high external magnetic field $\omega_0 \gg \omega_\mathrm{loc}$, where $\omega_\mathrm{loc} = \sqrt{\frac{\mathrm{Tr}\left(\bar{H}_\mathrm{d}^2\right)}{\mathrm{Tr} I_z^2}} = \frac{G}{2}\sqrt{3N}$ is a local field at the position of the nuclear spins, most of the energy of the nuclear-spin system belongs to the Zeeman order which is characterized by the averaged value of nuclear magnetization oriented along the external magnetic field. Initially, at thermal equilibrium at high temperature approximation [1] with the lattice, the density matrix is

$$\rho_\mathrm{eq} = 1 - \beta_1 \omega_0 \sum_\mu I_{z\mu}, \tag{10}$$

where $\beta_1 = \frac{1}{k_\mathrm{B} T}$. Applying a $\frac{\pi}{2}$-pulse with the RF field along the x-axis, the density matrix immediately after the pulse takes the form

$$\begin{aligned}\rho_1 &= \exp\left(-\mathrm{i}\frac{\pi}{2}\sum_\mu I_\mu^x\right)\rho_\mathrm{eq}\exp\left(\mathrm{i}\frac{\pi}{2}\sum_\mu I_\mu^x\right)\\ &= 1 - \beta_1\omega_0 \sum_\mu I_\mu^y .\end{aligned} \tag{11}$$

At time $\tau < T_2$ (here T_2 is the spin-spin relaxation time), the density matrix is governed by the equation

$$\rho(\tau) = 1 - \beta_1\omega_0 \exp\left(-\mathrm{i}\tau\bar{H}_\mathrm{d}\right)\sum_\mu I_\mu^y \exp\left(\mathrm{i}\tau\bar{H}_\mathrm{d}\right). \tag{12}$$

Using the identity

$$\exp\left(\mathrm{i}\varphi I_{\mu z}\right) = \cos\left(\frac{\varphi}{2}\right)E_\mu + 2\mathrm{i} I_{\mu z}\sin\left(\frac{\varphi}{2}\right) \tag{13}$$

and (9), then (12) may be rewritten as

$$\begin{aligned}\rho(\tau) = 1 - \beta_1\omega_0 \sum_\mu \Bigg\{ I_\mu^y \left[\cos^2\left(\frac{3}{8}G\tau\right)\right.\\ \left. + 4 I_z I_\mu^z \sin^2\left(\frac{3}{8}G\tau\right)\right] - I_\mu^x\left(I_z - I_\mu^z\right)\sin\left(\frac{3}{4}G\tau\right)\Bigg\}.\end{aligned} \tag{14}$$

Then a second pulse of angle ξ to the $\frac{\pi}{2}$-phase shift RF field is applied. Then the density matrix in (14) is changed according to

$$\begin{aligned}\rho_2 &= \exp\left(-\mathrm{i}\xi\sum_\mu I_\mu^y\right)\rho(\tau)\exp\left(\mathrm{i}\xi\sum_\mu I_\mu^y\right)\\ &= 1 - \beta_1\omega_0\sum_\mu \Bigg\{ I_\mu^y\left[\cos^2\left(\frac{3}{8}G\tau\right) + 4(I_z\cos\xi\right.\\ &\left. + I_x\sin\xi)\left(I_\mu^z\cos\xi + I_\mu^x\sin\xi\right)\sin^2\left(\frac{3}{8}G\tau\right)\right]\\ &- \left(I_\mu^x\cos\xi - I_\mu^z\sin\xi\right)\left[\left(I_z - I_\mu^z\right)\cos\xi\right.\\ &\left. + \left(I_x - I_\mu^x\right)\sin\xi\right]\sin\left(\frac{3}{4}G\tau\right)\Bigg\}.\end{aligned} \tag{15}$$

After a time $T_2 < t \ll T_1$ (here T_1 is the spin-lattice relaxation time), the density matrix is of the form [1]

$$\rho_f = 1 - \beta_\mathrm{d}\bar{H}_\mathrm{d} \tag{16}$$

with the inverse dipolar temperature

$$\beta_\mathrm{d} = -\frac{\mathrm{Tr}\left\{\rho_2\bar{H}_\mathrm{d}\right\}}{\mathrm{Tr}\left\{\bar{H}_\mathrm{d}^2\right\}} = \beta_1\frac{\omega_0}{4G}\sin(2\xi)\sin\left(\frac{3}{4}G\tau\right). \tag{17}$$

In the quasi-equilibrium (16), each nuclear-spin is oriented along an internal local field and most of the energy of the nuclear-spin system resides in the nuclear dipolar reservoir. The inverse dipolar temperature reaches its maximum $\beta_\mathrm{d} = \beta_1\frac{\omega_0}{4G}$ when $\xi = \frac{\pi}{4}$ [1] and $\tau = \frac{2}{3}\frac{\pi}{G}$.

4. Spin-Lattice Relaxation of the Dipolar Order

The quasi-equilibrium (16) corresponds to the spin system with an infinite temperature of Zeeman reservoir and a finite temperature dipole reservoir β_{d} (17). Since the magnitude of the Zeeman interaction is much larger than the DDI $\omega_0 \gg \omega_{\mathrm{loc}}$, we have $\beta_{\mathrm{d}} \gg \beta_{\mathrm{l}}$. Thus the dipole subsystem is in a state with low spin temperature. The spin-lattice interaction will bring the dipolar reservoir in equilibrium with the lattice, i.e. will align the inverse temperatures β_{d} and β_{l}.

The evolution equation for the dipolar energy and the spin-lattice relaxation rate will be derived by using the method of the non-equilibrium state operator [22], which gives

$$\begin{aligned}\frac{\mathrm{d}\langle \bar{H}_{\mathrm{d}}\rangle}{\mathrm{d}t} = {} & (\beta_{\mathrm{d}}-\beta_{\mathrm{l}}) \sum_{k=-2}^{2} \sum_{\mu\neq\eta} \int_0^1 \mathrm{d}\lambda \int_{-\infty}^{0} \mathrm{d}\tau\, \mathrm{e}^{-\varepsilon\tau} \\ & \cdot G_{\mu\eta}^{(q)}(\tau) \left\langle K_{\mu\eta}^{(q)}(\lambda) K_{\mu\eta}^{(q)} \right\rangle .\end{aligned} \tag{18}$$

Here the thermodynamic average $\langle \ldots \rangle$ corresponds to an average with the quasi-equilibrium density matrix (16), and the transition to the limit $\varepsilon \to +0$ should be made after the calculation of the integral.

The definition of operator K is given by [22]

$$K_{\mu\eta}^{(q)} = \mathrm{i}\left[A_{\mu\eta}^{(q)}, \bar{H}_{\mathrm{d}}\right], \tag{19}$$

$$K(\lambda) = \mathrm{e}^{\lambda \bar{H}_{\mathrm{d}}} K \mathrm{e}^{-\lambda \bar{H}_{\mathrm{d}}}, \tag{20}$$

$$G_{\mu\eta}^{(q)}(\tau) = \left\langle \Phi_{\mu\eta}^{(q)}(t) \Phi_{\mu\eta}^{(-q)}(t+\tau) \right\rangle_t . \tag{21}$$

The random functions $\Phi_{\mu\eta}^{(q)}(t)$ are assumed to be stationary and symmetric upon the time reversal, and the ensemble average is equal to the time average $\left\langle \Phi_{\mu\eta}^{(q)}(t)\, \Phi_{\mu\eta}^{(-q)}(t+\tau) \right\rangle_t$[1].

Assume that the spin-lattice relaxation is determined by the non-average part of the dipolar Hamiltonian. Then the operator $A_{\mu\eta}^{(k)}$ and functions $\Phi_{\mu\eta}^{(-k)}$ take the following form:

$$\begin{aligned} A_{\mu\eta}^{(0)} &= -\frac{2}{3} I_{z\mu} I_{z\eta} + \frac{1}{6}\left(I_{+\mu} I_{-\eta} + I_{-\mu} I_{+\eta}\right), \\ A_{\mu\eta}^{(1)} &= I_{z\mu} I_{+\eta} + I_{+\mu} I_{z\eta}, \quad A_{\mu\eta}^{(2)} = I_{+\mu} I_{+\eta}, \end{aligned} \tag{22}$$

$$\begin{aligned} \Phi_{\mu\eta}^{(0)} &= \alpha_{\mu\eta}\left(1 - 3\cos^2\theta_{\mu\eta}\right), \\ \Phi_{\mu\eta}^{(1)} &= \frac{\alpha_{\mu\eta}}{2} \sin 2\theta_{\mu\eta}\, \mathrm{e}^{-\mathrm{i}\varphi_{\mu\eta}}, \\ \Phi_{\mu\eta}^{(2)} &= \alpha_{\mu\eta} \sin^2\theta_{\mu\eta}\, \mathrm{e}^{-2\mathrm{i}\varphi_{\mu\eta}}, \end{aligned} \tag{23}$$

and $\Phi_{\mu\eta}^{(k)} = \Phi_{\mu\eta}^{(-k)*}$, $A_{\mu\eta}^{(k)} = A_{\mu\eta}^{(-k)*}$, $\alpha_{\mu\eta} = -\frac{3\gamma^2}{2r_{\mu\eta}^3}$. Taking into account that in the high temperature approximation

$$\langle \bar{H}_{\mathrm{d}} \rangle = -\beta_{\mathrm{d}} \mathrm{Tr}\left(\bar{H}_{\mathrm{d}}^2\right), \tag{24}$$

we obtain

$$\frac{\mathrm{d}\beta_{\mathrm{d}}}{\mathrm{d}t} = -W\left(\beta_{\mathrm{d}} - \beta_{\mathrm{l}}\right), \tag{25}$$

where W is the transition probability per unit time,

$$W = \frac{1}{2}\left(\frac{3G}{4}\right)^2 N\tau_{\mathrm{c}}, \tag{26}$$

and τ_{c} is the correlation time of the thermal molecular motion.

5. Conclusion

From (25), describing the evolution of the inverse temperature, it follows that the spin-lattice relaxation of the dipolar subsystem in a liquid entrapped into nanosize cavities occurs with a single-exponential law with a relaxation time $T_{1\mathrm{d}} = \frac{1}{W}$. It can be seen from (17) and (26) that the inverse dipolar temperature β_{d} and the spin-lattice relaxation time $T_{1\mathrm{d}}$ depend on the cavity size V, its shape F and orientation θ, $\beta_{\mathrm{d}} \sim V \frac{\sin\left(\frac{3}{4}\frac{\gamma^2\hbar}{V} P_2(\cos\theta) F\tau\right)}{P_2(\cos\theta)F}$ and $T_{1\mathrm{d}} \sim \left(\frac{V}{F(1-3\cos^2\theta)}\right)^2$, respectively. When the inverse temperature reaches the maximum, the dependence is greatly simplified to $\beta_{\mathrm{d}} \sim \frac{V}{\left(1-3\cos^2\theta\right)F}$, and it is convenient for practical application. For a large number of spins, in the limit $N \to \infty$, $V \to \infty$, and $\frac{N}{V} = C$ (the molecular concentration), we obtain that $W \sim \frac{C^2}{N}$. Therefore, measurements of the inverse dipolar temperature and the relaxation time in the local fields provide an important information about the cavity size V, its shape F, and the orientation θ (with respect to the external magnetic field) of the nanopores. It should be noted that the results of the calculation remain valid for other methods of transfer of spin order to the dipole subsystem, for example, using an adiabatic diagmagnetization or cross relaxation [1].

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