Proceedings of the 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13–17, 2016

Effect of Stochastic Dynamics on the Nuclear Magnetic Resonance in a Field Gradient

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In the present contribution, the attenuation function $S(t)$ for an ensemble of spins in a magnetic-field gradient is calculated through an accumulation of the phase shifts in the rotating frame resulting from the changes of the particle displacements. The found $S(t)$ is applicable for any kind of the stochastic motion of spins, including their non-Markovian dynamics with memory. Depending on the considered system, both the classical expressions valid for normal diffusion at long times and new formulae for the short-time Brownian motion can be obtained. Our method is also applicable to the NMR pulse sequences based on the refocusing principle. This is demonstrated by describing the spin echo experiment developed by Hahn.

DOI: 10.12693/APhysPolA.131.1111

PACS/topics: 76.60.–k, 76.60.Lz, 05.40.–a, 05.10.Gg

1. Introduction

Nuclear magnetic resonance (NMR) has proven to be an effective means of studying molecular self-diffusion and diffusion in various materials and has a wide range of applications ranging from characterization of solutions to inferring microstructural features in biological tissues [1–5]. The influence of diffusion on the signal of the NMR experiment, such as the spin echo, is described by the diffusion suppression function$S(t)$. In the literature, $S(t)$ is usually calculated by using the Bloch–Torrey equation for the spin magnetization. Another way is to evaluate $S(t)$ through the time-dependent resonance frequency offset in the rotating frame, which is expressed through the position $x(t)$ of the nuclear spin [3, 4]. It is assumed that $x(t)$ is a Gaussian random process. The known results in both the approaches are, however, valid only within the long-time (diffusion) approximation and are inapplicable for shorter times of the stochastic motion of spin-bearing particles, except the standard (memoryless) Langevin theory [5, 6].

No correct formulae are available for the attenuation function $S(t)$ describing the effect of the Brownian motion in the NMR experiments on systems in a magnetic-field gradient that would take into account possible memory effects in the dynamics of spins. The recent attempt [4] to overcome this limitation operates with the positional autocorrelation function (PAF), which is not defined for unbounded particle motion, described by the standard or generalized Langevin equation. In the present contribution, the function $S(t)$ for an ensemble of spins in a magnetic-field gradient is expressed through an accumulation of the phase shifts in the rotating frame due to the changes of the particle displacements. Instead of the PAF, we deal with the mean square displacement (MSD) $X(t)$, the well-defined and experimentally measured function. The obtained new formulae for $S(t)$ and the NMR line broadening due to the particle motion in a simple experiment, when the nuclear induction signal is read-out in the presence of a field gradient, significantly differ from the known ones and are applicable for any kind of the stochastic motion of spins, including their non-markovian Brownian motion and anomalous diffusion. The classical expressions valid for diffusion are just special cases within our consideration that can be easily obtained within the long-time approximation. The method is also applicable to the NMR pulse sequences based on the refocusing principle. This is demonstrated by describing the spin echo experiment developed by Hahn.

2. Nuclear induction signal in the presence of a magnetic-field gradient

Let us consider an experiment, in which the nuclear induction signal is read-out in the presence of a magnetic-field gradient [4]. The liquid or gaseous system is in a sufficiently strong external field and the gradient is unidirectional. The magnetization of an ensemble of spins is modulated by the gradient and the measurement of time evolution of this magnetization possesses the molecular self-diffusion coefficient D. The total magnetization determining the observed NMR signal is given by the product of the magnetization without the influence of diffusion and the diffusion suppression function $S(t)$. This function can be expressed as [2–7]:

$$S(t) = \langle \exp\left(\mathrm{i}\,\phi(t)\right)\rangle = \left\langle \exp\left(\mathrm{i}\int_0^t \omega(\tau)\,\mathrm{d}\tau\right)\right\rangle, \qquad (1)$$

where $\omega(t)$ is the time-dependent resonance frequency offset in the rotating frame and the brackets $\langle\ldots\rangle$ indicate

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an ensemble averaging. In the literature, see, e.g., [3, 8], the relation $\omega(t) = \gamma_n g x(t)$ is used, where g is the applied gradient strength, γ_n is the nuclear gyromagnetic ratio, and $x(t)$ is the position of the spin after time t. Then, for a Gaussian random process,

$$S(t) = \exp\left(-(1/2)\left\langle\phi^2(t)\right\rangle\right), \quad (2)$$

and, taking into account stationarity,

$$S(t) = \exp\left(-\gamma_n^2 g^2 \int_0^t \langle x(t')x(0)\rangle (t-t')\,\mathrm{d}t'\right). \quad (3)$$

Substituting here $\langle x(t)x(0)\rangle \approx 2Dt$ as the PAF [4], the classical "textbook" expression for the diffusion suppression is obtained,

$$S(t) = \exp\left(-(1/3)\gamma_n^2 g^2 D t^3\right). \quad (4)$$

However, beyond the $t \to \infty$ limit this approach is not applicable. Already within a more general standard Langevin theory for unbounded Brownian motion the PAF is ill defined [9]. The incorrectness of Eq. (3) is seen also from the following physical view. Let the spin-bearing particles are trapped in a harmonic well with the elastic constant k. At short times the motion of the particles is not affected by the trap. It is thus no reason that the influence of the trap would be reflected in $S(t)$. However, $S(t)$ from (3) is at $t \to 0$ determined mainly by k, since $\left\langle x^2\right\rangle \approx k_{\mathrm{B}}T/k$ [10].

The quantity that should be used in the description of the influence of stochastic motion of spins on the NMR experiments is the MSD, $X(t) = \left\langle [x(t)-x(0)]^2\right\rangle$. The normal diffusion MSD at $t \to \infty$ tends to infinity as $2Dt$, which is not consistent with the approximation $\langle x(t)x(0)\rangle \approx \langle x(t)x(t)\rangle = 2Dt$ [4]. In Eq. (1), $\omega(t)$ should be $\omega(t) = \gamma_n g\,(x(t)-x(0))$, the *change* of the phase in the rotating frame during the time t, instead of the phase given by the spin position at time t. The discussed controversy is then naturally resolved as follows. For the Gaussian random processes (or small ϕ) we use Eq. (2), where now

$$\left\langle\phi^2(t)\right\rangle = \int_0^t\int_0^t \mathrm{d}t'\,\mathrm{d}t''\,\langle\omega(t')\omega(t'')\rangle = (1/2)\gamma_n^2 g^2 \times \int_0^t\int_0^t \mathrm{d}t'\,\mathrm{d}t''\,(X(t')+X(t'')-X(t''-t')). \quad (5)$$

Since for stationary processes $X(t)$ is a symmetric function, we can use the following transformation:

$$\int_0^t\int_0^t \mathrm{d}t'\,\mathrm{d}t'' X(t''-t') = 2\int_0^t \mathrm{d}t'\,(t-t')\,X(t'). \quad (6)$$

Equations (6), (5) and (2) then give the final simple result

$$S(t) = \exp\left(-(1/2)\gamma_n^2 g^2 \int_0^t \tau X(\tau)\,\mathrm{d}\tau\right), \quad (7)$$

which is model-independent, applicable for any times and a character of the stochastic motion of spins. Most often, the normal (Einstein) diffusion is observed in liquids and gases. Then, at long times, $X(t) \approx 2Dt$ and we return to the classical formula (4). The measured spectral line broadening due to diffusion (half width at half maximum) is $\omega_{1/2} \approx \sqrt{6}a^{1/3}$, where $a \approx \gamma_n^2 g^2 D/3$ [11]. At short times, the motion of particles is ballistic [12], $X(t) \approx k_{\mathrm{B}}Tt^2/M$ as $t \to 0$ (M plays a role of the particle mass), so that

$$S(t) \approx \exp\left(-k_{\mathrm{B}}T\gamma_n^2 g^2 t^4/8M\right) \quad (8)$$

and $\omega_{1/2}^2 \approx 4\Gamma(5/4)\Gamma^{-1}(3/4)\left(k_{\mathrm{B}}T\gamma_n^2 g^2/8M\right)^{1/2}$.

Usually, the suitable description of the NMR experiments corresponds to long times. In Ref. [4], the stochastic motion of spins in gases was described by using the generalized Langevin equation, in which the friction force was modeled by the convolution of a memory kernel with the particle velocity. The kernel exponentially decreased in time. The induction signal has been obtained by using Eq. (3) for long times as $S(t) \approx \exp\left(-\gamma_n^2 g^2 \kappa t\right)$, where $\kappa = k_{\mathrm{B}}TM^2\gamma^{-3}$ (γ is the Stokes friction coefficient proportional to the gas viscosity). Since at high temperatures the viscosity of gases is $\approx T^{1/2}$, the authors conclude that $\omega_{1/2} \sim T^{-1/2}$. This prediction is not correct, since the MSD within the used theory behaves at long times as $X(t) \approx 2Dt$, the diffusion attenuation function is given by Eq. (4), and, consequently, $\omega_{1/2} \sim T^{1/6}$.

3. Hahn spin echo

Modern NMR pulse sequences come from the simple refocusing principle of the spin echo developed by Hahn [13]. In this experiment, at time $t = \tau$ after the first 90° rf pulse at $t = 0$ the spin phases are inverted by a 180° pulse. Measurements of the echo signal amplitude at time 2τ allow accurate determining of the diffusion coefficients of nuclear spins. During the experiment, a static magnetic field that creates macroscopic magnetization along the axis x and a constant linear magnetic field gradient g are applied. Acting as in the previous section, we express the attenuation of the signal due to the stochastic motion of spins (2) through the accumulation of the changes of spin phases $\phi(t)$. Instead of Eq. (5) we now have

$$\left\langle\phi^2(t)\right\rangle = \gamma_n^2 g^2 \left\langle\left[\int_0^\tau (x(t')-x(0))\,\mathrm{d}t' - \int_\tau^t (x(t')-x(0))\,\mathrm{d}t'\right]^2\right\rangle. \quad (9)$$

The sign before the second integral accounts for the fact that at time τ all phases are inverted. Equation (9) can be again expressed through the MSD. After the averaging and use of the stationarity condition one finds

$$\left\langle\phi^2(t)\right\rangle/\gamma_n^2 g^2 = \int_0^t \mathrm{d}t'(t'-2\tau)X(t') + 2\int_0^\tau \mathrm{d}t'(2t'-t)X(t') + 2\int_0^t \mathrm{d}t'\int_0^\tau \mathrm{d}t'' X(t'-t''). \quad (10)$$

Other equivalent forms of Eq. (10) are possible as well. In the special case of the Einstein–Fick diffusion we get from Eqs. (10) and (2) at $t = 2\tau$ the famous Stejskal–Tanner formula [14]:

$$S(2\tau) = \exp\left(-2\gamma_n^2 g^2 D\tau^3/3\right). \tag{11}$$

At arbitrary $t > \tau$:

$$S(t) = \exp\left(-\gamma_n^2 g^2 D(t^3 - 6t\tau^2 + 6\tau^3)/3\right). \tag{12}$$

It is interesting that the maximum of the function $S(t)$ is not at the echo time 2τ but at $t = \sqrt{2}\tau$. This result has been for the first time obtained and experimentally verified in [3].

4. Anomalous diffusion of spins

It is important that the obtained general formulae for the NMR induction decay and spin echo are applicable for any kind of the Brownian motion of spin-bearing particles. At long times, they can be used to interpret the experiments on system exhibiting both normal and anomalous diffusion.

Let us assume that at long time the MSD satisfies the formula $X(t) = Ct^\alpha$, where C is a temperature-dependent constant, $\alpha = 1$ corresponds to normal diffusion (then $C = 2D$), $\alpha < 1$ to sub-diffusion, and $\alpha > 1$ to super-diffusion [15]. In Ref. [16], the expressions for the attenuation of the NMR signal due to anomalous diffusion were obtained assuming that $X(t)$ is equal to the mean square distance $\langle x^2(t)\rangle$. Here, without this assumption, it is easy from (10) to find $\langle \phi^2(t)\rangle$ that determines the damping of the spin echo signal and generalizes (12). At the echo time it reduces to a simple formula obtained in [16] in a much more tedious way

$$\langle \phi^2(2\tau)\rangle = 4\gamma_n^2 g^2 C\left(2^\alpha - 1\right)\frac{\tau^{\alpha+2}}{(\alpha+1)(\alpha+2)}. \tag{13}$$

After substituting it in Eq. (2), at $\alpha = 1$ we return to Eq. (11).

5. Conclusions

For many experimental situations the description of the diffusion-based NMR experiments needs to properly take into account the stochastic motion of spins, which can be very different. Often the memory in the particle dynamics plays a significant role [12]. In such cases, the existing theories are suitable only at long times, when the particles are in the diffusion regime. We have shown that the attempt [4] to account for the memory effects as they are revealed at shorter times was not successful. In the present work, the attenuation function due to the stochastic motion of spin-bearing particles is evaluated for two examples: when the nuclear induction signal is measured in the presence of a field gradient, and for the Hahn spin echo experiment with a steady gradient. The observed damping of the signal is calculated through the accumulation of the spin phases in the frame rotating with the resonance frequency. Coming from the changes of the phases during the time of observation, this accumulation is represented through the mean square displacement for stationary and Gaussian random processes. The obtained formulae give known results in the case of normal and anomalous diffusion but its main application is aimed for systems described by other models, e.g., by the standard Langevin equation or its various generalizations.

Acknowledgments

This work was supported by the Agency for the Structural Funds of the EU within the project NFP 26220120033, and by the Ministry of Education and Science of the Slovak Republic through grant VEGA No. 1/0348/15.

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