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ANALYSIS OF NMR SELF-DIFFUSION MEASUREMENTS BY A DENSITY MATRIX CALCULATION

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The density matrix formalism with the Magnus expansion of the time evolution operator is used to study the nmr response in a pulsed magnetic field gradient (mfg) spin-echo experiment. The results show that the spin-echo cannot only measure the self-diffusion coefficient but can determine the spectrum of the single-particle velocity autocorrelation function as well. The proper combination of rf and mfg pulse sequences are proposed for measuring self-diffusion in spin systems with strong dipolar coupling where the classical method fails.

1. Introduction

The measurement of self-diffusion coefficients requires the labelling somehow of the diffusing species. In magnetic resonance this is accomplished by unique spin properties such as the Larmor frequency. If an inhomogeneous external magnetic field is applied the spin precession frequency changes with location. Thus the change of spin position is registered as a change in frequency. This idea has been exploited by using the spin-echo amplitude as an indication of translational motion [1]. With the spin-echo experiment it is possible to measure directly the self-diffusion coefficient of atoms or molecules containing the nuclear spin being observed.

A number of publications on nuclear magnetic resonance measurements of the self-diffusion coefficient shows a progressive interest in this method. The original method with the spin-echo in a gradient field [1] has been improved by using pulse gradients [2] rather than a steady magnetic field gradient (mfg). Some other improvements include the use of Fourier transform spectroscopy [3] to resolve the diffusion coefficient of different components, measurements of restricted diffusion [4], the use of various modifications of pulsed technique to remove the background field gradient [5], the use of the nonuniform radiofrequency field [6], the application of radiofrequency (rf) pulse sequences to destroy mutual spin interaction [7] etc. These techniques have been successfully applied to the studies of random nonlocalized molecular motions in liquids and gases.

When treating the self-diffusional damping of the spin-echo, the so-called Bloch–Torrey [1] equations are usually employed. These are the phenomenological Bloch equations, including terms due to the transfer of magnetization by particle migration. This approach explains the idea in a simple way but it does not show all the details. Here the density matrix formalism will be used to study the nmr response at the pulsed mfg spin-echo experiment. The results of this approach show that the spin-echo is feasible not only to measure the self-diffusion coefficient but also to determine the spectrum of the single-particle velocity autocorrelation function, at least in principle. The combination of the multiple rf pulse sequences and the mfg pulses, which was invented [7–9] to measure the self-diffusion in spin systems with strong dipolar coupling where the classical method fails, is considered in the last section, using the density matrix calculation and the Magnus expansion of the time evolution operator. The proper combinations of rf and mfg sequences are found and various spurious effects accompanying the experimental results are established.

2. Time-evolution operator

When treating the self-diffusion measurements by the mfg spin-echo experiment the system of nuclear spins is governed by the Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_z + \mathcal{H}_D^{(0)} + \mathcal{H}_G(t) + \mathcal{H}_{rf}(t) + \mathcal{H}_L, \tag{1}$$

where the first term is due to the spin interaction with the static magnetic field H_0

$$\mathcal{H}_z = -\gamma H_0 I_z, \tag{2}$$

the second term is the secular part of the spin dipole–dipole Hamiltonian*

$$\mathcal{H}_D^{(0)} = 2 \sum_{i>k} \beta_{ik} [\tfrac{1}{4}(i_+^i i_-^k + i_-^i i_+^k) - i_z^i i_z^k], \tag{3}$$

and the interactions with the external magnetic field gradient (mfg) are described by

$$\mathcal{H}_G(t) = -\gamma G(t) \cdot \sum_i r_i i_z^i, \tag{4}$$

where $G = \text{grad}\,|B(t)|$ and r_i denotes the location of the ith spin.

The interactions with the radiofrequency field are included in

$$\mathcal{H}_{rf}(t) = -\gamma H_1(t) I_x \cos \omega_0 t, \tag{5}$$

where $H_1(t)$ is the amplitude of the rf magnetic field and ω_0 is the spin Larmor frequency. The interactions with the remaining degree of freedom are included in the Hamiltonian $\mathcal{H}_L$.

The density matrix of the nuclear spin system is governing according to the Liouville equation

$$\frac{d\rho(t)}{dt} = [\mathcal{H}(t), \rho(t)], \tag{6}$$

(in units where $h = 1$), the formal solution of which may be written as

$$\rho(t) = U(t)\rho(0)U^+(t), \tag{7}$$

where $\rho(0)$ is the initial density matrix at $t = 0$ and $U(t)$ is the time developing operator

$$U(t) = T \exp\left[-i \int_0^t \mathcal{H}(t')\,dt'\right]. \tag{8}$$

Expression (8) includes the time-ordering operator T which orders to the left operators of greater time arguments in the exponential form, and which actually prevents the performing of the simple integration of the exponent in (8). Therefore some tricks should be used in order to evaluate $U(t)$. Part of the time dependence of $U(t)$ can be

* It is assumed that the static magnetic field is strong enough to take into account only the part of the spin dipole–dipole Hamiltonian commuting with $\mathcal{H}_z$.

removed by the transformation of the spin system into the frame rotating around the z-axis with frequency ω_0. This is accomplished by the separation of the time-evolution operator into two parts

$$U(t) = U_z(t)\, U'(t), \tag{9}$$

where the Zeeman part is

$$U_z(t) = \exp(-\mathrm{i}\mathcal{H}_z t), \tag{10}$$

and the part which includes the remaining interactions in the exponent is

$$U'(t) = T \exp\left[-\mathrm{i} \int_0^t \tilde{\mathcal{H}}(t')\, \mathrm{d}t'\right], \tag{11}$$

where

$$\tilde{\mathcal{H}}(t) = U_z^+(t)[\mathcal{H}(t) - \mathcal{H}_z]\, U_z(t). \tag{12}$$

Evaluation of (12) gives the rotating frame Hamiltonian

$$\tilde{\mathcal{H}}(t) = \mathcal{H}_D^{(0)} - \gamma G(t) \sum_i r_i i_z^i - \gamma H_1(t) I_x + \mathcal{H}_L, \tag{13}$$

where its time dependence is now due only to the pulse excitation of the rf field amplitude $H_1(t)$ as well as the applied magnetic field gradient $G(t)$. But the procedure of splitting the time-evolution operator into terms which are due to various kinds of spin interaction (9) can be repeated again as long as one gets the expression

$$U(t) = U_z(t)\, U_{\mathrm{rf}}(t)\, U_G(t)\, U_D(t) \tag{14}$$

with

$$U_{\mathrm{rf}}(t) = T \exp\left[\mathrm{i} \int_0^t \gamma H_1(t') I_x\, \mathrm{d}t'\right], \tag{14a}$$

$$U_G(t) = T \exp\left[-\mathrm{i} \int_0^t \tilde{\mathcal{H}}_G(t')\, \mathrm{d}t'\right], \tag{14b}$$

where

$$\tilde{\mathcal{H}}_G(t) = -U_{\mathrm{rf}}^+(t) \left[\gamma G(t) \sum_i r_i i_z^i\right] U_{\mathrm{rf}}(t) \tag{14c}$$

and

$$U_D(t) = T \exp\left[-\mathrm{i} \int_0^t \tilde{\mathcal{H}}_D^{(0)}(t')\, \mathrm{d}t'\right] \tag{14d}$$

with

$$\tilde{\mathcal{H}}_D^{(0)}(t) = U_G^+(t)\, U_{rf}^+(t)\, \mathcal{H}_D^{(0)}\, U_{rf}(t)\, U_G(t). \tag{14e}$$

Thus, the Hamiltonians in the exponents of (14a), (14b) and (14d) are in the interaction representation. The initial gradient Hamiltonian $\mathcal{H}_G(t)$ is transformed into the frame tilting according to the rf field pulse excitation (14c) while the dipolar Hamiltonian $\mathcal{H}_D^{(0)}$ is transformed, at first, into the tilting frame by $U_{rf}(t)$ and afterwards into the frame which is nonuniformly rotating by $U_G(t)$. The transformed dipolar Hamiltonian becomes time dependent which changes the effective dipole–dipole interactions in the spin system.

The separation of $U(t)$ into various terms (14), which are due to different kinds of spin interactions, makes sense only in the case when it simplifies further evaluation. Here we are dealing with an nmr pulse experiment where only the instantaneous values of the spin observables are monitored in some short time intervals, called the sampling points. And whenever the applied rf and mfg multipulse sequence has the property of being cyclic, i.e. at the sampling points, τ their time evolution operator is

$$U_{rf}(\tau) = U_G(\tau) \equiv 1. \tag{15}$$

Then at these particular points the spin time-evolution operator is defined only by the dipolar part of the interactions

$$U(\tau) = U_D(\tau). \tag{16}$$

In this way the problem has been reduced to the evaluation of the dipolar part of $U(t)$ only, with the effective time-dependent dipolar Hamiltonian in the exponent (14d). But the time-ordering operator T prevents us performing just a simple integration of the exponent. To overcome this, Magnus [9] was able to derive the expression for such cases in the form

$$U(t) = \exp(-iF(t)), \tag{17}$$

where $F(t)$ is the series

$$F(t) = F_0(t) + F_1(t) + F_2(t) + F_3(t) + \ldots. \tag{17a}$$

The first three terms of the expansion (17a) are explicitly

$$F_0(t) = \int_0^t \tilde{\mathcal{H}}_D^{(0)}(t')\,dt', \tag{17b}$$

$$F_1(t) = -\tfrac{1}{2} \int_0^t dt_1 \int_0^t dt_2\, [\tilde{\mathcal{H}}_D^{(0)}(t_1), \tilde{\mathcal{H}}_D^{(0)}(t_2)], \tag{17c}$$

$$F_2(t) = (1/6) \int_0^t dt_1 \int_0^{t_1} dt_2 \int_0^{t_3} dt_3\, [\tilde{\mathcal{H}}_D^{(0)}(t_1), [\tilde{\mathcal{H}}_D^{(0)}(t_2), \tilde{\mathcal{H}}_D^{(0)}(t_3)]] + [\tilde{\mathcal{H}}_D^{(0)}(t_3), [\tilde{\mathcal{H}}_D^{(0)}(t_2), \tilde{\mathcal{H}}_D^{(0)}(t_1)]]. \tag{17d}$$

Knowing the time dependence of $\mathcal{H}_D^{(0)}(t)$ it is possible to integrate $U(t)$ using the formulas (17)–(17d), thus obtaining a simple series expansion for the effective dipolar Hamiltonian.

3. Spin-echo with the magnetic field gradient

In this section the density matrix formalism will be employed to consider the self-diffusion measurement by a simple pulse–mfg spin-echo technique. This technique is the basic $90°-\tau-180°$ spin-echo rf sequence by adding magnetic field gradient pulses between 90° and 180° rf pulses and identical gradient pulses between 180° rf pulse and the spin-echo (fig. 1). The spin-echo signal which follows after time 2τ is induced by the transverse component of magnetization

$$\langle I_x(2\tau)\rangle = \langle \mathrm{Tr}_s I_x \rho(2\tau)\rangle_L. \tag{18}$$

Here the trace is running over the spin coordinates while $\langle\ \rangle_L$ is the average over the lattice and all other molecular degrees of freedom. In liquids the dipolar spin–spin interactions can be neglected, thus, the spin-echo damping is due merely to the dephasing which results from the migration of spins through the nonuniform magnetic field. Using the procedure developed in the previous section, the time-evolution operator governing the density matrix from (18) can be separated into the following parts

$$U(t) = U_z(t)\, U_{180°}\, U_G(t)\, U_{90°}. \tag{19}$$

Here

$$U_z(t) = \exp(i\omega_0 I_z t), \tag{20a}$$

$$U_{180°} = \exp[i\pi I_x], \tag{20b}$$

$$U_G(t) = \exp\left(i\gamma \sum_i \int_0^t G^*(t') r_i(t') i_z^i (dt')\right), \tag{20c}$$

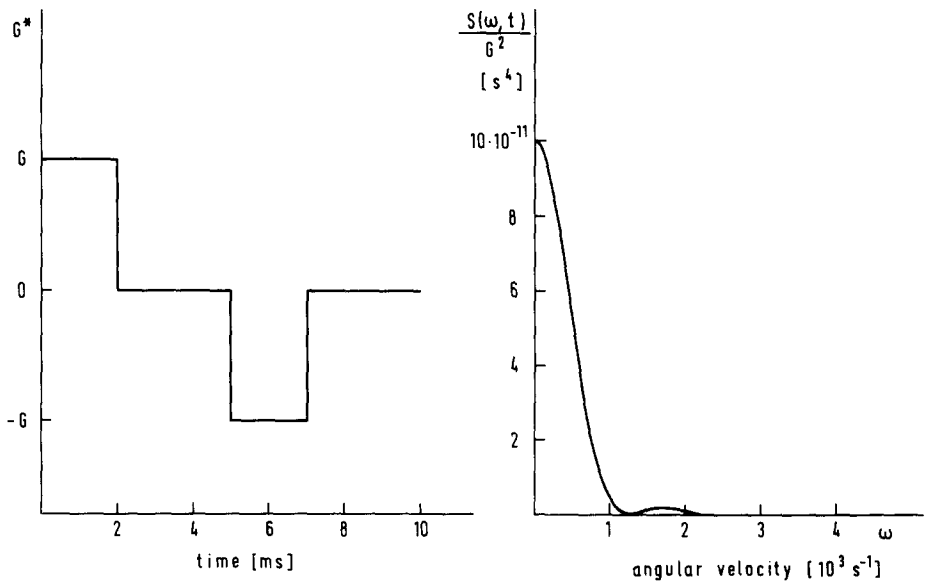


Fig. 1. The effective mfg of the usual two-pulse sequence and its frequency spectrum $S(\omega, t)$.

and

$$U_{90^\circ} = \exp\,(\mathrm{i}\tfrac{1}{2}\pi I_x), \tag{20d}$$

with the effective gradient field $G^*(t)$ obtained after the transformation (14c) which is reversing the sign* as

$$G^*(t) = \begin{cases} G(t) & 0 < t < \tau \\ -G(t) & \tau < t. \end{cases} \tag{21}$$

Taking the high-temperature approximation with the thermal equilibrium density matrix as

$$\rho(0) = 1 - \beta\omega_0 I_z, \tag{22}$$

the averaged value of the transverse magnetization is obtained by the substitution of (19) and (22) into (18)

$$\langle I_x(t)\rangle = -\tfrac{1}{2}\beta\omega_0 \sum_i \mathrm{Tr}_s\, i_+^i\, i_-^i \langle \sin\,[\omega_0 t + \varphi_i(t)]\rangle_L, \tag{23}$$

where

$$\varphi_i(t) = \gamma \int_0^t G^*(t') r_i(t')\,\mathrm{d}t'. \tag{24}$$

The average $\langle\ \rangle_L$ affects only the molecular coordinates $r_i(t)$ in (24); therefore, by using the cumulant expansion theorem [12], the average of the exponential functions in (23) can be replaced by the averages of the exponent in the following form:

$$\langle \exp\,[\mathrm{i}\varphi_i(t)]\rangle_L = \exp\,[\mathrm{i}\varphi_i(t) - \beta_i(t) + \ldots] \tag{25}$$

with

$$\varphi_i(t) = \gamma \int_0^t G^*(t') \langle r_i(t')\rangle_L\,\mathrm{d}t' \tag{26}$$

and

$$\beta_i(t) = \tfrac{1}{2}\gamma^2 \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \langle G^*(t_1) r_i(t_1)\, G^*(t_2) r_i(t_2)\rangle_L. \tag{27}$$

In stagnant liquids with $\langle r_i(t)\rangle_L = 0$ when the duration and height of both mfg pulses are identical the averaged phase shift at time 2τ is

$$\varphi(2\tau) \equiv 0, \tag{28}$$

* Two positive mfg pulses with the intermediate rf pulse have the same effect as two mfg pulses with the opposite sign but without the 180° rf pulse [4].

and the spin-echo signal is affected only by $\beta(2\tau)$ which is, in fact, the integral of the autocorrelation function between the molecular coordinate. By applying the gradient of the magnetic field along the x-axis the spin-echo damping close to $t = 2\tau$ is equal to

$$\langle I_x(t)\rangle = \tfrac{1}{2}\beta\omega_0 \sum_i \mathrm{Tr}_s\, i_+^i\, i_-^i \sin\omega_0 t \exp\left[-\beta(t)\right], \tag{29}$$

with

$$\beta(t) = \tfrac{1}{2}\gamma^2 \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 G^*(t_1) G^*(t_2) \langle x(t_1) x(t_2)\rangle_L. \tag{30}$$

The coordinate autocorrelation function can be expressed by the spectrum of the velocity autocorrelation

$$2D_{xx}(\omega) = \int_{-\infty}^{\infty} \langle v_{ix}(0)\, v_{ix}(t)\rangle_L \mathrm{e}^{\mathrm{i}\omega t}\, \mathrm{d}t \tag{31}$$

with v_{ix} being the molecular velocity along the x-axis as [7]

$$\langle x(t_1) x(t_2)\rangle_L = \frac{1}{\pi} \int_{-\infty}^{\infty} D_{xx}(\omega) \frac{\mathrm{e}^{\mathrm{i}\omega(t_1 - t_2)}}{\omega^2}\, \mathrm{d}\omega. \tag{32}$$

By the substitution of (32) in (30) and using the Fourier transformation of the effective mfg as

$$G(\omega, t) = \int_0^t G^*(t')\, \mathrm{e}^{\mathrm{i}\omega t'}\, \mathrm{d}t' \tag{33}$$

the spin-echo damping is defined by

$$\beta(t) = \frac{\gamma^2}{2\pi} \int_{-\infty}^{\infty} D_{xx}(\omega) S(\omega, t)\, \mathrm{d}\omega, \tag{34}$$

where $S(\omega, t)$ is the spectrum of the applied mfg field

$$S(\omega, t) = |G(\omega, t)|^2/\omega^2 \tag{35}$$

and $D_{xx}(\omega)$ is the spectrum of the velocity autocorrelation function. In the low-frequency approximation when the correlation time τ_c of molecular motion is short compared to the time scale of the spin-echo measurement, only the low-frequency part of the $D_{xx}(\omega)$ spectrum takes place in (34) and the damping coefficient can be written as

$$\beta_0(t) = \frac{\gamma^2}{2\pi} D_{xx}(0) \int_{-\infty}^{\infty} S(\omega, t)\, \mathrm{d}\omega, \tag{36}$$

where $D_{xx}(0)$ is identical to the self-diffusion coefficient along the x-coordinate. As expected, expression (36) is the same as the well-known Torrey result [1] if the Parceval identity is taken into account

$$\frac{1}{2\pi}\int_{-\infty}^{\infty}\frac{|G(\omega,t)|^2}{\omega^2}\,d\omega \equiv \int_0^t\left|\int_0^u G^*(t')\,dt'\right|^2 du; \tag{37}$$

The result (34) shows that the spin-echo with mfg makes it feasible not only to obtain the self-diffusion coefficient but also to determine the spectrum of the single-particle velocity autocorrelation function if the mfg pulse sequence with the appropriate frequency spectrum is applied.

The spectrum of the usual two mfg pulse sequence with the pulse width δ and the pulse interspacing τ (fig. 1) is

$$S(\omega,t)=\left[\frac{4G}{\omega^2}\sin(\tfrac{1}{2}\omega\delta)\ \sin(\tfrac{1}{2}\omega\tau)\right]^2. \tag{38}$$

It decays quickly with increasing frequency and, extracts only the low-frequency part of $D_{xx}(\omega)$. Therefore it is not very suitable for this purpose. The application of the Carr–Purcell sequence [1, 5] of 180° of pulses to the static mfg gives the effective field shown on fig. 2. Its frequency spectrum is

$$S(\omega,t)=\left[\frac{2G}{\omega^2}\,\mathrm{tg}\,(\tfrac{1}{4}\omega\tau)\sin(\tfrac{1}{2}n\omega\tau)\right]^2, \tag{39}$$

where $\frac{1}{2}\tau$ is the rf pulse interspacing and $2n$ is the number of applied rf pulses. When $n \gg 1$ $S(\omega, t)$ becomes

$$S(\omega,t)=\frac{n\pi^4}{\omega_m^2}\,t\left\{\delta(\omega)+\left(\frac{2}{\pi}\right)^4[\delta(\omega+\omega_m)+\delta(\omega-\omega_m)]+\ldots\right\}. \tag{39a}$$

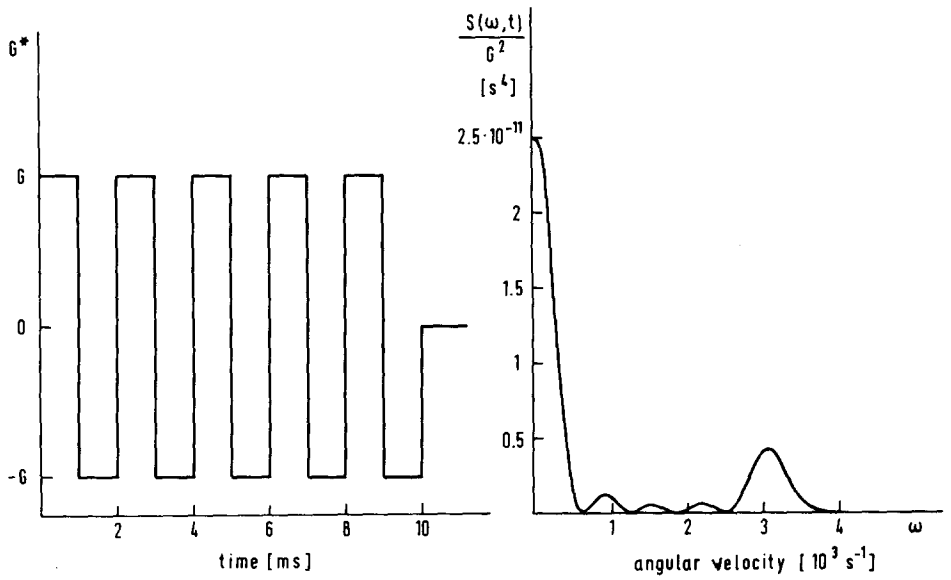


Fig. 2. The effective mfg of the Carr–Purcell sequence of 180° rf pulses applied to the static mfg and its frequency spectrum $S(\omega, t)$.

Substitution of (39a) into (34) gives the spin-echo damping

$$\beta(t) = \frac{\gamma^2 n\pi^3}{2\omega_m^2}\left[D_{xx}(0) + 2\left(\frac{2}{\pi}\right)^4 D(\omega_m) + \ldots\right]t, \tag{40}$$

which depends not only upon the self-diffusion constant $D_{xx}(0)$ but also upon the value of the velocity auto-correlation function at $\omega_m = 4\pi/\tau$.

By testing various mfg pulse sequences we have found out that just the simple mfg sinusoidal modulation of frequency ω_m can be suitable enough. It was shown in (21) that the combination of the positive and negative mfg pulses might replace the sequence of two positive mfg pulses with the intermediate 180° rf pulse. Thus, after each complete period of the mfg sinusoidal modulation, during which the defocusing and the refocusing of spin-free precession is produced, the spin-echo signal can be picked out. This mfg sequence has the frequency spectrum (fig. 3)

$$S(\omega, t) = 4G^2 \frac{\sin^2(n\pi\,\omega/\omega_m)}{\omega^2(\omega - \omega_m)^2}, \tag{41}$$

where n is the number of the applied periods. For $n \gg 1$ might be approximated by

$$S(\omega, t) = \frac{4\pi G^2}{\omega_m^2}\left[\delta(\omega) + \delta(\omega - \omega_m)\right]t. \tag{41a}$$

By the substitution of (39a) into (34) the spin-echo damping is equal to

$$\beta(t) = \frac{2\gamma^2 G^2}{\omega_m^2}\left[D_{xx}(0) + D_{xx}(\omega_m)\right]t. \tag{42}$$

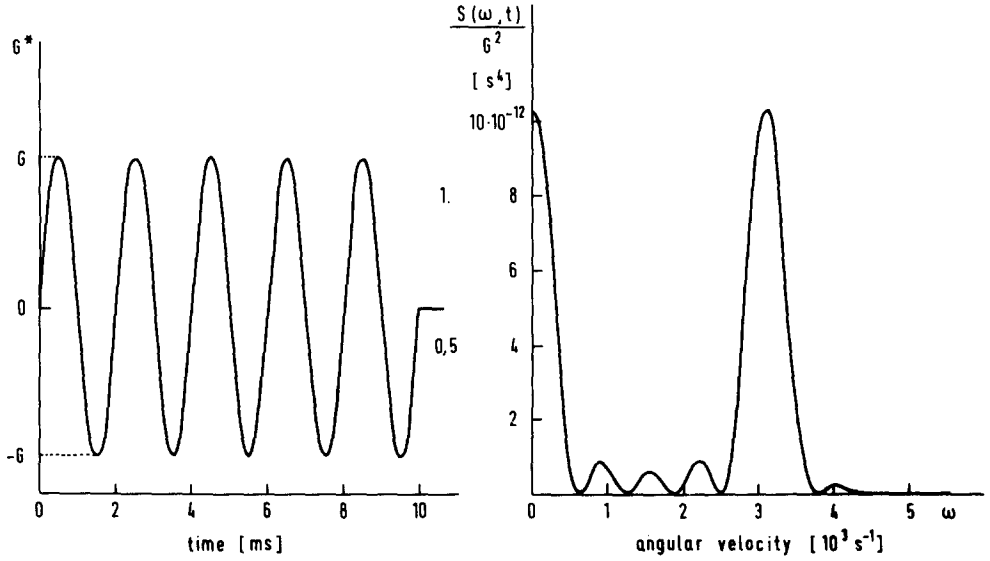


Fig. 3. The mfg sinusoidal modulation with its frequency spectrum $S(\omega, t)$.

It depends on the sum of the spectrum $D_{xx}(\omega)$ at zero frequency and at the modulation frequency ω_m. By changing ω_m the profile of the velocity autocorrelation function spectrum can be extracted from the damping of the spin-echo signal. Some other mfg pulse sequences have been tested too, but the sinusoidal modulation seems to be one of the most appropriate for this purpose.

4. Coherent averaging and self-diffusion measurement

The multipulse nmr method has been introduced [8–10] in order to measure the self-diffusion coefficients in systems with the strong dipolar spin–spin interaction where the classical spin-echo technique fails. This new technique combines the multipulse rf sequences with the mfg pulses in such a way as to reduce the dipolar damping of the spin-echo but retains the free precession dephasing which is due to the molecular migration across the gradient field.

Having examined this technique we have found out [10] that some precautions must be taken whenever the gradient pulses are superimposed on the multiple rf pulse sequence. Here this problem will be introduced and some appropriate combinations will be proposed.

The treatment of time-evolution in a system where the mixed sequences of the rf and mfg pulses are imposed requires a careful examination of the way in which $U(t)$ has been separated into parts. In ref. 10 it has been separated as

$$U(t) = U_z(t)\, U_{rf}(t)\, U_{G+D}(t) \tag{43}$$

and the part including the gradient and dipolar interactions together has been evaluated in terms of Magnus expansions (17) and (17a), assuming that the series (17a) is convergent. The critical parameter which determines its convergence is the value of the product $t_c GI$ where t_c is the cycling time of the sequences and I is the dimension of the sample. Whenever smaller than one, the series is convergent. Unfortunately, at the situations usually encountered in the experiment, it is much larger than one and, thus, the evaluations in ref. 10 only indicate the effects which the improper combinations of the rf and mfg pulses might bring about; but these results are not completely correct. To overcome this we have employed an approach in which the term $U_{G+D}(t)$ has been additionally separated as the time evolution operator takes the form

$$U(t) = U_z(t)\, U_{rf}(t)\, U_G(t)\, U_D(t)\, U_{90^\circ}, \tag{44}$$

where again the preparation 90° rf pulse has been removed from the term including multiple rf pulse sequences as well as the 180° rf pulse.

The simultaneous application of the multiple rf pulse sequences as well as the sequence of the mfg pulses to the spin system should accomplish the reduction of the spin-echo damping due to the dipolar spin–spin interactions as well as the spin-echo dephasing because of the molecular migration, but some precautions must be exercised to the eventual mutual interactions between the sequences of both kinds. It might happen either that the rf sequence reduces not only the dipolar damping but also the effective mfg, or that the mfg pulses remove the proper phasing of the rf pulses. The effect of the rf field on the gradient Hamiltonian is seen from the transformation (14c) (i.e., the effective mfg is obtained after the transformation of (4) into the tilting frame determined by the rf pulse excitations). The effect of the gradient on the rf sequence can be seen if a succession of the time-evolution operator separation is changed in the following way

$$U(t) = U_z(t)\, U'_G(t)\, U'_{rf}(t)\, U'_D(t)\, U_{90^\circ}, \tag{45}$$

where

$$U'_{rf}(t) = T \exp\left[-i \int_0^t \bar{\mathcal{H}}'_{rf}(t')\,dt'\right]. \tag{46}$$

The effective rf field

$$\mathcal{H}'_{rf}(t) = \exp\left(-i \int_0^t \mathcal{H}_G(t')\,dt'\right)\mathcal{H}_{rf}(t) \exp\left(i \int_0^t \mathcal{H}_G(t')\,dt'\right) \tag{47}$$

is transformed into the frame rotating around the z-axis. The inhomogeneous magnetic field (4) makes this rotation spatially nonuniform, (i.e., spins at various locations in the sample feel different magnetic fields) and, in addition to this, the mfg applied in pulses makes the rotation discontinuous. The nonuniform discontinuous rotation of the spin system changes the phasing of the applied rf pulses (i.e., in the interaction representation (47), the phases of two successive rf pulses are changed whenever the intermediate mfg pulse is applied). The removal of the proper alignment of the rf pulses inside the cycle reduces its ability for successful averaging of dipolar interactions since the important property of the rf Hamiltonian is changed, i.e. it is no longer cyclic

$$U'_{rf}(t_c) \neq 1. \tag{48}$$

In order to retain the proper rf pulse phasing within the cycle the mfg pulses should not be inserted inside the rf cycle but only in the time interval following the last rf pulse of a cycle. Using this simple recipe the multipulse rf sequence remains cyclic but there is a dephasing between different cycles that results in an additional effect known

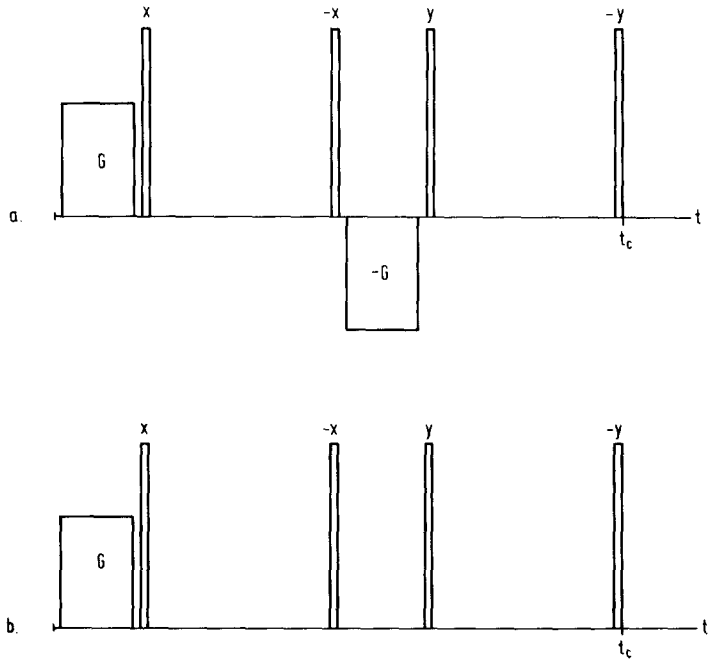


Fig. 4. (a) The combination of the mfg and rf pulses used in the ref. 7 and (b) its improvement.

from the resonance off-set experiment as the second averaging [13], which will be considered later on. In order to make these features more clear let us consider a few examples. In ref. 9 the so-called WAHUHA [13] rf pulse sequence has been combined with the mfg pulses placed in the time intervals between x and y rf pulses in such a way that the sign of mfg is alternating (fig.4a). The 180° rf pulse is applied after n WAHUHA cycles in order to accomplish the spin-free precession refocusing at time $2nt_c = 2\tau$, when the rf part of the time-evolution operator has the value

$$U_{rf}(2\tau) = \exp(-i\pi I_x), \tag{49}$$

while the mfg part of (42) is transformed into

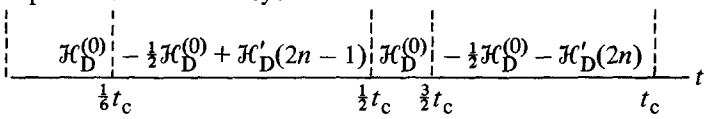
$$U_G(2\tau) = \exp\left(-i\gamma \sum_i \int_0^{2\tau} G^*(t') r_i(t') i_2^i\right) \tag{50}$$

with the effective gradient field $G^*(t)$ shown in fig.5. It consists of the train of mfg pulses the sign of which is changed after the time $\tau = nt_c$. The effective gradient field has the frequency spectrum (35)

$$S(\omega, t) = 16 \frac{\sin^2(\frac{1}{2}\omega\delta)\sin^4(\frac{1}{4}n\omega t_c)}{\omega^4 \sin^2(\frac{1}{4}\omega t_c)} \tag{51}$$

shown in fig. 5.

The Hamiltonian of the spin dipolar interaction in the interaction representation (14e) has the following time dependence in the nth cycle:



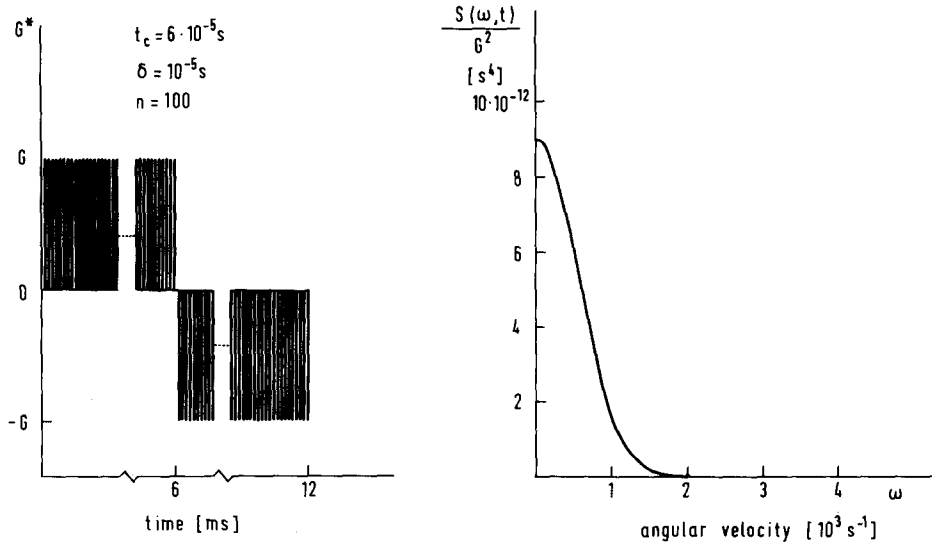


Fig. 5. The effective multipulse sequence and its frequency spectrum $S(\omega, t)$.

where $\mathcal{H}_D^{(0)}$ is identical to (3) and

$$\mathcal{H}'_D(n) = \tfrac{3}{4} \sum_{i>k} \beta_{ik}(i_+^i i_+^k \, e^{2in\varphi_i} + i_-^i i_-^k \, e^{-2in\varphi_i}), \tag{52}$$

where

$$\varphi_i = \gamma \int_0^{t_c/6} G^*(t') r_i \, dt' \tag{53}$$

is the angle of the spin system rotation due to the applied mfg pulse. (The mfg pulse of width 10^{-5} s and of magnitude 50 g/cm produces the phase shift φ_i of about 60° in 1 cm long sample.) Knowing the time dependence of $\mathcal{H}_D^{(0)}(t)$ the Magnus expansion (17–17d) can be employed in order to calculate the averaged dipolar Hamiltonian which defines the spin-echo damping. It is known [13] that the WAHUHA rf pulse sequence without mfg pulses reduces the dipolar Hamiltonian as much as the zeroth-order and first-order correction terms of the averaged Hamiltonian are equal to zero; $F_0 = 0$, $F_1(t) = 0$, while $F_2(t) \neq 0$. When the mfg pulses are applied as in the ref. 9, the zeroth-order correction term of the nth cycle is equal to

$$F_0^{(n)} = \tfrac{1}{2} i \, t_c \sum_{i>k} \beta_{ik}(i_-^k i_-^i \, e^{-i(4n-1)\varphi_i} - i_+^k i_+^i e^{i(4n-1)\varphi_i}) \sin \varphi_i. \tag{54}$$

However, because of the dephasing due to φ_i it is changing from cycle to cycle in the oscillatory way as it might be averaged off after many cycles. Similar oscillations have been found in the second-order term $F_1(t)$ but here is also the static part which is equal to

$$F_0^{(n)} \approx \tfrac{1}{8} t_c^2 \sum_{i>k} \beta_{ik}^2 [i_+^i i_+^k, i_-^i i_-^k] \sin 2\varphi_i. \tag{55}$$

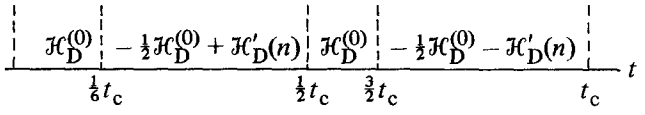
It determines the effective damping of the spin-echo signal, which is

$$\beta \cong \tfrac{1}{16} t_c M_2 \sin 2\varphi_i. \tag{56}$$

Here M_2 is the second moment of dipolar line broadening. When the typical experimental parameters are $n = 1000$, $G = 50$ G/cm, $t_c = 6 \times 10^{-5}$ s, $\delta = 10^{-5}$ s, $l = 1$ cm and $D = 10^{-6}$ cm^2/s, the self-diffusion damping

$$\beta_D = \frac{1}{12} (n\delta\gamma G)^2 D \tag{57}$$

is smaller than (56) for the dipolar field as small as 0.08 G. It means that, in this combination [8, 9], where the mfg pulse is applied inside the rf pulse cycle, the dipolar damping has just been partially reduced and could not be very effective for systems with considerable spin–spin interaction like solids or liquid crystals. But this sequence can be very simply improved by removing the second mfg pulse placed in the time interval inside the rf cycle (fig. 4b). If it is done the timing of $\mathcal{H}_D^{(0)}$ becomes



and the values of the Magnus expansion (17a) are

$$F_0(t) = 0,$$

$$F_1(t) = 0,$$

$$F_2(t) = \frac{t_c^3}{324} F_2^{(s)} + F_2^{(os)}, \tag{58}$$

with

$$F_2^{(s)} = \sum_i [\mathcal{H}_i'^{(2)}[\mathcal{H}_D^{(0)}, \mathcal{H}_i^{(-2)}]][\mathcal{H}_i'^{(-2)}[\mathcal{H}_D^{(0)}, \mathcal{H}_i'^{(2)}]] \tag{59}$$

and

$$F_2^{(os)} = \sum_i [\mathcal{H}_i'^{(2)}, [\mathcal{H}_D^{(0)}, \mathcal{H}_i'^{(2)}]]\, e^{4in\varphi_i} + [\mathcal{H}_D'^{(-2)}, [\mathcal{H}_D^{(0)}, \mathcal{H}_i'^{(-2)}]]\, e^{-4in\varphi_i}, \tag{60}$$

where

$$\mathcal{H}_i'^{(\pm 2)} = \sum_k \beta_{ik}\, i_\pm^i\, i_\pm^k. \tag{61}$$

We have seen that just a simple modification of the mfg pulse sequence reduces the dipolar damping to the second-order correction term of the averaged Hamiltonian (17d) which consists of two parts: i.e. the static part $F_2^{(s)}$ and the oscillating part $F_2^{(os)}$ which can be averaged out after many cycles. The result (58) becomes identical to that with the WAHUHA multiple pulse sequence without mfg [13] whenever φ_i is putting up to be zero, which means that $F_2^{(os)}$ is no longer averaged out and contributes to the dipolar damping. Thus, the applied mfg pulse sequences, in the modified form, bring about not only spin-echo dephasing which is due to the molecular migration but, in combination with the rf pulses, they additionally reduce the second-order correction term of the averaged dipolar Hamiltonian. This additional reduction of the second-order correction term is known from the resonance off-set experiments [13] as "second averaging" and must be taken into account when the self-diffusion coefficient is evaluated from the spin-echo data. Therefore with the same experimental parameters as in (56) and (57) the self-diffusion constant of about 10^{-6} cm^2/s can be measured in the system with the dipolar field as large as 1.5 G using this improved sequenee.

The examination of various combinations of rf and mfg pulse sequences reveals that the effect of the gradient field could be increased if the mfg pulse is applied in the longer time interval of the WAHUHA cycle between x and $-x$ rf pulse (fig. 6a) while all the evaluations of the averaged Hamiltonian remain the same as the one in (58). Sometimes the positive mfg pulses are not very convenient when applied to a magnet having field stabilization since they cause the static component of the mfg to be added to the main magnetic field. In this case it is better to employ the rf sequence which is in fact the doubled WAHUHA sequence with only positive rf pulses X, Y, Y, X, X, Y, Y, X (fig. 6b) and mfg pulses with alternating sign applied in the time intervals between the x rf pulses. This mfg pulse sequence gives only the oscillating components (the static one is zero) and can be realized easily with broad band power amplifiers.

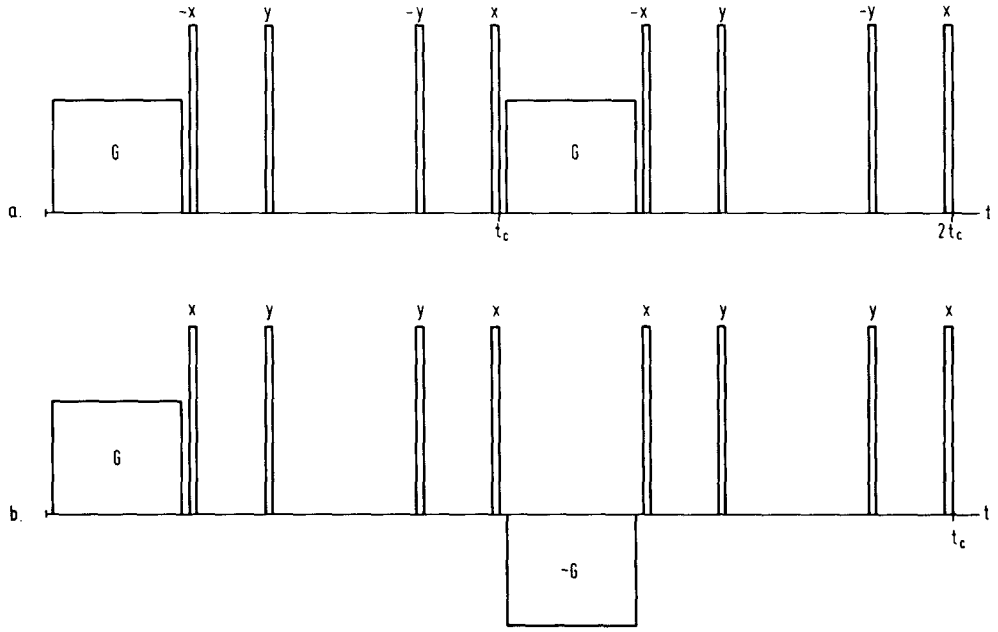


Fig. 6. Two combinations of the mfg pulses with the WAHUHA rf cycle (a) with the positive mfg pulses, (b) with the alternating positive and negative mfg pulses.

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