ON THE SELF-DIFFUSION MEASUREMENT BY MULTIPLE PULSE NMR

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Synopsis

The self-diffusion constant measurement by the new multiple pulse nmr technique[4] depends critically on the residual terms in the effective Hamiltonian which modify the spin-echo damping through the coupling of the dipolar and gradient fields, and can make the method useless for the self-diffusion measurement. Here, the alternative combination of the gradient and rf pulses is proposed where this coupling is suppressed.

Recent measurements of the self-diffusion constant in some smectic liquid crystals by the ordinary pulse-gradient spin-echo technique[1], as well as the measurements by the neutron[2] and light[3] scattering, give results inconsistent with those previously obtained by the new multipulse nmr method[4a,b,c] which was invented in order to measure the self-diffusion constants in systems with strong dipolar couplings where the classical nmr method fails. This cast some doubt on the effectiveness of the new method which combines the multiple rf pulse sequences[7], the gradient pulses, and the slow Carr-Purcell train of 180^{o} rf pulses in such a manner as to remove the dipolar damping of the spin-echo, but retains the free precession dephasing due to the molecular migration across the gradient field.

Having examined the new method we have found that some precautions must be exercised whenever the gradient pulses are superimposed to the multiple rf pulse sequence. Generally it leads to some effects among which the damping due to the cross-coupling between the gradient and the dipolar field can make the method useless for the self-diffusion constant measurement.

It is known[5,6] that the line-narrowing with the multiple rf pulse sequence critically depends on the resonance offset acting like an additional rotation of the spin system. This rotation misalignes the phases of the applied rf pulses and might change the mechanism of the dipolar reducation to a great extent[6]. The inhomogeneous magnetic field makes the resonance-offset spatially nonuniform, i.e. spins at various locations exhibit a different shift from the resonance and, when applied in pulses, it acts like a discontinuous rotation. Therefore, the combination of the gradient pulses with the multiple rf pulse cycle might bring about the effects known from the resonance-offset experiments[5,6], and can limit the usefulness of the proposed technique[4].

The system is governed by the rotating frame Hamiltonian

$$H(t) = H_D^{(o)} + H_{rf}(t) + H_G'(t) \qquad (1)$$

where $H_{rf}(t)$ depends on the nature of the multipulse rf exitation and $H_G'(t)$ is related to the applied magnetic field gradient pulses. $H_D^{(o)}$ is the secular part of the dipolar Hamiltonian. As Haeberlen and Waugh[7] have shown, if the multiple rf pulse sequence satisfies periodic and cyclic condition, the effective Hamiltonian becomes periodic as well, and one only needs to calculate the time development for a single cycle in order to be able to predict the system development for any time. The time evolution operator $U(nt_c)$ can be expanded using the Magnus formula[7]

$$U(nt_c) = \exp\left[-int_c(\bar{H}^{(o)} + \bar{H}^{(1)} + \bar{H}^{(2)} + \ldots)\right] \qquad (2)$$

where the average Hamiltonians $\bar{H}^{(n)}$ depends upon the multiple rf pulse sequence being used. For the proposed rf-gradient pulse exitation[4b]

$$\begin{array}{ll} \text{rf:} & P_y-(t-P_x-t-P_y-2t-P_y-t-P_x-t)^n \\ \text{gradient:} & \qquad \vec{G} \qquad\qquad\qquad -\vec{G} \quad . \end{array} \qquad (3)$$

$\bar{H}^{(o)}$ includes only the spin interactions with the magnetic gradient field:

$$\bar{H}^{(o)} = 2\frac{\delta}{t_c} \gamma \vec{G} \sum_{i=1}^{N} \vec{r}_i \, s_{yi} = 2\frac{\delta}{t_c} H_G \;, \qquad (4)$$

where t_c is the cycling time, δ is the gradient pulse width, $\vec{G}$ is the magnetic field gradient, grad B_z, and $\vec{r}_i$ is the location vector of the i-th spin. The sequence (3) is symmetric with respect to rf pulses, hence $\overline{H}^{(1)}$ is zero. The second-order correction

$$\overline{H}^{(2)} = H_{D^3} + H_{D^2G} + H_{DG^2} \quad (5)$$

contains purely dipolar term

$$H_{D^3} = \frac{t_c}{648}\left[(H_D^{(x)} - H_D^{(z)}),\left[H_D^{(y)}, H_D^{(z)}\right]\right], \quad (6)$$

and two cross terms of the type:

$$H_{D^2G} = \frac{t_c\delta}{54}\cdot\left[(H_D^{(y)} - 2H_D^{(z)}),\left[H_D^{(x)}, H_G\right]\right], \quad (7)$$

and

$$H_{DG^2} = \frac{\delta^2}{6}\left[H_G,\left[H_G, H_D^{(z)}\right]\right], \quad (8)$$

which couple the gradient and dipolar interactions. In the above expressions the dipolar Hamiltonians $H_D^{(\alpha)}$ ($\alpha = x,y,z$)

The use of the 180° rf pulse after the n multipulse cycles, removes the coherent spin dephasing caused by the terms linearly dependant upon the gradient magnitude. Thus, the terms $\overline{H}^{(o)}$ and H_{D^2G} do not affect the spin-echo damping directly, but the leading term $\overline{H}^{(o)}$, which dominates the time evolution of the spin system in the interval between the initial rf pulse and the spin-echo signal, brings about so called second averaging[7] whenever the gradient field exceeds the magnitude of the average dipolar field. According to this all parts of the remaining effective Hamiltonian, (6) and (8), not commuting with $\overline{H}^{(o)}$ should be neglected in the first approximation. Thus, the dipolar term (6) and the cross term

(8) are additionally reduced for the nondiagonal parts.

The above consideration shows that the gradient superposition to the multiple rf pulse sequence in the proposed manner[4b] brings about, in addition to the self-diffusion damping, also the modification of the spin-echo damping through:

i) the increase of the spin-echo damping due to the dipolar-gradient cross terms

ii) the reduction of the dipolar Hamiltonian (6) due to the second averaging.

Thus, the spin-echo damping no longer follows the law where the plot G^2 versus damping is a straight line with the slope proportional to the self-diffusion constant. In our case, by enlarging the gradient magnitude the damping decreases, at first, due to the second averaging, but when $\bar{H}^{(o)}$ exceeds the magnitude of the average dipolar field, it is governed mostly by the self-diffusion incoherent dephasing

$$\frac{1}{12}\,(n.\delta.\gamma.G)^2 D, \qquad (9)$$

and the cross dipolar-gradient terms. The last effect can be evaluated only if the higher-order corrections of the effective Hamiltonian (2) are also taken into account. Their closer examination[8] gives the cross-coupling damping proportional to

$$\frac{t_c}{16}\,M_2\,\sin(\gamma.G.\delta.\ell) \qquad (10)$$

Here D is the self-diffusion constant, M_2 is the dipolar second moment, and ℓ is the sample dimension. If the experimental parameters are: n = 1000, G = 20 gauss/cm, $t_c=6.10^{-5}$ s, $\delta = 10^{-5}$ s, ℓ = 1 cm, and if the typical value of the self-diffusion constant is 10^{-6} cm^2/s, then the cross-coupling damping (10) prevails over the self-diffusion dephasing (9) at the dipolar field as small as 0,03 gauss. The magnitude of the cross-coupling damping demonstrates the fact that the self-diffusion constant extraction from the spin-echo relaxation becomes troublesome and the additional information about the dipolar interactions is needed. Therefore, it is hard to believe that the proposed multipulse sequences[4a,b] can be a useful technique for the self-diffusion measurement in systems with the considerable dipolar damping.

These additional effects: (i) and (ii), have not been taken into account in the references (4), and we believe that this has made the results inconsistent with those taken by the standard techniques[1,2,3].

But the idea of the self-diffusion measurement by the technique which combines the gradient pulses with the multiple rf pulse sequence can work if a slightly modified sequence is used. Since the gradient field misaligne the phases of the rf pulses if the gradient pulses are inserted inside the rf cycle, we believe that the gradient pulse superimposed only at the beginning or the end of the rf cycle will not remove the proper rf pulse phasing inside the cycle. Thus, the dipolar averaging per cycle can be completed and the cross term (8) is expected to vanish. Closer examination of the various pulse sequences[8] reveals that the only requirement for this is a gradient pulse following the complete rf pulse cycle regardless of where the first gradient pulse starts. Thus, we propose the sequence of the double four rf pulse cycles:

$$\begin{array}{ll} \text{rf:} & P_y-(t-P_x-t-P_y-2t-\underset{\substack{\uparrow\\ G}}{P_y}-t-P_x-2t-P_x-t-P_y-2t-\underset{\substack{\uparrow\\ -G}}{P_y}-t-P_x-t)^n \\ \text{gradient:} & \end{array} \quad (11)$$

The application of the multiple pulse cycle with the positive and negative gradient pulses has some advantages with respect to the generation of the short and intense pulses of the electric current. Its effective Hamiltonian becomes

$$\bar{H}^{(o)} = \frac{\delta}{t_c} \gamma\vec{G} \sum_{i=1}^{N} \vec{r}_i \, s_{xi} = \frac{\delta}{t_c} H_G'' ,$$

$$\bar{H}^{(1)} = 0 \tag{12}$$

and

$$\bar{H}^{(2)} = H_D 3 + H_D' 2_G$$

with

$$H_D' 2_G = \frac{t_c}{108} \left[(H_D^{(y)} - H_D^{(x)}), \left[H_D^{(y)}, \; H_G'' \right] \right] .$$

In fact, the cross term, quadratic with respect to the gradient, does not appear in (12), therefore the sequence does not produce the cross-coupling damping of the spin-echo. It can be used for the self-diffusion constant measurements, but still, one has to have in mind the effect of the second averaging.

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