Spin Echo Formation in the Presence of Stochastic Dynamics

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Spin echo formation in magnetic field gradients in the presence of fast stochastic motion is studied for hyperpolarized ^{3}He gas at different diffusivities. The fast translational motion leads to frequency shifts already during echo formation, which can be described analytically for a linear gradient. Despite complete signal loss at the position of the spin echo itself, considerable intensity can be preserved at an earlier time ($\sqrt{2}\tau$ rather than 2τ, where τ is the pulse delay). Hence, the phenomenon is designated as a pseudo spin echo.

Today, nuclear magnetic resonance (NMR) is considered an indispensable tool in physics, chemistry, biology, and medicine [1]. Most modern NMR pulse sequences are based on the simple refocusing principle of the spin echo (SE) experiment, which was developed by Hahn in 1950 [2]. Moreover, echo formation is an important phenomenon in optical spectroscopy and neutron scattering [3,4]. Stochastic processes, however, can interfere with the echo formation and have to be handled properly. Indeed, the effect of slow spin motion on SE signals, caused by diffusion or other dynamical processes, has been the subject of many studies in liquids and solids [5,6]. In these motional regimes, this effect is well understood and described within an established theoretical framework [7,8]. Yet in the gas phase, the translational motion is about 4 orders of magnitude faster and can affect the SE signal on much shorter time scales. This regime of very fast diffusion has not been studied yet, although it is of special interest in the field of gas NMR and the uprising field of magnetic resonance imaging (MRI) with hyperpolarized (HP) noble gases [9,10]. Conventional theory, which considers only the signal at the echo maximum, predicts complete loss of the SE under such conditions. Nevertheless, in analogy to more complex dynamics in molten polymers [11], it is conceivable that significant signal intensity might be observable prior to the expected echo formation. Therefore, a theoretical and experimental examination of SE signals under fast motion in the gas phase has been performed, showing that this effect indeed occurs and can even be described analytically. This offers a way to extend the time scale over which dynamics can be studied by echo experiments.

In general, the signal $E(t)$ of the SE experiment, i.e., the total magnetization, is given by the product $E(t) = M(t)A(t)$, where $M(t)$ is the time evolution of the magnetization without the influence of diffusion, and $A(t)$ is the diffusion suppression function. A constant linear magnetic field gradient $G = \partial B / \partial z$ is assumed during the SE experiment in a constant external field $\mathbf{B} = B \cdot \mathbf{e_z}$. For an ensemble of spins with a homogeneous distribution along the gradient direction over a distance $2d$ (e.g., a cylindrical tube) the phases of the spins in the rotating frame are given

by $\phi(z, t) = \gamma G z t$, where γ is the magnetogyric ratio, and the initial phases $\phi(z, 0) = 0$. The total magnetization at times $t < \tau$ is given by the normalized integral over the whole sample,

$$M(t) = \frac{1}{2d} \int_{-d}^{d} dz \cos(\gamma G z t) = \frac{1}{\gamma G d t} \sin(\gamma G d t). \quad (1)$$

At time $t = \tau$, the spin phases are inverted by a 180° pulse, which leads to a simple substitution of t by $(t - 2\tau)$ as the argument of $M(t)$.

The diffusion suppression function $A(t)$ describes the effect of diffusion on isochromats of spins, depending on their motion, which is governed by stochastic motion. As is shown in Ref. [8], the function can be expressed as $A(t) = \exp[-1/2\langle \phi(t)^2 \rangle]$, where the brackets $\langle \ldots \rangle$ indicate an ensemble average. Therefore, it is sufficient to calculate $\langle \phi(t)^2 \rangle$. For the SE sequence, two different cases before and after the inversion pulse have to be considered,

$$\langle \phi(t)^2 \rangle = \begin{cases} \gamma^2 G^2 \langle (\int_0^t z(t')dt')\rangle, & t < \tau \\ \gamma^2 G^2 \langle (\int_0^\tau z(t')dt' - \int_\tau^t z(t')dt')^2 \rangle, & t > \tau \end{cases}. \quad (2)$$

The relative minus sign in the latter case accounts for the fact that at time τ all phases are inverted. Using the relation

$$\langle z(t')z(t' + T) \rangle = D[2t' + T - |T|], \quad (3)$$

which follows from the Einstein-Smoluchowski equation $\langle z^2 \rangle = 2Dt$, the solution of the resulting integrals leads to the diffusion suppression function for arbitrary times t,

$$A(t) = \begin{cases} \exp\left[-\frac{1}{3}\gamma^2 G^2 D t^3\right], & t < \tau \\ \exp\left[-\frac{1}{2}\gamma^2 G^2 D \left(4\tau^3 - 4\tau^2 t + \frac{2}{3}t^3\right)\right], & t > \tau \end{cases}. \quad (4)$$

This function also includes the Stejskal-Tanner equation [6] as a special case for time $t = 2\tau$.

The calculated SE signal $E(t)$ for typical values of an experiment with gaseous ^{3}He is shown in Fig. 1 ($\tau = 10$ ms, $D = 2$ cm^2/s, $G = 0.7$ mT/m, and $d = 8$ mm). The usual echo maximum at time 2τ is suppressed almost

completely by the function $A(t)$, which leads to an apparent shift of the SE maximum. The time t_{max} of the local maximum of $A(t)$ can be derived by setting its derivative to zero,

$$\left. \frac{dA}{dt} \right|_{t=t_{max}} = -\frac{1}{2}\gamma^2 G^2 D(-4\tau^2 + 2t_{max}^2)A(t_{max}) \overset{!}{=} 0, \quad (5)$$

which yields $t_{max} = \sqrt{2}\tau$.

The described effect has been detected experimentally by measuring SEs in HP ^{3}He for different diffusion coefficients D in the presence of a constant linear gradient. The gas mixing setup, similar to the one described in Ref. [12], allowed for a variation of D over a range of 1 order of magnitude (0.1–4 cm^2/s) by either admixing ^{3}He with a heavier buffer gas (SF$_6$) at elevated pressures or reducing the total pressure of the gas portion. A slice selective excitation pulse [7] (see Fig. 2) was applied to ensure that all excited spins stay in the detection volume during the experiment and that the assumption of a rectangular sample profile along the gradient direction is satisfied. A Gaussian smoothed sinc-shaped radio frequency (rf) pulse with 2 lobes and a duration of 600 μs was employed in combination with a gradient of 21 mT/m. Thus, a slice with a thickness of 10 mm in a 45 mm rf birdcage coil was selected. Therefore, precaution was taken to eliminate radiation damping effects [13]. The measurements were conducted in a magnetic field of 4.7 T with a typical ^{3}He polarization of 50%, obtained from the Institute of Physics in Mainz [14]. In order to check the influence of the magnetization on the signal, the measurements were also repeated with much lower polarization (less than 1%). The SE experiments were conducted with a 180° pulse of 67.5 μs, delay time $\tau = 10.3$ ms, and a constant linear gradient of 0.7 mT/m. All SEs were acquired with a two-

step phase cycle to remove the strong signal after the 180° pulse, which arises from pulse imperfections.

The magnitude signals of the experimental SEs for different diffusion coefficients are shown in Fig. 3. For a quantitative comparison of the experimental SEs with the derived diffusion suppression function $A(t)$ in Eq. (4), a proper approximation of $M(t)$ is required. Because of experimental imperfections, the acquired signal even for the slowest diffusion coefficient deviates substantially from the calculated function in Eq. (1), as the excited slice profile differs considerably from the ideal rectangular shape. Therefore, the experimental free induction decay (FID) before the inversion pulse for the lowest value of $D = 0.115$ cm^2/s is taken as the initial state and mirrored at time τ to obtain the echo signal without diffusion. This function is then multiplied by the analytical diffusion suppression function and compared with the experimental data. The parameters in the calculations equal the experimental values for the gradient strength, the diffusion coefficient, and the echo time τ. Indeed, the measured SEs show the behavior predicted by the calculations: The apparent signal maximum shifts with higher D to earlier times, which is caused by the increasing impact of the diffusion suppression function. Already for $D = 1.8$ cm^2/s the expected signal maximum at 2τ is suppressed to such an extent that the secondary maximum exceeds the main echo [Fig. 3(b)]. Even if the signal is completely lost at $t = 2\tau$, the correlation of the spin phases before and after the refocusing pulse can lead to a signal buildup at $t = \sqrt{2}\tau$ [Fig. 3(c)]. Typically, only the signal after the inversion pulse is acquired. In such an experiment, the maximum of the SE then seems to appear at an earlier time than $t = 2\tau$. Hence, we call this signal a *pseudo spin echo*, a term introduced in Ref. [11] to describe a similar effect in solid echoes of molten polymers due to rotational dynamics. Figure 3 clearly shows that the calculated signals agree almost completely with the experimental data, hereby approving the validity of the derived function for $A(t)$ with its local maximum at time $\sqrt{2}\tau$. Because of the loss of correlation no multiple SEs can be formed, which have been
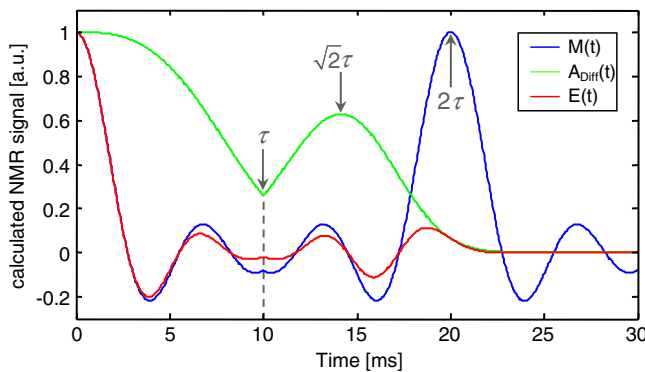

FIG. 1 (color online). Calculated SE signal $E(t)$ under the influence of diffusion for the typical ^{3}He parameter ($\tau = 10$ ms, $D = 2$ cm^2/s, $G = 0.7$ mT/m, and $d = 8$ mm); dashed line: SE signal of a cylindrical sample in a linear gradient without diffusion; dotted line: diffusion suppression function with a local maximum at time $\sqrt{2}\tau$; solid line: resulting SE signal showing an apparent maximum shift.
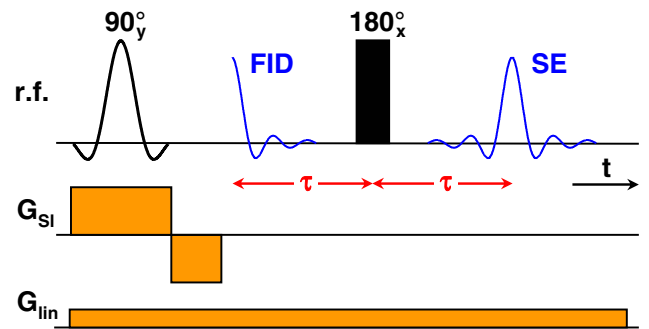

FIG. 2 (color online). SE sequence with a slice selective excitation pulse in the presence of a constant linear gradient. The times of the applied pulses are exaggerated in the illustration.
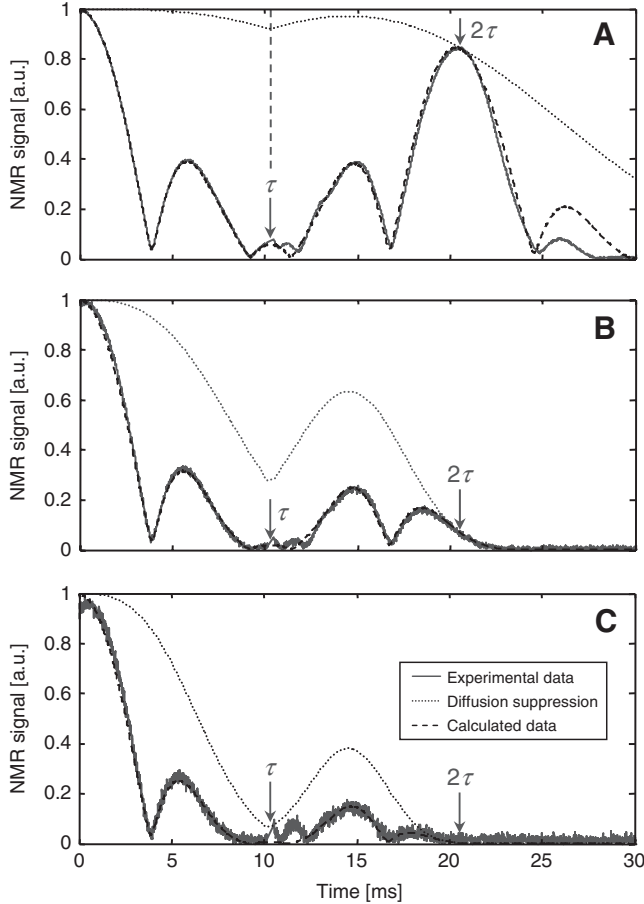
FIG. 3.   Comparison of experimental [solid line] and calculated [dashed line] SE magnitude signals in HP ^{3}He. The calculations are the product of the diffusion suppression function [dotted line] and the mirrored FID signal for times $t < \tau$ for $D = 0.115$ cm^2/s (see the text). The signal was acquired in the presence of a constant linear gradient of 0.7 mT/m from an excited slice with a thickness of 10 mm. The measurements were conducted with different diffusion coefficients D. (a) $D = 0.115$ cm^2/s, the deviation at long times arises from imperfections of the slice selection pulse; (b) $D = 1.8$ cm^2/s; (c) $D = 3.8$ cm^2/s.

observed in solid and liquid ^{3}He at high nuclear spin magnetization [15].

The main and the secondary maximum of the echo signal decay with different constants with respect to D. Thus, for a particular diffusion coefficient, the amplitude of the main echo maximum matches the amplitude of the secondary maximum. This special value, referred to as D_{12}, can then serve as an indicator for the motional regime of a certain spin system. Analytically, D_{12} can be derived from the intersection of the two exponential functions, which describe the decay of the signals with increasing D. The time t_2 of the secondary maximum is calculated approximately from the time of the first minimum of $\sin(\gamma G d t)$,

$$t_2 \approx 2\tau - \frac{3\pi}{2d\gamma G}. \tag{6}$$

By inserting these times into Eq. (4), one obtains the decay functions

$$A_1(D) = \exp\left[-\frac{2}{3}\gamma^2 G^2 \tau^3 D\right] = \exp[-D/D_{1\mathrm{dec}}], \tag{7}$$

$$A_2(D) = \exp\left[-\frac{1}{2}\gamma^2 G^2\left(\frac{4}{3}\tau^3 - \frac{18}{3}\tau_s\tau^2 + 9\tau_s^2\tau - \frac{27}{12}\tau_s^3\right)D\right]$$
$$= \exp[-D/D_{2\mathrm{dec}}], \tag{8}$$

$$\text{with} \quad \tau_s = \frac{\pi}{d\gamma G}.$$

The diffusion coefficient D_{12} is the value, where $M_1 A_1(D_{12}) = M_2 A_2(D_{12})$. M_1 and M_2 are the amplitudes of the main and the secondary echo maximum. Solving the equation for D_{12}, we find

$$D_{12} = -\ln\left(\frac{M_1}{M_2}\right)\frac{1}{\gamma^2 G^2 \tau_{12}^3}, \tag{9}$$

$$\text{with} \quad \tau_{12}^3 = -\frac{9}{3}\tau_s\tau^2 + \frac{9}{2}\tau_s^2\tau - \frac{27}{24}\tau_s^3.$$

In order to determine this value from the experimental data, the measured SE maximums for different values of D are fitted by exponential decay functions,

$$E(D) = E_0 e^{-D/D_{\mathrm{dec}}} + E_1, \tag{10}$$

yielding $D_{1\mathrm{dec}}$ and $D_{2\mathrm{dec}}$ in complete agreement with the calculated values from Eqs. (7) and (8), using the experimental parameters (see Fig. 4). Moreover, the calculated intersection value from Eq. (9) fits exactly the measured one. Note that the pseudo SE signal decays much less with
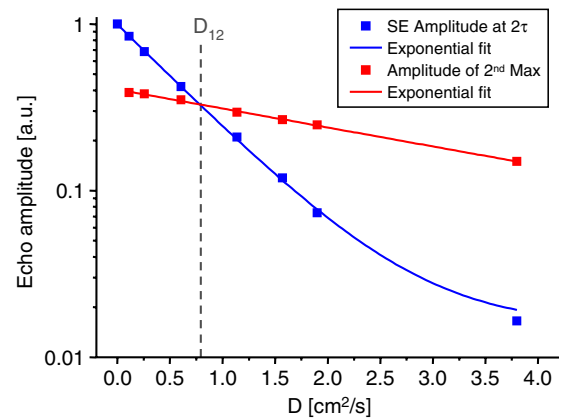

FIG. 4 (color online).   Amplitudes of the SE signal at time 2τ [gray line] and at the time of the secondary maximum [black line] in dependence of the diffusion coefficient D. The amplitudes are plotted on a logarithmic scale. The theoretical calculated intersection value D_{12} is marked by the gray dashed line.

D and thus provides a way of checking the stochastic process causing the dephasing at higher diffusivities.

Our study clearly shows that the effect of diffusion in gases on SE signals is substantial. However, it was not reported in literature to the best of our knowledge. In fact, SEs in gases can be studied conveniently only by using polarization enhancement techniques, as the signal from thermally polarized samples is so weak. Moreover, pseudo SEs have not been observed yet in experiments with HP ^{3}He, since these are usually conducted employing small flip angles and short timings. Indeed, the pseudo SE effect arises only if the additional phase resulting from stochastic processes is comparable with the spatial phase dispersion of the sample. Thus, the effect maximizes if the diffusion length $\sqrt{2Dt}$ is comparable with the sample size d.

In conclusion, the effect of diffusion on the usual SE signals in gases was studied for different motional regimes. It was verified that the observed changes in terms of amplitude, shape, and maximum position (designated as the *pseudo SE* effect) arise from the fast translational motion of the spins on the time scale of the dephasing and rephasing processes. Dipolar coupling effects were excluded since no dependence on the magnetization was observed. The pseudo SE signals were described by an extension of the Stejskal-Tanner equation which is valid for linear gradient fields and samples with a rectangular profile along the gradient direction. For the more complicated case of nonlinear gradients and other sample profiles, which applies to most NMR experiments in homogeneous magnetic fields, this analytical solution is insufficient, but the physics stays the same. In that case, the diffusion suppressed SE signals can be calculated using stochastic simulations, yielding similar results and complete agreement with the experimental data [16]. Details will be published separately.

The understanding of this strong diffusion suppression effect on SEs in gases opens the way to different new applications, e.g., SE experiments in MRI of HP gases, but also to the measurement of new fundamental effects, such as the detection of distant dipolar fields in gases [17]. Moreover, similar effects are expected in related echo experiments with photons and neutrons in the presence of stochastic dynamics on the time scale of the echo formation [18–20]. Thus, the observed phenomenon is not restricted to the case of spins in a magnetic field, but can occur in general in all echo processes, where the buildup of the signal relies on a remaining phase correlation that can be disturbed by stochastic dynamics. A proper description of pseudo SE formation then provides access to a dynamic regime which is not accessible by conventional SE spectroscopy.

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