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Generation and Application of Ultra-High-Intensity Magnetic Field Gradient Pulses for NMR Spectroscopy

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Two different concepts of gradient current power supplies are introduced, which are suitable for the generation of ultra-high intensity pulsed magnetic field gradients of alternating polarity. The first system consists of a directly binary coded current source (DBCCS). It yields current pulses of up to ±120 A and a maximum voltage across the gradient coil of ±400 V. The second system consists of two TECHRON 8606 power supplies in push–pull configuration (PSPPC). It yields current pulses of up to ±100 A and a maximum voltage across the gradient coil of ±300 V. In combination with actively shielded anti-Helmholtz gradient coils, both systems are used routinely in NMR diffusion studies with unipolar pulsed field gradients of up to 35 T/m. Until now, alternating pulsed field gradient experiments were successfully performed with gradient intensities of up to ±25 T/m (DBCCS) and ±35 T/m (PSPPC), respectively. Based on the observation of the NMR spin echo in the presence of a small read gradient, procedures to test the stability and the matching of such ultra-high pulsed field gradient intensities as well as an automated routine for the compensation of possible mismatches are introduced. The results of these procedures are reported for the PSPPC system.

Key Words: **PFG NMR; high-intensity pulsed field gradients; diffusion; mismatch.**

1. INTRODUCTION

The measurement of molecular diffusion has become a major issue of NMR spectroscopy. Among the 8174 citations of NMR papers in the 1999 issues of current contents (Physical, Chemical and Earth Sciences) as much as 422 papers deal with diffusion phenomena. As a consequence of the continuously enlarging spectrum of systems investigated (*1–4*), the requirements imposed on the measuring techniques have become more and more complex. Besides the pulsed field gradient (PFG) NMR technique (*5*), which is sometimes also referred to as pulsed gradient spin echo (PGSE) or diffusion ordered spectroscopy (DOSY), in the past few years the dramatic progress in NMR instrumentation has permitted a remarkable renaissance of NMR diffusion measurements in static magnetic field gradients; this means in the stray field of a superconducting magnet (*6, 7*). Though this latter technique allows the measurement of by far smaller diffusivities (*8*), the need of large accumulation numbers and the exclusion of selective diffusion measurement of multicomponent systems by high-resolution NMR (*9*) limit the range of applicability of this technique. Moreover, the application of gradients with alternating direction (*10*), which has turned out to be a very efficient method for overcoming the disturbing influence of internal field gradients brought about by the sample heterogeneity, is excluded by the very principle of the method.

Many of the applications of the PFG NMR techniques require the measurement of small diffusivities in systems where due to inherent small molecular mobilities also the transverse (T_2) NMR relaxation times are short (*3, 4*). Under these conditions, particular emphasis must be given to the generation of magnetic field gradient pulses with very high intensity and extremely short rise and fall times. Such field gradient pulse systems must fulfill very stringent requirements in respect to their mechanical and electronic stability. In particular, as a main requirement of PFG NMR diffusion measurement, the time integral over any pair of field gradient pulses must be identical, i.e., the pulsed field gradients must be "matched" (*11–13*). Any difference in these quantities ("mismatch") gives rise to artefacts of the measurements (*11–15*), which may result in an additional spin echo attenuation and, hence, may erroneously be interpreted as too large diffusion coefficients (*12, 16–18*). Recently, also the appearance of artefacts similar to the true "diffraction-like" effects in restricted diffusion analysis (*19*) were reported and correctly attributed to the mismatch of field gradient pulses (*15*).

Depending on the chosen approach to the PFG NMR experiment and its data evaluation, such artifacts manifest themselves in a phase shift of the NMR spectrum (frequency domain) and a shift of the spin echo position (time domain), which cannot be compensated by subsequent signal processing (e.g., "phasing") (*15*). It is well known that the presence of a small read gradient parallel to the direction of the strong pulsed gradient helps to prevent or reduce artifacts by mismatched pulsed gradients if both gradients are generated by the same gradient coil (*11–18*). But even in such experiments, mismatched pulsed gradients lead always to a phase shift (frequency domain) and a shift of the spin

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echo position (time domain) of the observed NMR signal (*12, 14, 18*), respectively.

In this contribution, we describe two hardware solutions to generate ultra-high pulsed field gradient intensities of high stability and an efficient automated experimental procedure to match the pulsed field gradient pairs. It is shown that this procedure works in time domain evaluation of PFG NMR measurements. Using these techniques, we demonstrate experimentally that high-quality PFG NMR measurements are possible with alternating pulsed field gradients of intensities of up to ± 35 T/m.

2. PULSE SEQUENCE MODIFICATION FOR ULTRA-HIGH-INTENSITY PFG NMR APPLICATIONS

Generally, PFG NMR measurements are based on the stimulated or primary (Hahn) spin echo pulse sequences. Both are commonly used with unipolar (*5*) or, more advanced, with alternating (bipolar) (*10, 20–22*) pulsed field gradients. Measurements with alternating pulsed field gradients (APFG) are known to suppress susceptibility-induced artifacts in diffusion studies, which is especially useful for investigations of materials with internal field gradients (e.g., porous media or metallic powders) (*10, 20, 22*). Since most APFG NMR pulse sequences require the application of at least two pairs of pulsed field gradients with opposite direction in conjunction with appropriate rf pulses, their demands to spectrometer hardware are larger than for unipolar PFG NMR sequences.

For ultra-high-intensity (alternating) pulsed field gradients, large current pulses must be generated, which may drive the gradient current power supplies up to their nominal limit. Besides other known effects, which are discussed in Section 3, instabilities in the electronics of the gradient power supplies may lead to a mismatch of the gradient pulses. Therefore, an efficient procedure for matching of the pulsed field gradients is indispensable. Moreover, the stability and reproducibility of the pulsed field gradient generation must be tested for successive individual scans using exactly the same measurement parameters.

In the following sections, such test and matching procedures are introduced and discussed for the 13-interval PFG NMR sequence published by Cotts *et al.* (*10*). However, these tests and matching procedures may easily be adapted to any other PFG NMR sequence for diffusion measurements. Unless stated otherwise, the results represented were obtained using phase-alternating pulse schemes and quadrature detection in order to remove signal distortions due to unwanted coherences.

In order to assist the matching of ultra-high-intensity alternating pulsed field gradients, this 13-interval PFG NMR sequence was modified by incorporating a small read gradient into the prepare and read interval of the sequence as reported by Stallmach *et al.* (*20*). This pulse sequence is plotted in Fig. 1. In addition to Ref. (*20*), the duration of the read gradient in the prepare interval $t_p + t_c$ is kept variable via the adjustable time interval t_c. While t_p is determined by the desired acquisition parameters, t_c is controlled automatically with the procedure to match the field gradients described below.

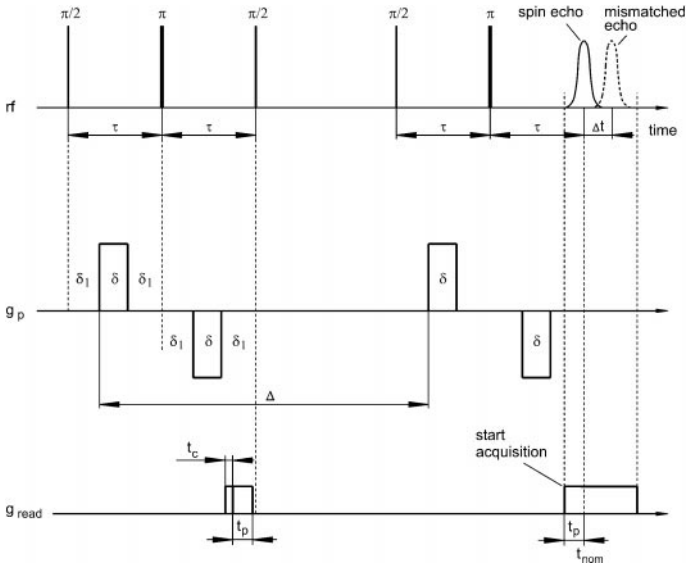

FIG. 1. Thirteen-interval NMR pulse sequence with additional read gradients in the prepare and read intervals. Please note that the definition of Δ is different in comparison with Cotts *et al.* (*10*).

Although the presence of the read gradient during the detection of the signal prevents direct multicomponent diffusion studies by FT APFG NMR, in Section 6 we will introduce a procedure how even this disadvantage may be circumvented.

3. THE TIME SHIFT OF THE NMR SPIN ECHO WITH MISMATCHED PULSED FIELD GRADIENTS

a. The Origin of the Time Shift of the Spin Echo

As already mentioned in the Introduction, the advantage of observing the NMR signal in the presence of a small read gradient in the time domain is that any mismatch of the pulsed field gradients is transformed into a well-defined shift of the spin echo position, which can easily be observed on the screen of the spectrometer computer. This shift is brought about by the fact that the spin echo arises at the instant of time at which the time integral of the effective read and pulsed gradients over the prepare and read period is a minimum (in ideal case equal to zero). Thus, due to the presence of the read gradient g_{read}, a mismatch Δm of the effective pulsed gradients g_p^{eff}, which (for the 13-interval pulse sequence) is given by

$$\Delta m = \int_0^{2\tau} g_p^{eff}(t)\,dt - \int_{t_{nom}-2\tau}^{t_{nom}} g_p^{eff}(t)\,dt, \qquad [1]$$

is compensated by a well-defined time shift Δt of the spin echo maximum. If t_{nom} denotes the instant of time where the spin echo maximum arises without any mismatch of the pulsed field

gradients, the time shift Δt is given by

$$0 = \Delta m + \int_{t^*-t_p-t_c}^{t^*} g_{read}\, dt - \int_{t_{nom}-t_p}^{t_{nom}+\Delta t} g_{read}\, dt\,, \qquad [2]$$

where t^* denotes the end of the read gradient in the prepare interval. For rectangular read gradient pulses of the pulse sequence in Fig. 1 and $t_c = 0$, Eq. [2] transforms into

$$\Delta t = \frac{\Delta m}{g_{read}}\,. \qquad [3]$$

Thus in the presence of a well-defined small read gradient, the time shift Δt of the spin echo can be used to measure the mismatch of the pulsed field gradients.

b. Estimation of the Sensitivity of the Time Shift

Assuming that the timing of the gradients in the pulse sequence is perfectly correct and a mismatch is caused only by a small deviation Δg_p of the intensity of one of the four pulsed gradients in the 13-interval APFG NMR sequence, the observed time shift Δt as indicated in Fig. 1 is related to the intensity of this mismatch by

$$\Delta g_p = \frac{\Delta t}{\delta} g_{read}\,. \qquad [4]$$

In order to estimate the sensitivity of this time shift, let us consider the following example: With a relatively strong read gradient of 50 mT/m in the 13-interval PFG NMR sequence, the position of the spin echo maximum t_{nom} can be determined very accurately. By applying rectangularly shaped alternating pulsed field gradients of a duration δ of 1 ms without any error in their timing, a shift of the spin echo by 1 μs corresponds to a mismatch in the intensities of the pulsed gradients of 5×10^{-5} T/m, which is independent of the actually applied pulsed field gradient intensity. In the APFG NMR experiments described below, current pulses of $\pm$100 A are necessary for the generation of gradient pulses of $\pm$35 T/m. Thus, with the observation of a time shift of the spin echo maximum of 1 μs, a mismatch of the current pulses on the order of 0.2 mA becomes detectable. To correct for this mismatch, the current of one of the four pulsed gradients must be adjusted by exactly this value, which requires that a $\pm$100 A current source must be driven by a 20 bit DAC. Thus, the observation of the position of spin echo maximum in the time domain is very sensitive to any instability in the electronics during the time scale of a single APFG NMR scan.

There are two classes of possible origins of such small instabilities. (i) Reproducible instabilities are caused by thermal effects in the whole gradient coil circuit (including the coil and power supply) and eddy currents in the room-temperature bore or in the sample itself (*23*). They can be minimized by carefully designing the gradient coil circuit, by using pregradients or shaped gradient current pulses (*15*). (ii) Stochastic influences caused by high- or low-frequency noise of the gradient current power supply as well as by the residual hum of its DC power supply are much more difficult to handle. However, as for the reproducible instabilities, their influence is also visible in the shift of the spin echo position.

Because of the special relevance of the stochastic instabilities for high-power gradient current power supplies, the influence of the noise and of the hum will be considered in particular. Such instabilities with frequency components large compared to the inverse width of a single pulsed field gradient ($f \gg 1$kHz) are averaged to zero during each single pulsed field gradient. Therefore, it is not expected that a residual high frequency noise (if present at all) influences the spin echo position. However, all signals with frequency components in the order of the inverse distances between two succeeding pulses in the APFG NMR sequence may result in unwanted small differences in the pulsed gradient intensities. In the 13-interval sequence, these time scales are the time τ between the 90° and the 180° rf pulses, which is typically in the 0.5 to 10 ms range corresponding to frequencies between about 2 kHz and 100 Hz, and the time Δ between the two pairs of the pulsed field gradients, which is typically in the 5 ms to 1 s range corresponding to frequencies between 200 and 1 Hz. Obviously, the main source of noise in these two frequency ranges is the residual hum of the DC power supply generated by rectifying the AC of the lab main power.

c. Exact Measurement of the Time Shift

In principle, the time shift Δt of the spin echo can be measured by comparing the positions of the echo maximum for the measurements with and without pulsed field gradients. This method is limited to sufficiently high signal-to-noise ratios and may yield problems if samples with small initial intensities and/or high attenuations due to the pulsed field gradients are observed. However, there is a very convenient way to calculate exactly the time shift even in cases of small signal-to-noise ratios, which can easily be implemented as automated routine: Consider the convolution of the observed signal without ($M_0(g\delta = 0, t)$) and with ($M(g\delta, t)$) pulsed field gradients:

$$A(t') = \int_{-\infty}^{\infty} M_0(g\delta = 0, t - t')M(g\delta, t)\, dt\,. \qquad [5]$$

Obviously, in the case of the convolution of M_0 with itself (autocorrelation function), the maximum of $A(t')$ which is given by the necessary condition

$$\left.\frac{dA(t')}{dt'}\right|_{t'_{max}} = 0 \qquad [6]$$

occurs at $t'_{max} = 0$. For small time shifts Δt of the spin echo caused by mismatched pulsed field gradients, the shape of the

spin echo envelope does not change significantly (this assumption holds for arbitrary time shifts, if any field gradients perpendicular to the pulsed gradient and transverse relaxation effects are negligible). Due to diffusion effects, only the total amplitude of the spin echo is reduced by a factor ψ. Therefore, the convolution in Eq. [5] may be written as

$$A(t') = \psi \int_{-\infty}^{\infty} M_0(g\delta = 0, t - t')M_0(g\delta, t + \Delta t)\, dt, \qquad [7]$$

which now has its maximum at $t'_{max} = -\Delta t$. Thus, the position of the maximum of the convolution of the spin echo without any pulsed field gradients with the spin echo observed with pulsed field gradients yields directly the shift of the spin echo position compared to t_{nom}. If the result is $\Delta t = 0$, no mismatch of the pulsed gradients occurred and the correct amplitude of the spin echo is measured. If $\Delta t \neq 0$, a mismatch of the pulsed gradient affected the spin echo position. Via Eq. [3] the value of this mismatch can be estimated. The advantage of this convolution compared to the direct observation of the spin echo shift for small signal-to-noise ratios is easily rationalized if one considers the general property of the convolution that uncorrelated signals (noise) do not contribute to the convolution function. Thus, the position of a maximum in a convolution is determined more accurately than the maximum of the corresponding original noise-containing signal.

The convolution and calculation of the position of the spin echo maximum can easily be automated with a software routine. We implemented it in the spectrometer with a Microsoft Visual Basic script, which is started from the spectrometer control software. It reads the measured time domain data and returns the time shift to the spectrometer control. The approach outlined in Eqs. [5]–[7] for time domain data works also with the Fourier transformed spin echoes. The convolutions are then simply given by the multiplication of the Fourier transformed spin echos:

$$A(t') = F^{-1}\{F[M_0(g\delta = 0, t - t')] * F[M(g\delta, t + \Delta t)]\}. \qquad [8]$$

d. A Convenient Approach to an Automated Compensation of the Mismatch of Pulsed Field Gradients

With pulsed field gradients switched on, a shift of the position of the echo maximum is observed, if and only if a mismatch of the effective gradient pulses occurred. The value of the shift is governed by Eq. [3] and can be measured exactly by the procedure described above. To achieve the matching of the pulsed gradients, one could now derive the necessary correction parameter for the pulsed field gradient width or intensity via Eqs. [2]–[4]. Due to the digitally limited resolution (16 bit) of the current amplifiers used, the perfect adjustment of the pulsed gradient intensity is not always possible when using ultra-high intensity pulsed field gradients (see Section 5). However, there is a completely identical and even more convenient way to achieve the same result: One can actually adjust the time of the read gradient in the prepare interval using the correction parameter t_c until the echo appears at the correct position t_{nom}. The necessary correction follows from Eq. [2]. For rectangular read gradient pulses it is given by

$$t_c = -\frac{\Delta m}{g_{read}}. \qquad [9]$$

By comparing Eq. [9] with Eq. [3], it turns out that the amount of the necessary correction time t_c is exactly the same as the observed time shift of the spin echo caused by mismatched field gradient pulses! Thus, by measuring the time shift in the first run of the pulse sequence one knows exactly the necessary correction for the duration of the read gradient in the prepare interval in a second, repeated run. It is simply $t_p + t_c$ and will correct exactly the mismatch if it is reproducible. This procedure is easily implemented and automated, since the time shift of the spin echo can be measured automatically and returned to the spectrometer control by the routine described above. If a time shift was observed, which exceeds a predefined, acceptable value, the experiment was repeated using this correction t_c thus abolishing the mismatch of the previous measurement. Now, the amplitude of the spin echo is registered and used for determination of self-diffusion coefficients from the spin echo attenuation.

4. HARDWARE REQUIREMENTS FOR ULTRA-HIGH INTENSITY PFG NMR APPLICATIONS

a. Gradient Current Power Supplies

Pulsed magnetic field gradients are generated by directing pulses of electric current through suitably arranged coil systems. High mechanical stability of both the coils (*24*) and the sample (*25*) are indispensable prerequisites for faultless diffusion measurements and are mainly an issue of PFG NMR probe design. Here, we focus on aspects of the electronics necessary to generate a high stability and reproducibility of the intensive current pulses.

Currently used gradient power supplies. Most modern NMR spectrometers provide the user with an interface which allows control of the timing (width), the shape, and the intensity of the pulsed field gradients via the pulse programmer. The desired pulse shapes and intensities are generated as a low-power analogue output signal in a DAC, which drives a suitable high-power current source. The achieved gradient intensities reach about 1 T/m (*22, 26*), which is strong for most imaging applications, sufficient for some diffusion applications, but not strong enough for measuring small diffusion coefficients, or substances with short spin relaxation times (*27*). Modern commercial systems as, e.g., described in Ref. (*15*) provide pulsed field gradients of up to about 10 T/m. However, as also pointed out in (*15*), care must be taken when pushing these systems up to their nominal limits.

Only in exceptional cases, higher pulsed field gradients are reported. They are based on homebuilt power supplies and/or specially designed gradient coils.

The homebuilt PFG spectrometer in the NMR group of the Max-Planck-Institut für Metallforschung in Stuttgart (as is described in (*28*)) was modified in 1990 to be capable of generating magnetic field gradient pulses of up to 50 T/m (*29*). It has been used for diffusion measurements in lithium with field gradient pulses of up to 35 T/m (*30*). Recently, the system was equipped with an actively shielded anti-Helmholtz gradient coil (10 mm sample diameter) and with a new gradient current power supply, which consists of a directly binary coded current source (DBCCS). Since the present spectrometer design is only reported in a German Ph.D. thesis (*31*), a brief description of the principles of the DBCCS may be found below.

Since 1993, magnetic field gradient pulses of up to 25 T/m are used in routine measurements at the university of Leipzig (*4, 24*). The gradient coil is an actively shielded anti-Helmholtz coil with 7.5 mm sample diameter. The power supply consists of a highly stabilized and adjustable voltage source providing the necessary current pulses of up to 70 A by discharging as many sets of capacitors as field gradient pulses are required.

In 1998, Callaghan (*27*) introduced a system which is capable of generating 40 T/m gradient pulses. It uses a small quadrupolar gradient coil (3 mm sample diameter) and is driven by a power supply suitable for 40 A current pulses. However, Ref. (*27*) actually reports only experiments with pulsed field gradients of up to 25 T/m.

DBCCS as current source for ultra-high-intensity pulsed field gradients. The DBCCS works like a conventional DAC (*31*). Current pulses of up to ± 120 A with a maximum duration of 9 ms can be adjusted in steps of ± 1.875 A. Currents of 1.875, 3.75, 7.5, 15.0, 30.0, and 60.0 A are provided by power MOSFETs (so-called Single-Die-MOSFETs, type 10026JN, APT, USA) in parallel connection. The 15.0, 30.0, and 60.0 A steps are produced by 2, 4, and 8 MOSFETs, respectively. An additional MOSFET with an adjustable current between 0 and 1 A is used for the generation of small read gradients.

This system is used in routine measurements with unipolar pulsed field gradients of up to 25 T/m. Most of the applications are in the field of hydrogen diffusion in metallic systems (see Refs. (*32–34*) and references therein). Recently it was used to accurately determine the diffusivity of hydrogen in paramagnetic intermetallic compounds by applying alternating pulsed field gradients of up to ± 25 T/m (*35*).

Since the effort for design and construction of the DBCCS makes this system very expensive, an alternative gradient power supply for generation of similar ultra-high alternating pulsed field gradients was designed. It is based on the combination of two (or more) commercially available gradient current power supplies in the so-called push–pull configuration (PSPPC).

PSPPC as current source for ultra-high-intensity pulsed field gradients. In order to increase the output voltage of commercially available gradient current power supplies one can connect two (or more) of them in series. For two TECHRON 8606 (*36*) used in the PSPPC, the supplier recommends the so-called push–pull configuration in which the gradient coil is wired in the middle of two power supplies (see Illustration 3–1 in Ref. (*37*)). Since each of the TECHRON power supplies is capable of generating ± 150 V, the effectively available voltage at the gradient coil is ± 300 V. Each amplifier is rated for currents of up to ± 100 A. The push–pull configuration does not change this maximum available output current. However, the increased voltage across the gradient coil has the advantage that the rise and fall times of the pulsed gradients are shorter than with a single amplifier.

The gradient coil driven by the PSPPC is the same as that used for the routine unipolar pulsed field gradient applications (*24*). It has an ohmic resistance of 1.4 Ω, an inductance of 220 μH, and a current-to-gradient conversion ratio of 0.35 (T/m)/A. With the maximum available output current of the PSPPC of ± 100 A, it yields a maximum gradient of ± 35 T/m. The gradient rise time from 0 to ± 35 T/m is 120 μs. To maintain the maximum current after the initial rise period, a voltage of ± 140 V is required across the coil, which is about a factor of two less than the maximum output voltage of the PSPPC. This ensures that the power amplifiers are still well protected from overloading when they supply their maximum output current. Moreover, it provides enough voltage gain for fast switching times required for nearly rectangularly shaped pulsed field gradients.

b. Triggering of the Pulse Sequence to the Phase of the Lab Main AC Power Source

As mentioned in Section 3b, a most prominent source for small mismatches of the pulsed field gradients might be the residual hum of the gradient current power supply. In principle, a gradient power supply with no hum would solve this problem. However, such a power supply is expensive or, most likely, even impossible to produce. But there is an easy way to circumvent this problem: The stochastic instabilities of the gradient current pulses, caused by the residual hum of the gradient current power supply, may be transfered into a reproducible mismatch if the pulse sequence is triggered to the phase of lab main AC. The gain of stability is demonstrated in Section 5. Such triggers are commercially available. A trigger designed by Resonance Instruments (GB), which is incorporated in the spectrometer console of the same manufacture, was used for the PSPPC.

c. The Spectrometer Electronics

The spectrometer designed for the NMR diffusion studies with ultra-high-intensity alternating pulsed field gradients is homebuilt using commercially available electronic components for the rf synthesizer (PTS 500, Programmed Test Sources, Inc., USA),

the rf-power amplifier (RF20000-150P, R.F.P.A.S.A., France), and the spectrometer console (MARAN ULTRA, Resonance Instruments, GB). The PSPPC as well as all other spectrometer components are directly controlled via the MARAN ULTRA console, which itself is controlled via a host PC running RINMR software (Resonance Instruments, GB) under WINDOWS operating software. The gradient control of the MARAN ULTRA console offers 16-bit resolution in the gradient power channel. This corresponds to a resolution of about ±3 mA at the output of the PSPPC which is sufficiently small for the generation of read gradients. The spectrometer is equipped with a wide bore 9.4 T sc magnet (Bruker, Germany) and operates at a ^{1}H resonance frequency 400 MHz. In a modification of the name of the previous system *FEGRIS 400* (*24*), this new spectrometer is called *FEGRIS 400 NT*. RF probe design and temperature control of the samples are very similar to the older system and may be found in (*24*).

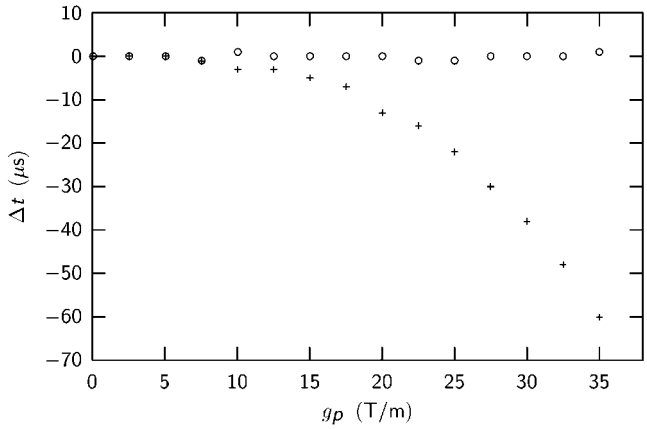

FIG. 3. The dependence of the spin echo position on the intensity of the bipolar pulsed field gradients. The uncompensated (initial) position, which is caused by stable remaining mismatch, is shown by crosses. Circles show the position after automated compensation. Residual deviations smaller than ±2 μs are permitted.

5. RESULTS AND DISCUSSION

a. Enhancement of Electronic Stability of Current Pulses

When only small read gradients are applied, instabilities of the spin echo generated by the 13-interval sequence (Fig. 1) are observed. In the PSPPC concept (and perhaps in most other power supplies connected to the main lab AC power lines), these instabilities are caused by a small ripple of the read gradient which arises from the hum of the current source. The appearance of the spin echo is also controlled by Eq. [2], but—due to the hum—the gradients do not exhibit well-controlled shapes, which prevents an easy prediction of the shift of the spin echo position.

However, the influence of the hum on the spin echo position can be observed experimentally. In Fig. 2, the distribution of the position of the spin echo maximum is plotted for 255 successive measurements with a single scan and pulsed field gradients switched off. The read gradient is set to 53 mT/m using the PSPPC. Under these conditions, the width (FWHM) of the spin echo in time domain is about 100 μs. Clearly, shifts of the spin echo position of up to ±35 μs are not acceptable for reliable diffusion measurements since they are connected to signal amplitude distortions due to inevitable inhomogeneities of the static magnetic field and transverse nuclear magnetic relaxation (*16, 17, 20*). Signal averaging in time domain is not possible under such conditions. Since the hum, which controls these shifts, is not a random process, the distribution of the shifts is not expected to be a Gaussian function.

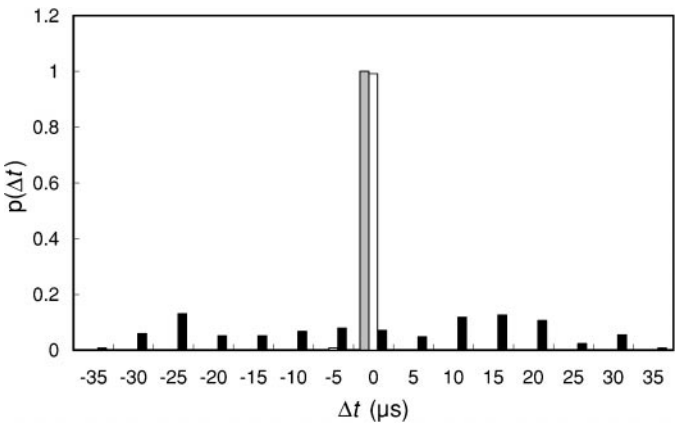

FIG. 2. The probability distribution $p(\Delta t)$ of the time shifts Δt of the spin echo position due to the hum of the gradient power supply. The large shifts, observed without pulsed gradients and without trigger (black bars) reduce significantly by using the trigger (white bars) and do not increase when applying the bipolar pulsed field gradients (gray bar).

By triggering the rf pulse sequence to the phase of the mains supply, the shifts of the spin echo positions are reduced by more than a factor of 10 (see Fig. 2). They are now smaller than ±2 μs for the used settings of the read gradient. Moreover, it is most remarkable that these shifts from scan to scan do not increase, when the pulsed field gradients are switched on. Figure 2 demonstrates this for the APFG NMR experiment with the 13-interval sequence using $\Delta = 21$ ms, $\tau = 3$ ms, $\delta = 0.8$ ms, and an intensity of the pulsed gradients of ±35 T/m. However, a stable shift of the spin echo position in respect to the observed position without pulsed field gradients occurs. According to Eq. [3] this stable and reproducible time shift must originate in slightly different field gradients during the prepare and read interval of the pulse sequence. These differences might be caused by thermal effects in the gradient coil/current source system and in residual eddy currents in the room temperature bore of the magnet, respectively. Because of its reproducibility this remaining time shift can not result from any stochastic process (e.g., noise). This time shift, which was calculated using the convolution of the spin echoes in the time domain according to the procedure described in Section 3c, was found to depend on the intensity of the pulsed field gradients. It is plotted in Fig. 3.

b. Automated Compensation of the Mismatch of Pulsed Field Gradients

According to Eq. [4], the observed time shift of 60 μs at $g_p = \pm 35$ T/m would correspond to a necessary adjustment in one of the four pulsed field gradients in the order of 10^{-3} T/m. This amounts to a necessary adjustment of the corresponding current pulse of 11 mA, which is in the order of magnitude of the available digital resolution of the PSPPC. Thus, it is not reasonable to adjust the amplitude of the pulsed field gradients. However, by changing the duration of the read gradient in the prepare interval as suggested in Section 3d, the mismatch is compensated and the spin echo arises at the correct position. The results of this procedure are also shown in Fig. 3. By applying the correction t_c of the read gradient in the prepare interval in the repeated, second experimental run, the deviation of the spin echo position from the position without pulsed field gradients is—even for the largest pulsed field gradients applied—smaller than ± 2 μs. This is acceptable since it is sufficiently small compared to the width of the spin echo in time domain and does not exceed the inevitable scatter of the spin echo position due to the read gradient alone (see Fig. 2).

c. Self-Diffusion Measurements

The test results described above evidence that pulsed field gradients with alternating polarity of an intensity of up to ± 35 T/m may be generated with high stability and reproducibility using the introduced hardware. Inevitable mismatches of such pulsed field gradients can be detected and compensated with a high accuracy by the proposed procedures, which were implemented as software routines in the spectrometer host PC. This concept's ability to yield reliable spin echo attenuations, which are needed for accurate self-diffusion measurements, is demonstrated in Fig. 4. It represents the spin echo attenuation measured with glycerol using the 13-interval pulse sequence.

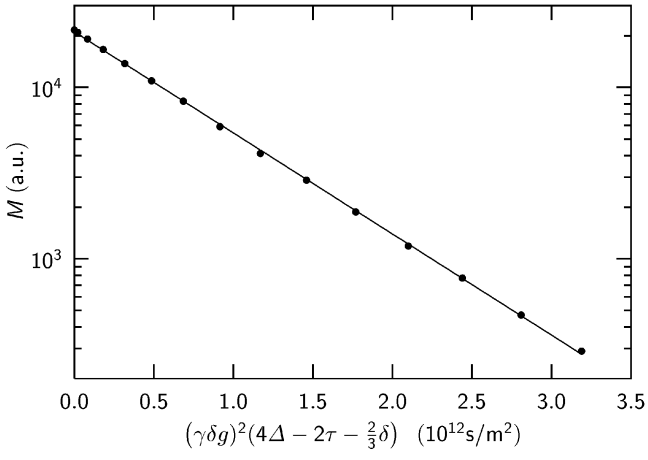

FIG. 4. Spin echo attenuation versus gradient intensity for glycerol by using the 13-interval sequence with $\Delta = 21$ ms, $\tau = 3$ ms, $\delta = 0.8$ ms, and $g_{pmax} = \pm 35$ T/m. The diffusion coefficient obtained is 1.36×10^{-12} m^2/s.

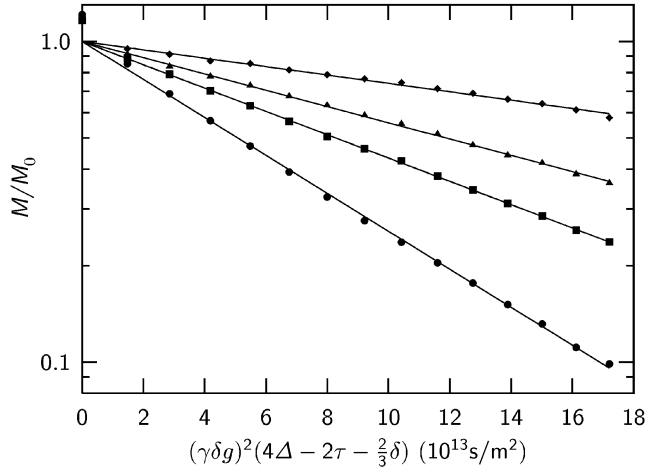

FIG. 5. Spin echo attenuation versus gradient intensity for PEE-PDMS by using the 13-interval sequence at different temperatures (with the increasing slope, at 285.5, 296.5, 304, and 310 K, respectively) with $\Delta = 500$ ms, $\tau = 2.5$ ms, $\delta = 1$ ms, and $g_{pmax} = \pm 35$ T/m. The relative intensities $M/M_0 > 1$ at the origin arise from a small, much faster part of the sample.

The semi-logarithmic plot shows that the observed spin echo attenuation is single-exponentially decaying with the square of the applied field gradient strength. The correlation coefficient obtained is 0.9997. Moreover, the self-diffusion coefficient of $(1.36 \pm 0.01) \times 10^{-12}$ m^2/s determined from the slope of the spin echo attenuation is in the range expected for dry glycerol (*38, 39*) at 298 K. It is most remarkable that even with the ultra-high pulsed field gradient intensities, the scatter in the experimentally determined spin echo attenuation is very small although the NMR signal is attenuated by two orders of magnitude. Thus, the inherent accuracy of these APFG NMR measurements is expected to be very good.

The newly developed method was applied to measure the temperature dependency of the self-diffusion coefficient of a dibloc copolymer PEE-PDMS (molar weight $\approx$ 10 kg/mol) in a temperature range from 285.5 to 317.5 K. The results for the applied 13-interval sequence with $\delta = 1$ ms, $\Delta = 500$ ms, $\tau = 2.5$ ms and $g_{pmax} = \pm 35$ T/m are shown in Fig. 5. The self-diffusion coefficient measured at the lowest temperature is $(3.0 \pm 0.1) \times 10^{-15}$ m^2/s. This corresponds to a mean square displacement of $\sqrt{\langle z^2 \rangle} = 55$ nm. It is most remarkable, that for such a small displacement the spin echo attenuation due to the pulsed field gradients is still 40%. Under consideration of the thermal limit set by the averaged power dissipation in the probe system, the maximum width of a single gradient pulse in the 13-interval PFG NMR sequence is $\delta = 2$ ms. Assuming, that an attenuation of the spin echo intensity of 25 % is large enough to determine the slope of the echo attenuation curve, displacements of down to $\sqrt{\langle z^2 \rangle} = 20$ nm become detectable theoretically.

In Fig. 6, the temperature dependence of the self-diffusion coefficients of PEE-PDMS obtained from the PFG-NMR measurements described above, is represented in an Arrhenius plot. Considering the uncertainty of both the temperature and the

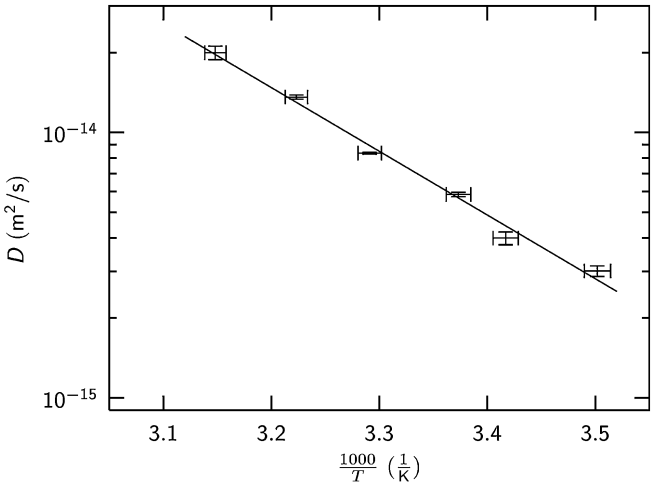

FIG. 6. Self-diffusion coefficient of PEE-PDMS as a function of the inverse temperature.

diffusion coefficients, the temperature dependency of the self-diffusion coefficient is found to follow an Arrhenius behavior with an activation energy of (46 ± 0.5) kJ/mol.

6. CONCLUSION

With the introduced PSPPC gradient power supply, alternating pulsed field gradients of up to ± 35 T/m with extremely short rise times can be used for PFG NMR diffusion studies. Except for the previously built system based on the DBCCS power supply, we are not aware of any other system, where high-intensity pulsed field gradients of this magnitude were successfully used in APFG NMR measurements. In the PSPPC power supply, the necessary current pulses of up to ± 100 A are generated from two single TECHRON 8606 in push–pull configuration. The triggering of the pulse sequence to the phase of the main AC power in the lab has turned out to be an indispensable hardware prerequisite for accurate PFG NMR measurements. It is necessary for both types of the gradient current power supplies. Remaining mismatches of the pulsed field gradients can be quantified accurately, since the spin echo is detected in the presence of a small read gradient. These remaining mismatches are stable and can be compensated by an automated routine, which finally leads to reliable spin echo attenuations and, thus, to high-quality APFG NMR self-diffusion measurements.

The described home-built spectrometer *FEGRIS 400 NT* is currently successfully used for diffusion studies of adsorbed species in microporous materials, of fluids in rocks and sediments and of polymer systems. The individual results will be published elsewhere. So far, the different users reported only two drawbacks of our approach to NMR diffusion measurements with ultra-high pulsed field gradients: (i) The triggering of the pulse sequence to the phase of main AC power may cause timing problems in the pulse sequence. Especially, short relaxation delays between individual scans may be longer than required, since the spectrometer waits after the relaxation delay until a predefined (fixed) phase of the AC power is reached before the new scan is started. (ii) The necessary detection of the spin echo in the presence of a read gradient prevents multi-component diffusion studies with high-resolution FT APFG NMR.

A possible way to enable such high-resolution APFG NMR diffusion studies might consist in the following procedure: Measurement and compensation of the mismatch of the pulsed field gradients is performed as described with the small read gradient in the prepare and read interval of the pulse sequence. After the correction time t_c was determined, a third run of the pulse sequence is performed in which the read gradient is only switched on during t_c. In the case that t_c is negative, a read gradient with opposite sign must be applied. Thus, the mismatch of the pulsed field gradients is compensated by the read gradient in the prepare interval, but, since during the detection of the spin echo no read gradient is applied, FT APFG NMR should allow the separate detection of species with different chemical shifts. This approach is currently being tested.

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