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# Constant time steady gradient NMR diffusometry using the secondary stimulated echo

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## Abstract

A pulse sequence producing a second stimulated echo is suggested for the compensation of relaxation and residual dipolar interaction effects in steady gradient spin echo diffusometry. Steady field gradients of considerable strength exist in the fringe field of NMR magnets, for instance. While the absolute echo time of the second stimulated echo is kept constant throughout the experiment, the interval between the first two radiofrequency pulses is augmented leading to a modulation of the amplitude of that second stimulated echo by self-diffusion only. The unique feature of this technique is that it is of a single-scan/single-echo-signal nature. That is, no reference signals neither of the same pulse sequence nor of separate experiments are needed. The new method was tested with poly(ethylene oxide) melts and proved to provide reliable data for (time dependent) self-diffusion coefficients down to the physical limit ($D \approx 10^{-15}\,\mathrm{m^2/s}$) when flip-flop spin diffusion starts to become effective.

*Keywords:* NMR; Fringe field; Diffusion; Stimulated echo; Field gradient; Poly(ethylene oxide)

## 1. Introduction

Pulsed field gradient spin echo (PGSE) pulse sequences form a popular and convenient class of techniques for the determination of self-diffusion coefficients in liquids [1–6]. However, in more viscous and anisotropic systems such as polymer melts and liquid crystals, respectively, the application of such techniques becomes more difficult: Diffusion is then very slow (diffusivities $\ll 10^{-11}\,\mathrm{m^2/s}$). The gradient encoding times are limited by transverse relaxation times often $\ll 1$ ms. Motional averaging of dipolar interactions tends to be incomplete on the time scale of spin echo evolution intervals. That is, extremely strong ($\gg 10$ T/m) and comparatively short field gradient pulses are required in order to achieve a sufficient echo attenuation by diffusion.

There are a number of problems arising on these grounds with pulsed gradient experiments. Apart from fluctuations of such strong and short gradient pulses in general, fields by eddy currents induced in metal components surrounding the probe must be compensated. Strong gradients stipulate strong currents through gradient coils which in turn may cause some thermal instability. A source of experimental artefacts of paramount importance are pulsed forces either directly on the sample and mobile constituents in it due to the magnetic susceptibility of the materials, or on the current leads and the gradient coils of the system.

All these problems can be safely avoided by employing steady gradients preferably in the fringe field of superconducting magnets [7–9]. The advantages of steady gradient spin echo (SGSE) diffusometry are: There are no time dependent forces. Using the fringe field gradients of superconducting magnets, the stability is perfect and only limited by building vibrations not screened off by damping units. Due to the strength of the available field gradients (about $G = 60$ T/m) in the fringe field of a wide bore 9.4 T magnet [9] or even $G = 180$ T/m in magnets especially designed for this purpose [10] on the one hand, and due to the fact that spatial encoding occurs throughout the whole free-evolution intervals without losses by finite switching periods on the other hand, one exploits the utmost possible echo attenuation efficiency.

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Advantages are unavoidably accompanied by disadvantages: The radiofrequency (RF) pulses used in SGSE diffusometry tend to excite the sample slice selectively. This tendency and the need to acquire inhomogeneously broadened signals with a broad bandwidth may restrict the sensitivity considerably [11]. The problem can be alleviated partly by the construction of special RF coils adapted to the sensitive slice. Note, however, that strongly viscous, cross-linked, and liquid crystalline samples tend to have broad lines, so that the bandwidth problem is intrinsic to the system anyway. The second disadvantage of using fixed steady field gradients is that echo times must be varied. That is, diffusive attenuation is superimposed by relaxation losses and, even worse, may be affected by residual dipolar couplings (the dipolar correlation effect [12–14]).

Self-compensating pulse sequences and experimental protocols for the elimination of relaxation losses have been proposed in [8,15,16]. The "*three-pulse SGSE diffusometry method*" reported in [8] was successfully employed for the examination of adsorbate diffusion in molecular sieves [17]. The self-compensating pulse schemes mentioned so far turned out to work well as long as there is no broad heterogeneous distribution of relaxation times and as long as the dipolar correlation effect can be excluded.

Non-exponential relaxation decays and the influence of residual dipolar couplings can reliably be accounted for with the aid of the "*two-gradient SGSE diffusometry protocol*" [9,18]. Applying this method, alternating measurements in the presence of a very strong and a very weak field gradient are related with each other under measuring conditions otherwise identical. In this way all relaxation and dipolar correlation effects can be eliminated. This solution of the problem is, however, time consuming and requires a second magnet whose resonance frequency in the central field with negligible gradient $G_z \approx 0\,\mathrm{T/m}$ happens to match the fringe field flux density. Corresponding applications are reported in [9,18] for polymer melts.

The feature common to all relaxation compensation methods mentioned above is that the echo signal to be examined is related to other echo signals generated by the same pulse sequence or acquired in separate experiments. The purpose of the present study is to report on a new self-compensating SGSE technique with constant total evolution times. With this method, all relaxation and residual dipolar coupling effects remain constant and can thus be eliminated without need of measuring separate reference signals. The method will be called "*constant time steady gradient (CTSG) NMR diffusometry*." In contrast to the secondary Hahn echo technique proposed by Norwood and Quilter [16] we employ pulse trains for a secondary stimulated echo which turned out to be particularly favourable for viscous materials with short transverse relaxation times and some residual dipolar coupling.

## 2. Principle of the CTSG method

The RF pulse sequence illustrated in Fig. 1 can be represented by

$$\frac{\pi}{2} - (\tau_{1,\min} + \Theta) - \frac{\pi}{2} - \tau_2 - \frac{\pi}{2} - (\tau_{1,\min} + \Theta)$$
$$- (\tau_{1,\max} - \Theta) - \frac{\pi}{2} - \tau_3 - \frac{\pi}{2} - (\tau_{1,\max} - \Theta)$$
$$- (\text{stim. echo}).$$

It is applied in the presence of a strong steady and spatially constant field gradient. In the experiments to be described below, the gradient in the fringe field of a superconducting magnet was used. The RF pulses are assumed to be "hard." That is, they excite the sample area of interest homogeneously. Off-resonance effects that may occur in reality are not considered explicitly because they affect the effective flip angles, but not echo attenuation by diffusion.

The above pulse sequence produces two consecutive stimulated echoes of which only the second is acquired as the measuring signal. The spatially and temporally constant gradient is assumed along the $z$ axis. The complex transverse magnetisation of a thin slice on resonance at a certain $z$ position after the first (nominally) $\pi/2$ pulse in the rotating frame is given by

$$m = M_{x'} + iM_{y'}. \tag{1}$$

It will immediately be dephased due to the strong gradient. Under on-resonance conditions, the second $\pi/2$ pulse stores half of the transverse magnetisation in the $z$ -direction. After a long $(\tau_2 \gg \tau_1)$ storage interval $\tau_2$ the magnetisation is recalled in the transverse plane with the aid of the third $\pi/2$ pulse. During the interval $\tau_{1,\min} + \Theta$ transverse magnetisation is refocused leading to the first stimulated echo with the amplitude

$$\hat{m}_1 = \frac{m_0}{2} \exp\left\{ -\frac{2(\tau_{1,\min} + \Theta)}{T_2} - \frac{\tau_2}{T_1} \right\} E_{\mathrm{diff}}\{(\tau_{1,\min} + \Theta), \tau_2\} E_{\mathrm{DCE}}, \tag{2}$$

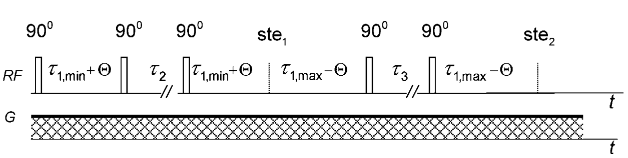

Fig. 1. Pulse sequence consisting of five equal (nominally $\pi/2$) RF pulses for constant time steady gradient (CTSG) NMR diffusometry. Two consecutive stimulated echoes are generated in the presence of a steady gradient. The secondary stimulated echo which is the only echo of interest here, arises at $t' = 2(\tau_{1,\min} + \tau_{1,\max}) + (\tau_2 + \tau_3)$. Varying the interval $\Theta$ while keeping $(\tau_{1,\min} + \tau_{1,\max})$, $\tau_2$, and $\tau_3$ constant, yields the attenuation curve of the second stimulated echo (ste$_2$) for diffusion, whereas relaxation losses and potential residual dipolar coupling effects are constant.

where

$$E_{\mathrm{diff}}\{(\tau_{1,\min}+\Theta),\tau_2\}=\exp\left\{-[\gamma G(\tau_{1,\min}+\Theta)]^2 D\left[\tau_2+\frac{2}{3}(\tau_{1,\min}+\Theta)\right]\right\}. \tag{3}$$

Here $D$ is the diffusion coefficient and $E_{\mathrm{DCE}}$ represents the influence of the dipolar correlation effect originating from residual dipolar couplings. Here and in the following we anticipate a Gaussian probability distribution for the diffusive displacements and mono-exponential relaxation curves for simplicity without loss of generality.

Further dephasing takes place in the interval $\tau_{1,\max}-\Theta$. Half of the dephased transverse magnetisation of a thin slice on resonance is again stored in $z$-direction by the fourth $\pi/2$ pulse. Similar to the time between the second and the third pulse, only longitudinal relaxation is present between the fourth and the fifth $\pi/2$ pulse. After the time interval $\tau_{1,\max}-\Theta$ after the fifth, i.e., last $\pi/2$ pulse, a second stimulated echo is observed depending on $\tau_{1,\min}$, $\tau_{1,\max}$, and $\Theta$ with an amplitude given by

$$\hat{m}_2=\frac{1}{2}\hat{m}_1\exp\left\{-\frac{2(\tau_{1,\max}-\Theta)}{T_2}-\frac{\tau_3}{T_1}\right\}E_{\mathrm{diff}}\{(\tau_{1,\max}-\Theta),\tau_3\}E_{\mathrm{DCE}}, \tag{4}$$

where

$$E_{\mathrm{diff}}\{(\tau_{1,\max}-\Theta),\tau_3\}=\exp\left\{-[\gamma G(\tau_{1,\max}-\Theta)]^2 D\left[\tau_3+\frac{2}{3}(\tau_{1,\max}-\Theta)\right]\right\}. \tag{5}$$

Taking all factors together, one obtains for the amplitude of the second stimulated echo of a thin, resonant slice the expression

$$\hat{m}_2=\frac{m_0}{4}\exp\left\{-\frac{2(\tau_{1,\min}+\tau_{1,\max})}{T_2}\right\}\times\exp\left\{-\frac{\tau_2+\tau_3}{T_1}\right\}E_{\mathrm{diff}}(\Theta,\tau_{1,\min},\tau_{1,\max},\tau_2,\tau_3)E_{\mathrm{DCE}}. \tag{6}$$

The second stimulated echo is then attenuated according to

$$\begin{aligned}E_{\mathrm{diff}}&(\Theta,\tau_{1,\min},\tau_{1,\max},\tau_2,\tau_3)\\&=\exp\left\{-\gamma^2G^2(\tau_{1,\min}+\Theta)^2D\left[\tau_2+\frac{2}{3}(\tau_{1,\min}+\Theta)\right]\right\}\\&\quad\times\exp\left\{-(\gamma G[\tau_{1,\max}-\Theta])^2D\left[\tau_3+\frac{2}{3}(\tau_{1,\max}-\Theta)\right]\right\}\\&=\exp\{-\gamma^2G^2D[\Theta^2(\tau_2+\tau_3)-2\Theta(\tau_{1,\max}\tau_3-\tau_{1,\min}\tau_2)\\&\qquad+2\Theta\vartheta(\Theta-\rho)]\},\end{aligned} \tag{7}$$

where $\rho=\tau_{1,\max}-\tau_{1,\min}$ and $\vartheta=\tau_{1,\min}+\tau_{1,\max}$. This is the evaluation formula for the new CTSG diffusometry technique.

Any overlap effect of second-order echoes need not be considered in this treatment because it can safely be neglected for $\tau_2\gg(\tau_{1,\min}+\Theta)$ and $\tau_3\geqslant(\tau_{1,\max}-\Theta)$.

Keeping $\vartheta=\tau_{1,\min}+\tau_{1,\max}$ and $\tau_2+\tau_3$ constant during the experiment, while varying $\Theta$, removes any influence of transverse and longitudinal relaxation, respectively, on the attenuation of the second stimulated echo. In [15], Demco et al. discuss constant-time relaxation procedures that have a similar purpose.

The formalism for the dipolar correlation effect, $E_{\mathrm{DCE}}$, is a bit more complicated [12,13] and will not be reported explicitly in this report. The argument is that this factor also remains constant under the above conditions of globally constant evolution intervals. The only interval varied in the CTSG experiment is $\Theta$. That is, echo attenuation by diffusive displacements can be experimentally examined directly without knowledge of any other molecular dynamics related parameters.

In the terminology common in PGSE NMR diffusometry [19,20], one distinguishes the gradient pulse width, $\delta$, and the diffusion time, $\Delta$, given as the total middle-to-middle interval between the gradient pulses [2–6]. With the CTSG technique these intervals correspond to

$$\delta\mathrel{\hat{=}}\tau_{1,\min}+\Theta \tag{8}$$

and

$$\Delta\mathrel{\hat{=}}\Theta+\tau_2+2\tau_{1,\min}+\tau_{1,\max}+\tau_3, \tag{9}$$

respectively. Note that the diffusion time normally is dominated by the longest intervals, $\tau_2$ and $\tau_3$, so that $\Delta\approx\tau_2+\tau_3$.

## 3. Experimental

Three practically monodisperse poly(ethylene oxide) (PEO) samples purchased from Polymer Standard Service, Mainz, were used as test substances. All measurements refer to proton resonance and were performed at $(80\pm1)\,^\circ\mathrm{C}$ well above the melting temperature of $\approx 65\,^\circ\mathrm{C}$. The weight average molecular weights were 10,000 ($M_W/M_n=1.2$), 41,500 ($M_W/M_n=1.14$), and 182,000 ($M_W/M_n=1.23$).

For the experiments the fringe field of a Bruker 9.4 T wide bore spectrometer and the central field of a tomograph Bruker BMT 47/40 (4.7 T) were used at a proton resonance frequency of $\nu_0=200\,\mathrm{MHz}$. The field gradients were $G=60\,\mathrm{T/m}$ and $G\approx0.1\,\mathrm{T/m}$, respectively. The $\pi/2$ RF pulse lengths were 2 and 2.5 μs, respectively. In the CTSG diffusometry experiments, the time interval $\Theta$ was incremented in 32 steps from $\Theta=0$ to $\Theta=(\tau_{1,\max}-\tau_{1,\min})$. In each case, $n=32$ scans were accumulated.

Different phase cycles have been tested. No improvement of the signals was found. The reason is that there is scarcely any echo or FID signal overlap due to the extremely narrow echo widths of only about 3 μs. The conclusion is that the CTSG pulse sequence does not produce coherence superposition artefacts and can be used without any phase cycle.

For comparison and reliability tests, the samples were also examined with other steady gradient diffusometry techniques based on the stimulated echo pulse sequence

$$\frac{\pi}{2} - \tau_1 - \frac{\pi}{2} - \tau_2 - \frac{\pi}{2} - \tau_1 - \text{(stimulated echo)}.$$

The three-pulse SGSE diffusometry version [8,17] as well as the two-gradient SGSE protocol [9,18] were employed for this purpose. The intervals $\tau_1$ were varied, whereas $\tau_2 \gg \tau_1$ was kept constant. The stimulated-echo amplitudes were normalized for $\tau_1 \to 0$ in each case. The echo attenuation decays by diffusion were determined by dividing the stimulated echo amplitude by the amplitude of the primary echo arising after the first two RF pulses (three-pulse method), or were extracted by forming the quotient of the normalized echo amplitudes recorded as a function of $\tau_1$ with a strong ($G = 60$ T/m) and a very weak ($G \approx 0.1$ T/m) field gradient (two-gradient compensation technique).

## 4. Results

Fig. 2 shows attenuation curves of the primary and stimulated echo amplitudes recorded after two and three pulses, respectively, in poly(ethylene oxide), $M_W = 182{,}000$, at 80 °C. The fact that the stimulated echo amplitude decays somewhat faster than the primary echo amplitude at a gradient of only $G = 0.1$ T/m, where attenuation by diffusion is negligible, indicates some influence of the dipolar correlation effect [12–14]. This influence is relatively weak with the samples examined in this study, but can be quite strong with larger molecular weights and, in particular, with anisotropic systems such as liquid crystals.

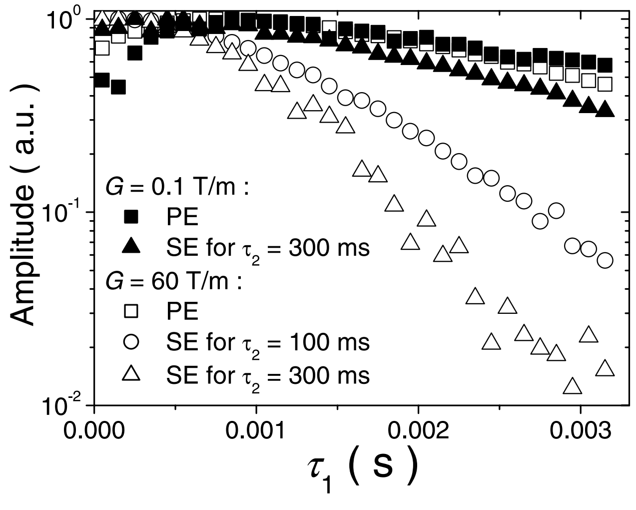

Fig. 2. Normalized attenuation curves of the conventional primary (PE) and stimulated (SE) echoes in poly(ethylene oxide), $M_W = 182{,}000$, at 80 °C, 200 MHz, and a strong and a weak steady field gradient of $G = 60$ T/m and $G \approx 0.1$ T/m, respectively.

Figs. 3 and 4 show echo attenuation curves of three poly(ethylene oxide) melts of different molecular weights, $M_W = 10{,}000$, 41,500, and 182,000. The data have been recorded using the three-pulse SGSE method [8] and the two-gradient SGSE protocol [9], respectively.

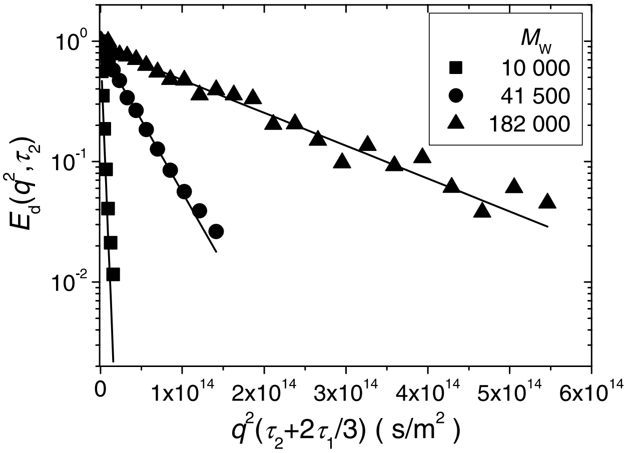

Fig. 3. Normalized echo attenuation curves for PEO melts with different molecular weights measured at 80 °C, 200 MHz, and $G = 60$ T/m with the aid of the "*three-pulse SGSE diffusometry*" method [8]. The data are plotted versus the squared wave number $q^2 = (\gamma G \tau_1)^2$ multiplied by the corrected diffusion time $\tau_2 + \frac{2}{3}\tau_1$. The straight lines represent mono-exponential decays.

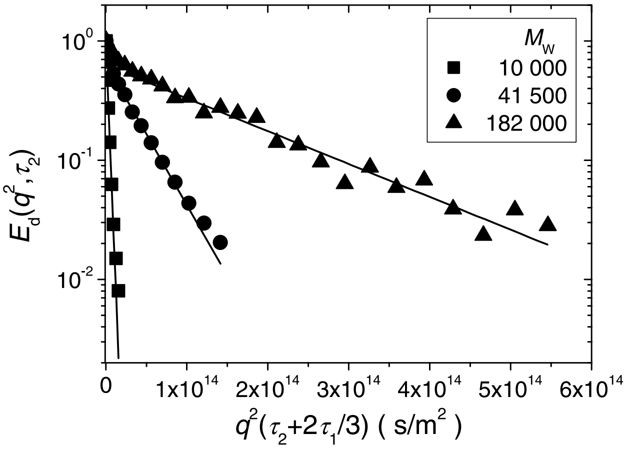

Fig. 4. Normalized echo attenuation curves for PEO melts with different molecular weights measured at 80 °C, 200 MHz, and $G = 60$ T/m. The data were evaluated with the aid of the "*two-gradient SGSE diffusometry protocol*" [9,18]. The data are plotted as a function of the squared wave vector $q^2 = (\gamma G \tau_1)^2$ multiplied by the corrected diffusion time $\tau_2 + \frac{2}{3}\tau_1$. They are calculated as the quotient of two (ordinary) stimulated echo amplitudes recorded at field gradients of $G = 60$ and 0.1 T/m, respectively. The straight lines represent mono-exponential decays.

The data can reasonably well be described by exponential functions from which self-diffusion coefficients can be evaluated (see Table 1).

The amplitude data of the secondary stimulated echo recorded with the CTSG method are shown in Figs. 5A–C. In this case the total diffusion time can be approximated by $\Delta \approx \tau_2 + \tau_3$. For $\tau_2 = \tau_3$ one obtains a symmetric echo modulation curve with a maximum in the middle of the range of the $\Theta$-values, $0 \cdots (\tau_{1,\max} - \tau_{1,\min}) = \rho$. For decreasing values of $\tau_2$ or $\tau_3$, the maximum is shifted to the right and to the left, respectively. In case of very small values of $\tau_3 \approx \tau_{1,\max}$, the maximum is located near the origin. One then obtains decay curves resembling those in ordinary pulsed gradient diffusion experiments.

Table 1
Comparison of (time dependent) diffusion coefficients $D$ (in units m$^2$/s) in poly(ethylene oxide) melts at 80 °C evaluated from the data shown in Figs. 4–6 for the three different measuring techniques

| $M_W$ | Three-pulse SGSE | Two-gradient SGSE | CTSG diffusometry |
|---|---|---|---|
| 10,000 | $3.9 \times 10^{-13}$ | $3.6 \times 10^{-13}$ | $3.4 \times 10^{-13}$ |
| 41,500 | $2.6 \times 10^{-14}$ | $2.7 \times 10^{-14}$ | $2.5 \times 10^{-14}$ |
| 18,2000 | $6.5 \times 10^{-15}$ | $6.8 \times 10^{-15}$ | $5.5 \times 10^{-15}$ |

For a given diffusion time (here e.g., $\tau_2 + \tau_3 = 100$ ms) the choice of $\tau_2 = \tau_3$ leads to an echo modulation curve that covers only about half an order of magnitude in the range of the experimental parameter, $\Theta = 0 \cdots \rho = (\tau_{1,\max} - \tau_{1,\min})$. In this respect, an asymmetric choice of the intervals $\tau_2$ and $\tau_3$ is more favourable since then one of these intervals dominates the total diffusion time which improves the evaluation accuracy. With asymmetric intervals $\tau_2$ and $\tau_3$, the dynamic range of the echo amplitude covers 1.5 decades for poly(ethylene oxide) with $M_W = 10{,}000$ and one decade for poly(ethylene oxide) with $M_W = 41{,}500$.

For comparison, an echo modulation curve of PEO $M_W = 182{,}000$ recorded in a magnetic field with a field gradient of only $G = 0.1$ T/m is shown in Fig. 5C in addition to the 60 T/m data. In this case no signal modulation is detectable apart from the overlap effect by secondary echo signals at very short values of $\Theta$ and for $\Theta = (\tau_{1,\max} - \tau_{1,\min})/2$. Such echo overlaps can safely be avoided at the high gradients used in the other experiments. The intervals $\tau_{1,\min}$, $\tau_{1,\max}$, and $\Theta$ can then be chosen precisely in a way avoiding any overlap due to the extremely narrow echo width of only ≈3 μs (full width at half maximum). Any phase

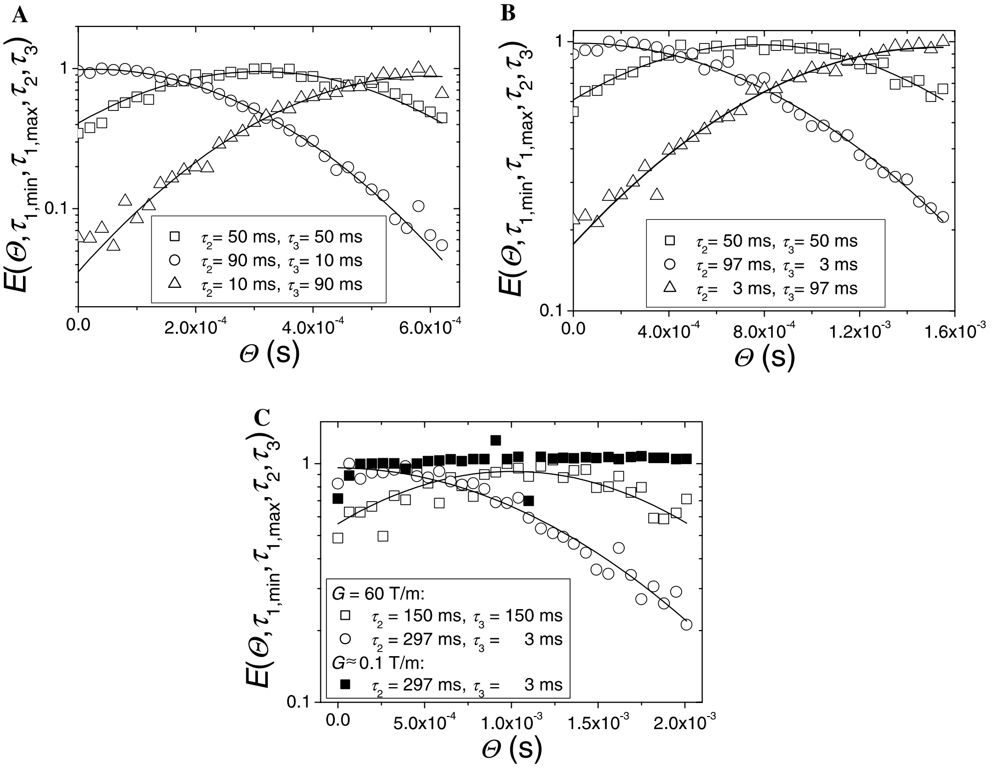

Fig. 5. (A) Normalized amplitude of the second stimulated echo, $E_{\text{diff}} = \hat{m}_2(\Theta)/\hat{m}_2(\Theta = 0)$, of a poly(ethylene oxide) melt, $M_W = 10{,}000$, at 80 °C, 200 MHz, and $G = 60$ T/m plotted versus the interval $\Theta$ (see the pulse scheme in Fig. 1). The intervals $\tau_2$, $\tau_3$ are experimental parameters chosen in such a way that $\tau_2 + \tau_3 = 100$ ms. All data refer to a fixed value $\tau_{1,\max} = 670$ μs. The solid lines represent fits of Eq. (7) to the experimental data. (B) Same as (A) but now for a poly(ethylene oxide) melt, $M_W = 41{,}500$, and $\tau_{1,\max} = 1600$ μs. (C) Same as (A) but now for poly(ethylene oxide), $M_W = 182{,}000$, $\tau_2 + \tau_3 = 300$ ms, and $\tau_{1,\max} = 2065$ μs. For comparison, the normalized amplitude of the second stimulated echo, recorded at 80 °C, 200 MHz, and a weak gradient of $G \approx 0.1$ T/m, is plotted versus the interval $\Theta$. Any attenuation by diffusion is negligible in this case. The few data points strongly scattering indicate overlap effects with secondary echoes as they are more likely with such weak gradients.

cycling curing overlap effects is therefore practically unnecessary.

Fig. 6 shows echo attenuation data recorded with strongly asymmetric diffusion intervals for all three PEO samples. The diffusion coefficients fitted to these data according to Eq. (7) are given in Table 1 in comparison to other data obtained with the other two SGSE techniques discussed above. The molecular weight dependence of the diffusion coefficient in PEO melts is plotted in Fig. 7. The good coincidence of the data obtained with the three techniques underlines the reliability of the CTSG method.

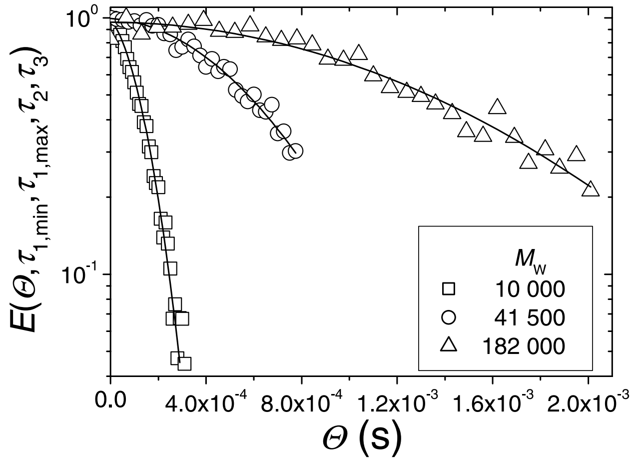

Fig. 6. Normalized amplitude of the second stimulated echo, $E_{\rm diff} = \hat{m}_2(\Theta)/\hat{m}_2(\Theta = 0)$, of poly(ethylene oxide) melts with different molecular weights at 80 °C, 200 MHz, and $G = 60$ T/m plotted versus the interval $\Theta$ (see the pulse scheme in Fig. 1). Experimental parameters are $\tau_2 = 297$ ms and $\tau_3 = 3$ ms. $\tau_{1,\rm max}$ was adjusted to $\tau_{1,\rm max} = 360$, 825, and 2065 μs for the molecular weights $M_{\rm W} = 10{,}000$, 41,500, and 182,000, respectively. The solid lines represent fits of Eq. (7) to the experimental data.

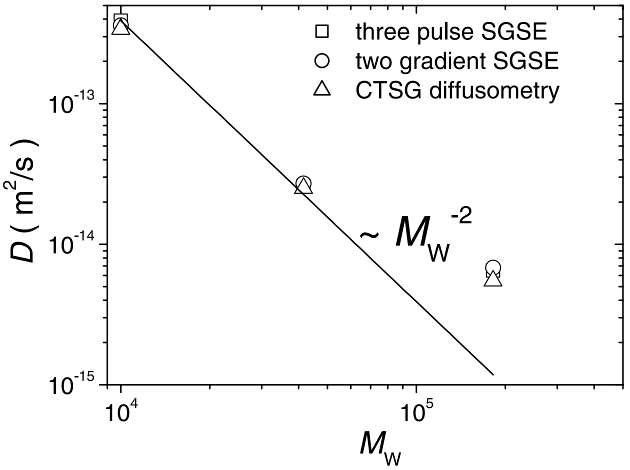

Fig. 7. Molecular weight dependence of the (time dependent) self-diffusion coefficients in PEO melts at 80 °C evaluated from the experimental data shown in Figs. 4–6. The data measured with the three different methods described in the text coincide very well. The straight line represents the molecular weight dependence $D \propto M_{\rm W}^{-2}$.

## 5. Discussion

A steady gradient spin echo method compensating for relaxation losses and potential effects by residual dipolar coupling has been presented and tested with PEO melts covering two orders of magnitude of the diffusion coefficient, $5 \times 10^{-13}\,\mathrm{m^2/s} < D < 5 \times 10^{-15}\,\mathrm{m^2/s}$. That is, the technique is applicable to diffusion coefficients down to the physical limit of any diffusion measurement based on spin echoes, namely to the limit where molecular diffusion is getting surpassed by immaterial flip-flop spin diffusion [9,22].

This *constant time steady gradient* (CTSG) diffusometry technique is based on two consecutive stimulated echoes. The principle is to have the total free-evolution time of spin coherences finally leading to the second stimulated echo constant in the course of the experiment. The amplitude of this secondary stimulated echo is evaluated. The unique feature of this method is that the amplitude of only a single echo is evaluated in the experiments and that all evolution and storage intervals of the pulse sequence remain globally constant. No reference signal is needed for the compensation of other attenuation mechanism.

The reliability of the technique was demonstrated by comparison with experimental data obtained with two other steady gradient methods, namely the three-pulse SGSE and the two-gradient SGSE techniques. It was also shown that signal overlap effects by secondary echoes can safely be avoided due to the extremely narrow echo widths characteristic for fringe field experiments.

A factor of two in the detection sensitivity is sacrificed relative to conventional stimulated echo methods. This deficiency is, however, overcompensated by the fact that all evaluation is based on a series of one and the same sort of spin echo, namely the secondary stimulated echo. The other techniques considered here for comparison are based on the record of different types of echoes or signals recorded under different experimental conditions. The CTSG diffusometry technique is therefore considered to be particularly robust, apart from the fact that steady gradient methods in general are not subject to any time dependent forces or eddy current fields accompanying pulsed gradients.

The interpretation of the diffusion data measured here with a series of poly(ethylene oxide) samples of different molecular weights is beyond the scope of this paper, but closely reproduce literature data. The intricacies of diffusion data for polymer melts and their relation to polymer dynamics models are discussed elsewhere [21–25].

The test experiments carried out in the present study were performed in the fringe field of a super-conducting laboratory magnet. The CTSG technique is also suitable for any other source of strong steady field gradients as they occur with applications of the so-called MOUSE [26,27] or with bore hole and out-of-the-lab NMR devices [27–30].

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## References

[1] I. Ardelean, R. Kimmich, Annu. Rep. NMR Spectrosc. 49 (2003) 43.
[2] W.S. Price, Annu. Rep. NMR Spectrosc. 42 (1996) 51.
[3] P. Stilbs, Progr. NMR Spectrosc. 19 (1987) 1.
[4] J. Kärger, H. Pfeifer, W. Heink, Adv. Magn. Reson. A 12 (1988) 1.
[5] P.T. Callaghan, Principles of Nuclear Magnetic Resonance Microscopy, Clarendon Press, Oxford, 1991.
[6] R. Kimmich, NMR Tomography, Diffusometry, Relaxometry, Springer-Verlag, Berlin, 1997.
[7] R. Kimmich, W. Unrath, G. Schnur, E. Rommel, J. Magn. Reson. 91 (1991) 136.
[8] R. Kimmich, E. Fischer, J. Magn. Reson. A 106 (1994) 229.
[9] E. Fischer, R. Kimmich, N. Fatkullin, J. Chem. Phys. 106 (1997) 9883.
[10] I. Chang, F. Fujara, B. Geil, G. Hinze, H. Sillescu, A. Tölle, J. Non-Cryst. Sol. 172–174 (1994) 674.
[11] P.J. McDonald, Prog. Nucl. Magn. Reson. Spectrosc. 30 (1997) 69.
[12] R. Kimmich, E. Fischer, P.T. Callaghan, N. Fatkullin, J. Magn. Reson. A 117 (1995) 53.
[13] F. Grinberg, R. Kimmich, J. Chem. Phys. 103 (1995) 365.
[14] E. Fischer, F. Grinberg, R. Kimmich, S. Hafner, J. Chem. Phys. 109 (1998) 846.
[15] D.E. Demco, A. Johansson, J. Tegenfeldt, J. Magn. Reson. A 110 (1994) 183.
[16] T.J. Norwood, R.A. Quilter, J. Magn. Reson. 97 (1992) 99.
[17] M. Ylihautala, J. Jokisaari, E. Fischer, R. Kimmich, Phys. Rev. E 57 (1998) 6844.
[18] E. Fischer, R. Kimmich, U. Beginn, M. Möller, N. Fatkullin, Phys. Rev. E 59 (1999) 4079.
[19] E.O. Stejskal, J.E. Tanner, J. Chem. Phys. 42 (1965) 288.
[20] J.E. Tanner, J. Chem. Phys. 52 (1970) 2523. Erratum: J. Chem. Phys. 57 (1972) 3568.
[21] M. Appel, G. Fleischer, Macromolecules 26 (1993) 5520.
[22] E. Fischer, R. Kimmich, N. Fatkullin, G. Ystsenko, Phys. Rev. E 62 (2000) 775.
[23] M. Doi, S.F. Edwards, The Theory of Polymer Dynamics, Clarendon Press, Oxford, 1986.
[24] R. Kimmich, N. Fatkullin, Adv. Polym. Sci. 170 (2004).
[25] N. Fatkullin, R. Kimmich, Phys. Rev. E 52 (1995) 3273.
[26] G. Eidmann, R. Savelsberg, P. Blümler, B. Blümich, J. Magn. Reson. A 122 (1992) 104.
[27] B. Blümich, NMR Imaging of Materials, Clarendon Press, Oxford, 2000.
[28] R.L. Kleinberg, A. Sezginer, D.D. Griffin, M. Fukuhara, J. Magn. Reson. 97 (1992) 466.
[29] M.D. Hürlimann, D.D. Griffin, J. Magn. Reson. 143 (2000) 120.
[30] M.D. Hürlimann, J. Magn. Reson. 148 (2001) 367.