On the Use of Pulsed Field Gradients in a High-Field NMR Spectrometer to Study Restricted Diffusion in Zeolites

J. Kärger, N.-K. Bär, W. Heink, H. Pfeifer, and G. Seiffert

Fakultät für Physik und Geowissenschaften der Universität Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany

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Dedicated to Prof. Dr. Werner Müller-Warmuth on the occasion of his 65th birthday on October 1st, 1994

A probe system is described which allows the application of magnetic field gradient pulses with amplitudes up to 24 T/m for self-diffusion measurements by means of a PFG NMR spectrometer operating at a proton resonance frequency of 400 MHz. It is demonstrated that PFG NMR measurements in the high field of a superconducting magnet necessitate precautions which are of minor relevance for measurements with iron magnets. Taking advantage of the large gradient intensity and the high sensitivity in signal detection of the described system, attenuation patterns of the NMR spin echo are observed for the first time that represent the PFG NMR analogue of the diffraction pattern of a sphere.

Introduction

The application of NMR spectroscopy to monitor the rate of molecular migration is based on the fact that in an inhomogeneous magnetic field the Larmor frequency of the considered spins is space dependent. Thus, by applying an intense inhomogeneous field (the so-called field gradient pulse) over a short time interval, the precessional phase accumulated by a spin during this time interval is determined by its location. In the pulsed field gradient (PFG) NMR technique, one monitors the effect of two succeeding field gradient pulses on the intensity of the NMR spin echo. The effective directions of the gradients [1] are chosen to be opposite to each other. This may be achieved, e.g., by applying field gradients of opposite sign or by applying gradients of the same sign before and after the π pulse in the primary spin echo sequence. Under the assumption that the considered spins have remained at the same positions, the phase shifts attained during the two field gradient pulses will compensate each other. However, any change of the locations of the spins at the instant of the second gradient pulse in comparison with their locations during the first gradient pulse will result in a remaining phase shift, which depends on the magnitude and on the direction of the displacement with respect to the direction of the magnetic field gradient. Molecular diffusion in the time interval between the two field gradient pulses (the "observation time") will therefore lead to a statistical distribution of the resulting phase shifts and hence to a decrease of the signal intensity in comparison to when no field gradients are applied.

Obviously, for a given mean molecular displacement, the signal attenuation becomes more pronounced with increasing intensity (g) and duration (δ) of the field gradient pulses. Thus, for the resolution of small molecular displacements and/or the observation of slow diffusion processes, the application of field gradient pulses with a large value of $g\,\delta$ is inevitable. The shape of the attenuation curve of the spin echo in dependence on the quantity $g\,\delta$ contains information about the pattern of molecular propagation, in particular about deviations from ordinary diffusion in the unconfined space. Therefore, the sensitivity of PFG NMR experiments with respect to such deviations also depends decisively on the accessible range of variation of the quantity $g\,\delta$, and, moreover, on the possibility to reliably measure signal intensities at large attenuations.

In the present communication a PFG NMR probe system operating in the field of a superconducting magnet is described, which allows the application of field gradient pulses with large amplitudes. The efficiency of the device is visualized by demonstrating that the pattern of the spin echo attenuation in the case of restricted diffusion passes through a minimum, as expected on realizing the analogy between the rela-

Reprint requests to Prof. J. Kärger.

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tions for the signal attenuation in PFG NMR measurement of restricted diffusion and the diffraction pattern of a hole.

Experimental

The application of field gradient pulses with large $g\,\delta$ values in the field of a superconducting magnet is limited by the following requirements [1, 2]:

(i) Since any mismatch $(g\,\delta)_2 - (g\,\delta)_1$ between the two field gradient pulses [3, 4] leads to an echo attenuation which may erroneously be interpreted as being due to molecular diffusion, the applied field gradient pulses must be stable and accurately adjustable with respect to each other.

(ii) The position of the sample in the magnetic field must be unaffected by the large forces appearing during the application of the current pulses that generate the magnetic field gradients. Moreover, any critical interference of the magnetic field generated by the field gradient coils with the superconducting magnet must be excluded in order to reduce the risk of quenching.

Requirement (i) has been met by applying a home-built electronic switch [5] producing current pulses up to 100 A with a decay time of 0.07 ms for the generation of the field gradient pulses. The amplitude of the current pulses could be regulated with an accuracy of 1 mA. The stability attained was better than 10^{-5} with respect to the maximum pulse amplitude and proved to be sufficient for the unambiguous resolution of molecular displacements on the order of 100 nm.

In order to fulfill requirement (ii), special care has been taken for the design of the probe. Figure 1 shows the cross-section through the probe applied for ^{1}H and ^{19}F PFG NMR self-diffusion measurements in the field of a superconducting magnet of 9.4 T. The NMR sample tubes are tightly inserted into a support (left part of the figure) which may be fixed within the probe. In this way, mechanical stability of the sample with respect to the probe is ensured. The sample temperature may be varied between $-160\,^\circ$C and $+200\,^\circ$C by a stream of evaporated liquid nitrogen or preheated air. Depending on the flow conditions and the chosen temperature, the difference in the temperature across the sample may attain several K.

During the current pulses the gradient coils are subjected to forces which are proportional to the intensity of the applied constant magnetic field. Consequently, in superconducting magnets with a large field

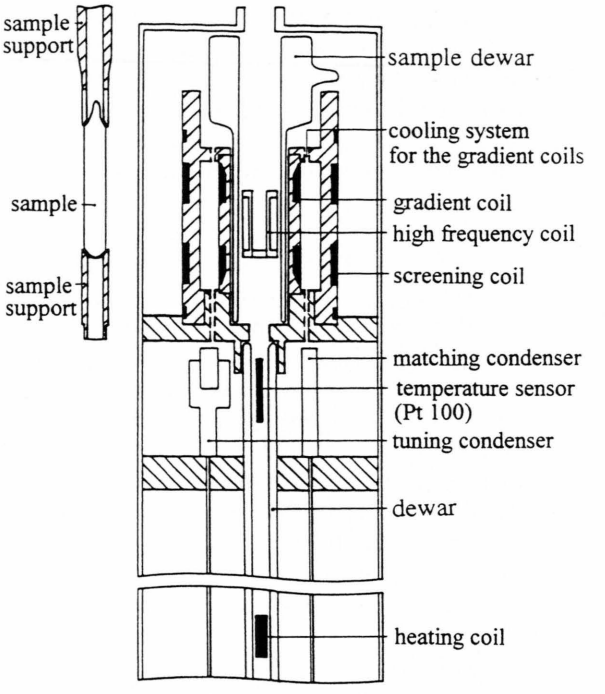

Fig. 1. Cross section through the probe applied for ^{1}H and ^{19}F PFG NMR self-diffusion measurements in a superconducting magnet.

intensity the mechanical pulses exerted on the sample during the field gradient pulses are much larger than in the case of an iron magnet. Similar to a shock wave, the mechanical pulse will also spread over the sample. Thus, even with completely fixed samples, this shock wave may lead to instabilities within the sample tube if the sample material is only loosely contained. Such behaviour was in fact observed with samples containing a loose bed of microporous crystallites, where a spin echo attenuation caused by the instability of the sample material could be observed. It is remarkable that this attenuation was completely reproducible and far from being random. After compacting the material within the sample tube, this effect could be suppressed and the genuine self-diffusivities of the molecules adsorbed on the inner surface of the crystallites could be measured. Looking for the same phenomenon in PFG NMR self-diffusion measurements in iron magnets it was found that due to the much smaller forces, indications of this effect become perceptible only under very special conditions (e.g. extremely small observation times).

The field gradients are generated by opposed Helmholtz coils. They may be cooled by a separate flow system so that, at a pulse rate of $0.2\ s^{-1}$ and with currents up to 70 A, stable field gradient pulses with amplitudes up to $g = 24$ T/m and a duration of $\delta = 10$ ms may be produced. When applying such intense field gradient pulses, any interruption of the cooling led to fluctuations in the values of $g\,\delta$, and hence to an irritating fluctuation in the signal intensity. Using shielding coils [6], even during the application of field gradients of maximum intensity, the additional magnetic field generated by the field gradient coils outside the probe could be kept below a value of 0.25 mT. This value turned out to be small enough, since the field gradient pulses did not lead to a quenching of the applied superconducting magnet (BRUKER AG, system BC-94/89, 89 mm bore).

As a substantial difference in comparison with probe heads used in iron magnets [4, 5], the sample tube in the present probe head is parallel to both the flow direction of the temperature-controlling gas stream (and hence to the direction of the temperature gradient) and to the direction of gravity. As a consequence of this situation, molecular diffusion may be superimposed by flow processes generated within the sample by the density differences due to the temperature gradient. For large temperature gradients this effect may even become dominant, so that a formal analyis of the spin echo attenuation would lead to diffusivities increasing linearly with the observation time.

PFG NMR as a Generalized Scattering Experiment

For sufficiently small magnetic field gradient pulse widths, i.e. when the mean molecular displacements during the field gradient pulses are much smaller than the displacements during the interval between the two field gradient pulses ("narrow-pulse approximation"), the spin echo attenuation in PFG NMR experiments is determined by the relation [1, 4, 7]

$$\Psi(\delta\,\boldsymbol{g}, t) = \int p(\boldsymbol{r}) \int P(\boldsymbol{r}, \boldsymbol{r}', t) \exp[i\gamma\,\delta\,\boldsymbol{g}\cdot(\boldsymbol{r}'-\boldsymbol{r})]\,\mathrm{d}\boldsymbol{r}'\,\mathrm{d}\boldsymbol{r}\,. \quad (1)$$

The quantities δ, $\boldsymbol{g}$, and t denote the duration, amplitude (and direction) and separation of the two field gradient pulses, respectively. γ stands for the magnetogyric ratio. $p(\boldsymbol{r})$ denotes the probability density to find a spin at position $\boldsymbol{r}$, and $P(\boldsymbol{r}, \boldsymbol{r}', t)$ denotes the probability density that a molecule which has been at position $\boldsymbol{r}$, will have migrated to position $\boldsymbol{r}'$ after a time interval t. This latter quantity has been termed the propagator [1, 4, 8].

If the diffusants are confined within regions with impenetrable walls, for sufficiently long times t the propagator will no longer depend on the starting position $\boldsymbol{r}$ and will coincide with $p(\boldsymbol{r}')$. In this case (1) becomes

$$\Psi(\delta\,\boldsymbol{g}, t\to\infty) = \int\int p(\boldsymbol{r})\,p(\boldsymbol{r}') \exp[i\gamma\,\delta\,\boldsymbol{g}\cdot(\boldsymbol{r}'-\boldsymbol{r})]\,\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}' = |S(\boldsymbol{q})|^2, \quad (2)$$

with the notations $\boldsymbol{q} = \gamma\,\delta\,\boldsymbol{g}$ (3)

and

$$S(\boldsymbol{q}) = \int p(\boldsymbol{r}) \exp(-\mathrm{i}\,\boldsymbol{q}\cdot\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\,. \quad (4)$$

Equation (4) is identical to the expression for the amplitude of a wave scattered in a medium with a distribution function $p(\boldsymbol{r})$ of the scattering centres, observed under the scattering vector $\boldsymbol{q}$. Consequently, the spin echo attenuation in PFG NMR studies of restricted diffusion as given by (2) may be interpreted as the intensity of a scattered wave with a scattering vector given by (3). Since the resolution of scattering experiments is determined by the magnitude of the scattering factor, this analogy visualizes the above stated requirement that the observation of small displacements (i.e. of small values for $\boldsymbol{r}' - \boldsymbol{r}$) necessitates large values of $\boldsymbol{g}\,\delta$. In addition we notice that the sensitivity is also proportional to the magnitude of the magnetogyric ratio.

Equation (4) may be applied to determine the diffraction pattern of a hole observed behind a nontransparent screen. In this case the function $p(\boldsymbol{r})$ is constant within the hole and zero outside. By analyzing (4) one may easily deduce the well-known diffraction pattern showing maxima and minima of the wave intensity as a function of the magnitude of the "scattering" vector $\boldsymbol{q}$. With respect to PFG NMR experiments such behaviour would mean that with increasing values $\boldsymbol{g}\,\delta$ the spin echo intensity should exhibit oscillations instead of decaying monotonically to zero.

PFG NMR attenuation patterns showing oscillations with increasing field gradient intensity have in fact been observed for diffusion through a regular arrangement of pores [1, 9–12]. Since the residence probability of the diffusants is clearly maximum within the pores and minimum within the connecting mouths, the analog of this situation is the diffraction pattern of a lattice. In this way, the formation of a

relative maximum of the signal intensity with increasing generalized scattering vector $\gamma \delta \boldsymbol{g}$ may be easily rationalized, and a relative maximum of the spin echo intensity may be shown to be brought about under the condition [1]

$$\boldsymbol{b} \gamma \delta \boldsymbol{g} = 2\pi, \tag{5}$$

where $|\boldsymbol{b}|$ denotes the spacing between the centres of adjacent pores.

The PFG NMR analogue of the diffraction pattern of a sphere would be attained, if the diffusants could be kept within the individual crystallites. We have simulated such a situation by considering the intracrystalline diffusion of tetrafluoromethane in zeolite crystallites of type NaX. The mean radius of the crystallites was 19 μm with a standard deviation of ± 1 μm. For sample preparation, the zeolite specimens were activated as usual (10 hours at 400 °C in vacuo, cf., e.g., [13]). Subsequently, at room temperature, the activated zeolite sample was brought into contact with CF_4 at atmospheric pressure. Finally, the intercrystalline space was blocked by imbedding the zeolite crystallites in an epoxy resin. In this way, a confinement of diffusion to the intracrystalline space could be ensured.

Using CF_4 as an adsorbate, the diffusion studies could be carried out using ^{19}F NMR. In this case any contribution of the blocking material to the NMR signal, which otherwise might have significantly reduced the lower limit of observable spin echo attenuation due to diffusion, could be excluded. The mobility of the diffusants ($2 \cdot 10^{-9}$ m^2 s^{-1} at the measuring temperature of 25 °C [14]) turned out to be sufficiently large. Using Einstein's relation

$$\langle l^2 \rangle = 6 D t, \tag{6}$$

with the maximum observation time $t = 640$ ms, it follows that the mean diffusion path without confinement is equal to 88 μm. This is substantially larger than the crystallite radius, so that the application of the large-time-limit approximation of the spin echo attenuation, (2), should be justified.

In the case of restricted diffusion within a sphere of radius R, the probability function is easily found to be [1]

$$p(z) = (3/4R^3)(R^2 - z^2) \quad \text{for} \quad -R \leq z \leq R \tag{7}$$

and zero outside, where z is the coordinate in the direction of the magnetic field gradient. Inserting this relation into (4), with (2) the spin echo attenuation is found to be given by

$$\Psi(q) = \frac{9\{qR\cos(qR) - \sin(qR)\}^2}{(qR)^6} \tag{8}$$

with the generalized scattering vector q as given by (3).

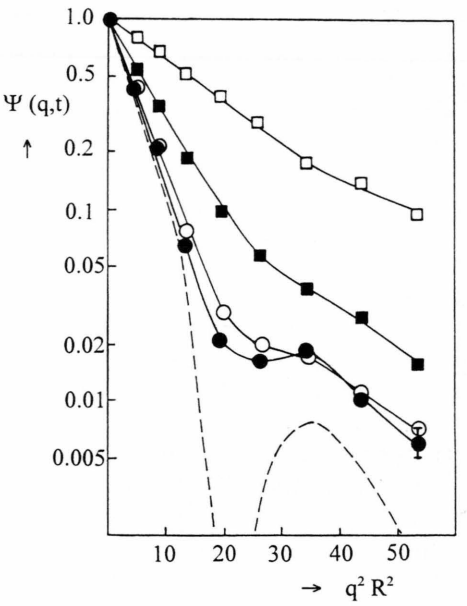

Fig. 2. Experimentally observed spin echo attenuation curves for tetrafluoromethane confined to zeolite crystallites of type NaX with a mean radius of 19 μm for the observation times $t = 10$ ms (□), 50 ms (■), 250 ms (○), and 640 ms (●). The broken line represents the curve calculated according to (8) for the case $t \to \infty$.

Figure 2 shows the experimentally observed spin echo attenuation for increasing values of the observation time together with the theoretical dependence (broken line) according to (8). The full lines connecting the experimental points are provided as guides for the eye. The accuracy of the experimental points in the vicinity of the relative maximum corresponds to the size of the symbols. The accuracy of the measurement for the largest echo attenuation is indicated by the error bar.

It is seen that with increasing values of the observation time the obtained attenuation curves approach a pattern which exhibits the typical features of a scattering experiment. Moreover, the magnitude q of the generalized scattering vector at the first maximum turns out to be in excellent agreement with the value expected theoretically on the basis of (8).

Presently we are not yet sure about the origin of the difference between the absolute values of the experimental and theoretical data of the spin echo attenuation in the vicinity of the relative maximum. A distribution of the crystallite diameters may be ruled out as a possible explanation since in this case the maximum of the theoretical curve would drop to even lower values. One should have in mind, however, that the difference between the experimental and theoretical values at the relative maximum in the echo attenuation curve is much smaller than the absolute value of the echo attenuation. It is most likely, therefore, that the observed deviation of the experimental data from the theoretical expectation may be caused by rather slight differences between the real system and the idealized conditions under which (8) has been calculated. These differences may concern the observation time (which is clearly not infinite), the shape of the crystallites (which are not ideally spherical), the existence of background gradients brought about by the differences in the susceptibility of the zeolite crystallites and the surrounding intercrystalline space [15, 16] and possible deviations from the narrow-pulse approximation. Recent numerical calculations [17, 18] of the spin echo attenuation for molecular diffusion confined by parallel walls have shown that a deviation from the narrow-pulse approximation may in fact lead to an enhancement of the relative maxima in the spin echo attenuation. The corresponding calculations for molecular diffusion under spherical confinement are in progress.

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