Self-Diffusion Coefficients in Plastic Crystals by Multiple-Pulse NMR in Large Static Field Gradients

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Measurements of self-diffusion coefficients in solids with the gradient spin echo technique have until now been limited due to short spin-spin relaxation times. Here we make use of multiple-pulse sequences, which average out the nuclear dipole interaction, to expand the measurable range for macroscopic self-diffusion coefficients by 2 orders of magnitude. By combining multiple-pulse NMR, in our case using the MREV-8 sequence, with a high static gradient we measured the self-diffusion coefficient in a molecular crystal of camphene down to a value of $D = 3 \times 10^{-16}$ m^2 s^{-1} at 219 K in the plastic phase.

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Self-diffusion of molecules or atoms in solids continues to be of considerable interest, both experimentally and theoretically. Recent examples include the particle exchange diffusion in molecular solids [1] and porous media [2] as well as the diffusive motion of modulation waves in incommensurate systems [3]. As a common feature of all these studies, information about microscopic length scales (lattice constants, modulation wave vectors, etc.) is used as input to deduce diffusion coefficients. For many, also technologically relevant, materials such as polymers and liquid crystals, such information is not easily available, so that methods operating on mesoscopic and macroscopic length scales, corresponding to intermediate and small wave vectors $\vec{Q}$, are required.

The classical method for studying slow macroscopic (quasi)self-diffusion is the isotope tracer technique. Besides the need to carry out an expedient isotopic substitution of the atoms and molecules under study, this method suffers from numerous experimental problems (for a detailed discussion, see [4]).

An alternative method for the study of macroscopic diffusion is the magnetic field gradient experiment. In the form of the pulsed gradient spin echo (PGSE) it is a standard method to investigate many aspects of diffusion in liquids [5]. Here on typical experimental time scales the molecules can move over large distances (corresponding to low $\vec{Q}$ vectors). After briefly describing the PGSE method and the major difficulties faced when trying to access large $\vec{Q}$ values, we present a multiple-pulse based NMR method, which circumvents the problem.

The PGSE technique is based on the stimulated echo pulse sequence [6]; see Fig. 1(a). As the wave vector in such an experiment is proportional to the delay between the first two pulses τ and the amplitude of the magnetic field gradient $\mathbf{g}$, the accessible range of the wave vector is limited by both. Since the magnetization is damped by spin-spin relaxation occurring during the dephasing and rephasing periods of length τ, the spin-spin relaxation time T_2 defines the maximum accessible wave vectors.

In liquids, PGSE takes advantage of relatively long relaxation times T_2 and rather large self-diffusion coefficients D, so that strong gradients or other refinements of the experimental method are not required. In solids, however, T_2 is usually shorter than 1 ms due to incomplete averaging of dipolar couplings which precludes application of classical PGSE methods. This can be partially compensated for by using a very strong field gradient as long as the echo damping of the transversal magnetization due to the migration of the molecules across the inhomogeneous magnetic field is larger than the damping due to the spin-spin interactions. In this context it is interesting to mention that a new magnet system using an anti-Helmholtz coil system has recently been installed in Mainz where static gradients up to 180 T/m at ^{1}H frequency of 90 MHz can be obtained [7]. This has allowed for diffusion measurements, e.g., in the plastic (i.e., orientationally disordered) crystal phase of adamantane at $T_2 = 0.7$ ms [7] and in supercooled *ortho*-terphenyl at $T_2 = 0.2$ ms [8].

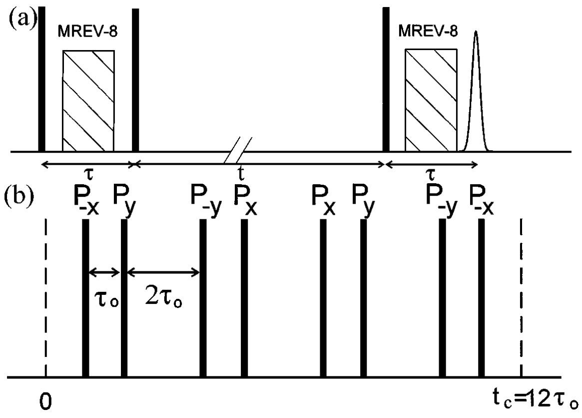

FIG. 1. (a) Superposition of the three pulse sequence (stimulated echo) and MREV-8 pulse sequence. N cycles of the MREV-8 sequence are inserted in the dephasing and rephasing periods of the stimulated echo, where $\tau \ll t$. (b) MREV-8 pulse sequence.

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In this Letter we report on measurements of self-diffusion coefficients of camphene by combining the high static field gradient with multiple-pulse NMR as a means for averaging out the static dipolar coupling. The latter had been used previously with PGSE in liquid crystals and liquid bilayers [9] where, however, the residual dipolar coupling is tiny in comparison with that in solids. Considerable progress has been made over the years to reduce the effects of dipolar broadening in solid state NMR. We have chosen the MREV-8 multiple-pulse sequence which is well known for its high efficiency in comparison with other multiple pulse sequences [10]. Some details of this pulse sequence are shown in Fig. 1(b). One cycle of the MREV-8 pulse sequence consists of a train of 8 $\pi/2$ rf pulses, which are phase shifted by 90° with respect to one another. The spacing between the first two pulses is τ_0 and the cycle time is $t_c = 12\tau_0$. According to the average Hamiltonian theory [10], the Hamilton operator can be replaced by an average Hamiltonian at observation windows $t = Nt_c$, N being the number of cycles. The cycle time here has to be small compared to the time scale of the internal interactions, e.g., dipolar coupling, i.e., $t_c\omega_{\mathrm{dip}} \ll 1$. The MREV-8 sequence averages the static dipolar interactions in a way so that the dipolar coupling only contributes to second order. The stimulated echo pulse sequence used in diffusion measurements [7] is composed of three $\pi/2$ pulses of the same phase; see Fig. 1(a).

For $\tau \ll t$ the amplitude of the echo represents the autocorrelation function which correlates the phase of a tagged spin at time $t = 0$ with its phase at a later time t. In a static field gradient the amplitude of the detected echo is given by [11]

$$S(\tau,t) = S_0(\tau,T_2)e^{-t/T_1}\langle e^{i\vec{Q}\cdot\vec{r}(t)}e^{-i\vec{Q}\cdot\vec{r}(0)}\rangle . \qquad (1)$$

$\vec{Q} = \gamma\tau\vec{g}$ corresponds to the momentum transfer vector in scattering experiments, $\vec{r}(t)$ is the position of the spin at time t, $\vec{g}$ the magnetic field gradient, and γ is the proton gyromagnetic ratio. Whereas the damping of the signal due to spin-lattice relaxation follows an exponential law e^{-t/T_1} with relaxation time T_1, the dipolar interactions in solids give rise to nonexponential decay, denoted by $S_0(\tau,T_2)$ in Eq. (1). The phase correlation function $\langle e^{i\vec{Q}\cdot\vec{r}(t)}e^{-i\vec{Q}\cdot\vec{r}(0)}\rangle$ is the well known Van Hove correlation function or intermediate incoherent scattering function [12]. In order to reduce the signal damping due to the spin-spin relaxation during the evolution (dephasing) and the detection (rephasing) periods, N cycles of the MREV-8 pulse sequence are superimposed on the stimulated echo pulse sequence [Fig. 1(a)]. In our experiments we have varied the diffusion time t, keeping the number of cycles in the dephasing and rephasing periods τ constant. Thereby it was unnecessary to determine the shape of $S_0(\tau, T_2^{\mathrm{eff}})$, provided that the decay time under the influence of MREV-8, T_2^{eff}, has been increased sufficiently that the signal amplitude is finite at $\tau = Nt_c$. The spin-lattice relaxation time T_1 was determined by the inversion recovery method. Since $2\pi/Q$ was sufficiently large (>250 nm) in our experiment, we can safely assume Fickian diffusion and formulate Eq. (1) as

$$S(t) = S_0 \exp\left(-\frac{t}{T_1}\right)\exp\left[-\left(\frac{\sqrt{2}}{3}\gamma g N t_c\right)^2 Dt\right], \qquad (2)$$

where $\sqrt{2}/3$ is the scaling factor for MREV-8 [10].

We have chosen polycrystalline dl-camphene as a first example to test the applicability of the technique. Here, an orientationally disordered (plastic) phase with bcc structure exists from the melting temperature of 324 K down to $T_c = 154$ K, below which the camphene molecules are orientationally ordered. The sample used in our experiments was reagent grade, 94% purity, from Aldrich Chemical Company.

Most of the dipolar coupling is averaged out by fast molecular reorientation in the plastic phase. However, the residual static coupling results in short T_2 values which prohibit application of the PGSE method and even the static gradient technique [7] can only be applied (in camphene) at temperatures $T > 260$ K where $T_2 > 400$ μs (see Fig. 4).

In order to determine the extent to which the line narrowing by MREV-8 is effective in an extremely strong field gradient, we used the conventional Hahn echo [13]. Here, the magnetization loss caused by the field gradient is recovered by applying a π pulse after the evolution time $\tau = Nt_c$. In all measurements the $\pi/2$ pulse length was 0.7 μs at the resonance frequency of 90 MHz. For the diffusion experiment t was varied keeping all other parameters constant, and thus it was necessary to determine T_1 separately. This was also done in the gradient magnet system in order to keep the systematic error in measuring the temperature as small as possible. Cycle times t_c of 96 and 72 μs were used and various numbers of cycles N ranging from 12 to 20, depending on the temperature. The magnetic field gradients were set to $g = 71$ or 111.5 T/m in our experiments.

Figure 2 demonstrates the efficiency of MREV-8 in the high magnetic field gradient in comparison with the homogeneous field case (inset in Fig. 2). Although further studies at variable g are necessary in order to investigate in detail the effect of the MREV-8 pulse sequence under strong off resonance conditions, it is apparent from Fig. 2 that the line narrowing efficiency is effective even in our large gradient. This is all we need for our diffusion studies using the stimulated echo sequence.

Shown in Fig. 3 is a measured curve from the composite pulse sequence consisting of 16 MREV-8 cycles and the stimulated echo compared with that of the T_1 curve measured with the inversion recovery method. The diffusion coefficient is calculated from the difference of the decay constants of the two measurements. It is noted that when too few ($N \leq 3$) MREV-8 cycles were used such a difference could not be detected.

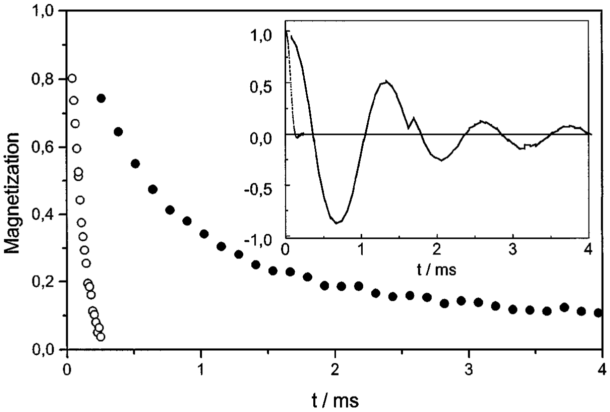

FIG. 2. Decay of the transversal magnetization due to spin-spin relaxation measured in the anti-Helmholtz magnet at 90 MHz, $g = 71$ T/m, $T = 230$ K. ○: T_2 measured with Hahn echo; •: T_2^{eff} measured with MREV-8 combined with Hahn echo. Inset: decay of the transversal magnetization measured in homogeneous field at 90 MHz, $T = 230$ K. Dashed line: FID. Solid line: decay under MREV-8. The curve was taken with stroboscobic detection.

The result of self-diffusion measurements in camphene is shown in Fig. 4. From immediately below the melting point down to the temperature where T_2 is approximately 400 μs the diffusion measurements could be carried out using the conventional stimulated echo pulse sequence. Below this, the measurements were done by incorporating the MREV-8 sequence. At the lowest value of $D = 3 \times 10^{-16}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ determined at 218.7 K the application of the MREV-8 sequence resulted in a prolongation of T_2 from 75 μs to $T_2^{\mathrm{eff}} \approx 1.4$ ms. We estimate the experimental uncertainty in the determination of D to be about ±70% at this temperature as indicated by the error bar in Fig. 4. Also shown in the figure are the radiotracer [14] and NMR relaxation diffusion data [15]. The theory and the experimental techniques for studying slow motion in low fields are described in a review by Ailion [16]. The discrepancy between the tracer measurements and the NMR relaxation method is known also in other plastic crystals [17]. Our D values are somewhat larger than those determined by NMR relaxation. We are not sure at present whether this difference is an impurity effect of due to the fact that the transport process monitored by NMR relaxation is seen on the length scale of the interparticle distance, whereas we are measuring particle displacement over much larger distances.

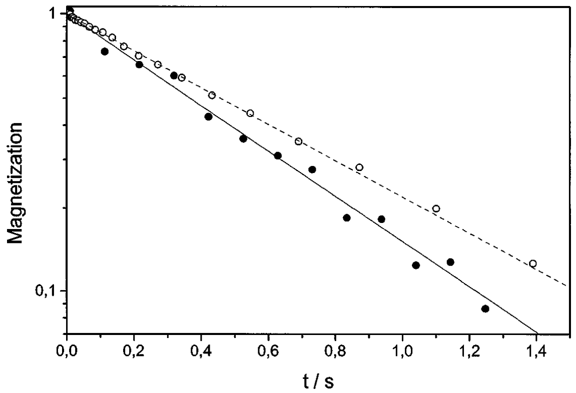

FIG. 3. ○: T_1 curve measured with inversion recovery; •: diffusion experiment made with 16 MREV-8 cycles and stimulated echo, $\tau = 8$ μs, $T = 239.5$ K, and $g = 111.5$ T/m. The diffusion coefficient was calculated from the difference in the decay constants of the two curves.

Our measurements of the diffusion coefficients in the plastic crystal phase of camphene have taken advantage of the fact that the averaging out of the dipolar coupling is already partially provided by nature. This partial averaging of the dipolar interactions is also found in polymeric systems or in liquid crystals. Here, the method presented in this Letter can be expected to be applicable very efficiently as well. Our technique, however, is not only well suited to extend the range of measurable self-diffusion coefficients, but can also serve as a way to enlarge the accessible range of $\vec{Q}$ values in magnetic field gradient experiments. Potential fields of application include such vastly different areas as materials research and biophysics. It is noted that the availability of a dedicated high gradient magnet is not a prerequisite for the application of the multiple pulse method itself. We expect that many experiments can also be carried out in the stray field of commercially available superconducting magnets. The use of stray fields is currently gaining much interest [18]. In this case the somewhat lower gradients (typically up to 60 T/m) will, however, not quite allow

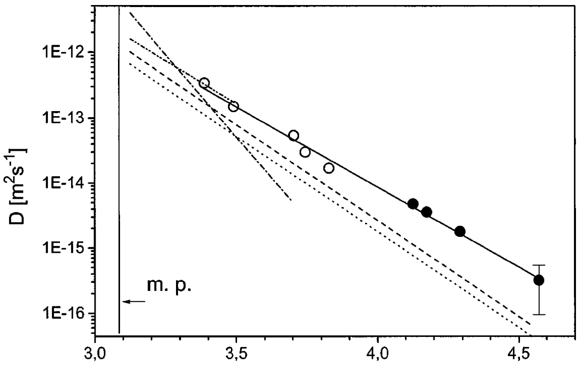

FIG. 4. Arrhenius plot of the diffusion coefficients of dl-camphene; ○: measured with the stimulated echo in static gradient of $g = 71$ T/m; •: measured with MREV-8; solid line: a fit with $E_a = 47.2$ kJ/mol; dashed line: NMR relaxation data on pure dl-camphene, $E_a = 56.5$ kJ/mol [15]; short dashed line: NMR relaxation data on dl-camphene/10% *d*-camphor, $E_a = 56.2$ kJ/mol [15]; dash-dotted line: ^{3}H-labeled tracer in pure dl-camphene, $E_a = 96.2$ kJ/mol [14]; dash-double-dotted line: tracer in dl-camphene/15% *d*–camphor, $E_a = 50.2$ kJ/mol [14].

attainment of the small D and large range of Q values accessible with anti-Helmholtz magnets.

In conclusion, we have shown that a combination of multiple-pulse line narrowing techniques and large static field gradient provides the opportunity of measuring extremely small self-diffusion coefficients in solids. The value of $3 \times 10^{-16}\,\mathrm{m}^2\,\mathrm{s}^{-1}$ is, to our knowledge, the smallest value of a macroscopic self-diffusion coefficient ever measured by magnetic field gradient NMR.

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