

● Invited Lecture

THE NMR-MOUSE: CONSTRUCTION, EXCITATION, AND APPLICATIONS

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A mobile nuclear magnetic resonance (NMR) device similar to a bore-hole probe has been developed for applications in materials science and biomedicine. Inhomogeneous polarizing and radio-frequency (rf) magnetic fields are applied to arbitrarily large samples from one side. Different experimental techniques have been tested to measure transverse and longitudinal relaxation times and translational diffusion constants. Good contrast for discrimination of material properties is gained when the residual dipolar coupling is retained in soft matter by avoiding spinlock effects in multi-pulse techniques. Applications to characterization of products from technical elastomers, skin, and coatings on iron sheets are reported. © 1998 Elsevier Science Inc.

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INTRODUCTION

Nuclear magnetic resonance (NMR) with spatial resolution is appreciated in materials science for its capability to identify material inhomogeneities and material change by a large range of accessible contrast parameters. The most important ones for material characterization are those which probe molecular dynamics. In particular, slow molecular motion and restricted, anisotropic motion carry the signatures from chemical reactions by aging, from local strain, temperature, and cross-link density in elastomers. They are probed by NMR relaxation times.^{1–3}

For generation of spatial resolution, magnetic field gradients are an asset, and their continuous presence poses little restriction for measurement of transverse and longitudinal relaxation as well as translational diffusion. Thus, NMR devices for spatially resolved materials characterization can be constructed with inhomogeneous magnetic fields, which obviates the superconducting magnet as the most expensive component in commercial imaging equipment.

Based on these considerations, the NMR Mobile Universal Surface Explorer (MOUSE) has been developed (Fig. 1),⁴ which applies the principles of inside-out NMR.⁵ A similar concept has been reported previously.⁶

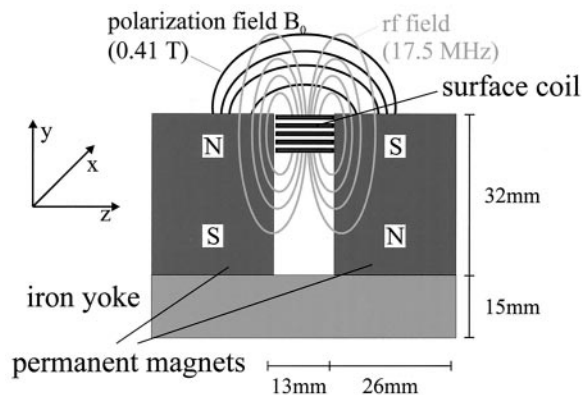


Fig. 1. Principle of the NMR-MOUSE: The static polarizing magnetic field B_0 and the rf field B_1 are approximately orthogonal to each other.

The static magnetic field is generated by two permanent magnets with anti-parallel magnetization. A solenoidal radio-frequency (rf) coil is positioned in the gap between the two magnets so that the static polarizing magnetic field B_0 and the rf field B_1 are approximately orthogonal to each other within a reasonably large volume above the surface of the sonde.

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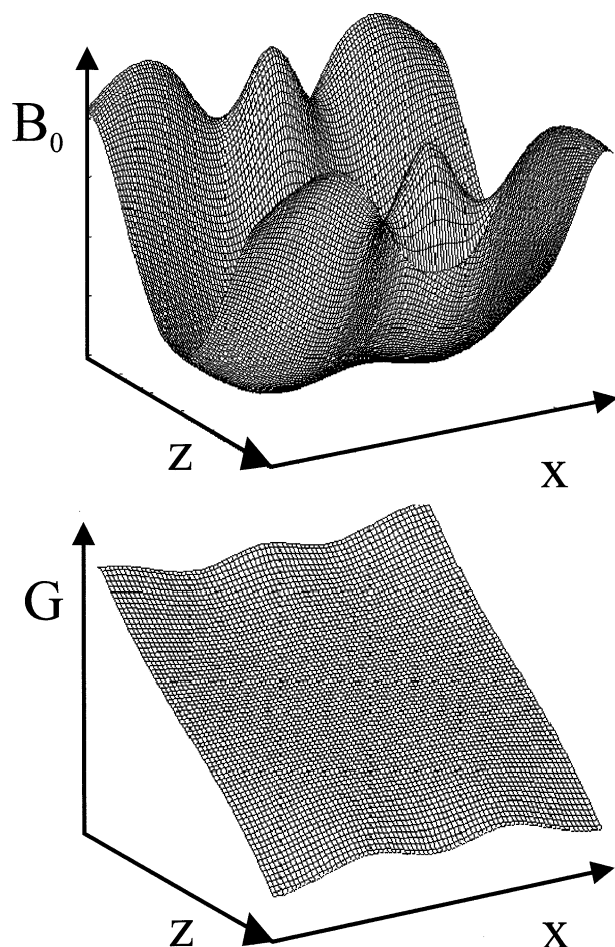


Fig. 2. Simulated profile of the polarizing magnetic field B_0 . Top: Dominating z component at a distance of $y = 2.5$ mm above the surface of the sonde. Bottom: Associated gradient profile at $y = 2$ mm. The magnetic-field gradient varies within the sensitive volume.

MAGNETIC FIELDS AND SENSITIVE VOLUME

The simulated profile of the dominating z component of the B_0 magnetic field is depicted in Fig. 2 at a distance of $y = 2.5$ mm above the surface of the sonde, together with the associated gradient profile. The field depends on space in an approximately quadratic fashion, so that the field gradient is nearly linear across the gap. Together with the B_1 -field distribution of the rf coil, an ellipsoidal shape of the sensitive volume is obtained in the vicinity of the surface coil (Fig. 3, top). The width of the sensitive volume is determined from the projection along the gap as 3.5 mm (bottom). The experimental values (left) determined by probing the sensitivity with a small piece of silicone rubber at different positions agree well with the ones obtained by computer simulations (right) (G. Eidmann and B. Blümich, manuscript in preparation).

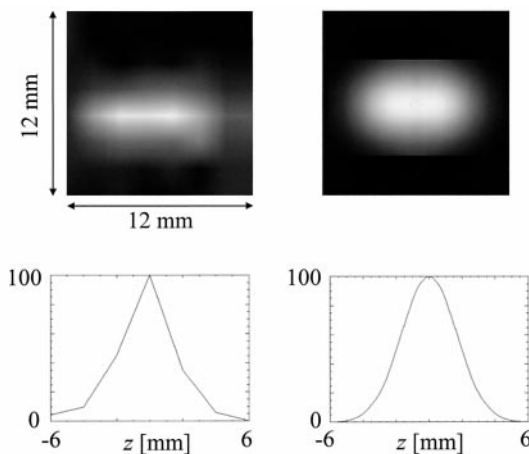


Fig. 3. Sensitive volume of the NMR-MOUSE. Left: Experimental values. Right: Values obtained from simulated B_0 - and B_1 -field distributions and the Bloch equations. Top: Two-dimensional representations. Bottom: Projections of the sensitivity profiles along the gap.

The magnetic-field gradient varies within the sensitive volume. By self-diffusion measurements the average field gradient has been determined to 10 T/m at 17.5 MHz, corresponding to 0.5 mm penetration depth and to 14 T/m at 17.0 MHz, corresponding to the 1.0 mm penetration depth.⁷ The slice thickness excited by a $2 \mu\text{s}$ long rf pulse in such a gradient corresponds to about 1 mm. Within this region, the B_1 field can be considered to be quite homogeneous, which is confirmed by an approximately sine-shaped flip-angle dependence of the NMR signal and the satisfactory use of phase cycles in rf pulse sequences.

EXCITATION

In principle any echo-based excitation scheme known from conventional NMR can be used in inhomogeneous fields. The echo is necessary to overcome B_0 -field inhomogeneities, while B_1 -field inhomogeneities introduce an additional flip-angle dependence. For applications in materials research, those pulse sequences are of particular interest which allow discrimination of different material properties with good accuracy in short time. Taking for granted that chemical shift information is inaccessible in inhomogeneous fields, relaxation and diffusion curves must be analyzed for contrast parameters. These parameters can be amplitudes of signal components, the associated decay constants, and combinations thereof. But the particular mechanism of signal decay can be influenced by the type of average Hamiltonian effective under multi-pulse excitation.

For high sensitivity, multi-pulse including steady-

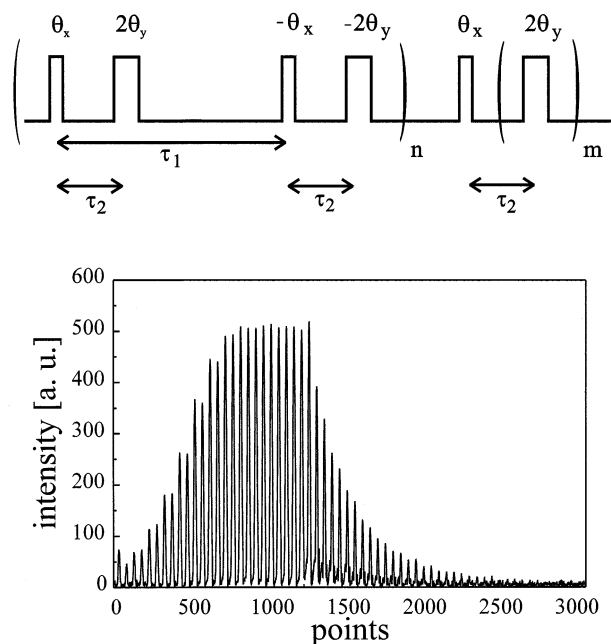


Fig. 4. Rapid measurement of longitudinal and transverse relaxation. Top: Pulse sequence. Bottom: Experimental data for styrene-co-butadiene rubber (SBR). Points 0 to 1250 show echoes with amplitudes increasing with T_1 and points 1251 to 3000 show echoes with amplitudes decreasing with T_2 .

state free-precession (SSFP) sequences are attractive, and for maximum contrast in soft-matter materials, the signal should decay only under the influence of the dipole-dipole interaction, while all other spin interactions are refocused, because the dipole-dipole interaction is the NMR parameter, which best monitors most macroscopic material properties. Given these criteria, three excitation schemes have proven to be most successful apart from schemes sensitive to translational diffusion:

1) Best signal-to-noise ratios are achieved by modification of the conventional SSFP techniques to include 2θ refocusing pulses for generation of echoes in the interpulse spacings between the original θ SSFP pulses (Fig. 4).⁸ Variation of the SSFP delay τ_1 introduces a T_1 weight for measurement of longitudinal magnetization build-up by changing τ_1 with increasing n . Multiple refocusing of magnetization within τ_1 produces T_1 -weighted multi-echo trains for measurement of transverse magnetization decays. The technique is closely related to the one used for rapid measurement of T_1 and T_2 in oil-well exploration.⁹

2) Rapid measurement of transverse magnetization decay under the influence of bilinear spin interactions and in the absence of linear spin interactions is achieved by the Carr–Purcell–Meiboom–Gill (CPMG) sequence.¹⁰ The dipole-dipole interaction is preserved and chemical shift and magnetic-field inhomogeneities are

refocused. But in inhomogeneous B_0 fields, turn-on effects^{8,13} are observed in the initial echo amplitudes similar to those in stray-field imaging, and spin-lock states arise, which lead to prolonged effective signal-decay times similar to line-narrowing in multi-pulse, solid-state NMR. The latter is avoided by use of a full phase cycle on the refocusing pulses. The corresponding sequence has been named XY-16.¹² It is particularly sensitive to changes in material properties.

3) An excitation scheme for use with the MOUSE, which is most sensitive to small differences in material properties, is that of the stimulated echo. The ratio of primary-to-stimulated echo has been shown to depend critically on the residual dipolar couplings in sheared liquids and polymer melts.¹³ Pulse spacings must be adjusted for each class of materials, and due to B_1 inhomogeneity, contrast depends on the nominal excitation flip angles. The method has been successfully applied to detect differences in cross-link densities of various industrial elastomers by the NMR-MOUSE (A. Guthausen and G. Zimmer, manuscript in preparation).

Applications

Almost any proton-containing material will give rise to a signal from the NMR-MOUSE.⁴ Polymers, elastomers, and biological materials are particularly suitable because they are rich in protons. Other nuclei have not been explored yet. Potential applications of the NMR-MOUSE are manifold. They are envisioned in nondestructive materials testing, process control, medicine, food processing, and agriculture. Selected examples are given below.

Elastomers. Elastomers and soft tissues give rise to the best signal-to-noise ratios. For elastomers the dependence of the transverse relaxation time on cross-link density, strain, and temperature has been verified.⁴ All these properties depend on the strength of the residual dipolar interaction, which determines the decay of the transverse NMR signal. At a given temperature the effective transverse relaxation times correlate well with cross-link density, which is affected by use and aging. It should be noted that, depending on the orientation of the B_0 field, magnetic steel cords in conventional tires may even have a beneficial effect on the ratio of signal-to-noise of the rubber signal, because field inhomogeneities may be reduced so that the width of the recorded echos increases.⁴ Therefore, an important area of use of the MOUSE is anticipated to be in the processing and testing of elastomer products, including tire characterization on the race track. A typical measurement time for an echo-train in a soft styrene-co-butadiene elastomer is 5 min.

As an example, transverse relaxation times are shown in Fig. 5 for a curing series of carbon-black-filled technical elastomer samples. The squares are the relaxation

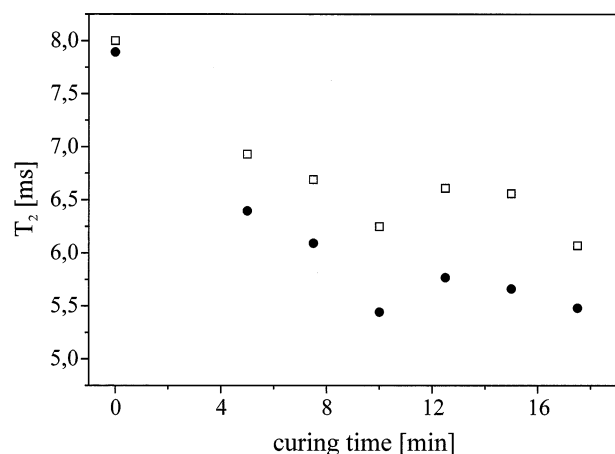


Fig. 5. Normalized transverse relaxation times of carbon-black technical elastomer for different curing times. Squares: MOUSE. Circles: DMX-300.

times measured by the MOUSE at 17.5 MHz; the circles are the relaxation times of the same samples measured on a conventional 300-MHz solid-state NMR spectrometer in homogeneous magnetic fields. The data measured by both methods compare favorably, taking into account the different field strengths. Furthermore, the onset of overcure in the surface-near-volume elements becomes visible after nine minutes curing time.

Rigid polymers. Stress whitening has been investigated in an impact-modified sheet of polystyrene.⁴ The MOUSE was repositioned in incremental steps across the region of stress whitening, where the value of the transverse relaxation time became smaller. This is in agreement with the fact that stress whitening is caused by the formation of creases which are crossed by micro fibrils of highly aligned macromolecular chain molecules.

The aging of polyvinylidene-difluoride (PVDF) samples by heat treatment in technical oil has been detected by T_2 measurements with the MOUSE. With increasing aging temperature, the relaxation time increased due to either chain scission or more oil entering the sample.⁸

Even polymer coatings on ferromagnetic steel can be characterized by the NMR-MOUSE. For example, polyvinylchloride (PVC) before and after weathering for 3000 h by cyclic treatment with humidity and UV irradiation has been analyzed without the presence of metal and as a 0.5-mm coating on a 1.5-mm iron sheet (Fig. 6).⁶ Due to eddy currents, the signal-to-noise ratio suffers a little for the coatings on the iron sheets as compared to the pure PVC samples. A consistent decrease in T_2 was observed for both of the aged samples compared to the reference samples, which may be explained by cross-linking reactions and a loss of volatile components like plasticiser. These preliminary studies are encouraging

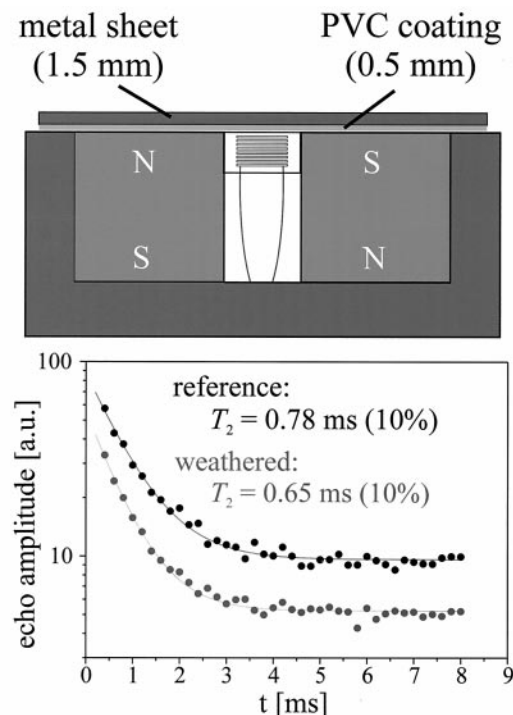


Fig. 6. Investigation of PVC coating on iron sheet metal by the NMR-MOUSE. Top: experimental setup. Bottom: Transverse relaxation curves for weathered and untreated PVC coatings.

evidence for use of the NMR-MOUSE in the investigation of even thinner coatings, also on magnetic metal.

Molecular self-diffusion. Because of strong field gradients, molecular self-diffusion leads to strong attenuation of the signal from the mobile component. Thus, in solid/liquid systems the liquid component is effectively suppressed. This property has been exploited to characterize the cross-link densities in polybutadiene/water emulsions.⁷ Furthermore, the strong field gradient can be used to measure constants of molecular self-diffusion by simple spin-echo methods. Because the field gradient varies in strength and direction within the sensitive volume, calibration of data on a system with a known diffusion constant is necessary. In this way the translation-diffusion constants of water and glycerol have been determined by the MOUSE within 2% accuracy of the literature values, according to R. Eymael (unpublished thesis).

Biomedical results. Exploratory studies on biomedical samples have been conducted in vitro. A two-dimensional image of a cross-section through a pork leg obtained from a butcher has been measured by repositioning the MOUSE in a point-wise fashion over the cross-section of interest. By extraction of parameters obtained from combined rapid measurement of T_1 and T_2

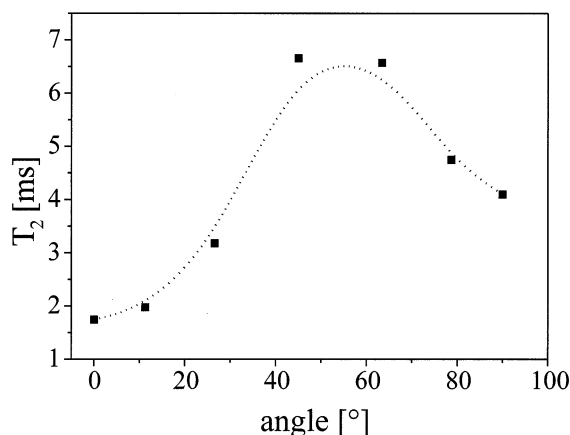


Fig. 7. Orientation-dependence of the transverse relaxation time in pork tendon. The angle measures the orientation of the long axis of the tendon with respect to the magnetic field B_0 of the MOUSE.

(Fig. 4), images with different contrast could be generated so that muscle, fat, bone, and marrow could be discriminated well. Furthermore, a depth profile through a sample of pork skin has been obtained by decreasing the resonance frequency and thus shifting the sensitive volume away from the scanner surface into the sample. Analysis of the transverse signal decay in terms of a biexponential function permitted the discrimination of signal contributions from the epidermis and the subcutis.⁷

The portability and open-magnet geometry of the instrument is of particular advantage for orientation-dependent studies. Many polymer materials, and also human tissues, show molecular orientation for mechanical reinforcement and biological functioning. For instance, the transverse relaxation time varies with the orientation of pork tendon with respect to the direction of the static magnetic field, B_0 , of the MOUSE (Fig. 7). The functional dependence can be approximated by the second Legendre polynomial, which defines the orientation dependence of second-rank tensor interactions of nuclear spins. With increasing age of the tendon, the anisotropy becomes smaller. These studies indicate that the state of health of tissues may be characterized by orientation-dependent relaxation studies with a simple NMR instrument like the NMR-MOUSE.

CONCLUSIONS

The NMR-MOUSE is a novel, mobile device for characterization of surface-near-volume elements of arbitrarily large objects. As a result of one-sided application of magnetic fields, both B_0 and B_1 are inhomogeneous,

and chemical shift information cannot be measured directly. Nevertheless, information about NMR relaxation and molecular translational diffusion is readily accessible in a broad variety of objects. Measurement schemes have been developed for discrimination of material properties based on the homonuclear dipole-dipole interaction. Encouraging evidence for use of the MOUSE is given by the nondestructive characterization of different materials:

- 1) Elastomer parts such as car tires on the track.
- 2) PVC coatings on magnetic iron sheets.
- 3) The discrimination of the solid components in suspensions with suppression of the fluid component by molecular translational diffusion.
- 4) The measurement of an anisotropy in the relaxation of a tendon.

These results promise interesting, novel applications of NMR in materials science, medicine, and process control.

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