Nuclear acoustic resonance in fluids using piezoelectric nanoparticles

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ABSTRACT

The influence of acoustic radiation in the form of ultrasound (US) on the nuclear magnetic resonance (NMR) signal of liquids in the presence of piezo- and ferroelectric nanoparticles was investigated. The NMR resonances of ^{1}H and ^{23}Na were influenced by US with a frequency of $\omega_{US} = 18.26$ MHz. For hydrogen, US with a frequency $\omega_{US} = \omega_0$ was used where ω_0 is the Larmor frequency of 18.26 MHz. For sodium, US with a frequency $\omega_{US} = 2\omega_{0,Na}$ was used with $\omega_{0,Na} = 9.13$ MHz. A detailed description of nanoparticle properties and sample preparation is given. The influence of US on the spin–lattice relaxation time T_1 was determined with an inversion recovery sequence for different concentrations of PZT. An elongation of T_1 of ^{1}H by 1.7% at a PZT concentration of 0.05% and an elongation of T_1 of ^{23}Na by 3% at a PZT concentration of 0.04% was observed. The elongation scales with the concentration of the PZT. An possible explanation of the effect of elongation is discussed.

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1. Introduction

Nuclear acoustic resonance (NAR) uses acoustic radiation (ultrasound) to induce transitions between Zeeman energy levels in the magnetic field B_0 where ultrasound (US) is applied with $\omega_{US} = \omega_0$ (dipole interaction) or $\omega_{US} = 2\omega_0$ (quadrupole interaction). ω_0 is the Larmor frequency. A first summarizing reflection on this subject has been published in 1952 by A. Kastler and experiments were proposed [1]. This method has been mainly used to investigate solids [2], namely ionic crystals. In 1965, Bowen published first results of NAR in an aqueous colloidal solution of As_2S_3 [3]. Furthermore, there were results reported on acoustic paramagnetic resonance in a dielectric liquid in [4].

Experiments on pure liquids conducted so far were not resonant [5] and it is accepted that NAR administered through phonons will not be relevant in liquids [6]. Recent calculations indicate that non-resonant acoustic waves with amplitudes small enough to avoid production of cavitation in the sample have no observable effect on proton nuclear relaxation rates of pure liquids [6]. In general, there have been limited publications on NAR in liquids, colloidal or pure.

This work presents results on the influence of piezoelectric nanoparticles on T_1 of ^{1}H and ^{23}Na when resonant US is irradiated into the sample during an inversion recovery sequence. The relaxation times of two elements were investigated to test the influence of lead zirconate titanate (PZT) dipoles on spin–lattice relaxation times. On the one hand, the well understood nuclear magnetic res-

onance of hydrogen was used to examine the magnetic interaction when US is applied with $\omega_{US} = \omega_0$. On the other hand, to examine the interaction of the electric fields of the nanoparticle through the quadrupole interaction, sodium was used due to its large quadrupole moment of $(0.14 - 0.15) \times 10^{-24}$ cm^2 [7]. Here, US was irradiated into the sample with $\omega_{US} = 2\omega_{0,Na}$.

A particle which is a lot smaller than the acoustic wavelength locally experiences the ultrasonic pressure changes as being spherically homogeneous [8]. PZT is both piezoelectric and ferroelectric and the PZT nanoparticles have approximately one domain. Due to the anisotropy in the piezoelectric response, they will produce an oscillating electric field when a periodic pressure change is applied. This radio frequency field will also induce an oscillating magnetic field.

To suspend the particles in water, an emulsifying agent was introduced.

A possible application of ferroelectric particles is as a contrast agent in magnetic resonance imaging (MRI) coupled with resonant US. The PZT particles are easily manufactured and can be produced following a top down approach (as done in this paper) and bottom up. Since the influence on ^{23}Na is larger, an MRI on the resonance of ^{23}Na is a possibility. The abundance of ^{23}Na is 100 g/70 kg in a human body and thus sufficient. PZT might be poisonous for humans, but other ferroelectric materials like barium titanate are also possible.

2. Particles and sample preparation

In contrast to magnetic nanoparticles which can be bought in abundance, there are no commercially available PZT nanoparticles.

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Furthermore, while the PZT bulk material is well researched, there is hardly any literature on PZT nanoparticles. Hence, we are giving a detailed description of their properties and of the sample production for reproducibility reasons.

2.1. PZT particle properties

The chemical formula of PZT is $Pb(Ti_{x-1}, Zr_x)O_3$. In our work, a composition with $x = 0.52$ was used. Here, the crystal has a morphotropic phase boundary between the tetragonal and rhombohedral phase [9]. The material is the calcinated product of a mixture of lead oxide PbO, titanium dioxide TiO_2, and zirconium dioxide ZrO_2 which is also used for producing piezoelectric transducers. The material is unpoled and not sintered.

PZT has a maximum in the dielectric constant at the morphotropic phase boundary [10] ($\varepsilon_r/\varepsilon_0 = 750$), which is due to the instability of the tetragonal phase, and it is responsible for the maximum in the electromechanical answer. The spontaneous polarization of PZT is an important parameter for this work. It can be obtained using the relationship between the distortion of the unit cell u, which creates the spontaneous polarization P_S, and the lattice parameters $a = 4.044$ Å and $c = 4.138$ Å [11]:

$$u = c/a - 1 = QP_S^2. \qquad (1)$$

Q is the electrostrictive coefficient and is specified as 0.049 m^4/C^2 in [12]. The spontaneous polarization P_S then amounts to 69 $\mu C/cm^2$. The average domain size of PZT is $l = 100$ nm [13]. This matches the size of the particles used in this work as seen in Fig. 1.

It is thus assumed that they are predominantly one domain particles. Also, the particles break more easily at domain boundaries

Fig. 1. FEG-SEM images of the PZT particles, taken with an inlens detector. The particles were coated with a 5 nm gold layer. (a) Accelerating voltage = 5 kV; (b) Accelerating voltage = 10 kV.

when the material is grinded, due to the mechanical stress involved at the domain boundaries. So, an average electric dipole moment p can be calculated with

$$p = V_0 P_S = 4/3\pi r^3 P_S = 2.9 \times 10^{-19} \text{ C cm}. \qquad (2)$$

It is orders of magnitude of the electric dipole moment of the water molecule which is 6.3×10^{-26} C cm [14].

It is well known that ferromagnetic coupling is possible even in a single unit cell, but the ferroelectric phase exists only with a larger number of unit cells. Thus, it is important to note that the diameter of the particles is above a critical diameter d_{crit} at which the Curie temperature tends to 0 K and thus the particle becomes paraelectric. The critical diameter has been calculated for $Pb(Ti_{0.48}, Zr_{0.52})O_3$ and is stated to be $d_{crit} = 4$ nm [15]. Some experiments have shown values for d_{crit} to be twice the above mentioned value (e.g. $PbTiO_3$ in [16]).

2.2. Sample preparation

The material provided by CeramTec AG, Lauf, Germany, was grinded in a ball mill for 60 min. Then, the PZT powder was added to 10 g of distilled water in different concentrations ranging from 0.01 to 0.05 mass percent. The nanoparticles in water can be easily separated by immersion of the fluid container in a standard ultrasound cleaning bath for 30 s. However, the PZT particles tend to coagulate and sediment completely in a few minutes. This can be counteracted by introducing an emulsifying agent. For this purpose, poly(acrylic acid) (PAA) with a molecular weight of 5000 was used. Its concentration in water was always chosen to be 0.1 mass percent because it yielded the best emulsion quality of the colloid. During the whole process of sample preparation, the water was kept in motion by a magnetic stir plate. First, PAA is added to the water. A change in the pH-value of a fluid leads to different relaxation times, and since the PAA changes the pH-value of water to approximately 3, a couple of drops of 2 M caustic soda solution were added to neutralize the pH-value. Second, the PZT particles were added to about 2 g water and separated through the immersion in the ultrasound bath. This was added to the PAA solution on the magnetic stir plate. Thus, a colloid consisting of PZT particles in water was produced.

With these samples, one can work for a couple of hours and they can be brought back to a proper emulsified state by immersing the sample container again in the ultrasound cleaning bath.

For measurements on the resonance of ^{23}Na, a saturated sodium chloride solution was produced and mixed with an equal amount of the PZT-in-water sample. To obtain an equal concentration of pure PZT-in-water sample, distilled water was mixed with the PZT-in-water sample. The liquid sample to be analyzed always had a volume of 100 μL.

3. Experimental setup

For the measurements, an NMR spectrometer was used that was specifically developed for this work so that all parameters could be changed and manipulated. This enabled us to have a large number of options. The constant magnetic field B_0 is provided by a superconducting magnet with a magnetic field varying from 0 to 5 T. A homogeneity better than 0.1 ppm can be achieved. The magnet has a cylindrical room temperature opening of 75 mm diameter which allows measurements at ambient temperature. The magnetic field can be varied by Helmholtz coils with a diameter of 1.914 m, separated by a distance of 0.8 m and 12 windings each. This is necessary to stabilize the constant magnetic field because it decreases over time due to Ohmic losses at the bridge contact of the superconducting coils. The NMR electronics is a standard signal
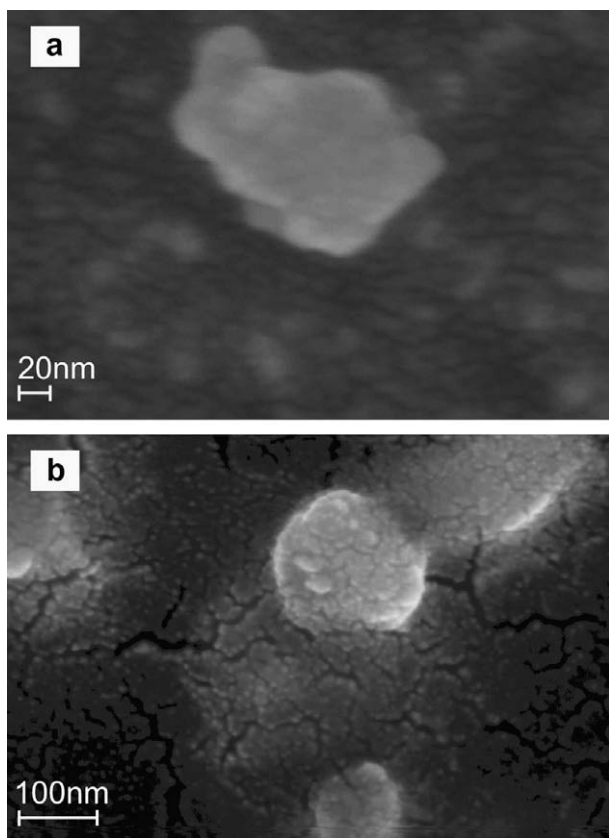
processing unit. Fig. 2, the sample container setup with the NMR coil and the direction of B_0 is shown.

For the measurements on the ^{1}H resonance line, the NMR circuit for the transversal magnetic field B_1 is a solenoid with 10 windings, a length of about 14.5 mm, and a radius of 4.5 mm. It has a resonance frequency of 18.26 MHz, which is adjusted to the system resonance frequency of piezoelectric ceramic and fused quartz rod together. A fused quartz rod is used to couple the US into the sample because it has a low loss factor and its acoustic impedance is similar to that of the aluminum shielding. For the measurements on the ^{23}Na resonance line at 9.13 MHz another solenoid was used. It has a length of 22 mm and a radius of 4.5 mm with 17 windings.

In this setup, the sound particle velocity is parallel to the magnetic flux lines of the NMR coil and perpendicular to B_0.

The ultrasound electronics is triggered by the same unit as in the case of the NMR pulse sequence. A separate HF-generator and amplifier are used to generate ultrasound. The signal is split, and one part is amplified and sent to the piezoelectric ceramic. The sound system produces considerable electromagnetic crosstalk in the NMR system. This coherent alternating field can influence the magnetization in the sample. To reduce the crosstalk through destructive interference, the other part of the split US signal is matched in phase and amplitude and sent to the interference antenna shown in Fig. 2. To further reduce crosstalk, an aluminum shielding is built around the antenna and sample. An aluminum shielding is also built around the US emitter separately. The reduction of crosstalk is shown in Fig. 3.

With the care taken and considering Fig. 3(c), it can be safely assumed that crosstalk does not influence the resonance signal.

4. Measurements

A standard inversion recovery sequence has been used as seen in Fig. 4. For ^{1}H NMR, the duration of the 90° pulse was 16 μs with a delay of 550 ms. The position of the US pulse was at 40 ms and its duration was 300 ms. The frequency was $\omega_{US} = \omega_0 = 18.26$ MHz with a sound intensity set to about 0.01 W/cm^2.

For measurements on the resonance of ^{23}Na, the US pulse and the 90° pulse were applied after the zero crossing of the magnetization at about 22 ms. The 90° pulses were irradiated at 200 ms, had a duration of 37 μs with a frequency of $\omega_{0,Na} = 9.13$ MHz. The US pulse had a duration of 100 ms at 50 ms after the 180° pulse with a frequency of $\omega_{US} = 18.26$ MHz in agreement with $\omega_{US} = 2\omega_0$. The sound intensity was set to 3.5×10^{-3} W/cm^2.

The free induction decays acquired after the 90° pulses were Fourier transformed. Subsequently, they will be called FT-FID$_{90°}$.

The maximum amplitude of the Lorentz peak with and without US influence was averaged separately for at least 15 spectra.

The results for different percentages of PZT-in-water or in NaCl & PZT-in-water are shown in Figs. 5 and 6. Error bars depict the variance of the amplitude. For the resonance on ^{1}H in Fig. 5, the amplitude of the FT-FID$_{90°}$ increases with US in the presence of the PZT nanoparticles. A higher amplitude of the FT-FID$_{90°}$ before the zero crossing of the magnetization represents an elongation of T_1. The influence also grows more evident with higher concentrations of PZT.

For the sodium resonance, the 90° pulse was irradiated after the zero crossing of the magnetization. Here, a diminishing amplitude of the FT-FID$_{90°}$ under the influence of US with increasing concentration of PZT nanoparticles represents also an elongation of T_1 as seen in Fig. 6. The effect is more pronounced with a higher concentration of PZT as well.

The T_1 relaxation time of water without PZT and with concentrations up to 0.1% PZT had been measured with a Bruker DRX 500 MHz. US was not applied. T_1 increased with increasing PZT concentration. A maximum increase of 10% was measured.

5. Discussion

Both graphs (Figs. 5 and 6) show similar results: the spin–lattice relaxation time T_1 is increased by a few percent under the influence of US in the presence of PZT nanoparticles. The T_1 relaxation time increased also under the influence of the PZT nanoparticles without US, but US augmented this elongating effect. It scaled with the concentration of PZT. The PZT nanoparticles can influence more H_2O molecules or ^{23}Na atoms in their vicinity. Their influence is short-range and thus a larger number of nanoparticles in the liquid leads to a greater effect. The maximum concentration was limited by sedimentation of the PZT nanoparticles. A significant change in the saturation magnetization due to US pulse lengths up to 3 s was not observed.

A principal problem in NAR measurements are systematic experimental errors such as electromagnetic crosstalk. This was studied in detail in our experiments. The possibility of electromagnetic crosstalk influencing the signal can be ruled out.

Our explanation of the results is that the water molecules around the PZT particle are not in a free liquid state and can "short circuit" the electric field. A short-range order is produced by electric dipole interaction between the water molecules and the ferroelectric particle. This ordering of the water molecule seems to diminish the energy transitions in the nuclear spin system and thus to an increased T_1 relaxation time.
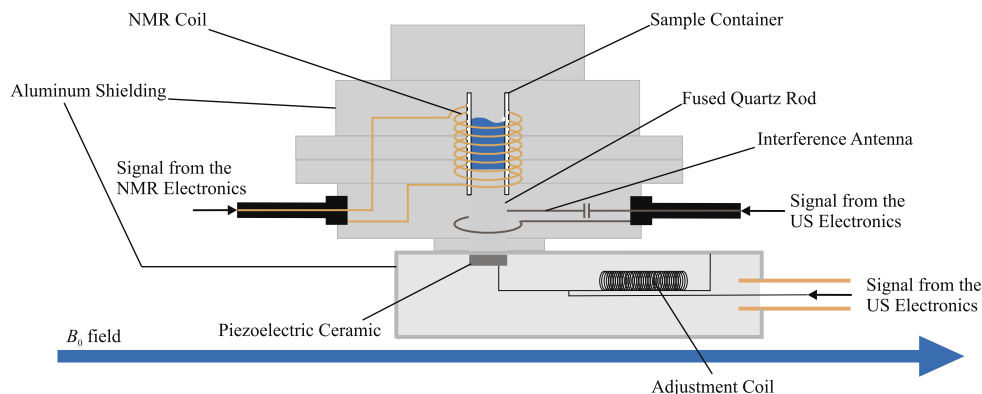

Fig. 2. The setup: sample container, NMR coil, and US emitter. The liquid sample is contained in a Teflon® tube fixed on top of the fused quartz rod. The US, which is produced by the piezoelectric ceramic, is coupled into the sample through the fused quartz rod. A coil is connected between the piezoelectric ceramic and the coaxial cable to adjust the impedance. The interference antenna serves to produce destructive interference to avoid electromagnetic crosstalk. For further reduction of crosstalk, two separate aluminum shieldings are present.
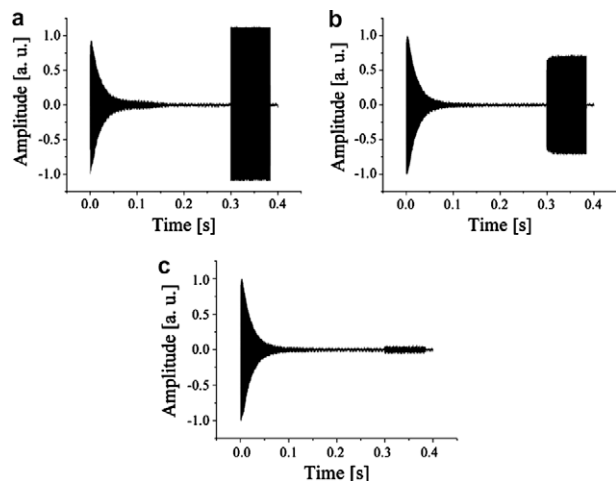
Fig. 3. Comparison of electromagnetic crosstalk and free induction decay: (a) without interference antenna and aluminum shielding. The amplifier is saturated; (b) aluminum shielding is present. A considerable reduction in amplitude of the crosstalk can be observed, the amplitude of the crosstalk is smaller than the maximum amplitude of the FID; (c) aluminum shielding and adjusted interference antenna are present. The crosstalk is hardly visible and can be neglected.
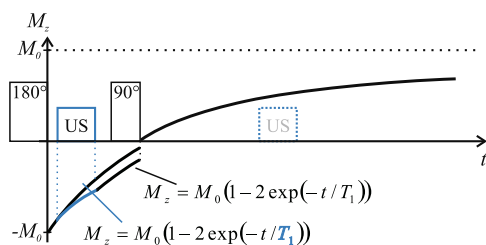

Fig. 4. Inversion recovery pulse sequence with the US pulse located between the 180° and 90° pulse. The magnetization in direction z of the magnetic field B_0 is plotted against the time t. The US pulse is applied before the 90° pulse for measurements on the ^{1}H resonance (solid line) and after the 90° pulse for measurement on the ^{23}Na resonance (dotted line).
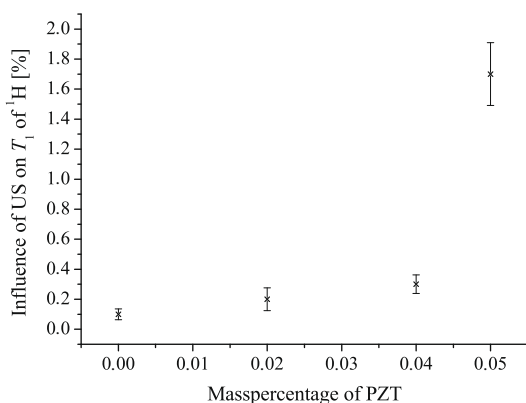

Fig. 5. The influence of US on the spin–lattice relaxation time T_1 of ^{1} in percent deduced from the difference in amplitude of Fourier transformed free induction decay after the 90° pulse with and without the influence of US. The error bars depict the variance of the amplitudes. With increasing mass percentage of PZT in water, T_1 is longer.

The PZT nanoparticles are 800 times smaller than the wavelength of the US. Thus, a particle experiences spherically homogeneous US pressure changes [8]. The anisotropy of the elasticity of PZT between the polarization direction and perpendicular to it
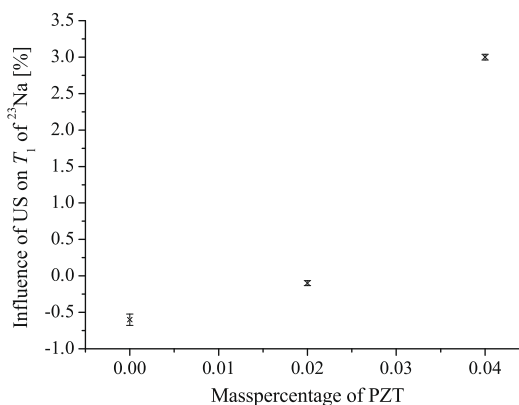

Fig. 6. The influence of US on the spin–lattice relaxation time T_1 of ^{23}Na in percent deduced from the difference in amplitude of Fourier transformed free induction decay after the 90° pulse with and without the influence of US. The error bars depict the variance of the amplitudes. With increasing mass percentage of PZT in water, T_1 is longer.

[17] leads to an anisotropy in the piezoelectric response. Due to this anisotropy, the particle produces a small oscillating electric field in addition to the static electric field. The H_2O molecules can follow the 18 MHz signal adiabatically, since the H_2O rotation lies at about 2.4 GHz. Also, the sound particle velocity due to US is very small (5 mm/s) and can be neglected. The polarized static arrangement can be considered as a metastable state. When US is applied, there is an input of energy to this arrangement. The result of T_1 elongation due to US application suggests that the area of influence of the polarized arrangement is increased.

For the ^{23}Na atoms, the interaction of the oscillating field of the PZT nanoparticle with the quadrupole field and electric field gradient of the sodium is more prominent, which leads to a larger effect under application of US. In our experiment, the influence on ^{23}Na is 43% stronger than the influence on the proton resonance. The effect of US on the T_1 relaxation time of ^{23}Na is comparable to the magnetic interaction of the protons.

At this stage, the observed effect is not large and prominent enough to consider using these nanoparticles in combination with US for example as a contrast agent in MRI like magnetic nanoparticles.

6. Conclusion

We found an elongation of the spin–lattice relaxation time T_1 of ^{1}H and ^{23}Na by 1.7% and 3%, respectively. The effect is reproducible and physically interesting since it has not been observed so far.

Acknowledgments

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