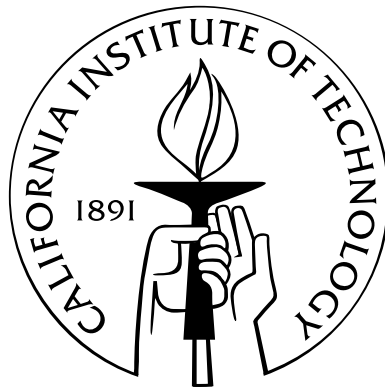


# Novel Methods for Force-Detected Nuclear Magnetic Resonance

Thesis by  
Mark C. Butler

In Partial Fulfillment of the Requirements  
for the Degree of  
Doctor of Philosophy



California Institute of Technology  
Pasadena, California

2008  
(Defended December 11, 2007)

© 2008

Mark C. Butler

All Rights Reserved

To my mom

# Acknowledgements

I would like to begin by thanking my advisor, Dan Weitekamp. Because of his deep scientific understanding and limitless creativity, I often found our discussions to be intellectually thrilling experiences. Dan consistently opened my eyes to new ways of looking at problems that I thought I already understood, and his first comments in response to my work would often give me startling moments of clarity. I eventually became used to the fact that for hours or days after a conversation with him I would find it very difficult to put down the work and return to the world of ordinary living because the questions that he brought up were so compelling to me. I would like to thank Dan for creating an environment in which I was free to grow intellectually, and also for encouraging me to stay focused on productive research. I enjoyed my research, and I thank Dan for the opportunity to work on these problems.

I would also like to thank several members of Dan's research group for their guidance and collaboration on a variety of projects. Gary Leskowitz and Lou Madsen graduated from the group around the time that I joined, but they remained available to me as mentors throughout my time in the group. They consistently helped me with experimental work in force-detected NMR. Gary, in particular, spent many hours helping me in the lab, giving me encouragement, and teaching me about experimental work. I regularly felt that I would have been lost without access to Valerie Norton's expertise with computers; on many occasions her ability to solve computer problems and use computers in clever ways saved me many hours of work. Choonsup Lee was endlessly patient in teaching me the basics of microfabrication and collaborating with me on the problem of fabricating a microresonator. Pratip Bhattacharya transformed my experience at Caltech. His positive energy, good-natured optimism,

practical wisdom, relentless encouragement, and his forceful generosity at restaurants are unique in my experience.

I thank my mom for her gentle confidence in me and the goals I was pursuing at every stage of my life, even when those goals were difficult to understand. My dad challenged me intellectually when I was a very young child; I have vivid memories of early conversations with him as some of the most intellectually intense experiences of my life. Together my parents introduced me to the world as a place that I could explore and understand. My dad was also very supportive throughout my time at Caltech, and I am grateful to him for proofreading this thesis.

During six years of marriage to my wife, Kendra, I have often felt that her commitment to my goals was even greater than my own. At times when those goals have seemed out of reach to me, she has been unstoppable in her confidence, her willingness to do whatever would support me and further my goals, and in her resourceful ability to find ways for us to function well in day-to-day life.

# Abstract

This thesis is concerned with the problem of extending methods for force-detected nuclear magnetic resonance (NMR) to the nanoscale regime. A magnetic mechanical resonator can be used both as a sensitive detector of spins and a means of inducing spin relaxation between detected transients. At the mK temperatures achievable in a dilution refrigerator, spin-lattice interactions are "frozen out," and resonator-induced relaxation can replace spin-lattice relaxation in returning the spins to equilibrium between detected transients. We analyze resonator-induced spin relaxation and the sensitivity of schemes which use a nanoscale mechanical resonator to detect spins.

Relaxation equations are derived from first principles, and a physical interpretation of the processes contributing to resonator-induced relaxation is given. The intrinsically quantum mechanical nature of the relaxation is highlighted by comparing the quantum mechanical relaxation equations with analogous equations derived using a semiclassical model in which all spin components have a definite value simultaneously. In the case where the spins all experience the same field, the semiclassical spins cannot become polarized as a result of their interaction with the resonator, and a quantum mechanical model is necessary even for a qualitative description of the polarization process.

Resonator-induced relaxation of spin systems is complicated by the fact that an indirect spin-spin interaction is present when all spins are coupled to the same resonator, since the resonator's field at a given spin is determined by the interactions which have occurred between the resonator and the other spins of the system. This indirect interaction can prevent the spins from relaxing to a thermal state characterized by a spin temperature. We present a physical interpretation of the mechanism

by which an indirect spin-spin torque develops during resonator-induced relaxation, and we estimate the magnitude of this torque and the time  $T_{\text{corr}}$  required for it to induce strong spin-spin correlations. A perturbation in the spin Hamiltonian which periodically reverses the direction of the indirect torques within a time period shorter than  $T_{\text{corr}}$  will prevent the development of resonator-induced correlations and allow the spins to relax to a thermal state.

The mechanisms by which the spin Hamiltonian  $H_s$  modifies resonator-induced relaxation are characterized. In the case where the eigenstates of  $H_s$  are weakly perturbed from product states, the system will relax exponentially to thermal equilibrium with the resonator, provided that resonator-induced couplings between populations and certain zero-quantum coherences are suppressed by terms in  $H_s$  which shift the frequencies of these coherences sufficiently far from zero. Analysis of longitudinal relaxation in example systems containing three dipole-dipole coupled spins shows that the relaxation occurs in two stages governed by different physical processes, and the three-spin systems do not relax to a thermal state. For substantially larger dipole-dipole coupled system (e.g.,  $N = 50$ ), we propose the hypotheses that the secular dipolar Hamiltonian will quickly equalize the population of states which lie in the same eigenspace of  $I_z$ . Simulations of the longitudinal relaxation predicted by this hypothesis suggest that a single resonator could efficiently relax dipole-dipole coupled systems to a thermal state.

Arguments based on general properties of the master equation suggest that the transverse relaxation induced by the mechanical resonator could occur on a shorter time scale than that of the longitudinal relaxation. We derive conditions which guarantee that the time constant for transverse relaxation will be  $2/R_h$ , where  $1/R_h$  is the time constant for resonator-induced longitudinal relaxation of a single-spin sample to thermal equilibrium. Under these conditions, transverse relaxation can be interpreted as the "lifetime broadening" associated with the shortened lifetime of energy eigenstates due to coupling with the resonator. For a two-spin system, however, we show analytically that "turning on" the dipolar coupling can accelerate resonator-induced transverse relaxation, and we give an interpretation of the mechanism by which this

occurs. Simulations of four-spin systems also show that the presence of dipolar couplings can substantially accelerate resonator-induced transverse relaxation, and that this accelerated relaxation can be distinguished from so-called radiation damping. In addition, we find that spin-locking limits the rate of resonator-induced transverse relaxation. In the case where the spin-locking field is large enough to average the dipolar Hamiltonian and the superoperator responsible for resonator-induced relaxation, we have  $T_{1\rho} = 2/R_h$ .

We propose a general definition of signal-to-noise ratio (SNR) which can be used to compare the sensitivity of methods that measure the amplitude of a signal with the sensitivity of methods that yield a continuous record of a signal. This definition is used to compare the sensitivity of three schemes for detecting the NMR signal of a sample consisting of a few spins: spin-locked detection of a transverse dipole, detection of a freely-precessing dipole, and detection of a correlated product  $\langle I_x(t_1) I_x(0) \rangle$ . The dependence of SNR and acquisition time on resonator parameters is analyzed. We find that when the time constant for decay of the signal during the detection period is  $2/R_h$ , with instrument noise substantially larger than spin noise, the only resonator parameter which appears in the SNR expressions is  $\omega_h/T_h$ , where  $\omega_h$  is the mechanical frequency and  $T_h$  is the temperature. This result suggests, in particular, that SNR for spin-locked detection will be insensitive to details of resonator design.

A torsional mechanical resonator design is presented. We discuss the advantages of using soft magnetic material and eliminating relative motion between the sample and the resonator, as well as the validity of the models used to characterize the resonator. The possibility of using non-metallic magnetic material as the source of the resonator's magnetic field is introduced. A numerical example is presented for which the calculated time constant for the longitudinal relaxation of a single-spin sample is  $1/R_h = 0.77$  s. Simulations of detected NMR spectra for two-spin samples suggest the possibility of chemical studies in which force-detected NMR spectroscopy is used with single-spin sensitivity.

The final chapter studies the possibility of using hyperpolarized spins to cool a single mechanical mode. Numerical examples suggest that cooling would be negligible



for resonators of size scale  $\sim 10 \mu\text{m}$  or larger. In the regime characterized by these examples, substantial cooling requires sufficiently strong spin-resonator coupling that neither a mechanical mode nor a spin mode can be distinguished in the spin-resonator system; instead, the modes of the system include equal contributions from the spins and the mechanical resonator. The spin-resonator correlations responsible for cooling make a significant contribution to the symmetric correlation function of the resonator coordinate, with the result that the noisy "thermal torque" acting on the resonator is increased rather than diminished by the presence of the hyperpolarized spins.

# Contents

<b>Acknowledgements</b>	<b>iv</b>
<b>Abstract</b>	<b>vi</b>
<b>1 Introduction</b>	<b>1</b>
<b>2 Description of the nanoscale spin-resonator system</b>	<b>7</b>
1 Average Hamiltonian . . . . .	7
2 Equations of motion for spin operators . . . . .	11
2.1 Reduced master equation for the spins . . . . .	11
2.2 Full master equation for the spin-resonator system . . . . .	16
3 Spontaneous and stimulated transitions . . . . .	18
4 Physical interpretation of the cooling process . . . . .	21
5 Semiclassical model . . . . .	24
6 Polarization of spins using an inductive resonator . . . . .	29
6.1 Rate constant for longitudinal relaxation . . . . .	29
6.2 Comparison of mechanical and inductive resonators . . . . .	31
<b>3 Resonator-induced spin relaxation</b>	<b>34</b>
1 Trapping of the spin system due to angular momentum conservation . . . . .	34
2 Indirect spin-spin interaction . . . . .	37
3 Modification of the relaxation processes by the spin Hamiltonian . . . . .	40
4 Longitudinal relaxation . . . . .	47
4.1 Noninteracting spins . . . . .	47

4.1.1	Two spins . . . . .	47
4.1.2	$N$ spins . . . . .	50
4.2	Dipole-dipole coupled spins . . . . .	54
4.2.1	Two spins . . . . .	54
4.2.2	Three spins . . . . .	56
4.2.3	$N$ spins . . . . .	58
5	Transverse relaxation of freely-precessing spins . . . . .	60
6	Transverse relaxation during spin-locking . . . . .	66
<b>4</b>	<b>Sensitivity of spin detection by a nanoscale resonator</b>	<b>69</b>
1	Definition of signal-to-noise ratio for measurement of an amplitude . . . . .	69
2	Generalization to measurement of a continuous signal . . . . .	74
3	Comparison with a standard definition . . . . .	77
4	Signal-to-noise ratio for amplitude detection . . . . .	82
4.1	Definition of the signal . . . . .	82
4.2	Definition of the noise . . . . .	85
4.3	Spectral density of the instrument noise . . . . .	86
4.4	Spectral density of the spin noise . . . . .	90
4.5	SNR formula for amplitude detection . . . . .	91
5	Signal-to-noise ratio for detection of a continuous signal . . . . .	94
6	Comparison of detection sensitivities . . . . .	96
6.1	Dependence of sensitivity on the energy in the signal . . . . .	96
6.2	Effect of resonator-induced transverse relaxation . . . . .	98
7	Dependence of signal-to-noise ratio and acquisition time on resonator parameters . . . . .	101
8	Signal-to-noise ratio for a product of correlated measurements . . . . .	104
8.1	Definition of the signal and the noise . . . . .	104
8.2	SNR formula . . . . .	107
8.3	Comparison of the first-order and second-order methods . . . . .	113

<b>5</b>	<b>Resonator design</b>	<b>116</b>
1	Description of the resonator and the detection scheme . . . . .	116
2	Selection of the resonator design . . . . .	119
3	Condition for resonance between the spins and the resonator . . . . .	121
4	Model of the resonator's magnetization . . . . .	124
4.1	Uniform magnetization . . . . .	124
4.2	Magnetization constant in the lab frame . . . . .	126
5	Strength of the spin-resonator coupling . . . . .	129
5.1	Effect of soft magnetic material on the coupling strength . . . . .	129
5.2	Upper bound on the torque between the spins and the resonator	133
6	Optimization of example resonators . . . . .	135
7	Use of non-metallic magnetic material . . . . .	140
<b>6</b>	<b>Simulations of spectra and spin relaxation</b>	<b>143</b>
1	Simulations of two-spin spectra . . . . .	143
1.1	Noninteracting spins . . . . .	144
1.2	Vinyl bromide . . . . .	147
2	Simulations of spin relaxation . . . . .	148
2.1	Relaxation of noninteracting spins . . . . .	150
2.2	Relaxation of dipole-dipole coupled spins . . . . .	155
<b>7</b>	<b>Cooling a single mode with hyperpolarized spins?</b>	<b>166</b>
1	Hyperpolarized spins as a cold bath . . . . .	166
2	Model of the spin-resonator system . . . . .	170
3	Steady-state number of quanta in the resonator . . . . .	174
4	Numerical example of cooling . . . . .	178
5	Modes of the spin-resonator system . . . . .	181
6	Response of the system to a torque acting on the resonator . . . . .	188
7	The cooled mode as a sensitive detector? . . . . .	193

<b>A</b>	<b>Derivation of the spin-relaxation equations from the full master equation</b>	<b>198</b>
<b>B</b>	<b>Relative magnitudes of the rate constants for lifetime and secular broadening</b>	<b>202</b>
<b>C</b>	<b>Longitudinal relaxation when the resonator's field is inhomogeneous</b>	<b>205</b>
<b>D</b>	<b>Derivation of the semiclassical equation for longitudinal relaxation</b>	<b>209</b>
<b>E</b>	<b>Longitudinal relaxation due to coupling between product-state populations</b>	<b>215</b>
<b>F</b>	<b>Transverse relaxation due to coupling between product-state coherences</b>	<b>218</b>
<b>G</b>	<b>Comparison between the use of an optimal filter and least-squares fitting</b>	<b>223</b>
<b>H</b>	<b>Spectral density in signal-to-noise ratio estimates</b>	<b>226</b>
<b>I</b>	<b>Statistics of a classical resonator</b>	<b>229</b>
	1 Correlation function of the oscillator's coordinate . . . . .	229
	2 Spectral density of the thermal torque . . . . .	232
<b>J</b>	<b>Contribution of the induced electric field to the resonator's kinetic energy</b>	<b>235</b>
<b>K</b>	<b>General formula for the magnetic spring constant</b>	<b>238</b>
<b>L</b>	<b>Spring constant and moment of inertia of a torsion beam</b>	<b>246</b>
<b>M</b>	<b>Eddy-current heating of metallic cylinders</b>	<b>250</b>
<b>N</b>	<b>Correlation function of the mechanical coordinate during cooling by hyperpolarized spins</b>	<b>257</b>



# List of Figures

1.1	Schematic representation of the energy flow during resonator-induced spin polarization. . . . .	3
5.1	Torsional resonator for force-detected NMR spectroscopy. . . . .	117
5.2	Torsional resonator for force-detected NMR imaging. . . . .	119
5.3	Comparison of magnetization orientation for hard and soft magnetic materials . . . . .	130
5.4	Comparison of the transverse field for hard and soft magnetic materials	131
6.1	Detection of two noninteracting spins without spin-locking. . . . .	145
6.2	Spin-locked detection of two noninteracting spins. . . . .	146
6.3	Two structures for dibromoethylene adsorbed on a silicon surface. . . .	148
6.4	Spin-locked detection of adsorbed vinyl bromide. . . . .	149
6.5	Longitudinal relaxation of noninteracting systems having $N = 36$ and $N = 144$ . . . . .	151
6.6	Transverse and longitudinal relaxation of four noninteracting spins which experience the same field and are initially aligned along the $x$ -axis. . .	153
6.7	Transverse and longitudinal relaxation of four noninteracting spins which have chemical shift offsets and are initially aligned along the $x$ -axis. . .	153
6.8	Longitudinal relaxation of four noninteracting spins which experience the same field and are initially disordered. . . . .	154
6.9	Longitudinal relaxation of four noninteracting spins which have chemical shift offsets and are initially disordered. . . . .	154

6.10	Longitudinal relaxation of four dipole-dipole coupled spins from an initially disordered state. . . . .	156
6.11	Transverse relaxation of four dipole-dipole coupled spins which are initially aligned with the $x$ -axis. . . . .	159
6.12	Longitudinal relaxation of four-spin systems when all spins are initially aligned along the $x$ -axis. . . . .	160
6.13	Accelerated transverse relaxation distinguished from radiation damping.	161
6.14	Resonator-induced relaxation of a spin-locked sample of four dipole-dipole coupled spins. . . . .	162
6.15	Longitudinal relaxation of 50 spins in the regime where dipolar interactions efficiently redistribute population within each eigenspace of $I_z$ during the relaxation. . . . .	164
6.16	Longitudinal relaxation of 150 spins in the regime where dipolar interactions efficiently redistribute population within each eigenspace of $I_z$ during the relaxation. . . . .	165



# List of Tables

3.1	Mixing of angular momentum systems. . . . .	58
5.1	Selected parameters for a resonator optimized with a separation of 50 nm between magnetic cylinders. . . . .	137
5.2	Selected parameters for a resonator optimized with a separation of 25 nm between magnetic cylinders. . . . .	137
5.3	Parameters for the optimized example resonator. . . . .	139
5.4	Sensitivity of the optimized example resonator. . . . .	139
7.1	Resonators cooled by hyperpolarized spins . . . . .	179
7.2	Scaled-up spin-resonator systems . . . . .	180
7.3	Dependence of rate constants on size . . . . .	181