

**SPIN-TEMPERATURE
AND NUCLEAR-SPIN
RELAXATION IN MATTER:**

**BASIC PRINCIPLES
AND APPLICATIONS**

**BY
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PREFACE

'Although all the first beginnings of things are in motion, the sum total seems nevertheless to abide in supreme quietude.'
Lucretius (94-40 BC), 'De Rerum Natura'

The use of n.m.r. techniques in materials science, solid-state physics, and chemical physics has progressed considerably during the last two decades. By their nature, most n.m.r. experiments represent rather indirect probes to gain information on static and dynamic microscopic properties of solid, liquid, and gaseous materials. Therefore, to interpret n.m.r. experiments in terms of the underlying microscopic events which determine the n.m.r. relaxation behaviour, considerable theoretical efforts are required.

In the past, many of the necessary theoretical concepts have been developed by experimentalists. This has the advantage that the basic concepts and models have been formulated in a language easily comprehensible to those for whom the theory is finally developed; namely, for the experimentalists. The disadvantages of this development lie in the apparent conflicting diversity of the different theoretical concepts and the variety of different experimental techniques developed.

As a theorist, I have always considered the variety of ideas as a challenge to find a more unified concept which would allow me to bring some order into the manifold of theoretical approaches used, which are conflicting in some respects and compatible in other ways. However, as Professor Alfred Seeger once pointed out to me, for good communication between theorists and experimentalists to be possible, both have to speak the same language. He reminded me that the word 'theory' derives from the Greek word 'θεωρία', which means 'overview' or understanding from a superior point of view, perhaps what the Germans call 'Weltanschauung'. In the original sense of the word 'theory', nuclear magnetic resonance in solids represents an ideal playground for a theorist trying to achieve a comprehensive understanding of the basic physical concepts applied in a

field in which, as in not too many other areas of physics, experimental and theoretical efforts may be so closely correlated. Keeping in mind this point of view, I wrote this book mainly for the experimentalist who is struggling to decide which kind of theoretical approach to apply to interpret his experimental results. In developing a language and a formalism which combines both intuitive and more formal theoretical concepts, my final goal was to encourage more physicists to adopt some of the extremely versatile n.m.r. techniques as a probe to gain a more microscopic picture of the static and dynamic properties of atoms, defects, and molecules in, for example, crystals.

In the past, the spin-temperature concept – a rather intuitive approach – has proved to be extremely fruitful in bringing some degree of order into the microscopic interpretation of a variety of different n.m.r. experiments performed in solids and liquids. However, because of the great number of different physical situations dealt with in these experiments, several apparently different types of spin-temperature theories have been developed. By reviewing the different approaches, a rather general spin-temperature formalism is developed in this book from which the different well known versions (which are restricted to particular experimental regimes) may be obtained as special cases. Since two weakly-coupled quantum systems may not interchange energy unless their interaction fluctuates, any kind of spin-temperature theory is only capable of describing the effects of 'lattice'-induced motions on the nuclear-spin system but not the static properties of matter. I shall therefore concentrate on situations in which, because of the motion-induced time dependence of the spin-lattice coupling, energy is exchanged between the spin system and the 'lattice'. Using the nuclear-spin system as a probe, we are able to gain microscopic insight into the mechanisms that allow atoms, molecules, point defects, dislocations, conduction electrons, etc. to move.

This book consists of four major parts. In Part 1, the basic interactions of spins with each other and with other degrees of freedom in a liquid or solid material are discussed. The basic ideas and assumptions underlying the spin-temperature concept are also reviewed and extended.

Part 2 begins with a summary of the basic assumptions common

to all theories of motion-induced nuclear-spin relaxation. As an example, the early theory of Bloembergen, Purcell, and Pound ('BPP theory') is used to illustrate how these basic assumptions affect the nuclear spin-lattice relaxation behaviour (Chapter 4). In Chapters 5, 6, and 7, the three most fundamental theories of nuclear-spin relaxation (Kubo-Tomita, Bloch-Wangsness-Redfield, and Hebel-Slichter theories) are reviewed from a common point of view. Part 2 is concluded by a comparison of and synthesis from these theories. This leads to the formulation of a rather general type of nuclear-spin-relaxation theory which includes the relaxation equations in a 'rigid lattice' and from which the usual theories of motion-induced nuclear-spin relaxation may be derived as special cases. As a limiting case of the latter, a unified spin-temperature theory of motion-induced nuclear-spin relaxation may be formulated (Chapter 8).

Throughout Part 2 neither the spin nor the spin-lattice interaction Hamiltonian had to be specified. Except for those theories which explicitly assume the existence of a spin temperature, the relaxation theories reviewed are of a very general nature and apply to relaxation processes in many areas of physics (most of which do not involve spins at all).

In the second half of this book the consequences of the 'unified spin-temperature theory' of Chapter 8 on a variety of commonly encountered physical situations are developed. As illustrated here, in effect all correlation-function expressions for T_1 and $T_{1\rho}$ follow from a single starting equation which is practically identical to the Hebel-Slichter equation. This leads to the development of a fairly comprehensive formalism for the derivation of correlation-function expressions for the nuclear-spin-relaxation behaviour. As demonstrated in some detail, laboratory and rotating-frame relaxation properties may therefore be determined in completely identical manners. In addition, the relaxation rates in the limiting 'ultra-slow motion' and 'motionally narrowed' regimes, respectively, are found to follow quite naturally as special cases from our general starting expression.

In Part 3, the relaxation due to fluctuating dipolar and quadrupolar interactions in systems containing one or two spin

species and in molecular crystals or liquids is investigated. The results of Chapters 9, 10, and 12 are applied to self diffusion in cubic crystals for which the dipolar and quadrupolar 'lattice' correlation functions are well known and particularly simple. Explicit analytical and numerical results for the entire relaxation behaviour (temperature, field, and orientation dependence of T_1 and $T_{1\rho}$) may thus be obtained.

Finally, Part 4 focuses on the relaxation properties associated with fluctuating hyperfine interactions. Owing to limited space, only the Fermi-contact interaction in metals or semiconductors and the relaxation due to fluctuating anisotropic chemical-shift interactions in non-cubic crystals are investigated. Common to the two related Hamiltonians is their linear nuclear-spin structure which is contrasted with the bilinearity of the dipolar and quadrupolar Hamiltonians. In spite of these differences it is found that the basic relaxation properties associated with fluctuating hyperfine interactions are very similar to those arising from time-dependent dipolar and quadrupolar interactions.

By developing both a language and the underlying formalism needed for the theoretical interpretation of n.m.r. experiments on the internal dynamical processes in solids, liquids, and gases, I hope that more experimentalists will in the future be inspired to use some of the very versatile n.m.r. techniques to investigate the microscopic dynamics of atoms, molecules, defects, and electrons in a great variety of materials.

I am grateful for the extremely helpful criticism and feedback which I have received from Professor Otmar Kanert of the University of Dortmund. During his sabbatical visit to the University of Utah, I benefited in numerous ways from his stimulating interest in this book and from his insistence on clarity and the use of a language familiar to experimentalists. During the two years in which I have focused a considerable share of my research efforts on this book, I have had two opportunities to test and improve its teachability: I am grateful for invitations from the 'Troisième Cycle de la Physique en Suisse Romande' to present a summer course in Lausanne in 1975, and from the Universidad Central de Venezuela to teach a course on the subject during the fall of 1976.

Salt Lake City,
February 1977

D.W.

NOTATION

$A_{ij}^{(q)}$	dipolar spin operators
A, B	spin operators
\tilde{A}	symmetrical second-rank tensor
$B_{I S}^{(q)}$	dipolar spin operators for different spin species I and S
C	Curie's constant
C_d	concentration of point defects in a crystal
e	elementary charge
$E = \langle \mathcal{H} \rangle$	energy (expectation value of Hamiltonian \mathcal{H})
$F_{ij}^{(q)}$	dipolar (geometrical) lattice functions
$G^{(q)}(t)$	'lattice' correlation function
H_0	external constant magnetic field
H_1	external rotating field
H_L	internal local field
H_D	dipolar local field
H_Q	quadrupolar local field
\mathcal{H}_D	dipolar-interaction Hamiltonian
\mathcal{H}_{ex}	exchange-coupling Hamiltonian
\mathcal{H}_{ind}	indirect magnetic-dipole Hamiltonian
\mathcal{H}_L	'lattice' Hamiltonian
\mathcal{H}_{psd}	pseudo-dipolar interaction Hamiltonian
\mathcal{H}_{psex}	pseudo-exchange interaction Hamiltonian
\mathcal{H}_Q	quadrupolar Hamiltonian
\mathcal{H}_S	Hamiltonian of the completely isolated spin system
\mathcal{H}_{SL}	spin-lattice interaction Hamiltonian
\mathcal{H}_Z	Zeeman Hamiltonian
I, S	spin quantum numbers for two-spin systems

I, \vec{S}	total angular-momentum operator
J	exchange integral
$J^{(q)}(\omega)$	dipolar spectral density (Fourier transform of $G^{(q)}(t)$)
\tilde{K}	Knight-shift anisotropy tensor
M	nuclear magnetization
Q	nuclear quadrupole moment
$Q_n^{(p)}$	quadrupolar spin operators
$Q_{\alpha\beta}$	quadrupole tensor
r	internuclear vector
T	absolute temperature
T_1	spin-lattice relaxation time
$T_{1\rho}$	spin-lattice relaxation time in the rotating frame
T_2	spin-spin relaxation time
T_{IS}	cross-relaxation time
T_m	thermal-mixing time
$V_{\alpha\beta}$	electric field gradient (e.f.g.) tensor
Z	Zeeman
γ	gyromagnetic ratio
$\delta_{\alpha\beta}$	Kronecker's symbol
η	asymmetry parameter of an electric field gradient
θ	off-resonance angle
θ_L	thermal-equilibrium 'lattice' temperature
θ_S	spin temperature
\vec{M}	magnetization operator
$\rho(t)$	hermitian density operator of the entire system (spins plus 'lattice')
$\sigma(t)$	density matrix of spin system
τ_c	correlation time
τ	mean time between successive jumps of an atom
τ_d	mean time between successive jumps of a point defect

χ_{eq}	thermal-equilibrium or 'Curie' susceptibility
$\psi_n(t)$	wave function of a spin n
ω	angular precession frequency
ω_0	Larmor angular precession frequency due to \mathbf{H}_0
ω_1	Larmor angular precession frequency due to \mathbf{H}_1
ω_D	precession frequency in the dipolar local field
ω_L	local-field precession frequency
ω_Q	precession frequency in a quadrupolar local field
$\langle \rangle_{\theta, \phi}$	solid-angle average

Subscripts and superscripts

'	transformed
*	interaction representation
★	complex conjugate
(0)	secular part of Hamiltonian
c	correlation
cr	cross relaxation
CS	chemical shift
D	dipolar
e	electronic
eq	thermal equilibrium
ext	external
FC	Fermi contact
HF	hyperfine
ind	induced
int	internal
L	'lattice'
(n)	non-secular part of Hamiltonian
orb	orbital

Q	quadrupolar
r	rotating frame
rf	radio frequency
ρ	doubly rotating frame
RL	rigid lattice
S	spin
SL	spin-lattice

CONTENTS

NOTATION

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PART 1: SPIN SYSTEMS IN SOLIDS, LIQUIDS, AND GASES AND THE CONCEPT OF SPIN TEMPERATURE

1. ON THE DESCRIPTION OF SPIN SYSTEMS	3
1.1. Introduction	3
1.2. Basic Hamiltonians of spin systems embedded in solids, liquids, and gases	6
1.3. Statistical description of spin systems	8
1.4. Rotating-coordinate representation of spin Hamiltonians	11
2. BASIC INTERACTIONS OF SPIN SYSTEMS AND RELATED HAMILTONIANS	13
2.1. Zeeman Hamiltonian of a system of non-interacting spins	13
2.1.1. Zeeman Hamiltonian in the rotating frame	14
2.1.2. Zeeman Hamiltonian in the doubly rotating frame	18
2.2. Direct magnetic-dipole Hamiltonian	19
2.2.1. Dipolar Hamiltonian in the rotating frame	22
2.2.2. Dipolar Hamiltonian in the doubly rotating frame	23
2.3. Nuclear-magnetic-exchange interaction and indirect magnetic-dipole Hamiltonians	28
2.4. Electric quadrupolar Hamiltonian	30
2.4.1. Quadrupolar effects on spin energy levels	33
2.4.2. Sternheimer's anti-shielding factor	34
2.4.3. Quadrupole Hamiltonian in cubic crystals	35
2.4.4. Quadrupole Hamiltonian in the rotating frame	37
2.4.5. Quadrupole Hamiltonian in the doubly rotating frame	37
2.5. Electron-nucleus (hyperfine) interactions	38
2.5.1. Magnetic hyperfine interactions	39
2.5.2. Electric hyperfine interactions	45
3. THE SPIN-TEMPERATURE CONCEPT	46
3.1. Spin-lattice relaxation in strong and weak Zeeman fields	46
3.2. Single-spin temperature in the laboratory frame in the absence of r.f. irradiation	48
3.2.1. Phenomenological aspects	48
3.2.2. Common spin temperature in a weak Zeeman field	53
3.2.3. Zeeman spin temperature in a strong Zeeman field	56
3.3. Single spin temperature in the doubly rotating frame in the presence of a saturating r.f. field	59
3.3.1. Redfield's spin-temperature concept	59
3.3.2. Consequences of Redfield's hypothesis	62
3.3.3. Common spin temperature in a weak r.f. field	66
3.3.4. Zeeman spin temperature in a strong r.f. field	67
3.4. Cases of more than one spin temperature	68
3.5. Validity and limitations of the spin-temperature concept	69

PART 2: BASIC THEORIES OF NUCLEAR-SPIN RELAXATION	
4. ON THE BASIC PHYSICAL CONCEPTS APPLIED IN NUCLEAR-SPIN RELAXATION THEORIES	73
4.1. Introduction	73
4.2. Theory of nuclear spin-lattice relaxation by Bloembergen, Purcell, and Pound (BPP theory)	76
4.2.1. Basic relaxation theory	76
4.2.2. Spin-lattice relaxation via time-dependent dipolar interactions	80
5. LINEAR-RESPONSE THEORY OF HIGH-FIELD NUCLEAR-SPIN RELAXATION BY KUBO AND TOMITA	82
5.1. Introduction	82
5.2. Basic linear-response formalism	82
5.3. Relaxation as the response to a step-function perturbation	86
5.4. Linear relaxation equations and the fluctuation-dissipation theorem	87
5.5. Symmetry properties of relaxation- and correlation-function tensor	89
5.6. Linear phenomenological relaxation equations	91
5.7. Relaxation equations in a rigid lattice	94
5.8. High-field perturbation expansion for weak spin-lattice coupling	96
5.8.1. Rigid-lattice contribution to relaxation	100
5.8.2. 'Lattice'-induced relaxation contribution	101
5.9. On the validity of Bloch's equations	102
6. DENSITY-MATRIX THEORY OF NUCLEAR-SPIN RELAXATION BY BLOCH, WANGSNES, AND REDFIELD	103
6.1. Introduction	105
6.2. Density-matrix master equation for the spin system	105
6.3. Redfield's high-field formulation of the master equation	109
6.4. Macroscopic equations of motion in Abragam's formulation	114
6.5. BWR theory and the assumption of a single spin temperature	116
6.6. BWR theory and systems characterized by two spin temperatures	117
6.6.1. Spin-lattice relaxation in systems with two non-mixing spin temperatures	121
6.6.2. Single-spin-temperature limit	122
7. SPIN-TEMPERATURE THEORY OF MOTION-INDUCED SPIN-LATTICE RELAXATION BY HEBEL AND SLICHTER	125
7.1. Introduction	125
7.2. Single-spin-temperature relaxation equation of Hebel and Slichter	126
7.3. Application of first-order perturbation theory	129
7.4. Schumacher's extension of the Hebel-Slichter theory to systems with two spin temperatures	130

8. FORMULATION OF A COMPREHENSIVE THEORY OF MOTION-INDUCED NUCLEAR-SPIN RELAXATION	135
8.1. Introduction	135
8.2. Kubo-Tomita and Bloch-Wangsness-Redfield theories: a synthesis	136
8.2.1. Linear-response formalism in the presence of fluctuating spin-lattice interactions	138
8.2.2. Relaxation equations in a rigid lattice	141
8.2.3. Motion-induced relaxation: BWR theory as limiting case	143
8.3. Relationship between the theories of Bloch-Wangsness-Redfield and Hebel-Slichter	144
8.4. Spin-lattice relaxation and spin-lattice cross coupling in systems with two non-mixing spin temperatures	148
8.5. Synthesis: formulation of a unified spin-temperature theory of motion-induced spin-lattice relaxation	153
8.6. Concluding remarks on the validity range of the unified relaxation theory	157
PART 3: APPLICATION TO SPIN-LATTICE RELAXATION ASSOCIATED WITH FLUCTUATING DIPOLAR AND QUADRUPOLEAR INTERACTIONS	
9. DIPOLAR SPIN-LATTICE RELAXATION IN THE LABORATORY FRAME AND DIFFUSION IN CRYSTALS CONTAINING ONE SORT OF EQUIVALENT SPIN	163
9.1. Formulation of the problem	163
9.2. Laboratory-frame spin-lattice relaxation due to fluctuating dipolar interactions	169
9.3. 'Strong collisions' and 'ultra-slow' motions in the laboratory frame	175
9.4. 'Weak collisions' and motional narrowing	180
9.5. Relationship between strong and weak collisions	184
9.6. Relaxation in the transition region: theory of low-field T_1 minimum	188
9.7. Application to random-walk diffusion in cubic crystals	191
9.7.1. Relaxation in the strong-collision region	197
9.7.2. Relaxation in the weak-collision region	199
9.7.3. Relaxation in powdered samples	202
10. DIPOLAR SPIN-LATTICE RELAXATION IN THE ROTATING FRAME AND DIFFUSION IN CRYSTALS CONTAINING ONE SORT OF EQUIVALENT SPIN	204
10.1. Introduction	204
10.2. Rotating-frame spin-lattice relaxation due to fluctuating dipolar interactions	205
10.3. 'Strong collisions' and 'ultra-slow' motions in the rotating frame	209
10.4. 'Weak collisions' in the rotating frame	211
10.5. Relationship between strong and weak collisions	214
10.6. Relaxation in the transition region: theory of low-field $T_{1\rho}$ minimum	216

10.7.	Comparison with the theories of Solomon-Ezratty and Slichter-Ailion	218
10.7.1.	Relaxation due to 'ultra-slow' motions	220
10.7.2.	Relaxation due to an arbitrary spin-lattice interaction	223
10.7.3.	Discussion	224
10.8.	Application to random-walk self diffusion in cubic crystals	228
10.8.1.	Relaxation in the strong-collision region	228
10.8.2.	Relaxation in the weak-collision region	232
11.	SPIN-LATTICE RELAXATION AND MOLECULAR MOTIONS IN CRYSTALS CONTAINING A SINGLE SPIN SPECIES	236
11.1.	Introduction and formulation of the problem	236
11.2.	Spin-lattice relaxation in the laboratory frame: general case	240
11.3.	Strong collisions of an arbitrary type	243
11.4.	Weak collisions of an arbitrary type	244
11.5.	Spin-lattice relaxation in the rotating frame: general case	246
11.5.1.	Strong collisions of type α	247
11.5.2.	Weak collisions of type α	248
11.5.3.	Relationship between line width and depth of a zero-field $T_{1\rho}$ minimum	249
11.6.	Application to random isotropic rotation and self diffusion of molecules in cubic crystals	250
12.	QUADRUPOLEAR AND DIPOLAR SPIN-LATTICE RELAXATION ASSOCIATED WITH DEFECT MOTIONS IN CUBIC CRYSTALS	261
12.1.	Spin-temperature concept and quadrupolar interactions	261
12.2.	Simultaneous dipolar and quadrupolar effects on T_1 : basic theory	262
12.3.	Strong versus weak quadrupolar and dipolar collisions in the laboratory frame	271
12.3.1.	Quadrupolar strong collisions	272
12.3.2.	Quadrupolar weak collisions	274
12.3.3.	Dipolar strong collisions	276
12.3.4.	Dipolar weak collisions	277
12.4.	Simultaneous dipolar and quadrupolar effects on $T_{1\rho}$	279
12.4.1.	Quadrupolar strong collisions	280
12.4.2.	Quadrupolar weak collisions	281
12.4.3.	Extrapolation from strong to weak collisions	282
12.4.4.	Dipolar strong collisions	283
12.4.5.	Dipolar weak collisions	284
12.4.6.	On the field dependence of relaxation rates	285
12.5.	Relaxation in the transition regions: theory of low-field $T_{1\rho}$ minima	288
12.6.	Quadrupolar relaxation contribution due to point-defect mechanisms of self diffusion in cubic crystals	290
12.6.1.	Orientation dependence of quadrupolar relaxation rates	293
12.6.2.	Temperature dependence of quadrupolar relaxation rates	295
12.7.	Dipolar effects on T_1 and $T_{1\rho}$ associated with point-defect mechanisms of self diffusion	299

13. LABORATORY-FRAME SPIN-LATTICE RELAXATION IN CRYSTALS CONTAINING TWO SPIN SPECIES	312
13.1. Internal spin dynamics of two-spin systems	312
13.2. Relaxation in the single-spin temperature limit: general theory	316
13.3. 'Strong collisions' with rapid cross relaxation	324
13.4. 'Weak collisions' with rapid cross relaxation	328
13.5. Spin-lattice relaxation in the absence of cross relaxation: general theory	329
13.5.1. Internal spin dynamics in the absence of cross relaxation	330
13.5.2. Basic expressions for relaxation rates	334
13.5.3. Discussion	337
13.6. 'Strong collisions' without cross relaxation	339
13.7. 'Weak collisions' without cross relaxation	340
13.7.1. Relaxation in a large Zeeman field	341
13.7.2. Discussion	342
13.7.3. Field dependence of relaxation rates	345
13.7.4. One spin species immobile	346
14. ROTATING-FRAME AND DOUBLE-RESONANCE RELAXATION IN CRYSTALS CONTAINING TWO SPIN SPECIES	347
14.1. Internal spin dynamics in the presence of one or two r.f. fields	347
14.2. Double-resonance relaxation in the single-spin temperature limit: general theory	350
14.3. 'Strong' versus 'weak' collisions with rapid cross relaxation	353
14.4. Spin-lattice relaxation in the absence of cross relaxation: general theory	358
14.5. 'Strong' versus 'weak' collisions without cross relaxation	361
14.6. Double-resonance relaxation in large r.f. fields	366
14.7. 'Ultra-slow' motions of rare spins	368
14.8. Rotating-frame spin-lattice relaxation in the presence of a single r.f. field	371
PART 4: SPIN-LATTICE RELAXATION VIA FLUCTUATING HYPERFINE INTERACTIONS	
15. RELAXATION VIA CONDUCTION ELECTRONS IN METALS AND SEMICONDUCTORS	379
15.1. Introduction	379
15.2. Combined effect of dipolar, quadrupolar, and Fermi-contact interactions on T_1 : basic theory	380
15.3. Field dependence of T_1	388
15.4. Electron correlation functions for metals (Fermi-Dirac case)	392