

Book Reviews

JEAN-JACQUES DELPUECH (Ed.)

Dynamics of Solutions and Fluid Mixtures by NMR

Wiley, Chichester, 1995, pp. xi + 587, \$95.00.
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This volume consists of 580 pages of text and figures and a seven-page subject index together with a table of contents, a preface and a list of 21 contributors, all of whom are affiliated to Western European laboratories.

The first few chapters deal with theory (*Introduction: Dynamic Phenomena in NMR* by J.-J. Delpuech, *Time-scales in NMR: Relaxation Phenomena in Relation with Molecular Reorientation* by D. Canet and J. B. Robert, *Time-scales in NMR: Nuclear Site Exchange and Dynamic NMR* by J.-J. Delpuech and *Nuclear Paramagnetic Spin Relaxation Theory. Paramagnetic Spin Probes in Homogeneous and Microheterogeneous Solutions* by P. O. Westlund) and the rest with applications but with some theory (*Quadrupolar Probes in Solution* by J. Grandjean and P. Laszlo, *Solvent Exchange on Metal Ions: A Variable Pressure NMR Approach* by U. Frey, A. E. Merbach and D. H. Powell, *Applications of Field Gradients in NMR* by D. Canet and M. Decroix and *Surfactant Solutions: Aggregation Phenomena and Microheterogeneity* by B. Lindman, U. Olsson and O. Söderman. In Chapter 9, M. A. Krajewski-Bertrand, F. Lauprêtre and L. Monnerie describe *Local Dynamics of Large Molecules: Synthetic Polymers in Solution and in Melts* and L. Y. Lian and L. Barkusov contribute *NMR and Dynamics of Biopolymers*. Chapter 10 is divided into three: *Swollen Polymers and Gels* by J. P. Cohen-Addad, *Fluids in and on Inorganic Materials* by J. P. Fraissard and *Magnetic Resonance in Food Science* by B. P. Hills.

On the back cover the publisher informs us that the book will be of great interest to analytical chemists and biochemists, and to researchers and students working specifically in the fields of application covered in the volume. The preface describes the volume as a textbook contributing to the development of dynamical aspects of NMR, especially for chemical and biochemical applications.

The introductory chapter is somewhat disappointing. The Zeeman Hamiltonian of Eqn (1.3), for instance, does not contain the magnetic field B_0 but does contain the mysterious constant \hbar_0 ; maybe this is a printing error, it could be shorthand for $\hbar B_0$ (a list of symbol

definitions would have been useful, not only here but in other parts of the book as well, where T_{12} , τ_{11} , $\delta\nu$, $\Delta\omega$ and such like abound). A minus sign goes missing from Eqns (1.3) to (1.5), but reappears in Eqn (1.11). Equation (1.17), $M_0 = \gamma^2 \hbar^2 I(I+1)N_0/3k_B T$, is described as the Langevin equation; the right-hand side of this, however, defines the susceptibility χ , not the induced magnetisation $M_0 = \chi H_0$. The reader, confused by the summary introduction of the Bloch equations and their steady-state solution, might well ask why a description of CW NMR, a technique which is seldom used today, is of interest to anyone. Chapter 1 does not provide an answer. The two final sections of the first chapter treat relaxation and exchange phenomena, and successfully provide a feeling for the time-scales involved.

Chapter 2 (relaxation phenomena in relation with molecular reorientation) does not contain as many printing mistakes as Chapter 1, although in Eqn (2.6) the '+' should be a superscript and the resulting V_i^\dagger is then a Hermitian conjugate, not a complex conjugate. The background knowledge expected of the reader is rather high, for although references to other sources are provided, several deductive steps are made without explanation. To tell us that 'the anti-symmetric and symmetric modes can be coupled only via csa-dipolar cross-correlation' and to let us fend for ourselves without a reference to a higher authority is not good practice. Neither is it likely that all prospective readers know what Liouville and von Neumann have to do with NMR. Unfortunately, this chapter does not provide the necessary introduction to relaxation theory which the rest of the book requires. The direction of the chapter becomes clear only after the second reading; it is roughly divided into a discussion on magnetization modes and a discussion on experimental methods, but even after a second reading I failed to see what I could do with magnetization modes.

Chapter 3 picks up the discussion of time-scales initiated in Chapter 1, and is devoted to the effects of chemical exchange. Starting with a historical introduction and going through the modern usage the range of applications is defined before being elaborated. The discussion of site exchange and exchange matrices is workmanlike with well chosen examples. The errors creep in again in the theoretical part: Eqn (3.34) has a G_2 too many and in Eqn (3.78) a G_i is missing. In the treatment of strongly coupled systems the density matrix ρ unavoidably raises its ugly head. The reader, being referred back to

Chapter 2 where the density operator σ has appeared, would have difficulty following the ensuing discussion. We are nowhere told whether these are the same thing or, if not, wherein lies the difference. It is unfortunate that this theme is not better treated. In general, though, this chapter makes a good impression and is supported by an extensive list of references (not all of which may be correct; for instance, D. Neuhaus is one of the authors of 'The NOE ...', not D. Nauhaus). Although it is stated that programs have been built to compute the lineshapes, none is offered and the only reference to a source points to the NMR textbook co-authored in 1980 by the Editor of this volume.

Having read my way through Chapters 1–3, I approached Chapter 4 with trepidation—how could I judge nuclear paramagnetic spin relaxation theory? From here on I stopped checking the equations for errors; this saved time for the equations are numerous in Chapter 4, which is written for the expert. Without at least some previous knowledge of relaxation theory one is just left wondering how the equations are derived. Equation (4.11), for instance, is a monster $[T_n^{1(\text{DD})}(t) = (-1)^{1+n} \sqrt{C^{\text{DD}}} 1/r_{\text{IS}}^3(t) \dots]$ which is supposed to be explained in Chapter 2—I searched in vain. Chapter 4 should have been expanded into a monograph and published separately.

In the short Chapter 5 (quadrupolar probes in solution, 30 pages), a review of the theory is followed by a review of applications to chemical exchange in such varied systems as proteins and clays as well as to molecular dynamics and ion transport in membranes. Chapter 6 (45 pages) is a review of the applications of variable pressure to solvent exchange on metal ions. The authors treat experimental methods, and both time-dependent methods as well as the static lineshape approach to determining kinetic data are dealt with. Several detailed relaxation rate measurements are also considered. The next chapter (35 pages) on field gradients contains an instructive description of imaging followed by a very condensed treatment of its application to systems undergoing motion—diffusion and flow.

The real meaty part of the book (pp. 345–580) starts with Chapter 8—surfactants (50 pages). This chapter offers a good overview of the subject and sufficient references to allow further reading. Chapter 9, dealing with polymers, is divided into two parts; the first (40 pages) treats synthetic polymers, the second (40 pages) biopolymers. In the first section the effects of local dynamics—mainly conformational

changes in chains—are related to relaxation time and NOE measurements, and the effects of structural changes on the measurements are also discussed. The second part of Chapter 9 is an informative treatment of exchange and relaxation in polypeptides. The last chapter is divided into three sections. The first, devoted to polymeric liquids and gels, consists of 20 pages, which are not sufficient to cover the subject (the author's article on the same theme in *Progress in NMR Spectroscopy* is over 300 pages long!). In the following 40 pages, the NMR of adsorbed species is treated concisely and the author provides an extensive list of references. The final 30 pages of the last chapter deal with NMR spectroscopy and imaging in food science: again, a concise treatment with useful references.

To sum up: this volume is not a textbook—most of the chapters are non-critical reviews written for connoisseurs, and those chapters dealing with theory are mainly also written as reviews. It is a compendium of largely independent descriptions of the applications of relaxation theory to dynamic problems. As such it will be of interest to researchers and students working in these fields, who thus obtain a large collation of equations and a comprehensive list of references. It will also be of use to those working in neighboring fields who wish to see what is going on 'on the other side of the fence.' Analytical chemists and biochemists should look elsewhere.

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RAY FREEMAN

A Handbook of Nuclear Magnetic Resonance

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It is too often the case that tomes covering NMR spectroscopy fall in the category 'I own one but seldom read it.' The reason is simple. The experts in the field, that is to say, those driving the theoretical and technical developments and consequently those in the best position to author such works, aim their publications at a level far beyond that needed by the bulk of the practising chemists and biochemists (many of whom suffer a phobia of Hamiltonians). At times, though, many of these researchers need to understand or themselves explain a theoretical concept in a simple or semi-theoretical way. For this purpose there are few references to which they can refer.

At a time when many works were published to disseminate the theoretical details of the emerging field of NMR, Ray Freeman's first edition of *A Handbook of Nuclear Magnetic Resonance* was a welcome arrival. It attempted to present the major ideas in as simple a language as was necessary, listing concise entries alphabetically rather than thematically. No attempt was made by the author to offer this as a comprehensive reference to the field, or as an introduction to the novice, but more as a *handbook* for those with a practical background in NMR—those very chemists and biochemists described earlier. This was its success.

This second edition, coming some 10 years after the first, builds on the original intentions. The format is largely

intact, although the contents have been altered to reflect the developments in the field since the first edition. Sections deemed less important have been merged into existing sections, or replaced by five new sections covering coherence spectroscopy, the measurement of coupling constants, nuclear susceptibility and pulsed field gradients.

Most of the original text has been revised and in almost every case to great effect. The author manages to condense into a few pages what others struggle to achieve in a hefty chapter. One such example is the entry describing the Product Operator Formalism. Here, the language could be simpler, but the ideas are presented well enough for someone without prior knowledge of this topic to understand. The graphics have been updated and in many cases make the description of the concepts clearer. On the whole, the production looks fresh and is well presented.

For the reviewer, the ultimate success of a handbook is not only the information it contains, but the reference listings that guide the reader to a more detailed treatment of a particular subject. To this end, the second edition is a significant improvement over the first, offering most of the original references in addition to many new ones. Some readers may also find the cross-referencing between topics covered in the book useful.

The second edition is a significant improvement on what was already a fine book, with ideas described clearly and eloquently by a scientist whose contribution to the field of NMR is as significant as that by any other.

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