

Physics, Chemistry and Magnetic Resonance: a New Zealand Perspective

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About the Author

Sir Paul Callaghan, GNZM, FRS, FRSNZ, is the New Zealand physicist who, as the founding director of the MacDiarmid Institute for Advanced Materials and Nanotechnology at Victoria University, holds the position of Alan MacDiarmid Professor of Physical Sciences. He is one of the country's most high profile and respected scientists showing outstanding leadership for over 30 years as a scientist, a teacher, a science administrator and communicator.

A native of Wanganui, Paul Callaghan took his first degree in physics at Victoria University of Wellington and subsequently earned his DPhil degree at the University of Oxford, working in low temperature physics. He returned to a lectureship in Physics at Massey University in 1974, reset his researches on the applications of magnetic resonance to the study of soft matter, and became Professor in 1984. He and his group relocated to Victoria University of Wellington in July 2001, but continue collaborations with colleagues at Massey. The group's laboratory is known as *The Magnetic Resonance of Materials Laboratory* and, while nuclear magnetic resonance (NMR) is the main technique they use, the laboratory has excellent rheometers as well as dynamic light scattering facilities. The work is dominantly directed towards developing NMR methodologies for the study of molecular dynamics and molecular organisation in soft matter and porous materials. It is performed by a mix of physicists and chemists and deals with a variety of physical and biophysical systems. The field is sometimes called *squishy physics*.

Sir Paul is a past president of the Academy Council of the Royal Society of New Zealand and has published over 240 articles in scientific journals as well as a 1994 book, *Principles of Nuclear Magnetic Resonance Microscopy*. He is also a founding director and shareholder of the Wellington-based technology company *Magritek*, which sells nuclear magnetic resonance and MRI instruments. He is a regular public speaker on science matters. In 2001 he became the 36th New Zealander to be made a Fellow of the Royal Society of London, was awarded the Ampere Prize in 2004 and the Rutherford Medal in 2005. He was appointed a Principal Companion of the New Zealand Order of Merit in 2006 and in 2007 was recognised by a KEA/NZTE World Class New Zealander Award and the Sir Peter Blake Medal. He was knighted on 14 August 2009. In 2010 he was awarded the Günther Laukien Prize for Magnetic Resonance and shared the inaugural NZ Prime Minister's Science Prize. In 2011 he was named Kiwibank New Zealander of the Year.



Photo: From The Dominion Post and provided by the author

I was born, and grew up in Wanganui, where physics seemed to surround me. I built my first crystal set radio while at primary school and was delighted to be able to pick up two radio stations. When I was 10 years old, Sputnik was launched, with many more satellites following, some of which could be seen at night with the naked eye, repeating their orbit after 90 minutes. In my early teens I was a boy chemist, with a backyard laboratory and pursuing adventures that would today be considered foolhardy at best, and criminal at worst. There was a 200-meter-long tunnel in a local hill that led to an elevator that allowed hilltop residents to avoid the 70-meter climb. It made wonderful echoes, over a second apart.

Among that mix of radio waves, molecules, echoes, and the evident triumph of the laws of physics may have been sown the seeds of a life in magnetic resonance (MR). Certainly I had never heard of it. I first came across MR as a final-year physics student at Victoria University of Wellington. But my interests then were in nuclear physics and solid-state physics. I discovered a field of research that combined them, the use of hyperfine interactions to orient radioactive nuclei. And so my doctoral ambitions took me, courtesy of a UK Commonwealth Scholarship, to the Clarendon Laboratory at Oxford University, where I joined the team of Nick Stone and grandfatherly mentor, Nicholas Kurti. There we used adiabatic demagnetization

of paramagnetic salts to get down to 10 milliKelvin, at which temperature the hyperfine interaction would overwhelm the Boltzmann energy to cause radioactive nuclei in a ferromagnetic host metal, attached to the cold finger of the apparatus, to align, so directing their gamma rays preferentially along the quantization axis. The degree of orientation could be used as a measure of the interaction strength, so that nuclear magnetic moments or local fields could be measured. But by far the best way of precisely measuring that interaction was by sweeping an RF field in the vicinity of the Larmor frequency. At resonance, the gamma rays would suddenly change their angular distribution and the axial count rate would change dramatically.

So that was my introduction to magnetic resonance, a phenomenon detected through gamma emissions! It wasn't until the last year of my DPhil that I came across Faraday detection and the mainstream. In 1973 I had the chance to go to a conference in Krakow, Poland, the 1st Specialized Colloque Ampere. It was a most remarkable meeting and one that completely changed my professional life. I knew only one person there, Erwin Hahn, a regular Oxford visitor of Nicholas Kurti. Alex Pines presented his work, *Proton Enhanced Nuclear Induction Spectroscopy*. Peter Mansfield spoke about nuclear magnetic resonance (NMR) diffraction in solids. Someone asked if he had seen the paper by Lauterbur, *Fourier Zeugmatography*, which had just come out in *Nature*. And a young graduate student from the Ljubljana group, Metka Luzar spoke about using pulsed magnetic field gradients to measure diffusion in liquid crystals. I was fascinated. Many years later, in the early 1990s, I met up with Metka at an NMR meeting in Portoroz, on the tiny coastline of her Slovenian homeland. I sat down next to her and said: *Metka Luzar, you changed my life*. I am sure she thought me quite mad. Sadly, she died of cancer less than a decade later.

I stayed in Oxford for another year as a postdoctoral fellow, but I was determined to go back to New Zealand to attempt the task of doing international science from my home base. My forebears, Rutherford included, just had to make the shift to expatriate status in order to do any serious science. But things were changing at home, not the least of which was the advent of cheap long-haul air travel. Suddenly NZ was connected to the world in a different way. And there were some brave pioneers from whom to take inspiration. Kiwi theoretical physicist Dan Walls had, in 1972, returned from Roy Glauber's group at Harvard to start a school of quantum optics in NZ. Dan later became a Fellow of the Royal Society and winner of the Dirac medal and prize. Cancer claimed him too, in 1999. I returned home in late 1974 to a lectureship in Physics at Massey University, an upstart institution with an agricultural college background, and a small but feisty science faculty led by a larger-than-life biochemist, Dick Batt. Dick came from my hometown of Wanganui. Maybe that's how I got the job. But I was grateful for the employment, and joined a small group of physics colleagues inside a larger Chemistry Department. There was no physics research equipment at all, but the chemists had just acquired a JEOL FX60 NMR spectrometer. It was just a remarkable machine, with a lovely light pen interface, the first for JEOL of the new generation of pulsed Fourier transform instruments.

The physical chemist in charge of the FX60 was a Lancastrian immigrant, Ken Jolley. I couldn't have had a better teacher or more generous colleague. He allowed me to share in this wonder and to start a research program using the spectrometer. And being in that chemistry environment could not have been better for me as I made my transition from a rather narrow-focused physicist to one who saw the wonders of chemistry, of the world of molecules, with all the opportunities for physics that this field of research presented. With Metka Luzar's talk in my mind, I set about building a pulsed field gradient system that we could attach to the FX60. In that I was assisted by an able graduate student named Craig Trotter. We built the electronics and gradient coil and quickly discovered that there were some technical problems plaguing this method that were ripe for tackling. These included gradient pulse area mismatch, sample vibration, and eddy current effects.¹ By good luck we made some progress, and that led to a fruitful period in which my collaborators and I measured polymer diffusion, as well as small molecule diffusion in anisotropic and heterogeneous environments.

It wasn't long before NMR micro imaging became a focus of our work. The apparatus building was result of a most remarkable graduate student named Craig Eccles. Craig was not only a fine physicist but also an electronics and software genius. In the mid-1980s, with Craig, and new Chinese student Yang Xia, we were using our NMR microscope to image flow in wheat grains *in vivo*, impossibly difficult but very effective.² This work helped start a new field of research in which sub-100 micron structure was revealed in soft materials and biological tissue from the perspective of the interpenetrating liquid molecules. NMR Microscopy was the subject of my first book, published by OUP in 1991.³

Another odd area of interest for me in the 1980s was Earth field NMR. We did the first spin echo experiments using 180° audio frequency pulses. Later, in 1994, Craig and I were to take this apparatus to Antarctica to measure brine content in sea ice. We were joined in 1996 by an American postdoctoral fellow, Joe Seymour. Joe not only contributed to our Antarctic program, measuring brine diffusion in sea ice,⁴ but also introduced me to chemical engineering, his own undergraduate specialty. Joe and I set out to see what we could do with pulsed-gradient spin echo (PGSE) NMR to measure dispersion, the process whereby molecules starting together are separated by flow.⁵ This collaboration was very fruitful, and porous media dispersion and diffusion studies became a major part of our research interests. My Slovenian link was also revived in a wonderfully productive sabbatical visit by Janez Stepisnik. We were able to demonstrate experimentally the validity of his idea that the spectrum of molecular velocity autocorrelation functions could be measured using modulated gradient spin echo NMR.⁶

By the 1990s we had been exploring the use of NMR microscopy to study heterogeneous flow in shear cells, combining rheology with NMR, inspired by Ed Samulski, a US sabbatical visitor to my lab. Our work in rheo-NMR led to another serendipitous collaboration that, in turn, generated a major field of research in my laboratory. In 1996 we

were introduced to worm-like micelles (WLMs) by visiting Dutch physicist, Bas Smeulders. Later, we used NMR microscopy to measure shear banding effects in WLMs,⁷ and we have been pursuing the complex rheodynamics of these systems ever since.⁸

Of all the work we have done, the most cited has been the *q*-space diffraction and *q*-space imaging research. The history of this is interesting. In a review paper⁹ on PGSE NMR, published in the *Australian Journal of Physics*, I pointed out the formal analogy between PGSE NMR and the incoherent fraction of inelastic neutron scattering. In neutron inelastic scattering, the symbol *q* is used as the reciprocal space dimension conjugate to dynamic displacement. The term *q*-space first appeared, in the NMR context, in the title of a paper on NMR velocimetry¹⁰ that I published with Craig Eccles and Yang Xia in *Journal of Physics E*, in 1988. But the impetus to see the potential of diffraction effects in diffusion studies came about as a result of a visit made in 1989 to Ken Packer's group at BP research in the UK. Ken, of course, had been the first to see non-Gaussian echo attenuation when he carried out a PGSE NMR experiment on pipe flow. Those 1989 discussions with Ken centered on the idea that the Fourier transform of the *q*-encoded echo was the propagator for displacements, and this led to speculation as to whether diffraction effects might be seen for small-molecule diffusion in porous media. I worked through the theory of this. A simple limiting case was that of the isolated pore, where it turned out that in the long diffusion time limit, the propagator reduces to the autocorrelation function of the pore structure. We dashed off a short paper¹¹ on *q*-space diffraction and oscillatory echo attenuation effects to the *Journal of Magnetic Resonance*. Concurrently (and submitted before us to *Magnetic Resonance in Medicine*), Al Garroway and David Cory¹² had come up with a similar idea, namely that the Fourier transform of the echo decay for an isolated pore was the pore autocorrelation function.

Of course, the key step was to do the experiment. Working on an isolated pore was difficult (that experiment came later). It was much easier to work on an interconnected porous medium imbibed with water. The interesting theory extension to interconnected porous media was based on the idea that, in effect, the pore structure factor is convolved with the pore lattice structure and modulated by a diffusive envelope. With a reasonably ordered system, diffraction effects might be seen there. On return to NZ, I suggested to my PhD student Andrew Coy that he try the diffraction experiment on a close-packed monodisperse latex sphere system. The oscillatory features of diffraction were immediately evident on the echo attenuation function, and a paper in *Nature*, jointly with the Packer group, resulted.¹³ In a later, more detailed paper on this in the *Journal of Chemical Physics*,¹⁴ we were greatly assisted by some subtle theory insights provided by BP theorist, Dave MacGowan. Later, Andrew and I verified the isolated pore predictions by using an array of rectangular glass microcapillaries, and this work subsequently led to a number of papers on the subject from our group.

The advantage of *q*-space imaging is that one is not constrained by voxel signal-to-noise limitation. These days,

the method is used as a contrast in medical imaging, where the distributions of displacements so obtained tell something about compartmentation of tissue, along with compartment size.

I moved my group to Victoria University of Wellington in 2001. I was ready for a change, but I had no idea just how big a change it would be. First, I ended up establishing a new research institute, the MacDiarmid Institute for Advanced Materials and Nanotechnology, named after Kiwi Nobel Laureate Alan MacDiarmid. Alan, who won his prize for co-discovering conducting polymers, was a national hero. Based at the University of Pennsylvania, Alan was a regular visitor to his homeland and a great communicator of science. Being in the capital city plunged me into the world of science communication as well. Motivated by Alan's example, I followed my route in trying to bring science to the general public, with a radio show, television documentaries, and popular science books.

Then something quite surprising happened. While at Massey University, I had started collaborating with a brilliant electronics engineer named Robin Dykstra. Robin had been with Craig and me on some of our Antarctic visits. In 2004, Robin, Craig, and I, along with my PhD student Mark Hunter, discussed the possibility of starting a company to commercialize the rheo-NMR attachments, a one-sided access NMR system that Mark had designed, and the Earth field spectrometer that Robin had improved so much, by comparison with its 1980s genesis. The company was formed in late 2004, headed by a CEO of great talent, the same ex-PhD student of mine, Andrew Coy, who was already well known in NMR circles for his work with me on *q*-space diffraction. Andrew had been in the business side of IT in Sydney and London for nearly a decade. He turned up in Wellington, heard we were starting the company, and expressed his interest in running it. *Magritek* has never looked back, in its 6th year now, with 21 staff and with export sales of NMR systems around the world. Suddenly I had entered the world of science commercialization, and my university research group was expanded to include NMR technology, along with our continuing work in soft matter and porous media.



The author (right) with his group at Massey University in 1993, from left Andrew Coy, Craig Rofe and Yang Xia.

I have had a wonderful life in magnetic resonance, learning so much from my students and collaborators. Much of what I have done, as well as the work of international colleagues, is summarized in a book I have just completed, to be published by OUP this year.¹⁵ I have always enjoyed dreaming up new ways of extracting information about molecules by manipulation of nuclear spins. And my particular interest in doing this is to gain insight regarding how molecules organize, align, and move about. Such insight is of some importance in helping physicists understand soft materials, self-assembly pathways to nanotechnologies, and the behavior of complex fluids and porous media. Of course, such understandings can assist a whole array of applications, from food science, to biotechnology, to biomedicine. That's a motivational factor, but for me, it's not the main one. It's the beauty of magnetic resonance that holds my interest, as well as its essential veracity.

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