The evolution of Neutron Reflectometry: personal reflections from Jeff Penfold

In the later 1970’s to mid 1980’s neutron reflectometry emerged and rapidly developed as dedicated technique for the study of surfaces and interfaces. What follows is a purely personal perspective of how it evolved and of my involvement in the development, with a particular emphasis on those early days. As such it is inevitably incomplete and I will have forgotten (not intentionally) some of the contributions.

In the early 1970’s most of the neutron scattering techniques now commonplace were already well established, but not neutron reflectometry. For some decades the optical properties of the neutron, such as reflection and refraction, had been well established. Neutron reflection was of course the basis of neutron guides, the neutron equivalent of fiber optics, through total external reflection; and their extensive installation at the Institute Laue Langevin, ILL, had transformed neutron instrumentation for both thermal and cold neutrons. However it was the spin dependent refractive index and total reflection from magnetic surfaces that drew Gavin Williams and myself at the newly formed Neutron Beam Research Unit at the Rutherford Appleton Laboratory, RAL, to an interest in reflectivity. We spent some time developing Fe/Co thin films deposited on different non-reflecting substrates as potential neutron polarisers. It was from this programme that we first became involved with John Hayter, then at the ILL. This was the start of a very exciting, stimulating and fruitful collaboration between John and myself. It was this collaboration that really ‘kickstarted’ my career in neutron scattering, and resulted in many of my most cited papers.

John was initially interested in our developments as potential polarisers / analysers for the newly developing spin echo instrument, IN11, which he was involved in with Feri Mezei. The aim was to produce efficient compact polarising soller guides. At the NBRU we developed a sputtering apparatus for depositing thin films of different Fe/Co alloys onto different substrates, mostly glass or plastic (1). During measurements at the ILL to evaluate the polarising properties of these films John and I observed for the first time interference fringes from a thin Fe/Co film, measured ironically by time of flight; and we reported the results in a letter to Nature (2).

We did spend some time trying to get rid of the effect as we initially thought that it may be an artefact of the way we were doing the measurements. When the ‘penny dropped’ we very quickly saw the potential for neutron reflectometry. The work did ultimately result in
I remember very clearly that meeting. Meeting potential of neutron reflectivity as a technique to probe surfaces and interfaces. I still become the British director of the ILL. He was very supportive and enthusiastic about some different areas of research. We presented our ideas to John White, who had just become the ILL director.

After John was challenging but stimulating and eventually became my PhD work. It was an exciting time to be at the ILL, and working with John was exciting and even more rewarding. To be involved in the early stages of neutron reflectivity and the application of SANS to the study of self-assembly at the same time was unbelievably lucky and exciting. Our work on SANS developed out of some early spin echo measurements, and I never returned to using spin echo; but that is another story.

Armed with a greater capability to calculate and predict neutron reflectivity profiles from different surfaces and interfaces, John Hayter and I started to think about the wider possibilities of using neutron reflectivity as a technique for studying a variety of surface and interfacial phenomena. We sketched out ideas for potential instrumentation and considered some different areas of research. We presented our ideas to John White, who had just become the British director of the ILL. He was very supportive and enthusiastic about the potential of neutron reflectivity as a technique to probe surfaces and interfaces. I still remember very clearly that meeting. However, we were unable at that stage, and for some time, adapting the optical matrix methodology, commonplace in light optics, for neutrons. The excellent books by Born and Wolf (4) and Heavens (5) and the seminal papers of Abeles (6) were invaluable guides. Curiously, we did not at that stage think to draw upon the analogy with X-rays and the earlier work of Kiessig et al (7) and others. We also had little or no contact with emerging developments of ‘supermirrors’ by Mezei and subsequently others. However, as a result, I developed the Fortran code, MULF, which has been the basis of the data analysis software at ISIS, and probably elsewhere, for the last 30 or so years (8, 9). I have a vivid memory of writing the heart of the code one night in the Hotel des Alpes in Grenoble when unable to sleep.

In the late 1970’s I went to the ILL to spend two years working with John Hayter, nominally on spin echo. I was formally the UK’s representative at the ILL; but by then this was not an onerous task. As they always do, things developed in other directions; and although I did some work on spin echo I spent most of my time with John Hayter developing our ideas for neutron reflectivity and on the use of SANS to study colloids and self-assembly. These areas eventually became my PhD work. It was an exciting time to be at the ILL, and working with John was challenging but stimulating and rewarding. To be involved in the early stages of neutron reflectivity and the application of SANS to the study of self-assembly at the same time was unbelievably lucky and exciting. Our work on SANS developed out of some early spin echo measurements, and I never returned to using spin echo; but that is another story.
years, to convince the rest of the ILL that this was a direction to support. John White did make one very important and crucial contribution at this stage when he introduced John Hayter and myself to Bob Thomas. Bob Thomas had recently taken responsibility for John White’s group in Oxford, and through a conversation with John Rowlinson, the head of Physical Chemistry in Oxford, had started to think about what could be done with neutron reflectivity in the context of surface chemistry. This resulted in a joint paper in Faraday Transactions (10) where we mapped out and calculated a whole range of different ideas for applying neutron reflectivity to study chemical surfaces and interfaces. In broad terms the contents of that paper has formed the basis of our joint research programme since that time in 1981. About the same time Gian Felcher at the Argonne National Laboratory’s Intense Pulsed Neutron Source, IPNS, was thinking about using neutron reflectivity to probe different aspects of surface magnetism (11).

Initial progress was slow for a number of reasons. The lack of dedicated instrumentation meant that at the ILL the initial experiments were done on D17, adapting the then SANS instrument temporarily into a reflectometer. Bob looked further afield and did some measurements of the Munich gravity reflectometer and at Brookhaven with Larry Passell. Not long after that John Hayter moved to Oak Ridge. For me, my wonderful two years at the ILL came to an end and I returned to the RAL to work on the early instrumentation for ISIS. Somehow I found myself working on Spectroscopy, as it was made clear to me that neutron reflectivity was unlikely to be relevant to ISIS. However, I was able to keep my interests in SANS and the developing collaboration with Unilever going. Fortunately I also kept in contact with John Hayter and Bob Thomas, and continued in my spare time to develop my interest in neutron reflectivity, thanks to some invaluable anarchic advice from Bob Thomas.

Schematic diagram of the CRISP reflectometer (12)

Around 1986 Bob Thomas and Rob Richardson lobbied the then head of ISIS, Alan Leadbetter, about the possibility of building a reflectometer at ISIS. Gavin Williams and I seized the opportunity and developed a proposal for the building of CRISP (named after a racehorse that should have won the Grand National). At that time Gian Felcher had already started running a reflectometer at IPNS and he generously gave me much invaluable advice during a crucial two week visit to Argonne. CRISP was a modest project, but was designed to have both polarised and unpolarised modes and view the cold moderator on ISIS. We were allocated a £80k budget, but in the end spent £250k; still a miniscule amount for a complete instrument even in the 1980’s. We measured the first spectrum in August 1986 (12, 13). It was still the early days of ISIS and
coupled with the limited automation available it is quite remarkable how good some of the data was. The early instrument collaborations with Richard Ward and Roberto Felici were vital contributions to the early and rapid progress. Another early contributor to the field was the group at Saclay led by Bernard Farnoux.

We quickly realised that the white beam time of flight method offered many advantages and the broad wavelength range including the shorter wavelengths was an important element. Early studies on L-B films, polymer films, solid state multilayers and magnetic thin films quickly established a vibrant and rapidly growing programme and community. It was for some time the fastest growing part of ISIS, and the support of many key users, including Thomas, Richardson, Stewart, Higgins, Cowlam, Jones, Bland, Richards and many others, was important. Industry showed a keen interest at an early stage, and ICI, BP, Unilever, Kodak and others quickly became involved. Neutron reflectivity remains an area of application of neutron scattering that still attracts a high level of industrial involvement. Important to my own future programme with Bob Thomas and Unilever was the ability to study the air-solution interface, unique at this stage. At an early stage in the exploitation of the instrument Rob Richardson published data on spread monolayers (14) and Bob Thomas produced the first comprehensive study of surfactant adsorption at the air-water interface (15).

CRISP, as an instrument, gradually evolved and incorporated more instrumentation and advanced sample environment equipment. However around 1995 ISIS secured funding for a new batch of instruments. This included a new reflectometer, SURF, which was partially funded by the Australian Government due to John White’s involvement from the ANU in Canberra.

Although reflectometers were now being built at most neutron sources, SURF, designed specifically to study chemical surfaces and interfaces, was a significant step forward from the capabilities of CRISP, and the experiment scope expanded enormously (16).

The combined research programme on surfactant, mixed surfactant and polymer-surfactant adsorption at different interfaces that has developed during a longstanding and ongoing research collaboration between myself, Bob Thomas and Unilever is well illustrated by two

![Schematic of the INTER reflectometer (16)](image)
relatively recent reviews (17, 18). However, apart from the instrumentation, the key element in its success and applicability has been the ability to manipulate the neutron refractive index by deuterium labelling. For us this has been possible due to the pre-eminence of the deuterium labelling facilities that Bob Thomas developed in Oxford.

The current suite of surface instruments on the second target station at ISIS, and the equivalent instruments at the other major neutron sources, are a testament to how the technique of neutron reflectivity has developed from those early beginnings at the ILL, ISIS and IPNS.

References.

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