FEBRUARY 2017, NO 1

Hellenic Neutron Association Newsletter

Editorial

The Hellenic Neutron Association (HENA) has as members scientists who use neutrons in their research field that includes, among others, neutron scattering, neutronic calculations, neutron activation analysis, neutron radiation damage studies, neutron production and detection. They are scientists from disciplines like physics, chemistry, material science and engineering, geology, archaeology and health science. The aim of the Association is to provide a platform for scientific information exchange, to promote co-operations and interdisciplinary relations and to exploit the opportunities offered at European and International Level as well as to pursuit the optimum access and use of the European Large Scale Neutron Facilities.

In an effort to bring the members of the neutron society closely together, inform them about relevant conferences, schools and events as well as better serve the aims of the association, a series of newsletters will be issued twice per year. In this effort, the contribution of Dr Alexandros Koutsioumpas has been valuable and I would like to thank him for his time, energy and devotion.

In the current first newsletter two research highlights are presented; the first one, by Prof. Chris Toprakcioglu (University of Patras), refers to the use of neutron reflectivity technique for the investigation of polymer films while the second one, by Dr Markos Skoulatos (Technical University Munich and Heinz Maier-Leibnitz Zentrum) shows how inelastic neutron scattering is used to reveal the magnetic properties of zigzag spin chains. We hope you enjoy reading it!

— Dr. Konstantina Mergia (NCSR Demokritos)

Research Note: Polymer brushes studied by neutron reflectivity *

by PROF. CHRIS TOPRAKCIOGLU †

More than four decades ago neutron scattering made its debut in soft matter research, and particularly in polymer science, most prominently with the experimental determination of the Flory exponent. By the 1980s neutron techniques had already become indispensible tools in the structural investigation of polymeric and colloidal systems. Given the differ-

*This research note summarises a long-term research project at the University of Patras using instrumentation at the Laboratoire Léon Brillouin, Saclay, France.

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ence in neutron scattering length between the isotopes of hydrogen (H and D), isotopic substitution provided unique investigative pathways in situations where x-ray scattering would be highly ineffective due to poor contrast.

An important method emerged early on that made full use of the wave nature of thermal neutrons and their ability to exhibit reflection, refraction, and interference in a manner quite analogous to the more familiar case of electromagnetic radiation. This was the technique of Neutron Reflectometry (NR) [1], which provides valuable structural information on surfaces and interfaces. NR is particularly useful in the study of polymer layers adsorbed at the solid/liquid interface. Such systems are of considerable practical importance in numerous industrial applications, apart from their theoretical appeal. In this note we briefly describe some of the results our group has obtained in the last twenty years or so on fundamental aspects of the behaviour of end-tethered chains using the technique of NR.

While it is more common for polymer chains to adsorb onto a solid surface from solution in a random conformation, under certain conditions end-tethering is the mode preferred by the system. An example is afforded by a block copolymer with a hydrophilic and a hydrophobic block in a selective solvent (i.e. a solvent that is good for one block and poor for the other). In such a case, one block adsorbs on the solid substrate while the other dangles in solution. The resulting structure depends on the 'grafting density' (i.e. the number of end-tethered chains per unit area of interface). In good solvent and at high grafting density, where the distance between grafting points is small compared to the chain radius of gyration, the repulsive monomer-monomer interactions cause the chains to strongly extend away from the surface forming a structure known as a 'polymer brush'. A number of fundamental questions arise in connection with such a system. How does the layer thickness ('brush height') vary with the chain molecular weight at equilibrium? What is the distribution of chain ends? What are the kinetics of brush formation? What happens to the brush when it is subjected to strong shear flow? Such questions can be answered decisively (and perhaps uniquely) by means of NR, and our group has endeavoured over the years to look for the answers.

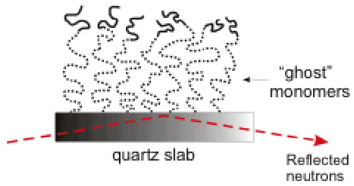

Figure 1. End-tethered 'ghost' chains with labelled end-segments. *(Adapted from ref. 3)*

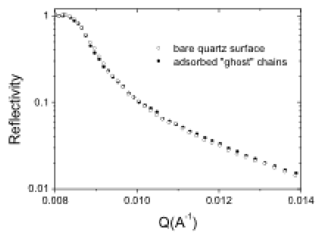

Figure 2.Neutron reflectance of the quartz/toluene interface, before and after 'ghost' chain adsorption. When ghost chains do not have their end-segments labelled, they are indistinguishable from the surrounding solvent. *(Adapted from ref. 3)*

It is now well-established that the brush height in good solvent varies with $M^{3/5}$, where M is the molecular weight of the brush chains. This was demonstrated using hydrogenated PS-PEO block copolymers with a short adsorbing PEO block in deuterated toluene [2]. However, the chain-end distribution, or the structure of the brush under shear have been far more challenging experimental problems to tackle. To solve the former we employed a PS-PEO block copolymer adsorbed onto quartz, where the dangling PS chain was contrast-matched to the deuterated toluene solvent except for a short segment at the end of the chain that was left hydrogenated [3] (see Fig.1). This rendered the chain 'invisible' to the neutrons apart from the hydrogenated end-segment (see Fig.2). The resulting chain-end distribution could then be measured and it was found to be in agreement with theory and simulation results[3] (see Fig.3).

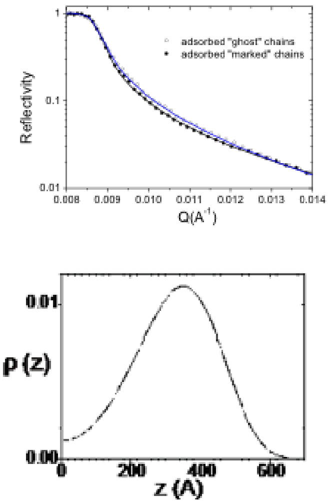

Figure 3.Neutron reflectivity profiles of ghost chains with (filled circles) and without (open circles) labelled end-segments, and the free-end distribution derived from the fit to the reflectivity profile of the former. *(Adapted from ref. 3)*

To study the behaviour of brushes in shear we constructed a flow cell in plane Poiseuille geometry, capable of reaching shear rates in excess of $6 \times 10^4 s^{-1}$, using quartz plates or silicon wafers as substrates on which brushes could be formed by adsorption. The brush profile could then be measured in situ under conditions of carefully controlled shear flow. We found that the brush structure remained unperturbed as the shear rate was increased, but rapid desorption took place at a critical shear rate that depended on the grafting density [4]. We further observed that bimodal brushes, formed by constituent block copolymers of two different molecular weights desorbed sequentially, with the longer chains detaching first at a lower critical shear rate, to be followed by the shorter chains at a higher critical shear rate [5]. These results may have important implications in a number of applications such as lubrication, wetting, adhesion, and stabilization of colloidal dispersions.

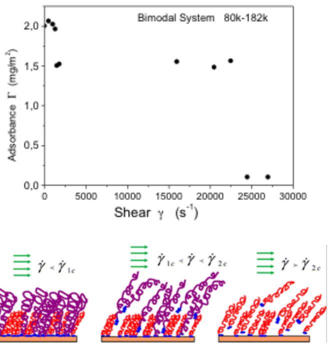

Figure 4.Adsorbance values of 80k-182k PS-PEO brush bimodal system calculated from the area under the volume fraction profile determined at each shear rate, and schematic representation of stepwise desorption process. The 182k PS-PEO polymeric chains detach from the surface at a critical shear rate of $1500s^{-1}$. The remaining 80k PS-PEO component desorbs at the much higher critical shear rate of $24500s^{-1}$. *(Adapted from ref. 5)*

In conclusion, NR has played a leading role in the study of adsorbed polymers and remains a powerful tool at the disposal of investigators interested in the structure of surfaces and interfaces in general. Furthermore, in view of recent advances in biophysics, biophysical chemistry and molecular biology, it is likely that NR will be increasingly used to good effect in these rapidly developing areas offering valuable insights into the structural details of complex systems.

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Effects of quantum impurity spin on the magnetic properties of zigzag spin chains ‡

by Dr. Markos Skoulatos §

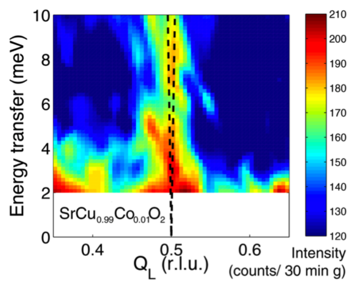
Low-dimensional quantum magnets show several unique and intriguing properties not found in their higher dimensional analogues [1]. Due to reduced dimensionality the quasiparticles in these systems are spatially confined, which makes them highly susceptible to any kind of disorder. Over the last few decades, this particular feature has been exploited successfully to uncover various exotic phenomena in low-dimensional spin systems [2, 3]. In the Heisenberg antiferromagnetic (HAF) spin-$1/2$ chain where the quantum fluctuations are particularly pronounced, the ground state and low-lying spin excitations are qualitatively reorganized in the presence of disorder [4-10].

Recently, it has been shown that merely 1% of Ni (spin-1) impurity in the quasi-1D antiferromagnet $SrCuO_2$ opens up a sizeable gap ($\approx 8meV$) in the spin excitation spectrum [10]. This gapping is proposed to be a manifestation of the Kondo-singlet state at the impurity site, predicted theoretically for an antiferromagnetically coupled spin-1 impurity in the spin-$1/2$ chain [7].

Interestingly, a spin-$1/2$ impurity shows a more complex renormalization behavior with the impurity spin either decoupled from the chain or over-screened via a two-channel Kondo effect [8, 9]. Here, we experimentally investigate the effect of Co^{2+} impurities with an effective spin-$1/2$ in the prototypical HAF spin-$1/2$ chain compound $SrCuO_2$. We show that the effect of Co^{2+} impurities (spin-$1/2$) is fundamentally different from the previously studied impurities Zn^{2+} (spin-0) and Ni^{2+} (spin-1) [10, 11]. Co-doping enhances the magnetic ordering and gives rise to a rich magnetic behavior which appears to be controlled by the Ising-like anisotropy of the Co^{2+} impurity. Unlike Ni, the spin excitations also remain gapless upon Co-doping.

Neutron scattering experiments were performed at SINQ (Paul Scherrer Institute, Switzerland) on oriented single crystals of $\approx 2g$. Inelastic neutron scattering experiments were performed at $T = 1.5K$ using the thermal triple-axis spectrometer EIGER, while the elastic neutron scattering experiments were carried out on the cold triple-axis spectrometer RITA-II.

Results of INS experiments on 1% Co-doped $SrCuO_2$ are shown in the figure. The vertical dashed lines originating at $Q_L = 1/2$ indicate the des Cloiseaux-Pearson characteristic dispersion of spinon excitations [12], for intrachain coupling, $J = 230meV$ [13]. Interestingly, the scattered intensity shows little variation as a function of the energy transfer, indicating a gapless spectrum down to the instrumental energy resolution of $2meV$. Contrary to this, 1% Ni-doped $SrCuO_2$ was recently reported to exhibit a gapped behaviour below $\approx 8meV$ (see Fig. 1 in ref. [10]).



Intensity color maps of the low energy excitation spectrum for $SrCu_{0.99}Co_{0.01}O_2$. The dashed lines correspond to the lower spinon boundary according to the "des Cloizeaux-Pearson" analytical result [12].

To conclude, we showed that Co-impurity has a rather strong and unexpected effect on the magnetic behavior of weakly coupled antiferromagnetic spin-$1/2$ chains. Dilute doping with Co leads to highly

‡based on a recently accepted paper: Koushik Karmakar, Markos Skoulatos, Giacomo Prando, Bertran Roessli, Uwe Stuhr, Franziska Hammerath, Christian Rüegg, and Surjeet Singh "Effects of quantum spin-1/2 impurities on the magnetic properties of zigzag spin chains", Phys. Rev. Lett. in press

§Physics Department, Technical University Munich and Heinz Maier-Leibnitz Zentrum (MLZ), FRM-II reactor anisotropic magnetization and a significantly enhanced magnetic ordering temperature, contrary to Ni or Zn-doping studied previously. These findings show that the ground state and magnetic excitations of the antiferromagnetic spin-$1/2$ chain depend sensitively on the spin state and symmetry properties of the doped impurity. This work should motivate further theoretical investigations on Ising spin-$1/2$ impurity in the spin-$1/2$ chains.

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Upcoming Events

International Conference on Neutron Scattering 2017, July 9-13, Daejeon, Korea

The ICNS 2017 will be the largest international platform for sharing and exchanging the latest exciting advances in neutron scattering science, which will bring together scientists from a wide range of disciplines including physics, biology, chemistry, materials science, engineering materials, earth science, neutron sources and instrumentations. The ICNS is held every four years cycling through Europe, America and Asia-Oceania regions. Previous ICNS includes ICNS2013 (Edinburgh, UK), ICNS2009 (Knoxville, US), ICNS2005 (Sydney, Australia), ICNS2001 (Munich, Germany), ICNS97 (Toronto, Canada), ICNS94 (Sendai, Japan), ICNS91 (Oxford, UK), ICNS88 (Grenoble, France), ICNS85 (Santa Fe, US), and ICNS82 (Hakone, Japan).

Neutrons in Structural Biology (NISB 2017), 7-9 June, Grenoble, France

Neutrons have become an increasingly powerful and sophisticated tool in structural biology in the recent years. In particular, over the last decade, improvements in sources, instrumentation and sample preparation have revolutionized the scope of neutron scattering studies of biological systems. As in all areas of modern structural biology there is now strong emphasis on interdisciplinarity with neutrons occupying a central role alongside the other major techniques including X-rays, NMR, EM. Over the years the focus of this meeting has shifted away from technical aspects relating directly to the development of neutron techniques towards a more science driven event where neutrons provide crucial information alongside the other techniques available.This 2017 edition will focus on highlighting recent results in fundamental biology, as well as considering the future of the field and the implications for the type of science that can be considered as well as for the instruments required. This meeting typically gathers mixture of researchers some of whom are experienced in the field of neutron scattering with others whose work may benefit from these approaches.

MLZ Conference Neutrons for Health, 27-30 June, Bad Reichenhall, Germany

The conference will cover major topics of neutron scattering and neutron radiation for health ranging from treatment of amyloid diseases, protein folding, details of enzyme behaviour, understanding of cell-membrane interactions, identification of new drug targets, development of advanced drug-delivery systems, antibiotic resistance, treatment of genetic diseases, implants and biocompatible materials, tissue regeneration, cancer diagnosis and therapy, radiopharmaceuticals as well as medical applications and treatments. In addition methodological instrument developments are an important contribution to enhance medical and health research with neutrons.

Neutron Schools

Here we present a list of Neutron School activities for the rest of 2017 that can be considered by students up to the doctoral level as an introduction to Neutron Science.

15th Oxford School on Neutron Scattering, 3 - 15 September 2017, St. Anne's College, University of Oxford, UK

The Oxford School on Neutron Scattering is intended for scientists and engineers who are new to the field of neutron scattering. Lectures and tutorials covering the theory and practice of neutron diffraction and spectroscopy are given by international experts. Students will gain a comprehensive grounding in modern techniques and applications at both continuous and pulsed neutron sources and have the opportunity to hear about the latest research being carried out with the technique.

21st JCNS Laboratory Course - Neutron Scattering 2017, 04 - 15 September 2017 Jülich/Garching - Germany

Each year, the Jülich Centre for Neutron Science at Forschungszentrum Jülich, Germany, in cooperation with RWTH Aachen University (Prof. T. Brückel, Prof. G. Roth, and Dr. R. Zorn) organizes a laboratory course in neutron scattering with experiments at the neutron scattering facilities of the Heinz Maier-Leibnitz Zentrum MLZ.

The course consists of two parts: a series of lectures, combined with the opportunity to take part in neutron scattering experiments. The lectures encompass an introduction to neutron sources, along with scattering theory and instrumentation. Furthermore, selected topics of condensed matter research are be presented.

Lectures are held at Forschungszentrum Jülich and the experiments take place at the neutron facilities of the Heinz Maier-Leibnitz Zentrum in Garching near Munich.

The laboratory course is part of the curriculum at the RWTH Aachen.

The aim of the course to give a realistic insight into the experimental techniques of neutron scattering and their scientific potential.

Forschungszentrum Jülich supports students coming from outside the Aachen area by offering free accommodation and half-board. Travel expenses will also be reimbursed within reasonable limits.

PSI Master School 2017 - Introducing photons, neutrons and muons for materials characterization, 4-15 September 2017, Villigen, Switzerland

The course runs for two weeks in a row in September before the regular semester lectures start. It takes place at the campus of the Paul Scherrer Institute. The first week consists of introductory lectures on the use of photons, neutrons and muons for materials characterization. Active participation of the students in the form of workgroups aimed at learning the basic concepts is also part of the first week program. The second week is focused on hand-on experiments on specific topics. The topical section includes tutorials and one to two experiments designed and performed by the students at one of the large scale facilities of PSI (Swiss Light Source, Swiss Spallation Neutron Source, Swiss Muon Source).

The aim of the course is that the students acquire a basic understanding on the interaction of photons, neutrons and muons with matter and how one can use these as tools to solve specific problems. The students will also acquire hands-on experience by designing and performing an experiment in a large scale facility of PSI (Swiss Light Source, Swiss Spallation Neutron Source, Swiss Muon Source).

Contact with the editorial board

The provisional editorial board welcomes articles and ideas about the contents of the HENA newsletter from fellow scientists in Greece and abroad. For this purpose please contact:

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