

HIGHLIGHTS OF ILL RESEARCH

# NEUTRONS UNRAVELLING THE SECRETS OF THE LAWS OF NATURE

Experiments with neutrons provide routes to testing theories describing the diverse behaviour of matter at the microscopic scale



NEUTRONS  
FOR SCIENCE

# FOREWORD



**T**hat science has to have societal impact is not to be debated. Any worthwhile human endeavour has to aim at improving our conditions of living. However, when it comes to laying out a precise plan on how to reach that goal, then opinions start to diverge. The question of how to choose the subjects to investigate is probably as old as science itself. One may naturally be tempted to ask for the immediate utility of scientific activity. But as the great French mathematician, Henri Poincaré, has explained in his book *Science and method* so well, this would have never led to the rapid technological evolution that we have witnessed over the past two centuries because: "if scientists had worked solely in

view of an immediate application, they would have left nothing behind them, and in face of a new requirement, all would have to be done again." To continue with Poincaré's words "...scientists believe that there is a hierarchy of facts, and (...) they are right for otherwise there would be no science, and science does exist." In this spirit, scientific activity, including that part aiming at immediate practical impact, has to have the ambition to continuously discover new concepts that are capable of describing phenomena in the most general terms.

We have assembled in this brochure examples of research that were recently carried out at the ILL. They cover domains ranging from fundamental physics to solid-state physics and soft-matter science. All these studies have in common that they aim at understanding fundamental relations in Nature, whether it is the intricate quantum mechanical behaviour of the neutron observed in an interferometer (p18), the emerging order of a magnetic spin system (p11) or non-equilibrium effects in polymer mixtures (p26).

I hope that you enjoy reading the articles and that you share my excitement about the continuous discovery of new phenomena emerging from our laws of Nature and their rationalisation in terms of new scientific concepts, from the intricate free fall of a neutron to the complex self-organisation of polymers.

*Helmut Schober*

Helmut Schober  
Associate Director, Head of Science Division



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# ABOUT THE ILL

**THE INSTITUT LAUE-LANGEVIN (ILL) IS AN INTERNATIONAL RESEARCH CENTRE AT THE LEADING EDGE OF NEUTRON SCIENCE AND TECHNOLOGY. IT IS LOCATED IN A SETTING OF OUTSTANDING BEAUTY IN THE COSMOPOLITAN CITY OF GRENOBLE IN SOUTH-EAST FRANCE.**

The Institute operates the most intense neutron source in the world, feeding neutrons to a suite of 40 high-performance instruments that are constantly upgraded.

As a service institute, the ILL makes its facilities and expertise available to visiting scientists. Every year, about 1400 researchers from over 30 countries visit the ILL. More than 800 experiments, which have been selected by a scientific review committee, are carried out annually. Research focuses primarily on fundamental science in a variety of fields; these include condensed-matter physics, chemistry, biology, materials science, engineering, nuclear physics and particle physics.

Neutron-scattering experiments have made significant contributions to our understanding of the structure and behaviour of a wide range of complex structures and systems at the atomic and molecular scale – from biological and soft-condensed matter and new chemicals such as drugs and polymers, to materials used in electronics and structural engineering. Neutron studies also offer unique insights into the nature of complex systems at the most fundamental level.

## NEUTRONS FOR EUROPE

The ILL was founded in 1967 as a bi-national enterprise between France and Germany with the UK joining later in 1973. As well as these three Associate Members, 10 Scientific Members now participate in the ILL: Spain, Switzerland, Austria, Italy, the Czech Republic, and more recently Sweden, Hungary, Belgium, Slovakia, Denmark and Poland.



# INTRODUCTION

THE POWER OF NEUTRONS AND THEIR ROLE IN EXPLORING NEW IDEAS IN FUNDAMENTAL SCIENCE

**N**eutrons are subatomic particles found in the nuclei of atoms. They are electrically neutral but have a magnetic moment, or spin. Scientists are interested in neutrons for many reasons: their structure and behaviour tell us about the fundamental nature of the building blocks of matter and forces in the Universe, and neutrons are emitted during various nuclear reactions – some of which are significant in the nuclear processes governing the evolution of stars and the creation of the elements needed for life. Using neutrons to initiate and probe nuclear processes also provides a means to study the structure of the nucleus and perhaps help identify new sources of safe nuclear energy.

However, there is another extremely important aspect to the use of neutrons in basic research: they provide a unique tool for probing the microscopic structure and behaviour of many kinds of complex matter – from sophisticated inorganic magnetic or electronic materials to large and intricate assemblies of organic molecules such as those found in living organisms.

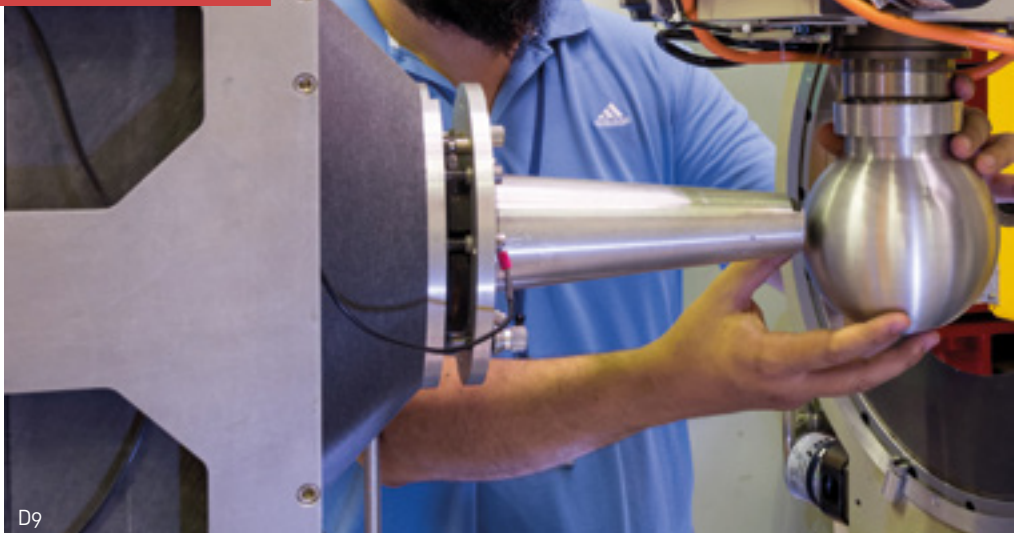
## NEUTRON DIFFRACTION

Like all subatomic particles, neutrons obey the laws of quantum mechanics, which means they behave like waves as well as particles. It so happens that the wavelength of neutrons (tens of nanometres) corresponds to the distances between atoms and molecules in solids and liquids. Consequently, when they interact with matter, for example, a regular array of atoms or molecules in a crystal lattice, the neutron waves are refracted, or scattered – a property known as neutron diffraction. Waves scattered from similarly oriented planes of atoms in the crystal interfere and re-enforce each other periodically to produce a characteristic diffraction pattern (like water waves on a lake that meet after being scattered off two rocks). The pattern can be recorded as a series of peaks of the scattered neutron intensity, which provides information about the positions of the atoms and the distances between them. The

scattering patterns are similar to those provided by X-rays, but the information obtained is slightly different because the neutrons have a mass and are scattered off the atomic nuclei in a material, while X-rays (electromagnetic radiation) are reflected from the outer electrons of atoms. Neutrons have a number of properties that makes them particularly useful as an experimental research tool (see opposite).

Such experiments require a powerful source of neutron radiation. Since neutrons are emitted during the fission of uranium-235, they can be obtained from a nuclear reactor designed especially for research purposes. The Institute Laue-Langevin (ILL) offers such a facility producing intense beams of neutrons, over a wide energy range – from hot (higher-energy or faster), thermal (medium energy), cold (lower energy or slower) to ultra-cold (very slow) neutrons.

During the past 50 years, neutron scattering has grown substantially as an analytical technique, developing into many variations (p9), each designed for investigating particular properties of matter. The ILL provides access not only to the advanced infrastructure and state-of-the-art instruments for neutron-scattering experiments, but also offers the means to study the nucleus and the fundamental behaviour of neutrons themselves (Box 2). Scientists thus come from all over Europe to use neutrons in particular ways in order to further knowledge in their research fields.



D9

S18





## ADVANTAGES OF NEUTRONS

- ▮ Low and medium-energy neutrons penetrate deep into most materials but do not damage their structure. They can be employed to investigate even quite delicate materials, and can follow relevant structural changes in a sample over a given period of time.
- ▮ The main advantage of neutrons is that they are scattered by the central nucleus of an atom, unlike X-rays which interact only with the surrounding atomic electrons. This means that X-rays do not easily detect very lightweight atoms with low numbers of electrons (such as hydrogen). Neutrons, however, are readily scattered by light atoms such as hydrogen or oxygen, the strength of the scattering being dependent only on the nature of the scattering nucleus. Many materials contain light elements whose structural arrangement may be critical to understanding, for example, their magnetic behaviour, so neutrons are particularly useful for these studies.
- ▮ Neutrons can distinguish between different isotopes of an element (which nevertheless have the same chemical and electronic properties). This allows researchers to replace significant atoms in a structure with an isotopic variation so that they can be 'picked out' in an experiment. Hydrogen is often replaced by its heavier isotope, deuterium, which gives a different scattering signal that is easily seen. 'Deuteration' is one of the most powerful techniques in the neutron-scattering toolbox. Selected components of a sample can be deuterated so that they are specifically highlighted.
- ▮ Experimental setups can be arranged so that diffraction is measured over specific ranges of angles of the scattered neutron beam. Measurements made at very small angles provide information about larger structural features in a material.
- ▮ Neutrons have a spin, or magnetic moment, which can interact with the electron spins in magnetic materials. Beams of polarised neutrons (in which all the spins are aligned) offer a unique tool for characterising exotic materials with complex magnetic structures and behaviour – an area of growing technological and theoretical interest.
- ▮ Neutrons can also be reflected off surfaces and interfaces to provide information about thin films and layers.
- ▮ The neutron energies (milli-electronvolts) are of the same magnitude as the motions of atoms and molecules. These include the diffusive motions of atoms and molecules in solids and liquids, the coordinated mechanical or magnetic oscillations in single crystals, or vibrations and rotations in molecules. Even the slow motions within larger molecular assemblies (down to 1 microelectronvolt) can be detected. Very small changes in energy measured at low temperatures may also be used to measure subtle quantum processes in exotic materials.

## FURTHERING OUR BASIC UNDERSTANDING OF NATURE

**Neutron science is playing a growing role in developing new materials and technologies. However, it is also helping to provide a deeper understanding of how Nature works at a fundamental level. This, in turn, opens up new frontiers of knowledge that may have a profound influence on how we live our lives in the future.**

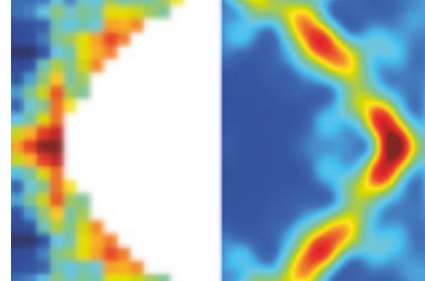
**F**undamental science is not just about elucidating the properties of subatomic particles and the origin and evolution of the Universe, it also encompasses efforts to uncover the organising principles behind the emergent properties associated with the diverse forms of complex matter in our everyday world. A simple example is a crystalline array of atoms, each with a magnetic moment, which couple together to produce bulk magnetism. In fact, neutron experiments have now demonstrated that many materials show much more intricate correlated magnetic behaviour, which is revealing new physical phenomena and principles, and is expanding our understanding of matter at a fundamental level.

Explaining such behaviour at the scale of electrons, atoms and molecules requires first designing a mathematical model that precisely describes the structure and interactions. Often the model is simplified to make the equations easier to solve, or approximation methods may be used in order to characterise systems consisting of many interacting particles. Statistical methods are important in understanding how the bulk properties of a material arise from the dynamic behaviour associated with the constituent particles, and how these properties change with temperature.

Ultimately, many of the phenomena of interest, such as magnetism, are quantum mechanical in nature. The equations of quantum mechanics are used to describe what happens when, for example, a highly correlated system is excited by imparting energy to it (by raising the temperature). The mathematical language developed is sophisticated but aims at descriptions that are as universal as possible, and can be applied to many complex systems. Indeed the descriptions used in one field of study often provide insights into another.

To prove the validity of a model for a given system requires testing its predictions for a real system. Neutron scattering experiments provide a very good platform. The theoretical model may be fed into a computer and the expected scattering patterns simulated so that they can be compared with the experimental results. The validity of, say, competing models can then be compared. If the data are a poor match, then modifications to the model may be required or even new theories developed. In this way, scientific knowledge moves forward.

In this booklet, we give recent examples of fundamental research that is cutting-edge from a theoretical point of view, and to which neutron experiments are contributing significant insights.



### MAGNETISM (P10-16)

In the field of magnetism, studies of mixed metal oxides are revealing remarkable insights into the complex nature of magnetic behaviour in these materials. In the high-temperature superconducting cuprates, neutron experiments show that exotic magnetic interactions clearly play a role in triggering the still mysterious superconducting behaviour.

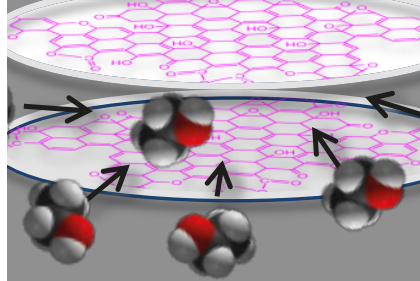
One increasingly important phenomenon ideally investigated with neutrons, which is exciting much interest because of its role in describing some exotic magnetic and electronic behaviour, is that of 'frustration' caused by competing magnetic interactions in a structure. The concept provides a theoretical tool for exploring complex quantum systems (as well as for developing new electronic technologies).

The role of another fundamental phenomenon, that of 'quasiparticles', which are the quantised excitations of highly correlated magnetic or electronic behaviour, can also be explored using neutron scattering.

FIGARO







## NUCLEAR AND PARTICLE PHYSICS (P18-20)

Because neutrons are subatomic particles, and can be manipulated in nuclear and particle physics experiments, they are proving invaluable for testing principles arising from the two fundamental theories of Nature: quantum theory and relativity. The experiments involve extremely accurate measurements carried out in highly controlled conditions, which the ILL can provide.

## MATERIALS (P21-22)

The physical properties of one and two-dimensional materials are of increasing interest both practically and theoretically. The broad applicability of neutron scattering to analyse a wide range of structures composed of layers, films and chains containing light elements is proving invaluable in testing theories of dynamic behaviour in low dimensions.

## SOFT MATTER (P23-27)

Soft matter systems represent some of the most structurally complex materials studied with neutrons. Many of them consist of organic polymers or molecular aggregates that self-assemble into elaborate nano-scale structures when dispersed in a solvent. Theories describing their often complicated interactions at a fundamental level can be tested using especially selected model systems. These, usually multi-component, systems can be selectively probed using neutron methods, which can follow structural and dynamic changes as a function of concentration, temperature or external forces. Again, fundamental theories of this kind of complexity can have applications in other fields.

## NEUTRON TECHNIQUES

Neutron scattering techniques can be divided into two types. **Diffractometry** maps the distances between atoms in a material to reveal its three-dimensional structure at the atomic or molecular level. **Spectrometry** enables the dynamics (both individual and coordinated motions or oscillations) of atoms, molecules and electron spins to be studied by recording the changes in energy in a neutron beam after it has been inelastically scattered by a sample.

### DIFFRACTOMETRY

**SINGLE-CRYSTAL DIFFRACTOMETRY** uses an instrument called a four-circle diffractometer, which allows the sample crystal to be oriented in all directions with respect to the incident beam. The scattered neutrons, which are then detected over a range of angles, give a diffraction pattern. It is a powerful method for investigating structural details in materials at the scale of atoms or molecules.

**SMALL-ANGLE NEUTRON SCATTERING (SANS)** measures diffracted neutrons at very small angles of scattering, and it requires a very long instrument to resolve the small angles. SANS is used to investigate structures with large interatomic distances such as polymers or large molecular assemblies.

**POWDER DIFFRACTOMETRY** records the scattered neutron beam from every angle simultaneously, and is used for powders and solids composed of tiny, randomly oriented crystals. The data are then processed and converted into a one-dimensional diffraction pattern from which the structure can be determined.

**LAUE DIFFRACTOMETRY** uses a multi-wavelength (white) neutron beam to map simultaneously the many diffractions in a crystalline sample with a large, complex molecular structure, such as a protein. The diffraction pattern is recorded using a large-area detector.

**REFLECTOMETRY** measures the variation in intensity of the reflected neutron beams from surfaces and interfaces to characterise the structure of surfaces and thin layers.

### SPECTROMETRY

**TRIPLE-AXIS SPECTROMETRY (TAS)** measures the difference in wavelength, and thus in energy, between the incident and scattered neutrons. An analyser is used to determine the wavelength composition of the diffracted neutron beam.

**TIME-OF-FLIGHT SPECTROMETRY (TOF)** measures the time that neutrons take to travel from the sample to the detector, and thus their velocity (usually kilometres per second) and energy.

**NEUTRON SPIN-ECHO (NSE)** measures the variation of the neutron spin orientation caused by transfers in energy associated with molecular movements over relatively long timescales, such as the slow movement of polymer chains.

**NEUTRON BACKSCATTERING SPECTROMETRY** measures the energies of neutrons that have been scattered nearly backward, and is used to analyse the dynamics of atoms in a range of materials.

### OTHER TECHNIQUES

**POLARISATION ANALYSIS** employs polarised neutrons (p29) to investigate the magnetic properties of materials.

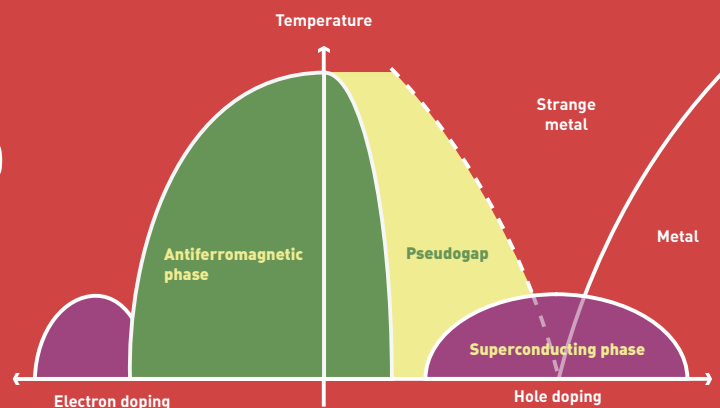
**GAMMA-RAY SPECTROMETRY** measures the energies of gamma-rays emitted in nuclear reactions in which neutrons participate

**INTERFEROMETRY** is a universal technique in physics for measuring minute separations in distance (p18). It is an important tool in some neutron experiments testing the fundamental properties of matter.

# WHAT GOES ON IN THE PSEUDOGAP

CUPRATES SHOW SOME UNUSUAL MAGNETISM ABOVE THEIR SUPERCONDUCTING TEMPERATURES, WHICH MAY BE KEY TO THEIR EXOTIC ELECTRONIC PROPERTIES

Lucile Mangin-Thro



It is 30 years since scientists discovered a family of metal oxides, the cuprates, that can conduct electricity without resistance up to temperatures much higher (138K) than those associated with metallic superconductors (maximum temperature, 30 K). However, even now, how the cuprates do it is still a subject of much debate and extensive research. The mechanism appears to be a good deal more complicated than in conventional superconductors, and is requiring new descriptions that extend the frontiers of fundamental physics.

One of the first high-temperature superconductors discovered was yttrium barium cuprate,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ , in which the oxygen content can be increased fractionally, which corresponds to an introduction of positive charges, or 'holes', that generate the necessary electron mobility. The level of such 'hole-doping' mediates the electronic (and magnetic) properties. To try to pin down what exactly goes on, physicists have mapped these properties over temperature and for different doping levels (top right).

What the phase diagram reveals is that just above the temperature at which cuprates stop becoming superconductors, the material acts like a 'bad metal', behaving neither as a metal nor an insulator. Within this strange region, there is an exotic phase called a pseudogap. This is quite different from low-temperature superconductors, which revert to normal metals above the transition temperature. This pseudogap is turning out to be the Rosetta Stone for discovering the physical principles that underlie the cuprates' complex behaviour, and so it is being extensively studied.

One aspect, becoming clear, is that subtle magnetic interactions, found within the square planar arrangements of copper and oxygen ions ( $\text{CuO}_2$ ) that form layers in the cuprate crystal lattice, are very significant (centre right). Polarised neutron scattering (p29) offers a way of studying these interactions because it can distinguish between normal and magnetic scattering.

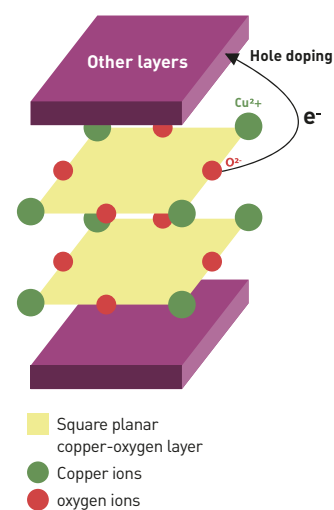
## CIRCULATING LOOP CURRENTS

Such experiments have been used to look at the magnetic behaviour in the pseudogap zone in four cuprate families, including  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . They have uncovered a curious type of antiferromagnetic order (that is, with ordered antiparallel magnetic moments, p28), which operates within each unit cell of the crystal, and whose appearance coincides with the onset of the pseudogap. This magnetic order could be the result of loop currents flowing within the unit cells, generating staggered static orbital magnetic moments (bottom right). The loop currents appear in pairs flowing clockwise and anti-clockwise, and the order is long-ranged at low doping levels but vanishes at high doping levels.

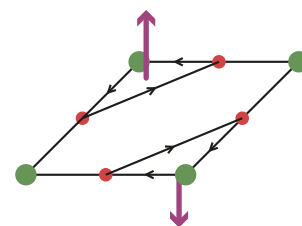
The existence of this intra-unit-cell magnetic order has now been well-documented over a wide hole-doping range. However, what happens to the proposed loop currents in compounds with optimal doping (where the superconducting 'dome' seen in the phase diagram shows its maximum) had not yet been addressed.

Our studies on optimally doped  $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$  showed that the intra-unit-cell magnetic order persists to relatively high temperatures. However, the magnetic intensity is strongly reduced compared to that in lower-doped samples, and the magnetic order is short-ranged. In addition, we confirmed previous reports that the magnetic moment does not just point vertically to the copper-oxygen planes, as originally expected from the loop-current model, but at low temperatures is tilted in an additional in-plane component. This may be due to a quantum superposition (p29) of different loop patterns – which would occur only at low temperatures. Whatever the reason, the discovery of these two sets of behaviours puts stringent constraints on any theoretical description of the pseudogap, and thus high-temperature superconductivity.

A phase diagram showing the electronic behaviour of a cuprate over temperature for different levels of doping



The square-planar structure of a superconducting cuprate



The loop current model: each loop induces an orbital magnetic moment perpendicular to the copper-oxygen planes

**RESEARCH TEAM:** L. Mangin-Thro and A. Wildes (ILL), Y. Sidis and P. Bourges (LLB, CEA Saclay, France)

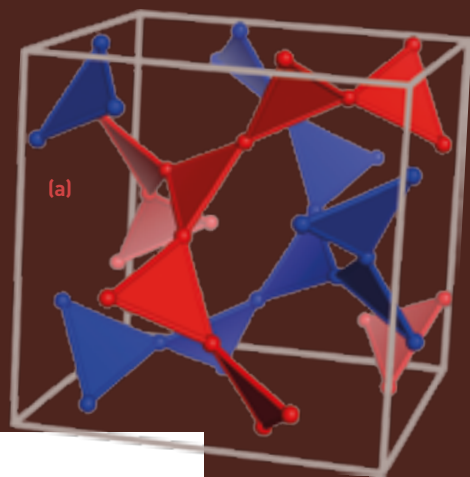
**ILL INSTRUMENT USED:** Diffuse scattering spectrometer D7

**REFERENCES:** C. M. Varma, *Nature*, 2010, **468**, 184; P. Bourges and Y. Sidis, *C. R. Physique*, 2011, **12**, 461; L. Mangin-Thro et al., *Nature Comm.*, 2015, **6**, 7705.

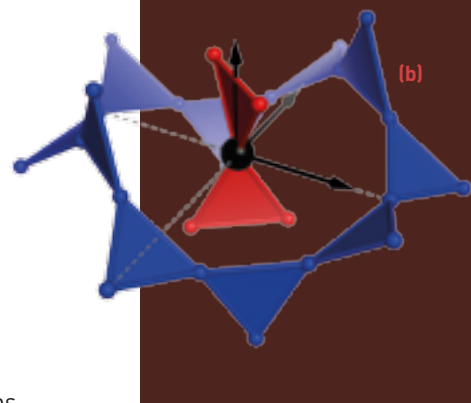
# SEEKING OUT SECRET SPIN ORDER

NEUTRON SCATTERING UNCOVERS THE COMPLEX SPIN STRUCTURE THAT LIES HIDDEN IN A FRUSTRATED MAGNET

Andrew Goodwin and María Teresa Fernández-Díaz



(a) The crystal structure of gadolinium gallium garnet and (b) the local environment of each gadolinium ion



The most familiar kind of magnetic behaviour, ferromagnetism, is the result of the magnetic moments (single electron spins) of neighbouring atoms in a crystalline structure interacting and aligning in a simple way. The ordering happens below a given temperature, and is revealed through measuring changes in thermodynamic properties such as specific heat. However, in some materials, such measurements have hinted at much more complicated magnetic ordering, which is not immediately obvious from their structure and not easily measured.

This kind of 'hidden' order could lurk in a class of systems – currently fascinating physicists – that show so-called frustrated magnetism. In such materials, the geometry of the crystal lattice leads to competing interactions between spins, so they continually change alignment – a magnetic state called a spin liquid. One well-known spin liquid is a synthetic garnet, gadolinium gallium garnet ( $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ ), shortened to GGG.

In GGG, the magnetic gadolinium ( $\text{Gd}^{3+}$ ) ions couple antiferromagnetically (neighbouring spins want to align in opposite directions), and occupy two interpenetrating three-dimensional networks of corner-sharing triangles (figure a). The key topological feature is that each gadolinium ion is surrounded by a loop of 10 gadolinium neighbours (figure b).

Now, thermodynamic measurements have suggested that there could be a long-range pattern of order hidden in the fluctuating spin-liquid state at low temperatures. We decided to look for this hidden order in GGG using neutrons. In the case of GGG, natural gadolinium readily absorbs neutrons, so a high-energy neutron beam is required to diminish the absorption. Fortunately, the four-circle diffractometer D9 is ideally suited because it employs an intense, high-energy neutron beam.

Single-crystal neutron diffraction offers an excellent method for probing magnetic behaviour (p9), and for simple ferromagnetism or antiferromagnetism, clear magnetic

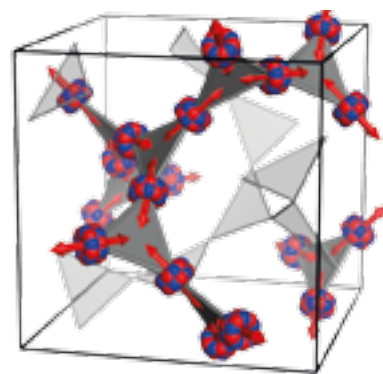
diffraction peaks would be expected. Unfortunately, hidden orders do not produce such peaks; instead, we have to pick through diffuse scattering patterns and compare the data with those predicted by a computational three-dimensional model of spin structures. We also used previously-published powder-diffraction data to refine the model, which had been collected using the D1B diffractometer. Our results turned out to show good agreement between calculation and experiment.

## A COMPLEX CONFIGURATION

Analysis of the spin configurations revealed two important features: first, the spins in each 10-gadolinium ion loop preferentially lie within the plane of the loop, and secondly, the antiferromagnetic alignment of the ions extends right around the loop.

We then calculated the average spin alignment of each loop by adding up the 10 spins in it, taking into account the antiferromagnetic alignment. This showed that the direction of the loop's spin alignment was preferentially vertical to it, leading to an overall order. Because this order is multipolar, neutron scattering is not directly sensitive to it. However, it can directly 'see' both the local antiferromagnetic spin correlations and the planar spin geometry, so we were able to show that it is precisely the combination of these two effects that leads to the hidden-order state.

The observation of hidden order in GGG helps to explain the anomalies seen in thermodynamic measurements. More generally, our results show that the diffuse contribution in the neutron diffraction pattern can indicate how the hidden long-range order of clusters of ions emerges from the complex coupling of the spins of their individual constituents.



Crystal structure showing the unit cell of the magnetic multipole crystal

**RESEARCH TEAM:** J. A. M. Paddison (University of Oxford and ISIS, UK and Georgia Institute of Technology, Atlanta, US), H. Jacobsen and P. P. Deen (Niels Bohr Institute, University of Copenhagen, Denmark and ESS, Lund, Sweden), O. A. Petrenko (University of Warwick, UK), A. L. Goodwin (University of Oxford, UK) and M. T. Fernández-Díaz (ILL).

**ILL INSTRUMENT USED:** Four-circle diffractometer D9

**REFERENCES:** J. A. M. Paddison, *et al.*, *Science*, 2015, **350**, 6257; O. A. Petrenko *et al.*, *Phys. Rev. Lett.*, 1998, **80**, 4570; J. A. M. Paddison and A.L. Goodwin, *Phys. Rev. Lett.*, 2012, **108**, 017204.

# QUANTUM MAGNETS DO THE SQUARE DANCE

**EVEN SUPPOSEDLY SIMPLE SQUARE-LATTICE QUANTUM ANTIFERROMAGNETS REVEAL COMPLEX QUANTUM BEHAVIOUR IN THEIR COLLECTIVE MOTION**

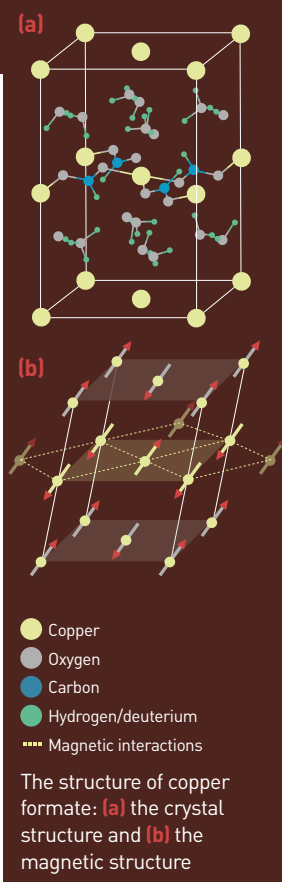
Mechthild Enderle

Exploring magnetic behaviour in materials has become one of the most flourishing areas of physics research. Correlated magnetism arises when the magnetic moments of incompletely filled electron shells belonging to atoms within the crystal lattice of a material interact. They may all align in the same direction (ferromagnetism), in collinear antiparallel pairs (antiferromagnetism), in more complex arrangements, or most intriguingly, in a quantum superposition of states (p29) where the direction of the individual magnetic moment is entirely undefined.

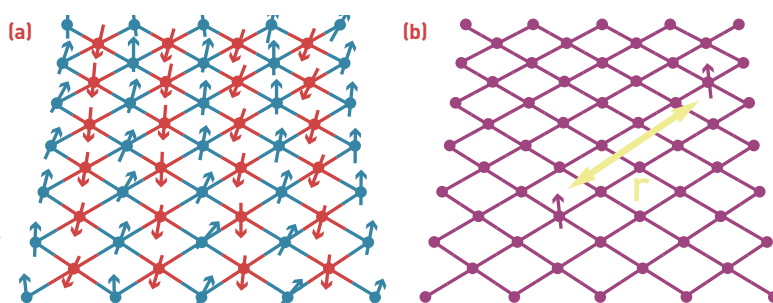
To probe magnetism at the quantum level, physicists start with simple model systems, for example, spins  $1/2$  (p29) arranged in chains or two-dimensional networks. Of the latter, one of the most basic is a square lattice of spins  $1/2$  interacting such that each spin wants to be antiparallel to its neighbour. The candidate material for this model is copper formate tetrahydrate  $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$ , which consists of square arrangements of copper ions carrying a spin  $1/2$  (figure a).

The simplest quantum picture of the antiferromagnetic interactions has described the excited energy states as propagating waves of spins flipping out of their original alignment to form collective 'quasiparticles' (p29) called magnons. The lowest-energy magnon wave moves the moments perpendicular to their preferential direction, but at higher energies, bound two-magnon excitations lead to oscillations of the length of the ordered moment parallel to the ordering direction, and three-magnon excitations are also generated, implicating a motion of the spins perpendicular to their preferential direction. These quasiparticles behave as so-called bosons, that is particles with spin 1 (p28).

The inelastic scattering of polarised neutrons provides a precise experimental method for exposing these excitations and thus testing the



A graphical representation of the two excitation models: (a) a triplet (fermion pair) excitation (b) a spin-wave excitation



theory. We carried out such experiments on single crystals of deuterated copper formate,  $\text{Cu}(\text{DCOO})_2 \cdot 4\text{D}_2\text{O}$ , using the ILL's polarised triple-axis spectrometer IN20. We substituted hydrogen with deuterium because it is a weaker scatterer, so does not mask the delicate detail of the magnetic scattering signal from the copper spins. The experiments are carried out at very low temperatures of about 1.4K.

## A DIFFERENT APPROACH

What the scattering data revealed was a much more complex spectrum of excitations than allowed by the magnon picture. We see a sharp peak at low energies, which is associated with magnons, but then at higher energies, the excitation spectrum broadens. Neither the pattern of the broadening nor the polarisation of the spectrum is matched in a magnon picture including up to three-magnon excitations.

There is, however, another approach, which was used to analyse the results, and which could be more fruitful in providing deeper theoretical insights. This approximation treats the lowest energy state (ground state) as if it were more like a single macroscopic quantum state composed of all the spins, in which the (quantum) entanglement of a spin with its neighbour continually resonates between different neighbours (forming a so-called singlet state, p29). This so-called resonating valence-bond model would account for the broadening of the spectrum, as well as the magnon peaks. The excitations are this time understood as quantum transitions, from the singlet to a so-called triplet state (p29), which dissociate (fractionalise) into individual quasiparticles with spin  $1/2$  (fermions), or form bound states resembling a magnon – similar to the bound electron pairs, bosons, associated with superconductivity.

Including higher and higher-order magnon or triplet states, and interactions between them, the magnon and resonating valence-bond pictures will eventually become equivalent, but the latter already captures the characteristic features of the excitation spectra at low order. Our results show that even apparently simple networks of spins  $1/2$  reveal a collective quantum behaviour that requires the introduction of new theoretical concepts.

**RESEARCH TEAM:** B. Dalla Piazza (EPFL, Switzerland), M. Mourigal (ILL and EPFL, Switzerland, now Georgia Institute of Technology, US), N. B. Christensen (DTU Denmark and PSI Switzerland), G. J. Nilsen (EPFL, Switzerland and ILL), P. Tregenna-Piggott (PSI Switzerland), T. G. Perring (ISIS, UK), M. Enderle (ILL), D. F. McMorrow (UCL, UK), D. A. Ivanov (ETH and University of Zurich, Switzerland and H. M. Morrow (EPFL, Switzerland).

**ILL INSTRUMENT USED:** Three-axis spectrometer IN20 with polarisation analysis

**REFERENCES:** B. Dalla Piazza *et al.*, *Nature Physics*, 2015, **11**, 62; M. Powalski, G. S. Uhrig and K. P. Schmitt, *Phys. Rev. Lett.*, 2015, **115**, 207202, M. Enderle and M. Mourigal, *ILL Highlight*, 2015.

# HOURGLASSES, CHECKERBOARDS AND NANO-ISLANDS

WITH SIMILAR STRUCTURES TO THE SUPERCONDUCTING CUPRATES, THE COBALTATES SHOW THE SAME HOURGLASS-SHAPED MAGNETIC SPECTRA, BUT THEY SEEM TO BE ASSOCIATED WITH DIFFERENT, RATHER COMPLEX STRUCTURAL CHANGES AT THE NANO-LEVEL

Andrea Piovano

The high-temperature superconducting cuprates (p10) have fascinated scientists for several decades now. The superconducting mechanism is still not well-understood, and physicists are trying to gain insights, for example, by comparing the behaviour of compounds with similar structures but in which the copper is substituted with a different metal.

A key issue is the magnetism. The prototypical cuprates are based on the parent compound lanthanum cuprate ( $\text{La}_2\text{CuO}_4$ ), which consists of planes of copper and oxygen ions with lanthanum ions sitting between the layers. The spins of the copper ions ( $\text{Cu}^{2+}$ ) are strongly antiferromagnetically coupled, rendering the parent compound insulating; however substituting a fraction of the lanthanum ions with a differently charged metal ion such as strontium (Sr) effectively removes electrons from the copper–oxygen layers, leaving positive charges (holes) behind.

Along with this ‘hole-doping’, the antiferromagnetic order vanishes and superconductivity appears. However, magnetic fluctuations can be still found in the hole-doped regime. Neutron inelastic scattering (p10) has been used to study these magnetic fluctuations, and they have revealed an intriguing hour-glass-shaped spectrum of magnetic excitations which have turned out to be a unifying property of the cuprates in general. It is widely believed that this phenomenon is related to another specific feature found in these cuprates – a pattern of spin and charge stripes.

We have studied a family of lanthanum compounds with a similar structure, in which the copper ions have been replaced by cobalt. In the cobaltates, there is also antiferromagnetic order similar to that in  $\text{La}_2\text{CuO}_4$ . However, these materials are strong insulators. This allowed us to study the equivalent magnetic excitation spectrum without the presence of effects associated with conductivity. The neutron measurements were carried out on a lanthanum cobaltate with one-third strontium doping –

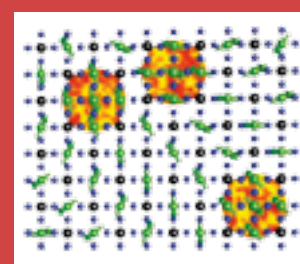
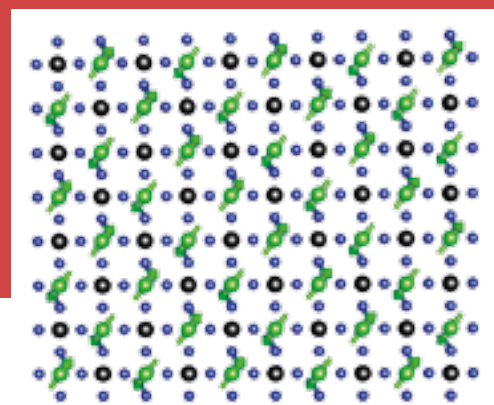
$\text{La}_{1.66}\text{Sr}_{0.33}\text{CoO}_4$  – with an hour-glass magnetic spectrum similar to that of the cuprates. However to our surprise, we did not detect the expected charge stripes.

## FROM STRIPES TO CHECKS

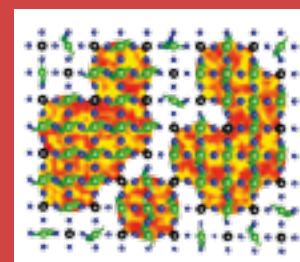
Instead, neutron scattering revealed magnetic peaks that indicated an electronic ordering in the cobalt–oxygen layers similar to that in half-doped cobaltates ( $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ ). These are known to have a robust checkerboard pattern of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions. Only the former are antiferromagnetically coupled. This arrangement seems to persist down to fairly low hole-doping levels. However, fewer holes imply that there are more electrons left in the cobalt–oxygen layers. In order to accommodate these additional electrons, we suggested that the structure consists of half-doped checkerboard-like regions, interspersed with nanometre-sized islands of the undoped parent material hosting the additional electrons.

Complementary X-ray measurements confirmed this scenario. Furthermore, using polarised neutrons (p29), we also observed an additional high-energy magnetic feature in the spectrum above the hour-glass shape, which resembles the magnetic excitation spectrum of undoped  $\text{La}_2\text{CoO}_4$ . Our nano-phase-separation scenario was supported by the fact that this extra magnetic excitation mode becomes weaker when the strontium doping is increased (to  $\text{La}_{1.6}\text{Sr}_{0.4}\text{CoO}_4$ ), thus reducing the fraction of the undoped  $\text{La}_2\text{CoO}_4$  islands. Further measurements of the temperature dependence of the magnetic excitations plus theoretical calculations also supported this novel nano-phase separation model.

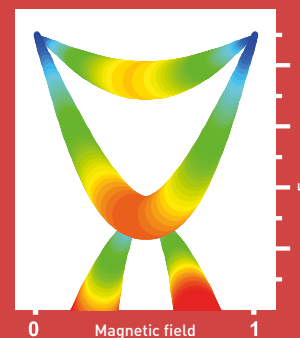
The hour-glass magnetic excitation phenomenon is thus yet another sign of just how complex the behaviour of cuprates and analogous materials like the cobaltates appears to be.



● nonmagnetic  $\text{Co}^{2+}$  ions  
● magnetic  $\text{Co}^{3+}$  ions



The checkerboard arrangement in a cobaltate at different doping levels showing the development of half-doped and undoped regions, which lead to the hourglass magnetic spectrum (below)



**RESEARCH TEAM:** A. C. Komarek, Y. Drees, Z. W. Li, H. Guo and L. H. Tjeng (Max-Planck-Institute for Chemical Physics of Solids, Germany), and A. Piovano and W. Schmidt (ILL)

**ILL INSTRUMENT USED:** Three-axis spectrometers IN8, IN12 and IN22

**REFERENCES:** A. T. Boothroyd *et al.*, *Nature*, 2011, **471**, 341; Y. Drees *et al.*, *Nature Commun.*, 2013, **4**, 2449; Y. Drees *et al.*, *Nature Commun.*, 2014, **5**, 5731; H. Guo *et al.*, *Phys. Status Solidi RRL*, 2015, **9**, 580.

# SPIN ICES, MAGNETIC MONOPOLES AND COULOMB GASES

**MATERIALS CALLED SPIN ICES REVEAL PHENOMENA ANALOGOUS TO FUNDAMENTAL ENTITIES LONG-DISCUSSSED BY THEORISTS – MAGNETIC MONOPOLES**

Tom Fennell and Steve Bramwell

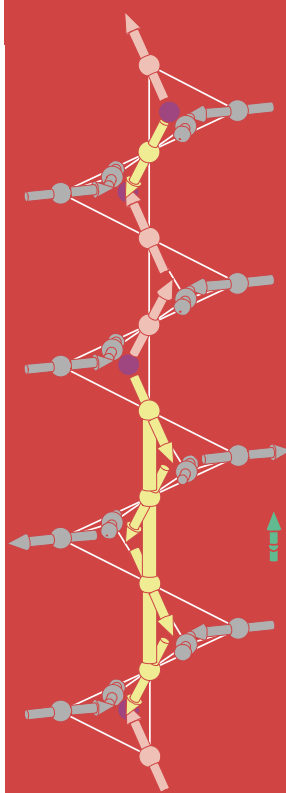
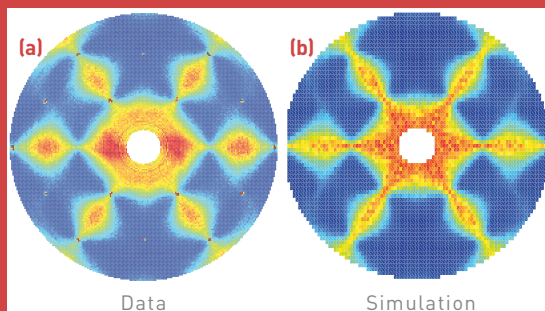
Everyone knows that bar magnets always have north and south poles, which are connected by lines of magnetic flux – a magnetic field. Nevertheless, theorists have speculated that a single magnetic pole – a free source, or sink, of magnetic field lines – could exist on its own. This magnetic monopole would be a microscopic particle, responding to magnetic fields or other monopoles, in the same way as electrons or protons (which are electrically charged) respond to an electric field or other electric charges. Particle physicists have searched for this hypothetical, rare and massive particle but have never detected it for certain.

Recently however, theorists working in condensed-matter research have suggested that materials called ‘spin ices’ should contain microscopic excitations analogous to magnetic monopoles. In a spin ice, such as the rare-earth oxide, holmium titanate ( $\text{Ho}_2\text{Ti}_2\text{O}_7$ ), the magnetic ions sit at the shared corners of connected tetrahedra – and on each tetrahedron, two moments (spins) point ‘in’, towards the centre of the tetrahedron, and two point ‘out’. In this arrangement, the spins are said to follow the ‘ice rule’ because this configuration is analogous to that of hydrogen bonds in an ice crystal.

Despite the apparent simplicity of the ice rule, it produces complex correlations amongst the spins. When the ice rule is satisfied everywhere, there is as much magnetic flux entering every tetrahedron as leaving it, so there are no magnetic poles of the sort that appear on the ends of bar magnets. Because of this, the low-temperature state of a spin ice can be thought of as a perfect ‘vacuum’ for magnetic poles. This means that the basic excitation of the system – a single spin flip – produces a north–south pair of magnetic pole ‘defects’ on adjoining tetrahedra (right). Subsequent spin flips on adjoining tetrahedra allow this dipole to ‘fractionalise’ into two monopoles, as the defects diffuse through the spin-ice state, and the ice rule is restored on tetrahedra in their wake.

The effective monopoles thus produced are microscopic and long-lived, with a magnetic charge that interacts according to the same inverse-square law as for electric charges,

Experimental data (a) and simulation (b) of spin-flip scattering in holmium titanate ( $\text{Ho}_2\text{Ti}_2\text{O}_7$ ). Clear pinch points indicate the existence of a Coulomb phase



The magnetic ions in holmium titanate are arranged in tetrahedra with two spins in and two out. Spin flips lead to ‘one in and three out’ (or vice versa), generating a pair of monopoles (top two tetrahedra). Subsequent spin flips separate the monopoles, leaving a ferromagnetic string (shown in yellow in the lower tetrahedra)

Coulomb’s law. A spin ice can therefore be thought of as a magnetic ‘Coulomb gas’ – a system whose dynamics are described by a gas of such charges diffusing and interacting, somewhat analogous to a dilute electrolyte.

## SEARCHING FOR SIGNATURES

The idea of a low-temperature state with a pole-free field, can be identified in various condensed-matter systems, which may collectively be described as ‘Coulomb phases’. However, in the case of a spin ice, the description gains particular power because the ‘monopoles’ issue a real magnetic field.

Using polarised neutron diffraction (p29), we searched for signatures of this Coulomb phase and the monopole excitations in the magnetic scattering patterns of a crystal of holmium titanate. An essential property is the presence of sharp ‘pinch points’ within the otherwise diffuse scattering pattern. However, they had never been clearly observed in previous experiments. Using polarisation analysis, we could distinguish between contributions to the spin correlations due to the ice rules and other contributions, and clearly see the sharp pinch points – in close agreement with computer simulations.

We could identify other signatures of the magnetic Coulomb gas. A very diffuse component, such as would be expected from the point-like magnetic defects in the ice-rule network, follows the expected temperature dependence for the thermal excitation of monopoles. The width of the pinch point, which characterises the length-scale of the ice-rule network diverges exponentially as the temperature decreases, as we expected for the string-like paths trailed by the diffusing monopoles.

**RESEARCH TEAM:** T. Fennell (PSI, Switzerland), P. P. Deen (Niels Bohr Institute, University of Copenhagen, Denmark, and ESS, Lund, Sweden), A. R. Wildes (ILL), K. Schmalz (Forschungszentrum Jülich, Germany); D. Prabhakaran, A. T. Boothroyd (University of Oxford, UK), and R. J. Aldus, D. F. McMorrow and S. T. Bramwell (UCL, UK)

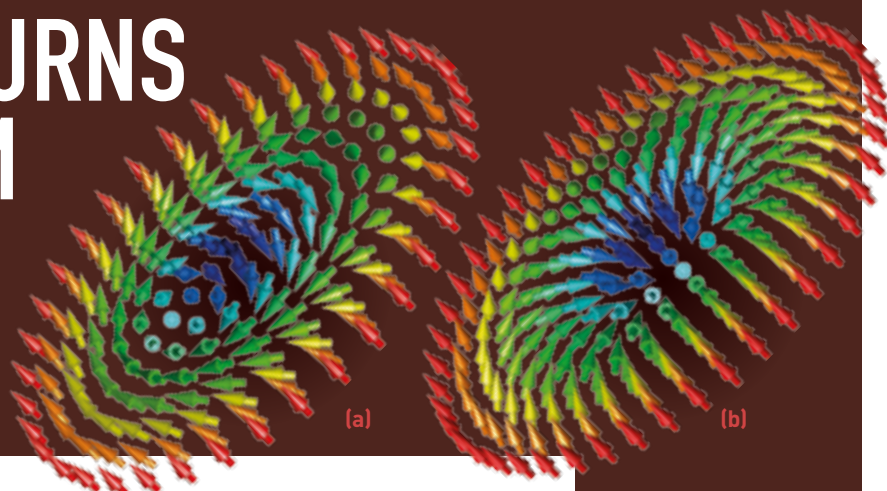
**ILL INSTRUMENT USED:** D7 polarised spectrometer and IN12 three-axis spectrometer

**REFERENCES:** A Rajantie, *Contemp. Phys.*, 2012, **53**, 195; C. Castelnovo *et al.*, *Nature*, 2008, **451**, 42; I. A. Ryzhkin, *J. Exp.Theo. Phys.*, 2005, **101**, 481; T. Fennell *et al.*, *Science*, 2009, **326**, 415.

# TWISTS AND TURNS IN MAGNETISM

STABLE ARRAYS OF TINY MAGNETIC TORNADOS CALLED SKYRMIONS, RECENTLY FOUND IN CERTAIN MATERIALS, ARE OPENING UP AN EXCITING NEW AREA IN THE STUDY OF COMPLEX QUANTUM INTERACTIONS

Jonathan White and Charles Dewhurst



**M**agnetism – the quantum phenomenon whereby the spins of single electrons on atoms in crystalline materials couple together in ordered arrays – is one of the most fertile areas of physics research. One reason is that in some types of minerals and alloys, the spins do not just form simple collinear patterns, as seen in ferromagnetism (spins parallel) and antiferromagnetism (spins antiparallel), but can also settle into more exotic types of ordering at low temperatures, especially if there are competing magnetic interactions that favour different ordering patterns.

This type of behaviour can lead to unusual emergent phenomena that provide intriguing examples of quantum behaviour, and so extend our understanding of the fundamental properties of matter.

Nowhere is this more apparent than with the recently discovered magnetic ‘skyrmions’ (named after the UK theoretician Tony Skyrme who formulated the basic idea). These are nanometre-sized swirls of spins, in which the spins at the edges and those in the centre are antiparallel (figures a and b). Perhaps unsurprisingly, they are found in real materials only under rather special conditions. A key ingredient is that the repeating units in the host material’s crystal structure must lack a centre of symmetry. This property promotes pivotal interactions that favour an ordering pattern of perpendicular spins. The competition between these interactions and other, generally stronger couplings favouring a parallel spin alignment, results in the rotating vortex spin-patterns of skyrmions.

A particularly fascinating and important aspect of skyrmions is that this kind of ‘wound-up’ spin configuration is difficult to ‘undo’, which means that they are very stable and resistant to external disturbance. Furthermore, despite being isolated magnetic objects, in solids they can also organise into a periodic lattice structure. Excitingly, skyrmions can then be controlled by applying tiny electric currents. All these properties mean they

could be ideal as data bits in very high-density magnetic storage applications.

## A NEW CONFIGURATION

At present, the hunt is on to expand the range of materials within which skyrmions can be stabilised. Until recently, they had been seen only in materials with the ‘whirlpool’ spin configuration which can spin left or right, as shown in figure (a) – a so-called Bloch-type skyrmion. However, another configuration is possible, where all the spins symmetrically lean towards the centre, as in figure (b) – a Néel-type skyrmion.

This latter configuration was recently uncovered for the first time in a series of studies using neutrons. Because skyrmions form lattice arrays, SANS (p9) can pick out the resulting magnetic scattering peaks. The material was a spinel, gallium vanadium sulphide ( $\text{GaV}_4\text{S}_8$ ), whose crystal structure consists of clusters of four vanadium atoms with a total single spin, arranged in a cubic lattice. On cooling below 44K, this distorts into a less symmetrical structure, which according to theory is just that required for skyrmion formation. This means that when the magnetic order finally sets in below 13K, the skyrmions form – and, moreover, they can survive over an unusually broad temperature range down close to absolute zero. We carried out SANS experiments under a range of magnetic fields and at different temperatures, and were also able to map out the magnetic phase diagram of the compound, showing that it could form several magnetic configurations dependent on the conditions.

This discovery is exciting because the spin ordering pattern of the Néel-type skyrmion can support alternative electrical properties compared with the Bloch-type skyrmion. These results demonstrate how neutron studies will continue to be crucial to the study of skyrmions, which display an increasingly diverse array of fundamental and functional properties.

The arrangement of spins in (a) a Bloch-type skyrmion, and (b) a Néel-type skyrmion



D33

**RESEARCH TEAM:** S. Bordács and I. Kézsmárki (BUTE, Hungary), H. M. Rønnow (EPFL, Switzerland), Jonathan White (PSI, Switzerland) and Charles Dewhurst (ILL)

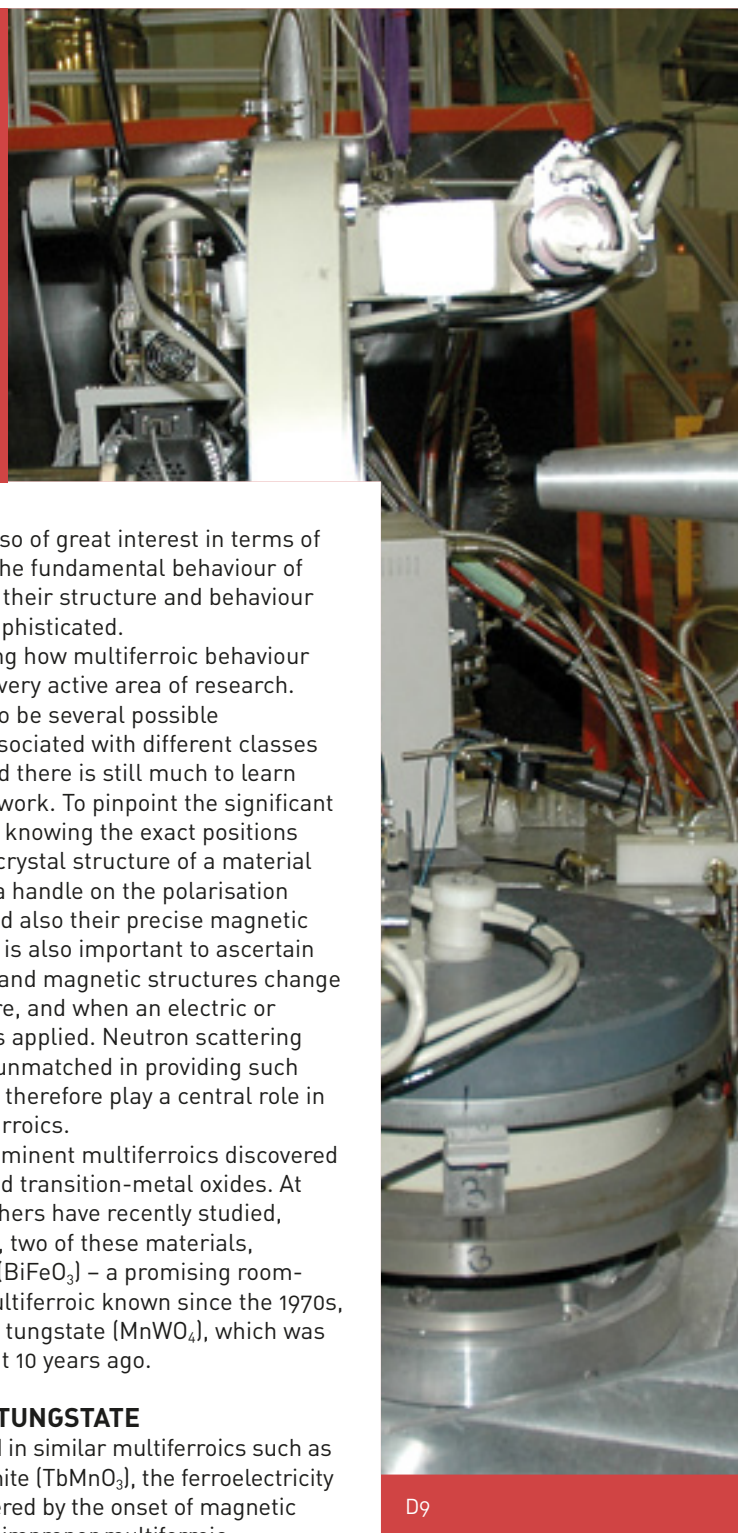
**ILL INSTRUMENT USED:** Small-angle diffractometer D33

**REFERENCES:** I. Kézsmárki *et al.*, *Nature Materials*, 2015, **14**, 1116; DOI: 10.1038/nmat4402ptions.

# INSIDE MULTIFERROICS

NEUTRON SCATTERING OFFERS ESSENTIAL INSIGHTS INTO MULTIFERROIC COMPOUNDS – MATERIALS IN WHICH MAGNETISM AND FERROELECTRICITY ARE COUPLED

Maria-Teresa Fernandez-Diaz and Laurent C. Chapon



**A**lthough it has been well-established since the seminal work of the British physicist James Clerk Maxwell that electricity and magnetism are expressions of the same fundamental force, it has been notoriously difficult to find materials that display, at the same time, electrical order (known as ferroelectrics) and magnetic order (ferromagnetic or antiferromagnetic substances) – the so-called magnetoelectric multiferroics.

Ferroelectricity appears in insulators if there is a spatial imbalance of electric charge (an electric dipole) arising when the electron clouds of the constituent atoms are distorted or when ions (which are charged) are slightly displaced from their regular positions in a crystal. The ordered alignment of these electric dipoles means that the material becomes electrically ‘polarised’ in a particular direction. Magnetically ordered systems, on the other hand, have a periodic arrangement of magnetic moments such that they are aligned in a particular direction over mesoscale-sized ‘domains’.

Multiferroics are very rare because ferroelectricity emerges typically in materials that contain ions with closed outer electronic shells (examples are the metals, bismuth and lead), whilst magnetism requires atoms or ions to have unpaired electrons in their outer shells. However, in the past decade, major advances in materials research has shown that it is, indeed, possible to combine such effects in a single compound. (Most multiferroics are, in fact, antiferromagnetic.)

## USEFUL APPLICATIONS

In ferroelectrics, the direction of polarisation can be altered by applying an external electric field. In ferromagnets, an external magnetic field can be used to alter the direction of magnetisation – a property used in electronic data-storage. The practical interest in multiferroic systems lies in the cross-control of magnetic and electric properties (an electric field can be used to change the magnetic alignment, and a magnetic field can be used to change the direction of polarisation). These possibilities offer the promise of novel electronic devices with lower energy consumption, and the prospect of encoding bits of information in both electrical and magnetic channels. Multiferroic

materials are also of great interest in terms of understanding the fundamental behaviour of matter because their structure and behaviour are inevitably sophisticated.

Understanding how multiferroic behaviour arises is thus a very active area of research. There appears to be several possible mechanisms associated with different classes of materials, and there is still much to learn about how they work. To pinpoint the significant factors requires knowing the exact positions of atoms in the crystal structure of a material (in order to get a handle on the polarisation mechanism), and also their precise magnetic configuration. It is also important to ascertain how the spatial and magnetic structures change with temperature, and when an electric or magnetic field is applied. Neutron scattering techniques are unmatched in providing such information and therefore play a central role in studying multiferroics.

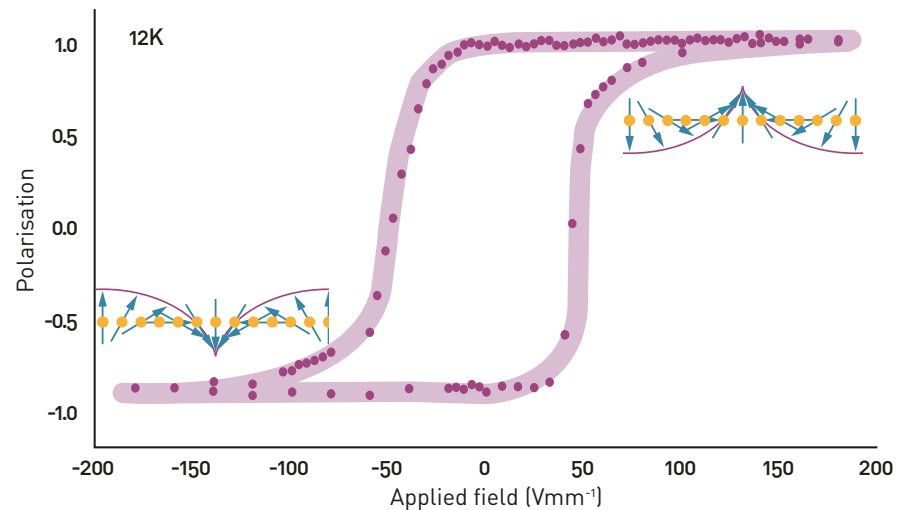
The most prominent multiferroics discovered to date are mixed transition-metal oxides. At the ILL, researchers have recently studied, amongst others, two of these materials, bismuth ferrite ( $\text{BiFeO}_3$ ) – a promising room-temperature multiferroic known since the 1970s, and manganese tungstate ( $\text{MnWO}_4$ ), which was discovered about 10 years ago.

## MANGANESE TUNGSTATE

In the latter, and in similar multiferroics such as terbium manganite ( $\text{TbMnO}_3$ ), the ferroelectricity is actually triggered by the onset of magnetic order (so-called improper multiferroic behaviour). Below about 12K, the arrangement of spins in manganese tungstate is cycloidal, but the periodicity of turns does not coincide with that of the crystal lattice (incommensurate modulation). The system gains energy due to magnetic interactions in this non-collinear state by displacing some ions. Since the cost in energy needed to bring about this physical deformation is smaller than the magnetic energy gain, such a distorted state is favoured at low temperatures. The ionic displacements lead to the charge imbalance necessary for the development of electrical order. The figure opposite illustrates the typical, long-period magnetic modulations found in this class of multiferroics.

D9





Neutron diffraction was used to confirm the exact spatial arrangement of the spins and the magnitude of the magnetic moments. ILL researchers also used polarised neutron scattering [p29] to determine the absolute direction of rotation of the spins (left or right with respect to the modulation direction). The high penetration of the neutron beam enabled the bulk magnetic response to be probed, while retaining atomic-scale information about the magnetic arrangement in each domain. Furthermore, the use of stroboscopic techniques (measurements over time) allowed them to follow the reversal of polarisation across domains driven by the application of an external electric field.

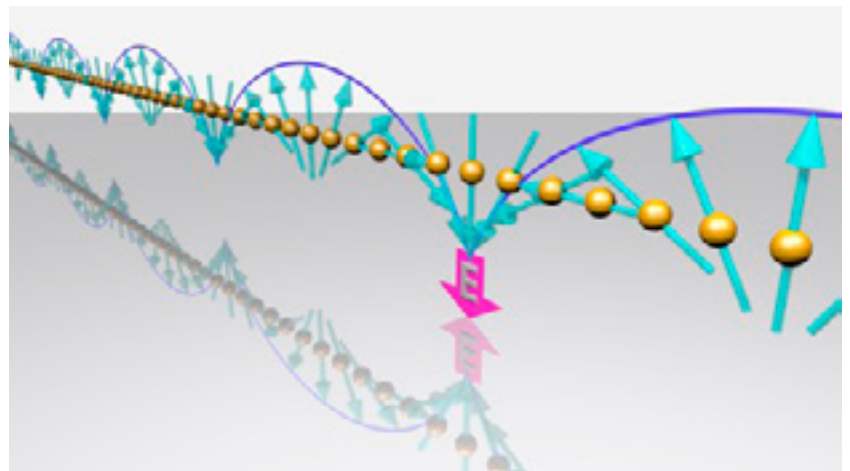
### BISMUTH FERRITE

Bismuth ferrite is typical of another class of system, in which ferroelectricity and magnetic ordering are driven by separate mechanisms and occur at different temperatures – 1100K and 640K respectively in this case.

Considered for a long time as entirely decoupled, it is now clear that these effects are, in fact, linked, and that the magnetic domains can be controlled by an electric field. Bismuth ferrite is particularly interesting because the switching has been demonstrated at room temperature. However, an unresolved question has been to understand how the magnetic ordering affects the ionic displacements already present in the ferroelectric phase.

The high sensitivity of neutrons to small atomic displacements, in particular for light elements like oxygen, is key to probing the interplay between these magnetic and electric responses. A detailed neutron diffraction

study recently shed light on this question by enabling the resolution of extremely small ionic displacements induced by the onset of magnetic order. Specifically, the researchers found that the iron ions undergo displacements that oppose the pre-existing electric polarisation. These small changes appear to arise from classical magnetostrictive effects (deformation of the crystal lattice due to the magnetisation of domains), rather than the intrinsic spiral magnetic structure as in manganese tungstate.



Understanding how the different contributions affect the overall ferroelectric response and the switching mechanisms is at the heart of materials discovery and design. Theoretical modelling of the magnetoelectric coupling, based on the magneto-structural results obtained with neutron scattering, will pave the way for future materials research in this field.

The cycloidal magnetic structure that gives rise to ferroelectricity (E) in the direction of the cycloid apex

**RESEARCH TEAM:** M. T. Fernandez-Diaz, A. Heiss (ESS, Lund, Sweden), Sanghyun Lee and Je-Geun Park (Seoul National University and SungKyunKwan University, South Korea), H. Kimura and Y. Noda (Tohoku University, Japan), D. T. Adroja (ISIS, UK), Seongsu Lee (Korea Atomic Energy Research Institute, Korea) V. Kiryukhin and S.-W. Cheong (Rutgers University, US), M. Mostovoy (University of Groningen, The Netherlands), T. Finger, M. Baum, P. Becker, L. Bohaty and M. Braden (University of Cologne, Germany), J. Leist and G. Eckold (Georg-August University at Göttingen, Germany), K. Schmalz (JCNS, Germany) and L. P. Regnault (CEA-Grenoble, France)

**ILL INSTRUMENT USED:** D9 diffractometer

**REFERENCES:** A. Poole *et al.*, *J. Phys.: Conf. Ser.*, 2009, **145**, 012074; S. Lee *et al.*, *Phys. Rev. B*, 2013, **88**, 060103; M. Baum *et al.*, *Phys. Rev. B*, 2014, **89**, 144406.

# QUANTUM CHESHIRE CAT CAPTURED

“WELL! I’VE OFTEN SEEN A CAT WITHOUT A GRIN”, THOUGHT ALICE, “BUT A GRIN WITHOUT A CAT! IT’S THE MOST CURIOUS THING I EVER SAW IN MY LIFE!”

Hartmut Lemmel and Tobias Jenke

Lewis Carroll’s character, Alice, in *Alice’s Adventures in Wonderland* was astonished by the Cheshire Cat who disappears in front of her, leaving behind only its smile. Our everyday experience tells us that the attributes of any object must always remain part of it. However, things are different in the microscopic world governed by the laws of quantum mechanics. In 2013, theorists proposed that the properties of a quantum particle could be measured independently from its physical location. Now, an experiment at the ILL has indeed revealed for the first time the existence of this quantum equivalent of the Cheshire cat and its grin.

The experiment exploited fundamental quantum properties: that particles can exist simultaneously in two different physical states – a so-called superposition; and that the quantum state or property observed is intrinsically linked to the mode of measurement or detection. Because quantum mechanics is based on probability, and the effects seen may be small, the experiment depends on large numbers of measurements, in this case, requiring the kind of neutron intensities available at the ILL.

We used a specialised device called a neutron interferometer to show that a neutron (the cat) could be spatially separated from its magnetic moment, or spin (the grin). The interferometer splits a beam of neutrons into two beams following different paths. The individual neutrons do not have to decide which of the two paths to take. Instead, they can travel along both paths at the same time in a quantum superposition. Because neutrons also have wave-like properties, differences between the neutron beams can be measured via interference fringes created when the beams are recombined at a detector.

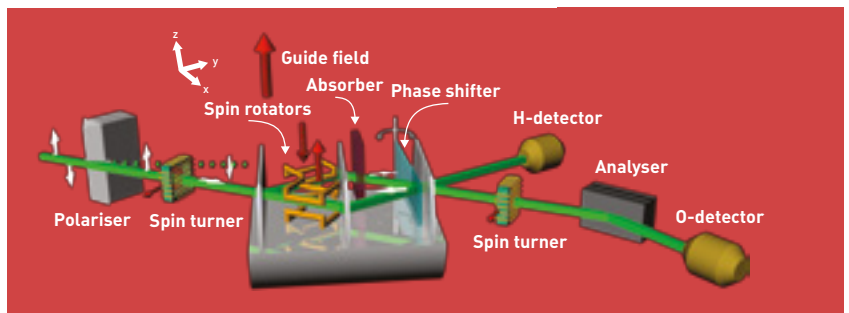
## SEPARATING THE CAT FROM ITS GRIN

Since our aim was to get the neutrons to travel along a different path from their magnetic moments, the neutron beam was split such that the two paths had different spin directions.

An upper beam path had spins parallel to the neutrons’ direction of flight, whilst the spins in the lower path pointed in the opposite direction.

After the beams were recombined, the detector was set up so that only neutrons with spins parallel to the direction of motion – that is those travelling along the upper path – were detected. We then introduced into the lower beam path a filter that absorbs some of the neutrons. This did not change the number of

The quantum Cheshire Cat: inside the interferometer, the cat takes the upper beam path, while its grin travels along the lower beam path

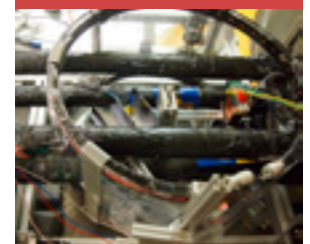


detected neutrons. However, when the same filter was introduced into the upper beam path, the number of detected neutrons was reduced. This indicated that the neutrons were travelling in the upper beam path.

To test the location of the neutrons’ spin component (the grin), we applied small magnetic fields to the paths of the interferometer to alter the spin direction, which would be detected in the interference fringes. When the field was applied to the lower beam path, the fringes changed. In contrast, there was no change when the field was applied to the upper beam path. Obviously, the neutrons’ spin component had taken the lower beam path.

The Cheshire Cat effect can be applied to any quantum system. Not only does it test the fundamental laws of quantum mechanics, it could be used to make high-precision measurements of quantum properties pertinent to sensitive systems such as those used in metrology – and increasingly in quantum information technology.

A schematic view of the experimental set-up for the observation of the quantum Cheshire Cat using single neutron interferometry



The experimental set-up at S18, with the neutron interferometer at the centre

**RESEARCH TEAM:** T. Denkmayr, S. Sponar, H. Geppert, and Y. Hasegawa (Atominstiut, Vienna University of Technology, Austria), and H. Lemmel (ILL and Vienna University of Technology, Austria)

**ILL INSTRUMENT USED:** Interferometer S18

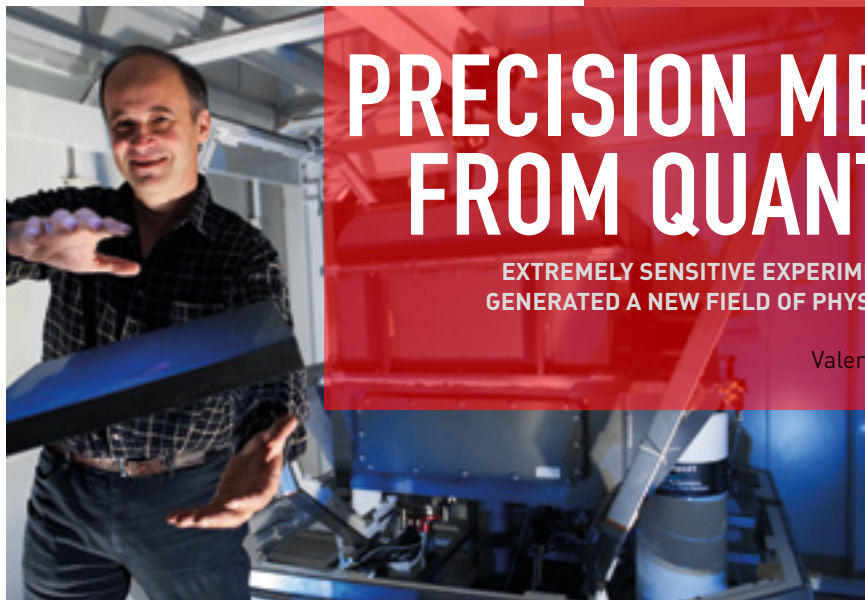
**NEUTRON ENERGIES:** Thermal neutrons

**REFERENCES:** Y. Aharonov, S. Popescu, D. Rohrlich and P. Skrzypczyk, *New J. Phys.*, 2013, 15, 113018. T. Denkmayr *et al.*, *Nature Communications*, 2014, 5, 4492. Y. Aharonov, D.Z. Albert and L. Vaidman, *Phys. Rev. Lett.*, 1988, 60, 1351.

# PRECISION MEASUREMENTS FROM QUANTUM BOUNCES

EXTREMELY SENSITIVE EXPERIMENTS EXPLOITING ULTRA-COLD NEUTRONS HAVE GENERATED A NEW FIELD OF PHYSICS – QUANTUM GRAVITATIONAL SPECTROSCOPY

Valery Nesvizhevsky, Peter Geltenbort and Tobias Jenke



Valery Nesvizhevsky with the equipment to measure quantum bounces

If we let a ping-pong ball drop gently onto a table, it accelerates under the Earth's gravity and is then reflected from the table surface. If the reflection were perfectly elastic and happened in a vacuum, the ball would then return to the surface due to gravity, and continue bouncing with a constant frequency independent of the ball mass. The smaller the initial drop-height is, the larger the frequency. Would this frequency approach infinity at very small heights? No, it would increase only up a certain limit when the height is so tiny that the laws of quantum mechanics take over.

For the ball in the Earth's field, the height at which this happens is too small, and quantum phenomena cannot be observed. However, this height increases as the object's mass decreases, so for a subatomic particle such as a neutron, quantum effects can be observed at heights of several micrometres at frequencies of a few hundred hertz. A neutron in such gravitational quantum states can have only certain, extremely small, values of energy (a few picoelectronvolts); it does not move but rather levitates above a surface.

So can such quantum bounces for neutrons be observed? Because gravity is very weak compared with the other fundamental forces, and numbers of low-energy neutrons available is low, such experiments are extremely challenging.

Nevertheless, using ultra-cold neutrons (UCNs) available at ILL's ultra-cold and very cold neutron facility, PF2, in a carefully designed experiment, pure gravitational quantum states could be selected and studied. This paved the way for further novel experiments: neutrons bouncing off a mechanically oscillating reflecting mirror revealed transitions between gravitational states. Furthermore, the visualisation of the bouncing ping-pong ball succeeded using track detectors with a high spatial resolution.

A complementary experiment was carried out, based on the 'whispering gallery' effect in which sound waves are reflected along a curved wall to create a standing wave. Neutrons, which also behave as waves, can be similarly reflected around the surface of a concave mirror. In this case, the same quantum states are seen, but due to acceleration from the centrifugal (inertial) force, rather than gravity.

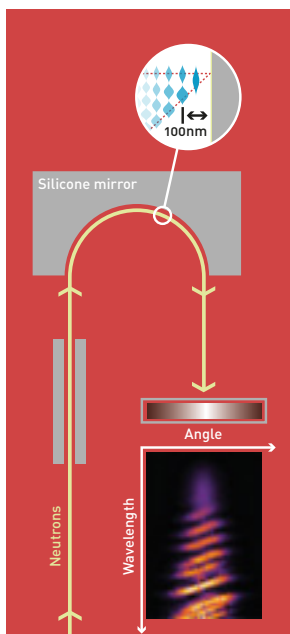
## HUNT FOR NEW FORCES

Such measurements are interesting because gravity is poorly understood at short distances. Any violation of Newton's law could indicate new, short-range fundamental forces that might suggest the existence of dark matter (predicted by some theories of fundamental particles and forces but not yet observed), or the mysterious dark energy apparently causing the expansion of the Universe to accelerate. The experiments have already set limits on these scenarios, and triggered new developments in other fields of physics.

Furthermore, they test a central tenet of Einstein's general theory of relativity – the 'equivalence principle' – which states that the gravitational force felt by an object is equivalent to the corresponding acceleration of its reference frame. If this principle is right also in the quantum regime, then the quantum states measured in the gravity and whispering-gallery experiments should be exactly the same. If short-range forces exist, the equivalence principle would not hold.

Our initial experiment has stimulated a whole new field of quantum gravitational spectroscopy, which allows us to make various precision measurements in fundamental physics, for example, measuring the gravitational states of antihydrogen at CERN to probe whether the properties of antimatter are an exact mirror image of those of matter.

At the ILL, an active community using the PF2 constantly pushes forward and extends the scope of this exciting new field, and a dedicated ultra-high resolution spectrometer, GRANIT, with its own UCN source, is being built.



The set-up for seeing the gravitational quantum states of ultra-cold neutrons when bounced off a curved mirror to create an analogous whispering gallery effect

**RESEARCH TEAM:** GRANIT, qBounce and the University of Tokyo

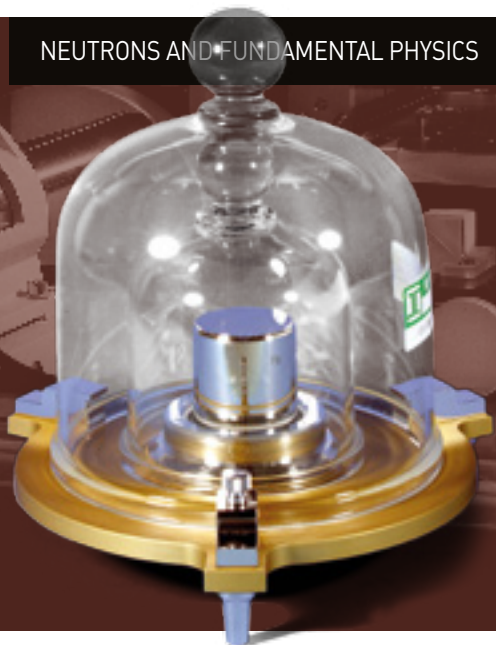
**ILL INSTRUMENT USED:** PF2, D17, GRANIT, PF1 instruments

**REFERENCES:** 1. V. V. Nesvizhevsky, and A. Yu. Voronin, *Surprising Quantum Bounces*, London: Imperial College Press, 2015. 2. V. V. Nesvizhevsky et al., *Nature*, 2002, 415, 297. 3. V. V. Nesvizhevsky et al., *Nature Phys.*, 2010, 6, 114. 4. T. Jenke et al., *Nature Phys.*, 2011, 7, 468.

# A NEW MASS STANDARD

NUCLEAR REACTIONS INVOLVING NEUTRONS ARE TESTING EINSTEIN'S FAMOUS MASS-ENERGY EQUATION TO CREATE A NEW DEFINITION OF A UNIT OF MASS

Michael Jentschel



**O**ur current definition of a unit of mass is based on the kilogramme-prototype held by the Bureau International des Poids et Mesures (BIPM) in Paris. It has several deficits, however. Variations in value, albeit tiny (of the order of one in a hundred million) show up in identical copies stored in the same place. Also, the concept of a definition based on a single monolithic object is rather outmoded and does not fit well with modern physics practices.

As a result, people are looking for a more suitable mass standard by linking the mass to the frequency of electromagnetic radiation via Einstein's mass-energy equation,  $E = mc^2$ . This first calls for a direct verification of this equation's validity. However, this is not as easy as it sounds because comparing energy and mass involves the 'c<sup>2</sup>' factor, which magnifies any variation in mass by 16 orders of magnitude. For this reason, any laboratory experiment is limited to measuring very small masses at the level of atomic nuclei.

Nuclear reactions, in which the nucleus of a given isotope captures a slow-moving neutron, are a good option. High-energy gamma-rays are released to create a new isotope that is almost one mass-number heavier. Here it is important to underline the word 'almost': there is a small measurable difference between the mass of the new isotope and the sum of the masses of the original isotope and neutron. To verify Einstein's equation requires comparing this little difference with the released gamma-ray energy.

## ULTRA-ACCURATE GAMMA-RAY ENERGIES

Neutron-capture reactions can be carried out using thermal neutrons supplied at the ILL, and its ultra-high-resolution gamma-ray spectrometers, GAMS, are equipped to obtain very accurate gamma-ray energies by measuring their wavelengths. These instruments use perfect single crystals of silicon with accurately known lattice spacings.

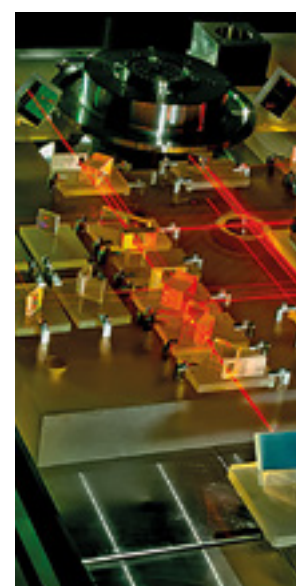
When the gamma-rays impinge on the crystals, they are diffracted at various angles, which are measured using highly sensitive optical-angle interferometers. Combining the measured diffraction angle with the known lattice spacing yields an absolute gamma-ray wavelength measurement, and thus the energy released in the nuclear reaction.

For the reasons given above, the isotope masses need to be measured 1000 times more precisely. This is done using a Penning trap. In this device, the charged atoms of the isotopes are held by electric and magnetic fields such that they circulate with a frequency that depends on their mass. The mass measurement gets calibrated by comparing this frequency with that of the isotope, carbon-12 (standardised as 12 mass units).

This method cannot be used for neutral neutrons, however. To overcome this problem, the neutron-capture experiments must be carried out twice with two different isotope combinations. The first set of data compares masses and energies of the first isotope combination and can be used to extract the neutron mass. This value can then be inserted into the data set of the second isotope combination. At the end, two results are obtained: an extremely precise determination of the relative atomic mass of the neutron and a validation of Einstein's formula.

The last result published in 2005 yielded a difference in mass-energy equivalence relation of a relative uncertainty of  $4.4 \times 10^{-7}$ . The main source of errors were the gamma-ray measurements. Since then, a new generation of GAMS spectrometers at the ILL, as well as Penning traps at the MPI in Heidelberg, have been developed. It is now time to start a new round of experiments to validate Einstein's formula at a precision level relevant to the new definition of the kilogram mass unit.

The prototype kilogramme at the BIPM in Paris



The GAMS6 spectrometer

**RESEARCH TEAM:** K. Blaum (MPI Heidelberg, Germany), M. Jentschel and P. Mutti (ILL), J. Krempel (ETH Zürich, Switzerland), and G. Mana and E. Massa, (INRIM Torino, Italy)

**ILL INSTRUMENT USED:** High-resolution gamma-ray facility, GAMS

**REFERENCES:** S. Rainville *et al.*, *Nature*, 2005, **438**, 1096; M. S. Dewey *et al.*, *Phys. Rev. C*, 2003, **73**, 044303; E. Massa and G. Mana, *Nature Physics*, 2016, **12**, 522.

# MELTING IN ONE DIMENSION

AN UNUSUAL CARBON-CARBON MOLECULAR SYSTEM IS PROVIDING  
TO CLUES TO THE DYNAMICS OF 1D SYSTEMS

Stéphane Rols

In order to understand the material world, physicists build mathematical models that describe how it works, and then test their predictions against experimental observations. However, because our world is three-dimensional, capturing the essence of physical phenomena may involve such complex interactions that any equations developed to describe them are difficult to solve.

Fortunately, it is possible to start with valid models that describe behaviour in just one dimension. Such models have the advantage of being mathematically solvable, and are often elegant as well. One example is the use of one-dimensional (1D) models in theories describing phase transitions (for example from a solid to a liquid). The starting-point might be a chain of interacting particles that acts like a vibrating spring when energetically excited as an effect of temperature. The model would then seek to characterise the types of excitations that trigger structural transitions.

Unfortunately though, Mother Nature is rather stingy in providing experimentalists with real 1D systems to test the theoretical predictions. Nevertheless, in recent years, a chain-like molecular assembly has been synthesised that is allowing us to examine the validity of a statistical-mechanical model that describes the structural and thermodynamic behaviour of a 1D crystal lattice.

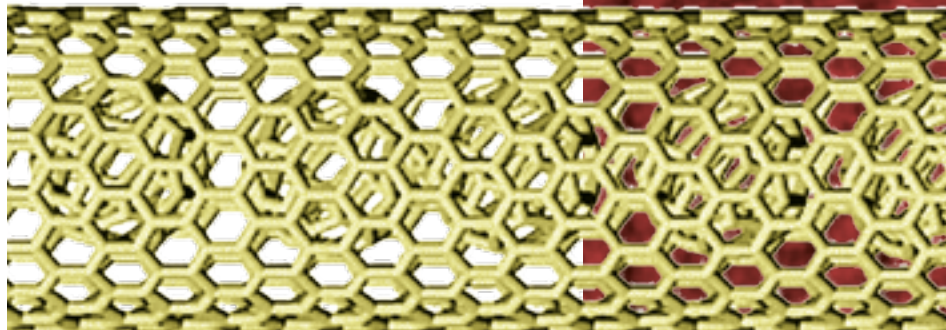
## CARBON NANO-PEAPODS

Carbon peapods represent an ideal 1D molecular arrangement. They consist of balls of 60 carbon atoms – so-called  $C_{60}$  fullerenes – sitting like peas in a carbon nanotube ‘pod’ that consists of a rolled-up sheet of graphene (p28). The  $C_{60}$  peas, at 0.7 nm across, fit snugly inside inside 1.4-nm diameter carbon nanotubes, and they are held in the central position by repulsive intermolecular forces which extend to 0.35 nm, to form a regular 1D lattice with a spacing of 1 nm. (If the  $C_{60}$  peas are made to polymerise so that they form a linked chain, the lattice spacing is reduced to 0.92 nm because of the tighter bonding.) Remarkably, the self-assembled carbon peapods are resilient up to a temperature of about 1000° C (above which they transform into double-walled carbon nanotubes). This makes them particularly

interesting for testing 1D models at high temperatures where few 1D materials (for example, DNA) are stable.

We used neutron inelastic scattering to follow the motions of the confined  $C_{60}$  peas. The IN4 time-of-flight (TOF) spectrometer (p9) was used to probe their rotations, while their motions along the nanotube were investigated with the TOF IN5 spectrometer and the IN11 spin-echo spectrometer (p9). In parallel, we also carried out X-ray and neutron diffraction (using D16) to follow what happened to the 1D lattice structure as it was heated up from 2 to 1000K.

We found that, as the temperature rises from 300 K, the  $C_{60}$  1D crystal lattice vibrates harmonically – the peas vibrate around preferential static positions. At 700 K, the chains ‘melt’ to form a highly correlated ‘liquid’ – that is, the individual spacing between peas starts to vary significantly while remaining constant on average. These findings match perfectly the phase diagram predicted by our 1D model.

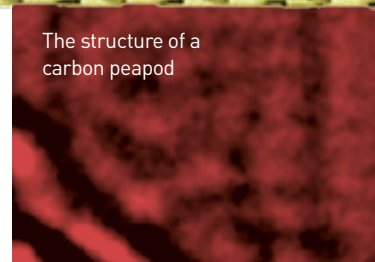


In the low-temperature range, at about 100K, we noted an additional transition – from a 1D harmonic crystal to a new, modulated phase that also accords with theoretical predictions. Increased interactions between the  $C_{60}$  peas and the nanotube walls, which are not commensurate with the 1D lattice spacings, break up the chains into domains with gaps, or defects, between them. These propagate along the nanotube axis rather like a single wave known as a soliton.



↔  
1nm

An electron micrograph  
of a carbon peapod



The structure of a  
carbon peapod

**RESEARCH TEAM:** S. Rols, C. Bousige, H. Schober, J. Ollivier, V. Cristiglio and P. Fouquet (ILL), P. Launois, E. Paineau and S. Rouziere (Université Paris-Sud, Orsay, France), J. Cambedouzou (ICSM, Bagnols sur Cèze, France), H. Kataura (AIST Tsukuba, Japan), V. Agafonov (University of Tours, France), V. Davydov (HPPI RAS, Troitsk, Moscow, Russia)

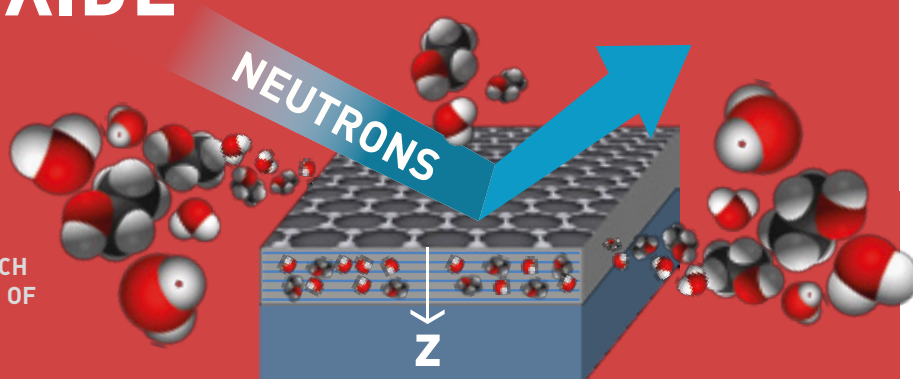
**ILL INSTRUMENT USED:** IN4 and IN5 time-of-flight (TOF) spectrometers, IN11 spin-echo spectrometer and D16 diffractometer

**REFERENCES:** C. Bousige *et al.*, *Phys. Rev. B*, 2012, **86**, 045446; C. Bousige *et al.*, *Phys. Rev. B*, 2013, **87**, 195438; S. Rols *et al.*, *Eur. Phys. J. Special Topics*, 2012, **213**, 77.

# GRAPHENE-OXIDE MEMBRANES AS FILTERS

NEUTRON REFLECTIVITY MEASURES HOW MUCH MORE EASILY WATER SLIPS INTO THE LAYERS OF GRAPHENE OXIDE THAN ETHANOL DOES

Alexei Vorobiev



Graphene oxide is the oxidised version of graphene – the remarkable material consisting of single layers of carbon atoms arranged in a chicken-wire structure. It can be easily dispersed in water and precipitated into multilayered membranes. In fact, paper-like graphene oxide had been tested as early as the 1960s for membrane applications; these experiments demonstrated promise for nano-filtration and the desalination of seawater.

Graphenea



A graphene-oxide film

Research results obtained during past few years have demonstrated that water molecules easily penetrate the graphene-oxide layers, while for other molecules such as ethanol (alcohol), the permeation is extremely slow. It was therefore proposed that graphene oxide was suitable for the purification of alcohol from alcohol–water mixtures, and potentially the separation of other solvent mixtures. For example, one can possibly eliminate some organic solvents contaminating waste waters by passing them through graphene-oxide filters.

Our study provides a quantitative evaluation of water sorption by graphene-oxide membranes exposed to water/ethanol vapour mixtures using neutron reflectivity (p9). Neutron-scattering methods are sensitive to hydrogen atoms in water and ethanol molecules. Furthermore, substituting the hydrogen in water ( $\text{H}_2\text{O}$ ) with its heavier isotope deuterium to form heavy water ( $\text{D}_2\text{O}$ ) allows us to evaluate precise amounts of water and ethanol absorbed by the graphene-oxide membrane.

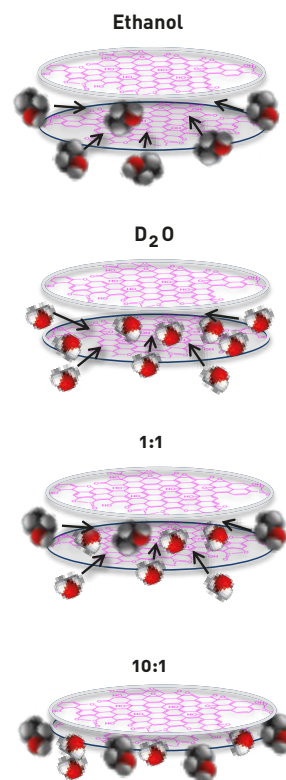
## SPEEDY WATER

The graphene-oxide thin films were exposed to a series of vapours consisting of pure  $\text{D}_2\text{O}$ , ethanol and a  $\text{D}_2\text{O}$ –ethanol mixture in various proportions. The reflectivity data collected under exposure to pure vapours were used to calculate the precise amounts of water and ethanol which was inserted into the films: 1.4 molecules per formula unit for pure  $\text{D}_2\text{O}$ , and 0.45 molecules per formula unit for ethanol.

The neutron data also clearly indicated that exposing the graphene-oxide film to a 1:1  $\text{D}_2\text{O}$ –ethanol vapour resulted in the absorption of both solvents but with the composition of absorbed solution remaining almost the same, thus showing poor selectivity. However, when a more concentrated ethanol solution was used (10:1 ethanol– $\text{D}_2\text{O}$ ), the composition of the solution absorbed into graphene-oxide films was found to be drastically different, at 0.79:1.

Our experiments therefore revealed significant selectivity in the absorption of water by graphene-oxide films when exposed to vapours of water–ethanol mixtures. Although far from perfect, this selectivity confirmed the potential of these membranes for the purification of ethanol, since water evaporates through the membrane much faster than ethanol.

These results provide the experimental background for understanding the fundamental mechanism behind the permeation properties of thin graphene-oxide membranes exposed to solvent vapours (for example, in humidity-controlled gas-separation experiments). Both water and ethanol penetrate between the membrane layers. However, when higher concentrations of ethanol are used, water is preferentially taken in, leaving behind an alcohol-enriched solution. When 10:1 vapour mixtures are used for experiments, a water concentration about 15 times higher is observed for the solution absorbed by the graphene-oxide film.



The sorption of water (deuterated), from a series of water–ethanol mixtures, into graphene-oxide layers

**RESEARCH TEAM:** A. Vorobiev and A. Dennison (Uppsala University, Sweden and ILL), D. Chernyshov (SNBL and ESRF, France), V. Skrypnichuk, D. Barbero and A.V. Talyzin (Umeå University, Sweden)

**ILL INSTRUMENT USED:** Reflectometer Super ADAM

**REFERENCES:** R. R. Nair *et al.*, *Science*, 2012, **335**, 442; V. F. Sears, *Neutron News*, 1992, **3**, 26.

# SMART NANOGELS FOR DRUG DELIVERY

NEUTRON REFLECTOMETRY PROBES THE MICROSCOPIC STRUCTURE OF GELS CONSISTING OF LINKED POLYMER PARTICLES AT THE AIR-LIQUID INTERFACE OF THE GEL SOLUTION

Richard Campbell

**G**els are materials found in many consumer products such as shampoos, sunscreens and food. They are formed by mixtures in which large amounts of liquid, usually water, are confined within a flexible network of polymer chains or colloidal particles. One particular type of gel consisting of minute polymer particles smaller than a micrometre, which are linked together, can incorporate and hold other large molecules in their network structure. Because they are both 'soft' and 'smart' – responding controllably to outside stimuli such as warmth – they have many attractive applications, including as drug-delivery agents.

One such group of nanogels are based on a polymer called *N*-isopropylacrylamide, or NIPAM, for short. They are considered to be 'smart' because they undergo a change in structure at a definite temperature close to that of the human body (37°C). This means that they can be made to release an active agent or drug by simple contact with the skin – for example, via a transdermal delivery system. However, the development of such systems requires a better understanding of the complex dynamic structure of these nanomaterials, and, currently, there is a lack of experimental data about how these materials actually behave at interfaces.

## IMPORTANCE OF INTERFACES

We have been carrying out studies with researchers at Queen Mary University of London to obtain important missing information on the behaviour of nanogels at interfaces, which may lead to a more patient-friendly route to administering drugs than in current methods. The samples investigated were solutions of NIPAM-based nanogels synthesised with different percentages (10 to 30 per cent) of a cross-linker molecule called *N,N'*-methylenebisacrylamide (MBA). Detailed structural studies of these systems at the molecular scale had not been attempted before.

Neutrons offer the ideal tool to investigate these microscopic structures. In particular, neutron reflectometry (p9) is the technique of choice for the study of surfaces and interfaces. Further, by selective deuteration (p7) of different structural parts of the samples, these components and their surroundings at interfaces could be highlighted, so that any changes in conformation related to concentration, or over time, could be evaluated.

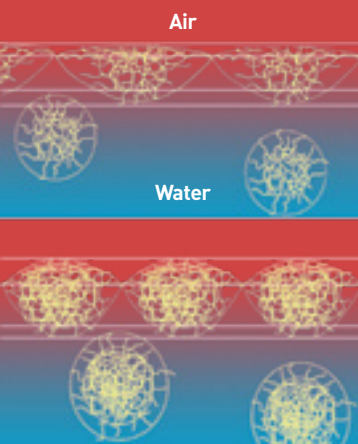
The experiments showed that there is a large structural change at the air-water interface of the sample solutions. Three distinct layers form; first, a densely packed collapsed layer in contact with air, then a second layer of polymer surrounded by water molecules, and finally a third layer of diffuse polymer chains extending into the bulk gel solution. This inner region is made particularly clear by the neutron reflectivity measurements.

The study also revealed that the structural changes at the air-water interface depend on the degree of cross-linking. As the percentage of cross-linker is increased, more rigid networks form and the amount of nanogel adsorbed at this interface increases.

Measurements with selective deuteration provided a sensitive means of determining the adsorbed amount. They also allowed the increase in the amount of nanogel at the interface to be followed with time, as more and more material reached it. Interestingly, the water content in the first layer increases with the amount of MBA (and a higher degree of cross-linking) – this can be attributed to a reduction in the ability of the nanogel to change conformation and thus repel water from polymer network. The structural data also suggest an extensive rearrangement of conformation of the nanogel particles at the interface during the adsorption process, resulting in structural deformation, which diminishes with increasing percentage of cross-linker.

This work is extended to studying the effects of temperature, with the aim of obtaining a comprehensive picture of how to design smart nanogels for use in transdermal drug delivery.

Polymer chain networks can be used to incorporate and deliver biologically active molecules to the body



A schematic representation of the nanogel structure

**RESEARCH TEAM:** M. Resmini, H. Sun, A. Zorbakhsh and K. Zielinska (QMUL, UK) and R. A. Campbell (ILL)

**ILL INSTRUMENT USED:** Reflectometer FIGARO

**REFERENCES:** K. Zielińska *et al.*, *Nanoscale*, 2016, **8**, 4951; DOI: 10.1039/C5NR07538F

# A RECIPE BOOK FOR SOFT NANO-COLLOIDS

MAPPING OUT THE BEHAVIOUR AND STRUCTURE OF COMPLEX FLUIDS CONTAINING SOFT NANO-PARTICLES IS HELPING IN THE RATIONAL DESIGN OF NEW MATERIALS

Jörg Stellbrink and Peter Lindner

**M**any everyday products, such as cleaning materials, foods and medicines, are colloids – materials composed of a fine suspension of one substance in another. The colloidal particles can be hard particles, self-assembled aggregates of molecules, or large molecules such as polymers. One currently active field of research is focused on the special class of colloids that consist of elastic and deformable nano-particles with characteristics lying somewhere between those of soft polymer molecules (long floppy chains) and hard spheres, dispersed in a solvent. Because of their physical and chemical characteristics, such soft nano-colloids have potential use as viscosity modifiers and drug-delivery agents.

To be able to design new nano-colloids for such applications, we embarked on a comprehensive experimental and theoretical study of these materials, with the aim of establishing a generalised view of how the morphology and concentrations of the constituent particles relate to their bulk properties – phase and viscosity – over wide length and timescales.

To do this, we developed a new nano-colloid that could act as a tuneable model system. The particles consist of aggregates of molecules (micelles) built from repeating blocks of two polymers, poly(butylene oxide), PBO, and poly(ethylene oxide), PEO, the former being more hydrophobic. Varying the ratios of the numbers of each block in the copolymer thus controls how the micelles interact with an aqueous solvent – that is, whether the individual polymer chains are attracted to water, and so spread themselves out in the liquid, form soft star-like aggregates with a hydrophobic core, or clump together in harder, more water-repellent balls. In this way, particles of varying softness and ‘clumpiness’ could be prepared.

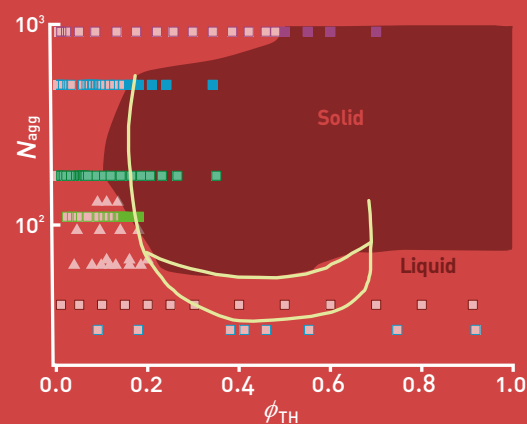
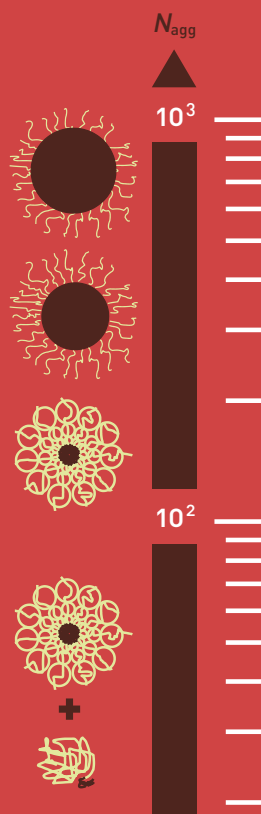
## FROM SOFT STARS TO HARD BALLS

We could then analyse their structure on the microscopic scale using small-angle neutron scattering (SANS, p9), for samples covering a wide range of block ratios from symmetrical to very asymmetrical (from 1:1 to 1:100

### Controlling viscosity with soft nanoparticles

(Top right) an experimentally derived diagram showing how star-like micelles control whether a colloid is a liquid or a solid, depending on the number of molecules in the micelle ( $N_{agg}$ ) and their size ( $\phi_{TH}$ ). The solid lines represent the ideal theoretical border between solid and liquid.

(Below) The graphic below shows how the structure of the micelle changes with  $N_{agg}$ , from a loose single polymer chain, through a star-like configuration, to a tight ball



PBO:PEO), and at various concentrations. The experiments used heavy water,  $D_2O$ , and the PEO blocks were selectively deuterated so as to highlight structural detail in the micelles (p29). The results confirmed that SANS is an ideal technique for characterising micellar structure. The size of the micelles and number of polymers in each micelle could be measured. The studies revealed that micelles with the most symmetrical block ratio closely resemble hard spheres, while increasingly asymmetric ratios lead to very soft star-like micelles and loose, non-aggregated polymer chains (left).

Another technique, dynamic light scattering, was employed to probe the diffusion characteristics of the micelles. These data could then be correlated with bulk viscosity measurements of the samples. We found a strong correlation between diffusion characteristics and viscosity, irrespective of their softness.

All the results were then combined to create a ‘phase diagram’ (above) showing quantitatively the physical state and bulk behaviour of nano-colloids across the full range of micelle softness and concentrations. This was then compared with the phase diagram predicted by a well-established model of colloidal particle interactions.

The two phase diagrams were reasonably close, confirming the validity of theoretical approaches employed for soft colloids. Of particular interest to us was the new information gained about the gel and glassy phases formed at higher concentrations. At a given concentration, the colloids containing the larger star-like micelles change from a gel to a glassy phase. However, as the clumpiness of the micelles increases so that they evolved into hard spheres, there is another transition back to the liquid phase.

These experimental results agree well with those from other similar model systems, confirming the usefulness of this fundamental approach in aiding the design of new soft colloidal materials.

**RESEARCH TEAM:** S. Gupta (JCNS-SNS, Oak Ridge National Laboratory, US), M. Camargo (Universidad Antonio Nariño, Santiago de Cali, Colombia), J. Stellbrink, J. Allgaier and D. Richter (JCNS-1 and ICS-1, Forschungszentrum Jülich, Germany), A. Radulescu (JCNS-FRM II, Forschungszentrum Garching, Germany) P. Lindner (ILL) E. Zaccarelli (CNR-ISC and Università di Roma La Sapienza, Italy) and C. N. Likos (University of Vienna, Austria)

**ILL INSTRUMENT USED:** Small-angle neutron diffractometer D11

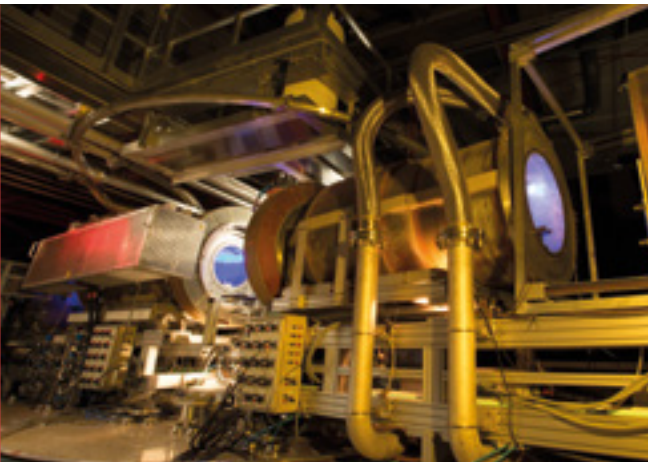
**REFERENCES:** S. Gupta *et al.*, *Nanoscale*, 2015, **7**, 13924; S. Gupta *et al.*, *Phys. Rev. Lett.*, 2015, **115**, 128302.



# HOW TO SIZE A POLYMER SNAKE

RING-SHAPED MOLECULES HELP PREDICT THE FLOW BEHAVIOUR OF INDUSTRIAL POLYMER MELTS

Dieter Richter, Andreas Wischnewski and Angela Wenzik



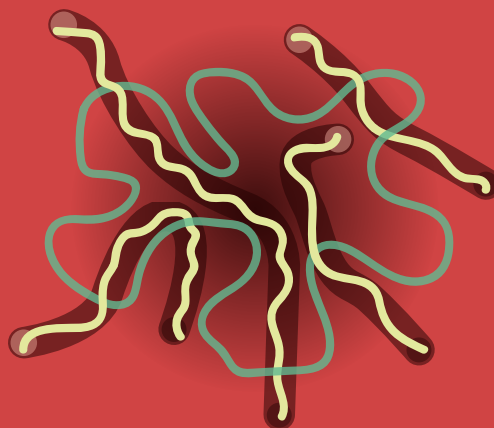
IN15 spin-echo spectrometer

**M**any of the products that we use in daily life, such as contact lenses, yoghurt pots, textiles and car tyres, are made of materials, partly or wholly, composed of long, chainlike carbon molecules – polymers. During their manufacture, polymer powders and granulates are melted together, and the resulting melt is then sent down pipes to the next process stage where it is squirted through nozzles, and sprayed or spun into shape.

Being able to predict and control accurately the flow properties, or viscosity, of this melt is important, because it allows the production plant and processing to be customised accordingly – thereby reducing costs. This viscosity depends on how easily the polymer chains can slide through the melt, and so a theoretical description of this motion is essential. Fortunately, the chain dynamics can be characterised using the concept of long ‘tubes’ through which the chains creep with snake-like movements – a motion called reptation. This term was coined by the 1991 Physics Nobel Prize-winner Pierre-Gilles de Gennes. The walls of these virtual tubes are formed from neighbouring polymer chains, which are tangled up together like spaghetti. The wider the tube, the more room there is for the molecule to slither about, and therefore the lower the viscosity.

The tube model has been extremely successful. However, many questions remain regarding the flow properties of complex polymers with a branched molecular structure – which are those most commonly used in manufacturing. The presence of polymer side-chains tends to increase tangling with neighbours, thus narrowing the tube and constraining movement. But how strong is this effect? Furthermore, these spatial constraints can vanish over time, the so-called ‘tube dilution effect’; how and why does this happen?

Previously, theoretical calculations of the tube diameter could not be verified from direct measurements of polymer-chain diffusion. The experimental values obtained were too high. The reason is that polymers move not only from side to side in the tubes but also along them, and are even able to break free at the tube ends.



In melts made up of polymer rings (green) and polymer chains (yellow), both types of molecules are entangled. The freedom of movement of the chains, which depends on the diameter of the virtual tubes, can be measured more easily and accurately with the help of the rings, compared with conventional methods

## RUNNING RINGS AROUND TUBES

However, we can overcome this problem by adding to the melt a small amount of ring-shaped polymers (1 to 10 per cent), made from the same building blocks as the chains. For our experiments, we used polyethylene oxide. Because the rings do not have any loose ends and therefore cannot escape out of the tubes, they make perfect probes; they can move only side-ways in the tubes, so can ‘feel’ their virtual walls.

Neutrons – in particular in neutron spin-echo experiments (p9) – can follow the motions of polymer molecules, both chains and rings, and distinguish between them. The ring probes can be highlighted by selectively deuterating (p5) the chains, which become the ‘background’. As a result, we could measure the circumference of the tube directly, which turned out to be in excellent agreement with our theoretical model. We expect that our methodology will make it possible to explain quantitatively, for the first time, the tube dilution effect.

Until now, it had been extremely difficult to produce the polymer rings in sufficient quantity and quality, as all known methods of making them produce a mixture of rings and chains. Nevertheless, using a new method, we were successful in separating the linear chains from the rings. The chain ends were modified so that they bonded with ion-exchange beads, and so could be filtered off, leaving behind a material of almost pure rings.



Understanding polymer-chain dynamics theoretically is vital for processing polymer materials

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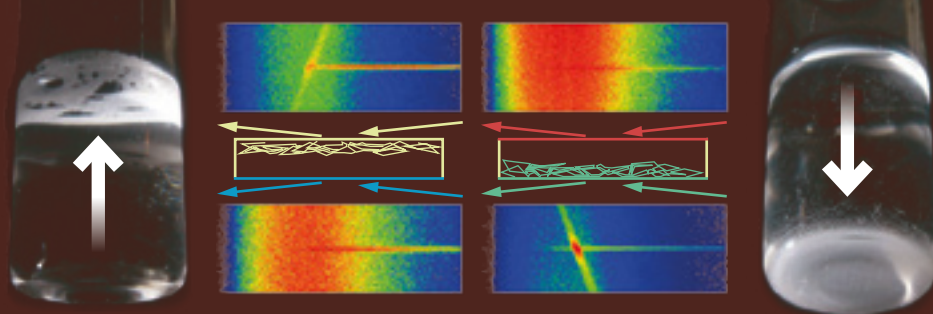
**ILL INSTRUMENT USED:** IN15 spin-echo spectrometer

**REFERENCES:** S. Goossen *et al.*, *Phys. Rev. Lett.*, 2015, **115**, 148302; DOI: 10.1103/PhysRevLett.115.148302

# MIXING THE PERFECT FORMULATION

**NON-EQUILIBRIUM EFFECTS CONTROL THE BEHAVIOUR OF MIXTURES OF POLYMERS WITH SMALL SURFACE-ACTIVE MOLECULES USED IN OUR EVERYDAY LIVES**

Richard Campbell



**M**ixtures of oppositely charged polyelectrolytes and surfactants have generated interest for more than a century, as a result of the huge commercial value of the formulations based on them. These include shampoos, cosmetics and foods, as well as constituents used in newer applications such as drug and gene delivery.

These materials, which consist of tiny complexes and slightly larger aggregates that are suspended in solution, are often used to modify the properties of surfaces, for example, to remove dirt in cleaning applications. As a result, their fundamental properties at the air-liquid interface have been the focus of several substantial bodies of research over the years. These have usually focused on rationalising their bulk behaviour assuming so-called equilibrium conditions, in which the configuration and location of the aggregates has stabilised.

Recently, however, there has been growing awareness that in many instances, the configuration of the components in these systems has not yet actually reached their final state, and that non-equilibrium effects strongly influence their properties. We set about demonstrating how non-equilibrium effects can dominate the interfacial properties of such mixtures, first focusing on one particular anomaly not easily explained using an equilibrium description.

A key role of a surfactant in one of these complex mixtures is to lower the surface tension at an interface. However, in some systems, adding more surfactant can cause an unexpected sharp rise in the surface tension at a given concentration. Using the ILL's FIGARO reflectometer, combined with selective deuteration (p7), we were able to look at the behaviour of these materials at the liquid surface in relation to this surface-tension peak. We found that the peak is related to the slow precipitation of aggregates that sink away from the interface.

## THE IMPORTANCE OF PREPARATION

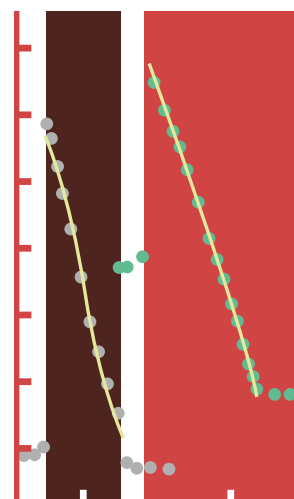
We then investigated a system in which the peak was apparently missing, and showed that if one waits long enough (one month in fact!), the feature does arrive. In other words, some systems take a really long time to stabilise. This result indicated that the method used to prepare the mixture was critically important. We then went on to study samples prepared in different ways. This involved using neutron reflectometry (p9) to measure the amounts of polyelectrolyte and surfactant at the air-water interface, and developing a new but very simple model to calculate the surface tension.

It turned out, however, that the ways in which the aggregates produced in solution reach the surface of the sample, and what happens to them when they get there, are extremely complicated. We uncovered three different mechanisms. First, some aggregates get stuck at the surface when the sample is first prepared. Secondly, aggregates containing more polyelectrolyte than surfactant interact spontaneously with a free surfactant layer on the liquid surface. Thirdly, the aggregates move in a specific direction when they sink – or sometimes float – because their density is different from that of the bulk liquid.

Further investigations showed that in certain cases the aggregates remained whole, and embedded in the surface monolayer, while in other cases they quickly broke up and spread material across the interface. In fact, it was shown, using a flow cell, that if the liquid surface was expanding – as happens when these products are actually used in formulations – even more polyelectrolyte can be delivered to it via aggregate-spreading than via diffusion and adsorption of small complexes from solution.

This work reveals the potential of exploiting non-equilibrium effects to tune the amount of a polyelectrolyte/surfactant mixture delivered to and remaining at an interface. Such insights will be invaluable in designing smarter soft materials, particularly for the targeted delivery of drugs and biomolecules.

Neutron reflectivity data recorded uniquely using the reflection up versus down modes of FIGARO to highlight the effects of gravity on the interaction of aggregates in the mixture with surfaces either above or below the sample



Data showing the surface tension peak for oppositely charged polyelectrolyte/surfactant mixture: the predictions from our simple model are shown as bold lines and the shadings mark where there are aggregates in the samples

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**ILL INSTRUMENT USED:** Reflectometer FIGARO

**REFERENCES:** R. A. Campbell *et al.*, *J. Phys. Chem. B*, 2011, **115**, 15202; R. A. Campbell *et al.*, *Langmuir*, 2014, **30**, 8664; R. A. Campbell *et al.*, *Soft Matter*, 2016, submitted.

# FROM CRAB SHELLS TO SMART SYSTEMS

COMPLEX MATERIALS BUILT FROM BIOLOGICAL POLYMERS CAN BE FINELY TUNED TO HAVE A VARIETY OF MICROSCOPIC STRUCTURES THAT UNDERLIE PHYSICO-CHEMICAL PROPERTIES USEFUL IN MEDICINE AND POLLUTION CONTROL

Leonardo Chiappisi and Michael Gradzielski

**S**oft complex matter composed of polymers make up not only many materials such as foods and medicines but also living organisms, including ourselves. A huge amount of research is ongoing to understand their properties, so as to glean insights into biological processes and to make new, tailored products that are biologically friendly.

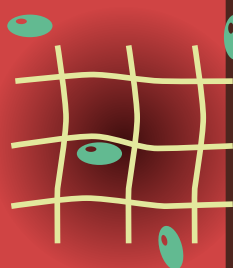
This requires probing the structure and behaviour of such systems over a range of scales. The constituent molecules often form elaborate hierarchical assemblies held together by weak ionic charges, which can be controlled by varying molecular structure, concentration and acidity (pH).

Neutrons are ideal for studying such molecular assemblies, because, using selective deuteration [p7], they can probe their shapes and configurations via SANS [p9], and follow their dynamics with neutron spin-echo [p9].

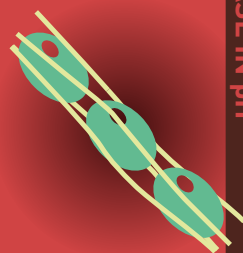
## POLYSACCHARIDE CO-ASSEMBLIES

In our studies, we focused on a group of materials of biological origin called polysaccharides. These sugar-based polymers are interesting because they are a relevant alternative to conventional petro-based polymers. Charged polysaccharides co-assemble with surfactants [p29] that are oppositely charged in a highly synergistic fashion. Surfactants collect into small aggregates – micelles – which readily bind to other charged polymers. This thus provides an easy route to making well-defined, hierarchically structured materials both in the solid state as well as in aqueous solutions, so they represent interesting candidates in the fields of drug delivery or waste recovery.

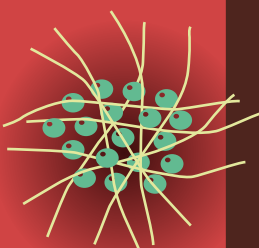
One subject of interest was the co-assembly processes of a cationic biopolymer called chitosan, (poly D-glucosamine), which is derived from seafood waste (for example, crab shells), and alkyl oligooxyethylene carboxylic acids. These surfactants behave rather like fatty acids, in being affected by the pH, but are more soluble in water (because of the ethylene-oxide units).



A loose network of chitosan chains decorated with surfactant molecules



A one-dimensional chitosan-surfactant aggregate



Surfactant micelles trapped in a chitosan corona

INCREASE IN pH

Moreover, by varying the pH and temperature, and also the molecular architecture of the surfactant, we can change the shape of the self-assembled micelles.

Using the ILL's small-angle diffractometer, D11, we elucidated the detailed structures found in mixtures of chitosan and the surfactant, nonaoxyethylene oleylether carboxylic acid ( $C_{18:1}E_9CH_2COOH$ ), in various mixing ratios and at different acidities. Three main structures can be identified (left): at low surfactant content and/or low pH – where the micelles carry a low charge density – we find a loose network of chitosan chains decorated with surfactant molecules. At high pH and/or mixing ratio, compact structures form with a core of micelles surrounded by a chitosan corona. At intermediate pH and mixing ratios, the components self-assemble into long, one-dimensional aggregates. It is worth noting that these remarkable structural changes take place within a range of only 1.5 units of pH but are associated with a huge variation in the physico-chemical properties of the system – for example, viscosity or the mobility of the surfactant micelles.

Another polysaccharide-surfactant system studied was composed of cationically modified cellulose ether, JR 400, and the oppositely charged surfactant SDS (sodium dodecyl sulphate). This forms highly viscous networks resembling honey after only tiny amounts of surfactant are added. SANS measurements showed that the change in viscosity is accompanied by the formation of rodlike mixed polyelectrolyte-surfactant aggregates. Using neutron spin-echo measurements to determine the diffusion coefficient of the aggregates, and knowing the radius of the rods, we could calculate their length. It turned out that they were only about 40 nanometres long, but they live long enough to yield an effective cross-linking system thus inhibiting movement and increasing viscosity.

**RESEARCH TEAM:** L. Chiappisi (TU-Berlin & ILL), M. Gradzielski and M. Simon (TU-Berlin), I. Grillo, I. Hoffman, P. Falus, B. Farago, R. Schweins and M. Sharp (ILL), and S. Prévost (ESRF).

**ILL INSTRUMENT USED:** Small-angle diffractometer D11, and spin-echo spectrometer IN15

**REFERENCES:** L. Chiappisi *et al.*, *Langmuir*, 2014, **30**, 1778; doi: 10.1021/la404718e; L. Chiappisi *et al.*, *ACS Applied Materials & Interfaces*, 2015, **7**, 6139; doi:10.1021/am508846r; I. Hoffmann *et al.*, *J. Chem. Phys.*, 2015, **143**, 074902; doi:10.1063/1.4928583.

# GLOSSARY

**Antiferromagnetism** A type of magnetic order in which the magnetic moments of unpaired electrons in atoms in a crystalline array are alternately oppositely aligned.

**Antihydrogen** The antimatter version of hydrogen, consisting of an antiproton and a positron (positively charged electron).

**Antimatter** Subatomic particles each have an antimatter partner (of opposite electrical charge, if the particle is charged).

**Block copolymer** A material consisting of alternating segments of more than one type of polymer.

**Boson** A quantum particle which has a spin of integer value (0,1,2....etc). Bosons include the particles that mediate the fundamental forces.

**Colloid/colloidal suspension** A fine dispersion of one material in another. The colloidal particles are less than a micrometre in size.

**Conformation** Molecules, such as polymers, with directional bonds that can rotate freely, can form different shapes or conformations depending on their immediate environment.

**Contrast variation** A technique in which certain atoms in a sample are substituted by another isotope with a different scattering strength in a way that preferentially enhances the scattering pattern of the particular components of interest.

**Crystal lattice** The regular three-dimensional array of atoms or molecules in a crystalline material.

**Deuteration** The (chemical) replacement of a hydrogen atom in a molecule with its isotope deuterium.

**Deuterium** A heavier isotope of hydrogen having a neutron as well as a proton in the nucleus.

**Diffuse scattering** The additional weak scattering effects in a diffraction pattern resulting from various kinds of disorder within a crystalline material.

**Doping** Replacing a small fraction of an element in a compound with another one.

**Elastic scattering** A neutron technique in which there is no (or almost no) exchange of energy between the neutrons and the molecules being studied, thus giving information about their structure – that is, their form and arrangement.

**Electron** An elementary particle which is a significant constituent of atoms.

**Electron hole** The positive charge left when an electron is removed from an atom. In a crystal lattice, it behaves like a positively charged electron and can be mobile.

**Electron shell** The electrons of an atom are arranged in shells composed of specific orbitals (*s*, *p*, *d* and *f*).

**Fermion** A particle which has half-integer spin. Examples are quarks and leptons (such as electrons), as well as composite particles like neutrons and protons.

**Ferroelectricity** A property of certain materials in which spontaneous electric polarisation is generated such that one side of a crystal is positive and the opposite side is negative. It arises from the correlated organisation of constituent atoms or molecules that have an uneven distribution of electric charge (are dipoles).

**Ferromagnetism** A type of magnetic order in which the electronic magnetic moments are all aligned.

**Frustrated magnetism** A phenomenon in which there are competing magnetic interactions in a crystal leading to complex ordering, or 'liquid-like' behaviour without long-range order of the magnetic moments on individual atomic sites.

**Fullerene** A molecule made of carbon atoms shaped like a hollow sphere or ellipsoid consisting of fused hexagonal and pentagonal units. The most common fullerene is buckminsterfullerene, C<sub>60</sub>.

**Gamma-ray** Very high energy electromagnetic radiation. Gamma-rays are emitted in nuclear reactions.

**Gel** A semi-solid solution in which large amounts of liquid solvent are confined within a flexible network of polymer or other colloidal particles.

**General Theory of Relativity** Einstein's theory, which shows that gravity is the result of the curvature of space-time.

**Glass** A solid that is non-crystalline with a random arrangement of constituent particles, as in a liquid.

**Graphene** A form of carbon in which the atoms are arranged hexagonally in single molecular sheets.

**Heavy water** Water in which hydrogen has been replaced by its heavier isotope, deuterium.

**Hertz (Hz)** A unit of frequency defined as one cycle per second.

**High-temperature superconductor** Materials that behave as a superconductor at temperatures above the boiling point of liquid nitrogen.

**Hydrophilic** Water-loving.

**Hydrophobic** Water-hating.

**Inelastic scattering** A neutron technique measuring the exchange of energy between the neutrons and the sample being studied, thus giving information about the motion of atoms, molecules or magnetic moments, and their respective interactions. (When a neutron is scattered elastically, there is no energy transfer.)

**Interface** The boundary between two phases of matter.

**Interferometer** An instrumental set-up for measuring the interference fringes created by the superposition of two sets of waves from a source. The phase difference between them is used to measure small changes in the source.

**Interference fringes** The pattern produced when waves are combined that are out of phase so that the crests of the combined waves are either reinforced or cancelled out.

**Insulator** A material that does not conduct electricity.

**Ion** An atom or molecule that has gained or lost electrons so that it has become electrically charged. A multivalent ion has gained or lost several electrons.

**Isotope** A particular form of an element as defined by the number of neutrons in its nucleus (an element is defined by the number of protons in the nucleus).

**Magnetic moment** A property arising from a spinning or orbiting electric charge. Atoms or ions with incompletely filled electron shells have a magnetic moment resulting from the spin and angular momentum of the unfilled electron shell. Atomic nuclei can carry a nuclear spin and magnetic moment. Neutrons have a magnetic moment due to their spin 1/2.

**Magnetism** A collection of phenomena related to the presence of electronic or nuclear magnetic moments.

**Magnetic monopole** A hypothetical particle that consists of a single isolated magnetic pole. Quasiparticles (see opposite) have been discovered in certain materials that behave like magnetic monopoles.

**Magnetic scattering/diffraction** Neutrons have a magnetic moment, which can interact with the magnetic moment of an unfilled electron shell of an atom. The periodic arrangement of these electron magnetic moments in a crystal lattice produces a characteristic magnetic diffraction pattern, in addition to the diffraction pattern generated by neutrons scattering off the atomic nuclei.

**Magnon** A quasiparticle (see opposite) that is the collective excitation of correlated magnetic moments in a crystal.

**Metal oxide** A compound of a metal and oxygen, and the usual form of metals in Nature.

**Micelles** Clusters of small molecules such as surfactants that assemble together in a solution, often with distinctive arrangements depending on chemical composition.

**Multiferroic** A material that shows more than one type of order, in particular, magnetic and ferroelectric order.

**Nanometre (nm)** One-billionth of a metre ( $10^{-9}$  metres).

**Nano-particle** Particles of matter at the scale of a nanometre. They often have specific properties connected with their size.

**Neutron** One of the two particles found in the atomic nucleus. Like all quantum particles, the neutron has both particle-like (mass, velocity, kinetic energy, gravitational effects) and wave-like (wavelength, diffraction and refraction effects) properties. Free neutrons decay into a proton, an electron and an antineutrino.

**Neutron diffraction** Neutrons can be reflected, or scattered, off a material in which the interatomic distances are similar to the neutron wavelength. The scattered waves interfere to produce a characteristic diffraction pattern. In standard neutron diffraction, a single crystal is oriented over a range of angles to collect neutron beams diffracted from different planes of atoms in the crystal.

**Neutron reflectivity, neutron reflectometry (NR)** A technique in which neutrons are reflected off a surface or interface. It is used to characterise the structure of surfaces and thin layers.

**Neutron time-of-flight spectroscopy** A technique in which bunches of neutrons with well defined initial energies are scattered by a sample and their arrival times at the detector are recorded. This allows any energy changes due to inelastic scattering (see left) to be calculated.

**Neutron spin-echo** A neutron technique that measures the changes in the spins of neutrons passing through a material caused by small changes in energy associated with molecular movements over relatively long timescales.

**Nuclear fission** A process by which heavy nuclei break up to produce smaller nuclei.

**Nucleus** A constituent of atomic matter consisting of protons and neutrons.

**Phase** A particular state of matter, which may be defined by its structure, constituents and dynamic behaviour.

**Phase diagram** A diagram in which the coordinates are external conditions, for example, temperature, pressure, magnetic field or composition of the system, displaying the different phases in equilibrium and the boundaries between them.

**Phase transition** A point on the boundary between two or more phases in a phase diagram. The point in terms of, for example, temperature or pressure at which a defined structure or set of properties of a system suddenly changes from one phase to another.

**Polarised neutrons** A beam of neutrons whose spins are all aligned.

**Polarised neutron diffraction** A class of neutron experiments using polarised neutrons to investigate the magnetic properties of materials.

**Polyelectrolyte** An electrically charged polymer – usually water soluble.

**Polymer** A molecule comprising repeating molecular units (monomers) usually in long chains.

**Powder diffraction** Coherent scattering from a polycrystalline material.

**Quantum mechanics** The theory that describes matter and energy in terms of probability ‘waves’ in space and time.

**Quantum state** The quantum mechanical energy state of an atom, nucleus or an assembly of these. A system can change from one energy state to another as the result of an external perturbation such as an interaction with a neutron, and it absorbs or emits energy in this process.

**Quantum superposition** Because particles behave as waves, any particle able to adopt two different quantum states exists in a wave-like superposition of the two states until an actual measurement is made.

**Quasiparticle** An elementary entity that is the basis of the collective excitations of a many-body (quantum) system. It is the quantum expression of this emergent behaviour, and is treated mathematically as though it has the same properties as a fundamental particle like an electron. The concept of quasiparticles provides an extremely powerful and useful description of complex interacting systems.

**Reflectometry** A technique in which neutrons or photons are reflected off a surface or interface.

**Reptation** The mechanism by which a single polymer chain moves through the entangled environment of other chains in melts or concentrated solutions. It is thought of as moving through a virtual tube defined the surrounding chains.

**Self-assembly** Molecules, such as surfactants, can spontaneously assemble themselves into complex structures at the nano-scale.

**Singlet state** A quantum state in which the spins of coupled spin-1/2 particles are paired (spin 0).

**Skyrmion** Quasiparticles consisting of vortex-like configurations of magnetic moments found in some materials.

**Small-angle neutron scattering (SANS)** The measurement of neutron scattering at small angles used to investigate large-scale structures such as polymers or biological molecular arrangements.

**Soft condensed matter, soft matter** Materials such as polymers, gels and colloidal dispersions that are soft at room temperature – in other words, can deform or change shape under mechanical pressure. Such materials often have complex structures at the nano or meso-scale.

**Spin** The term describing the internal angular momentum of a quantum particle such as the electron or neutron. It has the value of 0, 1/2, or multiples of those values.

**Spin liquid** A solid in which magnetic moments of the constituent atoms continually change alignment due to competing interactions, creating a disordered magnetic state.

**Superconductor** A material that has no electrical resistance below a certain temperature.

**Surface tension** The elastic force produced by intermolecular attraction in a liquid at its surface, such that it generates resistance to an external force, for example, mechanical pressure from an object on a water surface.

**Surfactant** A class of molecule that adsorbs at surfaces or interfaces. Surfactants are usually molecules with a hydrophilic head group and a hydrophobic tail. They dissolve in both water and oil, forming organised structures such as micelles. They stabilise emulsions and act as cleaning agents (soaps and detergents) by binding to oily materials and dispersing them in water.

**Triplet state** A quantum state in which coupled spin-1/2 particles have parallel spins.

**Ultra-cold neutrons** Neutrons of such low energies that they are totally reflected from material walls.

**Unit cell** The simplest repeating structural unit in a crystal.

# CONTACTS

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### WHAT GOES ON IN THE PSEUDOGAP

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## PAGE 11

### SEEKING OUT SECRET SPIN ORDER

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### QUANTUM MAGNETS DO THE SQUARE DANCE

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### HOURGLASSES, CHECKERBOARDS AND NANO-ISLANDS

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### SPIN ICES AND MAGNETIC MONOPOLES

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## PAGE 18

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### PRECISION MEASUREMENTS FROM QUANTUM BOUNCES

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### A NEW MASS STANDARD

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### A RECIPE BOOK FOR SOFT NANO-COLLOIDS

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### HOW TO SIZE A POLYMER SNAKE

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### MIXING THE PERFECT FORMULATION

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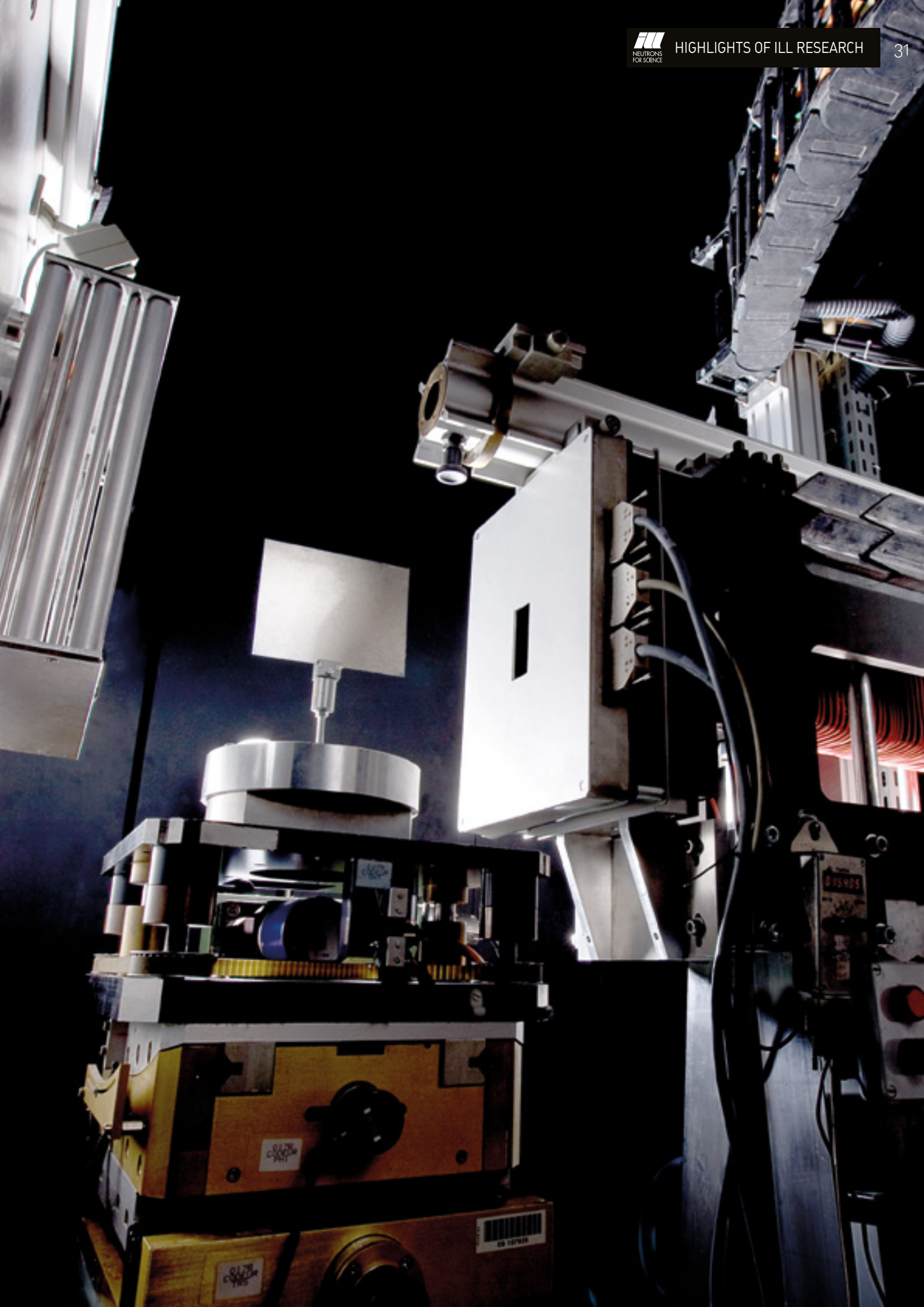
### FROM CRAB SHELLS TO SMART SYSTEMS

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