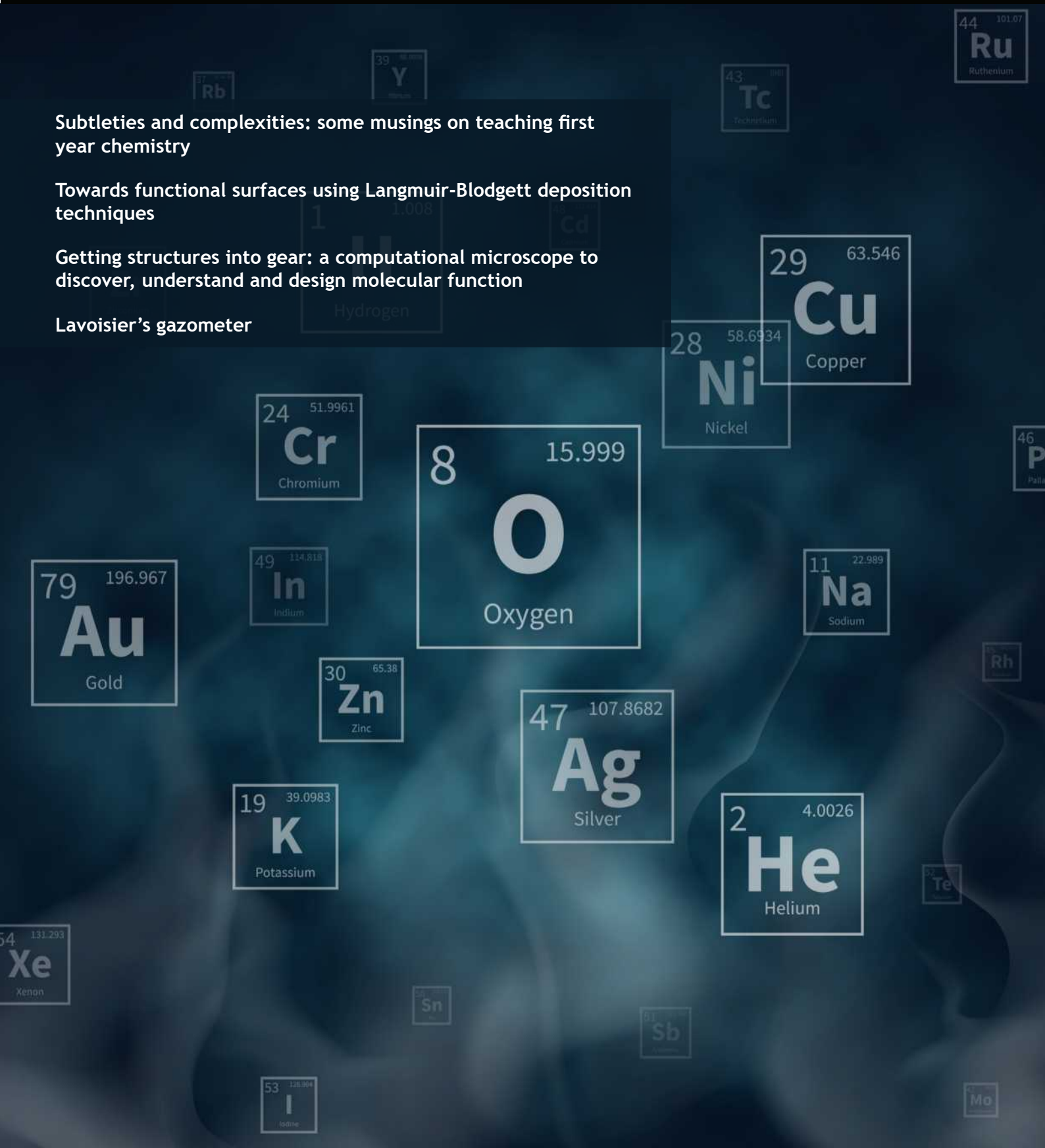
NZIC Chemistry IN NEW ZEALAND

ISSN 0110-5566 (Print) ISSN 2624-1161 (Online) Volume 83, No.3, July 2019



Published on behalf of the New Zealand Institute of Chemistry in January, April, July and October.

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Printed by Graphic Press

The International Symposium on Macrocyclic and Supramolecular Chemistry

On behalf of the local organising committee, you are invited to participate in the International Symposium on Supramolecular and Macrocyclic Chemistry (ISMSC-2020) to be held in Sydney, Australia from July 12 – 16, 2020.

ISMSC-2020 will provide a forum for the discussion of all aspects of macrocyclic and supramolecular chemistry, including nanoscience and materials science. It will follow the style of the preceding meetings in the series with a single scientific session running throughout the conference.

ISMSC, the International Symposium on Macrocyclic and Supramolecular Chemistry, came from a fusion of the International Symposium on Macrocyclic Chemistry (ISMC) and the International Symposium on Supramolecular Chemistry (ISSC). These meetings combined in 2006 and since then have been held on an annual basis in a different location. Join us for the meeting in Sydney in 2020!

https://www.ismsc2020.org/home

ISMSC 2020
15th International Symposium on Macrocyclic and Supramolecular Chemistry
12th - 16th July 2020 Sydney

NZIC Chemistry IN NEW ZEALAND

Volume 83, No.3, July 2019

Articles and features

Other columns

Comment from the President

Welcome to the July issue of *Chemistry in New Zealand*. 2019 is racing by and we are well into the **International Year of the Periodic Table** celebrations with continued contributions to the Radio New Zealand *Sonic Tonic* segment and subsequent discussion on the Friday evening *Nights* show with Bryan Crump. All of the interviews are available on the Radio NZ website in the Nights section. Professor Allan Blackman (AUT) is continuing his series of *Elemental* podcasts, also available on the Radio NZ website.

We recently launched our flagship **IYPT2019 competition** for schools and school-age children. To celebrate the International Year of the Periodic Table the NZIC and the Royal Society of Chemistry New Zealand Branch are running an exciting video competition. Entries will be in the form of a 1-2 min video about a favourite element from the periodic table. There are 118 elements to choose from, so we hope that there will be lots of diversity in the entries! There are two judging categories: Junior/Intermediate School (Years 1-8) and Senior School (Years 9-13). Individual and group/team/class entries are both welcome. Each category will have three cash prizes and entries close on 1 October 2019. Please see the following webpage for more details and conditions of entry: https://nzic.org.nz/iypt-video-competition/.

The **NZIC2019 National Conference** preparations are well under way, and the website can be found here: https://nzic2019.co.nz/. The clock on the front page is counting down to the opening ceremony so head over to the site, get your abstracts lodged and registrations in before the early bird pricing closes. We have a fantastic line-up of international plenary and keynote speakers, a great conference program including the popular student oral presentation competition, a conference dinner at the amazing Christchurch Town Hall and even a beer tasting event for all you craft beer lovers. All we need now is YOU!

Another conference looming on the horizon is **Pacifichem2020**, at which many NZIC members will be presenting and involved in organising symposia. I take this opportunity to remind members that the more of you attend, the more NZIC gets back in remuneration as a constituent organisation member, and therefore the more we can do for members in terms of financial support for future Pacifichem conferences and events.

Finally, a reminder that **NZIC is on social media**! We're on Facebook (search New Zealand Institute of Chemistry) and Twitter (our handle is @_NZIC). Please follow us. On Twitter, please tag @_NZIC in chemistry related tweets, and use the hashtag #nzchem to build up a record of exciting NZ chemistry related news. Use #NZIC2019 for the conference.

Sarah Masters

NZIC President

Editor's note

The April 2019 issue of Chemistry in New Zealand included an obituary for Professor Brian Halton. Doug Wright, a former NZIC President, has brought to our attention that NZIC was involved with Pacifichem well before Brian's contributions began in 1990. Doug was the NZIC delegate at the inaugural organising meeting of Pacifichem in the early 1980s. This meeting of the organising bodies was held in Tokyo and included delegates from USA, Canada, Japan, Australia and Malaysia.

New Zealand Institute of Chemistry
supporting chemical sciences
July News

AUCKLAND

The University of Auckland

Events

MOTAT STEM Fair

The School of Chemical Sciences participated in the Super STEM Fair at the Museum of Transport and Technology (MOTAT) on 8 April. Dr *Joel **Rindelaub*** initiated and organised the stand for the School of Chemical Sciences with the help of *Katrina **Graaf***, Dr *Pooja **Yadav***, *Thandeka **Mbangwa***, Dr *Mansa **Nair***, *Geraldine **Powell*** and *Stephen **Lo***. Our stand included hands-on chromatography, cabbage-water acid-base chemistry, and vitamin C analyses. The Photon Factory also had displays at the Fair, which included methylated spirits rockets, holographs and diffraction gratings. Dr *Viji **Sarojini*** also participated in the event, supervising the construction of catapults with the Association of Women in Science.

Chemistry Olympiad Training

During the week of 15 April, The School of Chemical Sciences hosted a training week for the Chemistry Olympiad. The students (32 in total, 14 from outside Auckland) received lectures and training in laboratory skills by a team that included Associate Professor *Duncan **McGillivray***, *Katrina **Graaf***, and Dr *Sheila **Woodgate***, together with teachers from the Auckland area and Associate Professor *Owen **Curnow*** from the University of Canterbury.

ChemComm Symposium 2019: Chemistry for Global Challenges

On 15 April the School of Chemical Sciences hosted members of the Editorial Board of ChemComm for a symposium, with talks ranging from fluorine radiochemistry to new materials for water and energy challenges. The event was organised by Professor *Penny **Brothers***, Professor *Christian **Hartinger*** and *Anna **Simcock***. Two students won poster prizes at the symposium: Kristel Mae Castillo (supervisor: Dr *Erin **Leitao***) with *Polysilanes: the unabridged version towards metallosupramolecular cages for anticancer drug delivery* and Antony Melton (supervisor: Professor *James **Wright***) with *Green hydrogen peroxide on demand.*

School of Chemical Sciences Seminars

The School of Chemical Sciences at the University of Auckland hosted several seminars between March and May 2019:

Dr Jakob Andersson (Austrian Institute of Technology, Austria): *Model membranes optimised for the study of ion channels.*

Dr Oleksandr Mykhaylyk (The University of Sheffield, UK): *Application of small-angle X-ray scattering (SAXS) for structural characterization of materials.*

Professor Greg Qiao (The University of Melbourne, Australia): *CAP for surface, RAFT for blood, and Star vs superbugs.*

NZIC Auckland Branch Seminars

The University of Auckland hosted the following NZIC Auckland Branch Seminars between March and May 2019:

Dr *Daniel **Foley*** (University of Canterbury): *Adventures in natural product-like chemical space.*

Dr *Sheila **Woodgate*** (The University of Auckland): *Use of web-based activities and data analysis to promote learning of chemistry*.

Dr Richard Hopkinson (University of Leicester, UK): *Studies on formaldehyde biosynthesis, metabolism and toxicity.*

Top: Prize giving at the ChemComm Symposium; bottom: ChemComm Symposium

Drug candidate ready for clinical trial

Congratulations to Distinguished Professor *Margaret* ***Brimble*** and her group for having another drug candidate ready for clinical trials. Neuren Pharmaceuticals announced that NNZ-2591 has shown positive effects in a pre-clinical mouse model of Phelan-McDermid Syndrome (PMS). PMS is a rare genetic condition in which the most common characteristics are intellectual disability, delayed or absent speech, symptoms of autism, low muscle tone, motor delays, and epilepsy. NNZ-2591 is a synthetic analogue of the natural neurotrophic peptide cyclic glycine proline (cGP), and has also shown efficacy in a range of other pre-clinical models including for Parkinson's disease, traumatic brain injury, and multiple sclerosis. NNZ-2591 was first synthesised in the Brimble research laboratory and is following trofinetide (NNZ-2566) into the clinic.

Public lecture webcast

Professor *Cather* ***Simpson*** gave a public lecture webcast at Perimeter on 6 March. She highlighted her research in exploring how recent advances in the physics of light are transforming our ability to feed the planet safely and sustainably. See: https://insidetheperimeter.ca/farms-food-and-photonics-cather-simpson-public-lecture-webcast/

Staff Successes

George & Christine Sosnovsky Award in Cancer Therapy

Distinguished Professor *Margaret* ***Brimble*** went on a lecture tour in April in recognition of her being awarded the George & Christine Sosnovsky Award in Cancer Therapy. This included giving a very well received Sosnovsky Distinguished Lectureship at the University of Wisconsin Milwaukee, where George Sosnovsky was on the Faculty.

Fellow of the New Zealand Institute of Chemistry

Dr *Marija* ***Gizdavic-Nikolaidis*** has been elected Fellow of the New Zealand Institute of Chemistry. Marija has been serving as the Auckland branch secretary since 2008. In this role she is well known to the Auckland membership, and has been very active in promoting the Institute's activities over the past 10 years.

Early Career Research Excellence Award

Dr *Ivanhoe* ***Leung*** received a University of Auckland Early Career Research Excellence Award. Ivan was recognised for his contributions in biological chemistry and in green chemical science at the School of Chemical Sciences.

Student Successes

9th International Conference on Advanced Materials & Nanotechnology (AMN-9), Wellington

PhD student Andrew Chen (supervisor: Professor *Cather* ***Simpson***) for winning a first place poster prize with his poster, *New on the physics menu: superconducting sandwiches!*

PhD student Roshan Khadka (supervisors: Professor *Jadranka* ***Travas-Sejdic*** and Dr Andrew Kralicek of Plant and Food Research), whose poster, Bioelectronic *nose using insect olfactory receptors* was highly commended.

Student Prizes at the School of Chemical Sciences

The School of Chemical Sciences held a prize giving function on 29 March to celebrate the prizes won by some of our students in 2018. These included the Baldwins Chemistry Prize for the top student in CHEM 392 (Kyle Fraser), the Dilshika Weerasekera Memorial Prize for the best Maori or Pacific Island student in CHEM 110 and CHEM 120 who continues on with stage 2 chemistry courses (Neihana Waitai), the Charmian J. O'Connor Scholarship for the top female student in CHEM 110 and CHEM 120 who continues on with second-year chemistry courses (Shanya Jayatissa), the Grace Phillips Memorial Prize Memorial Bursary to the top BSc(Hons) student (Tasha Steel) and the New Zealand Institute of Chemistry (Auckland Branch) Prize to the runner up BSc(Hons) student (Alex Mayer).

2018 LH Briggs Prize

Congratulations to Dr Emma Davison (supervisor: Associate Professor *Jon* ***Sperry***) for being awarded the 2018 LH Briggs Prize for Best Doctoral Thesis. Emma was also one of the five awardees of the Vice Chancellor's Prize for Best Doctoral Thesis and was placed on the Dean's List for the quality of her thesis. Congratulations also to Dr Samuel Davidson (supervisor: Associate Professor *David* ***Barker***), who was a close runner-up for the LH Briggs Prize. Samuel was also placed on the Dean's list and was a University finalist for the Vice Chancellor's Prize for Best Doctoral Thesis.

2019 Vice Chancellor's Best Doctoral Thesis Award

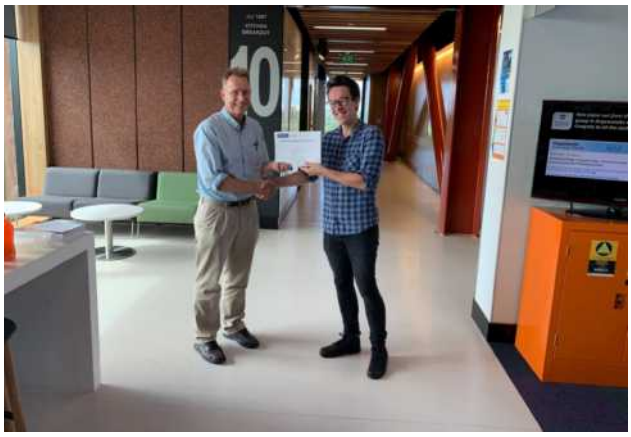
Dr Emma Davison (supervisor: Associate Professor *Jon* ***Sperry***) was awarded one of the University of Auckland Vice Chancellor's Best Doctoral Thesis awards, given to the top 5 PhD students of the 392 that completed the PhD examination process in 2018. Emma Davison received both the LH Briggs Prize and Vice Chancellor's Best Doctoral Thesis Award

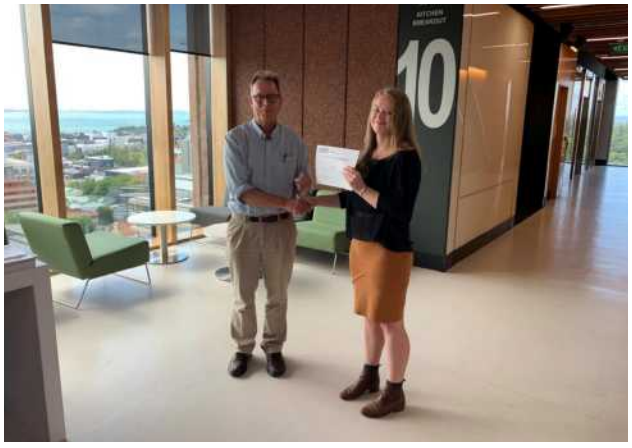
Massey University (Auckland Campus)

Professor *Peter* ***Schwerdtfeger*** has been awarded the Dan Walls medal by the New Zealand Institute of Physics (NZIP). The award is presented annually to the physicist working in New Zealand for at least the past ten years who is deemed to have made the greatest impact both nationally and internationally in his/her field of research. The medal is named after the late Professor Dan Walls (FRS) who made outstanding contributions to theoretical physics, in particular to the field of quantum optics.

Jon ***Kitchen*** welcomes MSc student Nethmie Jayasooriya to his group. Nethmie is working on luminescent lanthanide self-assemblies.

In April, *Marie-Anne* ***Thelen*** attended the ACS conference, *Chemistry for new frontiers*, held in Orlando. With around 15,000 attendees, the presentations covered diverse topics such as sensing human behaviour




Top left: Kyle Fraser receiving the Baldwins Chemistry Prize. Top right: Neihana Waitai receiving the Dilshika Weerasekera Memorial Prize. Middle left: Shanya Jayatissa receiving the Charmian J. O'Connor Scholarship award. Middle right: Tasha Steel receiving the Grace Phillips Memorial Prize Memorial Bursary. Bottom left: Alex Mayer receiving the NZIC Auckland Branch Prize.

Emma Davison received both the LH Briggs Prize and Vice Chancellor's Best Doctoral Thesis Award

with smart garments; the chemistry of finding extraterrestrial life; new transparent wood which absorbs and releases heat; transformation of mouse brains into fully intact, optically transparent material, and super-resolved fluorescence microscopy.

Auckland University of Technology

New Faces

We have welcomed three French interns to the AUT Chemistry Research Lab. Benoit Wagnon from Lyon will be working with Dr *Marcus* ***Jones*** and *Guillaume* ***Hopsort*** and Jules Martin from Toulouse will be working with Dr *Jack* ***Chen***.

In addition, we welcomed 3rd year research project students Alyssa Keenan and Joanne Salam who are working with Dr *Jack* ***Chen*** and Roisin Mooney (Bsc(Hons)) and Komalpreet Kaur (PgDipSc) who will be working with Dr *Marcus* ***Jones***.

Events

Nobel Laureate Seminar

AUT and the NZIC co-hosted a seminar by Nobel Laureate Professor Sir J. Fraser Stoddart (UNSW and Northwestern University) entitled, *The rise and promise of artificial molecular machines based on the mechanical bond* where he provided an overview of the research that led to his award of the Nobel Prize and some of the more recent results from his group relating to the preparation of molecular machines.

AUT Seminars

AUT hosted the following seminars from March to May 2019:

Associate Professor Arthur Winter (Iowa State University): *New strategies to achieve photocaging using visible light.*

Professor John Goodwin (Coastal Carolina University): *The N-bound peroxynitrito-cobalt intermediate in porphyrins*

Professor Paul Sampson (Kent State University): *Development of photoactivatable nitroxyl donors – new sources of HNO with spatial and temporal control.*

Invited Talks

Dr *Jack* ***Chen*** gave an invited talk at the University of Canterbury entitled, *Applying concepts from nature for the design of catalysts and smart chemical networks.*

Congratulations

Ruth Cink, PhD student of Professor *Nicola* ***Brasch***, successfully defended her PhD thesis.

Professor *Nicola* ***Brasch*** was appointed as an Associate Investigator of the Maurice Wilkins Centre for Molecular Biodiscovery.

Dr *Marcus* ***Jones*** and Dr *Jack* ***Chen*** were appointed as Associate Investigators of the MacDiarmid Institute.

An MBIE Smart Ideas proposal led by researchers in the Department of Chemical and Materials Engineering at the University of Auckland for which Dr *Cameron* ***Weber*** is a Key Researcher was successful in the concept stage and invited to the full proposal round.

CANTERBURY

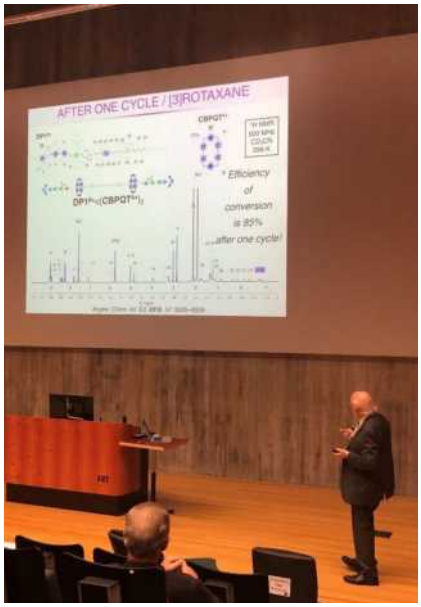
BBQ

The annual NZIC Canterbury Branch BBQ was held at the Ilam Homestead on 27 February. Another well attended gathering wherein numerous students and faculty were fed!

NZIC Seminar

Peter ***Saunders***, Distinguished Scientist, Measurement Standards Laboratory of New Zealand (MSL), gave an NZIC Seminar in association with the New Zealand Institute of Physics on 20 May entitled: *Cheese, platinum and fundamental constants; what is the redefinition of the SI units all about?*

Abstract: As of 20 May 2019, the unit of the kilogram will no longer rely on an unstable artefact guarded in a triple locked vault in Paris, but on the invariability of Planck's constant, *h*. Similarly, three other base units, the kelvin, the ampere and the mole will be redefined in terms of fundamental constants. This presentation will describe how we have reached this



Fraser Stoddart's visit to AUT

point and why, and what it means for the future. One advantage of using fundamental constants to define our units is that any physical relationship that relies on that constant can be used to realise the unit. This will be illustrated by looking at how several equations of state have been used to define Boltzmann's constant and can now be used to realise the kelvin.

Biography: Peter has been working at MSL since 1993 in the area of radiation thermometry, carrying out research in both metrological radiation thermometry and industrial applications. He has worked as a visiting researcher for eight months at IMGC (now INRiM – the National Institute of Metrological Research) in Italy, where he investigated the application of CCD cameras to radiation thermometry. Peter has published more than 70 papers and articles on radiation thermometry-related topics. He won the NZ Royal Society Cooper Medal in 2004 for research he carried out in understanding the physical basis of equations used in the calibration of radiation thermometers. He represents New Zealand on the International Committee for Weights and Measures (CIPM) Consultative Committee for Thermometry (CCT) and is an active member of the CCT Working Group on Non-Contact Thermometry. Peter is a technical expert for many IANZ accredited thermometry laboratories in New Zealand.

The seminar was well attended with some 50 attendees. A recording of the presentation can be seen here: https://echo360.org.au/media/a590d663-7391-4540-8d81-c3db-b1e0340c/public

University of Canterbury

Awards and appointments

Professor *Ian* ***Shaw*** has been awarded the degree of Doctor of Science from the University of Bath.

Ian's DSc was awarded for studies in toxicology and food safety with an emphasis on science communication. Well done!

MANAWATU

Paul ***Plieger*** was promoted to Deputy Head of the School of Fundamental Sciences at Massey University.

The ***Plieger*** group celebrated two graduations: Liam McGarry (BSc (Hons)) and Michael Brown (MSc). For his thesis, Liam worked on nickel(II) cages and Michael worked on pyrazine triangle complexes. There were three new additions to the group: Sidney Woodhouse (PhD), Marryllyn Donaldson (MSc) and Brodie Matheson (BSc (Hons)).

Anne Sophie Doyon joined the ***Filichev*** group as part of her internship. Suraj Patel joined the ***Rowlands*** group for his BSc (Hons)

Sam ***Brooke*** of the ***Waterland*** group was featured on *The Spinoff*. In the article Sam described the importance of nanomaterials like molybdenum disulfide.

Michael Hirscher of Max Planck Institute for Intelligent Systems, Germany, gave a seminar on *Hydrogen storage in nanoporous materials* on 27 February.

Duncan McMillan of Delft University of Technology, The Netherlands, gave a talk on, *Surface chemistry approaches for advanced enzymology* on 8 March.

David Thorn (Formerly of DuPont and retired from Los Alamos National Laboratory, USA) spent more than 3 months at Massey University hosted by *Geoff* ***Jameson*** and *Shane* ***Telfer*** and sponsored by the Massey University International Visitor's Fund and MacDiarmid Institute. He worked on perovskite growth in MOF pores and gave a talk entitled, *Analyzing patterns in awareness and adoption of technology* on 17 March.

The NZIC student event was held on 3 April. 32 people attended the event. The event was jointly organised by *Sam* ***Brooke*** and *Becky* ***Severinsen***. *Barry* ***Scott*** was the Master of Ceremonies. Sujin Lee of UCOL won the NZIC prize for Level 6 chemistry. Shikeale Harris of the ***Telfer*** group won the NZIC 300 Level prize.

Attendees at the NZIC Student Event with Barry Scott as MC

Left: Sujin Lee of UCOL receiving her NZIC Level 6 Chemistry Prize from Catherine Whitby. Right: Shikeale Harris receiving her NZIC 300 Level Chemistry Prize from Catherine Whitby.

On the 10 April *Daniel* ***Foley*** of the University of Canterbury gave a talk on, *Adventures in natural product-like chemical space.*

On 22 May, *Shane* ***Telfer*** gave a talk on metal-organic frameworks at Techweek Industry Interface, at the Aotea Centre, Auckland.

Te Papa featured metal-organic frameworks as part of its Future Cities exhibit. Staff at Te Papa consulted with members of the ***Telfer*** group for this exhibit.

Subo ***Lee*** attended the First International School on Advanced Porous Materials (MOFSchool) held at Lake Cuomo, Italy held on 17-21 June. The conference included lectures from internationally reputed scientists in the porous materials community.

OTAGO

University of Otago, Department of Chemistry

While announced earlier this year, the ceremony was held for the presentation of the Otago Teaching Excellence awards, where our very own *Dave* ***McMorran*** (Dr Dave to his students) was recognised for his outstanding contribution to teaching at Otago. Dave runs the highly successful CHEM191 course with over 2000 (!) students and always has an open door for any of them, as well as supporting wider teaching activities in the Department.

The special issue of *Chemistry - An Asian Journal* celebrating and highlighting the breadth and depth of NZ chemistry has been published, with a front cover feature and guest editorial by Professor *Sally* ***Brooker***. Thanks to all the authors from around the country who contributed to this impressive display of our chemistry. Please note that the NZIC is part of the society which publishes this journal, so always benefits financially for every paper published with an NZ corresponding author – so please continue to submit your papers to this journal!

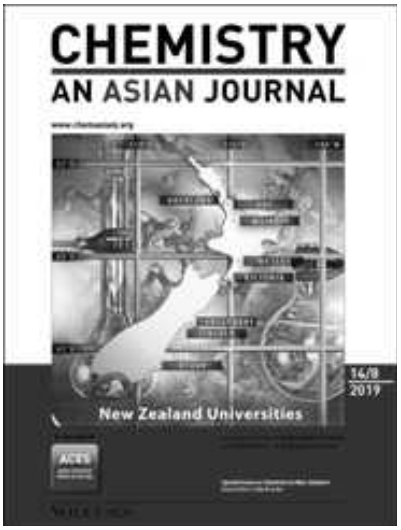
Rob Taylor (Deputy Principal, Musselburgh Primary School, Dunedin) is working with *Dave* ***Warren***, *Elaine* ***Burgess*** and *Nigel* ***Perry*** on the Royal Society Te Apārangi Science Teaching Leadership Programme. He is following up a discovery by Musselburgh students on plant growth promoters from mānuka, made in the Unlocking Curious Minds programme. MSc student *David* ***Rubin*** has started work with *Nigel* ***Perry*** and *Catherine* ***Sansom*** on chemotaxonomy of Celmisia, the endemic New Zealand alpine daisies. These are taonga plants – tikumu - for Ngai Tahu and other iwi.

Jaydee ***Cabral*** gave an oral presentation and was awarded "Best Presentation" by the program committee of the ICSB 2019: 21st International Conference on Bioengineering and Sustainability, Tokyo, Japan, 22-23 April 2019.

The group of *Anna* ***Garden*** welcomed *Calum* ***Gordon*** who started in the group as a BSc (Hons) student working on methods for modelling electrochemical potential in periodic DFT simulations. *Stephanie* ***Lambie*** and *Geoffrey* ***Weal***, also of the Garden group, published their first paper on the structures of Pt and Au nanoclusters in *Nanoscale Advances*.

The group of *Sally* ***Brooker*** has had a number of visitors. Professor Garry Hanan (Montreal) and two of his PhD students, Olivier Schott and Thomas Auvray, visited for the Otago Future Fuels (OFF) conference and to pursue collaborative research with Sally's team, supported by their joint Catalyst Seed grant from MBIE. In a reciprocal visit, Sally's PhD student *Abudullah* ***Abudayyeh*** is following in *Fola* ***Akoguns's*** footsteps, and is currently working with them in Montreal.

Dave McMorran (right) being presented with his Otago Teaching Excellence award from Professor Vernon Squire, outgoing DVC Academic at the University of Otago. Photo credit: Sharron Bennett



Front cover of the special "New Zealand" issue of *Chem. Asian J.*

Professors visiting the University of Otago, hosted by Professor Sally Brooker. Left to right: Garry Hanan (Montreal), Silvia Giordani (DCU), Ali Malik (KIT), Annie Powell (KIT), Sally (Otago).

Honorary Professor at the University of Otago, Professor *Annie* ***Powell*** (Karlsruhe Institute of Technology), was awarded a William Evans fellowship to visit us again in 2019, and presented a 4th year lecture course and department seminar. Professor Silvia Giordani (Dublin City University) also visited us briefly to further our nano-onion collaboration.

Brookers Bunch welcomed two Honours students in February, *Matt* ***Robb*** and *Lachlin* ***Gaudin***. Dr *Santi* ***Rodríguez-Jiménez*** finished working in Sally's team in May, to move to Cambridge University and take up a postdoctoral fellowship in the group of Professor Erwin Reisner in the area of solar fuels. Her second year PhD student, *Luca* ***Bondì***, (co-tutelle with Florence) has travelled to Florence, for the second period of 4 months working with Professor Totti in Florence.

Sally presented a plenary lecture at EsMolNa in Elche, Spain, and then travelled to Montreal to visit Professor Hanan, and then to Quebec City for the annual Canadian Chemical Society conference to give an invited keynote lecture at the Barry Lever celebration session.

The group of *Keith* ***Gordon*** is pleased to welcome Deok-Ho who has joined the group temporarily to attempt

to study recombination rates in dye sensitised solar cells.

Keith ***Gordon*** was awarded the 2019 Royal Society of Chemistry Australasian Lectureship. Keith will be giving lectures across New Zealand and Australia on his research over the next 12 months.

Fatema ***Ahmed*** has started her PhD journey with study on microencapsulated fish oil using vibrational spectroscopic techniques. *Samanali Garagoda* ***Arachchige*** has been writing up her study on consolidant penetration into harakeke fibres using Raman microscopy.

Joe ***Mapley*** had papers published in *Chemistry – An Asian Journal* (*RuII and IrIII complexes containing ADA and DAD triple hydrogen bonding motifs: potential tectons for the assembly of functional materials*) and *Journal of Coordination Chemistry* (*Triphenylamine-substituted 2-pyridyl-1,2,3-triazole copper(I) complexes: an experimental and computational investigation*). He gave a talk at the MacDiarmid Institute Cluster Hui in Kerikeri detailing the spectroscopic techniques employed within the Gordon group.

Georgina ***Shillito*** is currently preparing for her PhD defence. In July she will begin a three month internship funded by the MacDiarmid Institute at the Office of the Prime Minister's Chief Science Advisor. Her project will focus on the application of current and future solar energy technologies in New Zealand.

Sara ***Miller***, *Joshua* ***Sutton*** and *Kārlis* ***Bērziņš*** had a paper published in the *Journal of Physical Chemistry Letters* (*Application of low frequency Raman scattering spectroscopy to probe in situ drug solubilization in milk*).

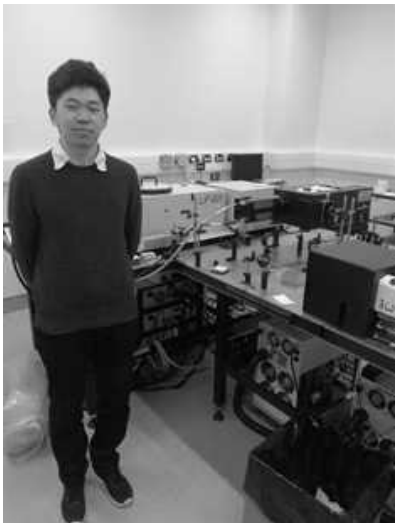
WAIKATO

The branch held a welcome barbecue for students as a joint venture with the Chemistry Social Club at Waikato. This was well attended and enjoyed by all.

Scion

Scion's polymer chemistry capability and links into the industry have been recognised at the New Zealand Plastics Industry Design Awards. A completely bio-based adhesive marketed as Ligate™ (led by *Warren* ***Grigsby***) won the Research and Innovation Award, and a biodegradable grape vine clip formulated for the wine industry (led by *Dawn* ***Smith***) picked up the Highly Commended – Best Supplier Partnership Award.

Professors visiting the University of Otago, hosted by Professor Sally Brooker. Left to right: Ali Malik (KIT), Annie Powell (KIT), Garry Hanan (Montreal), Sally (Otago), Silvia Giordani (DCU).



Deok-Ho (Korea University)

Ilena ***Isak*** and *Suzanne* ***Gallagher*** recently published work describing a new mechanism (retro Diels-Alder) that occurs in wood during kiln drying that causes an unsightly brown stain. This work will help develop new wood treatments and drying schedules that minimise wood loss.

Alankar ***Vaidya***, *Ibrar* ***Hussain***, and *Dawn* ***Smith*** along with *Marc* ***Gaugler*** have published on the grafting of chitosan to a biodegradable polymer to impart added functionality including potential antimicrobial action.

Kate ***Parker*** and *Jamie* ***Bridson*** have been off to the beach carrying out work into the distribution and types of microplastics that are washing up on New Zealand shores as part of a project to identify possible sources of contamination and to develop strategies to protect our coasts and sea life.

Stefan ***Hill*** and *Marie Joo* ***Le Guen***, along with Sean Taylor and Ashleigh Browne (AgriSea Ltd) have just returned from a visit to the Australian Synchrotron SAXS/WAXS beamline. The work carried out in Australia was to characterise the crystal structures of cellulose found in New Zealand seaweeds. Ashleigh braved the less than balmy waters, a swell, and a rip to gather fresh specimens. *Laura* ***Raymond*** and *Stefan* ***Hill*** travelled to Pharmalink in Nelson where a successful trial of extracting bark with supercritical CO_2 was undertaken – at near tonne scale.

In February, Scion hosted the conference, *Bioplastics and biocomposites – innovative building blocks of the emerging bioeconomy*. Around 100 delegates from Germany and New Zealand attended the one-day event. The conference covered topics on the sustainability of the growing biopolymer market and the ways that the European Union and New Zealand were integrating these fossil-based plastic replacements. Scion contributed five speakers: *Florian* ***Graichen***, *Marie Joo* ***Le Guen***, *Kate* ***Parker***, *Dawn* ***Smith*** and *Elspeth* ***MacRae***, along with *Lou* ***Sherman***

and *Jeremy* ***Warnes***. They covered areas ranging from the economics of biopolymers in New Zealand to chemically designed biopolymers for specific purposes.

Accepting the Awards for the Biopolymers and Chemicals team were (L-R): Dr Florian Graichen, Jeremy Warnes, Steve Wilson, Dr Dawn Smith, Marc Gaugler

WELLINGTON

VUW officially opened their brand-new suite of Jeol NMR spectrometers, comprising two 500 MHz and one 600 MHz magnets. In brief, there is a 2 channel 500 MHz NMR spectrometer with an inverse detection proton sensitive auto tuneable HC probe for routine analysis. The other 500 MHZ NMR spectrometer has 3 channels that can fit both a tuneable X-nuclei indirect detection probe with a variable temperature range from -120°C to 150C or a XPH broadband probe for P-X decoupling where X is between the ^{15}N and ^{13}C frequency, with a variable temperature range between -100°C and 150°C. The 600 MHz NMR spectrometer has a 5 mm SuperCOOL cryogenic (liquid nitrogen) probe and a room temperature indirect detection probe. All of the spectrometers are fitted with autosamplers, and the variable temperature units can be used on any of the instruments. Many thanks to *Ian* ***Vorster*** who had the vision of taking a hole-in-the ground and transforming it into a world-class NMR facility. The next step is the introduction of the helium recycling system to be incorporated later in 2019.

Of course, with the opening of the new suite, we had to say goodbye to our old 300 and 500 MHz Varian INOVA spectrometers. They have served VUW for the past 15 - 20 years!

Associate Professor *Peter* ***Northcote*** and Dr *Rob* ***Keyzers*** have been named among the top one percent of researchers cited in the field of pharmacology and toxicology. Their continual contribution to an annual review on "Marine Natural Products" in *Natural Product Reports*, in collaboration with scientists from the University of Canterbury, University of Auckland and University of Waikato, are routinely listed as "Highly Cited Paper" or "Hot Paper" in Web of Science. Well done Peter and Rob!

VUW continues to host students and interns from overseas. We recently said goodbye to Howard Leek (***Fulton*** group), Fergus Bramley (***Timmer*** group) and Amirita Datta (***Goreham*** group) who were here on a nine month exchange from the University of York. We welcome Malte Jürgenssen from Julius-Maximilians-University of Würzburg who is doing a 3 month internship in the ***Coles*** group.

SCPS was visited by Distinguished Professor *Bill* ***Denny*** in April. He talked about his involvement in bringing drugs to clinical trials.

VUW NMR spectrometer suite

Article

Subtleties and complexities: some musings on teaching first year chemistry

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Keywords: *first year chemistry, phase diagram, solubility product, teaching*

I've been teaching first year chemistry for over a quarter of a century. So you'd think I'd have it all sorted out by now. But no – every year I come across something that needs more thought, or that doesn't make obvious sense, or that appears to just be plain wrong. I generally put these oddities to one side and continue the lecture, but I've finally come to the conclusion that I should put these concepts up for discussion and see what others think. So what follows are eight topics that can be found in any first year chemistry course, with which I have problems.

Phase diagrams

Phase diagrams appear in all first year chemistry textbooks, generally in chapters on solids/liquids/gases, or, more generally, states of matter. And they are generally taught without any great comment, as they are pretty much self-evident – each region in a phase diagram shows under what conditions of pressure and temperature the solid, liquid and gaseous forms of a substance exist (not to mention the shadowy supercritical region!) But are they really self-evident?

Consider the phase diagram of bromine, shown in Fig. 1. I spent quite a bit of time with bromine during my PhD, making up countless aqueous solutions of the stuff to brominate metal-coordinated imidazoles.[1–3] And I always loved seeing the beautiful (but deadly!) red vapour above that very dense dark-coloured liquid (I've chosen bromine as my exemplar simply because of the fact that its vapour is visible, but what follows can be applied to any liquid). And this got me thinking one day. You see, the phase diagram of bromine shows that, at atmospheric pressure and room temperature, bromine exists as a liquid. So why can we see vapour above the liquid? The liquid isn't boiling, so the liquid and vapour phases are not in equilibrium. But yet it looks as though the vapour can co-exist with the liquid at atmospheric pressure and room temperature. But that's not what the phase diagram, at first glance, tells us. There's obviously more to this than meets the eye.

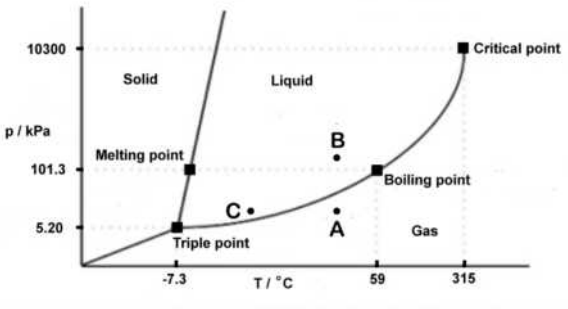

Fig. 1. An approximate phase diagram of bromine (Br_2), not to scale

Let's delve a little deeper then, and do a thought experiment. Let's take an evacuated flask, introduce some pure gaseous bromine, and then seal the flask, so that nothing else can be added. And let's assume the composition of the system is now given by point A on the phase diagram. This is the type of system to which unary phase diagrams strictly apply – a single- component closed system. Let's now suppose we want to move from point A to point B on the phase diagram. This will involve us increasing the pressure at constant temperature. How do we do this in a closed system, given that, in its current state, any pressure in the flask is exerted solely by the bromine vapour? We can't heat the flask, as our journey from A to B is going to occur at constant temperature. Therefore, our only option is to equip the flask with a mechanical piston, which will allow us then to vary the pressure by changing the volume. So let's do this. We will start at point A and slowly depress the piston, gradually increasing the pressure in the flask. The pressure will continue to increase until we encounter the equilibrium line – at this point the bromine vapour will start to condense to a liquid, and the system will now contain two phases – gas and liquid – that are in equilibrium. The condensation proceeds while constant pressure is maintained with the piston (the volume of the system will necessarily decrease as the condensation occurs) until *all* of the vapour has condensed. Further increasing the pressure takes us to point B on the phase diagram, where, again we have only a single liquid phase present – i.e. *no vapour*. But how can that possibly be? Surely all liquids have a vapour pressure, and therefore there must be some vapour above the liquid at all times? Well, in this case, no. We are altering the pressure mechanically, *as we have to do for an isothermal change in a single-component system*, and so as we increase the pressure to obtain complete liquefaction, the volume decreases to the point where the piston contacts the liquid and there is physically no room for vapour to be present.

Let's then try another thought experiment. This time, we're going to carry out the same change of phase, from gas to liquid, but this time we will accomplish this by decreasing the temperature while working at constant pressure – in other words, we will go from point A to C on the phase diagram. So, we begin with our enclosed sample of bromine vapour in a sealed container, and start decreasing the temperature. Obviously, the first thing that is going to happen is that the pressure in the vessel will decrease. Remember, it's a closed, single- component system, so we can't add more bromine gas (or any other gas, for that matter) to maintain the pressure. So again, we are forced to equip our vessel with a piston in order

to maintain the pressure in the vessel *mechanically*. And once we do this, we can make exactly analogous arguments to those above – as we lower the temperature, we must depress the piston in order to keep the pressure in the vessel constant. We do this until we hit the liquid/gas equilibrium line, at which point, condensation starts to occur at constant temperature (again, the volume of the system will change significantly during this process) and we have two phases coexisting in equilibrium. When condensation is complete, the temperature will again lower, and we will have only a single phase, liquid bromine, present again (no vapour), owing to the fact that the piston will again be contacting the liquid.[4]

There are two major misconceptions, in my experience, with phase diagrams. Firstly, the fact that they apply strictly to closed systems is rarely, if ever, specified, and secondly, the implications of the fact that only a single component is present are never explored. Phase diagrams are often explained in terms of a liquid in a beaker which can be heated or cooled, with the pressure of the system being the air pressure exerted by the atmosphere. And therefore, straight away we don't have a single-component system – we have both oxygen and nitrogen (and all the other components of air) which will be dissolved in the liquid, and this makes a difference! Likewise, it is assumed that the pressure in such a system can be regulated by altering the external air pressure – this again runs into the same problem. There are explanations in the literature involving the air above the liquid being saturated with the vapour of the liquid in question, but that's cheating – it's still not a single-component system![5]

So single component phase diagrams are only applicable to extremely specialised conditions, and it is imperative that examples be chosen very carefully in any discussion of these common first year concepts.

Solubility products

Let's start this section by looking at a multi-choice question that could be found in any first year chemistry exam anywhere in the world.

Use the following K_{sp} values to determine which of the salts has the greatest molar solubility in pure water at 25.0 °C.

Compound	**K_{sp} (25.0 °C)**
AgBr	5.0×10^{-13}
$HgBr_2$	1.3×10^{-19}
$AuCl_3$	3.2×10^{-25}
$Mg_3(PO_4)_2$	6.3×10^{-26}

A) AgBr

B) $HgBr_2$

C) $AuCl_3$

D) $Mg_3(PO_4)_2$

A pen and paper, calculator, and a little thought, should show that the correct answer is D. (A little hint to any students who may be reading this – the correct answer is always D in any multi-choice question that involves calculation – it means you have to do the maximum number of calculations to get the correct answer).

Now let's stop and think about this a little. We teach from day one in lectures on equilibrium that the magnitude of the equilibrium constant shows how far towards completion the equilibrium position lies – the larger the value of *K*, the further towards completion. And yet here, we find that the salt with the *smallest* value of *K* is the *most* soluble, meaning that a larger amount (and indeed mass) of $Mg_3(PO_4)_2$ will dissolve in 1 litre of water than any of the other salts. We must conclude from this that the equilibrium position for a saturated solution of $Mg_3(PO_4)_2$, the salt with the smallest K_{sp}, is further towards the right hand side than for any of the other salts. Does this not seem more than a little counterintuitive?

Well, to answer my own rhetorical question, yes it does. However, the reason for this supposed problem, as anyone who has ever taken first year chemistry should know, is that the K_{sp} expressions for all of the salts are different, and therefore we cannot simply compare their numerical values. In fact, this is a potential problem with all equilibrium constants, but is most often brought into focus in solubility product calculations, as the electrolytes involved can have different cation to anion ratios, in contrast to, for example, K_a expressions which refer overwhelmingly to monoprotic acids. Thus, it's easy to pick the strongest acid from a list, simply by looking at the K_a values, but, as shown in the example above, it's a little more complicated to choose the most soluble salt. So just what use are solubility products, other than providing a nice example of equilibrium for first year chemistry courses? Would you consult a table of K_{sp} values, or a table of solubilities in g/100 mL, if you wanted to know what mass of a particular salt will dissolve in a specific volume of water? I know which one I'd choose. Bear in mind also that K_{sp} values are only given for sparingly soluble salts, owing to the whole activity/concentration thing, making them even less useful in any practical situation. Possibly the only situation where K_{sp} values are useful is to debunk one oft-quoted fallacy – that silver chloride (or insert the name of any sparingly soluble salt here) is insoluble. No it's not. Its K_{sp} value is not zero, therefore *some* dissolves….

And finally on this topic, we need to be careful when working with the very low concentrations that are often found in solubility calculations. Consider, for example, the sparingly soluble salt Ag_2S, for which $K_{sp} = 8 \times 10^{-51}$ (measuring that must have been fun for starters!). Assume we stir some Ag_2S in a 0.00001 M solution of $AgNO_3$ and allow the system to come to equilibrium. Calculate the sulfide ion concentration in the resulting saturated solution.

Solving this problem using the usual methods gives $[S^{2-}] = 8 \times 10^{-41}$ mol L^{-1}. Having obtained this answer, most students would continue on to the next question without

a moment's thought. But let's look at what this answer actually means. Using the Avogadro constant, *L*, = 6.022 × 10^{23} mol^{-1}, we can calculate that, in 1 L of the above solution, we will have 8 × 10^{-41} mol × 6.022 × 10^{23} mol^{-1} = 5 × 10^{-17} S^{2-} ions. As one of my students once wrote in a dissertation, this is a truly homeopathic amount. Once we get below concentrations of ~10^{-23} mol L^{-1}, what do the numbers actually mean? To tell you the truth, I'm not exactly sure myself, but it is the sort of thing that better students will pick up on, and therefore you need an answer at the ready. And an answer of "I don't know" is perfectly valid, provided you can explain why it is you don't know.

Orbitals

This isn't so much a first year chemistry problem, as a problem with what is taught in earlier years. For some reason, many students come to university very much wedded to the idea of 'shells' when discussing atomic structure, and their knowledge of the electron configurations of the first 20 elements is given in terms of 2,8,8,2 electrons in K, L, M, etc shells. These are invariably accompanied by diagrams of the requisite number of electrons in circular orbits around a nucleus. Why do we persist in teaching this approach at High School when we could be teaching the students about orbitals from the very beginning? To my mind, *s*, *p* and *d* orbitals are not conceptually difficult, and the sets of quantum numbers that designate such orbitals can be obtained by following very simple rules. Why teach the students something that is demonstrably false in their early years, only to then have to teach them 'the truth' later on?

Formula triangles

Calculations are a central point of most chemistry exams, and in order to carry these out, students need to know how to remember (or figure out) the formulae to use. Even if the formulae are given to the students in the exam (something I'm totally against, but about which I'm slowly losing the battle), they will be of little use if the student cannot rearrange them. And this is where I have a huge problem with what students are being taught at High School by some teachers – formula triangles.[6]

$$a = \frac{b}{c}$$

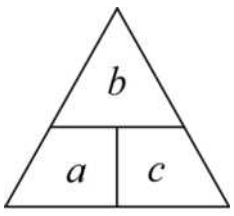

Fig. 2. Left: An equation (the right way). Right: a formula triangle (the wrong way)

Many is the time I've seen these triangles in exam scripts, where they have been used (or have been attempted to have been used) to rearrange simple equations such as $m = M \times n$, or $n = cV$. And invariably, there will be students who get this wrong. And the reason they get the rearrangement wrong is quite simple – *in order for these triangles to work, the student has to get the equation correct in the first place*. There's not much point in rearranging an incorrect equation correctly. The fact that these triangles appear so often in exams must mean that students are being taught this at school. So my question is, why are students apparently not being taught the 'correct' way of rearranging equations, namely multiplying or dividing both sides of the equation by one of the components of the equation (or adding or subtracting one of the components of the equation to or from both sides of the equation)? This is not difficult stuff - well I'd like to think that this was the case anyway, but in my experience, many students have difficulty with *anything* involving fractions. Teaching the students formula triangles merely provides them with a false sense of security, and, as they apply only to multiplication and division, most certainly doesn't prepare students to rearrange something as relatively straightforward as $H = U + pV$. I would implore all High School teachers to consign these triangles to the place where I'd like to see Venn diagrams go (hint: it's fiery and sulfurous).

Dimensional analysis

One of the most common questions I am asked by students is "What equations do I have to learn for the exam?" Well, if dimensional analysis were more widely taught, I'd say "You don't have to learn any." As implied in the above section, students do have trouble remembering equations. However, if they know the unit of a particular quantity, they can work out the equation involving that quantity rather than having to remember it. Let's use the stoichiometric equations to illustrate this. All that students have to know is that concentration and molar mass are measured in mol L^{-1} and g mol^{-1}, respectively, and they will never get the equations for these quantities incorrect. The unit mol L^{-1} implies a quantity measured in the unit of amount divided by a quantity measured in the unit of volume – in other words $\frac{n}{V}$.

Therefore, the equation for concentration is given by Eq. 1:

$$c = \frac{n}{V} \qquad \text{(Eq. 1)}$$

Likewise for molar mass. The unit g mol^{-1} implies a quantity measured in the unit of mass divided by a quantity measured in the unit of amount – in other words $\frac{m}{n}$.

Therefore, the equation for molar mass is given by Eq. 2:

$$M = \frac{m}{n} \qquad \text{(Eq. 2)}$$

Having obtained the correct forms of these equations, the students can now rearrange them (NOT using triangles) into any form, and there is now absolutely no excuse for these equations ever being written incorrectly ever again. This approach works for any equation, not matter how simple or complicated, and only involves knowing units. I would love to see this taught more, but given that the way of the future appears to be supplying equations to the students, I can't see it happening.

What does 'spontaneous' mean?

Thermodynamics is often 'sold' in first year chemistry on the fact that one can predict in which direction chemical reactions (or, less commonly, physical processes) will proceed. Thus, the students endure the concepts of *q*, *w*, Δ*U*, Δ*H*, and Δ*S*, before they finally get to the holy grail of Δ*G*, and the apparent ability to determine the direction of spontaneous change from the sign of this. They are told that if Δ*G* is negative, the reaction will proceed spontaneously in the forward direction, and if Δ*G* is positive, the reverse reaction will occur spontaneously. The problem then comes when Δ*G* = 0 and the system is at equilibrium. The better students will say at this point "But surely both the forward and reverse reactions are occurring spontaneously?" And they're right – they are. So how can this be? Well, in this case, it's more a matter of semantics as to what is meant by 'spontaneous', and we should really talk about 'a spontaneous change in the composition of the reaction mixture'. If we are at equilibrium, even though both the forward and reverse reactions are occurring, there is no net change in the relative amounts of the reactants and products, and so the composition of the mixture does not change. However, if Δ*G* for a particular process is negative, then we should say that the reaction mixture, which is initially at equilibrium, will undergo a change in composition that will give a greater amount of products and a smaller amount of reactants, and that this will continue until equilibrium is again attained. The same, but opposite, argument obtains for the situation where Δ*G* is positive.

Why do we pretend that organic reactions occur cleanly to give a single product?

Chemistry is a hell of a lot easier on a whiteboard than in the lab. On a whiteboard, you don't have to worry about incomplete reactions or by-products, and what one has to do in the real world to isolate pure products from reaction mixtures containing all sorts of possible impurities. We blithely show chemical equations (some of them are even balanced) depicting organic reactions involving substrates, catalysts and solvents, and from this melange magically emanates a single product. Let's be honest – who amongst us has ever carried out an organic reaction that didn't require some sort of purification procedure? We require that students know the mechanisms of (generally) S_N1 and S_N2 reactions backwards, but we don't teach them the reason why (for example) such reaction mixtures are washed with water, extracted three times with dichloromethane (and no – it's NOT called DCM…) and stirred over anhydrous magnesium sulfate – of course, it's all blindingly obvious to us, but, believe me, the average student in a first year laboratory hasn't got a clue! The reason why distillation works to separate compounds of differing volatility, or the theory behind chromatography are, in my experience, never broached in an organic laboratory, and are generally left to the physical or analytical chemists to explain. Organic reaction workups and purification/isolation techniques are a treasure trove of what used to be called 'applied chemistry' and the explanations of these should be embraced in all organic classes.

Nuclear chemistry

Why is nuclear chemistry nearly always relegated to occupying the final chapter in first year textbooks, if it's even in there at all? It is the absolute logical beginning to all of chemistry, and, as so, should be at the beginning of Chapter 1. Speaking as a textbook co-author myself,[7] I did try to do this, but encountered so much pushback from reviewers that the idea was shelved. What could be more fundamental to chemistry than the number of protons and neutrons in an atomic nucleus? The former is, after all, the ordering principle behind the periodic table. Radioactivity is one concept in chemistry that ALL first year students have encountered prior to enrolling in the course, and an explanation of the fact that the atomic nucleus can be either stable or unstable, and the ways in which unstable nuclei can decay to achieve stability, would surely make a relevant and interesting start to any first year chemistry course. Rutherford would feature significantly in such a course, with his Nobel Prize for the explanation of radioactivity, the gold foil experiment confirming the existence of the atomic nucleus, and his 'splitting of the atom' (I prefer the term "the first elemental transmutation") showing just what an extraordinary and underappreciated scientist he was. Once the constituents of, and processes that occur in, the nucleus have been studied, atomic structure logically follows. So why do chemists generally leave this fascinating topic to be pilfered by the physicists?

Chemistry is often viewed as the most difficult of the first year university subjects, and quite rightly so, for the subject contains subtleties and complexities that students find nowhere else in their curriculum. Hopefully the above eight topics will provide food for both thought and discussion amongst both students and educators. Please feel free to email me with any comments.

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Article

Towards functional surfaces using Langmuir-Blodgett deposition techniques

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Keywords: *Langmuir-Blodgett, functional surfaces, spin crossover, luminescence*

Introduction

Over the last few decades, numerous examples of complex molecular systems have been developed with many different applications in mind. These include luminescent, responsive (sensing), spin-labile, magnetically interesting, advanced electronics and antimicrobial systems. [1-6] Generally speaking however, for applications in the real-world to be realised, many of these systems need to move from being solution-based to being present on a surface. A number of techniques to introduce molecular systems onto surfaces are available, including spin-casting, vapour deposition, and self-assembled monolayers.[7-8] We are particularly interested in utilising the Langmuir-Blodgett (LB) technique to transition from solution-based applications to functional surfaces due to the inherent control this particular deposition method offers. In this article we will briefly familiarise the reader with the LB technique and how it can be used to introduce metal-based functionality, namely spin-crossover compounds and luminescent lanthanide systems, onto surfaces.

The Langmuir-Blodgett technique

Briefly, the Langmuir-Blodgett deposition technique involves the self-assembly of amphiphilic molecules into ordered monolayers (Langmuir films), typically at an air-water interface. These layers are subsequently transferred onto a solid substrate by sequential immersion/emersion of the substrate into/out of the Langmuir film (Fig. 1).[9] Using the LB technique, homogeneous highly ordered films can be introduced onto a range of solid supports (e.g. quartz, optical fibres, gold, highly oriented pyrolytic graphite [HOPG], fluorine-doped tin oxide [FTO]) of varying sizes and shapes.[10] However, unlike many surface coating methods, the LB technique allows precise control and quantification of film variables, including the composition and the number of layers deposited (film thickness), attributes which are important when fabricating functional devices.

In order to utilise the LB technique, the functional molecules typically need to display amphilicity. For metal-based systems, the hydrophilic moiety normally arises from the charged metal centre, with the hydrophobic moiety present in the form of long alkyl chains (normally C-16 or longer). In turn, the alkyl chains are typically introduced by either covalently tethering them to the ligand (Fig. 2a) or introducing them via an anionic component (Fig. 2b) when a charged species is present. In both cases, careful design of the complex is required in order to both preserve the metal-binding site and ensure the metal-based functionality is not suppressed via the addition of the hydrophobic group.

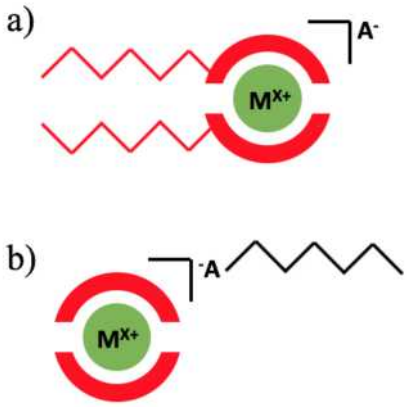


Fig. 2. Incorporation of amphilicity into metal-based systems by a) tethering the alkyl chain to the coordinated ligand or b) using a hydrophobic anion

Spin crossover complexes on LB surfaces

Spin crossover (SCO) compounds have a range of practical applications (including molecular switches, memory devices and sensors) which come about from the sensitivity the spin state of these compounds have to minor changes in a range of external stimuli (e.g. temperature, light, pressure). Many SCO applications rely on the spin

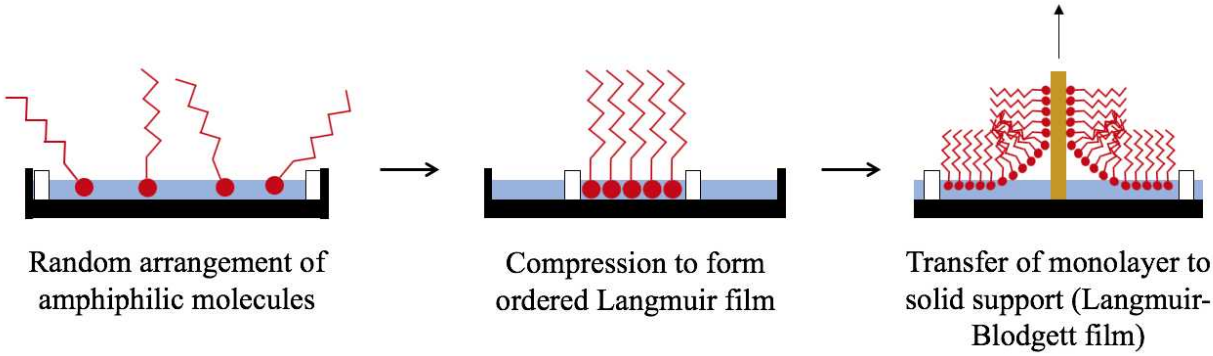
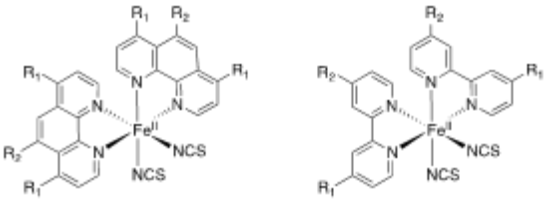


Fig. 1. Schematic showing the steps involved in the formation of a Langmuir-Blodgett film

state labile compound displaying a hysteresis loop, or bistability (i.e. the molecule can exist in either the high spin or low spin state depending on its immediate history). Although the presence of hysteresis is difficult to predict, it is well accepted that increasing the cooperativity (the degree to which the effects of a spin transition are conveyed through the material) within the system increases the probability of hysteresis occurring. Cooperativity can be introduced in a number of ways including linking metal centres through bridging ligands or via intermolecular interactions between discrete molecules (including lattice solvents). As such, the deliberate organisation of SCO molecules in ordered nano-structures (a bottom-up approach) has received much attention of late.[11-12] The LB technique is a particularly attractive approach to introducing SCO-functional devices onto surfaces as the deposition process results in stable, homogeneous and reproducible ordered layers of known thickness.

The initial studies of SCO complexes on surfaces were based upon Fe(II) complexes containing modified 1,10-phenanthroline (phen) ligands. The Fe(II) compound **1**, which was modified for LB deposition by the addition of three long alkyl chains onto the phen ligand showed no SCO event as an amorphous powder,[13] but when deposited onto a surface the transition took place over 75 K ($T_{1/2}$ 260 K) and was accompanied by a weak hysteresis loop of 4 K.[14] This result highlights that incorporation of compounds which do not exhibit SCO in powder form (i.e. no cooperativity) into ordered LB films gives rise to 2D cooperativity and hysteresis. Interestingly, the SCO event in the LB films differed from that in the parent compound, $Fe(phen)_2(NCS)_2$, **2** (the compound with no long chains appended) which showed an abrupt SCO event at 174 K with an associated hysteresis loop of 0.15 K.[15] This increased broadness of the spin transition within the LB film and was attributed to many small cooperative crystalline 2D domains present in the film, which all underwent transitions at slightly different temperatures.

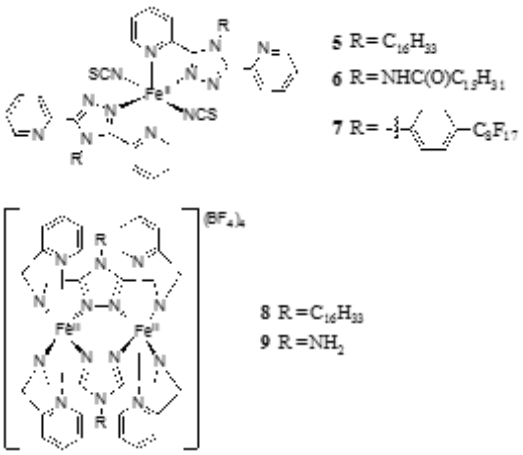
Taking a similar approach, the SCO properties of Fe(II) complexes containing modified bipyridine ligands were investigated after incorporation into LB films. Amorphous samples of **3** showed a continuous spin change over 250 K, with an SCO event centred around room temperature ($T_{1/2}$ *ca* 295 K), with the absence of hysteresis.[16] Y-type (head-to-tail, tail-to-head) multi-layered LB films of **3** were obtained and their SCO properties probed. During the first temperature cycle, the film showed SCO properties similar to the amorphous material, but a large proportion of HS residue was retained. However, when the sample was heated to over 340 K the properties were remarkably different, and rather than a gradual change a more abrupt spin transition was observed. Further experiments revealed that heating the sample above 340 K resulted in melting of the alkyl chains and a concurrent loss of LB layered film structure, so in this case it appears that incorporation of a SCO-active species into a film is not advantageous in promoting SCO.[17] Indeed, when the backbone was further modified to include fluoro-alkyl chains, **4**, in an effort to increase film stability, the subsequent LB films showed very little spin transition over the temperature range 2 – 300 K, with the majority of the molecules present in the LS state. Heating the film again resulted in melting which resulted in the SCO properties being somewhat similar to the bulk material.[18]



1 $R_1 = C_{17}H_{35}$, $R_2 = OC_{18}H_{37}$
2 $R_1 = R_2 = H$
3 $R_1, R_2 = C_{17}H_{35}$ or *trans* CH=CH-Ph
4 $R_1, R_2 = CH_3$ or $(CH_2)_{12}(CF_2)_5CF_3$

This early work produced somewhat contradictory results. In the case of the phenanthroline systems incorporating the compound into a LB film this resulted in promising changes to the SCO behaviours, whereas with the bipyridine systems the SCO events in the LB film were suppressed compared with the amorphous sample. Following these early results, a range of potentially SCO-active complexes with peripheral groups rendering them suitable for incorporation into LB films have been prepared by both the Brooker and Morgan groups (see below). However, detailed studies of SCO activity within the films have not been carried out to date.

Of particular promise are the observations from the Brooker group that appending alkyl chains to their extensively studied Fe(II) bis(2-pyridyl)-1,2,4-triazole systems had little adverse effect on the SCO properties of the complexes. In particular, compound **5** which contains a C-16 chain directly attached to the ligand backbone undergoes SCO close to room temperature (290 K).[19] Compounds **6** and **7** also demonstrate SCO activity ($T_{1/2}$ 182 K and 248 K respectively) and were shown to form LB films although adhesion to the surface was weak and the complex desorbed into the sub-phase during multi-layering deposition studies.[20] Along similar lines, appending a C-16 chain to the backbone of the dinuclear complex **8** still results in an SCO active complex ($T_{1/2}$ 224 K). However, in this case the half-SCO event (one metal centre undergoes SCO, the other does not giving mixed spin-state [HS-LS] complexes) is gradual compared with an abrupt event for the parent complex **9** ($T_{1/2}$ 224 K for the DMF solvate).[21]



5 R = $C_{16}H_{33}$
6 R = $NHC(O)C_{15}H_{31}$
7 R =
8 R = $C_{16}H_{33}$
9 R = NH_2

In a similar manner, Morgan and Albrecht demonstrated that while introduction of alkyl chains to $Fe(III)sal_2(trien)$

complexes suppresses SCO in the amorphous solids, a SCO event is present in solution – of particular interest is **13** which has a $T_{1/2}$ in a usable range (230 – 240 K).[22] Both **12** and **13** form stable films at the air-water interface, and in the case of **13** is able to be transferred onto either glass or silicon slides via LB techniques. A maximum of four layers could be transferred onto the surface, rendering the SCO studies carried out using UV-vis spectroscopy inconclusive.[23] When the alkyl chain is attached to the secondary amino nitrogen (rather than the phenolate), SCO is turned on ($T_{1/2}$ 125 K) in the molecule (the unsubstituted compound does not exhibit SCO).[24] An additional study from this group using Mn compounds provides direction for future research. A comparison between solid state structure (X-ray crystallography) and Langmuir film stability (Fig. 3) reveals that stability for those compounds with alkyl chains aligned in a cis arrangement (e.g. **15** and **17**) is greatly enhanced when compared to a trans orientation of alkyl groups (**16**).[25]

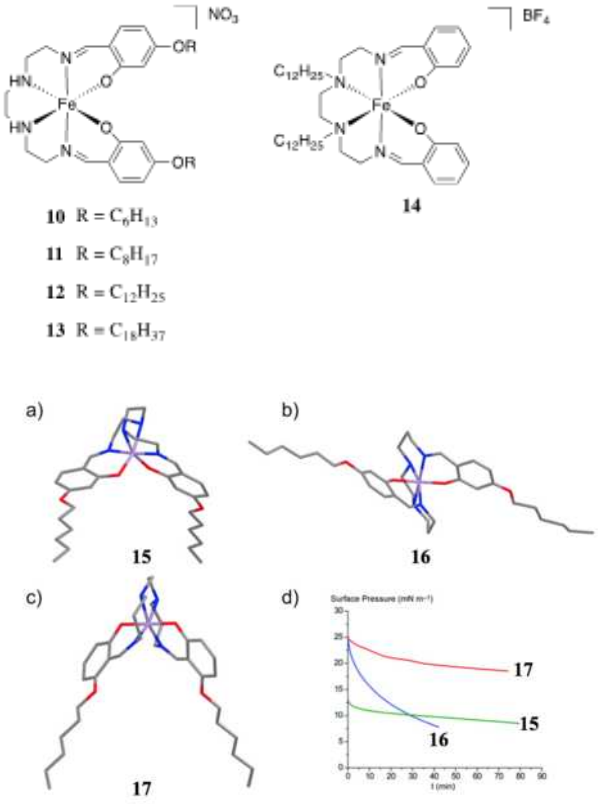
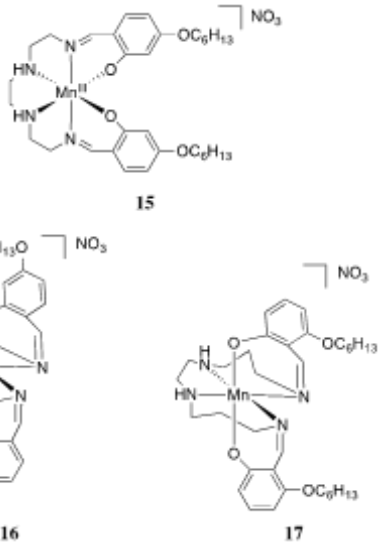


Fig. 3. Molecular structures of a) **15**, b) **16** and c) **17** showing special arrangement of hydrophobic chains and d) surface pressure isotherm showing the stability of Langmuir monolayers of **15**, **16** and **17** over time. Fig. d) reproduced from ref 25 with permission.

In the examples previously discussed, the hydrophobic chain has been introduced via the use of modified ligands (e.g. Fig. 2a), which in some cases has meant challenging synthetic chemistry prior to ligand coordination. The alternative method of introducing functionality via modified anions is less popular (e.g. Fig. 2b), even though it offers the benefit of being able to access a family of complexes with comparatively less synthetic effort (when simple ligands are employed). We have been able to demonstrate that using the commercially available hexadecane sulfonate anion, we are able to form stable Langmuir films of Fe(III) thiosemicarbazone complexes and successfully transfer single layers of the complex onto a LB surface.[26]

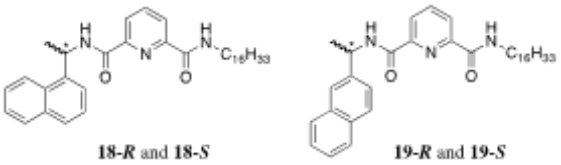


Langmuir-Blodgett films of luminescent lanthanide complexes

The Ln(III) cations are well known for their excellent photophysical properties, i.e. sharp narrow distinguishable line-like *f-f* emission, which are long lived, lasting in the millisecond region and occurring at long wavelengths.[27] This has seen complexes containing them used for applications such as biological probes, luminescent self-assemblies, luminescent sensors, and white light emitting materials.[28] Sensing and light-emitting devices are particularly attractive targets given the current interest in downsizing of devices and nanotechnology. However, many of these systems are again solution-based which vastly inhibits their ability to be used in 'real-life' applications. Much like for the aforementioned SCO systems, there is a need to immobilise these luminescent systems onto surfaces and the LB technique is particularly useful for this purpose. There are a few examples of Ln(III) systems immobilised onto surfaces using the LB technique, and the reader is directed to a recent review for a more comprehensive coverage of the topic area.[29] As such, we have chosen to highlight selected examples to give an overview of the types of layers which have been formed, and the applications they have found.

In a manner similar to that seen with the SCO compounds described above, Gunnlaugsson and coworkers demonstrated that addition of aliphatic chains to known lanthanide chelating systems produced Ln(III) complexes which were able to form LB monolayers.[30-32] The novel aspect of these complexes was that they were able to incorporate both a chiral centre and a long (C_{16}) chain onto 2,6-pyridine dicarboxamide scaffold to give the optically pure chiral ligands **18-*R***, **18-*S***, **19-*R*** and **19-*S***, which following self-assembly with Eu(III) ions gave chiral Eu(**L**)$_3$ (L = **18**-*R*, **18**-*S*, **19**-*R* or **19**-*S*) complexes that exhibited circularly polarised luminescence (CPL). Subsequent deposition of these chiral Eu(III) complexes onto surfaces (as mono-layers) gave the first examples of chiral at metal complexes organised into LB monolayers. Importantly, the complex-

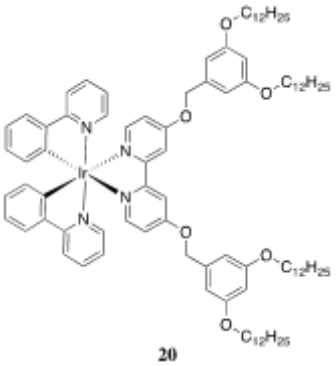
es retained their ability to undergo CPL within the film, lending themselves to be excellent candidates for chiral sensing platforms.[30-31]



18-*R* and 18-*S* **19-*R* and 19-*S***

Perhaps the most 'real-life' application of sensing on a Ln(III) containing LB surface comes from Caminati and Puggelli who developed a surface which mimics biological membranes and is capable of detecting trace amounts of the antibiotic tetracycline (TC).[33] Instead of pre-forming an amphiphilic metal complex then depositing onto the surface (as described in the previous examples), the films used in this particular system were constructed using dipalmitoylphosphatidic acid (DPPA) with Eu(III) cations in the subphase which subsequently coordinated to the DPPA film. In the absence of tetracycline, the Eu:DPPA films showed no emission but when exposed to tetracycline the Eu(III) emission was turned on (Fig. 4). Furthermore, tetracycline was able to be detected in trace amounts (as low as 1 x 10^{-8} M concentrations) and detection was ratiometric with emission increasing proportionally with increased antibiotic concentration. This study highlighted the applicability of Ln-LB films for developing responsive surfaces.

Indeed, the ability to incorporate different components into one film makes LB deposition a powerful technique for the development of advanced luminescent systems as it gives rise to the possibility of forming multi-emissive systems.[34-38] In one such system, a combination of an Ir(III) amphiphilic cationic complex ($[Ir(ddbpy)(ppy\text{-}CN)_2]^+$, **20**) and a (counter)anionic Eu(III) polyoxometalate (POM), $[Eu(W_5O_{10})_2]^{9-}$, gives rise to a dual emissive architecture.[39] In this system, the Ir(III) component is introduced via the amphiphile as $[Ir(ddbpy)(ppy\text{-}CN)_2]PF_6$ (added onto the sub-phase) whilst the Eu(III) POM is introduced as an anion in the aqueous sub-phase. On film formation the Eu(III) POM is incorporated as a counter anion to the Ir(III) complex. Initial films of the Ir(III)/Eu(III) system formed, however the Eu emission was masked by that of the Ir(III) complex. To overcome this the group included a non-luminescent cationic amphiphile, dimethyldioctadecylammonium bromide (DODA). Different ratios of DODA and the Ir(III) complex cation (1:5 and 1:20 of Ir(III):DODA), allowed for the characteristic emission of Eu(III) to be observed. This tri-component system displayed a dual emissive LB film with yellow emission from the Ir(III) complex and red from Eu(III) POM. Furthermore, the nature of the system means the emission can be tuned between red and yellow depending on the amount of DODA added. The formation of this advanced luminescent system highlights the versatility of the LB deposition technique. It not only further showcases the ability to use the sub-phase to introduce additional functionality (and indeed incorporate relatively large molecular species) but it also highlights how multiple amphiphile species can be used for fine tuning of the system.



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Fortunately, in the majority of cases, incorporating luminescent lanthanide complexes into LB films has not resulted in significant losses of the emissive properties of the system or a reduction in quantum yields. However, some groups have demonstrated that quenching of the lanthanide emission can occur either because of the presence of multi-layers (inner filter effect) or the close proximity of luminophores (aggregate quenching effect) when films are formed under high surface pressures. However, the LB technique allows for precise control over variables such as multi-layering and surface pressure so the issues described above can easily be overcome by making subtle changes during the LB film formation/deposition steps.[40-41]

Conclusions

The Langmuir Blodgett technique is an excellent method for immobilising amphiphilic metal complexes into ordered arrays on surfaces. It is a highly versatile "soft" deposition technique that can be applied to many systems and gives fine control over surface preparation. Whilst the examples showcased in this brief contribution have focused on SCO and luminescent lanthanide systems, the technique lends itself to many applications. Other application areas which have been investigated include the immobilisation of catalytically active species; immobilisation/ordering of nanoparticles (NPs) onto surfaces for a range of applications (emissive NPs, catalytic NPs, anti-microbial NPs, etc.); developing advanced surfaces

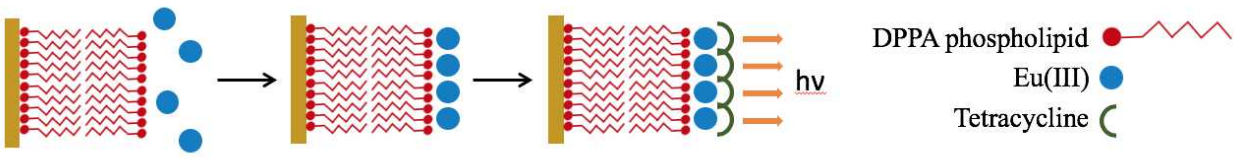

Fig. 4. Schematic showing the turn-on sensing mechanism for the antibiotic tetracycline (TC)

through deposition of mixed functional-amphiphile systems (e.g. combinations of SCO and luminescent amphiphiles) and templated surfaces/surface engineering where structure directing "templates" are introduced into the sub-phase so that programmed ordering of the amphiphiles occurs concomitantly with film formation thus giving a pre-arranged (engineered) surface. The scope for Langmuir-Blodgett deposition is enormous and we hope to further contribute to this field with more complex and interesting systems.

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Getting structures into gear: a computational microscope to discover, understand and design molecular function

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Keywords: *molecular dynamics, molecular simulations, high-performance computing, maximum entropy principle, integrative research*

Davide Mercadante completed his BSc and MSc in pharmaceutical biotechnology at the University of Naples Federico II, Italy. In 2008 he moved to the University of Auckland to undertake a PhD in chemistry, studying the interaction between proteins and polysaccharides using both experimental and computational approaches. During his PhD, he conducted research for one year in the group of Prof Chris Dobson at the University of Cambridge, UK, after being awarded an EMBO short-term fellowship. While there, he conducted computational studies on enzymatic processivity. For his postdoctoral training he first spent four years (2013-2017) at the Heidelberg Institute for Theoretical Studies (HITS) in Germany, specialising in computational biophysics. At HITS, he approached the study of intrinsically disordered peptides. His contributions as a postdoctoral fellow in Germany account for the development of methods useful to simulate the dynamics of intrinsically disordered proteins and for the identification of a new mechanism of protein-protein association. This mechanism promotes ultrafast binding between molecular partners and allows efficient nuclear transport in eukaryotic cells.

In 2015 he moved to the University of Zurich, Switzerland, where he conducted molecular simulations to investigate intrinsically disordered peptides and nucleic acids dynamics by directly integrating computations and single-molecule Förster energy transfer (smFRET) spectroscopy. Dr Mercadante has recently been appointed as a Senior Lecturer in the Food Science division of the School of Chemical Sciences at Auckland University. His research is focused on integrating his molecular simulations with the work of experimentalists, in order to understand how molecular dynamics mediates function and how such knowledge can be used for the design of new materials valuable to the fields of chemistry and food science.

Introductory note: why we shouldn't stop at molecular structure but should strongly focus on investigating molecular dynamics

Without going too far back in the history of physics, chemistry or biology, it is in most cases safe to state that molecular structure is essential for function. The continuous advancement of experimental techniques aimed at determining the structure of small to large molecules has produced an ever-growing list of structures. From X-ray crystallography, NMR and more recently cryo-electron microscopy (cryo-EM), all have refined an increasingly great amount of structures, garnished with explanations of working mechanisms.

However, in writing this article I face the challenge of describing why we should look beyond molecular structure.

Additionally, since I am a computational scientist, I also sometimes face the challenge of convincing experimental researchers about the importance of computations in defining molecular dynamics.

A prophetic quote published in 1963 by Richard Feynman states: *"[…] if we were to name the most powerful assumption of all, which leads one on and on in an attempt to understand life, it is that all things are made of atoms and that everything that living things do can be understood in terms of the jiggling and wiggling of atoms"*.[1] Contrarily to what can be imagined, this wasn't a thought exclusive to Feynman. Sometime in the first century BCE, the Latin author Lucretius described all things as composed by atoms, which have the property to continuously "swerve" (he used the Latin word *clinamen*).

Chemists are quite familiar with the concept of atomic/molecular motions as they drive chemical reactions through collisions between reactants.[2] However, from a structural perspective, rigid macromolecular structures are somehow counterintuitive with respect to molecular dynamics driving their function. Molecular dynamics, however, is at the very core of molecular function.[3] It is not only the collisions (driven by translational motions of molecules) that are important to Nature, but the internal fluctuations of macromolecules and their assemblies that are key to understanding molecular processes. For large molecules, such as nucleic acids, lipid assemblies or proteins, these motions can lead to function in a myriad of ways. I will therefore discuss in more detail what processes can be efficiently understood through sampling molecular dynamics using computational methods.

Enzymatic catalysis

A paradigmatic example is given by enzymatic catalysis. The role of internal protein dynamics and substrate entropy[4] in lowering the activation energy ($\Delta G^{\ddagger}$) of reactions to speed up substrates-to-products conversion, has been long debated.[5] In some cases, compelling evidence has suggested that internal dynamics, close to or far from the active site, are crucial for lowering $\Delta G^{\ddagger}$.[6] The element of connection between catalysis and internal enzymatic dynamics is the pre-exponential factor A in the Arrhenius formula of the kinetic rate (Eq. 1):

$$k = A(T)\, e^{\left(\frac{-\Delta G^{\ddagger}}{RT}\right)} \qquad \text{(Eq. 1)}$$

where k is the reaction rate. Dynamic effects lowering the activation energy can generally be ascribed to the pre-factor A. Understanding the relation between enzyme dynamics and the modulation of the pre-factor is difficult from an experimental perspective. This is mostly because experimental observables do not provide a resolution high enough to relate *A* to functional dynamics of enzymatic structures. To more clearly explain this I will mention one of the fundamental phenomena promoting catalysis: hydrogen tunnelling.[7] Hydrogen tunnelling can be ultimately related to the alignment, into the active site, of all the side chains providing the necessary chemical groups for a reaction: this mechanism has been proven true for a series of enzymes, from lipooxygenases[8] to alcohol dehydrogenase,[9] dihydrofolate reductase[10] and glucose oxydase.[11]

Clearly, the kind of resolution needed to achieve this understanding, can only be accessed if key experiments and a robust theoretical formalism are combined to provide a highly-resolved picture of the motions shaping the free-energy landscape of the active site. Such a highly-resolved picture can be yielded by the simulation of protein dynamics, which also crucially provide the opportunity to quantitatively relate motions to function.

Allostery

Allostery describes the transduction of a signal along a macromolecular structure, so as to regulate molecular activity directly or indirectly.[12] Allostery is therefore associated with short- or long-range conformational changes of a macromolecule.[13] In order to probe allostery, experimental techniques need to have the resolution to capture, upon molecular activation, concerted conformational changes of the structure. This is very difficult to pinpoint experimentally considering the level of resolution required.

On the other hand, molecular simulations can give detailed insights into conformational changes. Since the resolution limit of molecular simulations is up to the atomic level (in full-atom simulations), coupled motions in a molecular structure can be detected efficiently. Several ways have been proposed to understand allostery from molecular simulations.[14] For example, correlated motions of residues would reveal if the concerted activation of different parts of a structure dominates the overall dynamics. For this purpose, since molecular simulations provide the position, velocity and forces of each particle at each timestep (read further paragraphs in this article for details), calculating the correlation coefficient of the residue's pair positional vectors (r_i and r_j) as given in Eq. 2, comes in handy but is not without limitations:

$$C_{i,j} = \frac{\langle (r_i - \langle r_i \rangle) \cdot (r_j - \langle r_j \rangle) \rangle}{\sqrt{\langle (r_i^2) - \langle r_i \rangle^2 \rangle \cdot \langle (r_j^2) - \langle r_j \rangle^2 \rangle}} \qquad \text{(Eq. 2)}$$

Although the correlation coefficient $C_{i,j}$ would reveal correlated motions it may also give rise to false negatives. Two perfectly correlated oscillators that, however, would be placed orthogonal to each other, would still yield zero correlation ($\langle \sin\tau \sin\tau + \pi/2 \rangle = 0$). Therefore, a different but more useful method is used to compare probability distributions of positional vectors[15], $p(x_i, x_j)$, using Eq. 3:

$$I_{i,j} = \iint p(x_i, x_j) \log \frac{p(x_i, x_j)}{p(x_i) p(x_j)} \qquad \text{(Eq. 3)}$$

This gives the information about the mutual dynamic behaviour ($I_{i,j}$) of two particles (either single residues – these being nucleotides, lipids, amino acids, single atoms, or beads in coarse-grained simulations) without considering the geometric factors of the two oscillators involved. For non-correlated oscillators, the value of $I_{i,j}$ would go to zero, increasing towards infinity as the degree of mutual inference increases. Importantly, the mutual information can still yield a Pearson-like correlation coefficient (Eq. 4):

$$C_{i,j} = \sqrt{1 - e^{-(2/d) I_{i,j}}} \qquad \text{(Eq. 4)}$$

This coefficient is extremely important to relate the mathematical quantities describing allostery to a visual representation of signal transduction along the structure. One of the ways this can be achieved is to use the so-called graph theory where every residue is considered as a "node", while "edges" connect the residues characterised by correlated motions.[16] If we are to define a correlation-based distance, ($d_{i,j}$), between residues in a protein structure then we can use the correlation coefficient calculated previously (Eq. 5):

$$d_{i,j} = -\log |C_{i,j}| \qquad \text{(Eq. 5)}$$

The distance between two residues will be short if their correlation is high and vice versa. The "closest residues" can then also be coloured directly on the resolved molecular structure to identify which parts of the structure are crucially involved in allosteric behaviour. Overall, using one or more of the formalisms defined above to understand and visualise communication of residues in molecules that undergo allosteric behaviour, molecular simulations can be rightly considered the best techniques for the analysis and visualisation of communication pathways.

Nowadays, simulations cover a large range of length and timescales and are useful for a large variety of applications. According to the process under investigation and the level of detail required, different modelling and simulation approaches should be considered and carefully chosen, so as to retrieve complementary information about the examined molecular behaviour (Fig. 1).

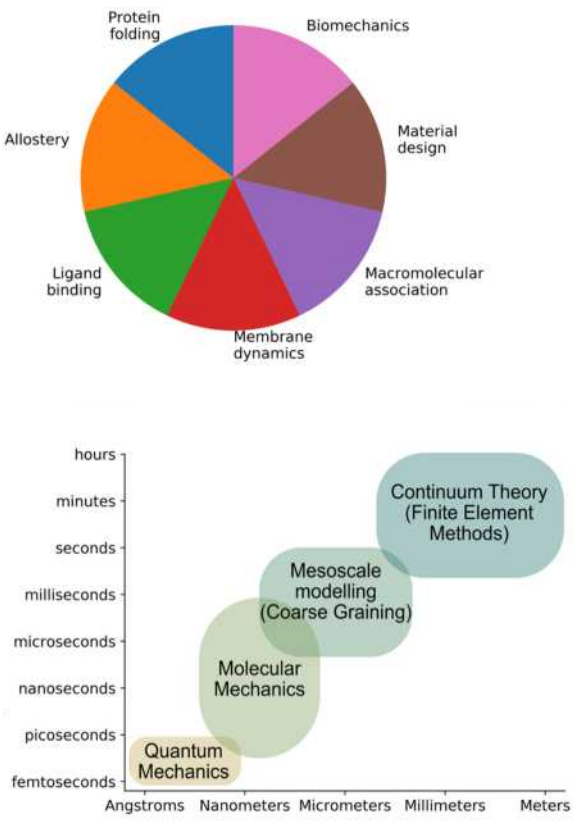

Fig. 1. The top panel shows some of the applications of molecular simulations. In the bottom panel, different types of modelling techniques and simulations are placed along a temporal and spatial scale. Quantum mechanics calculations simulate the behaviour of electronic orbitals in small molecules, while molecular mechanics and coarse-grained modelling are able to determine the dynamics of macromolecular systems in the timescale of ps to ms and are thus useful to study a variety of molecular processes. At larger lengthscale and timescales a continuous representation of matter has to be taken into consideration, and finite element methods are to be used.

Ligand binding

If there would be a single application for which molecular simulations are to be given strong consideration, this would be the study of ligand binding. Traditionally, ligand binding has been investigated computationally using molecular docking procedures. Molecular docking is a computational approach that allows multiple ligands to be screened in a very efficient way against a multiplicity of macromolecular targets.[17] In a docking run, the binding of thousands of ligands can be screened in hours, just employing a powerful workstation. The computational efficiency of molecular docking, however, comes with severe limitations.

The screening of active compounds with molecular docking algorithms often implies a high degree of rigidity of the molecular target and an implicit representation of the solvent (considering the solvent as a continuous medium having the dielectric constant similar to the one of water, without explicitly accounting for the presence of individual water molecules). The binding of compounds is usually scored using empirical energy functions,[18] which limit the accuracy and resolution of the factors determining binding.

The reason why ligand binding has not been tackled by molecular simulations in the past is that simulations of molecular dynamics are computationally demanding. Often these simulations sample protein dynamics adopting an explicit representation of water molecules (explicit solvent), and therefore need to solve the equation of motion for tens of thousands of particles. It is therefore not feasible to think, at this stage of computational development, to screen thousands of active compounds using molecular dynamics simulations. Nevertheless, within the context of drug design they are becoming increasingly useful. Binding and stability of a molecule in the active site of a target is hugely influenced by the target's dynamics, which is extremely important to take into consideration.

Simulations can therefore retrieve an ensemble of conformations that can be used for the molecular docking approach mentioned above.[19] Similarly, the best docked molecules can still be simulated in complex with their targets using molecular dynamics simulations to refine the binding pose and to identify further pharmacophoric elements that would enhance our ability to expand the structure of lead compounds creating "better" binders.

Additionally, one of the most serious limitations of molecular docking is that many protein targets, in their crystallised structures, do not show the presence of pockets in which compounds could be fitted by the docking algorithms. But this doesn't mean that these pockets do not exist. The ability of pockets to be formed along the explored conformational ensemble can indeed be investigated efficiently using molecular simulations. Specialised algorithms can be used to identify pockets in the retrieved ensemble[20] and docking can then be considered for a first screening of binding molecules, which can be further refined by simulations. This approach has been dubbed "ensemble docking" and is really improving our ability to target new drugs, hoping to reverse the deleterious trend defined by Eroom's law. While Moore's law describes how the number of transistors in circuits doubles every two years (giving an idea of how fast computing is developing), Eroom's law describes how the cost of developing new drugs doubles every nine years (where more than a billion US dollars is now required for the development of not even a single drug).

Universes beyond molecular structure: the bizarre but important case of the dark proteome

While at the beginning of this article I stated that the structure of a molecule provides insights about its function, in the universe of proteins this is not always the case. Some proteins, which have been identified in the

proteomes of all living organisms (including viruses), do not fold into three-dimensional structures but rather stay unfolded in solution.[21] Therefore they challenge the paradigm by which molecular structure is a necessary requisite for function. Nevertheless, they are still able to fulfil complex roles inside cells.[22]

These molecular entities are called intrinsically disordered proteins (IDPs). IDPs have peculiar sequence characteristics defining their highly dynamic nature. Aromatic residues that drive the formation of hydrophobic cores (and therefore three-dimensional folds) are under-represented, whereas polar and charged amino acids are abundant.[23] This generates "floppy molecules", which in solution explore a wide set of conformations. The high dynamics of IDPs makes their investigation difficult for most experimental techniques. Molecular simulations, on the other hand, can greatly help, as they are able to provide a highly detailed picture of molecular dynamics in solution. Nevertheless, the ability of simulations to provide experimentalists with meaningful ensembles of IDPs has been hindered by the fact that force fields (read following paragraph for more insight into force fields) have shown consistent limitations in reproducing the correct ensembles for IDPs. They tend to yield conformers that are too compact, confirming the tendency to overstabilise protein structure at the expense of dynamics.[24] Several improvements have characterised force fields for the correct simulation of both intrinsically disordered and folded proteins. Partially successful approaches have ranged from defining more precise parameters describing water-solute interactions[25] or dihedral terms,[26] to the deployment of force fields based on the Kirkwood-Buff theory of solution and parameterised following a rigorous experimentally-driven approach.[24b, 27]

The appearance of IDPs has been long debated in the scientific community. Although there were several indications about the existence of these highly dynamic molecules, it has taken more than 60 years to properly recognise IDPs as separate molecular entities. Structural biologists still try to reconcile the existence of IDPs associating their property of being structureless with terms such as "conditionally" or "transiently" disordered, stating the real functional state of intrinsically disordered proteins is their folded state.[28] In reality, from a biophysical perspective, IDPs are very different from "properly" structured proteins. Besides their diversity in the sequence space, their free energy landscape is hard to characterise as it is much shallower than that of structured proteins, with the lack of real minima that would lead to a more or less unique functional fold. Given this, intrinsic disorder cannot be considered an accident of evolution, even for folding-upon-binding IDPs, for which their binding partners play a crucial role in making them assume a fold. It has indeed been shown that positive evolution is precisely directed to more disordered rather than ordered protein regions, with the rate of positive selection differing up to four folds between structured and disordered proteins.[29] In other words, positive evolution doesn't inhibit disorder, but enhances it or at the most leaves it unvaried, but still expands the functional repertoire of proteins. Ultimately, disorder evolves towards disorder more rapidly than order (intended as structural moieties) evolves towards order. Stating that structure is still the predominant feature of these molecules just because they fold when binding other protein partners tends to diminish the importance of disorder in defining the functional repertoire of proteins._

In any case, without entering too much into the semantics of what disorder means and at what extent a protein is disordered, the occurrence of IDPs in organismal proteomes and their relative abundance in organisms of higher complexity[22b, 22e, 22g] suggests the importance of molecular dynamics and justifies the need of investigating molecular dynamics beyond the structural characterisation of macromolecules.

The appearance of IDPs in key and complex biological processes suggests how increased plasticity is useful to carry out functions that would otherwise be difficult to be mediated by more rigid, structured molecules. Additional abilities, such as the property to phase separate in mild conditions[30] make IDPs crucial molecules to investigate for the design of new functional materials in different fields of chemistry, from the creation of reaction chambers to the invention of new encapsulating materials.

Gold standards for understanding molecular dynamics: the working principles of a computational microscope

Sampling molecular dynamics means computing the position of each particle composing a molecule at a certain moment in time. We first need to define what are the particles that compose a system. Macromolecules are comprised of smaller building blocks, and each of these blocks is composed of atoms. Similarly, we can split the atoms further into their founding components such as subatomic particles: protons, neutrons and electrons. Assessing the dynamics of a molecular system ultimately means gaining information on how these entities influence each other's position concertedly. Paradoxically, the same experimental techniques that are so useful in defining the position of particles are similarly useless in defining the evolution of particles' positions over time. Highly dynamical stretches in macromolecules challenge experimental techniques such as X-ray crystallography and cryo-EM, while techniques that are able to resolve dynamics, i.e. NMR and single-molecule Förster energy transfer (smFRET) spectroscopy are limited by time-averaging effects, missing the fine details of molecular ensembles.

Computer simulations are therefore the best approach to gain detailed information about molecular dynamics. Once the structure (or model) of a molecule is available, it is in principle possible to compute particle dynamics by solving the fundamental equation of motions, such as those defining Newton's law of motion or Langevin dynamics. Molecular dynamics or Brownian dynamics simulations do exactly this: they solve the equation of motions of each particle of a molecular system in a vari-

ety of micro-environments, by integrating positions and velocities over time, so that, in the end, "a movie" of a molecule can be obtained. Besides these, Monte Carlo simulations which retrieve particles' positions using random moves and energy-based acceptance criteria for newly generated conformations constitute the other big branch of computational approaches based on classical mechanics.[31] From the collected trajectory is then possible to calculate any required observable, according to the achieved resolution, so that dynamics can be linked to function.

Computational techniques can therefore be considered as the gold standard to define molecular dynamics at high resolution and their potential is constantly increasing. What are then the current limitations of molecular simulations? Simulations unfortunately suffer from a so-called "force field problem". To integrate position and velocity of particles over time, the rules that define the interactions between particles of diverse types need to be set (Fig. 2). How do hydrogen bonds behave? How do hydrophobic interactions get arranged in an aqueous environment? How do charged particles attract or repel each other?

Simulations use force fields to define the principles governing the interaction between particles. They are a collection of equations (energy functions) and parameters that define how different particles would interact (what would their energy and force be) in space. Unfortunately, force fields are far from perfect. Their development is an active field of investigation, and the set of parameters that define particle interactions is continuously getting refined as new experiments and more advanced quantum chemistry calculations are carried out.

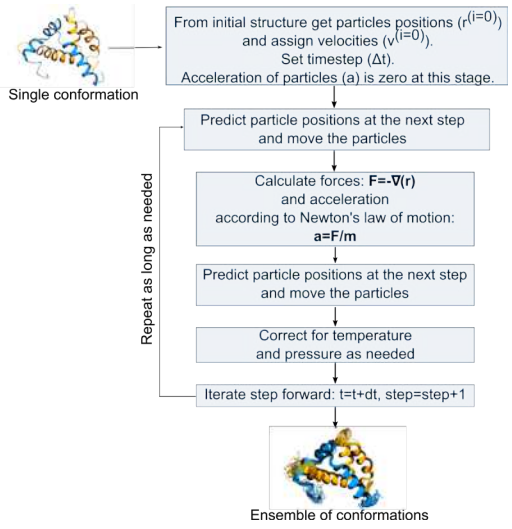

Fig. 2. Schematic workflow of a molecular dynamics (MD) simulations algorithm. In MD simulations, to each particle of an initial structure, which defines their positions in Cartesian space, a set of random velocities is assigned according to a Boltzmann distribution at a defined temperature. Particle positions and velocities are then updated at each step by calculating their force upon solving the Newton's equation of motion. The calculation of forces considers the rules and parameters defined in a physics-based model called a force field. At the end of a simulation, a "molecular movie" is obtained, yielding a set of conformations to be linked to the function of the investigated molecule. In the figure, the complex between the NCBD gene transcription co-activator (blue) and one of its binding partners ACTR (orange) is shown.[32]

Besides the reliability of force fields, the need to access relevant timescales constitutes the other limitation of computational research. This is also known as the "timescale problem". How long can we simulate for? Can we access timescales relevant to the processes of interest and that we sample experimentally? The problem of timescales has been affecting simulations for a long time. However, the field has seen major breakthroughs over the last decades. We have "broken the wall" of µs-long simulations[33] which can now be easily accessed, especially thanks to the use of graphics processing units (GPUs), which greatly accelerate simulations.[34] The challenge to access relevant timescales is additionally facilitated by enhanced-sampling simulation methods, aimed at accelerating the crossing of high-energy barriers, which separate low-energy states that are often responsible for molecular function. One of the most prominent examples is metadynamics simulations, in which energetic barriers are overcome by flooding the energy wells of a conformational landscape with gaussians of defined height and width.[35] The biasing, however, needs to be applied on relevant degrees of freedom (distance between molecules, dihedral angles, etc.) that well-describe the molecular process under investigation.

Therefore, enhanced-sampling methods mostly rely on the user knowing *a priori* the relevant degrees of freedom describing the molecular process of interest. In this way, the free-energy landscape defining a molecular process can be successfully reconstructed taking a mirror image of the applied bias. Other methods enhance sampling by simulating at higher temperatures and swapping conformations if the energy retrieved at higher temperature is lower than the energy of a conformation at lower temperature.[36] The swap between different replicas ensures that high-temperature conformations are accessible at the low-temperature ensembles. In this way, there is no need to know relevant degrees of freedom, even though sometimes the dynamics relevant to describe the molecular process of interest may not be exhaustively sampled. Although enhanced-sampling and increased computational power have improved and continue to boost our computing capabilities, simulations have another ace up their sleeve: direct integration with experimental observables. This is an effective way to retrieve a mechanistic understanding of a molecular system, through a highly interdisciplinary approach.

How can simulations help experiments and how can they be directly interfaced with them?

Within the universe of improving simulation accuracy and retrieving meaningful molecular ensembles, another powerful strategy can be considered. This is the direct integration of simulations with experiments (Fig. 3).

As outlined in the previous paragraph, simulations are often affected by the so-called "force field problem", which essentially states the limitation of the physics-based models used to describe interactions between particles. These physics-based models can then be corrected by adding a pseudo-energy term to the energy function of

the force field, to correct the ensemble yielded by the simulations and make it fit the experimental observables. The "correction energy term" derived from the experimental observables can be retrieved from different kinds of experiments, such as NMR, with the use of chemical shifts, NOEs or RDCs, small-angle X-ray scattering (SAXS), smFRET spectroscopy, electron paramagnetic resonance (EPR) and others. Ideally, any experimental quantity linking computational (i.e. distances, hydrodynamic radius etc.) and experimental (i.e. FRET, resonances, scattering, etc.) observables could be used to constrain/restrain a simulation so that the obtained ensemble satisfies the experimentally measured quantity.[37]

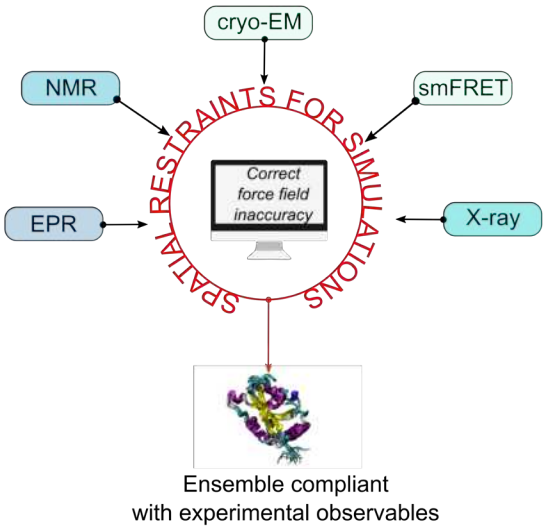

Fig. 3. Experiments and simulations can be directly integrated by using experimental observables coming from different techniques in order to guide simulations, so that ensembles of conformations respecting experimentally measured quantities can be obtained. These ensembles are therefore reflective of what experiments have observed and provide a structurally detailed picture of the investigated molecular processes.

It is important to note that most experiments only measure an ensemble-averaged quantity of an observable. For molecules characterised by low dynamics (mostly rigid), constraining/restraining simulations around an average value would yield a good experimentally-close approximation of an ensemble. However, for more flexible molecules simply constraining/restraining simulations to the experimental averages may lead to great inaccuracy. Respecting the ensemble average, does not necessarily mean that the single conformers of the ensemble always fluctuate close to the average.

To use a trivial example: if I spend half of my time in Dunedin and the other half in Auckland, computing my average position using the two cities' coordinates would tell me that I have spent most of my time somewhere in the Kahurangi National Park, even though I have never been there. For cases where restraining or constraining around an average would yield great inaccuracy, another theoretical formalism, equivalent to restrained-ensemble simulations[38] comes to the rescue: the maximum entropy principle. In 1957 E.T. Jaynes stated a link between the thermodynamic entropy and information-theory entropy, which is the speed at which a stochastic source of data produces some information (in this case our observables).[39] This information-theory entropy is also called Shannon entropy. Going back to molecular ensembles, Jaynes formulated that the best probability distribution is the one that maximises Shannon's entropy.[40] An *a priori* probability distribution of a conformational state is therefore constrained/restrained such that the Shannon entropy is maximised and is still compatible with the experimental constraints/restraints. The probability distribution retrieved *a posteriori* is therefore the best one satisfying the experimental constraints/restraints. In this way, the *a posteriori* probability distribution doesn't shift (like in the case of experimentally constrained/restrained simulations) to values close to the experimental average but gets reweighted such that the relative weights of each population reflect the observables obtained in experiments (Fig. 4).[41]

The maximum entropy principle provides a robust framework to directly integrate experiments and simulations. Taking it a step further, rather than enforcing experimental averages it could be possible to directly enforce entire distributions of an arbitrary shape, so that the *a posteriori* distribution is obtained applying constraints/restraints that would satisfy a continuous distribution of points matching the experimental observable distribution. To obtain the enforcement of a distribution rather than of single ensemble averages as explained above, several methods have either been developed or are under development. A possibility would be to variationally enhance

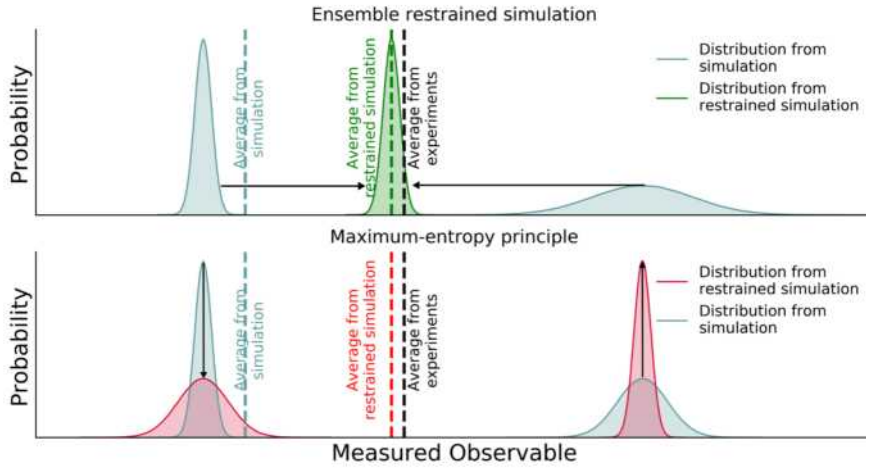

Fig. 4. Schematic representation of approaches that correct the force field energy term with experimental restraints (top panel) or using the maximum-entropy principle (bottom panel). For systems characterised by low dynamics, the application of experimental restraints to the force field energy, shifts the relative populations to respect the experimental average in order to match it as best as possible (green vs. black dashed lines). This leads to large errors when the investigated system is characterised by high dynamics. The maximum entropy principle, on the other hand, assures that a reweighing of the relative populations yields computed averages in line with experimental averages (red vs. black dashed lines). Adapted with permission from ref 37.

the sampling with adaptive potentials.[42] Overall, either enforcing ensemble-averages or entire distributions, the maximum entropy principles allows a meaningful correction of force field terms, easing the force field problem and providing a meaningful representation of the conformational dynamics of molecules in solution. This approach can therefore directly and powerfully integrate computational and experimental work.

The landscape of New Zealand's computational research: what has been done and what is still needed

Looking past the inaccuracy of physics-based models (force fields), the other considerable challenge in molecular simulations is the accessibility of long timescales. This relates to our ability to simulate small to large molecular systems at a certain level of structural detail, long enough to cover, at equilibrium, timescales meaningful to the processes investigated experimentally. The obvious advancement needed to ease the "timescale problem" is the availability of powerful computing infrastructures.

Since New Zealand's research universe is characterised by strong experimental expertise in diverse and complementary fields of science, complementing this expertise with capable computational research would constitute an extremely powerful opportunity to further enhance scientific investigations.

The country has made great strides in developing new computing infrastructures that will now allow computational researchers in the fields of chemistry, food science and biophysics to explore molecular dynamics using cutting edge approaches. An important and needed change in the philosophy of computing has occurred, with the New Zealand eScience Infrastructure (NeSI) consortium actively involved in working together with researchers to meet their needs. Computing infrastructures have been recently renewed and centralised in Wellington, at NIWA's Greta Point campus. Two new high-performance computing (HPC) platforms have been built with the aim of satisfying the many needs that constellate the universe of computational research in New Zealand. This includes but is not limited to numerical weather predictions, fluid dynamics, quantum chemistry and molecular mechanics simulations. The new clusters are called Maui and Mahuika, Maori deities with a strong symbolic power. These clusters feature thousands of CPUs interconnected by systems that allow fast intercommunication between computing nodes working in parallel, which can satisfy computational research with low to high parallel computational requirements.

What can further be done to improve this already promising and powerful scenario? I have already mentioned that a great advancement in scientific computing has been promoted by the use of graphics processing units (GPUs). GPUs have a very high parallel architecture where thousands of arithmetic units can process multiple pieces of information at the same time. Although GPUs have been used in the past to optimise graphics processing, their use in numerical computations has been sped up by a parallel change in philosophy of numerous software, which have been translated into "GPU programming languages". GPUs have an additional advantage: they can be cheaper than CPUs for some computing needs, with the benefit of much greater computing power.

It is therefore almost obvious to think that a future expansion of computing capabilities in New Zealand needs to take GPU computing into account. Maui and Mahuika already feature 8 GPU Nvidia Tesla cards in their configurations and is very likely that they will include more in the future. However, computing centres and consortia (like NeSI) need to carefully plan the integration of GPUs into existing clusters, to provide the maximum benefit for researchers with the minimum cost, avoiding over-spending for features that are not needed by some research communities and ducking the complicated market strategies of monopolising companies which may be trying to lock them into unfavourable licensing agreements. An example of this can be given by the licensing agreement drafted by Nvidia and imposed on the builders of computing clusters. Single-precision GPU units, which are much cheaper than their double-precision counterparts (double-precision is in many cases not needed), won't be under warranty if integrated into computing servers. They weren't designed for high-performance computing and long-lasting performance but their low cost compared to high-end cards (with differences of a factor 10 in the worst case) still makes them a valid alternative to purchasing expensive cards, at the expense of breaking the licensing agreement and losing support.

It is therefore also required that, in the future, when building infrastructures is in the planning stage, alternatives are considered. Instead of Nvidia graphic cards, AMD cards have the advantage of working on open source driver stacks and are being coupled with very powerful new 7nm chipsets (Rome architecture). Alternatively, but against the philosophy of centralising computing infrastructures, single computational groups could think about starting to build small GPU clusters that would target the simulations of smaller systems particularly suited to GPU computing through the use of dedicated software. This would offload the large, centralised computing infrastructures from molecular systems that do not show good scalability.

Another opportunity worth mentioning is the possibility of using cloud computing resources such as those provided by Amazon Web Services (AWS). The advantage of using cloud computing resides in reducing the management costs of an infrastructure and have computing nodes that are always up-to-date, at the expense of a slightly higher cost. Nevertheless, the problem of cost can be overcome if researchers consider booking cloud infrastructure in the so-called "spot market". It is indeed possible to "bet" on spare instances that are unused in a particular moment (spot instances). The advantage of this is a heavily discounted price on the instances requested for computations, but running the risk of "losing" the instance (while the computation is running) if somebody else is willing to pay more for it. Although this is surely annoying, writing checkpoint files more fre-

quently would enable the possibility of re-submitting a simulation every time a spot-instance becomes available again, reducing the costs enormously (sometimes five times less than the market price of the instance as an exclusive resource). The choice to use cloud infrastructures for scientific computing will need, however, to consider other "hidden" costs. Examples include the stowage of the collected results into instances dedicated to storage (bucket instances) and the requirement to access the data efficiently when needed. Last but not least, cloud infrastructures need to insure a good level of parallelism, which is a pre-requisite for scientific computing. Unfortunately, the very nature of cloud computing does not always assure good performances as the requested computing instances could happen to be placed on different electrical units, sometimes at a physical distance that is too large to provide fast intercommunication between instances and ultimately efficient scalability.

Overall, a lot has been done in New Zealand for scientific computing and future action will provide a robust legacy for computations. This will flank the pre-existing experimental expertise characterised by a long-standing tradition, greatly boosting the scientific output of the country.

Closing remarks: what will the future hold? A call for interdisciplinarity to raise research quality

The closing remarks of an article almost exclusively focused on the importance and advantages of molecular simulations could well be dedicated to the positive impact of computational sciences on society. However, I feel that such a closing remark would be short-sighted and, at the same time, not entirely reflective of the potential of what I have stated so far. This is essentially because computations, like any other experimental approach you may be thinking of, are limited within their sphere of competence. It is clear to me that the level of resolution and dimensionality of molecular simulations combined with the ever-increasing amount of computational power and its continuedly decreasing costs provide enormous advantages if embraced wholeheartedly. Nevertheless, computations alone won't go very far. On the contrary, the best possible combination of simulations and experiments will provide an unprecedented understanding of molecular systems. The closing remarks of this article are therefore a call for interdisciplinarity.

Integrative approaches, like those outlined in the previous paragraphs, already provide a starting framework that scientists can build upon. Fully embracing interdisciplinary work will provide a powerful, comprehensive and multifaceted understanding of molecular behaviour. On this premise, scientific research that embraces interdisciplinarity at any level is earmarked for success, increasing its quality and its impact beyond the scientific community. On the one hand, scientists themselves need to be open-minded enough to take on board highly cross-collaborative (and sometimes risky) work and on the other hand, institutions need to instigate collaborations by thinking about building working environments where collaborations are favoured.

As a computational scientist working side by side with experimental investigators, I am convinced that the undertaking of this philosophy will pave the way for excellence.

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Lavoisier's gazometer

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By the early eighteenth century, European chemists were very skilled at handling, transforming, and isolating solid and liquid substances working in an ancient, but evolving, tradition, parts of which dated back to the beginnings of metallurgy, distillation and extraction. But little thought was given to the airs that many processes and reactions produced because there were no containers or instruments to capture and then meaningfully manipulate and analyse these airs.

The invention that did so, thereby opening up a whole new realm for chemical analysis seems, in retrospect, to be so simple; yet no one thought of it until the early eighteenth century. It was the pneumatic trough and its first convincing form was announced by an English clergyman, Stephen Hales, in his *Vegetable Staticks* of 1727.[1]

A thought experiment can conjure a pneumatic trough into existence. Imagine washing a glass and idly submerging it allowing all the air to escape. Then lift it up with the bottom facing upwards but the top of the glass still fully submerged; the water stays in most of the glass, but leaves a gap between it and the bottom of the glass. Mightn't one let the air from a reaction be guided by a tube into this intriguing space? Rather than hold the glass by hand (or a piece of string as did Hales), perhaps a means to support it permanently is possible.

By the end of the century the pneumatic trough was routinely found in chemistry laboratories; Lavoisier transformed it by joining it to a powerful and sophisticated instrument, the "gazometer", which weighed the captured airs.

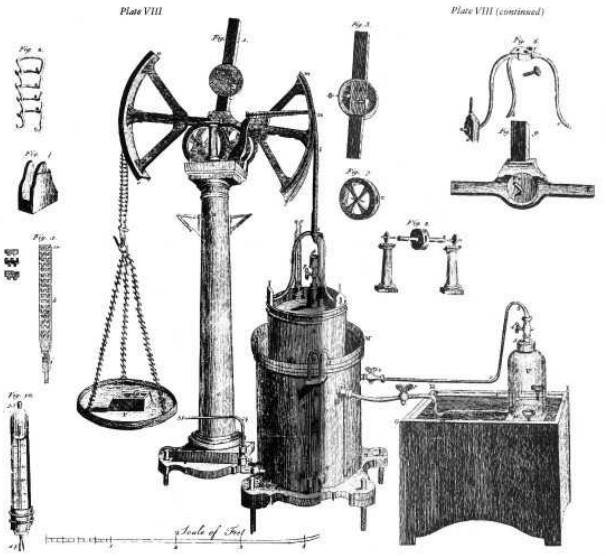

Fig. 1. Lavoisier's gasometer[7]

Lavoisier devotes a full third of his treatise to instrumentation.[2] He fully acknowledges that such descriptions (accompanied by engravings) can only give an indication of what it actually means to do chemistry, sternly advising the novice to "familiarise themselves to the performance of experiments by actual experience" and to recall the

motto which his predecessor Rouelle painted conspicuously in his laboratory "*nihil est in intellectu quod non prius fuerit in sensu*."[3]

As Jan Golinski points out, many of the instruments that Lavoisier discusses (particularly the gazometer) were so sophisticated and expensive that they were the only ones in existence; it would be a long time before other experts, let alone novices, could afford or operate them and check his assertions.[4]

Lavoisier himself acknowledges this paradox: innovative science requires unique instruments which are "too costly and too complicated for being generally used in laboratories", but universal science (the means by which novices learn and colleagues can copy or affirm) requires "more simple and more readily applicable methods."[5]

The gazometer lay at the centre of Lavoisier's chemistry because it enabled him to apply the simple logic of accountancy to chemistry. Just as accounts must be balanced, so too must chemical reactions. When wood burned in the atmosphere, under the old system, it disaggregated into its constituent elements of earth (the ash), fire (or heat), air and water (the hot air being given off was moist). The ash was lighter than the wood but that was all that could be confidently be stated. For Lavoisier the weight of the wood and the air it consumed must equal, in total, the weight of the resulting ash, air given off, heat and water.

It is essential to note that, until a chemist could capture and weigh various airs, then there was no point in adopting a chemistry that took as axiomatic that reactants before and afterwards must weigh, in total, the same, as some of those reactants could well be escaping up a chimney. Lavoisier was right to state that:

"we may lay it down as an incontestable axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment: the quality and quantity of the elements remain precisely the same; and nothing takes place beyond the changes and modifications in the combination of these elements …. We must always suppose an exact equality between the elements of the body examined and those of its products of its analysis."[6]

However, prior to the pneumatic trough and the gazometer, such an axiom was of little use.

The gazometer is too complex to easily describe; it is best left to read the pages themselves that explicate *Plate VIII* (Fig. 1) which depicts the great instrument.[7] A balance dominates *Plate VIII*, with weights in a pan to the left balancing the pressure of the airs on the right and hence giving them a numerical weight. Lavoisier did not make the instrument himself (he was trained as a lawyer, not a mechanic); it was made for him by an instrument maker, Meignie, and is indicative of the intelligence and enterprise of the best French instrument makers of the time.

Chapter VIII of Part 1 displays Lavoisier at his brilliant best; it is the chapter that deploys the gazometer to destroy water's status as an element.[8] Lavoisier places 28 grains of dried and heated charcoal in a special glass tube and passes water over the charcoal. The bottle from which the water came is later weighed and has lost 85.7 grains, so that must be the weight of the water that passed over the charcoal. The water and the charcoal disappear to produce gases which are collected and analysed by the gazometer. They are of two types: carbonic acid gas weighing 100 grains and "a very light gas" which is "susceptible of combustion" weighing 13.7 grains. Earlier in the work he had shown that "100 grains of carbonic acid gas consists of 72 grains of oxygen [gas]" hence it follows that "85.7 grains of water are composed of 72 grains of oxygen [gas] combined with 13.7 grains of a gas susceptible of combustion."[9]

Lavoisier named this "gas susceptible of combustion" hydrogen (from the Greek "generator of water") which, in combination with the caloric (what we would now call energy), was the hydrogen gas he had collected in bottles and which combusted readily with oxygen gas to produce water; a perfect example of synthesis being the mirror image of analysis.[10]

Further demonstrations confirmed the elemental status of oxygen and hydrogen; in their gaseous state and under any chemical operations Lavoisier could arrange, they only became heavier, never lighter. Water, on the other hand, fell apart under chemical operations and thus lost its ancient, elemental status.

Just as a new instrument, the gazometer, helped bring into being new elements at the end of the Enlightenment, so too would a radically new device, the voltaic battery, conjure up myriad new elements under the direction of Humphry Davy. It is to Davy and his pursuit of the elemental in the Romantic era I next turn.

References and notes

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2. Part 3, entitled the "Description of the Instruments and Operations of Chemistry," Antoine Lavoisier, *Elements of Chemistry*, translated by Robert Kerr, Edinburgh, 1790 (hereafter, *Elements*).
3. Nothing is grasped by the mind which is not first apprehended by the senses; *Elements*, p. 293
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5. *Elements*, pp. 319-320.
6. *Elements*, pp. 130-131.
7. *Elements*, pp. 308-319. All the plates were drawn by Lavoisier's wife, Marie-Anne-Pierrette.
8. "Of the Radical Principle of Water, and of its Decomposition by Charcoal and Iron", *Elements*, pp. 83-96.
9. *Elements*, pp. 85-87.
10. *Elements*, p. 89; the synthesis is described pp. 91–96.

International Year of the Periodic Table

#IYPT2019

Video Competition

Help us celebrate the 150th birthday of the Periodic Table and submit a short 1-2 min video about your favourite chemical element!

1869 is considered the birth of the Periodic Table of Elements. 2019 is the 150th anniversary of the Periodic Table of Chemical Elements and has therefore been proclaimed the "International Year of the Periodic Table of Chemical Elements (IYPT2019)" by the United Nations General Assembly and UNESCO.

To celebrate this the **New Zealand Institute of Chemistry (NZIC)** and the **Royal Society of Chemistry New Zealand Branch** are running an exciting video competition. **We would like you to put together a 1-2 min video about your favourite element from the periodic table.**

You have 118 elements to choose from, let your imagination run wild.

There are two judging categories: Junior/Intermediate School (Years 1-8) and Senior School (Years 9-13). Individual and group/team/class entries are both welcome.

Each category will have a first, second and third prize.

1st Prize $300 and a copy of Scientific Sleuthing (http://clerestorypress.co.nz/scientific-sleuthing)

2nd Prize $200 and a copy of Scientific Sleuthing

3rd Prize $100 and a copy of Scientific Sleuthing

You have until 1st October 2019 to complete and submit your video. When you are ready contact Joanna Dowle nzic.office@gmail.com for the details on where to upload the video for judging.

There are many resources you could use to find information for your video, some of these are collected on the NZIC website (https://nzic.org.nz/). We have also provided a few example videos which can be seen by following the link on the NZIC website. Once the judges have decided the winners all the videos will be posted onto the NZIC website (and YouTube channel) and they will also be played at the NZIC conference in November 2019. The judges' decision will be final.

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