Research in the School of Mathematics and Physics in Lincoln, UK.

The School of Mathematics and Physics of the University of Lincoln opened in 2014 as part of the ambitious expansion of College of Science.

In less than three years the School established itself as a centre for cutting-edge research, ranging from pure mathematics to applied nanoscience at the interface between biology, chemistry, physics and mathematics.

We collaborate with research institutions in Brazil, Canada, France, Germany, India, Iran, Iraq, Italy, Japan, Netherlands, Norway, Singapore, Spain, and USA.

This booklet of research highlights contains brief description of some of the best achievements of our members of staff over the last couple of years, as well as reports on our first mathematics conference and graduation in 2016.

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Length Parameters of Finite Groups and Fixed Points of their Automorphisms

One of the most fruitful directions in group theory is the study of the influence of fixed points of automorphisms on the structure of the group. This research [1] establishes a connection between important length parameters of a non-soluble finite group and the corresponding parameters of the fixed point subgroup of its coprime automorphisms.

The structure of an arbitrary finite group $G$ can be described in terms of length parameters related to normal series with `nice' sections. One way of constructing such a series is based on the generalized Fitting subgroup $F^*(G)$. Recall that $F^*(G)$ is the product of the Fitting subgroup $F(G)$ and all subnormal quasisimple subgroups; here a group is quasisimple if it is perfect and its quotient by the centre is a non-abelian simple group. Then the generalized Fitting series of $G$ is defined starting from $F_1^*(G) = F^*(G)$, and then by induction, $F_{i+1}^*(G)$ being the inverse image of $F^*(G/F_i^*(G))$. The least number $h$ such that $F_h^*(G) = G$ is naturally defined as the generalized Fitting height $h^*(G)$ of $G$. Clearly, if $G$ is soluble, then $h^*(G) = h(G)$ is the ordinary Fitting height of $G$. Bounding the generalized Fitting height of a finite group $G$ greatly facilitates using the classification of finite simple groups (and is itself often obtained using the classification). One of such examples is the reduction of the Restricted Burnside Problem to soluble and nilpotent groups in the Hall–Higman paper, where the generalized Fitting height was in effect bounded for groups of given exponent (using the classification as a conjecture at the time). A similar example is John Wilson's reduction of the problem of local finiteness of periodic profinite groups to pro-$p$-groups. (Both problems were solved by Efim Zelmanov.)

Another useful, more rough, length parameter is the non-soluble length of a finite group $G$, which is defined as the minimum number of non-soluble factors in a normal series each of whose factors either is soluble or is a direct product of non-abelian simple groups. (In particular, the group is soluble if and only if its non-soluble length is 0.) Bounding the non-soluble length was one of the steps in Wilson's paper; more recently we used this parameter in the study of both finite and profinite groups in joint work of E. Khukhro and P. Shumyatsky.
This research [1] considers the generalized Fitting height and non-soluble length of a finite group $G$ relative to the same parameters of the fixed-point subgroup $C_G(A)$ of a soluble group of automorphisms $A$ of coprime order. The results are modelled on Thompson's paper, where in the case of soluble groups $G$, $A$ of coprime orders, a bound for the Fitting height of $G$ was obtained in terms of the Fitting height of the fixed-point subgroup $C_G(A)$ and the number of prime factors of $|A|$ counting multiplicities.

This research makes a definitive contribution to the direction in group theory described above. Several open questions are stated, by analogy with improving the bounds for the non-soluble length and generalized Fitting height (similarly to how Thompson's bounds for the Fitting height were dramatically improved later by various authors).

The results of this research were obtained in collaboration of E. I. Khukhro and P. Shumyatsky (Brazil). Some of them were obtained during E. I. Khukhro's visits to University of Brasilia in the framework of the CNPq-Brazil programme “Researchers without borders”.

Additive Subgroups and Inversion in Finite Fields

The inversion map in a finite field (mapping \(a\) to \(1/a\), supplemented by sending 0 to 0) plays a role in various cryptographic tools. A notable instance is the Advanced Encryption Standard, the block cipher adopted by the U.S. government in 2002 and later become a worldwide standard. One of the reasons is the high nonlinearity of the inversion map, in various appropriate senses. The set of inverses of the nonzero elements of an additive subgroup of a finite field may thus be expected, as a rule, to be a very nonlinear subset. This generic expectation may take various concrete expressions depending on the specific context. The results in [1] make one such nonlinearity characteristic of the inversion map explicit in terms of certain bounds.

This line of research originated with a description of all inversion-closed additive subgroups of an arbitrary field which I gave in 2007. A more general result with a division ring in place of a field was independently and simultaneously proved in a paper of Goldstein, Guralnick, Small and Zelmanov, the noncommutative case relying on Zelmanov’s classification of prime Jordan triple systems.

In the simpler commutative case of a field the gist is that inversion-closed additive subgroups are rather close to being subfields. More precisely, they are either subfields or kernels of the trace map in a quadratic field subextension. (A simple example is given by the additive subgroup of purely imaginary numbers within the field of complex numbers.) This occurs because, roughly speaking, subtraction and inversion in a field are, together, almost enough to recover multiplication: a classical identity of Hua (1949) expresses the product \(aba\) in terms of \(a\) and \(b\) (in an associative but not necessarily commutative ring) using only subtractions and taking inverses.

In the special case where the field is finite one can replace the use of Hua’s identity with an elementary polynomial argument. The finite setting, and this type of polynomial proof, allow cryptographically relevant refinements where the same conclusion can be obtained on the weaker assumption that \(a^{-1}\) belongs to \(A\) for most nonzero elements \(a\) of \(A\) rather than for all. How weak this assumption can be made was investigated by Bence Csajbók (2013). He noted that the following more general setting involving two subspaces rather than one is actually more natural and simpler to work with. Let \(A\) and \(B\) be \(\mathbb{F}_q\)-subspaces of a finite field \(F\) (where \(\mathbb{F}_q\) denotes the field of \(q\) elements, contained in \(F\)), of the same size \(q^d\), let \(A^{-1}\) denote the set of inverses of nonzero elements of \(A\). If \(A^{-1}\) is contained in \(B\) then clearly \(|A^{-1}\cap B| = |A^{-1}| = q^d - 1\), and this case is well-understood as a straightforward generalization of the case described above of \(A = B\) being inversion-closed. Assume therefore that \(A^{-1}\) is not contained in \(B\). The goal then becomes obtaining a good upper bound on \(|A^{-1}\cap B|\). Csajbók’s proved that \(|A^{-1}\cap B| \leq 2q^{d-1} - 2\), and produced examples to show that the bound is best possible for \(d\) not exceeding three.
Thus, according to Csajbók’s bound, at most about a fraction $2/q$ of the elements of $A^{-1}$ belong to $B$. The main achievement of [1] is to roughly halve Csajbók’s bound for $d > 3$, namely, proving the general bound $|A^{-1} \cap B| \leq q^{d-1}(1 + O(q^{-1/2}))$ for each $d > 3$. However, this could only be achieved by developing a novel algebro-geometric approach to the problem, which I hope might prove useful for similar investigations in finite fields.

The essence of the argument is viewing the image of the intersection $A^{-1} \cap B$ in the $(d - 1)$-dimensional projective space associated with the $\mathbb{F}_q$-linear space $B$ as an algebraic set $S$. After some technical work required to extend the field of scalars to the algebraic closure of $\mathbb{F}_q$, the special structure of $S$ gives an amount of control on the structure and dimensions of its various irreducible components, whose number of $\mathbb{F}_q$-rational points can then be estimated using the Lang-Weil bound.

A nontrivial part of the argument is showing that, in essence, $S$ has only one top-dimensional irreducible component when $d > 3$, which accounts for the main term in the final bound. The argument also sheds further light on the case $d = 3$ and the geometry of the examples produced by Csajbók. In fact, in that case the curve $S$ cut by $A^{-1}$ in the two-dimensional projective plane associated with $B$ is a cubic with possibly two irreducible components, a line and a nonsingular conic, each contributing up to half of Csajbók’s bound $|A^{-1} \cap B| \leq 2q^{d-1} - 2$. Furthermore, the arguments of [1] allow a full classification of the geometric possibilities in case $d = 3$, producing a complete list of the possible values attained by $|A^{-1} \cap B|$ in the reducible case.

A natural open question is whether the technique employed can be extended to prove bounds on $|A^{-1} \cap B|$ in case $A$ and $B$ are $\mathbb{F}_q$-subspaces of a finite field $F$ having different sizes, say $|A| > |B|$. For that situation I can presently only prove the weaker bound $|A^{-1} \cap B| < \frac{(d-1)|B|}{q} + q - d$ (under a natural assumption which serves to exclude trivial configurations), using more elementary arguments which I presented in a separate recent paper.

A classification of primitive permutation groups with finite stabilizers

When looking at permutation groups, researchers typically focus on primitive permutation groups. These are indecomposable in some sense, and so they are like the "atoms" of permutation group theory.

A permutation group $G$ on a set $\Omega$ is primitive if the only $G$-invariant partitions on $\Omega$ are the trivial or universal relations. For example, the group consisting of all permutations of the integers is primitive; the group consisting of the symmetries of a 4-cycle is not primitive because a bipartition of the vertices is invariant under the action of the group.

In the finite case, primitive groups are the fundamental actions from which all permutation groups are constituted. The finite primitive permutation groups were classified by the famous Aschbacher–O’Nan–Scott Theorem. This theorem describes in detail the structure of finite primitive permutation groups in terms of finite simple groups. It underpins all of modern finite permutation group theory. A simplification of the theorem says that such groups are either "basic" or they are constructed from basic groups using the wreath product in its product action (the groups described here as being basic can in fact be quite complicated).

The research in [1] focuses on infinite primitive permutation groups, and describes the structure of those that have finite point stabilizers. These groups are precisely those primitive groups whose subdegrees are bounded above by a finite cardinal. This class of groups also includes all infinite primitive permutation groups that act regularly on some finite self-paired suborbit (there is an old problem in the Kourovka Notebook, Problem 7.51, asking for a description of these groups).

The main result in [1] is a classification of all infinite primitive permutation groups with finite point stabilizers, describing in detail their structure in terms of finitely generated simple groups. Intuitively it shows that such groups are either almost simple (that is, they act as a "large" group of automorphisms of a finitely generated simple group) or they are built from a smaller infinite primitive permutation group (which also has finite point stabilizers) using the wreath product in its product action. The precise statement of the theorem follows.

**Theorem.** If $G$ is a group of permutations of an infinite set $\Omega$, and the action of $G$ is primitive with some point stabilizer finite, then $G$ is finitely generated by elements of finite order and possesses a unique
(non-trivial) minimal normal subgroup $M$; there exists an infinite, nonabelian, finitely generated simple group $K$ such that $M$ is the direct product of $m$ copies of $K$, where $m \geq 1$ is finite; each stabilizer acts transitively on the components of $M$ by conjugation; and $G$ falls into precisely one of the following categories:

(i) $M$ is simple and acts regularly on $\Omega$, and $G$ is equal to the split extension $M.J$ where $J$ is any point stabilizer and no non-identity element of $J$ induces an inner automorphism of $M$;

(ii) $M$ is simple, and acts non-regularly on $\Omega$, with $M$ of finite index in $G$ and $M \leq G \leq \text{Aut}(M)$;

(iii) $M$ is non-simple. In this case $m > 1$, and $G$ is permutation isomorphic to a subgroup of the wreath product $H \text{Wr}_{\Delta} \text{Sym}(\Delta)$ acting via the product action on the Cartesian product of $\Gamma^m$, where $\Delta = \{1, ..., m\}$, $\Gamma$ is some infinite set and $H \leq \text{Sym}(\Gamma)$ is an infinite primitive group with a finite point stabilizer. Here $K$ is the unique minimal normal subgroup of $H$. Moreover, if $M$ is regular, then $H$ is of type (i) and if $M$ is non-regular then $H$ is of type (ii).

For each type (i), (ii) and (iii) there exist examples of infinite primitive permutation groups with finite point stabilizers. For permutation groups which lie in classes (i) and (iii) there are known conditions which guarantee primitivity. For any group $G$ of type (iii), an explicit permutation embedding of $G$ into the product $H \text{Wr} \text{Sym}(\Delta)$ is described.

This paper showed, for the first time, that infinite primitive permutation groups that satisfy a finiteness condition might have a structure that is very similar to that of the finite permutation groups. It has inspired other work in a similar direction, looking for example at the structure of quasiprimitive permutation groups with finite stabilizers.

Automorphisms of Finite $p$-Groups

From the 1970s, the following question began to take form: Does every finite non-cyclic $p$-group $G$ of order $|G|$ at least $p^3$ have $|G|$ dividing the order of its automorphism group, $\text{Aut}(G)$?

Notice that every non-central element of $G$ induces a non-trivial automorphism of $G$ via conjugation. This defines an inner automorphism of $G$. Let $\text{Inn}(G)$ denote the subgroup of inner automorphisms of $G$, which is normal in $\text{Aut}(G)$. Certainly as $\text{Inn}(G)$ is isomorphic to $G/\text{Z}(G)$, that is $G$ modulo its centre, one can rephrase the question to whether $|\text{Z}(G)|$ divides $|\text{Aut}(G)/\text{Inn}(G)|$.

Over the past forty years, this question was partially answered in the affirmative for specific families of $p$-groups, for instance $p$-abelian $p$-groups, $p$-groups of class 2, $p$-groups of maximal class, etc. This led many to believe that the complete answer might be yes, which is why the question was reformulated as a conjecture: If $G$ is a finite non-cyclic $p$-group with $|G| > p^2$, then $|G|$ divides $|\text{Aut}(G)|$.

What is more, Eick proved in 2006 that all but finitely many 2-groups of a fixed coclass satisfy the conjecture. Couson generalized this to $p$-groups for odd primes, but only to infinitely many $p$-groups of a fixed coclass. The coclass theory shed new light on the conjecture, and provided more evidence as to why it could be true. Looking at past efforts, it could also be said that an underlying theme was cohomology, which hinted that the full conjecture might be settled using such means.

However, it came as a surprise that the conjecture is false. Very recently, Gonzalez-Sanchez and Jaikin-Zapirain disproved the conjecture using Lie methods, where the question was first translated into one for Lie algebras. The main idea was to use the examples of Lie algebras with derivation algebra of smaller dimension, from which they constructed a family of examples of $p$-groups with small automorphism group. Their proof incorporates pro-$p$ groups and $p$-adic analytic groups.

Now a new question may be formulated: Which other finite non-cyclic $p$-groups $G$ with $|G| > p^2$ have $|G|$ dividing $|\text{Aut}(G)|$? In [1], we prove that for $G$ a finite non-cyclic $p$-group with $|G| > p^2$, if $G$ has an abelian maximal subgroup, or if $G$ has elementary abelian centre and is not strongly Frattinian, then $|G|$ divides $|\text{Aut}(G)|$. The latter is a partial generalization of Gaschütz’ result that $|G|$ divides $|\text{Aut}(G)|$ when the centre has order $p$. Our proofs make significant use of works by O. Mueller and U. H. M. Webb.

Apart from classifying finite non-cyclic $p$-groups which have $|G|$ dividing $|\text{Aut}(G)|$, another direction that one might take is to tackle the following related conjecture: Every finite $p$-group admits a non-inner
automorphism of order $p$. This conjecture, dated back to 1973, naturally extends the aforementioned result of Gaschuetz: every non-abelian finite $p$-group admits a non-inner automorphism of order some power of $p$. When $G$ is a finite $p$-group of class at most 3, it was shown by Liebeck and Abdollahi et al that this conjecture holds. Further, Abdollahi et al proved that any finite $p$-group of coclass 2 possesses a non-inner automorphism of order $p$. A few other special cases of finite $p$-groups have been confirmed to satisfy the conjecture, the most recent being $p$-groups of coclass 3 excluding the prime 3 by Ruscitti, Legarreta and Yadav in 2006, but in large the conjecture remains unconfirmed.

Also there are other many other open questions regarding the automorphism group of finite $p$-groups. For instance, there are infinitely many $p$-groups for which $|G|$ equals $|\text{Aut}(G)|$, but it is an old problem whether there exists a finite $p$-group, other than $D_8$, whereby $G$ is isomorphic to its automorphism group $\text{Aut}(G)$.

Moon Induced Vorticity in Saturn’s Rings

Saturn’s rings are known to show remarkable real-time variability in their structure. Many of their perturbations can be associated to interactions with nearby moons and moonlets (large coherent bodies smaller than typical moons with sizes $\sim 10^2 m \) ). Possibly the most interesting and dynamic place in the rings, probably in the whole Solar System, is the F ring. A narrow ring situated at the edge of the main rings shepherded by the two nearby moons Prometheus and Pandora. A highly disrupted ring with large asymmetries both radially and azimuthally. This is partly due to the close radial proximity of the F ring to the Roche limit of water ice around Saturn and the nearby shepherd moons which constantly stir up ring material. The Roche limit is the minimum distance a satellite can be from a planet without it being tidally pulled apart. For a planet with density $\rho_M$ and a purely fluid satellite consisting of ice with density $\rho_m$, it is taken as $d = R \cdot 2.46 \sqrt[3]{\frac{\rho_M}{\rho_m}}$.

Numerically we found that the curl of the velocity vector field (vorticity) in the perturbed area of the F ring after a close encounter of Prometheus (inner shepherd moon) was non-zero. Here the vorticity is shown as the curl of the velocity vector field $\nabla \times V = \frac{\partial V_y}{\partial x} - \frac{\partial V_x}{\partial y}$. It should be noted that due to the
orbits of ring particles around Saturn a background vorticity is always present. This background vorticity is measured at \( \sim 1.23 \times 10^{-4} \text{ rad/s} \), and decreases with increasing radial location \( r \) from Saturn due to the Keplerian velocities required for circular orbits \( |V| = \frac{GM}{r} \). However, after the inner moon Prometheus gravitationally stirs up ring material local rotations in the F ring are significantly above these background levels. Within the perturbed area rich distributions of local rotations is seen located in and around the channel edges. The gravitational scattering of ring particles during the encounter causes a significant elevated curl of the vector field above the background F ring vorticity for the first 1–3 orbital periods post encounter. After 3 orbital periods vorticity reverts quite quickly to near background levels. This newly found dynamical vortex life of the ring will be of great interest to planet and planetesimals formation in proto-planetary disks where vortices and turbulence are suspected of having a significant role in their formation and migrations.

Additionally, we also find that the immediate channel edges created by the close passage of Prometheus actually shows high radial dispersions in the order \( \sim 20–50 \text{ cm/s} \), up to a maximum of 1 m/s. This is much greater than the value required by Toomre for a disk to be unstable to the growth of axisymmetric oscillations. However, an area a few hundred km away from the edge shows a more promising location for the growth of coherent objects. This is because radial dispersions here are well below those required for a disk to be unstable to the self-gravity and the growth objects.

Computational Physics

Covalent assembly of functionalized molecules on a copper surface

We investigated the assembly of highly functionalised porphyrin molecules on a copper surface, forming structures with distinct directional properties and stabilized by covalent interactions (Figure 1). Given the strong nature of the covalent bond, covalent assembly has a great promise of producing robust nanostructures, as opposed to fragile assemblies mediated by weaker interactions. The ability of controlling the features of such networks is important from a technological point of view as it would allow the realization of stable and self-assembled structures to be exploited in molecular devices operating at extreme conditions (e.g., high temperature). The aim is to uncover how covalent assembly work at surfaces and understand the underlying mechanism(s) that control bond-breaking and bond-making processes at specific positions of the molecules. In particular, we studied the reaction of TMTPP molecules (Figure 2), which create connected networks utilizing the 4-methyl groups as unique connection points. We used density functional theory (DFT), Nudged Elastic Band (NEB) calculations and scanning tunneling microscopy (STM) to show that the unique directionality of the bonding stems from a chain of highly selective C-H activation and dehydrogenation processes, followed by specific intermolecular C-C coupling reactions (Figure 3). These are facilitated by the surface, by steric constraints and by anisotropic molecular diffusion. These insights provide the first steps towards developing synthetic rules for complex two-dimensional covalent organic chemistry that can be enacted directly at a surface to deliver macromolecular structures designed for specific functions.

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Figure 1: Covalent assemblies of differently functionalized porphyrins on Cu(110) surface. At high temperatures (T >550K), three molecules assemble in a completely different way. TMTPP (left) form diagonal chains, COMP (centre) horizontal chains, while COD, (right) form strictly vertical structures.
These investigations have been performed in collaboration with Prof L. Kantorovich (KCL London), with the experimental STM group of Prof R. Raval (University of Liverpool) and the synthesis group of Prof. D. Amabilino (University of Nottingham).

Figure 2: Minimum energy profiles and reaction paths calculated with Nudged Elastic Band (NEB) bringing two TMTPP molecules to the bonded configuration via dehydrogenation (left), diffusion and bonding (right). The insets highlight the bonding region(s).

Figure 3: Left: Experimental and DFT-simulated STM images of a TMTPP porphyrin. Centre: different hydrogens which “activate” selectively to form the diagonal structures after diffusion and bonding (right).

Disk-shaped bicelles in block copolymer/homopolymer blends

Mixtures of micelle-forming and lamella-forming amphiphilic molecules in solution can form disk-shaped bilayers known as bicelles (see, for example, U. H. Dürr, R. Soong and A. Ramamoorthy, *Prog. Nucl. Mag. Res. Sp.* 69 (2013), 1–22). These structures are widely used in biophysical experiments as model membranes. However, it is not clear if and under what conditions they are thermodynamically stable, and making detailed comparisons between theory or simulations and experiments on aqueous systems proves difficult. In a paper published in Macromolecules in 2016, we take a step towards bridging this gap. Following an approach that has been successfully applied to the study of micelle formation, we perform self-consistent field theory (SCFT) calculations on bicelle formation in a blend of two types of diblock copolymer (a polymer composed of two sections joined end-to-end) with homopolymer.

We find that, if the segregation between the different sections of the copolymer is strong and the hydrophilic block of the micelle former is large, the free energy of the bicelle can drop below those of the competing micelle and bilayer structures. This region of parameter space is found to correspond to a PDMS-PS/PDMS blend at experimentally accessible temperatures. We also find that the centre of each disk is mainly composed of lamella former, while its thicker rim has a higher concentration of micelle former. Finally, we show that the presence of the micelle former is necessary for the bicelle to be stable with respect to further aggregation. The system also has the potential to show new mechanical properties at low temperatures, where it will have a clay-like structure, being composed of a dispersion of hard disks in a fluid polymer.

This work was presented at the Physical Aspects of Polymer Science conference in Manchester, the Recent Appointees in Polymer Science meeting in Loughborough and in an invited seminar at the University of Sheffield, and was listed as one of the most-read articles on the Macromolecules website.
Figure 1. A disk-shaped bicelle found in SCFT calculations. The inset shows the segregation of the two hydrophobic groups at the rim of the bicelle core.

Experimental and Theoretical Analysis of Hydrogen-Bonding in Two-Dimensional Chiral 4',4''"-(1,4-Phenylene)bis(2,2':6',2''-terpyridine) and Self-Assembled Nano-architecture

Engineering novel organic nano-architectures through bottom-up strategy and molecular self-assembly is attracting increasing interest over the last decade. Predicting and controlling self-assembly is a prerequisite to fabricate well-defined nano-architectures with specific local electronic properties.

In this paper we investigated experimentally with Scanning Tunneling microscopy (STM) and Density functional theory (DFT) the two-dimensional self-assembly of 4',4''"-(1,4-Phenylene)bis(2,2':6',2''-terpyridine) on graphite surface (Fig 1). Scanning tunneling microscopy (STM) shows that this molecular building blocks form a compact chiral supramolecular network on graphite at the 1-octanol/graphite interface. Molecules adopt a side-by-side arrangement inside the monolayer but are arranged perpendicularly at the domain boundary. Experimental observations and calculations reveal that molecule forms a close-packed structure stabilized by double and single hydrogen-bonds.

Calculations show that the molecular conformation is less planar in the perpendicular molecular packing than in the molecular parallel packing (Fig 2). The flexibility of terpyridine groups open new opportunities to engineer new organic nano-architectures on surfaces.

Figure 1. 4',4""-(1,4-Phenylene)bis(2,2':6',2''-terpyridine) molecule (C36H24N6) and experimental STM images on graphite surface.
Figure 2. STM images of the two enantiomeric domains in parallel and perpendicular packing and the respective configurations obtained using Ab-initio methods.

Phase separation of a binary mixture on triply periodic surfaces

If you pour olive oil in water, it will not mix but instead form multiple oil patches at the water surface. Two things then happen: over a short period of time, these oil patches will tend to have circular shapes because of a phenomenon that tries to minimise the perimeter length of the patch while keeping the amount of oil molecules in the patch constant. Mathematically, this is analogous to a famous mathematical problem of the antiquity called the isoperimetric problem and whose goal was to determine the shape of a closed curve with fixed perimeter length that would enclose the biggest possible area (one can easily imagine a shepherd trying to enclose as many sheep as possible given that he only has a rope of a given length). The solution to this problem, on a flat even surface, is a circle and so it is as well the shape took by our small oil patches. Another thing that happens over a much longer time scale is the lumping of the small oil patches into a single big circular oil patch; essentially because of the same underlying phenomenon.

Now, these two specificities (circular shape of disconnected domains and merging of previously disconnected lipid domains into a final single patch) are not restricted to oil and water but are expected to occur at sufficiently low temperature for every mixture of different molecules confined on a two dimensional liquid film. As everybody knows from playful experiences with soap and water, liquid films are not necessarily flat. In fact, in the same way that a flat sheet of paper can be curved and rolled to form a cylinder so can a liquid film adopt curved shapes: from spherical shapes for bubbles to more exotic shapes called minimal shapes that look like a saddle at every point. Amongst these exotic shapes, some called triply periodic minimal surfaces appear naturally in detergent mixtures and biology and are made of “stitched” pieces of minimal surfaces repeated periodically in the three dimensions of space (cf. Figure 1 for the known repeating elements of liquid film phases observed in lipid mixtures).
In a work done in collaboration with the University of Durham [1], we asked ourselves what would be the behaviour of a mixture of two molecules that do not like each other if they lived on an exotic surface like the ones represented in Fig. 1. By combining numerical simulations and a strong mathematical analogy with magnetic systems we found that, although small patches of a substance may form (in green in Fig. 2), they would neither necessarily merge together on the surface nor would they have a circular shape. The underlying reason is that different molecules have different preferences for curved regions: some don’t mind being in curved regions while some don’t like it at all. This makes certain areas of the surface more suitable for one type of molecules while the remaining surface is more suitable for the other type. If we were to focus on the molecular species that prefers to be in the flattest possible regions of the surface (and assign colour green to it), it would require extra work to get it out of such a cosy area. Graphically, this can be represented by trying to imagine where would “rain water” settle in a corresponding virtual “topographic” map where zero curvature means zero height and very strong curvature means great height (Top left of Fig. 2). The outcome is that small green patches form but tend to remain trapped at the bottom of the valleys if they don’t have enough incentive to climb the hills separating them from their neighbours (Top right of Fig. 2). If, however, the two substances dislike each other very much, then bridges can form between patches (Bottom left and right of Fig. 2).

Lastly, it can be seen that the green patches adopt quasi-polygonal shapes instead of the usual circular shape (Top right of Fig. 2). We propose that this is due to the underlying surface which has a quasi-hexagonal symmetry and thus the minimising bounding curve of an isolated patch ought to be made of six repetitions of the same piece of curve, which itself should be as short as possible given two particular end points. Such a minimising piece of curve is called a geodesic and thus the bounding curve of a patch is made of six stitched pieces of geodesics on the underlying triply-periodic surface.

These results are important for understanding how geometry may be exploited to understand and control composition in biological systems and may have applications for pattern formation in the design of smart materials.

Multipod Structures of Lamellae-Forming Diblock Copolymers in Three-Dimensional Confinement Spaces.

In collaboration with the experimental group based in Tohoku University, Sendai and in Tokio (Japan) the three-dimensional (3D) confinement effect on the microphase-separated structure of a diblock copolymer was investigated both experimentally and computationally. Block copolymer nanoparticles were prepared by adding a poor solvent into a block copolymer solution and subsequently evaporating the good solvent.

The 3D structures of the nanoparticles were quantitatively determined with transmission electron microtomography (TEMT). TEMT observations revealed that various complex structures, including tennis-ball, mushroom-like, and multipod structures, were formed in the 3D confinement. Detailed structural analysis showed that one block of the diblock copolymer slightly prefers to segregate into the particle surface compared with the other block (see Figure 1).

To compare the experimental and theoretical results, the structures in the 3D confinement spaces were determined using CDS. The $f_{ni}$ is chosen to match the experimental data.

From the experiment it is known that PST segments prefer the outer surface of the particle. Therefore, we chose the boundary condition $\psi_0=0.2$ to mimic that experimental behaviour and more specifically to match the experimental structures in Figure 1; see Figure 2.

This paper [1] suggests a tandem approach in designing new structures in confinement spaces: Computer simulations can be used to predicted block copolymer structures in confinements prior to real experiments.

Figure 1. TEM and 3D structures of block copolymer nanoparticles obtained with TEMT. The blue and Green Phases in 3D images correspond to the PST and PI phases respectively. Scale Bar: 100 nm.

Figure 2. Cell dynamics simulation of diblock copolymer in spherical confinement for the boundary parameter $w_{050.2}$. The green and blue blocks correspond to the major (PI) and minor (PSt) phases, respectively, in the experiments. The volume fraction is $f_{PI}=0.60$. 
Structure, Dynamics and Function of the P450 BM-3 Enzyme

Monooxygenase P450BM-3 is an enzyme present in *Bacillus megaterium*, a big rod-like bacterium that lives in widely diverse habitats. Its ability to insert with high specificity and selectivity an oxygen atom to a hydrocarbon chain makes it a very attractive enzyme for possible biotechnological and biomedical applications. In the last 12 years, we have studied different functional aspects of this enzyme using computer simulations and molecular modelling. More recently, we have studied the effect of inter-domain conformational changes and dynamics of complex between the Heme and the FMN reductase domain and its effect on the inter-domain electron transfer (ET) mechanism. The simulations evidenced an inter-domain conformational rearrangement (see Figure 1) that reduces the average distance between the FMN suggesting that the crystallographic FMN/heme complex is not in the optimal arrangement for a favourable ET rate under physiological conditions. We have also calculated, using semi-empirical calculations of electron tunnelling, the changes in the ET rate caused by the protein dynamics. The results showed the occurrence of ET pathways (red dashed lines in the Figure 1) between the heme iron and cobalt atoms having calculated ET rates comparable with the experimental one. We also observed a neat correlation between the largest protein functional movements and the activation of the most effective ET pathways.

![Figure 1.](image_url) The purple colour arrow shows the displacement of the FMN domain (represented with an orange secondary structure) towards the HEME domain (represented with a pink molecular surface containing the secondary structure in purple) after conformational rearrangement occurring within 100 ns of MD simulation. The secondary structure coloured in blue represent the FMN in its starting crystallographic conformation.

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Finally, in one of our latest study of the protein [1] the interaction of the Heme domain with the soluble electron mediator mediator cobalt(II) sepulchrate (CoSep) was analyzed. One of the principal limitations to exploit this enzyme in industrial processes is its dependence on the expensive reduction cofactor NADPH to drive its catalytic cycle. Soluble electron-transfer mediators like the CoSep have been proposed as a cost-effective alternative to shuttle electrons between an inexpensive electron source (Zn powder) and the enzyme’s redox center. Our study provided a detailed map of ET mediator binding sites on the protein surface. The CoSep did not show a preferential binding to these sites. However, among the observed binding sites, only few of them provide efficient ET pathways to heme iron (see Figure 2 and Ref. [1] for details). The results of this study could be used to improve the ET mediator efficiency of the enzyme for possible biotechnological or biomedical applications.

Fluctuation effects in polymers

This research considers extending a successful theoretical approach to experimentally relevant quantities. Polymers consist of building blocks that are chained together. Diblock copolymers are a special variant, in which the chain consists of two subchains, each with its own building blocks, see Figure 1.

![Figure 1. Diblock copolymer chain](image)

The two subchains effectively repel each other. The strength of repulsion is controlled by the parameter $\chi N$. Their linkage prevents them from separating completely as in water and oil. Instead, they form intricate structures at sizes comparable to the extent of a chain. One of the theoretical approaches to model such systems is called self-consistent field theory (SCFT). It is a highly successful theory, but does lean on an important assumption: the chains are infinitely thin. Together with the assumption of an incompressible melt this implies that the number of neighbours a chain has is infinite too and as a result the mean field-description becomes exact in this limit.

In experiments, however, chains are not infinitely thin and hence the number of neighbours is finite. Here the effect of limiting the number of neighbours is studied. This characteristic is captured in a parameter $C$, the number of chains per volume that is equal to the radius of gyration of a chain cubed. The motion of a single neighbouring chain will have a noticeable effect on the tagged chain; it induces fluctuations of its surroundings.

The theoretical approach that I use to study these effects is called Field-Theoretic Monte Carlo (FTMC). Like SCFT it is a field-based description, where the fields are describing the interaction of a building block with its surrounding blocks. However, instead of taking the saddle point approximation, as is the case with SCFT, one averages over different field configurations using the so-called Metropolis algorithm. Another technique would be to do particle-based simulations (PBS). PBS do have limitations, however: only relatively small values of $C$ can be studied. In this sense it is complementary to FTMC, since the latter technique has no problems to simulate intermediate to infinite values of $C$. 

Bart Vorselaars is a Lecturer in applied mathematics. Bart received his PhD in 2008 in Physic from Eindhoven University of Technology in the Netherlands. Subsequently he worked at the University of Reading and the University of Warwick in the UK and the University of Waterloo in Canada.
An important characteristic of field-theoretic approaches is that they contain an ultraviolet divergence. As a result physical observables depend on the grid spacing. This can be resolved for FTMC by renormalizing the repulsion parameter $\chi N$. We found that the renormalization procedure that is typically in use does not work for realistic values of $C$. We introduced a new renormalization method that solves this problem.

Upon studying the results we find that the lamellar surfaces for finite $C$ roughens, fig 2. It is also observed that the transition from a disordered structure to ordered lamellae depends on $C$. The fluctuations destabilize the ordered phase, so that the transition shifts towards larger values of $\chi N$ upon decreasing $C$. The shift in transition is considerably, and for small values of $C$ the results agree nicely with particle-based simulations, fig. 3. This illustrates that FTMC is capable of bridging the gap between SCFT and PBS.

Although the FTMC technique has been demonstrated here for diblock copolymers with symmetric composition, it can easily be extended for more complex block copolymer architectures, which exhibit a myriad of ordered morphologies with numerous applications (e.g., compatibilizers, adhesives, lithography, porous materials and photonic crystals).

A relationship between three-dimensional surface hydration structures and force distribution measured by atomic force microscopy

Hydration plays important roles in various solid–liquid interfacial phenomena. Very recently, three-dimensional scanning force microscopy (3D-SFM) has been proposed as a tool to visualise solvated surfaces and their hydration structures with lateral and vertical (sub) molecular resolution.

Scanning force microscopy is an ingenious technique where tiny changes in the frequency of an oscillating cantilever arm can be used to amplify the miniscule changes in atomic forces as an atomically sharp tip attached to the cantilever is scanned over the surface. By scanning in 3D a full map of the force over the surface can be constructed (see Figure 1).

However, the relationship between the 3D force map obtained and the equilibrium water density distribution above the surface remains an open question. Work from Matt Watkins and international theoretical and experimental collaborators investigated this relationship at an interface of an inorganic mineral, fluorite (commonly used in toothpaste), and water.

The force maps experimentally measured in pure water were directly compared to force maps generated using the solvent tip approximation (STA) model.

![Figure 1. By combining experimental atomic force microscopy (left panel) and theory (right) we can map out the likely locations of water molecules above a mineral surface.](image)
Comparison of experiment and theory showed that the simulated STA force map describes the major features of the experimentally obtained force image. The agreement between the STA data and the experiment establishes the correspondence between the water density used as an input to the STA model and the experimental hydration structure and thus provides a tool to bridge the experimental force data and atomistic solvation structures. This means that a macroscopic microscope is capable of determining with sub atomic precision the location of water molecules above a structured surface, and without disturbing the surface.

Further applications of this method should improve the accuracy and reliability of both interpretation of 3D-SFM force maps and atomistic simulations in a wide range of solid–liquid interfacial phenomena.

Towards directed self-assembly in block copolymers

Supramolecular structures of nanometric size are of great interest due to potential applications in nanotechnology, which range from nanopatterned surfaces, nanocrystals with exotic optoelectronic properties, to functional foods and pharmacological products. The main technological problem is to achieve the control and reliability of the final product when traditional manufacturing processes cannot be down-scaled to the nanometric size. Hence, physical systems that spontaneously form supramolecular assemblies under appropriate conditions are so important, as far as they can be externally controlled to produce the desired target structure. Block copolymers (BCP) are one of these valuable materials because of their ability to self-assemble into different nanostructures.

BCP consist of blocks of chemically different monomers covalently bond. The simplest system is (A-B) diblock copolymers. If monomers A and B are highly incompatible, the system can spontaneously segregate into two distinct nanodomains (microphase separation). The size of such nanodomains is on the range between 10 and 100 nm. Depending on the nature of the monomers, such as their degree of polymerization, interaction between the components, and the relative size of each block, these microphases can be either lamellae, cylinders, or spheres, although other more exotic morphologies, like the gyroid phase, can be observed in bulk samples. Morphologies not accessible in the bulk can exist under confinement due to the additional constraints on the system imposed by the bounding surfaces.

In our article [1] we have theoretically analyzed the morphology of sphere-forming block copolymers assembled in thin films on patterned surfaces. The patterns on the lower surface are alternating bands of a given width distinctively attracting or repelling a given block (Figure 1). We find that long-range order can be achieved, and it depends on the commensurability of the characteristic length of the block domains with both band periodicity and slit thickness. The comparison of the simulation results with experimental data shows a very good agreement. Furthermore, we show that the proper selection of the band periodicity and, consequently, of the film thickness permits the system to switch from hexagonal packing to body-centered orthohedra (Figure 2). The analysis carried out in this article suggests that the use of chemical masks on surfaces, together with the control of the thickness can be a useful tool to create the desired structure from the self-assembly of BCP. We believe that this is a step forward towards the applications of this systems in well controlled fabrication of nanoscopic devices.
Figure 1. Simulation setup (top) and example of BPC assembly (bottom).

Figure 3. Example of CDS simulation of non-bulk morphology of sphere-forming BCP confined by solid surfaces (top and side views).

EXPERIMENTAL NANOSCIENCE

PEGylated graphene oxide for tumor-targeted delivery of paclitaxel

The graphene oxide (GO) sheet is considered to be one of the most promising carbon derivatives in the field of material science for the past few years and has shown excellent tumor-targeting ability, biocompatibility and low toxicity. In this research [1] we have endeavored to conjugate paclitaxel (PTX) to GO molecule and investigate its anticancer efficacy.

We conjugated the anticancer drug PTX to aminated PEG chains on GO sheets via covalent bonds to get GO-PEG-PTX complexes. The tissue distribution and anticancer efficacy of GO-PEG-PTX were then investigated using a B16 melanoma cancer-bearing C57 mice model.

The GO-PEG-PTX complexes exhibited excellent water solubility and biocompatibility. Compared with the traditional formulation of PTX (Taxol.), GO-PEG-PTX has shown prolonged blood circulation time as well as high tumor-targeting and -suppressing efficacy.

PEGylated graphene oxide is beneficial for anticancer therapy. Owing to its good water solubility, highly dispersed ability, high drug-loading efficacy and passive tumor-targeting ability, graphene oxide (GO) can be used as a carrier to deliver certain drugs into tumor tissues. PEGylation of GO can improve both its solubility in saline and biocompatibility. The GO-PEG obtained can be utilized for biomedical applications.

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Figure 1. PTX loading on GO-PEG: (A) Schematic illustration of PTX modified by succinic anhydride at 2’-OH; (B) Schematic illustration showing how GO was modified by NH2-PEG4k-NH2 and 2’-succinyl PTX was conjugated on GO-PEG through a cleavable ester bond.
GO-PEG substantially improves the use of paclitaxel in anticancer chemotherapy. Indeed, the side effects, toxicity and severe anaphylaxis of paclitaxel (PTX) injections used in clinic limit their application. PTX was covalently conjugated onto GO-PEG to optimize the solubility and biocompatibility. GO-PEG-PTX can deliver PTX molecules to tumor tissues resulting an improved therapeutic effect.

In vivo investigation showed that GO-PEG-PTX exhibited prolonged blood circulation time, much higher tumor distribution and better anticancer efficacy compared with Taxol®. GO-PEG-PTX did not show any obvious or severe in vivo toxicity in the current investigation.

PEGylated graphene oxide is an excellent nanocarrier to load PTX for cancer targeting. More detailed in vivo toxicity investigation will be carried out to improve its safety. Further investigations in the future will include other anticancer drugs and differently surface-engineered graphene oxide.

Defect-related excited state dynamics in CuInS2 quantum dots

Colloidal semiconductor nanocrystals have emerged over the last few decades as promising materials for many applications, ranging from fluorescence probes for bio-imaging to the absorbing components in next generation solar cells. As the dimensions of a semiconductor are reduced below a characteristic, critical size (typically 2-10 nm), the optoelectronic properties are transformed in relation to the bulk; the band gap becomes larger due to quantum confinement effects, enabling the absorption and emission spectra to be tuned by varying the crystal size, and the electronic states become increasingly discrete. Semiconductor nanocrystals are therefore also known as ‘quantum dots’ or ‘artificial atoms’.

The discrete nature of the energy levels within the conduction band produces various effects not observed in bulk semiconductors. For example, if a photon with energy greater than twice the band gap energy is absorbed, two excitons can be created instead of one. This phenomenon may allow quantum dot sensitised solar cells to exceed the Shockley-Queisser theoretical limit for solar cell efficiency.

Colloidal quantum dots can be synthesised in solution by wet chemical methods and are therefore suitable for continuous ‘in-line’ or ‘reel-to-reel’ manufacturing processes. A high degree of control over their morphology and thus their optoelectronic properties can be achieved by controlling the reaction kinetics and by carefully selecting the solvent and surfactant.

Prominent quantum dot materials include cadmium and lead based chalcogenides. These heavy metals are toxic and therefore their use is being increasingly legislated against around the world. There is therefore a need to develop more biocompatible quantum dot materials with comparable optical properties.

Copper indium disulfide (CuInS2) colloidal quantum dots show promise as low-toxicity sensitising components in solar cells, since they exhibit very strong, broad absorption that can be tuned to match the solar spectrum. However, the excited state dynamics are still not well understood in comparison to binary materials such as CdS or ZnS.
CuInS$_2$ quantum dots display remarkably broad, long-lived photoluminescence in addition to a large Stokes shift, suggesting that the de-excitation dynamics do not involve the so-called ‘band edge emission’ observed in simple QD systems. Rather, this suggests that the exciton recombination pathway involves intra-gap trap states most likely related to point defects. The origin of these trap states has remained uncertain and various models have been put forward in the literature.

Building on previous work that identified In$_{Cu}$ antisite defects as the most likely candidate for the long-lived trap state, I.T.Kraatz, M.Booth, B.J.Whittaker, M.G.D.Nix and K.Critchley, Sub-Bandgap Emission and Intraband Defect-Related Excited-State Dynamics in Colloidal CuInS$_2$/ZnS Quantum Dots Revealed by Femtosecond Pump–Dump–Probe Spectroscopy, J. Phys. Chem. C, 2014, 118 (41), 24102–24109. This research sought to image the defect population within CuInS$_2$ quantum dots [1]. Working with colleagues from the University of Leeds in collaboration with staff at the national Super-STEM (aberration corrected Scanning Transmission Electron Microscopy) facility in Daresbury, UK, an Electron Energy Loss Spectroscopy (EELS) map was created that shows defect-rich regions within individual quantum dots, in support of the model of defect-mediated excited state dynamics previously reported. More specifically, indium rich regions consistently coincided with copper-poor regions, supporting the hypothesis that a large population of In$_{Cu}$ antisite defects are formed during synthesis.

These results showed compositional heterogeneity alongside the preservation of the chalcopyrite crystal structure, demonstrating that the defect tolerant nature of bulk CuInS$_2$ can be extended to CuInS$_2$ nanocrystals.

A comprehensive understanding of the excited state dynamics of these technologically important materials is essential if optimised performance in specific applications is to be achieved. For example, knowledge of the dominant de-excitation pathways of hot electrons is vital to designing efficient solar cell architectures.

![Elemental maps of copper and indium in individual CuInS2 quantum dots obtained using electron energy loss spectroscopy. Scale bars 2nm.](image)

Figure 2. Elemental maps of copper and indium in individual CuInS2 quantum dots obtained using electron energy loss spectroscopy. Scale bars 2nm.

MATHEMATICS CONFERENCE

International conference “Groups, rings, and their automorphisms”

On 31st August—2nd September 2016 Lincoln School of Mathematics and Physics has conducted its first mathematics conference “Groups, rings, and their automorphisms”, which was dedicated to Evgeny Khukhro’s 60th birthday. The conference proved to be a resounding success for our new school, attracting leading mathematicians from all over the world, including Brazil, France, Germany, Italy, Russia, Spain, Thailand, Turkey, UK, USA.

The conference was organized by the School of Mathematics and Physics of University of Lincoln and the Sobolev Institute of Mathematics of the Siberian Division of the Russian Academy of Sciences, with main organizers Sandro Mattarei and Natalia Makarenko, respectively. Partial support was provided by the College of Science of the University of Lincoln and the Russian Science Foundation, project no. 14-21-00065.

Talks and poster presentations were given on groups, rings, their automorphisms, and related problems. The three days of talks took place in the Minerva building in the Brayford Pool campus of the University of Lincoln. The main speakers were Alexandre Borovik (Manchester), Otto Kegel (Freiburg, Germany), Evgeny Khukhro (Lincoln), Charles Leedham-Green (Queen Mary, London), Natalia Makarenko (Novosibirsk, Russia, and Mulhouse, France), Victor Mazurov (Novosibirsk), Pavel Shumyatsky (Brasilia), Andrei Vasil'ev (Novosibirsk), Michael Vaughan-Lee (Oxford), John Wilson (Oxford), Efim Zelmanov (San Diego, USA). Apart from the main speakers, a number of shorter talks were given, as well several posters were presented at a special session at noon of 31 August.

One of the highlights of the conference was a talk by Efim Zelmanov, a Fields Medal laureate, and a member of the external advisory board of Lincoln School of Mathematics and Physics; after the conference on 5 September he received an honorary doctorate of the University of Lincoln.
As part of the conference, in the afternoon of 1 September Efim Zelmanov unveiled a plaque inaugurating the new School of Mathematics and Physics in the presence of Deputy Vice-Chancellors Andrew Hunter and Sue Rigby.

Later in the afternoon of 1 September the participants had a chance to go sight-seeing in the historic centre of Lincoln, including the famous Lincoln cathedral and Norman Castle, housing one of the original copies of Magna Carta. In the evening the participants enjoyed the conference dinner.
GRADUATION

At the graduation ceremony on 5 September 2016 in the magnificent Lincoln cathedral Roberta Dessi received her PhD degree. She is the first graduate of our School of Mathematics and Physics in Lincoln. Years of hard work were celebrated during this wonderful day!

At this graduation ceremony, an Honorary Doctorate of the University of Lincoln was bestowed on Efim Zelmanov (Fields Medallist).