Imperial College London

DEPARTMENT OF CHEMICAL ENGINEERING

Department of Chemical Engineering Postdoc Symposium 2017

27 April 2017, 09:30–13:00

Talks in Lecture Theatre 1 (ACEX 250)

Programme and book of abstracts

Contents

Programme 2
Speaker abstracts 3
Liquid Phase Oligonucleotide Synthesis with Membrane Separation for Efficient Large Scale Manufacturing 3
Piers Gaffney 3
The dynamic formation of iterated structures in thin films 4
Michael Dallaston 4
Measuring gas adsorption isotherms in three dimensions by X-Ray computer tomography 5
Lisa Joss 5
Cooperation and full transparency for climate change mitigation 6
Carlos Pozo 6
Combined CO_2 Capture and Photocatalytic Conversion using advanced materials 7
Konstantinos Christoforidis 7
From basic enzymatic building blocks to bacterial signalling pathways: a systematic elucidation of spatial regulation and compartmentalization of biochemical pathways 8
Aiman Alam Nazki 8
Computational statistical mechanical framework for soft condensed matter. Mean-field description of wetting at the nanoscale 9
Peter Yatsyshin 9
Hierarchically porous carbon foams *via* emulsion-templated polymers 10
Robert Woodward 10

Organising committee

Postdocs: Alex Brogan, Peter Yatsyshin

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Support staff: Geneviève Timmins, Nathalie Simpson

Programme

09:30–10:00	*Keynote presentation: Professor Nilay Shah, Head of Department*	
10:00–10:20	Piers Gaffney	Liquid Phase Oligonucleotide Synthesis with Membrane Separation for Efficient Large Scale Manufacturing
10:20–10:40	Michael Dallaston	The dynamic formation of iterated structures in thin films
10:40–11:00	Lisa Joss	Measuring gas adsorption isotherms in three dimensions by X-ray computed tomography
11:00–11:15	*Coffee break*	
11:15–11:35	Carlos Pozo	Cooperation and full transparency for climate change mitigation
11:35–11:55	Konstantinos Christoforidis	Combined CO2 Capture and Photocatalytic Conversion using advanced materials
11:55–12:15	Aiman Alam Nazki	From basic enzymatic building blocks to bacterial signalling pathways: a systematic elucidation of spatial regulation and compartmentalization of biochemical pathways
12:15–12:20	*Presentation of Sir William Wakeham awards*	
12:20–12:40	Petr Yatsyshin	Computational statistical mechanical framework for soft condensed matter. Mean-field description of wetting at the nanoscale
12:40 – 13:00	Robert Woodward	Hierarchically porous carbon foams via emulsion-templated polymers

Speaker abstracts

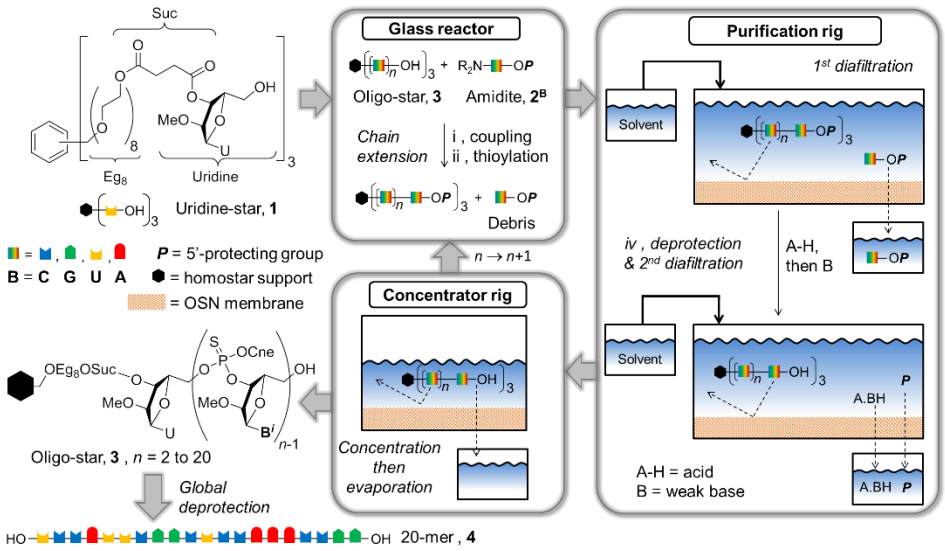
Liquid Phase Oligonucleotide Synthesis with Membrane Separation for Efficient Large Scale Manufacturing

Piers R. J. Gaffney[a], Patrizia Marchetti[a], Jeong F. Kim[a], Daniela Negru[b], Mike S. Anson[b], Andrew G. Livingston[a].

10:00–10:20

Abstract

Oligonucleotides (oligos, 18 to 25-mers, 4) are a new class of pharmaceutical, but cannot be prepared in greater than 5 Kg per batch. We introduce a liquid phase oligo synthesis (LPOS) strategy that rivals classical solid phase oligo synthesis (SPOS) for both yield and purity, but unlike SPOS is readily scaled. After each chain extension the growing oligo is separated from reaction debris using a two-stage nanofiltration apparatus, and the 5'-protecting group is then unblocked in the rig. To enhance the separation, three oligos are linked to a central hub in a three arm oligo-star (3). The purified oligo-star is then concentrated in a second membrane rig ready for the next chain extension. This process enables LPOS in standard chemical process plant; in-process reaction monitoring is facile; and building block usage is minimised. A new class of membranes was developed that efficiently retains oligo-stars but permeates large reactant debris (MW *ca.* 600 Da) in strong organic solvents over more than 19 synthesis cycles. The synthesis cycle was repeated up to a 20-mer.



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The dynamic formation of iterated structures in thin films

Michael Dallaston[a], Marco Fontelos[b], Dmitri Tseluiko[c], Zhong Zheng[d,e], Serafim Kalliadasis[a]

10:20–10:40

Abstract

A thin liquid film coating a solid surface may become unstable due to a number of physical effects. The dynamical behaviour of the film thickness depends on the nature of the destabilizing force; for instance, a film that dewets due to intermolecular interactions will rupture at a point, before the dry spot expands, whereas a film that is destabilized by gravity (for instance, a thin layer of paint on a ceiling) breaks up into spatial structures of geometrically shrinking size, reminiscent of self-similar fractal shapes from mathematics.

In this talk I will describe recent theoretical work on the self-similar analysis of idealized (lubrication) models of thin film instability, which uncovers the transition in behaviour from rupture at a point, to the formation of iterated structures, which can be interpreted as periodic behaviour in a logarithmic time variable.

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Measuring gas adsorption isotherms in three dimensions by X-ray computed tomography

Lisa Joss[a], Ronny Pini[a] 10:40–11:00

Abstract

Imaging techniques constitute a novel paradigm in characterization methods of porous media; X-ray computed tomography is of particular interest because it allows for the non-destructive determination of spatially resolved properties such as macropore space[1] and mineral distribution[2]. While the resolution is being continuously increased moving from medical scanners towards monochromatic synchrotron micro-CT and nano-CT setups, bench scale laboratory systems are still limited to voxel sizes above 1μm^3, and therefore do not allow visualising nanoporosity (≤ 100 nm) that is ubiquitous in porous materials used in the chemical industry (e.g. adsorbents, catalysts), and from natural sources (e.g. coal, shale). The most widespread technique for the characterization of nanoporous solids indeed is gas adsorption. While the interpretation of sub-critical adsorption isotherms in terms of pore size and connectivity is being continuously refined[3], gas adsorption remains a technique that only provides bulk (macroscopic) measures and can therefore not provide any information regarding the distribution of these properties.

The images obtained from X-ray CT scans contain spatially resolved quantitative information of the linear attenuation coefficient. Based on this observation, Pini[4] showed in a recent communication that it is possible to extract the excess adsorption from the difference images of porous solids in the presence of an adsorbate and of an inert, respectively.

This work has been extended here by developing the relevant experimental and analysis protocols to measure full excess adsorption isotherms by X-ray CT imaging. By applying the devised protocols to fixed beds of commercial zeolite 13X pellets (ZeoChem, Switzerland) and activated carbon rods (Norit, USA), we measure spatially distributed adsorption isotherms – one isotherm for each cubic millimeter – by means of X-ray CT imaging with a medical CT scanner. This work provides the framework to characterize nanoporosity (pore volume, size distribution, specific surface area) present in heterogeneous media in three dimensions and in a non-destructive way.

References

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3. Thommes, M. et al. W. *Pure and Applied Chemistry* **2015**, *87*, 1051–69.
4. Pini R. *Langmuir* **2014**, *30*, 10984–89.

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Cooperation and full transparency for climate change mitigation

Carlos Pozo[a], Ángel Galán-Martín[b], Ignacio E. Grossmann[c], Adisa Azapagic[d], Niall Mac Dowell[a], Gonzalo Guillén-Gosálbez[a]

11:15–11:35

Abstract

Coordinating global efforts in climate change mitigation is a major challenge facing the world today. We envision an approach to aid negotiations based on quantifying the benefits of transnational cooperation and providing full transparency on how the associated efforts would be distributed among the parties involved. To illustrate how such an approach would work in practice, we developed a mixed-integer linear programming (MILP) model (referred to as ERCOM, as an acronym for Emission Reduction Cooperation Model), which finds the most cost-effective way of meeting the U.S. electricity demand for different levels of cooperation while not exceeding the total CO_2 emissions ceiling imposed by the Clean Power Plan. Taking as starting point this solution and allocating costs and emissions among states, we study the implications of global cooperation on every individual state and discuss policies that could spur such cooperation. From the analysis, it becomes clear that significant benefits can be attained even for low levels of cooperation with cost reductions of 10% for 25 states cooperating. We argue that quantifying the benefits of such cooperation could help reach better agreements by which the most cost-effective technologies would be implemented in the right places and savings from cooperation equitably shared through compensation mechanisms. Domestic initiatives for climate change mitigation offer a unique opportunity to test, refine and validate effective approaches that could be used later at the international level to tackle more challenging endeavours.

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Combined CO_2 Capture and Photocatalytic Conversion using advanced materials

Konstantinos Christoforidis [a], Angus Crake [a], Camille Petit [a] 11:35–11:55

Abstract

The levels of carbon dioxide (CO2) in the atmosphere have been increased considerably over the past century as a result of mankind activities mainly in energy production and use. This has raised great concerns since CO2 is one of the main greenhouse gases with severe impact on global warming. CO2 capture and storage process is currently considered the most promising approach to carbon management. Among the different adsorbents suggested for CO2 capture, metal organic frameworks (MOFs) have emerged as suitable candidates due to their inherent properties (i.e. high surface area, adsorption selectivity). As with any capture process, a net input of energy is required to regenerate the sorbent. Considering this, our approach consists in coupling CO2 capture with CO2 conversion (especially via photocatalysis) within a single process. Following this approach, the energy required to convert CO2 into chemicals is also used to regenerate the adsorbent. To achieve this goal, bifunctional absorbent-catalytic MOF-based materials were developed and photocatalysis was applied for CO2 reduction. An in situ growth strategy was adopted to couple TiO2 nanosheets (NS) with NH2-UiO-66. Materials synthesis was optimized and the photocatalysts were fully characterized in an effort to elucidate how the preparation process affects activity. Results indicated that the introduction of TiO2 NS did not affect the porosity of the MOF, maintaining the high CO2 uptake, while a heterojunction was formed. XPS revealed the tight interaction between the two parts and charge transfer and separation under illumination was verified by transient absorption spectroscopy. Using a gas/solid set-up, the prepared composite materials were proven more active than the corresponding pure counterparts in CO2 photoreduction. This was linked to the enhanced abundance of photogenerated charges driven by the efficient charge transfer via interface.

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From basic enzymatic building blocks to bacterial signalling pathways: a systematic elucidation of spatial regulation and compartmentalization of biochemical pathways

Aiman Alam Nazki[a,b], J. Krishnan[a,b] 11:55–12:15

Abstract

In cells, complex networks of proteins govern essential processes. A vital organizer of these networks and their function is a mechanism known as compartmentalisation. Compartments are an evolutionary hallmark and experimental effort to understand natural systems and build synthetic compartments is growing. For example, artificial compartments are designed to function as “chemical microreactors” with spatially segregated reaction pathways.

In mathematical modelling studies, the role of compartments either goes unacknowledged, or is subsumed in model kinetics. Typically, purely kinetic models, with a few exceptions, are used to study naturally compartmentalised systems. This work was motivated by the widespread presence and the important role of compartmentalisation in natural systems. Our aim was to understand the role compartments play in controlling enzymatic modification pathways- basic building blocks of larger signalling networks that drive cellular processes.

Our study considers a wide array of typical enzymatic pathways. We built explicit spatial models to mimic compartmentalisation and transport of reaction components between compartments- a common theme in biological systems. This allowed us to gain insight into the capabilities and constraints arising from compartmentalising an array of pathways. We show that compartmentalisation significantly effects pathway characteristics and ignoring it may result in misleading model predictions.

We applied the investigation of building blocks (and their extensions) in studying compartmentalisation in the bacterium, Caulobacter. Compartmentalisation is seamlessly integrated into the spatiotemporally choreographed phases of the Caulobacter cell cycle. By building a bridge from building blocks to bacterial enzymatic pathways, we sought to understand the logic of control of key enzymatic pathways by compartmentalisation. This part of the work has implications in understanding spatial organisation of pathways in other bacterial organisms, as well.

Our work acts as a scaffold to build on exploring more complex enzymatic modification pathways, and a potential design framework to build synthetic compartments.

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Computational statistical mechanical framework for soft condensed matter. Mean-field description of wetting at the nanoscale

Peter Yatsyshin

12:20–
12:40

Abstract

Since the days of van der Waals, it is known that interfaces between the different phases of matter (gas and liquid, liquid and solid, solid and gas) are directly linked to the workings of the atomic world, and provide one of the most striking manifestations of the existence of molecules in the first place. Indeed, the shape and width of interfaces are determined by the complicated interplay of intermolecular forces and various fluctuation effects, such as thermal noise and capillary waves. In many experimentally accessible cases of wetting, where a third phase (liquid) intrudes into the interface between the other two phases (solid and gas), the interplay between the substrate geometry, and fluid—substrate and fluid—fluid intermolecular interactions can lead to the appearance of exciting interface phase transitions. Moreover, small-scale geometric dimensions of sculpted substrates, as well as the parameters of the interaction potentials often act as thermodynamic fields, and, according to the Gibbs phase rule, bring about a vast zoo of phase transitions associated with adsorption on patterned and sculpted substrates. Practical applications of wetting at small scales are numerous, from the design of superhydrophobic surfaces and miniature lab-on-a-chip devices, to vapour-liquid-solid growth of semiconductor nanowires, to capillary filling of microchannels, adsorption in nanoporous materials, and so on. In this talk, we present interesting new results, obtained in a number of recent studies of wetting on patterned and sculpted walls, capillary pores and wedges. We demonstrate that in sculpted substrates, such ubiquitous interfacial transitions as planar pre-wetting and capillary condensation can change order and become continuous phenomena, characterised by non-universal critical exponents.

Our research tool is a formulation of statistical mechanics, commonly known as classical density functional theory (DFT). In short, DFT allows one to introduce the spatial dependence of fluid density into the thermodynamic equation of state. More importantly, classical DFT provides a computationally-friendly framework, suitable for investigating a wide variety of soft-matter systems, from simple liquids with Lennard-Jones interactions, to solutions of colloids, macromolecules and polymers, to even non-equilibrium phenomena within the Smoluchowsky dynamical picture, e.g., crystallisation, colloid sedimentation and self-assembly. Although vanilla DFT is fully *ab initio*, approximations, such as mean-field, are often necessary in practice, in order to derive computationally tractable models. We shall briefly discuss the philosophy of simple DFT approximations, and the challenges one faces when trying to solve the resulting non-linear and non-local governing equations in the regions of metastability and phase transitions. As a footnote, we shall also provide illustrative DFT computations, relating to several highly debated problems in homogeneous nucleation, and diffusion-driven dynamics of nanodrops.

Hierarchically porous carbon foams *via* emulsion-templated polymers

Robert Woodward

12:40–
13:00

Abstract

High performance carbonaceous materials are of significant interest as they show great potential in a plethora of applications, ranging from water purification and gas sorption to catalysis and energy storage. Many routes to produce such carbons have thus far been devised, however it has proven more difficult to synthesise carbons with designable architectures and/or tuneable pore sizes. The carbonisation of macroporous poly(divinylbenzene) (DVB) templated from high internal phase emulsions (HIPEs) presents an exciting new route to tailored carbon foams, or 'carboHIPEs'. The use of a pourable, aqueous emulsion-template enables simple moulding of the polymers, minimises waste and avoids strong acid treatments commonly employed to remove many conventional solid-templates. Moreover, the poly(DVB)HIPE's macropore diameters, interconnectivity and surface chemistries are all easily controlled by careful selection of the emulsifier used to stabilise the initial HIPE systems. The translation of these desirable polyHIPE features during carbonisation, coupled with the introduction of significant microporosity, produces hierarchically porous carboHIPEs with designable pore structures ranging from the macro- to the microporous regime.

By employing poly(DVB)HIPEs as carbon precursors, emulsion-templated carboHIPEs with high surface areas (approaching 2000 m^2/g), tuneable pore sizes, various surface chemistries and excellent electrical conductivities of up to 450 S/m, were produced. The hierarchical porosity and excellent surface areas make carboHIPEs suitable for a wide range of applications as sorbents and electrodes. Various carboHIPEs were tested in energy storage applications, which revealed crucial design parameters when considering their application as supercapacitor electrodes.