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KEYNOTE PRESENTATIONS

MULTI-SCALE AVERAGING METHODS FOR CHEMICAL REACTORS AND REACTING FLOWS

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Due to the fact that the length and time scales associated with continuum models of chemical reactors and reacting flows vary from the molecular scale to the macro scale, for most cases of practical interest, even with the present day computational power, it is impractical to solve such detailed models consisting of several nonlinear partial differential equations (PDEs) and explore all the different types of solutions that exist in the multi-dimensional parameter spaces. Accurate reduced order models that retain the multi-scale physics and expressed in terms of measurable variables are desired for the purpose of design, control and optimization of these systems.

We have recently shown that the Liapunov-Schmidt (L-S) technique of classical bifurcation theory is an excellent multi-scale averaging technique for diffusion-convection-reaction (DCR) models described by coupled nonlinear PDEs. This procedure starts with detailed models based on the fundamental laws and takes advantage of the separation of the length or time scales (expressed in terms of one or more small parameters in the dimensionless form of the model) to reduce the spatial and/or temporal degrees of freedom and to obtain multi-mode multi-scale low-dimensional models in terms of measurable quantities (such as cup-mixing temperature/concentrations). This procedure is rigorous and is equivalent to the McClaurin series expansion of a more detailed model in terms of the small parameters representing separation of length/time scales. The multi-mode averaged models derived by such an expansion have not only low-dimensional state spaces (due to elimination of the local degrees of freedom associated with smaller length/time scales) but also a smaller number of effective/lumped parameters characterizing the system behavior, while including the physical phenomena occurring at the smaller scales.

In the first part of this talk, we discuss the theoretical/mathematical aspects of the L-S reduction with focus on how to include the initial/inlet/boundary conditions in the averaging procedure, proper scaling of the model and the use of multiple small parameters or extension to multi-phase averaging with multiple-zero eigenvalues. In the second part, we present specific examples of low-dimensional models from the areas of multiphase reaction engineering, transport in porous media and coupled homogeneous-catalytic reaction systems. By comparing the solutions of the full PDE models with those of the low-dimensional models derived by the L-S method for some selected cases, we show that the low-dimensional models are robust and accurate with practically acceptable error, speed up the calculations by several orders of magnitude, and can be used for real time (and faster than real time) simulations of many physical systems with infinite number of degrees of freedom. The limitations of the averaged models in capturing the solutions of highly nonlinear systems with fine scale spatial and time scales will also be discussed.

FROM REGULATORY NETWORK TO MATHEMATICAL MODELS: APPLICATIONS TO CANCER BIOLOGY

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Mathematical models serve to explain complex biological phenomena and provide predictions that can be tested experimentally. They can provide plausible scenarios of a complex biological behaviour when intuition is not sufficient anymore. The process from the definition of a biological hypothesis to the construction of a mathematical model is challenging.

In this talk, I will discuss a possible workflow that describes the steps that can be taken starting from biological experimental data to the construction of a mathematical model using the appropriate mathematical formalism (ordinary differential equations vs. logical rules). The model can then be used to identify the driver genes, anticipate the impact of individual or combinations of gene alterations in the cell fate decision, and predict the effect of drugs on a particular patient.

I will illustrate the workflow with a logical model of the early steps of metastasis. The model recapitulates published experimental results of known gene perturbations on local invasion and migration processes, and predict the effect of not yet experimentally assessed mutations. Using a modelling tool, MaBoSS¹, that simulates continuous or discrete time Markov processes applied on a Boolean network, we have systematically explored the single and double mutant landscape to identify the alterations that favour the most metastasis. In particular, we have shown that the double mutation Notch gain-of-function and p53 loss-of-function has the highest probability to acquire metastasis, which is in agreement with a recent published experiment in a mouse model of gut cancer^{2,3}. The model predicts new gene perturbations that affect the early steps of metastasis underlying potential intervention points for innovative therapeutic strategies in oncology.

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MODELING THE STRUCTURE FORMATION PROCESS OF TWIN POLYMERIZATION

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Polymer hybrid materials, i.e. materials combining organic polymer structures with inorganic components on the nanoscale, play an important role in reinforcing, coating and barrier materials. The production of such nanostructured polymer hybrid materials is a challenging task, since two different components must be merged together, while suppressing phase separation processes on the molecular level. The established way is either a simultaneous polymerization of two different monomers in one procedure or the chain (or step-growth) polymerization of heterobifunctional monomers, where each polymerizable functional group of these monomers polymerizes independently and by another mechanism.

In recent years a more elegant technique called twin polymerization [1] has been developed to synthesize these hybrid materials with organic and inorganic structure domains. Twin polymerization is a special process that utilizes twin monomers containing differently polymerizable groups in one molecule, where only one initialization step is necessary to start the process.

Due to the intrinsic coupling of different structure elements a special feature of the polymers obtained by twin polymerization is that the inorganic and the organic structure domains have a defined size of 0.5 to 3 nm. Thus, polymer hybrid materials structured on the nanoscale can be created. Then, just a simple post-treatment, like combustion of the organic phase or HF treatment of the inorganic phase is necessary in order to obtain nanoporous carbon or oxide.

The theoretical understanding of the overall twin polymerization process and especially of the structure formation of the composite material is still at the beginning. After introducing the basic concepts of twin polymerization, I will show different modeling approaches for the complex reaction mechanism of twin polymerization. The utilized methods range from density functional theory (DFT) calculations [2] via reactive molecular dynamics simulation [3] to reactive Bond-Fluctuation-Models (rBFM). I will present and discuss obtained results and validate them with experimental results. Doing so insights to the structure formation process on different levels of length scale can be obtained.

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SYNCHRONIZATION ENGINEERING: DESIGN OF PATTERN FORMATION WITH OSCILLATORY CHEMICAL REACTIONS USING EXPERIMENT-BASED PHASE MODELS

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Description, control, and design of weakly interacting dynamical units are challenging tasks that play a central role in many physical, chemical, and biological systems. Phase models have been shown to be an efficient way of description of complex dynamic structures that can handle hierarchical complexities and predict emergent, system-level properties. In the presentation, we show the use of experiment-based phase models for engineering the synchronization properties of nonlinear oscillator populations.

External signals can be used to control the behavior of complex rhythms, both to tune essential behavior, such as by heart pacemakers, or to alter pathological behavior, such as by deep-brain “antipacemakers” in tremors or Parkinson’s disease. In such applications, a mild control is desired so that the system can be tuned to a desired behavior without destroying its fundamental nature. A methodology is presented that applies phase models to describe and tune complex dynamic structures to desired states; weak, nondestructive signals are used to alter interactions among nonlinear rhythmic elements. Experiments on electrochemical reactions on electrode arrays are used to demonstrate the power of mild model-engineered feedback to achieve a desired response. Applications are made to the generation of cluster states¹, restoring rhythmicity in diffusively coupled dynamical networks², and to the design of rotating waves in regular rings and small-world type networks. Finally, phase model analysis is combined with calculus of variation to derive a waveform with which robust or fast entrainment of an oscillator is achieved with minimum power, area, and magnitude forcing signal³. The theory is tested in electrochemical entrainment experiments in which sinusoidal and higher harmonic nontrivial optimal waveforms are obtained depending on experimental conditions. The proposed method will give a convenient way to obtain optimal waveform for entrainment (e.g., in design of cardiac pacemakers and injection locked electronic oscillators) and could test the optimality of current waveforms used in many applications.

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SELF-ORGANIZED REGULATION RESULTING FROM LOCAL CONTACTS

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One of the fundamental problems in biology concerns the method by which a cluster of organisms can regulate the proportion of individuals that perform various roles or modes as if each individual is aware of the overall situation without a leader. In various species, a specific ratio exists at multiple levels, from the process of cell differentiation in multicellular organisms to the situation of social dilemma in a group of human beings. This study determines a common basis for regulating collective behavior that is realized by a series of local contacts between individuals. In this theory, the most essential behavior of individuals is to change their internal mode by sharing information when in contact with others. Our numerical simulations with a cellular automata model regulate the proportion of individuals in either of two modes. Using theoretical analysis and numerical calculations, we show that asymmetric properties in local contacts are essential for adaptive regulation in response to global information such as group size and overall density. Furthermore, a discrete system is crucial in allowing flexible regulation in no-leader groups, and the critical condition that eliminates overlap with other individuals (the excluded volume effect) also affects the resulting proportion at high densities. The foremost advantage of this strategy is that no global information is required for each individual, and minimal mode switching can regulate the overall proportion. This simple mechanism indicates that proportion regulation in well-organized groups in nature can be realized through and limited to local contacts, and has the potential to explain various phenomena in which microscopic individual behavior results in orderly macroscopic behavior.

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QUENCHING ANALYSIS OF SMALL-AMPLITUDE CHEMICAL AND BIOCHEMICAL OSCILLATIONS NEAR A SUPERCRITICAL HOPF BIFURCATION

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Experimental studies of detailed kinetic mechanisms underlying complex chemical and biochemical reactions are often limited by our capacity to simultaneously monitor changes in the intensity of a handful of dynamical variables. New experimental approaches are therefore

needed, which yield quantitative results that can be interpreted in terms of quantities closely related to the kinetics of the investigated reactions. One such method is quenching analysis, also known as quenching of small amplitude oscillations, a perturbation analysis technique that relies on controlled addition of chemical species to determine the amplitudes and phases of the oscillatory parts of the concentrations of these species [1–3].

Quenching is an instantaneously induced perturbation of an oscillating chemical system by which limit cycle oscillations around a supercritical Hopf bifurcation are temporarily suspended. For the oscillations to stop by the addition, the change in concentration of the species added and the phase at which the addition is made must each have a unique value, so that the state of the system is shifted from a point on the limit cycle to a point on the stable manifold of the saddle focus that exists near the centre of the nearly elliptical limit cycle. The result of an experimental quenching analysis is a set of quenching concentrations and quenching phases for each investigated species. Such a set of data is closely related to an important dynamical property of the system at the operating point, the left eigenvector of the Jacobi matrix corresponding to the oscillatory mode [1–3].

In my talk, I will first introduce the theoretical background behind quenching analysis and present its application for the study of detailed kinetic mechanisms of complex chemical reactions [1–3]. Thereafter, I will discuss the potential of this method for understanding the behaviour of a complex neuroendocrine dynamical system, the Hypothalamic-Pituitary-Adrenal (HPA) axis, under normal physiology and in response to internal and external stimuli [4–6].

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ORAL PRESENTATIONS

Systems Biology

NUMERICAL CALCULATION OF TIME-RESOLVED LIGHT REFLECTANCE FROM BIOLOGICAL TISSUE USING THE RADIATIVE TRANSFER EQUATION

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Numerical modelling of light reflectance (and/or transmittances) at boundary of biological tissue is crucial for *in-vivo* determinations of the optical properties of biological tissue by model-based inverse analysis¹. Among the optical properties, recovery of absorption and scattering coefficients of a target organ is a basis for optical imaging such as diffuse optical tomography² because they have relations to chemical components and structural properties of biological tissue. For the accurate determination, short source-detector distances are desirable to measure less scattered light including rich information over diffused light and to suppress effects of other tissue surrounding the target tissue. Meanwhile, this condition requires an accurate light propagation model in turbid media with highly forward-peaked scattering like biological tissue and an accurate treatment of refractive index mismatching at boundary between tissue and air. The radiative transfer equation (RTE) provides accurate descriptions of light propagation in turbid media, but the RTE usually needs high computation loads because of the integro-differential form in the phase space.

In this presentation, we construct a numerical model of light reflectances at boundary of the three dimensional and highly forward-peaked scattering media using the time-dependent RTE under the refractive index mismatched boundary condition. The RTE is numerically solved by the finite difference and discrete ordinates methods, and highly forward-peaked scattering is treated by the first order renormalization approach of the phase function, which is recently developed by the authors³. The numerical schemes developed in this study are verified by comparing the numerical solutions of the RTE with the approximated analytical solutions of the RTE for semi-infinite media. Influences of numerical aperture and source-detector distance will be investigated.

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OPTIMAL ENZYME ALLOCATION IN KINETIC METABOLIC NETWORKS

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When a cell optimizes rates of specific metabolic target reactions, it must appropriately partition enzymes to reactions, since enzyme abundance determines reaction velocities. Since total enzyme is limited, this becomes a constrained enzyme allocation problem. Understanding the optimization of rates (rather than yields) helps in making sense of important adaptive scenarios. It also is significant from a biotechnological perspective.

In our modeling approach, we combine bioengineering and theoretical biology. In mathematical terms, we build on dynamical systems theory and combinatorial optimization. This repertoire enables us to go beyond studying optimality with linear methods such as flux balance analysis (FBA). We explicitly consider kinetic information, leading to a nonlinear optimization problem with a surprising result.

In fact, for arbitrary kinetics, solutions that optimize rates are elementary flux modes (EFMs), representing minimal metabolic pathways. This is surprising precisely because such flux modes only depend on stoichiometry and yet they show up as optimal states for arbitrary enzyme kinetics, including arbitrary allosteric regulation. Most importantly, our result predicts discontinuous metabolic switches and explains the occurrence of low-yield pathways as observed in the Crabtree and Warburg effects.

Multiscale modeling

QUASI-HARMONIC AND SPIKY OSCILLATIONS IN A HARVEST MODEL WITH EQUABLE RESOURCE SUPPLY

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We study a model for the population of autotrophs fed on an abiotic resource with constant rate of supply. The population is subject to harvesting, or to consumption by a holozoic predator. Model equations are: $dS/dt = a - (b/Y) S N - d S$, $dN/dt = b S N - h H(N)$, where S is the substrate concentration, N is the species density, a is the resource influx rate, b is the population specific growth rate (the substrate is supposed to be taken up with a simple mass-action functional response), Y is the yield constant, d is the substrate dilution rate, h is the maximum possible harvesting rate, $H(N)$ is the functional response of the harvester. We assume the intake function be of Holling's type II, $H(N) = N/(K + N)$, where K is the half-velocity constant, although the precise form of the relationship is not important, provided H is a monotonous increasing function of N , with a limiting value. Employing the algebraic functional response actually means that the harvester relaxes much faster to its quasi-stationary value than the substrate and the species. Upon a proper scaling, the model is brought to the nondimensional form: $ds/d\tau = 1 - s((1 - \delta)n + \delta)$, $dn/d\tau = \gamma n(s - (\kappa + 1)/(\kappa + n))$. The timescale parameter, $\gamma = b(h - a Y)^2/(a(b K - d Y)^2)$, is a key property of the model showing to what extent the dynamics of the population is faster as compared with that of the substrate. It has been found that sustained oscillations are possible through a Hopf bifurcation. Depending on the value of γ the system may operate in two qualitatively different oscillatory regimes. At $\gamma \sim 1$, the population density executes sustained quasi-harmonic fluctuations about a single positive equilibrium. In this case, for $\varepsilon = \gamma/(\kappa + 1) - 1 \ll 1$, close to the Hopf bifurcation, an analytical solution could be obtained in the second approximation of the Krylov-Bogoliubov-Mitropolski technique. At $\gamma \gg 1$, when the substrate is "slow", oscillations are characterized by high-density pulses separated by long time intervals, where the density is almost zero. Between successive spikes, the substrate concentration slowly increases exponentially. For high values of the timescale parameter, when the system is singularly perturbed, the approximate limit-cycle solution could be constructed using two separate approximations: the low density approximation and the high density approximation. It is believed that the described phenomenon could be reproduced experimentally in a chemostat-like system. The short pulse widths and the giant peak output biomass densities could be found interesting for applications in microbiology and biotechnology.

The present results are part of the research project 0116RK00250 performed under the auspices of the Ministry of Education and Science of the Republic of Kazakhstan.

COMPARATIVE STUDY OF ADSORPTION AND SCATTERING TECHNIQUES TO DETERMINE THE SURFACE FRACTAL DIMENSION OF NANOSTRUCTURED MATERIALS

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In this study small-angle X-ray scattering (SAXS) and N₂ adsorption techniques are compared as appropriate methods for the characterization of the surface roughness of different type nanostructured materials [1]. The surface roughness can be quantitatively characterized by a well-known mathematical concept, namely the non-integer dimensions or fractals. In this work three different types of materials were investigated:

1) TiO₂/Hydroxyapatite(Hap) nanocomposites, 2) mesocellular and hexagonally ordered SiO₂ supports and 3) ZnO₂ and ZnO nanoparticles (NPs) synthesized by different methods. The catalytic properties of a semiconductor particle may be significantly influenced by the physical (not only the chemical) surface properties, so this study attempts to look for correlation between the surface fractal properties and catalytic activity.

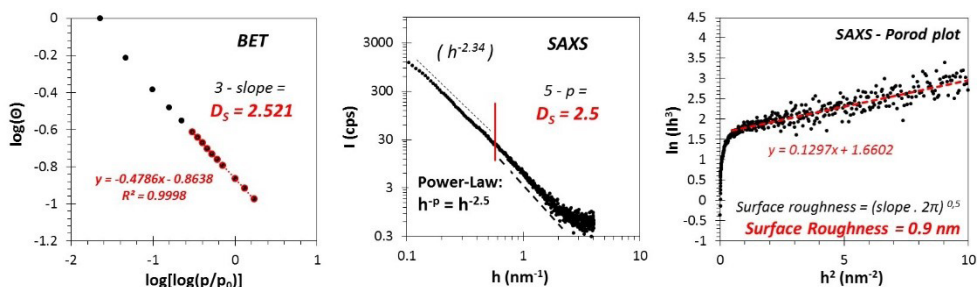


Fig 1. Double logarithmic plot of the adsorption isotherm (A) and the SAXS curve (B) of TiO₂/HAp nanocomposite for the determination of the surface fractal dimension ($2 < D_s < 3$), and the Porod plot of the SAXS pattern (C) to calculate the surface roughness

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Stochastic kinetics and simulation

EXPERIMENTAL AND MODELLING OF NO REDUCTION ON SILVER AND GOLD CATALYSTS

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Nitrogen oxides are one of the most toxic pollutants causing several health and environmental hazards. Among various sources, automobiles are the biggest contributors to the emission of nitrogen oxides. Automobile exhausts need treatments which can simultaneously reduce emissions of NO as well as other major pollutants such as carbon oxides, unburnt hydrocarbons etc. One of the most effective methods is selective catalytic reduction (SCR) using a reductant (CO, HC, NH₃ etc.), where NO selectively gets reduced to N₂ by a reductant on a catalyst.

Here we propose to perform experimental and modelling studies of selective catalytic reduction of NO using CO as a reductant over Au/Al₂O₃ and Ag/Al₂O₃ and compare the performance of the catalysts.

We have already developed the microkinetic model for NO-CO consisting of 16 elementary reactions in our group for Pt/Al₂O₃ [1], which is further extended to silver and gold catalysts by incorporating modifications in the reaction parameters (activation energy and pre exponential factor). The activation energy of each reaction on Au/Al₂O₃ and Ag/Al₂O₃ is calculated using a semi empirical method, UBIQEP (unity bond index quadratic exponential potential) [2]. The pre-exponential factors for the respective reactions are maintained at an approximate value as per the transition state theory. The packed bed reactor simulations are done using a commercial software CHEMKIN PRO, incorporating the micro-kinetic model.

To validate the modelling results on both Au/Al₂O₃ and Ag/Al₂O₃ catalysts, lab scale experiments will be performed. In the experimental setup we have three inlet gases (NO, CO, O₂) which are passed through a pre-heater followed by a packed bed reactor placed within a quartz glass tube inside the furnace. The temperature is varied from 200°C to 650°C and the exhaust gases from the packed bed reactor are passed through a chemiluminescent detector which detects the reduced NO emissions from the catalytic reactor. Furthermore we will be studying the effect of oxygen and hydrocarbons on the catalytic performance of silver and gold catalysts.

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STRONG APPROXIMATIONS OF STOCHASTIC MODELS OF REACTION NETWORKS

Enrico Bibbona

For large values of the volume of reaction stochastic models of mass-action chemical kinetics converge to deterministic systems of differential equations (Kurtz, 70). Moreover for moderate V they can be approximated trajectory by trajectory by paths of a diffusion process (Kurtz, 76).

We will review such approximations and discuss a case where they fail.

Indeed when the state space is bounded (e.g. because concentrations cannot be negative or because conservation of mass prevents concentrations to become arbitrarily large), if the process visits the boundaries with non-negligible probability both the deterministic and the diffusion approximation fail.

We present a strong approximation by jump-diffusion processes which is robust to this event (joint work with colleague at University of Torino).

HYBRID MODELS: USING KRIGING TO IMPROVE ODE-BASED KINETICS

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Catalytic hydrocracking is used to convert heavy Vacuum Gas Oil (VGO) residue to more valuable middle distillate and/or naphtha cuts. Hydrocracking of VGO residue is performed in a two-step process: a hydrotreatment (HDT) section followed by a hydrocracking step in a separate reactor. Models are mainly developed to optimize process design and operating conditions to maximize desired cuts and product characteristics. Historically, ODE-based kinetic models were used to predict the nitrogen content in the output of the HDT section¹. The advantage of these models is the ability to insure known experimental trends. However, many phenomena are not taken into account due to incomplete description of the entire physico-chemical system. This leads to inaccurate predictions. Recently, new modeling approaches, such as Kriging², allow to increase precision using advanced mathematics. Unfortunately, these models lack in robustness and cannot ensure known trends.

The goal of this study is to develop a hybrid model which preserves the advantages of both methods while moderating the inconvenient.

Prior to this study, an ODE-based kinetic model was developed to represent well-known trends. The idea is to use this model as a predictor and then correct the output using a Kriging model. The correction should represent the lack of knowledge about reactivity. For this reason, it is applied as a multiplication factor on the prediction: $Y(x) = F(x) \cdot K(x)$ where Y stands for the outlet nitrogen content, F is the ODE-based kinetic and K : the Kriging model. It is imposed that the correction is stronger near the calibration database. To do so, when x is far from experimental data, $K(x)$ tends to 1.

This methodology was applied to 114 experimental data points acquired in a fixed-bed pilot plant at IFPEN using a commercial HDT hydrocracking catalyst and 13 VGO feedstocks from different geological origins. Feedstock characteristics (SIMDIS, sulfur/nitrogen content, aromatic carbon content etc.) are known. Experimental data covers a wide range of operational conditions (reactor temperature, liquid hourly space velocity...). A validation set was created using 25% of the available points by random selection.

Results show an important improvement on the learning set evolving from 70% of the points in the experimental uncertainty range ($\pm 15\%$ wt) to 100%. The overall robustness is preserved since the quality of the simulations on the validation set stays similar when compared to the original ODE-based system (about 82%). This shows that it is possible to improve traditional models accuracy using hybrid approaches without losing precision, even outside the leaning database (extrapolation).

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STOCHASTIC THERMODYNAMICS OF REACTIVE SYSTEMS: AN EXTENDED LOCAL EQUILIBRIUM APPROACH

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In small systems, the relevant physical quantities are subjected to fluctuations. Over recent years, progress in experiments along with new theoretical developments led to the emergence of a new field known as stochastic thermodynamics. The aim of this framework is to try and generalize the laws of thermodynamics to small systems.

Not long ago a novel approach to stochastic thermodynamics was introduced [1], which is based on the extension of the local equilibrium hypothesis to state variables in mesoscopic systems. Starting from macroscopic non-equilibrium thermodynamics, the approach enables to derive Langevin equations for thermodynamic variables of interest such as heat or entropy.

In this talk, we will show how this formalism can be applied to single variable and multivariate chemical reactions in small networks [2]. More particularly, we will focus on the fluctuating entropy production of those systems. The probability distribution of entropy production was analytically derived in different states of the network: at equilibrium, in non-equilibrium steady states or near a criticality. In each case, the shape of the probability follows a specific law. Moreover, the different statistical moments can be related to the macroscopic parameters of the network. Furthermore fluctuations theorems for entropy production were derived and compared to other existent theorems. The non-linearities in the network

coupled with fluctuations are also shown to modify the mean of the entropy production compared to the deterministic predictions. Numerical simulations reinforced the analytical results discussed.

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THE INTERPLAY BETWEEN TOPOLOGY AND FLUCTUATIONS IN THE THERMODYNAMICS OF CHEMICAL NETWORKS

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Large chemical networks subtend complex biochemical processes crucial to life, such as metabolism, respiration, and signal transduction. All such processes operate thermodynamic cycles far from equilibrium that transform environmental resources into valuable products, at the expense of high-entropy waste. While the chemistry of an Avogadro’s number of molecules is well described by macroscopic rate equations, at the cellular level the number of molecules involved might be small, allowing for significant fluctuations that are better described by means of the Markovian Chemical Master Equation. It is now well-understood that certain topological properties of the network, such as the deficiency, play a crucial role for chemical dynamics.

In this talk we analyze chemical networks under the light of Stochastic Thermodynamics, a rigorous theory of the thermodynamics of nonequilibrium systems subject to fluctuations. Assuming that closed macroscopic chemical networks “in a box” abide by elementary laws of physics (the second law of thermodynamics, mass conservation, the mass-action law), we provide a framework to describe open chemical networks subjected to the influx of chemostats, chemical species steadily provided by the environment [1]. We describe the effect of chemostats on the topology of the network, in particular on cycles that support thermodynamic transformations of the free energy differences. We discuss the effect of topology on efficiency and conservation laws. We then consider small numbers of molecules, showing that at steady states the surplus production of entropy due to fluctuations is related to the deficiency of the network [2].

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Reaction-diffusion systems

A NOVEL SOLUTION STRATEGY FOR THE SIMULATION OF BULK RAFT POLYMERIZATION

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Reversible addition fragmentation chain transfer (RAFT) polymerization allows to synthesize polymer products with a well-defined microstructure within comparable reaction times as Free Radical Polymerization. Using the pseudo steady state assumption a novel deterministic approach is presented to calculate the concentrations of all individual macrospecies in RAFT polymerization, using chain length dependent apparent rate coefficients to fully account for the impact of diffusional limitations.^[1] For RAFT polymerization of styrene initiated by 2,2'-azobis(2-methylpropionitrile) and 2-cyano-2-propyl dodecyl trithiocarbonate, this solution strategy is successfully applied to model experimental data over a broad range of conditions. The changes in dispersity profiles for less controlled conditions can be better understood by focusing at the fraction of short macroradicals. Additionally when comparing FRP with RAFT polymerization it is clear that the impact of the differences in chain length always result in a rate retardation of the latter. The solution is compared to the conventional (extended) method of moments in combination with an a priori assumed Poisson or Flory-Schulz distribution to calculate average properties of the polymer product.^[2] For polymerizations with a strong gel-effect (e.g. methyl methacrylate) it is demonstrated that a full kinetic model taken into account all chain lengths explicitly is needed to accurately represent the RAFT polymerization kinetics.

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NEW, SIMPLE METHOD OF DETERMINING NECESSARY CONDITIONS OF DEAD ZONE FORMATION

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The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids. Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. It is worth to notice that diffusion of reactants into catalyst pellet affect overall rate of these production processes as well as reaction rate. If intrinsic diffusion is much slower than reaction rate, concentration of reactant inside pellet decreases rapidly. For sufficiently strong diffusional limitations concentration in the pellet can even vanish to zero. Then in a pellet centre zone without reaction (so called 'dead zone') is formed. Fundamental investigations on dead zone were carried out already by Aris (1975).

Dead zone is a central part of catalyst pellet where chemical reaction does not occur.

As a consequence, the pellet is not fully utilized and efficiency of catalytic process decrease. Conditions of dead zone formation still have not been fully formulated. Usually, in literature, there are presented the types of kinetic equations for which such zone could appear (i.e. necessary conditions of dead zone formation). To meet them is insufficient to be sure that dead zone appears in the pellet. Additionally diffusional limitations must be sufficiently large i.e. Thiele modulus value should be larger than critical Thiele modulus.

Extensive investigations on necessary conditions of dead zone formation were done by Andreev (2013). He applied Lagrange theorem to mass- and thermal-balance equations of catalyst pellet. In this way he obtained procedure of determining necessary conditions based on calculations of two appropriate function limits. Results of applying his method to few well known reaction systems with Langmuir-Hinshelwood and power law kinetic equations were summarized in (Andreev, 2013).

For simple kinetic functions Andreev's algorithm work well, but for more complex ones particular cases could be easily omitted. We present a new method of determining necessary conditions of dead zone formation (Król and Szukiewicz, 2016). The new method is based on simpler mathematics and is more intuitive than presented formerly. It allows to find the necessary conditions for commonly used in biochemistry kinetic equations (yet undiscussed in literature) as well as to find and fill some gaps in already published results, e.g. for two-reagent reaction system (Andreev, 2013).

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EXPLORING THE FUNDAMENTALS IN CATALYTIC PARTIAL OXIDATION OF METHANE: THE INTERACTION BETWEEN DIFFUSION AND REACTION IN A PACKED BED REACTOR

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Catalytic partial oxidation of methane (CPO) on Rh is a promising route for syngas production. Its high reactivity and short space time operation offer interesting opportunities, yet, simultaneously present significant challenges. E.g., in the reactor design irreducible diffusion limitations caused by high surface reactivity dramatically impact on the reactor performance. A heterogeneous packed bed reactor model explicitly accounting for internal and external diffusion limitations was used to obtain inter- and intra-particle species and temperature profiles along the reactor axis in the following range: $P_{\text{tot}} = 0.1\text{--}1$ MPa, $T_{\text{in}} = 773\text{--}1273$ K, $W/F_{\text{CH}_4,0} = 0.774$ kg s mol⁻¹, $V/F_{\text{tot},0} = 1.73 \cdot 10^{-4}$ m³ s mol⁻¹, $\text{CH}_4/\text{O}_2/\text{N}_2 = 2/1/4$ (v/v/v), $d_p = 0.4\text{--}1.2$ mm. Microkinetics for CPO on Rh and methane homogeneous combustion were employed.¹ The model was validated by comparing the simulation results with the literature reported experimental information. On the pellet scale, external and internal gradients for both reactants and products were observed indicating that the reaction was highly limited by diffusion at typical CPO operating conditions. Increasing the Rh active surface area shifted the reactor behaviour from hybrid to transport control regime in the entrance zone. A further increase had little impact on O_2 profile along the reactor length, while it slightly increased CH_4 conversion due to slow steam reforming. Increasing the catalyst pellets diameter strongly reduced the reactor

performance because larger catalyst pellets and larger void space between these pellets enhanced diffusion limitations. Particularly for these larger catalyst pellets, homogeneous combustion reactions become very important at elevated pressures, i.e., a true ignition is observed at about 1/3 of the total bed length for catalyst of 1.2 mm at 1 MPa, see (Fig.1).

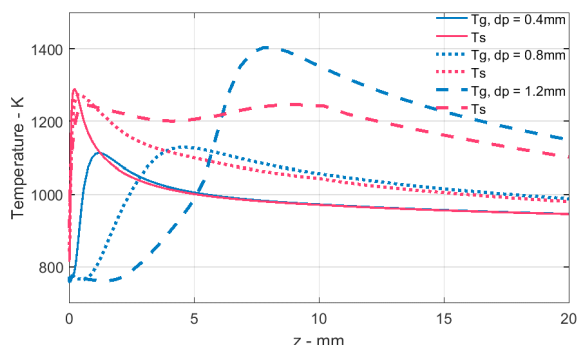


Fig. 1. Gas and solid temperature profiles along the reactor length for different particle size. ($P_{\text{tot}} = 1$ MPa, $T_{\text{in}} = 773$ K, $W/F_{\text{CH}_4,0} = 0.774$ kg s mol⁻¹, $V/F_{\text{tot},0} = 1.73 \cdot 10^{-4}$ m³ s mol⁻¹, $\text{CH}_4/\text{O}_2/\text{N}_2 = 2/1/4$ (v/v/v))

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MODELLING OF THE HYDROGENASE FRONT REACTION

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Hydrogenases are natural metalloenzymes that catalyze the reversible reaction between molecular hydrogen and hydrogen ion. It was shown experimentally¹ that the hydrogen oxidation of HynSL hydrogenase from *Thiocapsa roseopersicina* proceeds through autocatalytic steps. Furthermore, carrying out the reaction in thin layer in the presence of reduced benzyl viologen yields reaction fronts propagating with constant speed. The reaction is unique, since the autocatalyst is inside the enzymatic cycle and the autocatalyst and the intermediates are different forms of the enzyme. The reaction also exhibits different pH dependence in oxidation and reduction directions.²

A chemically realistic model is constructed to corroborate the experimental findings. The model not only describes the enzyme and electron acceptor concentration dependence of the front velocity, but also reproduces the experimental values within the experimental error. The critical enzyme concentration, where the reaction front disappears, is explained considering the stability of the reactant state, while the nearly constant front velocity at low electron acceptor to enzyme concentration ratios is associated with the change in the shape of the front in this region. The pH dependence of the enzyme activity is also reproduced both in the acidic and in the basic regions.

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AN ANALYTICAL METHOD FOR OPTIMIZING THE PORE NETWORK ARCHITECTURE OF LITHIUM-ION BATTERY ELECTRODES

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With advantages of high energy density, long cycle life, and environmental benignity, lithium ion battery (LIB) has been widely used in consumer electronics since it was firstly commercialized by Sony in 1991. At present, an emerging application of LIB is to power the electric vehicle that demands LIB with higher energy and power densities to extend its driving range and speed range. Among the various approaches to improve energy and power densities, optimizing the pore network architecture of electrodes is very effective, attracting attention from both academy and industry. In most of these studies, numerical methods are used to investigate the effects of pore network architecture on the performance of LIB. However, these numerical methods are inefficient in terms of optimizing the pore network, because the structural variables for optimization are large in number, including pore size, porosity, thickness etc. Therefore, an analytical method is needed to effectively optimize the pore network with various structural variables.

In this contribution, an analytical method is proposed to optimize the hierarchical pore network of LIB electrodes. This analytical method is based on the 2D Newman model [1], which describes the coupled processes of Li^+ diffusion in electrolyte and active material, electron conduction, and electrochemical reaction. An effective tortuosity is introduced to reflect the overall Li^+ diffusion resistance in an electrode, and subsequently to correspond to the performance of the electrode. To obtain the analytical expression of this effective tortuosity that includes all the structural variables, the parallel resistor principle is applied to integrate the Li^+ diffusion resistances in the hierarchical pore network [2]. This analytical method is validated by comparing the analytical solutions with the numerical ones calculated by using COMSOL. Finally, employing this analytical method, the pore network architecture of a commercial LIB, i.e., Sony UP383562, is optimized. The volumetric power density increases by 60% with a favourable energy density for the electrode with a low thickness (61 μm); while the energy density increases by 110% at 0.2 C for the electrode with a high thickness (305 μm).

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Chemical reaction networks and chemical reactor network theory

EXISTENCE, UNIQUENESS, AND STABILITY OF STEADY STATES OF MASS-ACTION SYSTEMS

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We give an overview on the existence, uniqueness, and stability results on the steady states of mass-action systems. The theory goes back to Feinberg, Horn, and Jackson, they started to derive general results on chemical reaction networks in the 1970's. In the last two decades, a renewed attention has been paid to the theory, and significant results have been developed. We touch the Deficiency-Zero- and Deficiency-One Theorems, the Deficiency-One Algorithm, the Global Attractor Conjecture, the Deficiency-Zero Theorem for generalized mass-action systems, and other famous results.

KINETIC INTERSECTIONS AS A SOURCE OF INFORMATION ON RATE COEFFICIENTS

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New results in extracting kinetic parameters of complex reactions based on the intersections of kinetic CSTR-dependences are presented. A general type of mechanism is described, assuming that it is possible to extract the rate coefficients from the CSTR-kinetic dependences. This mechanism has two parts bridged by a special step. The concept of the *gateway substance* is introduced. Different types of kinetic intersections are categorized. Special attention is paid to the so-called *end intersection*, i.e., the intersection between the concentrations of chosen substance and product concentration.

In accordance with the property theoretically discovered, all possible intersections of chemical species in a single sequence of reactions occur at values of space time which depend only on the kinetic parameters of the sequence itself. Requirements are formulated for the chemical mechanisms and corresponding initial compositions. A mathematical method is

proposed to obtain numerically the kinetic parameters from the values of space time related to the intersection points. The approach is illustrated by examples of complex reactions, especially of typical consecutive and parallel reactions, and complex reactions of catalytic synthesis as well. This approach is a further development of concepts of *joint kinetics* originated in 2011 [1–7].

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GLOBAL KINETIC MODELLING AND REACTOR ANALYSIS OF LEAN NO_x TRAPS CATALYSTS

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Lean NO_x traps (LNT) are one of the after-treatment techniques used for NO_x abatement in lean burn gasoline engines. The challenge in the exhaust gas treatment of lean burn engines is to selectively reduce the ppm levels of NO_x in the presence of percentage levels of oxygen. Traditional catalytic converters like TWC fail to yield good NO_x reductions at these conditions. The reactions that take place in LNT are not well established. The aim of this work is to develop a generic kinetic model for LNT and use it to design and analyse the LNT reactor for NO_x after-treatment. In this work, we propose an overall reaction scheme consisting of 16 global reactions that are modelled using LHHW Kinetics.

They can be categorised as oxidation reactions, NO_x reduction reactions, Barium oxide-NO_x storage reactions and Ceria-oxygen storage reactions. They are a simplified version of the model proposed by [1]. The reactor considered is a monolith channel for which a 1D Heterogeneous model is used. The proposed model is validated against experimental data in literature [1–3]. It is demonstrated that the model is capable of predicting the performance of several catalyst formulations including Pt/BaO/Al₂O₃, Pt/Rh/BaO/Al₂O₃ and Pt/Rh/BaO/Al₂O₃/Ce₂O₃ with only a slight modification of parameters. Next the contribution of each of the proposed reactions in the scheme to the overall observed phenomena is analysed in order to determine the important steps.

A complete reactor level analysis is performed to look into the ways of extending the time scale of lean phase, reducing the time scale of rich phase and reducing the dimensions of the reactor. The major aspects taken into consideration for analysis includes improving the fuel efficiency, reducing NO_x emissions to meet the upcoming stringent emission standards and cost reduction by reducing the dimensions of the reactor which in turn reduces the amount of catalyst used. Analysis is done by varying the dimensions (length, diameter and cpsi) and operating conditions (temperature and flow rate) from the base set of conditions within a certain range.

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OPTIMAL CONTROL PROBLEMS FOR GROUNDWATER STRESSED BY AGRICULTURAL FERTILIZERS

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The talk is devoted to a problem driven by contrasted time scales (fast reaction time scale, medium transport time scale, short-term profit and long-term environmental policies).

An optimal control problem of underground water contaminated by agricultural pollution is considered. The spatio-temporal objective takes into account the economic trade-off between fertilizer use and cleaning costs. It is constrained by a hydrogeological model which consists in a parabolic partial differential equation which is non linearly coupled through the convection term and the dispersion tensor with an elliptic equation, in a three-dimensional domain.

The model of pollutant transport is fine-tuned, defining the dispersion operator depending nonlinearly of the velocity of the fluid which itself derives from another unknown of the problem giving the flow potential. To take into account long run consequences of the optimal policy, we consider the economic objective on an infinite time length.

$$\max_{p \in E} \int_0^T \left(\int_{\Omega} (f(x, p(x, t)) - D(x, c(x, t))) \, dx \right) e^{-\rho t} \, dt$$

The model is the following:

subject to:

$$\begin{cases} R\psi\partial c + v \cdot \nabla c - \operatorname{div}(\psi S(v)\nabla c) = -r(c) + (p + \gamma)(1 - c) - gc \\ \operatorname{div}(v) = p + \gamma + g, v = -\kappa \nabla \phi \end{cases}$$

with reaction term r , initial and boundary conditions that we choose in a wide variety.

Taking into account the low-concentration of the pollutant in the underground, we derive rigorously the appropriate upscaled model and prove the existence and the uniqueness of its solution using singular perturbations and asymptotic analysis.

$$E = \{q \in L^2(0, T; L^2(\Omega)); 0 \leq q(x, t) \leq \bar{p} \text{ a.e in } \Omega \times (0, T)\}$$

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DYNAMICS AND THERMODYNAMICS OF OPEN CHEMICAL NETWORKS

Massimiliano Esposito

Université du Luxembourg

I will present a rigorous nonequilibrium thermodynamic description for open chemical reaction networks of elementary reactions described by deterministic rate equations with mass action kinetics. The most general framework considers open networks driven by time-depen-

dent chemostats. I will establish the energy and entropy balance and introduce a nonequilibrium Gibbs free energy. The difference between this latter and its equilibrium form will be shown to represent the minimal work done by the chemostats to bring the network to its nonequilibrium state. It is minimized in nondriven detailed-balanced networks (i.e., networks that relax to equilibrium states) and has an interesting information-theoretic interpretation. The importance of the network topology (algebraic properties of the stoichiometric matrix) on the thermodynamics will be emphasized.

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HYDROTREATMENT OF C₆ KETONES AND SECONDARY ALCOHOLS OVER SULPHIDED NiMo CATALYST: FIRST-PRINCIPLES SUPPORTED MICROKINETIC STUDY

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Using renewable feedstock for production of platform chemicals has recently been a topic of wide scientific research efforts. Cellulose and its monomer unit glucose is a promising component of biomass for conversion into platform chemicals, due to high amount of oxygen-containing functional groups.¹⁻³

Hydrotreatment of ketones (2-hexanone, 3-hexanone) and alcohols (2-hexanol, 3-hexanol) as a biomass model compounds was investigated in the presence of sulfided NiMo/ γ -Al₂O₃ catalyst and hydrogen atmosphere in the temperature range between 225 °C and 275 °C. Hydrotreatment of ketones proceeded through alcohols and olefins into alkene. Different isomers of olefins (1-hexene, *cis*-2-hexene, *trans*-2-hexene, *trans*-3-hexene and *cis*-3-hexene) were identified and quantified, showing the same selectivity regardless of the initial functional group position. Experiments were performed in a cylindrical 300 mL batch stainless steel autoclave, reactants, intermediates and products were analysed by gas chromatograph and gas phase was analysed by FTIR analysis. Furthermore a microkinetic model for three-phase slurry reactor was developed based on mass transfer from dispersed bubbles to the bulk liquid, mass transfer from bulk liquid to the catalyst surface, adsorption and desorption kinetics and surface reaction kinetics and fitted to the experimental data in order to obtain the corresponding parameters. *Ab initio* quantum chemical calculations were performed to complement experimental data. Density functional theory (DFT) calculations were used to calculate the activation energies and equilibrium constants for comparison with calculated values from modelling and in turn for explanation of reaction mechanisms, which were compared with their values from microkinetic modelling, showing remarkable agreement.

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OSCILLATIONS IN THE LOTKA-FARKAS REACTION

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The simplest chemical oscillator goes back to Lotka.

Farkas and Noszticzius (1985) and Dancso et al (1991) considered generalized Lotka reactions with power-law kinetics and provided a local stability and bifurcation analysis as well as first integrals.

We continue their investigations. In particular we solve the center problem: For which Lotka-Farkas systems is the unique positive equilibrium surrounded by periodic orbits only? As a byproduct we obtain systems with two limit cycles.

This is joint work with Balazs Boros, Stefan Müller and Georg Regensburger.

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BIFURCATION ANALYSIS OF DETAILED COMBUSTION MECHANISMS

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Performing bifurcation analysis of complex detailed chemical mechanisms that are used for simulation of combustion systems is a computationally difficult task. The difficulty arises from the fact that species concentrations in these non-isothermal systems may span 10–20 orders of magnitude. It is general that many of the species that are important at certain conditions may become irrelevant at different ones along a solution branch. Nevertheless, the continuity of the solution demands that the relevant species be present for the whole solution branch. Handling these species numerically becomes a very difficult task during computation of both steady states, and eigenvalues that are used for detecting various bifurcation points. Here we present a general methodology that enables us to reliably perform numerical bifurcation analysis on these systems. The method is based on easy to adopt coordinate transformations that utilizes numerical algorithms' built-in handling of machine precision. The method is tested on combustion mechanisms consisting of up to 250 species and over a thousand reactions. The method also allows us to simplify complex mechanisms to the most relevant species and reactions that replicates the bifurcation behavior of the more complex mechanism as redundant species along solution branches can be identified and eliminated subsequently. Examples are shown for partial oxidation of hydrocarbons.

MOLECULAR POTENTIAL ENERGY SURFACES AS FRAMEWORKS FOR REACTION KINETICS

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Potential energy hypersurfaces, where the energy functions belonging to a given stoichiometry are dependent on the nuclear coordinates, provide a general framework for the study of chemical reactions, molecular rearrangements, and conformational changes. These hypersurfaces are typically of high dimensions where visualization is difficult, however, their mathematical properties provide useful shortcuts, simplifications, and important rules on the interrelations among reaction mechanisms, including an algebraic structure, the Fundamental Group of Reaction Mechanisms, derived from the algebraic topology of such hypersurfaces. Alternative group-theoretical properties are exploited in the symmetry-conservation relations

along reaction paths and two generalizations of symmetry, syntopy and symmorph, serve as tools for identification of optimality conditions in a family of reactions occurring along these hypersurfaces.

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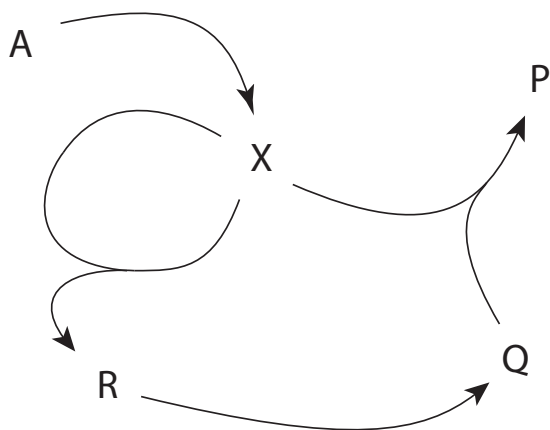
THE MODEL OF “MINIMAL OSCILLATOR” OF THE $\text{H}_2\text{O}_2 - \text{NaSCN} - \text{NaOH} - \text{CuSO}_4$ DYNAMICAL SYSTEM

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Oscillatory chemical reactions are usually characterized with complicated kinetic mechanisms. However, the essential source of the oscillations can often be reduced to only a few reaction steps providing the alternative domination of the positive and negative feedback loops. In an extreme case such a reduction leads to the so-called “minimal oscillator”. In our work we studied the $\text{H}_2\text{O}_2 - \text{NaSCN} - \text{NaOH} - \text{CuSO}_4$ homogeneous oscillator, discovered by M. Orbán [1]. Our aim was to reduce significantly the original mechanism proposed by Luo et al. [2] and engaging 26 intermediates as dynamical variables. In a series of recent papers we have described the nine-variable [3], five-variable [4] and the three variable mechanisms [5], the latter one considered by us a minimal oscillator for this dynamical system. The methodology involved intuitive analysis of the reaction mechanism, supported by numerical calculations of the reaction dynamics, linear stability analysis, as well as comparative spec-

trophotometric measurements. The proposed minimal oscillator model includes the autocatalytic loop involving X species and negative feedback caused by competitive interaction of X with Q, produced from R formed together with X (the so-called “coproduct autocontrol”). The model includes also the adjustable stoichiometric parameter m that controls the presence of autocatalysis and determines the Hopf bifurcation limits. Finally we show that the three-variable model is really a minimal oscillator since its further reduction to two-variable variant by adiabatic elimination of one more dynamical variable is not possible.



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INHERITANCE OF BISTABILITY IN MASS ACTION REACTION NETWORKS

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This talk focuses on the question of bistability, or existence of multiple (stable) positive equilibria, a dynamical property that underlies important cellular processes, and a recurring theme in recent work on reaction networks. Namely, we consider the question: "when can we conclude that a network admits multiple stable positive equilibria based on analysis of its subnetworks?" We identify a number of operations on reaction networks that preserve bistability as we build up the network, and we illustrate the power of this approach on the much-studied Huang-Ferrell MAPK cascade. Work in this direction is an essential step towards a rigorous theory of "motifs", a central theme in systems biology.

SYSTEMATIC DESIGN OF REACTION SYSTEMS WITH PRESCRIBED BEHAVIORS: DETERMINISTIC AND STOCHASTIC METHODS

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**Talk given by Tomislav Plesa.*

In this talk, I will discuss methods for systematic design of reaction systems with desired dynamics. Two types of dynamical models of reaction systems will be considered: (i) the deterministic model, taking the form of the kinetic ordinary-differential equations, which govern the time-evolution of the species concentrations, and (ii) the stochastic model, taking the form of the chemical master equation, which governs the time-evolution of the species copy-numbers distribution, and which is consistent with the Gillespie stochastic simulation algorithm. The methods presented may play an important role in the growing field of synthetic biology, where the designed systems may be physically realized (for example, using the so-called strand-displacement DNA computing).

Relatively simple reaction systems with exotic dynamics will be constructed. More precisely, I will present reaction systems whose deterministic models display multistability and oscillations (e.g. multiple oscillating solutions), and undergo specific bifurcations (e.g. a homoclinic bifurcation). I will then present the so-called noise-control algorithm, which structurally modifies any given reaction network under mass-action kinetics, in such a way that (i) the deterministic model is preserved, and (ii) controllable state-dependent noise is introduced

into the stochastic model. The algorithm will be used to redesign some of the exotic reaction systems at the stochastic level, in order to achieve noise-induced multistability, and noise-induced oscillatory monostability.

GLUCANS MONOMER-EXCHANGE DYNAMICS AS AN OPEN CHEMICAL NETWORK

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We describe the oligosaccharides-exchange dynamics performed by so-called D-enzymes on polysaccharides. To mimic physiological conditions, we treat this process as an open chemical network by assuming some of the polymer concentrations fixed (chemostatting). We show that three different long-time behaviors may ensue: equilibrium states, nonequilibrium steady states, and continuous growth states. We dynamically and thermodynamically characterize these states and emphasize the crucial role of conservation laws in identifying the chemostatting conditions inducing them.

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SOME COMPUTER ALGEBRA TOOLS FOR INVESTIGATION OF BIOCHEMICAL MODELS DESCRIBED BY SYSTEMS OF ODES

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We give an introduction to algorithms of the elimination theory and methods for solving of polynomial systems and show how they can be used for the qualitative investigation of autonomous systems of ordinary differential equations arising in modeling of biochemical networks. An application to the study of the May-Leonard system, which models some ecological and chemical processes, is considered in more details. Some first integrals and periodic solutions in the system are found. Hopf bifurcations are discussed.

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POSITIVE LINEAR ELIMINATION OF SPECIES

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The steady states of a chemical reaction network with mass-action kinetics are solutions to a system of polynomial equations. Even for small systems, finding the steady states of the system is a very demanding task and therefore methods that reduce the number of variables are desirable. In [1] the authors give one such method, in which so-called non-interacting species are eliminated from the system of steady state equations.

We extend this method for the elimination of what we call reactant non-interacting species and give some conditions that ensure the positivity of the elimination obtained, that is, for positive values of the reaction rate constants and the non-eliminated species, we ensure that the eliminated species are positive as well. In particular, if enough species can be eliminated, then this method provides a parametrisation of the positive part of the steady state variety.

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PARAMETER FITTING IN MODELS OF COMPLEX REACTIONS TO EXPERIMENTALLY OBSERVED OSCILLATORY DYNAMICS USING REACTION NETWORK THEORY

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Oscillatory enzyme reactions frequently have complex mass action based mechanisms. A model based on such a mechanism has the problem of difficult identification of rate coefficients that would provide dynamics consistent with experimentally observed oscillations.

The rate coefficients of elementary steps are typically unavailable, instead, equilibrium constants for some of the reversible steps may be known. One way of overcoming this difficulty is to reduce the model using quasi-steady-state assumption resulting in a simplified enzyme mechanism for which some parameters, such as maximum rate, Michaelis constant and various inhibition constants may be obtained by fitting to measured data. We adopt a different approach based on the mass action kinetics that makes use of stoichiometric constraints and the theory of stability of reaction networks. For a system where oscillatory dynamics were experimentally observed, the mass action mechanism is formulated and the corresponding network is decomposed into subnetworks. The original parameters – the rate coefficients – are replaced by convex parameters – the weights of the convex combination of the subnetworks and steady states. Next, oscillatory subnetworks are identified, which implies preferred choices for the steady state concentrations, and a convex combination of all the subnetworks is sought such that a suitable oscillatory subnetwork is dominant. By varying the extent of its dominance, a Hopf bifurcation is eventually found and the rate coefficients of all the reaction steps are determined from the convex parameters. This formulation requires certain constraints implied by known data either from literature (some kinetic or equilibrium constants) or from the experiment (inflow rates of reactants, some measured steady state concentrations) to be satisfied. We have been able to find kinetic parameters for oscillatory conditions in models consistent with experiments for the catalase-hydrogen peroxide-glucose-oxidase-glucose system and for the urea-urease system.

FLATNESS-BASED MODEL SELECTION OF A BENZALDEHYDE LYASE CATALYSED BIOCHEMICAL REACTION NETWORK

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Profit margins in the highly competitive pharmaceutical industry have been constantly declining over the last decades because of increasing research and development costs [1]. In the development and production of active pharmaceutical ingredients (APIs) biochemical pathways play an important role. Mathematical models have been proven beneficial to optimal bioprocess design and to system understanding. Biochemists, however, often face a plurality of mathematical models that attempt to describe the complex biochemical reaction network of an experimental outcome. The identification of the best model candidate, that reproduces closest the physical process, is a crucial task for identifying the underlying system mechanisms and predicting its behaviour – in particular in the strongly regulated pharmaceutical market. Conducting model-revealing experiments, in turn, is in general time-intensive and expensive. In this work, we analyse a benzaldehyde lyase catalysed reaction network with-

in the framework of optimal experimental design (OED) for an improved model selection outcome. We falsified improper models from a set of model candidates by 1) showing that the individual models satisfy differential flatness conditions and 2) solving an optimisation problem that makes use of the flatness property and its mathematical basics. Flatness-based methods have been widely applied in nonlinear control problems since the introduction of differentially flat systems by Fliess et al. in the 1990s, especially in the field of mechanics [2], and were recently introduced for model calibration problems of (bio)chemical systems [3]. Flat outputs of a dynamic system parameterise its states and control functions entirely, thus, enabling straightforward analytic trajectory planning and controller design. We successfully transferred the mathematical principles of the flatness concept to a model selection problem and a model-revealing optimal experimental design framework, respectively. We analytically obtained the best available model candidate without the limitations of linearising or integrating non-linear differential equations, and derived optimal experimental conditions for subsequent validations at the same time. Moreover, we used this concept as an analysis tool to measure limits and applicability of the different models leading to an analytic insight where and how well the models had been defined in state-space.

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APPROXIMATION OF DELAYED CHEMICAL REACTION NETWORKS

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Chemical reaction network models in the form of ordinary differential equations are widely used in the modeling of (bio)chemical processes or other nonnegative systems such as ecological, disease or even transportation dynamics [1,2]. It is known that important dynamical phenomena occurring in nature or in technological systems can often be explained in a satisfactory way by using explicit time-delays in the equations. To support the computational treatment of delayed models, it is common to approximate the original system's dynamics by a set of ordinary differential equations through introducing auxiliary state variables. One

popular approach for doing this is the so-called chain method [3] for which there exist useful results on the quality of approximation depending on the non-linearities and the number of additional approximating equations [4]. In this contribution we define and study a class of delayed reaction network models derived from classical mass action kinetic systems by allowing different (but constant) delays corresponding to certain reactions of the network. More precisely, we assume that the source and product complexes of delayed reactions contain exactly one species, while there are no constraints on the source and product complexes of non-delayed reactions in the network. Applying the modified chain method [4], we show that the approximating ODE of the delayed reaction network remains kinetic (i.e., it is always a mass action model), and therefore it is straightforward to obtain its reaction graph. The approximation involves n new state variables which correspond to n additional complexes in the reaction graph, where the positive integer n is a design parameter determining the precision of the approximation. We show that the approximation preserves the number of linkage classes, deficiency and weak reversibility of the original network. Additionally, we define the notion of complex balance for delayed kinetic systems. As a main result, it is shown that the proposed approximation preserves the complex balanced property of the system for any finite number of n .

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DISSIPATION IN NOISY CHEMICAL NETWORKS: THE ROLE OF DEFICIENCY

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In the interior of biological cells, various chemical reactions take place fulfilling tasks like energy transport and transduction, sensing, information storage and processing, as well as regulation tasks and production of biomass. These reactions can be considered complex chemical reaction networks since they involve hundreds to thousands of chemical species and thousands of reactions. The dynamics of these systems is typically modelled either on the

microscopic level with stochastic processes including all the intrinsic noise, or on a coarse-grained level using deterministic rate equations thus neglecting any noise or correlations. On both levels there is a natural thermodynamic description. We study the effect of the microscopic noise on the thermodynamic balances in these processes and compare the stochastic to the deterministic description from a thermodynamic perspective.

For reaction networks one defines a topological quantity known as *structural deficiency*, which is known to determine the possibility of complex behavior such as multistability and oscillations. We show that this quantity also characterizes the entropic balance. In particular, when the deficiency is zero the average stochastic dissipation rate equals that of the corresponding deterministic model. [1]

At steady state the topological cycles in the network play a key role in quantifying the thermodynamic dissipation in terms of the entropy-production rate [2]. We give a classification of cycles based on the two concepts of deficiency and dissipation. Thus capturing their dynamic and thermodynamic contributions to the steady state of the system without the need to explicitly calculate the steady state.

We illustrate our findings with a toy model for cellular metabolism, allowing us to briefly comment on the implications on linear response close to equilibrium. While it was known in the literature that coarse graining typically underestimates dissipation, we show that for a class of systems including our toy model dissipation is systematically overestimated when performing the large scale limit. This phenomenon highlights that there is a close interplay between deficiency and the activation of new dissipative processes at low molecule numbers.

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LINEAR OR NON-LINEAR: PROCEDURES FOR DISTINGUISHING THE MODELS OF CHEMICAL KINETICS AND CHEMICAL ENGINEERING

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In chemical kinetics and chemical engineering, it is crucial to solve problems related to distinguishing linear and non-linear behavior:

1. to distinguish a linear process from a non-linear one based on experimental data;
2. to determine the linear domain of a non-linear process based on computational or experimental data

Presently this differentiation is made only statistically using model discrimination.

For typical chemical reactors, ideal (CSTR and PFR) and non-ideal, we propose procedures, experimental or computational, that are special sequences of different experiments, parallel or consecutive, in particular experiments of type “one step forward – one step back”. It was found that in linear cases the linear combination of non-steady-state concentration dependences gives a simple time invariance. Such an invariance is a rigorous fingerprint for distinguishing a linear model or the linear domain of the non-linear model from non-linear ones.

In a batch reactor (BR), for linear kinetic models of reversible transformations, the ratio of special non-steady-state dependences that start from symmetrical initial conditions, “Y produced from X” / “X produced from Y”, provides a thermodynamic time invariant (equilibrium-like constant) [1–3] This invariant is proposed as a fingerprint of linear models in the setting of reversible chemical reactions.

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A SKELETAL KINETIC MECHANISM FOR THE “SO_x-NO_x-O₂-H₂O-CO₂” SYSTEM AT ELEVATED PRESSURES

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Pressurized oxy-combustion (POC) is a promising technology that can significantly reduce the energy penalty for CO₂ capture in coal-fired power plants. In pressurized oxy-combustion, coal is burned in the mixture of oxygen and recirculated flue gas, by replacing air, at high pressure. Such a condition results in much longer residence time and higher SO_x and NO_x partial pressures¹. This tends to enhance the production of strong acid gases, including SO₃ and NO₂, aggravating the corrosion threat during flue gas recirculation (FGR); on the other hand, the strong interaction between SO_x and NO_x at high pressure enables integrated SO_x/NO_x removal. However, the mechanism of SO₃ and NO₂ formation during POC process is not well understood. In this study, after validating the ‘full’ mechanism, which includes

nitrogen and sulphur chemistry based on GRI 3.0, and 72 species and 428 reactions, the formation of SO_3 and NO_2 was kinetically evaluated under representative conditions for the POC process. Sensitivity analysis and rate of production analysis (ROP) were conducted to demonstrate the formation pathway of SO_3 and NO_2 and develop a skeletal mechanism for the “ $\text{SO}_x\text{-NO}_x\text{-O}_2\text{-H}_2\text{O-CO}_2$ ” reaction system. Finally, the skeletal mechanism was coupled with a computational fluid dynamics (CFD) model to evaluate the formation of SO_3 and NO_2 in a new concept for POC. Previous results identified the regions of 700–1100°C as the critical temperature window. Sensitivity and ROP analysis in this region indicate that for the “ $\text{SO}_x\text{-NO}_x\text{-O}_2\text{-H}_2\text{O-CO}_2$ ” system at elevated pressures, there is a ‘strong’ cycle which consists of three reactions $\text{HO}_2+\text{NO}=\text{NO}_2+\text{OH}$, $\text{SO}_2+\text{OH}+\text{M}=\text{HOSO}_2+\text{M}$, $\text{HOSO}_2+\text{O}_2=\text{HO}_2+\text{SO}_3$ with the global reaction $\text{NO}+\text{SO}_2+\text{O}_2\rightarrow\text{NO}_2+\text{SO}_3$. The radical HOSO_2 can be considered as a quasi-steady state intermediate. This cycle is the major route for the formation of both of SO_3 and NO_2 at elevated pressures, while the reversible reaction $\text{SO}_2+\text{NO}_2=\text{SO}_3+\text{NO}$ can be treated as in equilibrium. There are also two ‘weak’, non-negligible cycles of NO_2 consumption and SO_3 formation: (A) $\text{NO}_2+\text{M}=\text{NO}+\text{O}+\text{M}$, $\text{SO}_2+\text{O}+\text{M}=\text{SO}_3+\text{M}$ and (B) $\text{NO}_2+\text{M}=\text{NO}+\text{O}+\text{M}$, $\text{NO}_2+\text{O}=\text{NO}+\text{O}_2$ with global reactions $\text{NO}_2+\text{SO}_2=\text{NO}+\text{SO}_3$ and $2\text{NO}_2\rightarrow 2\text{NO}+\text{O}_2$, respectively. Neglecting these two ‘weak’ cycles results in a maximum error of SO_3 and NO_2 formation by no more than 25%. Two skeletal mechanisms of 10 or 6-steps have been developed. Results of modelling of POC furnace using CFD model coupled with the reduced kinetic model agree well with calculations based on the ‘full’ mechanism.

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RATIONAL CATALYST DESIGN FOR PROPANE DEHYDROGENATION FROM FIRST PRINCIPLES AND MICROKINETIC MODELING

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Abstract: Propylene is an important chemical intermediate in the chemical industry, which is conventionally produced either as a co-product to ethylene in steam crackers or byproduct in refineries. With the increase in exploration of shale gas, new cracker projects for ethylene production are based primarily on ethane feedstock, which yield almost no propylene^[1,2]. On the other hand, the demand for propylene worldwide is growing by 5–6 % each year, so that on-purpose propylene production technologies such as propane dehydrogenation (PDH) have been proposed to fill the supply-demand gap. PDH has been successfully commercialized,

and the catalysts used in industry are platinum- or chromium oxide-based catalysts. However, Pt is precious and Cr^{6+} has harmful effects on environments. Therefore, searching for novel non-precious metal alloy catalysts with increased catalytic activity and improved selectivity for propylene production would make this process more competitive.

In this contribution, volcano curves for the PDH process are obtained through density functional theory (DFT) calculations coupled with descriptor-based microkinetic analysis. The formation energies of $\text{CH}_3\text{CH}_2@(\text{111})$ and $\text{CH}@\text{(211)}$ scale linearly with the energetics of other species involved in PDH and are found to be good descriptors to describe the reaction kinetics. Among the elemental metals, Ir and Pt achieve the highest turnover frequencies (TOFs) for propylene production. However, if a compromise is made between catalytic activity and selectivity, Pt is the best monometallic catalyst, which offers an explanation for the usage of Pt in industry^[3]. On the basis of the derived activity and selectivity maps, promising PDH catalysts can be singled out by screening a large number of metal alloys.

Keywords: Rational catalyst design; Microkinetic modeling; Volcano curve

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Other

COMPARTMENTAL MODELING OF TOP SPRAYED FLUIDIZED BED GRANULATOR USING POPULATION BALANCES

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Mathematical modelling has proven as a powerful tool in pharmaceutical industry for understanding various types of fluidized bed granulators. In this present exercise, the modelling and simulation of a two-compartment model, i.e., the wet zone and the dry zone of a top sprayed fluidized bed granulator (SFBG) has been analysed. In the wet zone, only aggregation mechanism is considered whereas breakage is chosen to be the dominant mechanism in the dry zone. The particle mass flow between both zones is assumed to be exchange at a steady rate and the residence time of the particles in each compartment is defined using a mass balance. For solving the two-compartment population balance model, a new discretization scheme based on number distribution is proposed. The idea of the discretization is to conserve some desired property such as total number and total mass of the system by introducing certain correction factors to the formulation. Moreover, the numerical discretization is verified using newly derived analytical solutions for various moments corresponding to different combinations of aggregation and breakage kernels. It is shown that the predicted numerical moments show good consistency with the analytical moments. In addition to this, various sizing of the compartments of SFBG as well as different flow rates have been investigated to check the behaviour of various order moments derived from the number distribution function.

FULL MATHEMATICAL DESCRIPTION OF THE PH-STAT KINETIC TRACES IN THE PHOTOCHEMICAL REACTIONS OF QUINONE DERIVATIVES

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The aqueous photoreactions of substituted 1,4-benzoquinone derivatives produce a mixture of hydroquinones and hydroxy-quinones, both of which are weak acids [1, 2]. The pH of aqueous solutions often has a major influence on the rates of chemical reactions, thus it is

desirable to keep it at a controlled, constant value during a single experiment. Buffers are usually used for this purpose, but they frequently interfere with the studied process as well, which is especially a problem for photoreactions. Therefore, it is very advantageous to monitor these processes without using buffers by time dependent pH-stat titrations. In this technique, a suitable automatic system continuously adds just enough base or acid to the system to keep the pH constant. In the photoreactions of quinones, the formation of hydroxy-quinone can be readily monitored by this technique. Mathematical models were set up to describe the pH-stat measurements, which facilitates the determination of the differential quantum yield of the reaction and the ratio of the two photo-products through a detailed analysis of the base consumption as a function of time. The parameters of the equation are practically pH-independent, which is in good agreement with the fact that 2,5-dichloro-1,4-benzoquinone itself is not a weak acid or base, so its absorption spectrum does not depend on the pH of the solution. This technique and the mathematical model could be suitable for studying other photochemical reactions when the reaction includes the formation or consumption of acid or base.

Acknowledgements

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AN INNOVATIVE KINETIC MODEL FOR NR-HIGH CIS PB BLENDS

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In this paper, an innovative kinetic model for the numerical interpretation of the curing behaviour of NR-high cis polybutadiene (PB) rubber blends is presented.

For each rubber component, the model bases on consolidated kinetic approaches available in the technical literature and merged linearly in the same procedure, having demonstrated a linear interaction fairly good agreement with experimental evidences. In particular for NR, a kinetic model by Han's and co-workers [1], which bases on the determination of three kinetic constants, is adopted, whereas for PB a recent kinetic scheme proposed by the authors [2] is utilized. This latter procedure is based on four kinetic parameters. The derived mathematical

model is therefore characterized by seven constants, to be estimated against experimental rheometer data. The benchmark blend used to assess the numerical results is a NR mixed with high-cis polybutadiene at variable NR-PB ratios (50–50% and 70–30%) and vulcanized in presence of sulphur and two accelerants (TBSS and DPG) at different concentrations and different temperatures. Quite good agreement is found, meaning that the approach may be useful for practical purposes, because expensive and cumbersome experimental investigations can be avoided.

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DIFFERENT AVAILABLE COMPLETION ROUTES IN COMPLEX CHEMICAL REACTIONS

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Abstract: This work address the construction of slow manifold in a complex chemical reaction based on different available routes [1] with the same decomposition techniques of entropy maximum along with certain constraints (lies on the manifold or given by slowest eigenvectors) at equilibrium point as well as measuring the variation of their eigenvalues at each point. The goal of this paper is to bring together different available mathematical ideas and methods [2-6], commonly used to transform the complex chemical problems from one way to the other, so as to enhance progress in understanding. For a case study the behaviour of the ‘four step reversible reaction’ is summarized in the form of the two (different) available routes in order to get rid of stiffness as well as complexity in the system. Together with nonlinear effects such as reaction rate oscillations and concentration pattern formation we apply the modern model reduction techniques to get the slow invariant manifold (SIM). Finally, combining and comparing these techniques, we get better estimates (dimensional curves) lies in the complex problems.

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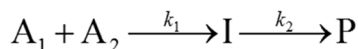
DOUBLE EXPONENTIAL EVALUATION UNDER NON-FLOODING CONDITIONS: A MIXED SECOND ORDER PROCESS FOLLOWED BY A FIRST ORDER REACTION

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In the present work, a double exponential approximating approach is described for a quite common kinetic model, when a mixed second order formation of an intermediate (I) is followed by its first order decay [1, 2]:



The kinetic curves are described under non-flooding conditions (when the initial ratio of the two reactants is between 1 and 10).

The exact kinetic curves predicted by the two-step model were first calculated and then fitted to a double exponential function. The goodness of the fits and the estimated parameters of the double exponential function for both I and P concentrations were determined as a function of the rate constants and initial concentrations in the two-step model. It was found that the fit of the double exponential function is acceptable or very good under these conditions despite the fact that none of the reagents is in a large excess.

Since UV-vis absorption spectroscopy is probably the most common technique to follow kinetic traces, we also made efforts to deal with the typical properties of monitoring the process through UV-vis. It was found that the experimental curves can be fitted quite well with a double exponential function if the reagents have minor absorption compared to the intermediate and/or product, which is very common case. The connection between the observed rate constants and the rate constants of the above mentioned mechanism is also studied.

Acknowledgements

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A MODEL-BASED EXPERIMENTAL DESIGN APPROACH FOR THE IDENTIFICATION OF KINETIC MODELS OF AU CATALYSED HMF OXIDATION IN A MICROPACKED BED REACTOR

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Oxidation of HMF (5-hydroxymethylfurfural), a key intermediate of lignocellulosic biomass, is recognized as a promising route towards transformation of biomass into fine chemicals. FDCA (2,5-furandicarboxylic acid), the total oxidation product of HMF oxidation, is identified as a non-phthalate cellulosic plasticizer, capable of replacing terephthalic acid (TPA) in the production of polyesters^[1]. In this study, HMF oxidation reaction was carried out in a micropacked bed (PTFT tubing, 0.8 mm i.d) reactor over Au/TiO₂ catalyst. Preliminary experiments identified the major side products and suggested the reaction pathway as a consecutive series reaction with FDCA as the final product. Furthermore, reactions conducted at 25-80°C, over varying gas (1-6 ml/min of O₂) and liquid (5-15 µm/min of HMF) flow rates corroborated the existence of considerable gas-liquid mass transfer resistance. Some attempts of modelling the reaction kinetics under batch reaction conditions can be found in the scientific literature^[1]. However, a precise identification of reaction kinetics can be achieved only when the kinetic parameters involved in the model are estimated with satisfactory accuracy. In this study, model-based design of experiments (MBDoE)^[2] techniques are applied to the micro-reactor platform^[3] to accomplish the complete modelling description of the HMF oxidation in the microfluidic device. This implies: *i*) elucidating the complex (only partially known) reaction pathways; *ii*) understanding underlying hydrodynamics and relationship with mass

transport properties; *iii*) the precise estimation of kinetic parameters. A simulation model is developed in gProms where the micropacked bed reactor is modelled as dynamic plug flow reactor (PFR). The rate laws are formulated based on Eley-Rideal mechanism in which O₂ reacts with HMF adsorbed on the catalyst surface. The framework aims at eliminating unnecessary experimentation and modelling effort as it enables the optimal design of experiments for model discrimination and parameter estimation for the development of a predictive model of the HMF oxidation process.

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APPLICATION OF PARTIAL LEAST SQUARES REGRESSION FOR UNDERSTANDING AND PREDICTION OF FOULING IN THE TRANSFER LINE HEAT EXCHANGER OF A STEAM CRACKER

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Advanced data analysis is crucial to identify hidden information in complex data. Multivariate techniques, such as Partial Least Squares Regression (PLSR), are the preferred data analysis techniques for dimensionality reduction and compression of data structure [1]. The mathematical concepts of PLSR method is able to handle highly correlated (collinear) and noisy data even when the number of measurements highly exceed the number of samples, thereby enabling quantitative multivariate linear modelling. To illustrate the capabilities and limitations, PLSR has been applied for evaluation and prediction of fouling tendencies of gas condensates during steam cracking. The latter is governed by their chemical composition, however, establishing the relation between molecular composition and observed fouling is a challenging task due to the vast amount of compounds in these mixtures. Gas condensates are characterized using two-dimensional comprehensive gas chromatography (GC×GC) indorsing the high separation power of the technique. Furthermore, pixel based analysis of GC×GC

data enabled a direct unbiased approach for chemical evaluation without loss of information. The large amount of data prevents easy interpretation of variations between the samples and correlating the composition with the experimental observation, i.e. fouling in the steam cracker transfer line heat exchange (TLE). The initial PLRS model is build using complete characterization matrix for seven gas condensate samples and consequently seven pilot scale steam cracking fouling measurements. However, evaluation of root mean square error of cross-validation showed that the model did not give promising predictions. The model focused on describing fouling through correlations with the most abundantly present paraffinic molecules that are not recognized as fouling precursors. By scaling the chromatography data by inverse within-sample standard deviation, the regions with a large amount of random variation have a reduced influence whilst the impact of regions with chemical differences between samples is increased. Next, the regression vector was used as a variable selection method on a logarithmical transformed chromatography and fouling data, providing a prediction model with 20% of error on average. Variable selection indicated that elution regions of aromatic compounds, monoaromatic and naphthenic compounds with a long alkyl chains bonded and paraffin compounds with high boiling point are the best TLE fouling predictors.

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TIME SCALES FOR FREE ENERGY LANDSCAPES

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The connection between rate constants and free energy landscapes is discussed in a context that brings in explicitly a time scale of interest. The free energy of activation is seen to depend crucially on this time-scale. The example of Holliday junction resolution is used to illustrate the arguments.

FINITE VOLUME APPROXIMATION OF TWO-DIMENSIONAL AGGREGATION POPULATION BALANCES ON TRIANGULAR MESH

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A finite volume scheme for approximating the solution of a two-dimensional (2D) aggregation population balance equation on a regular rectangular mesh was introduced by Singh et al. (2016). Recently, Chakraborty and Kumar (2007) proposed a framework known as 'smart discretization' which shows that the accuracy of the numerical scheme highly depends on the choice of the mesh taken into consideration. In this present work, the first application of the finite volume scheme for solving a 2D aggregation population balance equation on a regular triangular mesh is demonstrated. The triangular mesh is generated by slicing the rectangular mesh along the diagonal. To test the accuracy and efficiency of the scheme with the triangular mesh, the numerical results are compared with the sectional method namely Cell Average Technique (Singh et al., 2014) for various analytically tractable kernels. The results reveal that the finite volume scheme is computationally less expensive and predicts the number density function along with the different order moments more accurately than the cell average technique. Furthermore, the numerical comparison is extended by comparing the finite volume scheme with the rectangular mesh. It also reveals that the finite volume scheme using the regular triangular mesh computes the numerical results more accurately and efficiently than the finite volume scheme using a rectangular mesh. In conclusion, the finite volume scheme with regular triangular mesh shows good consistency with the exact results for number density as well as with different order moments and is computationally less expensive.

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MODELING THE ENZYMATIC HYDROLYSIS OF PROTEINS CONSIDERING VARIABLE PRODUCT INHIBITION

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The enzymatic hydrolysis of proteins is an attractive alternative to valorising food residues because it generates functional properties [1]. The reaction has been characterized kinetically and the main mechanisms have been unveiled. The reaction system consisted in the substrate salmon muscle proteins and the enzyme subtilisin [2]. The methodology involved initial reaction rate experiments to estimate the maximum rate (V_{max}), the Michaelis-Menten constant (K_m) and the substrate inhibition constant (K_s). The product inhibition was tested adding hydrolysate at the beginning of reaction and the initial rate experiments repeated at this condition to estimate the product inhibition constants (K_p). Progress curves were carried out to test the product inhibition and its variation during reaction. The mechanisms of uncompetitive substrate inhibition, mixed product inhibition and modulation of the thermal inactivation of subtilisin were verified [2]. The estimated kinetic constants were $V_{max} = 0.581$ mM/min (for 0.6 mAU/ml), $K_m = 4.39$ mM and $K_s = 826$ mM at 40 °C and pH 8.0. Estimated values for competitive inhibition constant K_i and uncompetitive inhibition constant K_2 were 14 mM and 85 mM when a 20 % degree of hydrolysis hydrolysate was used. The product inhibition was the main cause of the dramatic decreasing on the reaction rate during the batch reactor operation due to the low-value of the inhibition constants [2]. A variation of the K_i values was inferred from this results. The variation of K_i values was modelled correlating the inhibition constant with the degree of conversion (X) [3]. A mathematical model was developed and fitted to conversion curves by using least squares method for the calculation of linear functions of both K_i versus conversion. A significant improvement on prediction were achieved with the present approach using functions for both K_i . These results confirmed the variation of both K_i values during the hydrolysis reaction. The quality of prediction with this mathematical model was improved. The model can be used to characterize, evaluate and design the enzymatic hydrolysis of proteins in batch reactor.

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POSTER PRESENTATIONS

Multiscale modeling

QUICK WAY TO COMPUTE THE AXIAL DISPERSION COEFFICIENT USING LAPLACE TRANSFORM AND MAPLE®

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The Laplace transform is applicable in many disciplines like mathematics, physics, mechanics, process control, chemical engineering and biosciences. It is a useful *tool of mathematics* in solving of many problems which are described by a system of differential equations. In many complex cases, an analytical transform to the time domain can be difficult or even impossible to obtain, so numerical methods have to be used. According to literature reports, there are many methods for numerical inversion of the Laplace transform. According to literature reports, and authors own experience, different algorithms can be recommended for solution of a specific type of problem, e.g. dispersion problem [1, 2].

In this paper, we presented the application of the Laplace transform to solve the model of gas flow describing dispersion of a gas tracer pulse in a real measurement system. We used the Gaver-Stehfest algorithm of inverse Laplace transform to obtain the solution in the time domain. Axial dispersion coefficients D_L were estimated by comparing model solution with recorded TCD signal (inverse method). The values of parameter D_L was determined using an optimization procedure of the program Maple® (*NLPSolve*).

The results show that the Laplace transform is very effective tool for solving the inverse boundary value problems associated with the diffusion equation. The axial dispersion coefficients can be easily determined. The values of axial dispersion coefficients indicate that under operational conditions, neither plug-flow nor perfect mixing can be assumed.

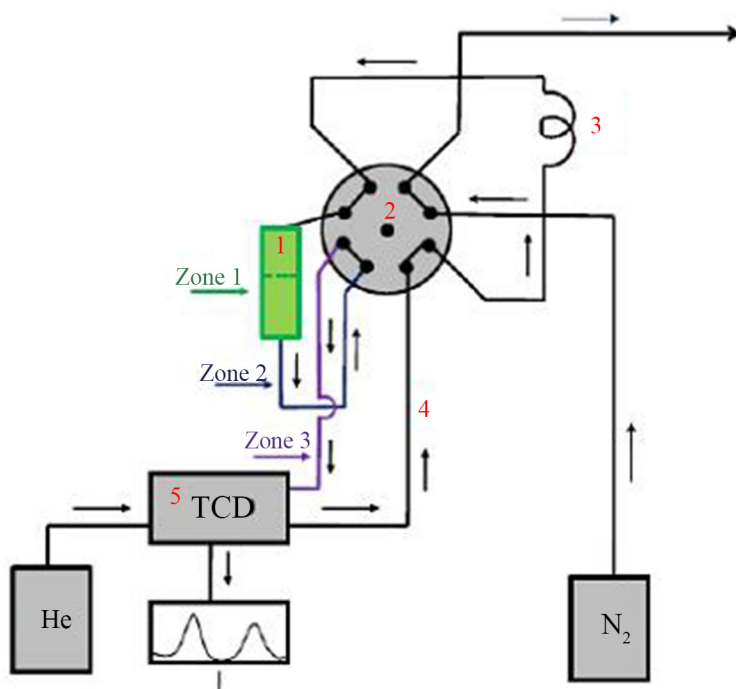


Fig. 1. The simplified schematic representation of apparatus (Micromeritics' AutoChem 2950HP): 1 – a unit called vessel, which consisting of two steel pipes, 2 – the 8-way valve, 3 – the sample loop, 4 – pipes, 5 – the thermal conductivity detector (TCD).

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Stochastic kinetics and simulation

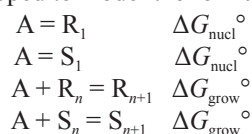
CHIRAL SYMMETRY BREAKING IN CRYSTALLIZATION EQUILIBRIUM

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Chiral symmetry breaking during the crystallization of non-chiral chemicals in forming structures belonging to enantiomorphic symmetry groups is an experimentally detected phenomenon. The best known example is the case of solid sodium chlorate. [1]

To following model was developed to model the formation of chiral crystals:



In this model, A is the non-chiral substance in solution, whereas R_n and S_n mean crystals of opposite chirality containing n units. Only two different standard free energies are used in the model: that of nucleation ($\Delta G_{\text{nucl}}^{\circ}$) and that of crystal growth ($\Delta G_{\text{grow}}^{\circ}$). It is assumed that this latter energy is independent of the size of crystal (n).

The system was fully characterized from a combinatorial point of view: the number of possible states and the state multiplicities were determined. Equilibrium calculations were carried out based on the methods of statistical thermodynamics. The expectation for the overall enantiomeric excess was calculated as a function of the two standard enthalpies in a small system where all the possible states could be handled within reasonable computation time.

Acknowledgements

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Reaction-diffusion systems

SIMULATION OF REACTION-DIFFUSION PATTERNS IN AN INITIALLY SEPARATED LANDOLT-TYPE PH OSCILLATOR

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Pattern formation in reaction-diffusion systems has been widely investigated owing to its theoretical and practical importance in geological and biological systems. It is known that the initial and boundary conditions determine the basic properties of the developing pattern. Now we use a general reaction-diffusion model of the well-known Landolt-type pH oscillators,¹ and simulate the effect of a special initial condition: namely when the reactants are spatially separated at the initial moment.² Our one-dimensional calculations show the time development of the reaction-diffusion patterns perpendicular to the interface.

The general mechanism of the Landolt-type pH oscillators includes a positive and a negative feedback concerning on the H^+ autocatalytic species. This ensures the possibility of bistability and periodicity even in continuously fed homogeneous media, or in reaction-diffusion systems where the concentrations are fixed at one of the boundaries.¹ In our setup the reaction-diffusion system is divided into two parts, which are filled homogeneously with different reactants at the initial moment: the OX part contains the oxidant (the partner of H^+ in the autocatalytic reaction) and the ACID part contains extra H^+ (in bonded form). The initial concentrations of the other reactants are equal in both parts. There is no external reagent supply.

The initially separated reactants diffuse due to the cross-gradient of the concentrations, and the autocatalytic reaction results in a narrow acidic band in the counter-diffusion zone. In the presence of the H^+ -consumer species the width of the acidic band remains constant. Depending on the initial concentrations, the behaviour of the band changes dramatically. We present a phase diagram to show the following dynamical behaviours:

- 1) propagation of the acidic band towards the OX part or towards the ACID part;
- 2) damped oscillation (forming needles) at the beginning of the acidic band;
- 3) spatial separation of the autocatalytic region (the acidic band splits up).

We analyse qualitatively the spatial/temporal concentration profiles and the reaction rate profiles to understand how the diffusion and the autocatalytic reaction interact to form these nonlinear phenomena. We conclude that the appropriate autocatalytic kinetic is crucial for the oscillation, while the kinetic of the H^+ -consuming step has less importance.

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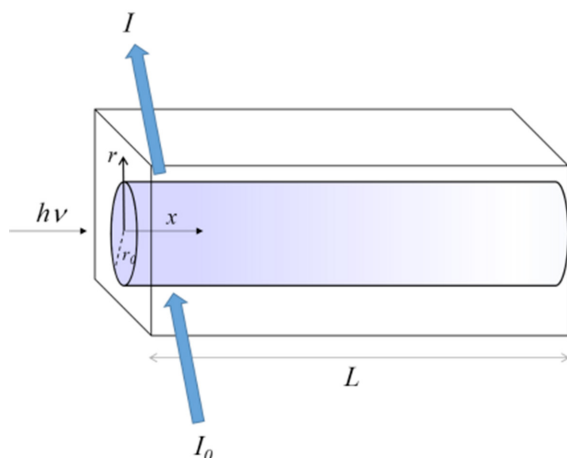
A REACTION-DIFFUSION APPROACH TO THE INHERENT INHOMOGENEITIES DURING LASER FLASH PHOTOLYSIS EXPERIMENTS

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Laser flash photolysis (LFP) is an experimental method for generating highly reactive intermediates, transient species or free radicals by a very short, high energy laser pulse. The concentrations of the transients reach a sufficient level to apply spectrophotometric detection.



This work presents a detailed mathematical study of the effect of inhomogeneities in LFP studies, which are of two different kinds: the first arises from diffusion, whereas the second one has geometric origins (the shapes of the excitation and detection light beams). Both of these are taken into account in our reported model, which uses reaction-diffusion type partial differential equations to describe the chemical process between sulfate ion radical and iodide ion using cylindrical coordinates to match the symmetry properties of the system:

$$\frac{\partial c_s}{\partial t} = D_s \left(\frac{\partial^2 c_s}{\partial x^2} + \frac{1}{r} \frac{\partial c_s}{\partial r} + \frac{\partial^2 c_s}{\partial r^2} \right) - k c_s c_1$$

$$\frac{\partial c_1}{\partial t} = D_1 \left(\frac{\partial^2 c_1}{\partial x^2} + \frac{1}{r} \frac{\partial c_1}{\partial r} + \frac{\partial^2 c_1}{\partial r^2} \right) - k c_s c_1$$

These equations were solved by a specially developed finite volume method. The results showed that diffusion is too slow to influence the kinetic curves on the usual time scales of LFP experiments. However, the use of the absorbances measured requires very detailed mathematical consideration and the full knowledge of the geometrical details. The pseudo-first order approach could be used to evaluate the kinetic traces successfully even if the large excess condition was not met in the reaction cell locally. [1]

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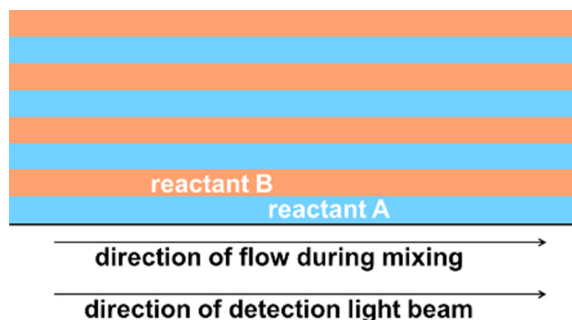
A REACTION-DIFFUSION APPROACH TO MICROMIXING DURING STOPPED-FLOW EXPERIMENTS

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The stopped-flow technique is the state-of-the-art instrumental method for measuring the kinetics of reactions for processes where mixing of two solutions is unavoidable. The performance of this method is limited by the efficiency of mixing. [1]



In this work, a stopped-flow experiment was modelled by assuming that thin layers of solutions form in the cell as a result of macromixing, but then the homogeneous state is achieved through the diffusion of reactants (micromixing). This process is described by a one-dimensional diffusion-reaction equation for two substances (A and B), which react in a mixed second order process:

$$\frac{\partial A(t,x)}{\partial t} = D_A \frac{\partial^2 A(t,x)}{\partial x^2} - kA(t,x)B(t,x)$$

$$\frac{\partial B(t,x)}{\partial t} = D_B \frac{\partial^2 B(t,x)}{\partial x^2} - kA(t,x)B(t,x)$$

$A(t,x)$ and $B(t,x)$ are the concentrations of the two reactants, D_A and D_B are the diffusion coefficients, whereas k is the second order rate constant.

This equation was solved numerically and attempts were also made to find approximate analytical solutions by Fourier transformation. It is shown that the approximate analytical solutions are in excellent agreement with the numerical calculations. The simulation results were compared with experiments done in the calibration process of the stopped flow instrument.

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DYNAMICS OF PH OSCILLATORS IN A TWO SIDE FED REACTOR

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Pattern formation in chemical reaction–diffusion systems with positive and negative feedback serve as a prototype of non-equilibrium self-organization. Hydrogen ion autoactivated systems with appropriate negative feedback, pH oscillators, are preferably used to study reaction-diffusion phenomena.¹ These systems are capable to show a wide range of spatiotem-

poral phenomena from spatial bistability and oscillations to the formation of stationary patterns. The experiments are typically performed in open spatial reactors, which allow to feed all space points of a porous material (e.g a hydrogel) in order to maintain the system far from equilibrium, without introducing macroscopic fluid motion. The feed can only be made by diffusive exchanges of matter with the environment at the boundaries of the system. The spatiotemporal dynamics of pH oscillators have been mostly explored in one-side-fed-reactors, where all reagents are fed through a unique continuous-flow stirred tank reactor (CSTR) and the feed composition at the CSTR/gel boundary relies on the chemical state of the CSTR. Here, apply a two side fed reactor (TSFR) geometry, where complementary sets of chemicals are provided at opposite faces of the gel. This configuration induces cross composition ramps of the chemicals between the feed boundaries. This asymmetric feeding mode avoids the development of the temporal instabilities in the feed tanks and allows us to study pattern formation in presence of cross gradients. It is widely accepted, that the graded distributions of morphogens play important roles in biological pattern generation.² By using numerical simulations with a general model of the pH oscillators we observed spatial bistability and oscillations in a presence of counter gradients of the chemicals. The nonequilibrium phase diagram of the system shows a typical cross shaped topology. Two types of spatiotemporal oscillations have been found, one with large and the other with small amplitude. The interaction of them leads to the formation of mixed mode oscillations. We discuss the role of gradients of the chemicals in the development of the observed phenomena.

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Chemical reaction networks and chemical reactor network theory

ANALYSIS OF BIOCHEMICAL ADAPTATION

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We study two specific measures of quality of chemical reaction networks, Precision and Sensitivity. The two measures arise in the study of sensory adaptation, in which the reaction network is viewed as an input-output system. Given a step change in input, Sensitivity is a measure of the magnitude of the response, while Precision is a measure of the degree to which the system returns to its original output for large time. High values of both are necessary for high-quality adaptation. We focus on reaction networks without dissipation, which we interpret as detailed-balance, mass-action networks. We give various upper and lower bounds on the optimal values of Sensitivity and Precision, characterized in terms of the stoichiometry, by using a combination of ideas from matroid theory and differential-equation theory. Among other results, we show that this class of nondissipative systems contains networks with arbitrarily high values of both Sensitivity and Precision. This good performance does come at a cost, however; since certain ratios of concentrations need to be large, the network has to contain many species and reactions, or the network should show strongly different time scales.

UNCERTAINTY QUANTIFICATION FOR QUANTUM-CHEMICAL MODELS OF COMPLEX REACTION NETWORKS

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For the quantitative understanding of complex chemical reaction mechanisms, it is, in principle, necessary to accurately determine free energies for all elementary processes, and to solve the corresponding continuous-time reaction-rate equations, which are generally highly coupled and spread over several time scales. It is computationally hard to fulfill these two requirements. However, it is possible to approximately address these challenges in a physically consistent way. On the one hand, it may be sufficient to consider approximate free energies if a reliable uncertainty measure can be provided. On the other hand, a (quasi-)continuous-time evolution may not be necessary to still determine quantitative fluxes in a reaction network if one is interested in specific time scales.

Here [1], we present discrete-time kinetic simulations for a coarse-grained state space taking free-energy uncertainties [2] into account. The method builds upon thermo-chemical data obtained from electronic-structure calculations in a condensed-phase model. Our ap-

proach supports the analysis of complex chemical reaction networks [3] spanning multiple time scales, which is here demonstrated at the example of the formose reaction. An important application of our approach is the detection of regions in a reaction network which require further investigation, given the uncertainties introduced by both approximate electronic structure methods and kinetic models. Such cases can then be studied in greater detail on the basis of more sophisticated first-principles calculations and reaction-rate theories.

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INTERMEDIATES, ENZYMES, BINOMIALITY AND MULTISTATIONARITY

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In this poster we consider reaction networks with intermediates (as described in [1]), with enzymes (as described in [2]) and networks with toric steady states (as considered in [3]). Specifically, given a core reaction network and an extension of it obtained by adding intermediates or enzymes, we study how the Gröbner bases of the steady state ideal of the core reaction network relate to the Gröbner bases of the steady state ideal of extended networks. We use this to (1) find Gröbner bases of large networks from Gröbner bases of simplified versions of them, thereby reducing substantially the computational cost; (2) infer when extensions of networks with toric steady states also have toric steady states; (3) pinpoint what/whether intermediates can be target as responsible for multistationarity.

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STRONG REACHABILITY OF CHEMICAL REACTIONS

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Controlling chemical reactions is important both for chemical engineering, pharmacology and in some other parts of chemistry, as well. Studying strong reachability is necessary to decide if we can have any effect on the states (described by the vector of concentrations) of the system. As a first step we have chosen temperature and the inflow rates of some species as control input. The analysis is based on the Lie-algebra generated by the vector fields related to the induced kinetic differential equation of the reaction.

First we give conditions for strong reachability with temperature input. It turned out that the chemical reactions are strongly reachable on a subspace that has the same dimension as the number of independent reaction steps in every point except where the concentration of reactant species is zero. Next we analysed the continuously stirred tank reactors. We have shown that the same result holds for these cases, as well. Finally, we analyse a simple model of polymer electrolyte membrane fuel cells, using the inflow rates as control.

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Other

TIME-PROGRAMMED SELF-ASSEMBLY

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We present a general concept to drive the self-assembly of various building blocks from molecular level to nanoscopic level by combining a pH clock reaction and lactone hydrolysis in a closed system. The time scale separation of these two processes (fast pH jump provided by the clock reaction and a delayed decrease of pH by lactone hydrolysis) ensures the existence of a transient alkaline state. This chemical system can be used to control and drive autonomously the self-assembly of pH switchable self-assembling components: fatty acid molecules, carboxyl group terminated gold nanoparticles and amine functioned polymer chains in a network. We demonstrated that the proper control over the electrostatic interaction between the building blocks can govern and induce reversible transformation of vesicle-to-micelle, dispersion/aggregation of nanoparticles and contraction/reswelling of gel filaments.

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KINETICS OF THE REACTION BETWEEN 2,5-DICHLORO-1,4-BENZOQUINONE AND SULFITE ION

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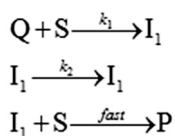
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The reaction between variously substituted quinones and sulfite ion in water is a special type of the quinone-bisulfite addition reactions.[1] The kinetics of the reaction was investigated under slightly acidic conditions (pH 3.8 and 4.5 in acetate buffer). Both the rate and

the stoichiometry of the reaction depend on the substituents of the quinone derivative. This process clearly involves intermediates[2], the existence of which can be proved by UV-vis spectroscopy.

The observed absorbance-time traces showed a very fast (stopped-flow time scale) absorbance increase and decrease in a wide wavelength region (380-500 nm) for 2,5-dichloro-1,4-benzoquinone (Q). The kinetic traces can be fitted well to a double exponential function in a wide concentration range: $c(2,5\text{-dichloro-1,4-benzoquinone}) = 0.5 \text{ mM}$, $c(\text{SO}_3^{2-}) = 0.02\text{-}50 \text{ mM}$. The kinetic traces measured at 420 and 320 nm were simultaneously fitted to the following mechanism using the multipurpose program package ZiTa:[3]



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QUANTITATIVE KINETIC DESCRIPTION OF THE REDOX (PHOTO)REACTION BETWEEN CERIUM(IV) AND WATER

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The acidic aqueous solutions of Ce(IV) salts give Ce(III) and dioxygen gas when illuminated by polychromatic light, even if it comes from the detection beam of a diode array spectrophotometer (total photon flux of $1.7 \times 10^{15} \text{ s}^{-1}$). [1] This reaction is part of the photocatalytic

water splitting cycle which gives O₂ and H₂ gas when an acidic aqueous Ce(III) solution is illuminated by UV light.[2]

The rate of the photoreaction and also the spectrum of the reactant and product Ce complexes depend on the chemical identity of the strong acid. A detailed mathematical evaluation was developed to interpret the experimental findings in perchloric acid of different concentrations, based on the general quantitative description of photoreactions assuming a single initial excitation process, which leads to the following differential equation:

$$\frac{d\xi}{dt} = \frac{\Phi}{Vc_0} \int \left(1 - 10^{-(1-\xi)A_{\lambda}^{ini} - \xi A_{\lambda}^{fin}} \right) \frac{q_{P,\lambda}(1-\xi)A_{\lambda}^{ini}}{(1-\xi)A_{\lambda}^{ini} + \xi A_{\lambda}^{fin}} d\lambda$$

$$A_{det} = (1 - \xi)A_{det}^{ini} + \xi A_{det}^{fin}$$

In this formula, ξ is the extent of reaction (*i.e.* the reaction coordinate), Φ is the differential quantum yield, $q_{P,\lambda}$ is the spectral photon flux at wavelength λ , c_0 is the sum of the initial concentrations of cerium(III) and cerium(IV), V is the volume, A_{λ} is the *initial* and *final* absorbance at wavelength λ , A_{det} is the absorbance at the wavelength of detection and β is the ratio of the path length of illumination and detection.

The rate of the reaction in the absence of light is also investigated using not only diode array but also scanning double beam spectrophotometer (total photon flux < 1% compared to a diode array spectrophotometer).

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EXPERIMENTAL AND MODELLING STUDY OF SYNTHESIS GAS PRODUCTION FROM CATALYTIC STEAM REFORMING OF METHANE

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In the latest years, the environmental problems derived from useful energy generation sources and from the increment of fossil fuels prices, have enhanced the development of new technologies for energy production. Steam reforming of methane produced by biomass gasification is one of the most employed processes to produce hydrogen and synthesis gas. Synthesis gas, constituted by different quantities of carbon monoxide and hydrogen, can also be used to produce high purity hydrogen streams and chemical products. In this research, experimental and theoretical studies of steam methane reforming reactions with different amount of hydrogen sulfide in the feed gas are presented. A two dimensional pseudo-heterogeneous model is developed to simulate methane steam reforming reactions in a packed bed tubular reactor. This model is based on mole and energy balance equations for the catalyst and the fluid phases. Attention is given to the analysis of sulfur negative effects on methane conversion when Ni-based catalysts are used. A parametric study is done and effects of different steam to carbon ratios, space velocities, temperatures on methane conversion and temperature distribution within the reactor are investigated. The results are verified comparing to the experimental results. It is shown that even presented in the gas at very low concentration levels (ppm), sulfur drastically decreases the conversion of methane. The obtained results play a key role in design and optimization of an actual reactor.

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APPLICATION OF VARIOUS MATHEMATICAL METHODS ON MODELING OF FULLEROLE DEHYDROXYLATION

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Fullerols, derivatives of fullerenes with hydroxyl group, possess number of extremely important properties, such as: antioxidant [1], antimicrobial [2] and anti-cancer [3] activity. It is well-known that physical, electronic and functional properties, as well as reactivity of a ful-

lerols are strongly dependent on number of hydroxyl group attached per surface [4]. Thus, it is important for one to develop methods by which fullerol with certain number of OH groups can be obtained. With that in mind, we investigated non-isothermal kinetics of $C_{60}(OH)_{27}$ dehydroxylation. Fullerol dehydroxylation thermogravimetric curves were recorded at different heating rates ranging from 5 K min^{-1} to 25 K min^{-1} . Dependence of energy activation on dehydroxylation degree was calculated by Vyzovkin's method [5], from which it is clear that investigated reaction has complex kinetic mechanism consisting of a few reaction steps. Reaction rate curves were further decomposed by Suzuki-Fraser method [6] and two reaction steps were distinguished. It has been concluded that in reaction step which dominates at lower temperatures 14 OH groups leave fullerol surface, whereas dehydroxylation of the rest of OH groups takes place in other step (i.e. one which dominates at higher temperatures) and that temperature program by which fractions with high content of fullerol with desired number of OH groups may be designed.

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