# Final Report

1. DE-SC0002339, University of Massachusetts-Amherst

2. Project Title: "**Multiscale Mathematics for Biomass Conversion to Renewable Hydrogen**" , PI: **Markos Katsoulakis**

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## 4. Progress and Accomplishments

Our two key accomplishments in the first three years were towards the development of, (1) a mathematically rigorous and at the same time computationally flexible framework for *parallelization of Kinetic Monte Carlo methods*, and its implementation on GPUs, and (2) *spatial multilevel coarse-graining methods* for Monte Carlo sampling and molecular simulation. A common underlying theme in both these lines of our work is the development of numerical methods which are at the same time both computationally efficient and reliable, the latter in the sense that they provide *controlled-error approximations* for coarse observables of the simulated molecular systems. Finally, our key accomplishment in the last year of the grant is that we started developing (3) *path-wise information theory*-based and *goal-oriented* sensitivity analysis and parameter identification methods for complex high-dimensional dynamics and in particular of non-equilibrium extended (high-dimensional) systems. We discuss these three research directions in some detail below, along with the related publications.

### 1. Hierarchical fractional-step approximations and parallel kinetic Monte Carlo algorithms

**Publication 1a:** G. Arampatzis, M. A. Katsoulakis, Petr Plechac, Michela Taufer, Lifan Xu *Hierarchical fractional-step approximations and parallel kinetic Monte Carlo algorithms*, **J. Comp. Phys.,** 231, 7795-7814, (2012).

We present a new framework for constructing parallel algorithms for lattice Kinetic Monte Carlo (KMC) simulations. These algorithms have the capacity to simulate a wide range of spatio-temporal scales of spatially distributed, non-equilibrium physiochemical processes with complex chemistry and transport micro-mechanisms, while they can be tailored to specific hierarchical parallel architectures such as clusters of GPUs. The proposed parallel algorithms are controlled approximations of kinetic Monte Carlo algorithms, departing from the predominant paradigm of creating parallel KMC algorithms with exactly the same master equation as the serial one. Instead, our methodology relies on first developing a spatio-temporal decomposition of the Markov operator underlying the KMC algorithm into a hierarchy of operators corresponding to the processors' structure in the parallel architecture. Based on this operator decomposition, we formulate Fractional Step Approximation schemes by employing the Trotter Theorem; these schemes, (a) determine the communication schedule between

processors, and (b) are run independently on each processor through a serial KMC simulation, called a kernel , on each fractional step time-window. The hierarchical structure can be easily derived and implemented for very general physicochemical processes modeled by lattice systems, allowing users to input as the algorithm's KMC kernel their serial algorithm of choice.

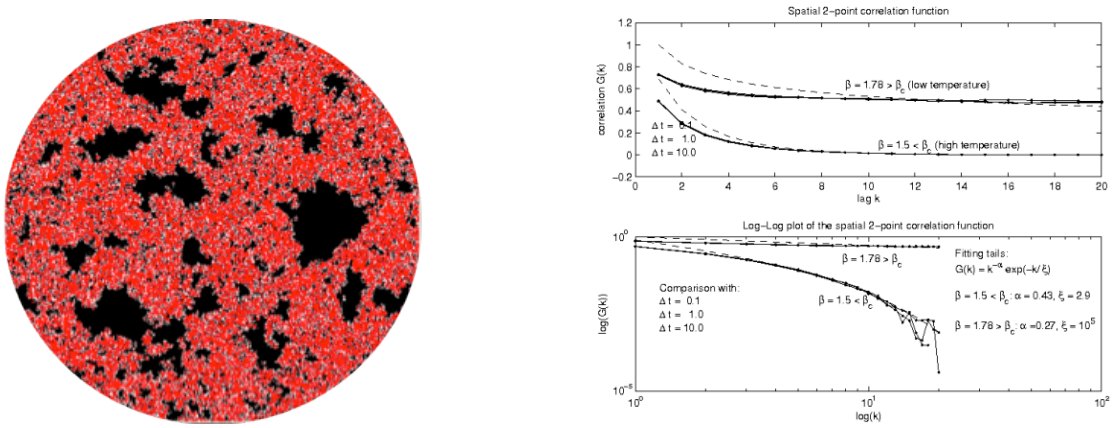


**Figure 1** (a) Snapshot of the simulation of a catalytic process on 1024x1024 lattice (zoom of the lattice with two species of molecules and vacant sites.) (b) Accuracy testing: spatial correlations in 2D Ising model in sub and super-critical temperatures.

This flexibility and hierarchical structure, see Fig. 3(b), are key advantages for tailoring our framework to particular parallel architectures with complex memory and processor hierarchies, e.g. clusters of GPUs. Temporal multi-scale methods such as Trotter-based algorithms for systems with well-separated fast and slow processes can be recombined with the proposed Fractional Step methods into a spatio-temporal hierarchy of operators.

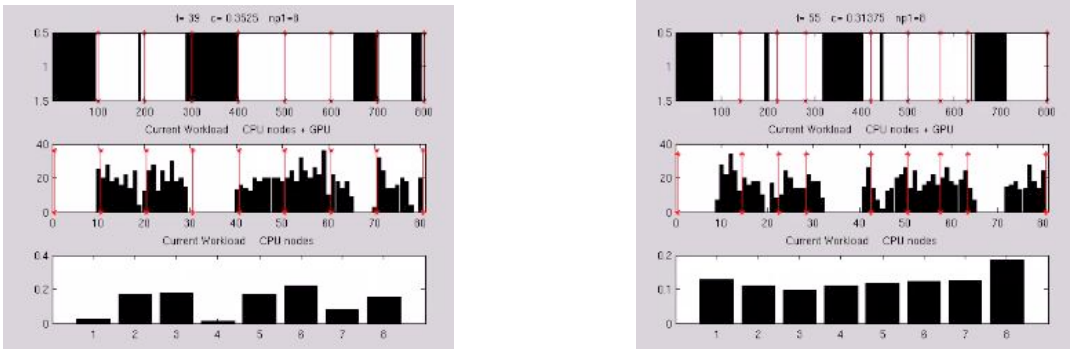


**Figure 2** Dynamic load balancing: example of an algorithm in 1D: (a) no balancing, (b) Dynamic load balancing using probabilistic mass transport framework by refining adaptively the sub-lattice of our Fractional KMC framework.

Furthermore, the numerical and statistical consistency of the proposed algorithms is rigorously justified, showing the convergence of our approximating schemes to the

original serial KMC algorithm. In this paper we also include detailed benchmarking using available exact solutions, for example, in Ising-type systems and we demonstrate the capabilities of the method to simulate complex spatially distributed reactions at very large scales on GPUs. Finally, we discuss work-load balancing between processors and propose a re-balancing scheme based on probabilistic *mass transport* methods.

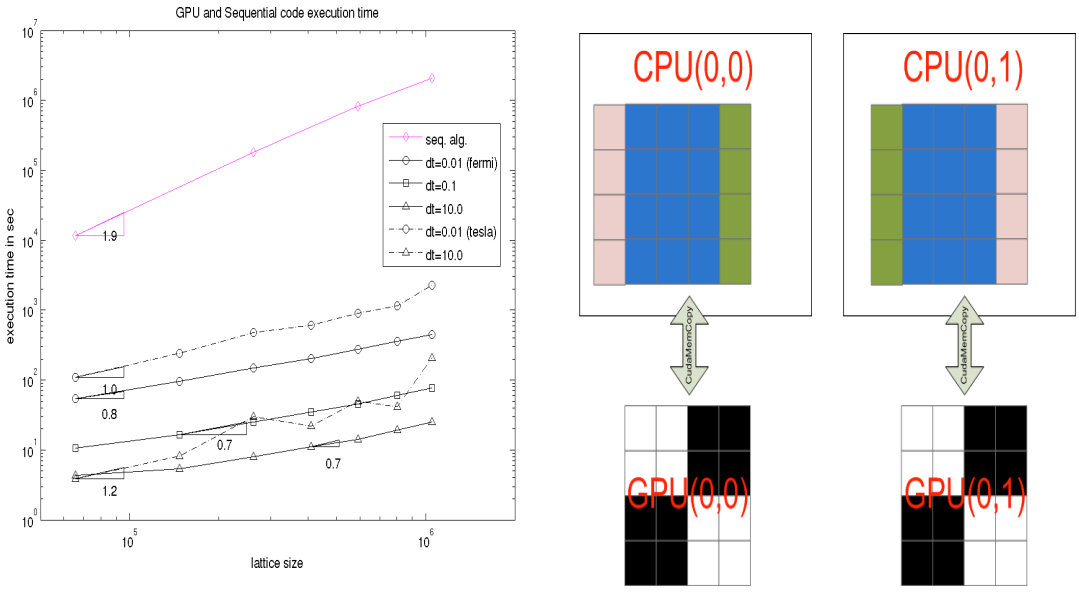


**Figure 3** (a) Efficiency evaluation on NVIDIA GPUs achieving speed-up 10000x.Capability of simulating 1000x1000 lattice models of a heterogeneous catalysis example up to a steady state on a single GPU. (b) Two GPU units and two independent sublattices (B&W) on GPUs.

***Publication 1b.*** G. Arampatzis, M. A. Katsoulakis, Petr Plechac, *Parallelization, processor communication and error analysis in lattice kinetic Monte Carlo*, **SIAM, Num. Analysis**, 52, no. 3, 11561182, (2014).

In this paper we study from a numerical analysis perspective the fractional step kinetic Monte Carlo (FS-KMC) algorithms proposed in Publication 1a for the parallel simulation of spatially distributed particle systems on a lattice. FS-KMC are fractional step algorithms with a time-stepping window $\Delta t$, and as such they are inherently *partially asynchronous* since there is no processor communication during the period $\Delta t$. In this contribution we primarily focus on the error analysis of FS-KMC algorithms as approximations of conventional, serial KMC. A key aspect of the presented analysis relies on emphasizing a goal-oriented approach for suitably defined macroscopic observables (e.g., density, energy, correlations, surface roughness), rather than focusing on strong topology estimates for individual trajectories. The presented error analysis allows us to compare different parallelization strategies and their processor communications by relating the

algorithm partial asynchrony to the time step $\Delta t$ and a prescribed error tolerance, see for instance Figures 4a and 4b below.

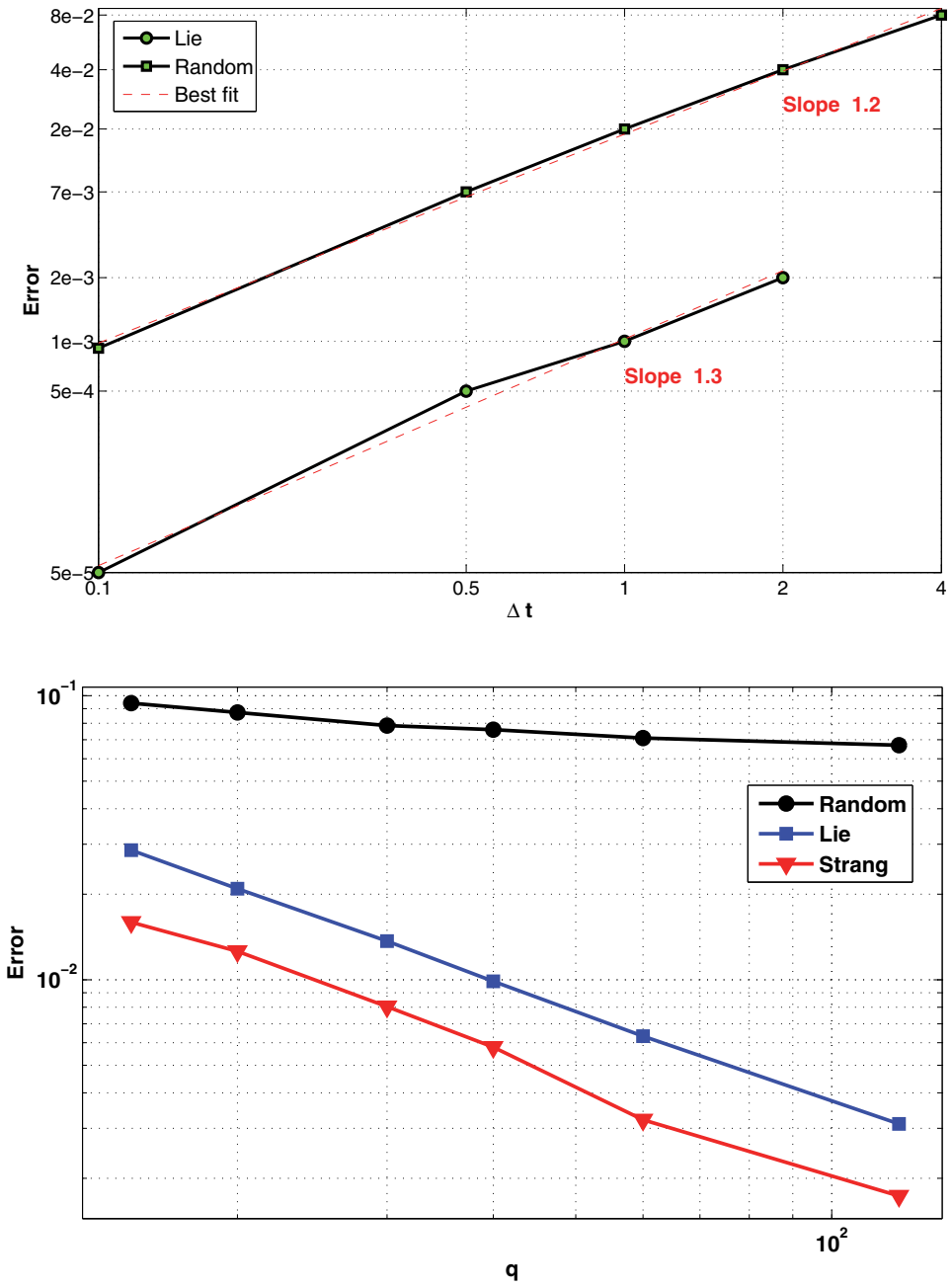


**Figure 4** (a) Convergence of the weak error for deterministic and randomized Lie splitting. (b) Dependence of the weak error on the sub-lattice size parameter q for three different parallelization schemes. The related numerical analysis is carried out in our SIAM Num. Analysis publication.

Furthermore, the presented results show that previously developed KMC algorithms based on domain decomposition principles also allow for simulations with controlled errors for macroscopic of observables, such as coverage, Hamiltonian, surface roughness, spatial correlations, etc, while their partial asynchrony also can be demonstrated and quantified. Finally, this paper also provides the rigorous underpinnings for the SANDIA parallel KMC solver SPPARKS, while it provides a flexible framework for its future extension to concurrent (hybrid) PDE-KMC models, as well as architectures that may require different sub-lattice decompositions with distinct time-stepping windows $\Delta t$, e.g. clusters of GPUs or GPU/CPU architectures.

## 2. Multilevel Coarse-Graining and Error Quantification for lattice dynamics

***Publication 2a.*** E. Kalligiannaki, M. A. Katsoulakis, P. Plechac, *Spatial two-level interacting particle simulations and information theory-based error quantification*, **SIAM Sci. Comp.,** Vol. 36, No. 2, pp. A634-A667, (2014)

In this article we propose a hierarchy of multi-level kinetic Monte Carlo methods for sampling high-dimensional, stochastic lattice particle dynamics with complex interactions. The method is based on the efficient coupling of different spatial resolution levels, taking advantage of the low sampling cost in a coarse space and by developing local reconstruction strategies from coarse-grained dynamics, see Figure 5. Microscopic reconstruction corrects possibly significant errors introduced through coarse-graining, leading to the controlled-error approximation of the sampled stochastic process. In this manner, the proposed multi-level algorithm overcomes known shortcomings of coarse-graining of particle systems with complex interactions such as combined long and short-range particle interactions and/or complex lattice geometries, see Figure 6.

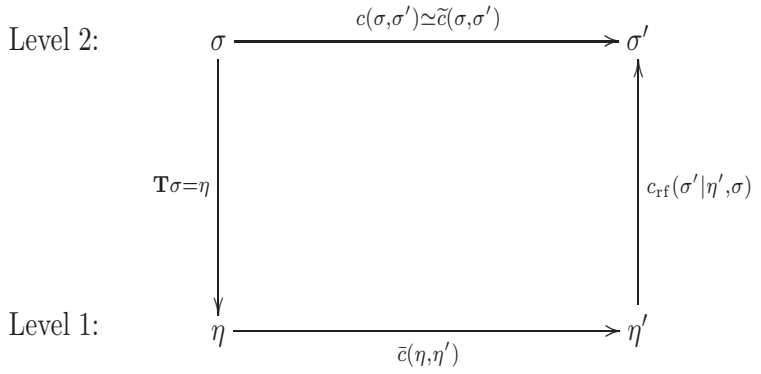


**Figure 5** Two-level decomposition, compressing with T and reconstructing of the evolution process per event, as described in the publication

Specifically, we provide error analysis for the approximation of long-time stationary dynamics in terms of relative entropy and prove that information loss in the multi-level methods is growing linearly in time, which in turn implies that an appropriate observable in the stationary regime is the *information loss of the path measures per unit time*, i.e. the Relative Entropy Rate (RER). We also refer to the use of this important observable for *sensitivity analysis* and in general *uncertainty quantification* in Section 3 below. We show that the observable defined as RER can be either estimated a priori, or it can be tracked computationally a posteriori in the course of a simulation. The stationary regime is of critical importance to molecular simulations as it is relevant to long-time sampling, obtaining phase diagrams and in studying meta-stability properties of high-dimensional complex systems. Finally, the multi-level nature of the method provides flexibility in combining rejection-free and null-event implementations, generating a hierarchy of algorithms with an adjustable number of rejections that includes well-known rejection-free and null-event algorithms.

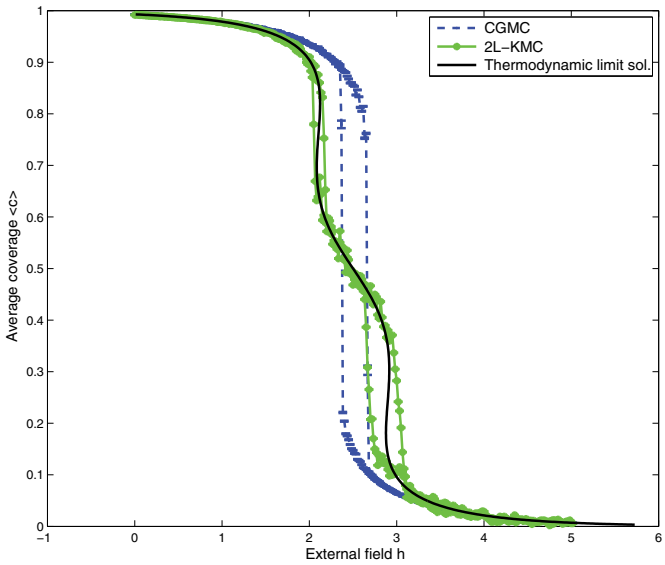


**Figure 6** Comparing the proposed multi-scale coarse-grained Kinetic Monte Carlo method to a one-scale coarse-graining and direct numerical simulation. Here we depict a hysteresis simulation in a bi-stable regime.

***Publication 2b.*** M. A. Katsoulakis, P. Plechac, L. Rey-Bellet and D. Tsagkarogiannis, *Coarse-graining schemes for stochastic lattice systems with short and long-range interactions,* **Math. Comp.,** 83, no.288, 17571793, (2014).

In this manuscript we develop coarse-graining schemes for stochastic many-particle microscopic models with competing short- and long-range interactions on a d-dimensional lattice. First, we focus on the coarse-graining of equilibrium Gibbs

states and using cluster expansions we analyze the corresponding renormalization group map. We quantify the approximation properties of the coarse-grained terms arising from different types of interactions and present a hierarchy of correction terms. We derive semi-analytical numerical schemes that are accompanied with *a posteriori* error estimates for coarse-grained lattice systems with short and long-range interactions. These semi-analytical methods are based on a multi-level decomposition of the microscopic Gibbs states which is in turn induced by the cluster expansion.

On one hand, this is a key mathematical and algorithmic tool towards efficient and accurate simulation of self-assembly in materials and surface processes at mesoscales. Pattern formation in such systems arises typically due to competing short- and long-range interactions. Furthermore, this work also addresses the coarse-graining of systems with short-range interactions, such as the ones arising in catalysis; it is demonstrated that multi-body coarse-grained interactions and transition rates are unavoidable for coarse-grained simulations with desired accuracy, due to the sub-grid particle/particle correlations, and can be calculated through semi-analytical formulas. A notable result of our error analysis is the quantification of the role of multi-body terms in coarse-graining schemes, and the relative ease to implement them. Finally the *a posteriori* error analysis identifies and quantifies the regimes where multi-body terms need to be included in coarse-graining schemes and allows for on-the-fly adaptive coarse-graining of microscopic lattice systems.

## 3. Uncertainty Quantification (UQ) for Non-equilibrium Complex Systems

Our key accomplishment in the last year of the grant is that we started developing *path-wise information theory*-based and *goal-oriented* sensitivity analysis and parameter identification methods for complex high-dimensional dynamics and in particular of non-equilibrium extended systems. The combination of these novel methodologies provide the first methods in the literature which are capable to handle UQ questions for stochastic complex systems with some or all of the following features: (a) stochastic models with a *very large number of parameters*, (b) spatially distributed systems such as Kinetic Monte Carlo or Langevin Dynamics, (c) *non-equilibrium processes* typically associated with coupled physico-chemical mechanisms, driven boundary conditions, etc. The first two such publications sponsored by the grant, have just been published:

***Publication 3a.*** A Relative Entropy Rate Method for Path Space Sensitivity Analysis of Stationary Complex Stochastic Dynamics, (Y. Pantazis and M. A. Katsoulakis), **J. Chem. Phys.,** 138, 054115, (2013).

In this paper we proposed for the first time a new sensitivity analysis methodology for complex stochastic dynamics based on the relative entropy rate. The method becomes computationally feasible at the stationary regime of the process and involves the calculation of suitable observables in path space for the relative entropy rate and the corresponding Fisher information matrix. The stationary regime is crucial for stochastic dynamics and here allows us to address the sensitivity analysis of complex systems, including examples of processes with complex landscapes that exhibit metastability, non-reversible systems from a statistical mechanics perspective, and high-dimensional, spatially distributed models. All these systems exhibit, typically non-Gaussian stationary probability distributions, while in the case of high-dimensionality, histograms are impossible to construct directly.

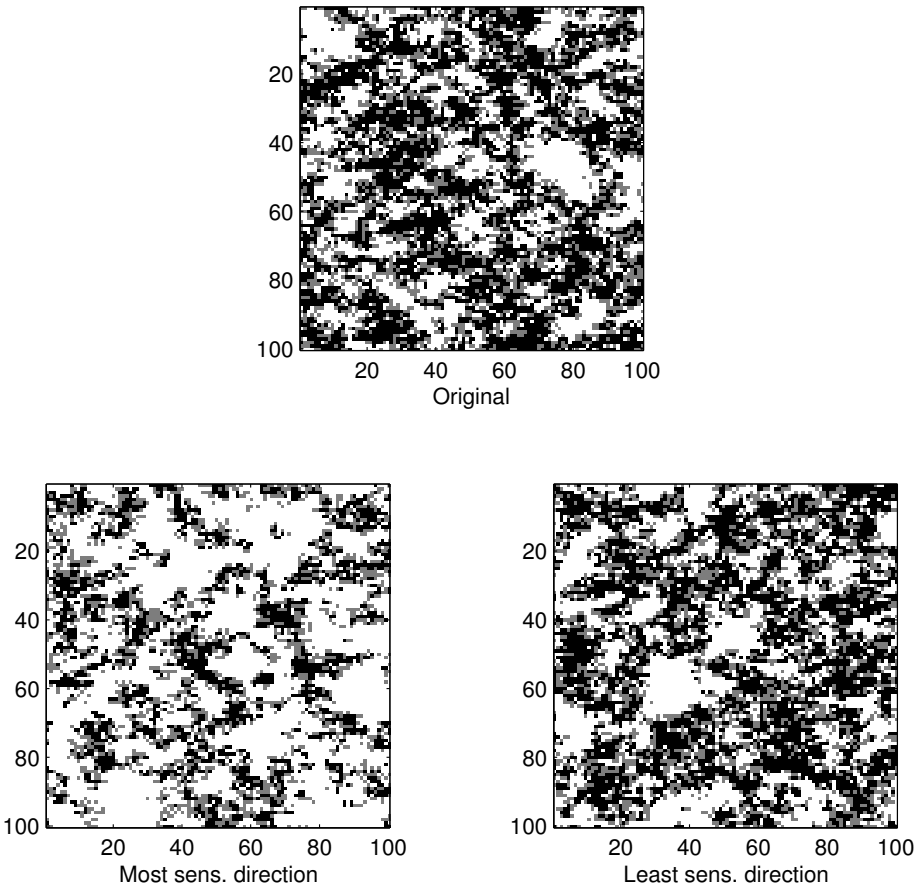


**Figure 7** Typical configurations in a spatial KMC system (ZGB catalysis model) obtained by perturbations of the most and least sensitive parameters. The comparison with the reference configuration reveals the differences between the most and least sensitive perturbation parameters.

Our proposed methods bypass these challenges relying on the direct Monte Carlo simulation of rigorously derived observables for the relative entropy rate and Fisher information in path space rather than on the stationary probability
distribution itself. We demonstrated the capabilities of the proposed methodology by focusing here on two classes of problems: (a) Langevin particle systems with either reversible (gradient) or non-reversible (non-gradient) forcing, highlighting the ability of the method to carry out sensitivity analysis in non-equilibrium systems; and, (b) spatially extended kinetic Monte Carlo models (see Figure 7), showing that the method can handle high-dimensional problems.

***Publication 3b.*** *Parametric Sensitivity Analysis for Biochemical Reaction Networks based on Pathwise Information Theory*, (Y. Pantazis, M. A. Katsoulakis and D.G. Vlachos), **BMC Bionformatics**, 14:311, (2013).

Stochastic modeling and simulation provide powerful predictive methods for the intrinsic understanding of fundamental mechanisms in complex biochemical networks. Typically, mathematical models involve networks of coupled jump stochastic processes with a large number of parameters that need to be suitably calibrated against experimental data. In this direction, the parameter sensitivity analysis of reaction networks is an essential mathematical and computational tool, yielding information regarding the robustness and the identifiability of model parameters. However, existing sensitivity analysis approaches such as variants of the finite difference method can have an overwhelming computational cost in models with a high-dimensional parameter space.

We developed a sensitivity analysis methodology suitable for complex *stochastic reaction networks* with a large number of parameters, e.g. Figure 8. The proposed approach is based on Information Theory methods and relied on the quantification of information loss due to parameter perturbations between time-series distributions. For this reason, we need to work on path-space, i.e., the set consisting of all stochastic trajectories, hence the

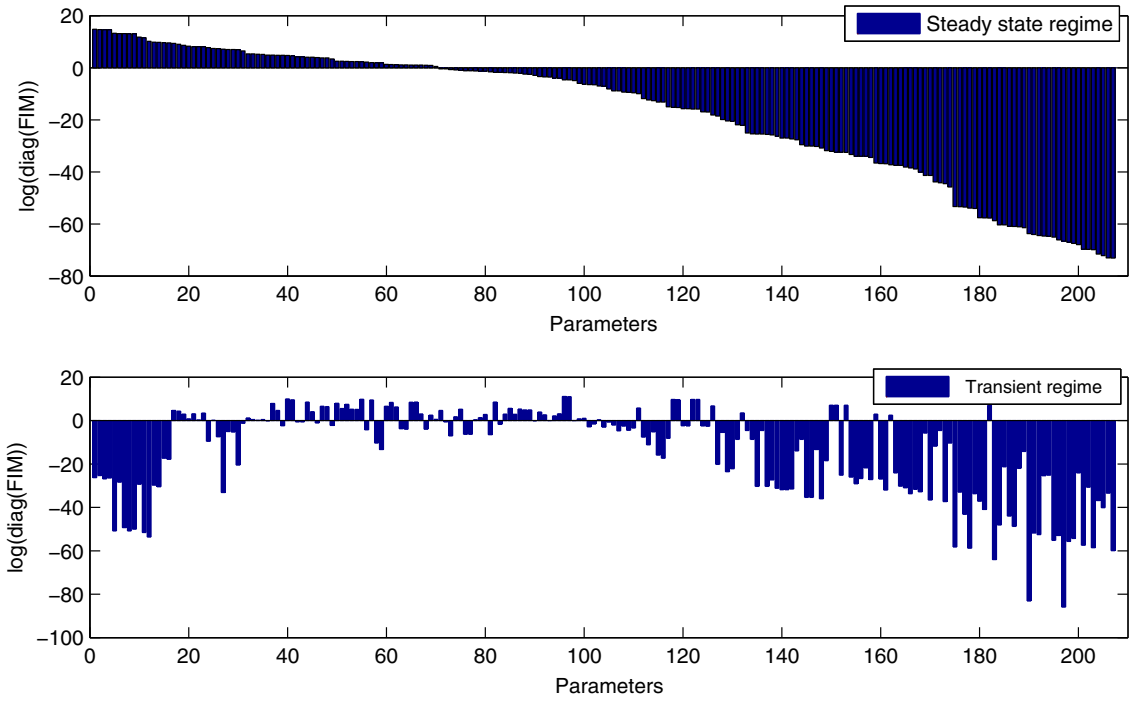


**Figure 8** Diagonal elements of the path-wise FIM for the EGFR model computed at a steady state regime (upper plot) and at a transient regime (lower plot); The EGFR model is a signaling biochemical network with 207 parameters. This analysis would have been computationally prohibitive with earlier UQ methodologies for stochastic systems.

proposed approach is referred to as ``pathwise". The pathwise sensitivity analysis method is realized by employing the rigorously-derived Relative Entropy Rate, which is directly computable from the propensity functions. A key aspect of the method is that an

associated pathwise Fisher Information Matrix (FIM) is defined, which in turn constitutes a gradient-free approach to quantifying parameter sensitivities. The structure of the FIM turns out to be block-diagonal, revealing hidden parameter dependencies and sensitivities in reaction networks. Furthermore, we suggested using not only exact stochastic simulation algorithms but also multi-scale numerical approximations of stochastic reaction networks (mean field, stochastic Langevin, $\tau$-leap, etc.) in order to derive efficient statistical estimators for the FIM.