FINAL REPORT

DOE Award: DE-SC0007046
Recipient: UNIVERSITY OF DELAWARE

Project Title: Multiscale Mathematics for Biomass Conversion to Renewable Hydrogen

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1 Summary of research objectives

The research reported here covered the mathematical and computational aspects of the collaborative project *Multiscale Mathematics for Biomass Conversion to Renewable Hydrogen,* with coPIs D.G. Vlachos (UD Chemical Engineering) and M.A. Katsoulakis (University of Massachusetts, Amherst).

The overall objective of this project was to develop multiscale models for understanding and eventually designing complex processes for renewables. To the best of our knowledge, our work is the first attempt at modeling complex reacting systems, whose performance relies on underlying *multiscale mathematics* and developing rigorous mathematical techniques and computational algorithms to study such models. Our specific application lies at the heart of biofuels initiatives of DOE and entails modeling of catalytic systems, to enable economic, environmentally benign, and efficient conversion of biomass into either hydrogen or valuable chemicals. Specific areas of contributions and achievements included:

1. Development of *rigorous spatio-temporal coarse-grained* kinetic Monte Carlo (KMC) algorithms and simulation for microscopic processes encountered in biomass transformation.
2. Development of mathematical tools for *coarse-graining of systems with non-equilibrium steady states.*
3. Development of *hybrid multiscale simulation* that links KMC simulation with quantum density functional theory (DFT) calculations (primarily D. G. Vlachos)
4. Development of *parallelization of models* of 1. and 3. to take advantage of new generation of computing architectures (multi-core and GPU) in order to enable real world applications of complex, multiscale models.

2 Research accomplishments for the UD-based work

Below we describe our major accomplishments in the development and analysis of mathematical and computational techniques.

2.1 Mathematical and Computational Methods

2.1.1 Accelerated Monte Carlo simulations for systems with complex chemistry

We developed and implemented new approach to simulations of large lattice systems with complex chemistry using parallel architectures. The primary focus was on demonstrating applicability of the developed method on multi-core architectures and Graphical Processing Units (GPUs). We presented a mathematical framework for constructing and analyzing parallel algorithms for lattice Kinetic Monte Carlo (KMC) simulations. The fractional time step algorithms have the capacity to simulate a wide range of spatio-temporal scales in spatially distributed, non-equilibrium physiochemical processes with complex chemistry and transport micro-mechanisms. The algorithms can be tailored to specific hierarchical parallel architectures such as multi-core processors or clusters of GPUs. The proposed parallel algorithms are controlled-error 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. The approach provides a systematic evaluation of different processor communicating schedules. We discussed work load balancing between processors and proposed a re-balancing scheme based on probabilistic mass transport methods. This flexibility and hierarchical structure, are key advantages for tailoring our framework to particular parallel architectures with complex memory and processor hierarchies, e.g. clusters of GPUs. We have also developed a test suite of benchmarks that can be used for performance evaluation and code validation of KMC simulators for lattice models with complex chemistry. The details of algorithms, implementation and numerical analysis have been published in [4,8].

To overcome computational bottleneck caused by the presence of long-range interactions in the lattice models with complex chemistry we developed an efficient Markov Chain Monte Carlo method for sampling equilibrium distributions for stochastic lattice models with complex spatial particle interactions. The proposed method is a Metropolis-type algorithm with the proposal probability transition matrix based on the coarse-grained approximating measures. We prove that the proposed algorithm reduces the computational cost due to energy differences and has comparable mixing properties with the classical microscopic Metropolis algorithm, controlled by the level of coarsening and a suitably defined reconstruction procedure. The developed mathematical tools and their application to algorithmic development and implementation are described in [3,5,7,9].

2.1.2 Coarse-graining methods for molecular systems with non-equilibrium steady states.

Coarse-grained models plays an important role both from the computational point of view as well as a bridge to building mesoscopic models. While widely used a systematic mathematical analysis for models with complex chemistry has not been yet presented. We developed coarse-graining schemes for stochastic many-particle microscopic models with competing short- and long-range interactions on a d-dimensional lattice. Using cluster expansions we analyzed the corresponding

renormalization group map. We quantified the approximation properties of the coarse-grained terms arising from different types of interactions and presented a hierarchy of correction terms. We derived semi-analytical numerical schemes that were accompanied with *a posteriori* error estimates for coarse-grained lattice systems with short and long-range interactions allowing for adaptive coarse-graining in the hierarchy of models. The multiscale decomposition of Gibbs measures and its application to error analysis of coarse-graining schemes were published in [5].

We also contributed to understanding and mathematical description of coarse-graing procedures in off-lattice systems. Using the probabilistic language of conditional expectations, we reformulated the force matching method for coarse-graining of molecular systems as a projection onto spaces of coarse observables. A practical outcome of this probabilistic description is the link of the force matching method with thermodynamic integration. This connection provides a way to systematically construct a local mean force and to optimally approximate the potential of mean force through force matching. We introduced a generalized force matching condition for the local mean force in the sense that allows the approximation of the potential of mean force under both linear and non-linear coarse graining mappings (e.g., reaction coordinates, end-to-end length of chains). Furthermore, we studied the equivalence of force matching with relative entropy minimization which we derived for general non-linear coarse graining maps. The information theoretic tools developed and applied to coarse-graining molecular systems are described in detail in [1,2,6].

3 Publications acknowledging this award

1. V. Harmandaris, E. Kalligiannaki, M.A. Katsoulakis, P. Plechac, Path-space variational inference for non-equilibrium coarse-grained systems. **J. Comp. Phys.** 314 (2016) 355-383
2. E. Kalligiannaki, V. Harmandaris, M.A. Katsoulakis, P. Plechac, The geometry of generalized force matching in coarse-graining and related information metrics**, J. Chem. Phys.**, 143, (2015), 8, 084105
3. E. Kalligiannaki, M.A. Katsoulakis, P. Plechac, Spatial multi-level interacting particle simulations and information theory-based error quantification. **SIAM J. Scientific Comp.** 36(2014), No. 2, pp. A634--A667,
4. G. Arampatzis, M.A. Katsoulakis, P. Plechac Fractional time step approximation in parallel kinetic Monte Carlo simulations, **SIAM J. Numer. Analysis**, 52, (2014), 3, 1156—1182
5. M.A. Katsoulakis, L. Rey-Bellet, P. Plechac, D.K. Tsagkarogannis, Coarse-graining schemes for stochastic lattice systems with short and long-range interactions. **Mathematics of Computations** 83 (2014), 1757--1793
6. M. A. Katsoulakis, P. Plechac, Information-theoretic tools for parametrized coarse-graining of non-equilibrium extended systems. **J. Chem. Phys.** 139 (2013), 074115

7. E. Kalligiannaki, M. A. Katsoulakis, P. Plechac, D. G. Vlachos, Multilevel coarse graining and nano–pattern discovery in many particle stochastic systems. **J. Comp. Phys.** 231, (2012),6, 2599-2620.
8. G. Arampatzis, M.A. Katsoulakis, P. Plechac, M. Taufer, L. Xu, Hierarchical fractional-step approximations and parallel kinetic Monte Carlo Algorithms, **J. Comp. Phys.**, 231 (2012), 23, 7795-7841
9. E. Kalligiannaki, M.A. Katsoulakis, P. Plechac, Coupled coarse-graining and Markov chain Monte Carlo for lattice systems. in Numerical Analysis and Multiscale Computations, Ed. B. Enguist, O. Runborg, R. Tsai, Lecture Notes on Computational Science and Engineering (LNCSE), Springer, 2011

High impact journal publications: Mathematics of Computations 83 (2014), 1757–1793, SIAM J. Numer. Analysis, 52, (2014), 3, 1156—1182

4 Invited conference talks acknowledging this award

1. Coarse-graining and multilevel Monte Carlo simulations, Workshop on Multiscale computations, Banff, Canada, Dec 2009.
2. Hierarchical multiscale modeling of surface pattern formation resulting from complex particle-particle. Interactions. DOE Applied Mathematics Research – PI Meeting: Berkeley, CA, Oct 2010.
3. Accelerated Monte Carlo Methods: Multilevel approximations, coarse-graining and parallel algorithms. Plenary talk, Applied Math Center, Heraklion, Crete, Greece, June 27-July 1, 2011.
4. Parallel kinetic Monte Carlo simulations: algorithms and numerical analysis. DOE Applied Mathematics Research – PI Meeting: Washington, DC, Oct 17-19, 2011.
5. SIAM Conference on Parallel Processing for Scientific Computing – Savannah, Georgia, Feb 15-17, 2012.
6. Parameterization and multilevel approximations of coarse-grained dynamics in KMC simulations. IPAM Workshop on multiscale computations, UCLA, Dec 2012.
7. Parallelization and Error Analysis in Lattice Kinetic Monte Carlo. SIAM Conference on Computational Science and Engineering, Boston, Feb 2013.
8. Information-theoretic tools for parametrized coarse-graining of non-equilibrium extended systems. International Conference on Applied Mathematics, Archimedes Centre for Applied Mathematics, Heraklion, Crete, Sep 2013.
9. Information-theoretic error analysis for coarse-graining of stochastic systems. Workshop on Computational coarse-graining of many-body systems, Warwick University, UK, Dec 2013.
10. Information-theoretic tools for coarse-graining and parametrization of non-equilibrium systems. Multiscale Computational Methods in Materials Modelling, Jun 2014, Edinburgh, Scotland, UK.
11. Information-theoretic tools for coarse-graining and parametrization of non-equilibrium systems. Plenary session talk. Materials Research Society

annual meeting, Boston, Nov 2014.

5 Personnel funded by this project budget

Graduate students
Angelos Athanosopoulus (MSc 2013)
Yan Song (PhD 2014)
Michael DePersion (PhD expected 2016)
Lifan Xu (in collaboration with Prof. Michela Taufer UD-Computer Science)

Postdoctoral fellows
Dr Evangelia Kalligiannaki

Undergraduate students
Giorgos Arampatzis (summer internships)