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RNMC: kinetic Monte Carlo implementations for complex reaction networks

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Summary

Macroscopic chemical and physical phenomena are driven by microscopic interactions at the atomic and molecular scales. In order to capture complex processes with high fidelity, simulation methods that bridge disparate time and length scales are needed. While techniques like molecular dynamics and *ab initio* simulations capture dynamics and reactivity at high resolution, they cannot be used beyond relatively small length (hundreds to thousands of atoms) and time scales (picoseconds to microseconds). Kinetic Monte Carlo (kMC) approaches overcome these limitations to bridge length and time scales across several orders of magnitude while retaining relevant microscopic resolution, making it a powerful and flexible tool.

Here, we present `RNMC`, an easy-to-use, modular, high-performance kMC simulation framework that enables modeling of complex systems. `RNMC` consists of a core module defining the common features of kMC algorithms, including an implementation of the Gillespie algorithm (Gillespie, 1977), input/output operations leveraging SQLite databases, random number sampling, threading logic for parallel execution, and dependency graphs for efficient event propensity updates. In addition, there are currently three modules defining kMC implementations for different types of applications. The `GMC` (Gillespie Monte Carlo) module enables simulations of reaction networks in a homogeneous (well-mixed) environment. `GMC` is a basic tool that is appropriate for general simulations of solution-phase chemistry. The `NPMC` (NanoParticle Monte Carlo) module enables simulation of dynamics in nanoparticles with 3D statistical field theory and supports one- and two-site interactions. Finally, the `LGMC` (Lattice Gillespie Monte Carlo) module is designed for simulations of multi-phase systems (especially at solid-fluid interfaces) where chemical and electrochemical reactions can occur between a lattice region and a homogeneous region. We have designed `RNMC` to be easily extensible, enabling users to add additional kMC modules for other diverse chemical and physical systems.

Statement of need

Three are many existing kMC implementations, including several open source examples (e.g. the Stochastic Parallel PARticle Kinetic Simulator or `SPPARKS` (Garcia Cardona et al., 2009) and `kmos` (Hoffmann et al., 2014)). `RNMC` began as a fork of SPPARKS but differs in several important ways. First, because `RNMC` uses the widely supported SQLite database engine for simulation inputs and outputs, it facilitates the automation of simulations. Second, `RNMC`

has a focus on modularity. All simulators leverage the small core library, which serves as a common interface through the use of templating. As long as they can operate through this shared core, different simulation implementations are totally independent. This means that new developers need only read and understand the core library to be able to add new capabilities to RNMC, lowering the barrier to entry, and further reduces the likelihood that new additions will adversely affect pre-existing code.

The simulation modules already implemented in RNMC provide unique capabilities that are not widely available in other open source codes. NPMC is specifically designed for 3D simulations of the complex photophysical interaction networks in nanocrystals (Teitelboim et al., 2019), particularly multi-domain heterostructures whose optical properties cannot be calculated deterministically (Skripka et al., 2023). NPMC can be used to simulate energy transfer interactions between dopants in nanoparticles, their radiative transitions, and nonlinear processes such as upconversion (Chan, 2015) and photon avalanching (Skripka et al., 2023). LGMC is also somewhat unique in that it can simulate multi-phase systems and electrochemical processes. Simulations using LGMC can include a lattice region and a homogeneous solution region which can interact *via* interfacial reactions. Electrochemcial reactions can be treated using Marcus theory (Marcus, 1965) or Butler-Volmer kinetics (Newman & Balsara, 2021). Because it allows for a dynamic lattice region, LGMC is also appropriate for simulations of nucleation and growth, dissolution, precipitation, and related phenomena.

We have already used the GMC module in a number of prior works in applications related to Li-ion and Mg-ion batteries (Barter et al., 2023; Spotte-Smith et al., 2022, 2023). We note that these simulations included tens of millions of reactions, demonstrating that RNMC is able to scale to large and complex reaction networks. In addition, we have used NPMC to perform Bayesian optimization of upconverting nanoparticles (Xia et al., 2023).

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