**Acceleration of a kinetic Monte Carlo
Master Equation Solver for Gas Phase Chemical Kinetics**

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**Highlights**

* The MCRRKM stochastic master equation solver is adaptively accelerated.
* Speedup factors reach 1E+25 for low temperature simulations (300 K).
* Rate constant computation is now feasible in the full temperature range.
* Calculated k(T,P) with acceleration are accurate within a factor of 1.2.

**1. Introduction**

The calculation of pressure and temperature dependent rate constants of gas phase reactions requires the solution of a Master Equation, which describes the energy transfer dynamics between molecules as a continuous time Markov Process[1]. The stochastic approach, or kinetic Monte Carlo (kMC) integration[2], allows to directly extract rate coefficients, but suffers from intrinsic time scale separation between reaction events and internal energy relaxation by strong collisions. The Markov process converges on rare event dynamics[3] and molecules reach thermodynamic equilibrium. In these cases, especially at low temperatures, the stochastic simulation explores energies well below the reaction thresholds, requiring approximately 1020 iterations before reaching a reactive event. It is therefore necessary to search and implement solutions that will allow a speedup, or acceleration, of the stochastic simulation algorithm while maintaining high accuracy for the extracted rate coefficients. As such, a validation must be performed with existing solvers, possibly with method-independent (deterministic) ones, to eliminate sources of statistical error.

This problem also arises for deterministic solvers, e.g. MESS[4], that numerically solves the Master Equation as a linear matrix ODE problem, exploiting the physics of the reactive system. Different approaches have been proposed to speed up master equation solvers; the most commonly used one is the Reservoir State Approximation[5], as it defines a fictitious set of energy states, called reservoir, which is treated as a single macrostate. The reactant energy distribution within that state is assumed at thermal equilibrium, thus described with the Boltzmann distribution.

The reservoir dimensions, or the number of lumped energy states under a threshold, are usually taken as an input data and are inherently system dependent. They are directly linked to the reaction barrier energies, thus the chemical mechanism or energy profile. It should be preferable to skip the setting of the reservoir threshold by an adaptive calculation, employed within the code.

**2. Methods**

The present work examines an existing RRKM Master Equation solver, called MCRRKM[6], which adopts the stochastic solution method. MCRRKM is a research code, developed by prof. Cavallotti at the Applied Physical Chemistry Lab. An acceleration protocol was developed that allows speeding up the kMC integration by introducing an analytical correction for the time the random walkers spend in the Boltzmann equilibrated portion of the energy distribution function.

**3. Results and discussion**

The acceleration protocol was implemented within MCRRKM with an adaptive calculated threshold, the Thermal Energy Limit, below which energy levels are treated as populated according to the Boltzmann distribution and binned as a single macrostate. The Speedup was found to be dependent only on thermodynamic quantities: the partition function ratio of the unperturbed and perturbed energy states. Below are two main results of the acceleration protocol on two test reactions:

 

**Figure 1.** (left) Speedup factor as a function of simulation temperature and thermal energy limit (in 1/cm) for two reactions [C2H3 = C2H3 → C2H2 + H, and C2H5 = C2H5 → C2H4 + H]. The speedup is super-exponential with temperature, thus at low temperatures the rare-event dynamics problem is solved. The acceleration protocol is effective at low T.
(right) estimated simulation time [red] and actual simulation time [blue] for the reaction C2H3 → C2H2 + H at 0.1 bar.

**4. Conclusions**

This work led to the development of a new acceleration protocol for the Monte Carlo integration of the master equation for reactive systems that drastically reduces computational times, from approximately 1020 to 102 iterations to reach a reactive event, making the stochastic solution of the Master Equation feasible at all temperatures. The protocol was validated with respect to MESS, a solver developed by Georgievskii and Klippenstein[4], employing the deterministic approach over two reactions of combustion interest: hydrogen dissociation from vinyl (C2H3) and ethyl (C2H5) radicals. With temperature and pressure ranges of 300-2500 K and 0*.*001-1000 bar, rate constants differ by a maximum 1.2 factor (0-20% relative error) from MESS results in all cases.

**References**

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