Conclusion

This thesis presented the Uncoupling-Coupling Method (UC), which is a new algorithmic approach for drawing samples from high-dimensional probability distributions based on Markov Chain Monte Carlo (MCMC) and transfer operator techniques.

The Algorithm. Addressing directly the trapping problem inherent to MCMC methods, UC hierarchically decomposes the state space into metastable sets. This allows for a fast and parallel sampling via restricted Markov chains on identified metastable sets. Theoretical investigations on an upper bound of the 2nd largest eigenvalue for associated Markov operators revealed rapidly mixing properties for restricted chains. The coupling step performs data analysis on the various samples obtained in a UC simulation. Coupling factors determining weights for all samples are extracted from the stationary distribution of a coupling matrix, which can be estimated from the samples. This enables to set up an overall sample for the probability distribution.

The Application. We have applied UC to draw samples from the canonical distribution of biomolecules. For n-butane we reproduced analytical known expectation values, and for n-pentane we analyzed in detail the hierarchical decomposition process and the interplay of UC's algorithmic parts. Moreover, we applied UC to epigallocatechin, a constituent of green tea, which is a more complex biomolecule with potential use in drug design. Together with the Hybrid Monte Carlo method UC has provided not only static, but also dynamic information: identified metastable sets, which are used in UC solely for the purpose of a fast sampling, are strongly connected to physical relevant metastable conformations of the biomolecule.

Outlook. The general concept of UC consists of uncoupling Markov chains into their rapidly mixing parts and of regaining seemingly lost coupling factors via a coupling matrix. Though important in practice, UC does not rely on a specific MCMC or discretization method; even the use of a hierarchical decomposition can be replaced by any patchwork of distributions. UC should therefore also provide a flexible framework in other application fields from Statistical Physics or Bayesian Analysis.