

[An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions](#)

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1. Auflage 2012. Taschenbuch. xvii, 254 S. Paperback

ISBN 978 3 642 29487 7

Format (B x L): 15,5 x 23,5 cm

Gewicht: 421 g

[Weitere Fachgebiete > Physik, Astronomie > Thermodynamik > Festkörperphysik,
Kondensierte Materie](#)

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Preface

Kinetic Monte Carlo (kMC) simulations form still a quite new area of research. Figure 1 shows the number of publications (articles or reviews) with “kinetic Monte Carlo” in the title or abstract according to the abstract and citation database Scopus. There are two things to note. On the one hand it is not a very extensive area of research yet. A very diligent researcher can still keep track of all publications that appear. On the other hand, the number of publications is rapidly growing.

Figure 1 shows that there were no publications before 1993 that used the term kMC. This does not mean that there have been no kMC simulations before that year. There have been some but the term was not used yet. In fact, there are still people, who do what we will call kMC simulations here, but who do not use the term. One mundane reason for that is probably that they use an algorithm that they regard as one of many possible algorithms for doing Monte Carlo (MC) simulations. Why give it a special name? Another reason may be historical. Instead of kMC, people have used and still use the term dynamic MC. This is a term introduced by D.T. Gillespie for his algorithms that use MC to solve macroscopic rate equations. These algorithms are often almost identical to the ones we will describe in Chap. 3, and it seems reasonable to use the same term even when the algorithms are used for different problems. There has been a tendency to be more strict in the terminology however. For example, the term Stochastic Simulation Algorithm is now often used when using MC for rate equations. There are even people that restrict the term kMC to one particular algorithm, the Variable Step Size Method in our terminology (see Sect. 3.2), even though all other algorithms in Chap. 3 give exactly the same results. But the term kMC has also been used for rate equations. So the situation concerning terminology is still fluent.

So what do we mean when we use the term kMC? There are always two aspects to kMC as we will discuss it here. We will regard a system as a set of minima of a potential-energy surface (PES). The evolution of a system in real time will then be regarded as hops from one minimum to a neighboring one. These are the elementary events of kMC. The second aspect concerns the algorithms. The hops in kMC will be seen to be stochastic processes and the algorithms use random numbers to determine at which times the hops occur and to which neighboring minimum they go. This is

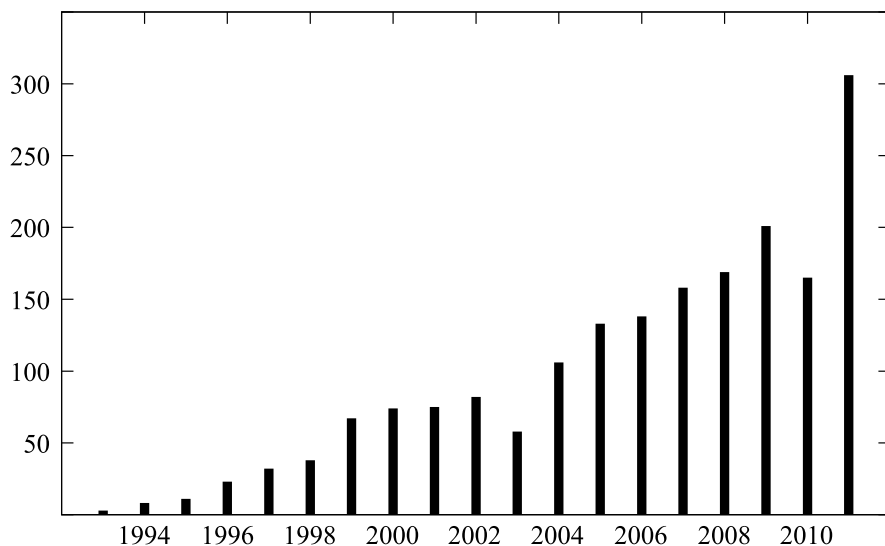


Fig. 1 Number of publications (articles or reviews) with “kinetic Monte Carlo” in the title or abstract as a function of the year of publication

our general definition of kMC. We will use it however only in Chap. 2 and Sect. 8.4. In the rest of this book we will make an additional assumption. This is where the surface reactions in the title of this book come in. The surface on which the reactions take place is often periodic and has translational symmetry in two directions. The minima of the PES are related to the adsorption sites of the surface. The latter form a lattice and the reactions can be modeled with a lattice-gas model. We will see that this is even possible if the periodicity of the surface is not perfect. So kMC in this book stands for a lattice-gas model that describes the evolution of the system in real time and with elementary events that are stochastic and that correspond to reactions and other processes.

This book has two objectives. First, it is about the kMC method. A derivation of the method will be given from first principles, and we will discuss various algorithms that can be used to do actual simulations. This means that much of the book is also supposed to be useful to people who use kMC for other systems than surface reactions. For example, the derivation of the master equation in Chap. 2, which forms the basis of our theory of kMC, does not use any information particular to surface reactions. It only assumes that you have a system that can be described by a single-valued PES. This includes a very large majority of all systems one encounters in chemical physics. Chapter 8 also has a section that discusses kMC for when this is all one knows about a system.

Most of the book does however assume that a lattice-gas model is used, because this simplifies the applicability of kMC enormously. However, this still does not restrict the usefulness only to surface reactions. In fact, most publications using lattice-gas kMC are not about surface reactions. There are many applications

of kMC in crystalline solids, polymers, crystal growth, chemical vapor deposition, molecular-beam epitaxy, ion implantation, etching, nanoparticles, and non-reactive processes. The discussions of algorithms in Chap. 3 and the way processes can be modeled in Chaps. 5, 6, 7, and 8 are just as useful for those applications as for surface reactions. However, the second objective of this book is to show what kMC simulations can teach us about the kinetics of surface reactions that one finds in catalysis and surface science. The book was mainly written with this in mind. This means that there are aspects that are relevant for the application of kMC to other areas that will not be found here, whereas some aspects that are discussed here may not be relevant for these areas.

The book is called an introduction because it is meant to give all information on kMC simulations of surface reactions that you need if you want to start from scratch. A lot of space is devoted to the basics, which are discussed in detail. The term “introduction” is not meant to imply that everything in this book is low level or easy. Some things are but others definitely are not. It is for example quite easy to implement the algorithms of Chap. 3 for a simple system of surface reactions, and the resulting code will probably yield very useful and interesting information on the kinetics of the system. Writing a general-purpose code however is much harder. Also the theoretical derivation of the master equation on which we base kMC, advanced aspects of the algorithms, and certain new developments in Chap. 8 are anything but easy.

The structure of this book is as follows. Chapter 1 discusses why one would want to do kMC simulations. The kinetics of surface reactions is normally described with macroscopic rate equations. There are different ways in which these equations can be used, but it is shown that they all have substantial drawbacks.

Chapter 2 deals with the basic theory. It introduces the lattice gas as the model for the systems in this book, and it gives the derivation of the master equation. This is the central equation for kMC. It forms the basis of all kMC algorithms, it relates quantum chemical calculations of rate constants to kMC, and it relates kMC to other kinetic theories like microkinetics.

Chapter 3 discusses kMC algorithms. kMC generates a sequence of configurations and times when the transitions between these configurations occur. This solves the master equation. There are many algorithms that yield such a sequence of configurations and which are statistically equivalent. We discuss a few in detail because they are the ones that are efficient for models of surface reactions. Time-dependent rate constants are discussed separately as the determination of when processes take place pose special problems. Parallelization is discussed as well as some older algorithms. Some guidelines are given of how to choose an algorithm for a simulation.

Chapter 4 shows how the rate constants that are needed for kMC simulations can be obtained. It shows how rate constants can either be calculated or be derived from experimental results. Calculating rate constants involves determining the initial and the transition state of a process, the energies of these states, and their partition functions. The phenomenological or macroscopic equation is the essential equation to get rate constants from experiments. Lateral interactions can affect rate constants substantially, but because they are relatively weak and special attention needs to be given to the reliability of calculations of these interactions.

Chapters 5 and 6 discuss ways to model surface processes. These chapters deal with the same topic, but approach it from different angles. Chapter 5 shows the tools that we can use in modeling. For simple systems there is a lattice corresponding to the adsorption sites and the labels of the lattice points describe the occupation of the sites. The labels can however also be used to model steps and other defects and sites on bimetallic substrates. The lattice points don't need to correspond to sites however, but can also be used to store other information like the presence of certain structures in the adlayer. Processes need not always to correspond to reactions or other actual processes, but when they have an infinite rate constant they can be used in a general-purpose code to handle exceptional situations that are normally hard-coded in special-purpose codes.

Chapter 6 discusses typical surface processes and how each of them can be modeled in different ways using the tools from Chap. 5. The way to model many processes for kMC simulations is straightforward. There are however also processes that one encounters regularly and for which there are more modeling options and for which it is not always clear which the best. We discuss several of them.

Chapter 7 shows how the modeling of various surface processes can be integrated. We discuss a number of complete surface reaction systems and show the benefits of kMC simulations for them. Chapter 8 finally discusses some aspects of kMC that one might want to improve and some likely new developments. kMC is a very versatile and powerful method to study the kinetics of surface reactions, but there are nevertheless some systems and phenomena for which one would like it to be even more efficient or one would like to extend it.

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