Lecture Notes in Physics 856

An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions

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Chapter 2
A Stochastic Model for the Description of Surface Reaction Systems

Abstract The most important concept for surface reactions is the adsorption site. For simple crystal surfaces the adsorption sites form a lattice. Lattices form the basis for the description of surface reactions in kinetic Monte Carlo. We give the definition of a lattice and discuss related concepts like translational symmetry, primitive vectors, unit cells, sublattices, and simple and composite lattices. Labels are introduced to describe the occupation of the adsorption sites. This leads to lattice-gas models. We show how these labels can be used to describe reactions and other surfaces processes and we make a start with showing how they can also be used to model surfaces that are much more complicated than simple crystal surfaces. Kinetic Monte Carlo simulates how the occupation of the sites changes over time. We derive a master equation that gives us probability distributions for what processes can occur and when these processes occur. The derivation is from first principles. Some general mathematical properties of the master equation are discussed and we show how a lattice-gas model simplifies the master equation so that it becomes feasible to use it as a basis for kinetic Monte Carlo simulations.

2.1 The Lattice Gas

We start the discussion of the way how we will model surface reactions by specifying how we will describe our systems. We want an atomic scale description of our systems and relate this to the macroscopic kinetics: i.e., we want to be able to talk about individual atoms and molecules reacting on a surface, and then link this to global changes and reaction rates of the layer of adsorbates. It turns out that the proper way to described a system is related to the different time scales with which things change on the atomic and on the macroscopic scale. We will see that we need to do some coarse-graining on the atomic length scale to bridge the gap in time scales.

If we regard the evolution of a layer of atoms and molecules adsorbed on a surface on an atomic scale, we will notice that there is a huge difference in time scale of the motion of individual atoms and molecules on the one and of the macroscopic properties on the other hand. For most systems of interest in catalysis, for example, the latter typically vary over a period of seconds or even longer. Motions of atoms occur typically on a time scale of femtoseconds. This enormous gap in time scales

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poses a large problem if we want to predict or even explain the kinetics (i.e., reaction rates) in terms of the processes that take place on the atomic scale.

The conventional method to simulate the motions of atoms and molecules is Molecular Dynamics (MD) [1–3]. This method generally discretizes time in intervals of equal lengths. The size of this so-called time step, and with it the computational costs, is determined by the fast vibrations of chemical bonds [1]. A stretch vibration of a C-H bond has a typical frequency of around 3000 cm^{-1}. This corresponds to a period of about 10 fs. If one wants to study the kinetics of surface reactions, then one needs a method that does away with these fast motions.

The kinetic Monte Carlo (kMC) method that we present here does this by using the concept of sites. The forces working on an atom or a molecule that adsorbs on a surface move it to well-defined positions on the surface [4, 5]. These positions are called sites. They correspond to minima on the potential-energy surface (PES) for the adsorbate. Most of the time adsorbates stay very close to these minima. If we would take a snapshot of a layer of adsorbates at normal temperatures, only about 1 in 10^{13} of them would not be near a minimum at normal reaction conditions. Only when they diffuse from one site to another or during a reaction they will not be near such a minima, but only for a very short time. Now instead of specifying the precise positions, orientations, configurations, and motions of the adsorbates we will only specify for each sites its occupation. A reaction and a diffusion from one site to another will be modeled as a sudden change in the occupation of the sites. These changes are the elementary events in a kMC simulation. The vibrations of the adsorbates do not change the occupations of the sites. So they are not simulated in kMC, and hence they do not determine the time scale of a kMC simulation. Reactions and diffusion take place on a much longer time scale. Thus by taking a slightly larger length scale, we can simulate a much longer time scale.

If the surface has two-dimensional translational symmetry, or when it can be modeled as such, the sites form a regular grid or a lattice. Our model is then a so-called lattice-gas model. This chapter shows how this model can be used to describe a large variety of problems in the kinetics of surface reactions.

2.1.1 Lattices, Sublattices, and Unit Cells

If the surface has two-dimensional translational symmetry then there are two linearly independent vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, with the property that when the surface is translated over any of these vectors the result is indistinguishable from the situation before the translation. It is said that the system is invariant under translation over these vectors. In fact the surface is then invariant under translations for any vector of the form

$$n_1\mathbf{a}_1 + n_2\mathbf{a}_2 \tag{2.1}$$

where n_1 and n_2 are integers. If all translations that leave the surface invariant can be written as (2.1), then $\mathbf{a}_1$ and $\mathbf{a}_2$ are so-called primitive vectors or primitive translations, and the vectors of the form (2.1) are the lattice vectors. Primitive vectors are not uniquely defined. For example a (111) surface of a fcc metal is translationally invariant for $\mathbf{a}_1 = a(1, 0)$ and $\mathbf{a}_2 = a(1/2, \sqrt{3}/2)$, where a is the lattice spacing. But one can just as well choose $\mathbf{a}_1 = a(1, 0)$ and $\mathbf{a}_2 = a(-1/2, \sqrt{3}/2)$. The area defined by

$$x_1\mathbf{a}_1 + x_2\mathbf{a}_2 \tag{2.2}$$

with $x_1, x_2 \in [0, 1\rangle$ is called the unit cell. The whole system is obtained by tiling the plane with the contents of a unit cell.

Expression (2.1) defines a simple lattice, Bravais lattice, or net. Simple lattices have just one lattice point, or grid point, per unit cell. It is also possible to have more than one lattice point per unit cell. The lattice is then given by all points

$$\mathbf{s}^{(i)} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 \tag{2.3}$$

with $i = 0, 1, \ldots, N_{\text{sub}} - 1$ and N_{sub} the number of lattice points in the unit cell. Each $\mathbf{s}^{(i)}$ is a different vector in the unit cell. The set $\mathbf{s}^{(i)} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ for a particular vector i forms a sublattice, which is itself a simple lattice. There are N_{sub} sublattices, and they are all equivalent: they are only translated with respect to each other. (For more information on lattices, also for a discussion of their symmetry, see for example references [4] and [6].) All points of the form (2.3) from a composite lattice.

The sites of a simple crystal surface form a lattice. The description so far suggests that the different lattice points in a unit cell, corresponding to sites, are all in the some plane, but that does not need to be the case. As we will see in Sect. 4.6.3, that different lattice points may also correspond to positions for adsorbates in different layers that are stacked on top of each other. Lattices can also be used to model surfaces that are much more complicated than simple crystal surfaces (see Sects. 5.5.2 and 5.5.3). In fact, we will see that sometimes lattice points do not correspond to physical adsorption sites at all (see Sect. 5.5.4).

2.1.2 Examples of Lattices

Figure 2.1 shows top and hollow sites of the (100) surface of an fcc metal. Such a surface has $\mathbf{a}_1 = a(1, 0)$ and $\mathbf{a}_2 = a(0, 1)$ as primitive translations with a the distance between the surface atoms. CO for example prefers the top sites on such surface if the metal is rhodium [7–10]. We have $N_{\text{sub}} = 1$ if we would only include these top sites. We can choose the origin of our reference frame any way we want so we take $\mathbf{s}^{(0)} = (0, 0)$ for simplicity. If we would want to include the hollow sites as well then $N_{\text{sub}} = 2$ and $\mathbf{s}^{(1)} = a(1/2, 1/2)$.

Figure 2.2 shows bridge sites of the same surface. Some CO moves to these bridge sites at high coverages [7–10]. If we would include the top and bridge sites to describe all adsorption sites for CO/Rh(100), then we would have $N_{\text{sub}} = 3$ and $\mathbf{s}^{(0)} = (0, 0)$, $\mathbf{s}^{(1)} = a(1/2, 0)$, and $\mathbf{s}^{(2)} = a(0, 1/2)$ for the top and the two types of bridge site, respectively.

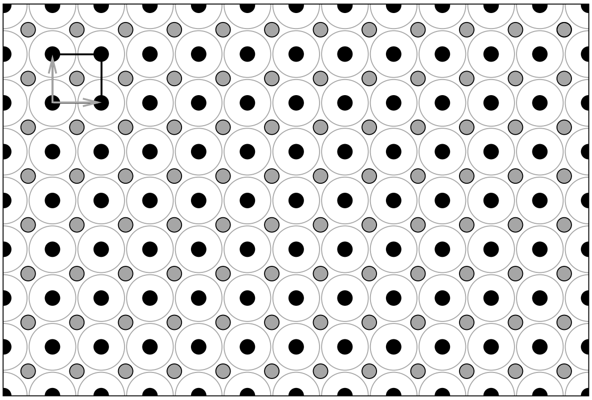

Fig. 2.1 The large *white circles with gray edges* depict the atoms of the top layer of a (100) surface of an fcc metal. The *black circles* indicate the positions of the top sites, and the *gray circles with black edges* the positions of the hollow sites. The top sites form a simple lattice as do the hollow sites. In the *top-left* corner the unit cell and the primitive translations of the surface are shown

Figure 2.3 shows a (111) surface of an fcc metal. CO on Pt prefers to adsorb on this surface on the top sites [4]. We can therefore model CO on this surface with a simple lattice with the lattice points corresponding to the top sites. We have $\mathbf{a}_1 = a(1,0)$ and $\mathbf{a}_2 = a(1/2, \sqrt{3}/2)$. As $N_{\mathrm{sub}} = 1$ we choose the origin of our reference frame so that $\mathbf{s}^{(0)} = (0,0)$ for simplicity. Each lattice point corresponds to a site that is either vacant or occupied by CO.

NO on Rh(111) forms a (2 × 2)-3NO structure in which equal numbers of NO molecules occupy top, fcc hollow, and hcp hollow sites [11, 12]. Figure 2.3 shows all the sites that are involved. We now have three sublattices with $\mathbf{s}^{(0)} = (0,0)$ (top

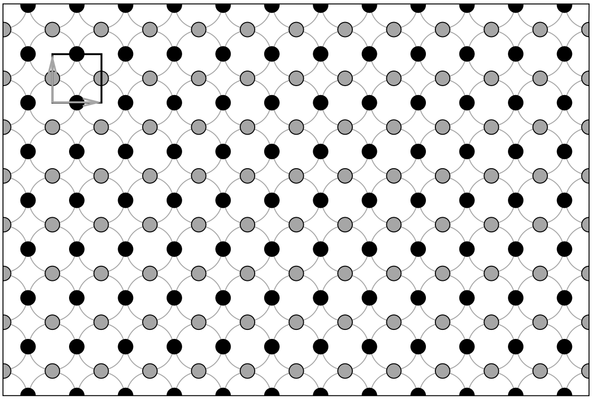

Fig. 2.2 The *large white circles with gray edges* depict the atoms of the top layer of a (100) surface of an fcc metal. The *black circles* and the *gray circles with black edges* indicate the positions of the bridge sites. Although all bridge sites have the same adsorption properties, together they do not form a simple lattice, but a composite lattice. This is because the relative positions of the surface atoms with respect to the "black" bridge sites is different from those of the "gray" bridge sites. However, if we ignore the surface atoms, then all bridge sites together from a square simple lattice. In the *top-left* corner the unit cell and the primitive translations of the surface are shown

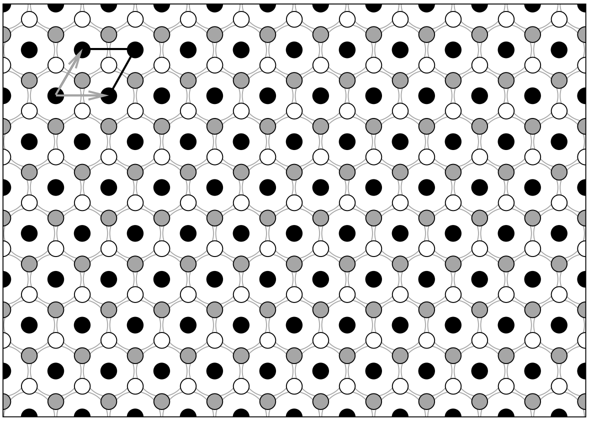

Fig. 2.3 The *large white circles with gray edges* depict the atoms of the top layer of a (111) surface of an fcc metal. The *black circles* indicate the positions of the top sites, and the *gray circles with black edges* the positions of one type of hollow site, say fcc, and the *small white circle with black edges* the positions of the other type, say hcp, of hollow site. The top sites form a simple lattice as do the fcc sites and the hcp sites separately. The top and hollow sites together also form a simple lattice if we disregard the different adsorption properties of the sites and the different positions with respect to the surface atoms. Otherwise they form a composite lattice with three sublattices. In the *top-left* corner the unit cell and the primitive translations of the surface are shown

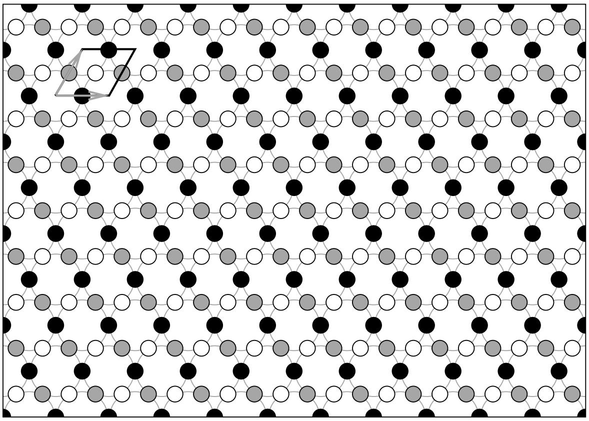

Fig. 2.4 The *large white circles with gray edges* depict the atoms of the top layer of a (111) surface of an fcc metal. The *black circles*, the *gray circles with black edges*, and the *small white circle with black edges* indicate the positions of the bridge sites. Together they form a composite lattice even though they have the same adsorption properties. In the *top-left* corner the unit cell and the primitive translations of the surface are shown

sites), $\mathbf{s}^{(1)} = a(1/2, \sqrt{3}/6)$ (fcc hollow sites), and $\mathbf{s}^{(2)} = a(1, \sqrt{3}/3)$ (hcp hollow sites).

At high coverages the repulsion between the CO molecules on Pt(111) forces some of them again to bridge sites [13]. Figure 2.4 shows the bridge sites. We have now four sublattices with $\mathbf{s}^{(0)} = (0, 0)$, $\mathbf{s}^{(1)} = a(1/2, 0)$, $\mathbf{s}^{(2)} = a(1/4, \sqrt{3}/4)$, $\mathbf{s}^{(3)} = a(3/4, \sqrt{3}/4)$. The first one is for the top sites (not shown in the figure, but see Fig. 2.3). The others are for the three sublattices of bridge sites. The four sublattices together form a simple lattice, but only when we do not distinguish between top and bridge sites.

The examples here are of simple single crystal surfaces. It would be wrong however to assume that a lattice-gas model can only be used for such surfaces. The unit cell can be much larger and with many more sites. This makes it possible to model a surface with steps. But it is even possible to model systems with no translational symmetry at all with a lattice-gas model. It is possible to model steps at variable distances, point defects, bimetallic surfaces, and many more systems through the use of labels as explained in Sect. 2.1.3.

2.1.3 Labels and Configurations

The sites are the positions where the adsorbates are found on the surface, but for each site we need something to indicate if it is occupied or not, and if it is occupied with which adsorbate. We use labels for this.

We assign a label to each lattice point. The lattice points correspond to the sites, and the labels specify properties of the sites. A particular labeling of all lattice points together we call a configuration. The most common property that one wants to describe with the label is the occupation of the site. We use the short-hand notation $(n_1, n_2/s : \mathrm{A})$ to mean that the site at position $\mathbf{s}^{(s)} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ is occupied by an adsorbate A.

The labels are also used to specify reaction. A reaction can be regarded as nothing but a change in the labels. An extension of the short-hand notation $(n_1, n_2/s : \mathrm{A} \to \mathrm{B})$ indicates that during a reaction the occupation of the site at $\mathbf{s}^{(s)} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ changes from A to B. If more than one site is involved in a reaction then the specification will consist of a set changes of the form $(n_1, n_2/s : \mathrm{A} \to \mathrm{B})$. Not only reactions can be specified in this way. Also other processes can be described like this. For example, a diffusion of an adsorbate A might be specified by $\{(0, 0/0 : \mathrm{A} \to *), (1, 0/0 : * \to \mathrm{A})\}$. Here $*$ stands for a vacant site, and the diffusion is from site $\mathbf{s}^{(0)}$ to $\mathbf{s}^{(0)} + \mathbf{a}_1$. We will also write this as $(0, 0/0), (1, 0/0) : \mathrm{A}* \to *\mathrm{A}$.

There are many other uses for labels as will be discussed in Sect. 2.1.4 and Chaps. 5, 6, and 7. Most kMC programs are special-purpose codes with hard coding of the processes. Labels play only a minor role in these programs. Labels are however an important and very versatile tool in general-purpose kMC codes. They allow great flexibility in creating models for reaction systems, and a clever use of them can greatly enhance the speed of simulations.

2.1.4 Examples of Using Labels

Desorption of CO from Pt(111) can be written as $(0, 0 : \mathrm{CO} \to *)$ when we use a model of the top sites shown in Fig. 2.3. We have left out the index of the sublattice,

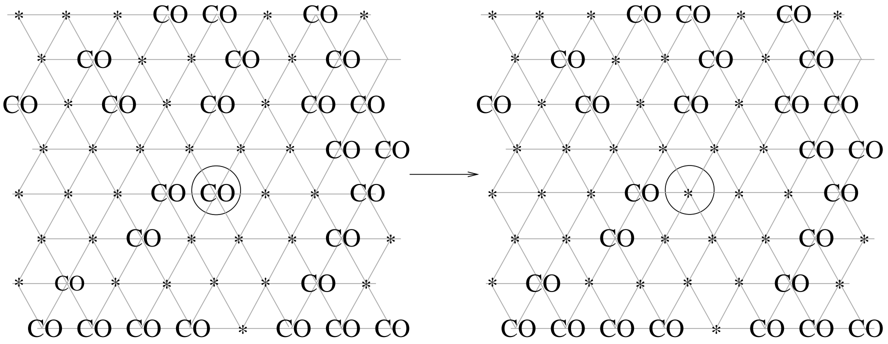

Fig. 2.5 The change of labels for CO desorption from a Pt(111) surface. The *encircled* CO molecule on the *left* desorbs and the label becomes $*$ indicating a vacant site. The *lines* are guides for the eyes

because, as there is only one, it is clear on which sublattice the reaction takes place (see Fig. 2.5). Desorption on other sites can be obtained by translations over lattice vectors: i.e., $(0,0\!:\!\mathrm{CO} \to *)$ is really representative for $(n_1,n_2\!:\!\mathrm{CO} \to *)$ with n_1 and n_2 arbitrary integers. Diffusion of CO can be modeled as hops from one site to a neighboring site. We can write that as $\{(0,0\!:\!\mathrm{CO} \to *),(1,0\!:\!* \to \mathrm{CO})\}$ or $(0,0),(1,0)\!:\!\mathrm{CO}* \to *\mathrm{CO}$. Hops on other sites can again be obtained from these descriptions by translations over lattice vectors, but also by rotations that leave the surface is invariant.

Specifying adsorbates is the most obvious and most frequent use of labels, but other properties can be modeled by labels to great effect. Note that in the case of NO on Rh(111) (Fig. 2.3) the lattice is a composite one, but if we ignore the difference between the sites we get a simple lattice with $\mathbf{a}_1 = a(1/2,\sqrt{3}/6)$ and $\mathbf{a}_2 = a(\sqrt{3}/3,0)$. It is possible to use the simple lattice and at the same time retain the difference between the sites. The trick is to use labels not just for the occupation, but also for indicating the type of site. So instead of labels NO and $*$ indicating the occupation, we use NOt, NOf, NOh, $*$t, $*$f, and $*$h. The last letter indicates the type of site (t stands for top, f for fcc hollow, and h for hcp hollow) and the rest for the occupation. Instead of $(0,0/0\!:\!\mathrm{NO})$ and $(0,0/1\!:\!*)$ we have $(0,0\!:\!\mathrm{NOt})$ and $(1,0\!:\!*\mathrm{f})$, respectively. It depends very much on the processes that we want to simulate which way of describing the system is more convenient and computationally more efficient.

Because a lattice is used to represent the adsorption sites, one might think that only systems with translational symmetry can be modeled. That is not the case however. Figure 2.6 shows how to model a step [14, 15]. The difference in the top sites can be modeled with different labels just as for the NO/Rh(111) example above. If the terraces are small then it might also be possible to work with a unit cell spanning the width of a terrace, but when the terraces become large this will be inconvenient as there will be many sublattices. If the width of the terraces varies this is even impossible. In a similar way as in Fig. 2.6 bimetallic surfaces can be modeled [16]. Notice that some distances between the sites on the left in Fig. 2.6 are different

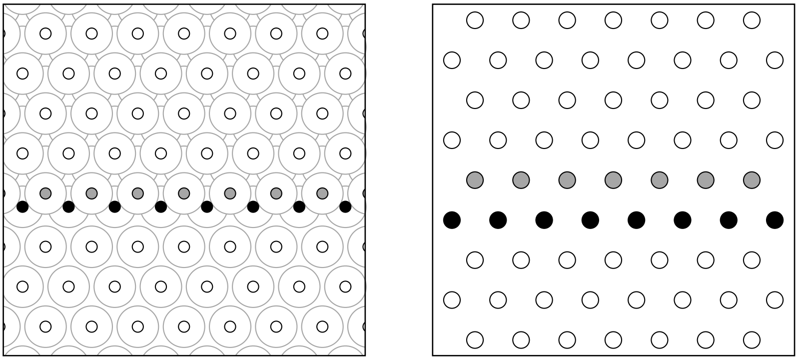

Fig. 2.6 A Ru(0001) surface with a step with the top sites indicated on the *left*. On the *right* is shown the lattice. The *large open circles* are the atoms. The *small open circles* indicate top sites on the terraces, the *small black circles* top sites at the bottom of the step, and the *small gray circles* top sites at the top of the step. Notice the difference in distance between the top sites at the step on the *left* and on the *right*

from those on the right. The distance between the sites on the top and bottom of a step is smaller on the left than on the right. On the right this distance is increased so that the sites form a lattice. Such a distortion of the system is quite acceptable in kMC simulations. The elementary events (reactions, diffusion, and possibly other processes) are described in terms of changes of the labels of sites. We only need to know which sites and how the labels change. Distances between sites are not part of the description of events.

Site properties like the sublattice of which the site is part of and if it is a step site or not are static properties. The occupation of a site is a dynamic property. There are also other properties of sites that are dynamic. Bare Pt(100) reconstructs into a quasi-hexagonal structure [17]. CO oxidation on Pt(100) is substantially influenced by this reconstruction because oxygen adsorbs much less readily on the reconstructed surfaces than on the unreconstructed one. This can lead to oscillations, chaos, and pattern formation [17, 18]. It is possible to model the effect of the reconstruction on the CO oxidation by using a label that specifies whether the surface is locally reconstructed or not [19–21].

Chapters 5, 6, and 7 will show more esoteric uses of labels. Labels can be used as flags or as counters as well. Very often this use is combined with fictitious processes and fictitious sites, which can either be a way of modeling actual physical and chemical processes, or a way to get kinetic information.

2.1.5 *Shortcomings of Lattice-Gas Models*

The lattice-gas model is simple yet very powerful, as it allows us to model a large variety of systems and phenomena. Still, not everything can be modeled with it.

Let's look again at CO oxidation on Pt(100). As stated above this system shows reconstruction which can be modeled with a label indicating that the surface is reconstructed or not. This way of modeling has shown to be very successful [19–21], but it does neglect some aspects of the reconstruction. The reconstructed and the unreconstructed surface have very different unit cells, and the adsorption sites are also different [22, 23]. In fact, the unit cell of the reconstructed surface is very large, and there are a large number of adsorption sites with slightly different properties. These aspects have been neglected in the kinetic simulations so far. As these simulations have been quite successful, it seems that these aspects are not very relevant in this case, but that need not always be so. Another example would be catalytic partial oxidation (CPO), which takes place at high temperatures at which the surface is so dynamic that all translational symmetry is lost. In this case using a lattice to model the kinetics seems inappropriate.

The example of CO on Pt(111) has shown that at high coverage the position at which the molecules adsorb change. The reason for this is that these positions are not only determined by the interactions between the adsorbates and the substrate, but also by the interactions between the adsorbates themselves. At low coverages the former dominate, but at high coverages the latter may be more important. This may lead to adlayer structures that are incommensurate with the substrate [4]. Examples are formed by the nobles gases. These are weakly physisorbed, whereas at high coverages the packing onto the substrate is determined by the steric repulsion between them. At low and high coverages different lattices are needed to describe the positions of the adsorbates, but a single lattice describing both the low and the high coverage sites is not possible. Simulations in which the coverages change in such a way from low to high coverage and/or vice versa then cannot be based on a lattice-gas model except by making substantial approximations.

Although not all systems can be modeled well by a lattice gas, it is a much more flexible model than might initially appear. Figure 2.6 already shows some of this flexibility. Note that the sites in the system in the figure have only translational symmetry in the direction parallel to the step, whereas in the corresponding lattice-gas model there is the usual two-dimensional periodicity. This is accomplished by displacing the sites at the step somewhat from their real positions. As has been explained above, this is perfectly acceptable. Similarly, it is possible to describe with a lattice-gas model a layer of adsorbates that have been displaced from their normal site positions by the interactions between them, and that have formed an adlayer with a structure that is incommensurate with that of the preferred adsorption sites. The reason for this flexibility is the labels that we attach to each lattice point. It will be shown in Chaps. 5, 6, and 7 that these labels make it possible to model a very large variety of systems with a lattice gas. Whether or not a system can be described by a lattice-gas model depends very much on one's ingenuity.

2.1.6 Boundary Conditions

The surface of a real catalyst will very often contain many more sites than we can include in a kMC simulation. In fact, such a surface is generally regarded as infinite in two directions. In a kMC simulation we need to restrict ourselves to a much more limited number of sites. It is possible to do kMC simulations with all sites in a small part of the catalyst's surface. This gives an acceptable description except for the sites at the edge. It is more customary to use periodic boundary conditions. In that case all sites $\mathbf{s}^{(i)} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ with $n_1 = 0, 1, \ldots, N_1 - 1$ and $n_2 = 0, 1, \ldots, N_2 - 1$ are explicitly included in the simulation. Sites with values of n_1 and/or n_2 outside this range are thought to have the same label as those of $n_1 \bmod N_1$ and $n_2 \bmod N_2$. The system can be thought as if being rolled up on a torus. The values of N_1 and N_2 in real simulations vary. Sometimes they can be smaller than 100, but simulations with $N_1 = N_2 = 8192$ have been reported as well [24].

2.2 The Master Equation

2.2.1 The Definition and Some Properties of the Master Equation

The derivation of the algorithms and a large part of the interpretation of the results of kMC simulations are based on a master equation

$$\frac{dP_\alpha}{dt} = \sum_\beta [W_{\alpha\beta} P_\beta - W_{\beta\alpha} P_\alpha]. \tag{2.4}$$

In this equation t is time, α and β are configurations of the adlayer (i.e., different ways in which adsorbates are distributed over the sites, or more generally ways in which labels can be assigned to lattice points), P_α and P_β are their probabilities, and $W_{\alpha\beta}$ and $W_{\beta\alpha}$ are so-called transition probabilities per unit time that specify the rate with which the adlayer changes due to reactions and other processes. The master equation is the single most important equation in kMC. It relates everything that we do in kinetics to each other as will be shown below. Here we start with looking at some of its mathematical properties. The master equation is a loss-gain equation. The first term on the right stands for increases in P_α because of processes that change other configurations into α. The second term stands for decreases because of processes in α. From

$$\frac{d}{dt}\sum_\alpha P_\alpha = \sum_\alpha \frac{dP_\alpha}{dt} = \sum_{\alpha\beta} [W_{\alpha\beta} P_\beta - W_{\beta\alpha} P_\alpha] = 0 \tag{2.5}$$

we see that the total probability is conserved. (The last equality can be seen by swapping the summation indices in one of the terms.)

The master equation can be derived from first principles as will be shown below, and hence forms a solid basis for all subsequent work. There are other advantages

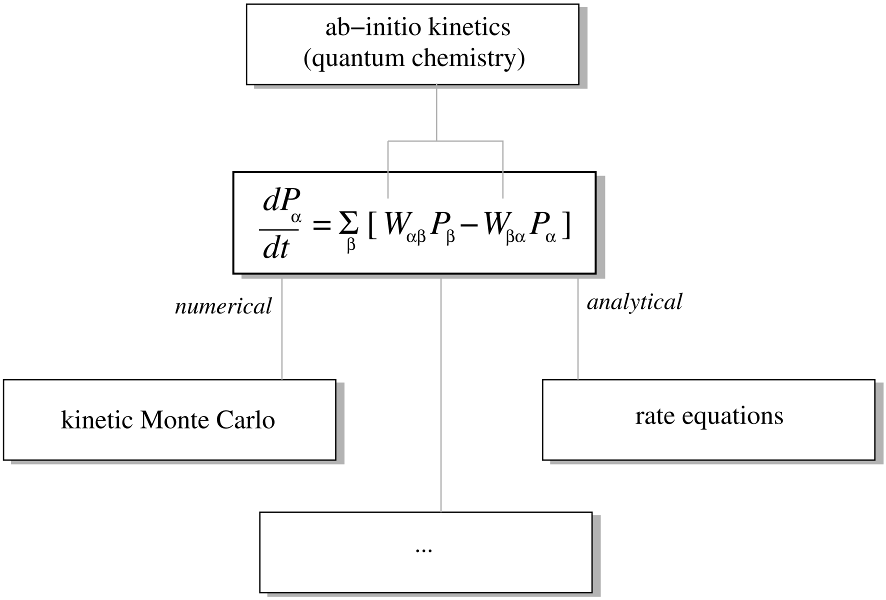

Fig. 2.7 Scheme showing the central position of the master equation for kinetics. Quantum chemical calculations yield the rate constants of the master equation, and kMC, rate equations, and other kinetic theories, methods, and approaches can be regarded as ways to solve the master equation

as well. First, the derivation of the master equation yields expressions for the transition probabilities that can be computed with quantum chemical methods [25]. This makes ab-initio kinetics for catalytic processes possible. Such calculations generally use the term rate constants instead of transition probabilities and we will use that term for the W's in the master equation as well. We will show however that these rate constants are generally not the same as the rate constants in macroscopic rate equations (see Sect. 4.6). Second, there are many different algorithms for kMC simulations. Those that are derived from the master equation all give necessarily results that are statistically identical. Those that cannot be derived from the master equation conflict with first principles. Third, kMC is a way to solve the master equation, but it is not the only one. The master equation can, for example, be used to derive the normal macroscopic rate equation (see Sect. 4.6), although this generally involves the introduction of approximations. In general, it forms a good basis to compare different theories of kinetics quantitatively, and also to compare these theories with simulations. Figure 2.7 shows that the master equation can be regarded as the central equation of the kinetics of surface reactions and that it relates the quantum chemical calculation of rate constants, kMC, and other kinetic theories to each other.

There is an extensive mathematical literature on the master equation. This literature also often talks about continuous-time Markov chains. If a system is in configuration α_n then the master equation gives the probabilities that the system will move to another configuration α_{n+1}. These probabilities do not depend on the configurations that the system was in before α_n. This makes $\alpha_n \to \alpha_{n+1}$ a Markov process [26, 27]. Continuing the transitions from one configuration to another gives a series $\alpha_n \to \alpha_{n+1} \to \alpha_{n+2} \to \dots$ that is called a Markov chain.

We discuss here only a few basic properties [26, 27]. The reader should be aware however that even these properties have only a limited use in relation to kMC simulations and should not be overinterpreted. For example, the Ziff–Gulari–Barshad (ZGB) model of CO oxidation has been extensively studied with kMC simulations (see Sect. 7.4.3). The physics literature mentions three states. Two of these states correspond to CO poisoning and oxygen poisoning of the surface. The third corresponds to a reactive state. The point here is that strictly speaking this reactive state is not stable. This means that it can not represent a steady state. The ZGB model might therefore seem a rather useless model for CO oxidation. However, the time it takes for the reactive state to turn into one of the poisoning states is so enormously long, even for small system sizes, that it can effectively be regarded as a stable state. This is what is actually done in the literature.

We start with a discussion of the class structure [27]. Suppose we mean by $\alpha \to \beta$ that there is a chain of processes that can convert configuration α into β. (Note that we normally use this notation to indicate a change of configuration by a single process.) We then define $\alpha \leftrightarrow \beta$ to mean $\alpha \to \beta$ and $\beta \to \alpha$. This relation $\leftrightarrow$ defines an equivalence relation [28]. This means $\alpha \leftrightarrow \alpha$ for all α, if $\alpha \leftrightarrow \beta$ then $\beta \leftrightarrow \alpha$, and if $\alpha \leftrightarrow \beta$ and $\beta \leftrightarrow \gamma$ then $\alpha \leftrightarrow \gamma$. Because of these properties we can partition all configurations into equivalence classes: i.e., α and β belong to the same class if and only if $\alpha \leftrightarrow \beta$.

A class is closed if α is in the class and $\alpha \to \beta$ implies that β is also in the same class as α: i.e., $\beta \to \alpha$ also holds. If the system ends up in a closed class, then it will never leave it. Such a situation may for example arise when no reactions are possible in a system anymore, and the adsorbates can only hop from one site to another. A system in a closed class visits each of the configurations in the class an infinite number of times. This does not hold for configurations in a class that is not closed. If a closed class consists of a single configuration, then the configuration is called an absorbing state. The poisoned states mentioned above for the ZGB model are examples of such absorbing states.

If all configurations can be partitioned into two or more sets such that neither $\alpha \to \beta$ nor $\beta \to \alpha$ holds if α and β are in different sets, then the system is said to be reducible or decomposable. This terminology is related to the way in which the master equation can be written in matrix-vector form. With the vector $\mathbf{P}$ with components $\mathbf{P}_\alpha = P_\alpha$, and the matrix $\mathbf{W}$ with components

$$\mathbf{W}_{\alpha\beta} = \begin{cases} W_{\alpha\beta}, & \text{if } \alpha \neq \beta, \text{ and} \\ -\sum_\gamma W_{\gamma\beta}, & \text{if } \alpha = \beta, \end{cases} \tag{2.6}$$

we can write the master equation as

$$\dot{\mathbf{P}} = \mathbf{WP}. \tag{2.7}$$

For a completely reducible or decomposable system the matrix **W** can be written in the form

$$\begin{pmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{0} & \mathbf{B} \end{pmatrix} \tag{2.8}$$

with **A** and **B** square matrices by appropriately ordering the configurations. The configurations in the different sets can be treated completely independently from each other. A system that is not reducible is called irreducible.

If there is a closed class, but the system is irreducible, then we can write **W** in the form

$$\begin{pmatrix} \mathbf{A} & \mathbf{D} \\ \mathbf{0} & \mathbf{B} \end{pmatrix} \tag{2.9}$$

with **D** a non-zero matrix, **A** and **B** square matrices, and the rows and columns of **A** indexed by the configurations in the closed class. Such a system is called (incompletely) reducible. If there are two closed classes, then **W** can be written as

$$\begin{pmatrix} \mathbf{A} & \mathbf{0} & \mathbf{D} \\ \mathbf{0} & \mathbf{B} & \mathbf{E} \\ \mathbf{0} & \mathbf{0} & \mathbf{C} \end{pmatrix} \tag{2.10}$$

with **A**, **B**, and **C** square matrices, **D** and **E** non-zero matrices, and the rows and columns of **A** and **B** being indexed by the configurations in the two closed classes. Such a system is called splitting, because it ends up in one closed class or the other.

The definition of **W** immediately gives

$$\sum_{\alpha} \mathbf{W}_{\alpha\beta} = 0. \tag{2.11}$$

Matrices with this property can be shown to have at least one right eigenvector with eigenvalue equal to zero [26]. The components of such eigenvector are all non-negative and by proper normalization can be identified with the probabilities to find the system in a configuration when the system is in a steady state. It can also be shown that the system will evolve toward such an eigenvector.

There are various ways to prove this [26]. One way is to write the solution of the master equation as

$$\mathbf{P}(t) = e^{\mathbf{W}t}\mathbf{P}(0), \tag{2.12}$$

where $\mathbf{P}(0)$ are the probabilities of the configurations at $t = 0$. If we can diagonalize **W** and write

$$\mathbf{WU} = \mathbf{UV}, \tag{2.13}$$

then this becomes

$$\mathbf{P}(t) = \mathbf{U}e^{\mathbf{V}t}\mathbf{U}^{-1}\mathbf{P}(0). \tag{2.14}$$

The matrix **V** is diagonal and all matrix elements on the diagonal are non-positive. This means that for large t, all components of $\exp[\mathbf{V}t]$ vanish, except those with zero on the diagonal of **V**. **P** evolves to the corresponding eigenvector in **U**.

Note that an eigenvector with eigenvalue equal to zero does not exclude the existence of an oscillation. Suppose we have configurations $\alpha_1, \alpha_2, \dots, \alpha_N$ with $N \geq 2$ and the system always moves from α_n directly to α_{n+1} for $n = 1, 2, \dots, N-1$ and from α_N directly to α_1. This means that we have a cycle. The eigenvector with zero eigenvalue has $W_{\alpha_{n+1}\alpha_n} P_{\alpha_n} = W_{\alpha_1\alpha_N} P_N$ for $n = 1, 2, \dots, N-1$. Although the system has a cycle, this can still be regarded as a stationary state because the time it takes the system to move through the cycle will not always be exactly the same. It can be shown (see Sect. 3.7.3) that on average this will take a time equal to

$$T = \sum_{n=1}^{N-1} W^{-1}_{\alpha_{n+1}\alpha_n} + W^{-1}_{\alpha_1\alpha_N}. \tag{2.15}$$

If we would start the system in α_1 at time $t = 0$ and follow the system, then after a time T we would find it most likely again in α_1, but also with some small probability in α_N and α_2, with an even smaller probability in α_{N-1} and α_3, et cetera. After another period T the probability of finding the system in α_1 would be reduced and the probabilities for configurations before and after α_1 would be increased. After many periods T we would find the system in one of the configurations with a probability corresponding to the one given by the eigenvector with zero eigenvalue.

2.2.2 The Derivation of the Master Equation

The master equation can be derived by looking at the surface and its adsorbates in phase space.[1] This is, of course, a classical mechanics concept, and one might wonder if it is correct to look at the processes on an atomic scale and use classical mechanics. The situation here is the same as for the derivation of the rate equations for gas phase reactions. The usual derivations there also use classical mechanics [29–33]. Although it is possible to give a completely quantum mechanical derivation formalism [34–37], the mathematical complexity hides much of the important parts of the chemistry. We therefore give only a classical derivation. It is possible at the end to replace the classical expressions by quantum mechanical ones, in exactly the same way as for gas phase reactions. The new expressions will depend on the type of motion (vibration, rotation, et cetera). This will be shown in detail in Chap. 4.

The derivation of the master equation is usually based on the observation that there is a separation between the time scale on which reactions take place and the time scale of much faster motions like vibrations [38, 39]. The longer time scale of reactions defines states, in which the system is localized in configuration space, and the transitions between them can be described by a master equation. The rates of the individual transitions can each be computed separately by one of the methods

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[1] Parts of Sect. 2.2.2 have been reprinted with permission from X.Q. Zhang, A.P.J. Jansen, Kinetic Monte Carlo method for simulation reactions in solutions, Phys. Rev. E **82**, 046704 (2010). Copyright 2010, American Physical Society.

of chemical kinetics: e.g., Transition-State Theory (TST) [38–40]. We present here a different derivation that incorporates all process at the same time [41–43]. It is a generalization of the derivation of Variational TST (VTST): i.e., we partition phase space in many regions [29, 32, 33], and it is an alternative to the derivation using projection operators [44, 45]. It has the advantage that the result is somewhat more general. We will use this in Sects. 2.2.3 and 8.2. The derivation does not use the fact that we are interested in surface reactions, and has a much more general validity. We will show in Sect. 2.2.3 how the results simplify for surface reactions.

A point in phase space completely specifies the positions and momenta of all atoms in the system. In MD simulations one uses these positions and momenta at some starting point to compute them at later times. One thus obtains a trajectory of the system in phase space. We are not interested in that amount of detail, however. In fact, as was stated before, too much detail is detrimental if one is interested in simulating many processes. The time interval that one can simulate a system using MD is typically of the order of nanoseconds. Reactions in catalysis have a characteristic time scale that is many orders of magnitude longer. To overcome this large difference we need an approach that removes the fast processes (vibrations) that determine the time scale of MD, and leaves us with the slow processes (reactions). This approach looks as follows.

Instead of the precise position of each atom, we only want to know how the different adsorbates are distributed over the sites of a surface. So our physical model is a lattice. Each lattice point corresponds to one site, and has a label that specifies which adsorbate is adsorbed. (A vacant site is simply a special label.) This gives us a configuration. As each point in phase space is a precise specification of the position of each atom, we also know which adsorbates are at which sites: i.e., we know the corresponding configuration. Different points in phase space may, however, correspond to the same configuration. These points differ only in slight variations of the positions and momenta of the atoms. This means that we can partition phase space in many regions, each of which corresponds to one configuration. The processes are then nothing but the motion of the system in phase space from one region to another.

More generally and in line with the idea of different time scales mentioned above, we can start with identifying the regions in configuration space where the fast motions take place. Figure 2.8 shows a sketch of a PES of an arbitrary system. We assume that only the electronic ground state is relevant, so that the PES is a single-valued function of the positions of all the atoms in the system. The points in the figure indicate the minima of the PES. Each minimum of the PES has a catchment region. This is the set of all points that lead to the minimum if one follows the gradient of the PES downhill [46].

We now partition phase space into these catchment regions and then extend each catchment region with the momenta. Let's call $\mathcal{C}$ the configuration space of a system and $\mathcal{P}$ its phase space [47, 48]. The minima of the PES are points in configuration space. We define C_α to be the catchment region of minimum α. This catchment

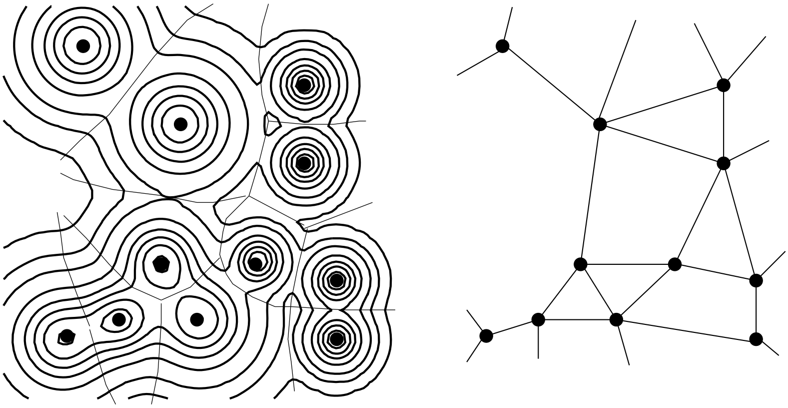

Fig. 2.8 A sketch of a potential-energy surface of an arbitrary system and its corresponding graph. The *points* are minima of the potential-energy surface. The *edges* in the graph connect minima that have catchment regions that border on each other. They correspond to reactions or other activated processes

region is a subspace of configuration space $\mathcal{C}$, and all catchment regions form a partitioning of the configuration space.

$$\mathcal{C} = \bigcup_{\alpha} C_{\alpha}. \tag{2.16}$$

(There is a small difficulty with those points of configuration space that do not lead to minima, but to saddle points, and with maxima. These points are irrelevant because the number of such points are vanishing small with respect to the other points. They are found where two or more catchment regions meet, and we can arbitrarily assign them to one of these catchment regions.) With $\mathbf{q}$ the set of all coordinates and $\mathbf{p}$ the set of all conjugate momenta we can extend the catchment region C_{α} to a corresponding region in phase space R_{α} as follows.

$$R_{\alpha} = \left\{ (\mathbf{q}, \mathbf{p}) \in \mathcal{P} | \mathbf{q} \in C_{\alpha} \right\}. \tag{2.17}$$

We then have for phase space

$$\mathcal{P} = \bigcup_{\alpha} R_{\alpha}. \tag{2.18}$$

If we use the regions R_{α}, we can derive the master equation exactly as for the lattice-gas model. This starting point based on the PES for the derivation of the master equation is more general than the one that defines the regions in phase space in terms of configurations of adlayers. It applies in principle to any molecular system. However, for an adlayer both lead to the same partitioning of phase space.

The probability to find the system in region R_{α} is given by

$$P_{\alpha}(t) = \int_{R_{\alpha}} \frac{d\mathbf{q}\, d\mathbf{p}}{h^{D}} \rho(\mathbf{q}, \mathbf{p}, t), \tag{2.19}$$

where h is Planck's constant, D is the number of degrees of freedom, and ρ is the phase space density. The denominator h^D is not needed for a purely classical description of the kinetics. However, it makes the transition later on from a classical to a quantum mechanical description easier [47].

The master equation tells us how these probabilities P_α change in time. Differentiating Eq. (2.19) yields

$$\frac{dP_\alpha}{dt} = \int_{R_\alpha} \frac{d\mathbf{q}\,d\mathbf{p}}{h^D} \frac{\partial \rho}{\partial t}(\mathbf{q}, \mathbf{p}, t). \tag{2.20}$$

This can be transformed using the Liouville-equation [48]

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{D} \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right] \tag{2.21}$$

into

$$\frac{dP_\alpha}{dt} = \int_{R_\alpha} \frac{d\mathbf{q}\,d\mathbf{p}}{h^D} \sum_{i=1}^{D} \left[\frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} - \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} \right], \tag{2.22}$$

where H is the system's classical Hamiltonian. To simplify the mathematics, we will assume that the coordinates are Cartesian and the Hamiltonian has the usual form

$$H = \sum_{i=1}^{D} \frac{p_i^2}{2m_i} + V(\mathbf{q}), \tag{2.23}$$

where m_i is the mass corresponding to coordinate i. The area R_α has been defined above by coordinates only, and the limits of integration for the momenta are $\pm\infty$. Although R_α can be defined more generally (we would like to mention reference [49] for a more general derivation), the definition here allows us to go from phase space to configuration space. The first term on the right-hand-side of Eq. (2.22) now becomes

$$\begin{aligned}
\int_{R_\alpha} \frac{d\mathbf{q}\,d\mathbf{p}}{h^D} \sum_{i=1}^{D} \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} &= \sum_{i=1}^{D} \int_{R_\alpha} d\mathbf{q} \frac{\partial V}{\partial q_i} \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \frac{\partial \rho}{\partial p_i} \\
&= \sum_{i=1}^{D} \int_{R_\alpha} d\mathbf{q} \frac{\partial V}{\partial q_i} \int_{-\infty}^{\infty} \frac{dp_1 \ldots dp_{i-1}\, dp_{i+1} \ldots dp_D}{h^D} \\
&\quad \times \left[\rho(p_i = \infty) - \rho(p_i = -\infty) \right] \\
&= 0,
\end{aligned} \tag{2.24}$$

because ρ has to go to zero for any of its variables going to $\pm\infty$ to be integrable. The second term becomes

$$-\int_{R_\alpha} \frac{d\mathbf{q}\,d\mathbf{p}}{h^D} \sum_{i=1}^{D} \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} = -\int_{R_\alpha} \frac{d\mathbf{q}\,d\mathbf{p}}{h^D} \sum_{i=1}^{D} \frac{\partial}{\partial q_i} \left(\frac{p_i}{m_i} \rho \right). \tag{2.25}$$

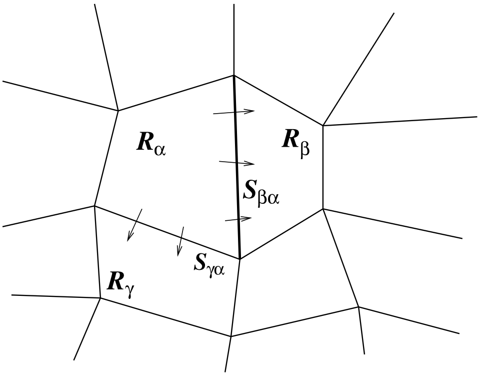

Fig. 2.9 Schematic drawing of the partitioning of configuration space into regions R, each of which corresponds to some particular configuration of the adlayer or catchment region of a minimum of the potential-energy surface. The process that changes α into β corresponds to a flow from R_α to R_β. The transition probability $W_{\beta\alpha}$ for this process equals the flux through the surface $S_{\beta\alpha}$, separating R_α from R_β, divided by the probability to find the system in R_α

This particular form suggests using the divergence theorem for the integration over the coordinates [50]. The final result is then

$$\frac{dP_\alpha}{dt} = -\int_{S_\alpha} dS \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \sum_{i=1}^{D} n_i \frac{p_i}{m_i} \rho, \tag{2.26}$$

where the first integration is a surface integral over the surface of R_α, and n_i are the components of the outward pointing normal of that surface. Both the area R_α and the so-called dividing surface S_α are now regarded as parts of the configuration space of the system [32, 33]. As $p_i/m_i = \dot{q}_i$, we see that the summation in the last expression is the flux through S_α in the direction of the outward pointing normal (see Fig. 2.9).

The final step is now to decompose this flux in two ways. First, we split the dividing surface S_α into sections $S_\alpha = \bigcup_\beta S_{\beta\alpha}$, where $S_{\beta\alpha}$ separates R_α from R_β. Second, we distinguish between an outward flux, $\sum_i n_i p_i/m_i > 0$, and an inward flux, $\sum_i n_i p_i/m_i < 0$. Equation (2.26) can then be rewritten as

$$\begin{aligned} \frac{dP_\alpha}{dt} = {} & \sum_\beta \int_{S_{\alpha\beta}} dS \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \left(\sum_{i=1}^{D} n_i \frac{p_i}{m_i} \right) \Theta \left(\sum_{i=1}^{D} n_i \frac{p_i}{m_i} \right) \rho \\ & - \sum_\beta \int_{S_{\beta\alpha}} dS \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \left(\sum_{i=1}^{D} n_i \frac{p_i}{m_i} \right) \Theta \left(\sum_{i=1}^{D} n_i \frac{p_i}{m_i} \right) \rho, \end{aligned} \tag{2.27}$$

where in the first term $S_{\alpha\beta}$ $(= S_{\beta\alpha})$ is regarded as part of the surface of R_β, and the n_i are components of the outward pointing normal of R_β. The function Θ is the Heaviside step function [51]

$$\Theta(x) = \begin{cases} 1, & \text{if } x \geq 0, \text{ and} \\ 0, & \text{if } x < 0, \end{cases} \tag{2.28}$$

Equation (2.27) can be cast in the form of the master equation

$$\frac{dP_\alpha}{dt} = \sum_\beta [W_{\alpha\beta} P_\beta - W_{\beta\alpha} P_\alpha], \tag{2.29}$$

if we define the transition probabilities as

$$W_{\beta\alpha} = \frac{\int_{S_{\beta\alpha}} dS \int_{-\infty}^{\infty} d\mathbf{p}/h^D (\sum_{i=1}^D n_i p_i/m_i) \Theta(\sum_{i=1}^D n_i p_i/m_i) \rho}{\int_{R_\alpha} d\mathbf{q} \int_{-\infty}^{\infty} d\mathbf{p}/h^D \rho}. \tag{2.30}$$

The expression for the transition probabilities can be cast in a more familiar form by using a few additional assumptions. We assume that ρ can locally (i.e., in R_α and on $S_{\beta\alpha}$) be approximated by a Boltzmann-distribution

$$\rho = N \exp\left[-\frac{H}{k_B T}\right], \tag{2.31}$$

where T is the temperature, k_B is the Boltzmann-constant, and N is a normalizing constant. We also assume that we can define $S_{\beta\alpha}$ and the coordinates in such a way that $n_i = 0$, except for one coordinate i, called the reaction coordinate, for which $n_i = 1$. The integral of the momentum corresponding to the reaction coordinate can then be done and the result is

$$W_{\beta\alpha} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q}, \tag{2.32}$$

with

$$Q^\ddagger = \int_{S_{\beta\alpha}} dS \int_{-\infty}^{\infty} \frac{dp_1 \ldots dp_{i-1}\, dp_{i+1} \ldots dp_D}{h^{D-1}} \exp\left[-\frac{H}{k_B T}\right], \tag{2.33}$$

$$Q = \int_{R_\alpha} d\mathbf{q} \int_{-\infty}^{\infty} \frac{d\mathbf{p}}{h^D} \exp\left[-\frac{H}{k_B T}\right]. \tag{2.34}$$

We see that this is an expression that is formally identical to the TST expression for rate constants [52]. There are differences in the definition of the partition functions Q and $Q^\ddagger$, but they can generally be neglected. For example, it is quite common that the PES has a well-defined minimum in R_α and on $S_{\beta\alpha}$, and that it can be replaced by a quadratic form in the integrals above. The borders of the integrals can then be extended to infinity and the normal partition functions for vibrations are obtained. This is sometimes called harmonic TST (see Chap. 4) [53]. The dividing surface $S_{\beta\alpha}$ is then chosen so that it contains the transition state of the process, which is then also where the PES has its minimum on $S_{\beta\alpha}$.

The W's indicate how fast the system moves from (the catchment region of) one minimum to another. We will often call them therefore rate constants. The system can only move from minimum α to minimum β if the catchment region of these minima border on each other. Only in such a case we have $W_{\beta\alpha} \neq 0$. The right-hand-side of Fig. 2.8 shows the minima of the PES as points. Two minima are connected if their catchment regions border on each other, and the system can move from one to the other without having to go through a third catchment region. The result is the graph in Fig. 2.8. The vertices of the graph are the minima of the PES and the edges indicate how the system can move from one minimum to another.

Although we have presented the partitioning of phase space based on the catchment regions of the PES, this is actually not required. In fact, we have not used this particular partitioning in the derivation up to Eq. (2.30) anywhere. One can in principle partition phase space in any way one likes and derive a master equation. It is the partitioning that defines the processes that the master equation describes. Of course, most partitionings lead to processes that are hard to interpret physically, but there are variations in the partitioning above that are useful.

The dividing surface $S_{\beta\alpha}$ was split to distinguish fluxes in opposite directions. If there is a trajectory of the system that crosses the surface and then recrosses it, then effectively no process has occurred, but both crossings contribute to the rate constants of $\alpha \to \beta$ and $\beta \to \alpha$. For surface reactions such a recrossing is well known for adsorption and leads to the definition of a sticking coefficient (see Sect. 4.4.3). The idea of VTST is to move $S_{\beta\alpha}$ to remove recrossings and to minimize the rate constants [29, 32, 33, 40]. It can be shown that when we have a canonical ensemble, this is equivalent to locating $S_{\beta\alpha}$ at a maximum of the Gibbs energy along the reaction coordinate [54, 55]. The transition state need then not be on $S_{\beta\alpha}$. The transition state need then generally not be on $S_{\beta\alpha}$. As our derivation is a generalization of VTST, it has the same limitations and possible ways to deal with them. We refer to Chap. 4 of [40] for a fuller discussion.

2.2.3 The Master Equation for Lattice-Gas Models

In the derivation of the master equation above the subscripts α and β refer to minima of the PES. We want however a master equation with subscripts referring to configurations. We have already stated that using configurations to derive the master equation gives the same result, but there are some subtleties. So we take a closer look at how minima of the PES and configurations relate to each other. As the coordinates of all atoms have well-defined values for a minimum of a PES, we also know which adsorbate is at each site: i.e., we know the corresponding configuration. So it is easy to go from the minima of the PES to the configurations. The reverse is not true in general.

The first problem is that not all configurations need to correspond to a minimum of the PES. For example, suppose that we have an adsorbate that is so large that there is a very high repulsion when another adsorbate is at a neighboring site. A configuration with two adsorbates at such relative positions may then not correspond to a minimum. The forces between them may push them farther apart and to other sites.

This however does not prevent us from identifying the subscripts in the master equation with configurations. We only need to make sure that the rate constant $W_{\alpha\beta}$ for the process $\beta \to \alpha$ equals zero when the configuration α can not be identified with a minimum of the PES.

The other problem is that there may be more than one minimum of the PES that leads to the same configuration. This is the case when an adsorbate has different (meta)stable structures or adsorption modes. For example, an NO molecule on Rh(100) may be adsorbed perpendicular to the surface with the N end down or it may be adsorbed parallel to the surface [56, 57]. In this case we have a choice. We may regard the different geometries as different adsorbates. This solves the problem, because we then do get a 1-to-1 correspondence between configurations and minima of the PES. Alternatively we may ignore these differences in geometry. We can deal with this by redefining the areas R_α in the partitioning of configuration space. Instead of the catchment region of one minimum, we define them as the union of the catchment regions of all the minima leading to the same configuration. We can also first regard the different geometries as different adsorbates as before and then do a coarse-graining as explained in Sect. 8.2. The result is the same. The advantage of disregarding these differences is that it leads to a simpler model and faster kMC simulations. We need to point out however that disregarding the difference in geometry may constitute an approximation that needs to be justified.

Now that we have established that the master equation can be regarded in terms of configurations of lattice-gas models, we can discuss the advantage this gives us. The number of rate constants $W_{\alpha\beta}$ is enormous even if we use only a small model. Suppose that we do a simulation with a modest 100×100 lattice. Also suppose that we have only one type of adsorbate so that each site can either be occupied or vacant. This gives us $2^{100\times 100}$ different configurations and $2^{2\times 100\times 100} \approx 10^{6000}$ rate constants $W_{\alpha\beta}$. In general, if we have a number of sites S and each site can be occupied in A ways then the number of configurations equals A^S and the number of rate constants is A^{2S}. A lattice model allows us to reduce this number by the same order of magnitude, because what matters is only the number of different non-zero values that the rate constants can have.

First we note that $W_{\alpha\beta} = 0$ unless the change $\beta \to \alpha$ corresponds to an actual physical or chemical process like a reaction or diffusion of an adsorbate. This means that for a configuration β the number of configurations α with values $W_{\alpha\beta} \neq 0$ does not equal the number of possible configurations, but only the number of processes that can actually take place in β. This number is only proportional to the number of sites, and not to an exponential function of the number of sites. So the number of rate constants is thereby reduced to cSA^S with c a constant depending on the number of types of process but not on S.

This is still a huge number of values for the rate constants. Using translational symmetry only reduces this number by a factor S. Point-group symmetry only reduces it by a factor of the order of unity. To reduce it to a workable number of rate constants, we need to make some assumptions. Fortunately, such assumptions are almost always valid and easy to find. The reason why the number of values for the rate constants depends exponentially on the number of sites is that so far we have assumed that the occupation of each and every site in the system can affect these values. This will often be unlikely however. If we have a process involving one site or a pair of neighboring sites, then the occupation of a site well away from this site or these sites will not be relevant. The extreme case is where we only need to look at the sites that change occupation, and which define the process, to determine the rate constant. This means that we have just one value for a desorption of a particular adsorbate, one value for the reaction of two adsorbates, et cetera. Adsorbates that do not desorb, react, et cetera do not affect the value of the rate constant. In such a case the number of different values of the rate constants reduces to c, the proportionality constant introduced above. A large majority of kMC simulations done so far have assumed that this case is valid.

Suppose that the occupation of S_{env} sites in the environment of a process does not change but does affect the value of the rate constant because of interactions with the adsorbates that change in the process. These interactions are called lateral interactions. The number of values of the rate constants is then $cA^{S_{\text{env}}}$. This number need not be large. Suppose we look at CO desorption from a Rh(100) surface. At low coverage we can model this with a square lattice representing the top sites which CO prefers [10]. We also assume that only interactions between CO molecules at nearest-neighbor positions need to be included. We then have $A = 2$. For desorption we have $S_{\text{env}} = 4$ so that there are at most $2^4 = 16$ possibly different values for the rate constants for desorption. For diffusion modeled as a CO hopping from one site to a neighboring one we have $S_{\text{env}} = 6$ and $2^6 = 64$ possibly different values. We can use point-group symmetry to reduce the number of values further.

This example shows that there are situations in which the number of values of rate constants is relatively small even with lateral interactions, but the exponential dependence on S_{env} will often necessitate another approach. We want to reduce the number of values for the rate constants, because these values are generally hard to determine as will be shown in Chap. 4. For a lattice-gas model it is often possible to split the effect of the lateral interactions from the determination of a rate constants without lateral interactions. The determination of rate constants even without lateral interactions is difficult, but need only be done for a few processes. The determination of lateral interactions is also difficult, but here too often only few values need to be determined. It is the large number of combinations of lateral interactions that leads to a very large number of possible values for rate constants with lateral interactions. These combinations can however often be determined quite easily. This is shown explicitly in Chap. 4 and in particular Sect. 4.5. However, the number of values of the rate constants does also determine which kMC algorithm is the most efficient. If the number of values is small, faster algorithms can be used than when we have a large number of values of the rate constants even if these values can be determined easily and fast. See Chap. 3.

To summarize. The reason why kMC simulations of surface reactions can be done much more efficiently than simulations of systems without translational symmetry has to do with the number of rate constants. For surface reactions this number is either very limited when there are no lateral interactions, or can often be computed easily from a limited set of parameters when there are lateral interactions. In both cases only a relatively small number of values need to be determined, although they require costly calculations or time-consuming experiments (see Chap. 4). This can however be done before and separately from the kMC simulations. This is not the case for simulations of other systems.

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