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Lattice gas models and Kinetic Monte Carlo simulations of epitaxial growth

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Abstract. A brief introduction is given to Kinetic Monte Carlo (KMC) simulations of epitaxial crystal growth. Molecular Beam Epitaxy (MBE) serves as the prototype example for growth far from equilibrium. However, many of the aspects discussed here would carry over to other techniques as well. A variety of approaches to the modeling and simulation of epitaxial growth have been applied. They range from the detailed quantum mechanics treatment of microscopic processes to the coarse grained description in terms of stochastic differential equations or other continuum approaches. Here, the focus is on discrete representations such as lattice gas and Solid-On-Solid (SOS) models. The basic ideas of the corresponding Kinetic Monte Carlo methods are presented. Strengths and weaknesses become apparent in the discussion of several levels of simplification that are possible in this context.

1. Introduction

An impressing variety of methods is applied in the theory, modeling, and simulation of epitaxial growth. They range from the faithful quantum mechanics treatment of the microscopic dynamics to the description in terms of coarse grained continuum models. An overview of the field can be obtained from, e.g. [1, 2, 3, 4] and this volume.

The purpose of this contribution is to provide a brief introduction to one of the most widely used approaches: the Kinetic Monte Carlo (KMC) simulation of lattice gas models. It is not intended to give a detailed exhaustive review or historical summary of the many aspects of this line of research. The aim is to introduce and illustrate some of the basic concepts of the method and to provide a starting point for the interested reader. The selection of examples from the literature also reflects this purpose and the list of references is far from being complete in any sense. It is the result of a very personal and often random choice of examples. Numerous important contributions to the advancement of the KMC technique and its applications cannot be mentioned here and the interested reader is directed to, e.g. [1, 2, 3, 4, 5] for further references.

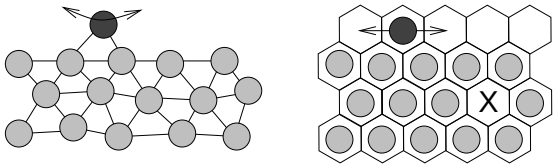

FIGURE 1.
Cartoon of hopping diffusion on a flat surface (cross section).
Left: Particles can assume continuous positions in space, straight lines correspond to nearest neighbor bonds. In an MD simulation, thermal fluctuations of the entire system may result in a jump of the adatom (dark) to a neighboring pair of surface atoms.
Right: Simplifying lattice gas representation of the same situation. Atoms can only occupy pre-defined lattice sites as represented by the hexagonal cells, here. In a KMC simulation, the adatom jumps to the left or right neighbor cell with a given rate. The cross marks a vacancy in the bulk which would be, like overhangs, *forbidden* in Solid-On-Solid models.

Among the different realizations of epitaxial growth, Molecular Beam Epitaxy (MBE) is a particularly clear-cut one [1, 2, 3, 4]. In this technique, one or several adsorbate materials are heated in an oven which is contained in an ultra-high-vacuum chamber. The evaporating particles form an atomic or molecular beam which is directed onto a substrate crystal. Arriving particles are incorporated and contribute to the growing film upon the substrate. The term homoepitaxy is used if the deposited adsorbate and the substrate material are identical, whereas in heteroepitaxy they differ. Apart from the selected materials, the most important experimental control parameters in MBE growth are the substrate temperature and the flux of incoming particles.

MBE has become a well-established technique for the production of high-quality crystals, as it allows for a very precise control of the growth conditions. It is, for instance, possible to add monoatomic layers of a compound semiconductor to the growing film by alternating deposition of the elements in Atomic Layer Epitaxy (ALE).

Molecular Beam Epitaxy is applied, for example, in the growth of layered semiconductor heterostructures for electronic devices or in the development of thin magnetic films for novel storage media. MBE plays also a significant role as a tool in the design of nano-structures, such as Quantum Wires or Dots [6]. The range of materials used in MBE includes conventional semiconductors, elementary metals, metal-oxides, and organic molecules.

Growth in an MBE environment is clearly far from equilibrium, as the system is constantly driven by the deposition flux and an extremely low pressure is maintained in the vacuum chamber. This is different from, say, growth from the

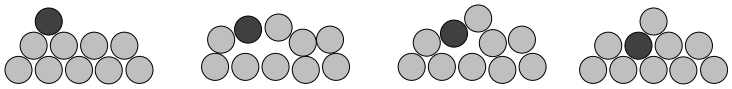

FIGURE 2. Illustration of an exchange diffusion process (cross section). A concerted move of several particle leads to the exchange of the adatom (dark) with a surface atom. Note that, if all atoms represent the same chemical element, the final states of hopping and exchange diffusion in this illustration would be identical whereas the transition states differ significantly.

vapor which can be much closer to thermal equilibrium. This feature makes MBE highly attractive from a theoretical point of view. It provides a workshop in which to put forward analytical approaches and develop tools for the simulation of more general non-equilibrium systems.

In the following section, relevant atomistic processes and some approaches to the theory and modeling of MBE growth are discussed. Many aspects would directly carry over to the physics and modeling of similar growth techniques. In section 3, the basic features of lattice gas models and the corresponding Monte Carlo kinetics are presented and a short conclusion is given in section 4.

2. Atomic scale processes in MBE growth

In MBE, physical processes in a very wide range of time and length scales are relevant. Accordingly, a set of quite different methods of modeling is required when aiming at a more or less complete realistic picture of the growth process.

Ultimately, all macroscopic features of the growing surface emerge from the interactions of atoms and their microscopic kinetics. Therefore, a faithful quantum mechanical description on the atomistic level is clearly desirable. The so-called *Density Functional Theory* (DFT) is particularly suitable in this context [7]. This method is based on the, in principle exact, description of many electron systems in terms of the electron density only. Despite the clear advantage over an explicit treatment of the many particle Schroedinger equation, the computational cost of the method is significant. It is therefore often applied to relatively small systems of a few atoms or molecules, or to unit cells of periodic structures. [1]

As just one example for the latter, by means of DFT calculations it is possible to evaluate and compare the specific ground state energies of different reconstructions of a particular material surface. The calculation yields also the precise structure of the reconstruction, i.e. the location of the atoms. Clearly such information is valuable in the development of models describing the surface or its

[1] The use of relatively vague terms like *relatively small systems* relates to the fact that their meaning steadily changes with the rapid evolution of available computer power.

evolution in a non-equilibrium situation. For examples in the context of compound semiconductor surfaces see [8, 9] and references therein.

The analysis of dynamical properties such as diffusion processes is obviously more involved than the investigation of ground state properties only [10]. Impressing progress has been achieved in recent years in the combination of the DFT approach with other methods such as Kinetic Monte Carlo simulations. Reference [10] gives an introduction to this promising line of research.

Often, the results of DFT calculations depend crucially on the quality of the actual approximations made, which can lead to significant discrepancies in the literature. As an example, a discussion and comparison of energy barriers obtained for diffusion on various fcc(111) metal surfaces is given in [4].

One of the most important tools for describing the temporal evolution of many particle systems is Molecular Dynamics (MD), see for instance [11] and the contribution by K. Albe to this volume [12]. In its simplest version it amounts to the numerical integration of Newton's equations of motion based on classical interactions of the particles. Methods have been devised that allow for imposing a constant temperature or other physical conditions on the system [11].

Frequently, the interactions are given in terms of classical pair or many particle potentials. These can range from simple model interactions to highly sophisticated material specific potentials. The latter can be obtained from first principles, e.g. by means of DFT calculations, or result from fitting suitable parameterizations to experimentally observed material properties. It is also possible to incorporate the quantum mechanics of the system directly into the MD scheme, as for instance in the celebrated DFT-based Car-Parrinello method [13].

Efficient implementations and modern computers allow for the simulation of relatively large systems. However, a serious restriction of all MD techniques remains: the physical real time intervals that can be addressed are usually quite small, see the discussion in [12] (this volume). Even with sophisticated acceleration techniques, such as proposed in [14], it seems currently infeasible to reach MBE relevant time scales of seconds or minutes. MD aims at a faithful representation of the microscopic dynamics in continuous time. The relevant time scale of atomic vibrations in a solid is, for instance, $10^{-12}s$. Hence, an MD procedure should advance time by even smaller steps in the numerical integration.

Consider, as an example, a single adatom on top of a flat surface as sketched in Figure 1. Thermal fluctuations may result in a *jump* of the adatom to a neighboring pair of surface atoms. However, such an event will occur quite rarely. A large portion of an MD computation will be used to simulate the collective vibration of the crystal which does not change the system significantly over relatively long periods of time. It is precisely this difficulty which motivates the basic idea of KMC simulations, see section 3.

As the discussion in section 3 will show, perhaps the most attractive advantage of Molecular Dynamics over standard KMC techniques is that no *a priori*

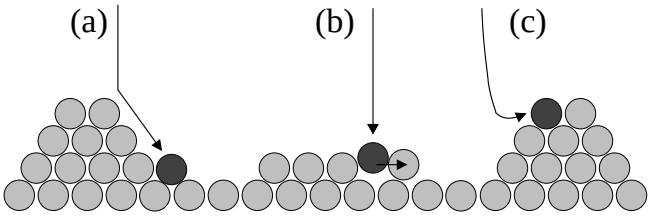

FIGURE 3. Some kinetic effects that may play a role in the incorporation of deposited adatoms.
(a) *Downhill funneling*: the deposited particle slides down a slope until a local minimum of the surface height is reached.
(b) *Knockout process*: the momentum of the arriving particle suffices to push out a surface adatom at a terrace edge.
(c) *Steering effect*: attractive forces can influence the trajectory of the arriving particle significantly. Obviously, (a) and (c) are unlikely to occur both under the same conditions.

assumptions about the possible microscopic processes have to be made. As an example, it is not necessary to know in advance whether adatom diffusion occurs by *hopping* or by concerted *exchange processes* involving many particles, see Figure 2 for an illustration. A similar problem is that of island mobility: in several materials it has been observed that, after mobile adatoms meet and coalesce, they may perform diffusion as a more or less rigid cluster on the surface. Such cluster diffusion can influence the growth kinetics significantly [12]. In principle, an MD simulation which is based on a faithful representation of atomic interactions will produce all relevant single particle or concerted moves *automatically* [12, 14]. In contrast, one usually has to pre-define a catalogue of possible events in KMC simulations, see section 3.

Molecular Dynamics should also be the natural technique for simulating processes which cannot be described as thermally activated. This concerns in particular the *transient mobility* of freshly deposited adatoms on the surface. A more detailed discussion of such processes can be found in [4], which also provides references to related experimental studies of specific materials.

A deposited particle may arrive with a certain momentum at the surface. Not only was the particle part of a directed beam, it may also pick up additional kinetic energy when it is attracted by the surface. The term *downhill funneling* describes one possible consequence: an adatom that arrives at an inclined portion of the surface may slide down the slope until it reaches a local minimum in surface height, see Figure 3 (a) for an illustration of the process. It is clearly to be distinguished from thermally activated diffusion which occurs only after the particle has been incorporated into the crystal surface.

Another possible effect is sketched in Figure 3 (b): the arriving particle may *knock out* an atom at a terrace edge. This process will smoothen a surface and would favor layer-by-layer growth, effectively.

The interaction of the deposited atom with the surface may have a significant impact on the particle's trajectory and may lead to a deviation of the adatom position from the deposition site, cf. Figure 3 (c). Such *steering effects* have been observed explicitly in, e.g., metal epitaxy, see also [4] for references.

The capture of arriving adatoms in weakly bound intermediate states may play an important role as well. For several compound semiconductors it is assumed that one of the elements may reside in a highly mobile state close to the surface before a regular lattice position is reached. Examples in the literature discuss the role of mobile As in GaAs epitaxy [8] or Te in ALE growth of CdTe [9].

Frequently, the deposition process is complicated by the fact that molecules or small clusters of atoms, e.g. dimers, arrive at the surface. Their dissociation may be a highly complex process which is not governed by thermal activation. Again, MD should be the method of choice for the simulation and understanding of the deposition kinetics. In lattice gas models and KMC simulations such processes can be implemented in a highly simplifying effective fashion, at best.

In spite of its practical restrictions, Molecular Dynamics has been and continues to be extremely useful in the context of epitaxial growth, see [12] for specific examples. Simplifying faster techniques like Kinetic Monte Carlo simulations rely in general on the *a priori* knowledge of the catalogue of relevant microscopic processes. In particular when aiming at material specific investigations, MD can provide valuable detailed insights in this context.

3. Kinetic Monte Carlo simulations and lattice gas models

3.1. Thermally activated processes

The Kinetic Monte Carlo method extends the range of accessible time scales by implementing appropriate *short cuts* in the treatment of thermally activated processes. Only those configurations are explicitely taken into account, in which the system resides for significant time intervals. A stochastic process is defined which takes the system from one such state to a neighboring one in configuration space. Obviously, the physical properties must be taken care of when specifying the transition rates.

In order to illustrate the basic idea of the KMC approach, we return to the above example of hopping diffusion, c.f. Figure 1. A simplifying interpretation of such a situation is illustrated in Figure 4: if we assume the rest of the crystal is *frozen*, the adatom moves in a potential energy surface (PES) that results from its interactions with the other atoms. In reality, the underlying crystal rearranges and reacts to any movement of the adatom. However, as long as this does not lead to topological changes, the *frozen crystal picture* is essentially valid and appropriate for the following considerations, see also [16] (this volume). The local minima in the

PES, cf. Figure 4, correspond to the relevant configurations in the KMC approach and are termed the *binding states*. As discussed above, thermal fluctuations will occasionally provoke a jump from one such minimum to a neighboring one. One implicitly assumes that the time required for the actual transition can be neglected in comparison with the time spent in the binding states. Under further simplifying assumptions, only some of which will be discussed below, the typical waiting time for a transition is given by an Arrhenius law of the form

$$\tau = \tau_o \exp\left[\frac{(E_t - E_b)}{k_B T}\right] \qquad \text{or} \qquad r = \nu_o \exp\left[-\frac{(E_t - E_b)}{k_B T}\right] \tag{3.1}$$

for the corresponding rate, respectively, where k_B is Boltzmann's constant. The rate r decreases exponentially with the height $(E_t - E_b)$ of the energy barrier that has to be overcome in the process , cf. Figure 4. E_b is the energy of the so-called *binding state*, whereas E_t corresponds to the *transition state*. The barrier is compared with the typical thermal energy $k_B T$ in the system, i.e. the higher the temperature T the more frequent becomes the event. The prefactor ν_o is termed the *attempt frequency*. In the Arrhenius law it is assumed to be independent of the temperature.

Figure 4 displays the PES as for a single particle in the vicinity of a terrace edge. In the center of the upper or lower terrace, the potential is oscillatory with equivalent minima at the regular lattice sites and identical barriers. Near the edge, however, the shape of the PES shows some distinct features: a very deep minimum is found right at the step due to the good coordination, i.e. the interaction with many neighbors. Consequently, a particle that has attached to the upper terrace will detach with a relatively low rate only. A second pronounced feature is the additional, so-called Ehrlich-Schwoebel barrier E_S [1, 2, 3, 4] for hops from the upper to the lower terrace (or vice versa). Here, the transition state is very weakly bound and hence *interlayer diffusion* is hindered effectively. This can result in the formation of pronounced mounds in the course of growth, see [2, 3, 4] for discussions of the effect.

In Transition State Theory, the Arrhenius law is motivated by arguing that the occupation of binding and transition states should correspond to an effective thermal equilibrium situation. Following this line of thought one obtains directly the form of Eq. (3.1). This and other approaches to the evaluation of transition rates are discussed briefly in [4, 10, 14] and in greater detail in e.g. [17, 18].

In principle it is also possible to determine the attempt frequency by taking into account the (vibrational) entropies, i.e. the free energies of binding and transition state, see [4, 10, 17, 18] and references therein. However such an evaluation can be quite involved and has to go beyond the frozen crystal approximation. Consequently, good estimates of attempt frequencies are hardly available in the literature. Very often it is therefore simply assumed that the attempt frequency is the same for all possible diffusion processes in the system. A popular choice is $\nu_o = 10^{12}/s$, corresponding to the typical frequency of atomic vibrations. Usually,

there is no obvious justification for this crude simplification. In fact, several authors have argued that it is simply incorrect in particular cases, see [4] for example references.

From a practical point of view, the simple picture of a single attempt frequency has several striking advantages: with only one ν_o in the system this quantity can be taken to define the unit of time and does not have to be taken care of explicitly. More importantly, Arrhenius rates with identical attempt frequency are guaranteed to satisfy the condition of detailed balance [4, 5]: for two neighboring binding states b_1 and b_2 with energies E_1, E_2 one obtains directly

$$\frac{r(b_1 \to b_2)}{r(b_2 \to b_1)} = \frac{e^{-E_2/(k_B T)}}{e^{-E_1/(k_B T)}} \tag{3.2}$$

as ν_o and the dependence on E_t cancel in the ratio. The detailed balance condition is by no means a necessary requirement for meaningful simulations, especially not in situations far from equilibrium. However, it conveniently guarantees that the system – in absence of deposition and desorption – would approach the correct thermal equilibrium eventually, i.e. a Boltzmann distribution of binding states [5]. If it is violated one might have to worry, for instance, about unphysical cycles of diffusion events in which the system could pick up (free) energy constantly [20].

Note that deposition and desorption in MBE models necessarily violate detailed balance. Deposition is not an activated process anyway and the discussion of detailed balance is meaningless, the same is true for the kinetic processes illustrated in Figure 3. In desorption a particle has to overcome a barrier which is simply identical with its binding energy at the surface. Hence, desorption can be implemented with the corresponding Arrhenius rate. However, the process is irreversible: in an ideal MBE environment a perfect vacuum is maintained in the chamber and desorbed particles will be removed immediately. The situation differs significantly from a surface that may exchange particles with a surrounding vapor or melt.

The validity of the Arrhenius law for thermally activated processes, Eq. (3.1), hinges on several assumptions, which will not be discussed in detail, here. A more thorough discussion of these conditions and further references can be found in [4, 14, 17, 18], for instance. One important requirement is, loosely speaking, that the minima in the energy surface have to be deep enough to guarantee that
(a) the system remains in the binding state for a significant time interval – Arrhenius rates describe only *infrequent events* correctly.
(b) once the transition state is reached, the system is caught in the neighboring minimum, indeed.
The importance of these conditions can be demonstrated by a counter-example: if an adatom moves in a PES with very shallow minima, thermal fluctuations might very well provoke double or multiple jumps directly to more distant binding states. According to [19] the rate for double jumps can still be written in a form similar to Eq. (3.1) but with an explicit temperature dependence of the prefactor: $\nu_o \propto \sqrt{T}$.

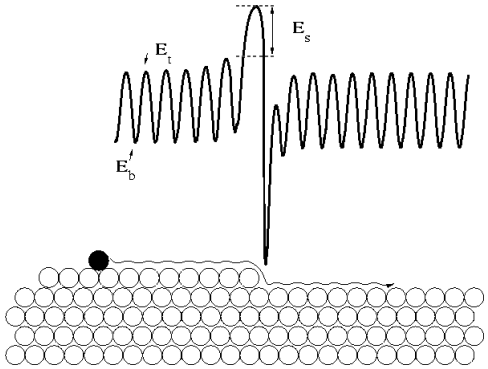

FIGURE 4. Sketch of the potential energy surface (PES) for single adatom hopping diffusion on a terraced surface, courtesy of Florian Much [15]. In this particular example, pairwise interactions according to a Lennard-Jones potential were assumed, see [15] for details. E_b is the energy of a binding state, whereas E_t corresponds to the transition state of hopping diffusion. The Ehrlich-Schwoebel barrier E_S hinders inter-layer hops at the terrace edge.

Most KMC simulations in the literature are indeed based on the above simple Arrhenius picture. In fact, further simplifications are frequently applied, some of which will be discussed in the following section.

3.2. Lattice gas and Solid-On-Solid models

In principle it is well possible to implement the above basic ideas of KMC in off-lattice models with continuous particle positions, see [16] for an example in this volume. It requires the evaluation of the relevant barriers from the PES *on the fly*. The vast majority of KMC studies, however, applies important additional simplifications.

If the material is expected to crystallize in a regular lattice without dislocations or other defects, one might as well pre-define the set of potential lattice sites. In such lattice gas models, a particular site is either occupied or empty and particles can only be placed precisely at one of the sites as illustrated in Figure 1. Diffusion processes are then represented by hops between lattice sites.

The popular class of Solid-On-Solid (SOS) models fulfills further conditions. Assuming that vacancies in the bulk or *overhangs* do not occur in the system, one ends up with a crystal that is uniquely described by the height of the surface above the substrate. A simple cubic model crystal, for instance, is then fully specified by an integer array of variables above a substrate square lattice, see Figure 5 for an illustration.

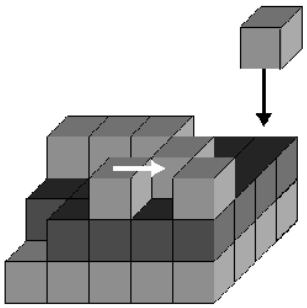

FIGURE 5. Illustration of a simple cubic Solid-On-Solid lattice gas model. For clarity alternating layers are colored differently. As overhangs and bulk vacancies are excluded, the surface is fully characterized by an integer array of height variables above a square lattice substrate. As example processes, the deposition of a new particle (black arrow) and the diffusion hop of an adatom attaching to neighboring particles (white arrow) are shown.

The layout of the actual lattice structure, the design of a catalogue of relevant events, and the assignment of rates can be more or less closely related to the physical reality. The necessary or adequate level of sophistication clearly depends on the problem under investigation. The following paragraphs highlight only a few of the many choices one has to make in the design and simulation of lattice gas models.

The lattice

In principle, all relevant lattice structures can be implemented in a Solid-On-Solid fashion. When aiming at material specific simulations, the correct topology should be represented in the model as it determines, for instance, neighborhood relations and the potential diffusion events. The practical implementation of several lattice types is discussed, for instance, in [5]. To name just one specific example: the (001) surface of a compound zinc-blende structure is represented as an SOS model in reference [9]; the system can be treated as the superposition of four simple cubic sublattices.

One aspect that deserves particular attention is the geometry of the substrate and the use of appropriate periodic boundary conditions in order to reduce boundary effects in the simulation of finite systems. Imposing an inadequate geometry, e.g. using a square shape substrate in the SOS representation of an fcc(111) surface, may result in subtle difficulties. For example, the shape of large islands that align with the lattice axes might conflict with the substrate geometry. In order to avoid such artefacts, the design of the substrate should reflect the lattice symmetries, see [5] for recipes in particular cases.

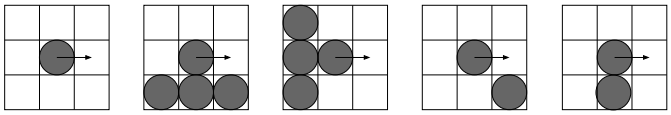

FIGURE 6. Diffusion hops of an adatom on a crystal surface with cubic symmetry, illustration after [24]. In each picture, the adatom in the center is assumed to hop to the right, and four different configurations of the neighborhood (3×3 sites) are shown. In principle there are $2^7 = 128$ possible configurations, due to symmetry only 72 situations are distinct. From left to right, the illustrations correspond to diffusion on a flat surface, movement along a terrace (step edge diffusion), detachment from an edge, and one possibility for the formation of a pair and its dissociation.

Monoatomic simple cubic models are employed frequently in the literature. Whereas they obviously cannot describe any real material faithfully, they serve as prototype systems for the investigation of many basic and qualitative features of epitaxial growth. Several properties of growth processes are believed to be *universal*, i.e. they should not depend on the lattice type and other details of the model, see e.g. [21] and references therein. In the investigation of, for example, scaling laws in kinetic roughening one resorts to the simplest models available [2, 3].

Deposition and transient mobility

An ideal beam of particles in MBE growth deposits, on average, the same amount of adsorbate material per unit time and area everywhere on the substrate. Fluctuations on the atomistic level are usually represented in SOS models by choosing one of the substrate lattice sites with equal probability for each deposition event. Almost always it is assumed in MBE models that single atoms arrive at the crystal, despite the fact that the beam often contains molecules or small clusters of a few atoms which dissociate at the surface.

Effects of transient mobility upon deposition, like the above discussed *downhill funneling* or *knockout* at terrace edges, can be represented very conveniently in SOS models. A simplifying realization of funneling, for instance, amounts to the deterministic search for the lowest surface height in a neighborhood of the deposition site. Clearly, such implementations cannot take into account the microscopic details faithfully, it is only possible to capture the most essential features.

Adatom mobility

In the conceptually simplest models, only the most recently deposited particle is considered mobile at a given time. It may, for instance, move to an available empty site of lower height in a neighborhood of the deposition site and then become immobile. Thereafter, the simulation proceeds with the deposition of another single adatom. Often, only the immediate incorporation of the particle upon arrival at the

surface is modeled, whereas activated diffusion over longer distances is completely neglected. Clearly, this is computationally very cheap and allows for the simulation of large systems and very thick films of, say, 10^6 layers or more. Consequently, such *limited mobility models* are employed, for example, in the investigation of basic phenomena like kinetic roughening of self-affine surfaces, see e.g. [2]. Their applicability in material specific modeling is, however, rather limited in general.

In contrast, *full diffusion models* consider all atoms mobile at the same physical time, in principle. In the simulation, deposition is only one possible event among all other processes and has to be implemented with the corresponding rate. As many adatoms move simultaneously the system displays a much broader spectrum of possible events.

In the standard SOS approach only atoms right at the surface are considered mobile. Bulk particles are surrounded by occupied lattice sites and vacancies are excluded. Unless concerted moves or exchange processes are implemented explicitly, the entire bulk remains fixed. In the example of the simple cubic lattice this could mean that only particles with less then six nearest neighbors are considered mobile at all.

In fact, in many cases the adatom mobility is further restricted due to simplifying assumptions in the model design, see the discussion in the next session. Some of these are made for practical reasons mainly, others reflect peculiarities of the non-equilibrium growth conditions.

The catalogue of events and rates

The key step in designing a KMC lattice gas model is the setting up of the catalogue of possible events. Closely related and equally important is the assignment of rates to the considered processes.

As an illustrative example we consider the diffusion of a single adatom within one layer of a monoatomic crystal surface with cubic symmetry, cf. Figure 6. Already simplifying, let us assume that only hops to nearest neighbor sites occur and that their rates depend only on the configuration of a very small neighborhood of, say 3×3 sites. Only four examples are shown in the illustration, Figure 6, in total there are 72 essentially different neighborhood configurations. For each of those a different rate has to be specified in the model, in principle.

For several material systems, such detailed catalogues of rates have indeed been worked out. For the particular example of diffusion of a single adatom on an fcc(001) metal surface, see for instance [22, 23, 24]. Note, however, that the evaluation of rates by first principles or approximate methods requires a careful analysis of the physical process. For instance, the rate of hopping and potential exchange processes must be compared for each of the configurational changes and the task of finding the correct transition path can be very demanding, see e.g. [25].

The faithful representation of all relevant events in a KMC simulation can be quite involved. In our example, inter-layer hops at terrace edges and the like have not even been included yet. The potential extension to island mobility and other concerted processes would make the catalogue of events even more complex.

For practical reasons or because the required detailed information about the rates is simply not available, one frequently resorts to simplifying schemes. The aim is to capture the essential features of a material system or to study qualitative properties of the growth process.

In some cases it is possible to find efficient parameterizations of the relevant barriers in terms of a small number of independent quantities. *Bond counting schemes* have been particularly successful in this context [4, 5, 23, 26]. The idea is to consider only very few distinct barriers, but to take into account the energies of the involved binding states explicitly. In particularly simple schemes only the energy of the initial state determines the rate, whereas, in general, initial and final configuration are considered. In our example we could assume that the quantity E_o plays the role of the characteristic barrier for all nearest neighbor hops within the layer and assign a rate of the form

$$r = \nu_o \exp[-E/(k_B T)] \qquad \text{with} \qquad E = \max\{E_o, E_o + (E_f - E_i)\}. \tag{3.3}$$

Here, E_i and E_f are the energies of the initial and final state, respectively. In the simplest cases, their determination amounts to counting nearest or next nearest neighbor bonds adding up the associated binding energies. The rate (3.3) is of the Arrhenius form, where the diffusion barrier is directly given by E_o if the number of bonds decreases or remains the same in the process. In the opposite case the energy gain adds to the barrier. Note that the rates in Eq. (3.3) satisfy the detailed balance condition by construction. Apart from the extra barrier, which cancels out in (3.2), the prescription is equivalent with Metropolis like rates in equilibrium MC simulations [5].

If only one characteristic E_o is present in the system, the factor $e^{-E_o/(k_B T)}$ appears in all rates and might be taken to re-define the time scale. However, several such barriers may apply to different types of events, e.g. to planar diffusion or hops along the border of an existing terrace (step edge diffusion). The above discussed Ehrlich-Schwoebel effect, for instance, would be represented by a distinct barrier for inter-layer diffusion.

Often, several processes are excluded explicitly from the simulation. For large enough flux, for instance, the time required for adding an entire monolayer may be much smaller than the typical waiting time for a desorption event. In such a case, desorption may be disregarded or considered *forbidden*, whereas in a vacuum chamber without incoming flux it is clearly relevant and the crystal sublimates, see [9] for the discussion of an example.

One can also expect that the detachment of an atom from a terrace edge or from a small island will occur with a very small rate if typical binding energies are large. Hence, one might consider all detachment processes *forbidden* in an extreme case, which reduces the number of possible events considerably. Note that the implementation of irreversible attachment immediately violates detailed balance as only one of the rates in Eq. (3.2) is non-zero. Again, the justification of the simplification hinges on a comparison of the relevant time scales which are mainly determined by the incoming flux and the substrate temperature.

The risk of missing relevant microscopic processes is one of the main dangers in KMC simulations, especially in the context of material specific investigations. Complicated and – at first sight – counter-intuitive concerted moves may be very well relevant in a specific system. This can lead to an oversimplified catalogue of events. In addition, wrong rates can be assigned to the implemented events whenever alternative pathways to the same final state have been ignored.

On the other hand, the potential to explicitly *allow* or *forbid* certain processes is one of the major strengths of the KMC approach. It allows to investigate the relevance of particular microscopic processes and their influence on the macroscopic properties of the growing crystal systematically. As just one example for this strategy, the role of step edge diffusion on the morphology and scaling behavior of surfaces can be studied by *switching* the process *on* and *off* in simulations, see e.g. [27] and references therein.

Implementation of the Monte Carlo Kinetics

The standard textbook realization of the stochastic Monte Carlo kinetics in computer simulations amounts to (a) suggesting one of the possible events with equal probability, and (b) evaluate or look up its rate r_i and accept or reject it with a corresponding probability.

This conceptually simple strategy is easy to implement and has been widely used in both equilibrium and off-equilibrium simulations [5]. In terms of efficiency its major drawback is that quite frequently a suggested event is rejected and potentially expensive computations have been performed without changing the system at all.

In contrast, *rejection-free* or *event-based* methods do perform one of the possible n events at each step of the procedure. Given a certain configuration of the system, the next process, say event number i, has to be selected with the correct probability $r_i \,/\sum_{i=1}^{n} r_i$. Next, the associated waiting time t_i is evaluated and the physical time in the model is advanced accordingly. For infrequent events as considered here, elementary considerations show that the time t_i is exponentially distributed with mean value $1/\sum_{k=1}^{n} r_k$ [4, 5].

The simplest realization of the correct selection requires only one random number $z \in [0,1]$: the event i which satisfies the condition

$$\sum_{k=1}^{i-1} r_k \leq z \sum_{k=1}^{n} r_k \leq \sum_{k=1}^{i} r_k \tag{3.4}$$

is chosen and performed. The costly linear search can be replaced by more sophisticated tree-like representations of the catalogue of events [5]. In simulations with a limited number of distinct processes it is efficient to group the events according to their rate. However, the basic idea of rejection free simulations remains the same.

The price paid for the gain in efficiency is that, at any given time, all possible processes must be known and stored. Their number and nature as well as their rates can change with every event that occurs in the system. Depending on the structure

of the model this can require sophisticated bookkeeping and costly frequent re-evaluations of all rates.

4. Conclusion

Kinetic Monte Carlo simulations of lattice gas systems constitute one of the most widely used tools in the modeling of epitaxial growth. The success of the approach is due to the fact that it is extremely flexible and versatile.

Conceptually very simple models can be used in the investigation of basic, perhaps universal properties. It is quite straightforward to set up, for instance, a simple cubic model with only a few distinct rates. Such a system can be implemented very efficiently and already allows for the study of various essential phenomena.

On the other hand, lattice gas models offer the potential for material specific simulations, as well. The success of such attempts depends on the availability of detailed information about the microscopic processes. To a certain extent, this knowledge can arise from comparison with experiments. In turn, simulations allow for testing hypotheses about the microscopic causes of macroscopic surface properties.

First principle calculations or approximate theoretical treatments are clearly most desirable as a basis of material specific models. A particularly promising route seems to be the incorporation of such methods into the on-going simulation.

A complete description of epitaxial growth requires the consideration of processes on many different time and length scales. Lattice gas models and Kinetic Monte Carlo simulations in general, will certainly play an essential role in the further development of the multi-scale approach.

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