ELSEVIER

Computer Physics Communications 97 (1996) 82-100

Computer Physics Communications

Numerical simulations in the theory of crystal growth

M. Kotrla[1]

Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 180 40 Prague 8, Czech Republic

Abstract

The methodology of computer simulations of crystal growth is described. Two main methods, kinetic Monte Carlo and molecular dynamics, are discussed. The principle of kinetic Monte Carlo simulations is explained in detail, including recent developments of algorithms. Particular attention is paid to approximations which are made in the construction of discrete growth models. Applications of the Monte Carlo method for three different kind of problems: kinetic roughening, near equilibrium growth, and far-from-equilibrium molecular beam epitaxy growth are presented together with examples of representative results. Possibilities of employing molecular dynamics simulations are discussed as well, and examples of results are also given. The range of applicability of different methods on present-day computers is evaluated.

1. Introduction: microscopic theory of crystal growth

Crystal growth is a very old branch of science and has many important practical applications. In particular, to this field belongs the preparation of new artificial materials by modern technologies that allow to design structures on the nanometer scale. Theory of crystal growth developed from a simple phenomenological description on the macroscopic level to more complex methods [1,2]. In the last two decades more and more effort has been devoted to the understanding of growth phenomena on the microscopic level. This is caused on one side by pure theoretical interest in nonequilibrium phenomena, and on the other side by increasing demands of industrial applications directed to the preparation of well defined structures on smaller and smaller scales.

The main theoretical tool of the microscopic theory are numerical simulations involving the application of two basic methods: *kinetic Monte Carlo* (KMC) and *molecular dynamics* (MD). Both these methods take explicitly into account atomistic processes such as deposition, surface diffusion, adatom attachment and detachment at step edges, desorption, and so on. Both methods also deal with the dynamics of the growth process; however, from the methodological point of view they are different. In MD simulations deterministic dynamical equations of motion for a set of particles are solved, whereas in KMC the growth process is treated as a stochastic process and a probabilistic description based on more or less complicated growth models is used.

The goal of the microscopic theory of crystal growth is a detailed understanding of the mechanisms of growth and of the effects arising from the change of physical quantities and material parameters. To achieve this goal an iterative modeling procedure is used, which consists of the following steps:
(i) formulation of a microscopic model,
(ii) calculation of quantities of interest,
(iii) direct or indirect comparison of the results of

---

[1] E-mail: `kotrla@fzu.cz`

PII S0010-4655(96)00023-9

calculation with experimental data,

(iv) correction or modification of the model.

These steps are repeated until the desired agreement with experiment is obtained. The procedure allows to evaluate the importance of different microscopic processes, to explain experimental results from an atomistic point of view, and possibly even to predict results for a new situation (material).

To be more specific, one is typically interested in the time dependence of theoretical quantities characterizing the morphology of the surface (adatom coverage, average island size, roughness, step density, structure factor, height-difference correlation function and so on) which can be experimentally measured either indirectly using, for example, diffraction measurements (RHEED, TEAS, LEED) or by direct visualization (STM, AFM). Eventually the interest lies in the stationary values of dynamical quantities like, for example, the rate of growth (the average velocity of the interface between solid and fluid). These quantities depend on physical parameters as substrate temperature, supersaturation (difference of chemical potentials, $\Delta\mu = \mu_{\mathrm{solid}} - \mu_{\mathrm{fluid}}$), or flux of incoming particles. The time evolutions (eventually the stationary values) of theoretical quantities which are calculated in some model are compared with corresponding experimental data, usually for several values of the physical parameters. For example, the evolution of the step density is compared with the evolution of RHEED intensity for different substrate temperatures.

Computer modeling of the crystal growth has already a long history (for a review of the older results see Refs. [3,4]) during which, however, mainly MC simulations have been used. The first applications of MC concerned thermal surface roughening [5], growth-rate dependence on supersaturation and temperatures [6-8], equilibrium and growth morphologies of crystals [9], transitions between modes of growth [10] and the effect of a screw dislocation on growth [11]. Most of these studies were only qualitative, not related to any specific material. Later MC simulations were applied to molecular beam epitaxy (MBE) growth in far-from-equilibrium conditions (see [12-14] for reviews and Subsection 4.3 for further references). Models for specific semiconducting materials were developed and activity in this field is still continuing. Another more academic application of MC simulation of growth, which began in the middle of the eighties, is the study of kinetic roughening [15-19] (see Subsection 4.1). As far as molecular dynamics is concerned, it cannot be used for a realistic simulation of the crystal growth but it has been applied to the study of elementary dynamical processes during the crystal growth, as diffusion or impact phenomena (see Section 5).

Due to the complexity of the phenomena studied, some approximations are necessary. In almost all works quantum effects are disregarded and the classical description is used. In order to estimate a possible importance of quantum effects a full ab initio calculation taking into account electronic degrees of freedom is required. Molecular dynamics calculations of this kind are, however, extremely demanding in computer power and even simulations of elementary growth processes on ab initio level are quite rare up to now. Nevertheless, a lot of electronic structure calculations of static properties of surfaces have been performed, and these results provide valuable information about the states of the system. Hence, ab initio calculations constitute another approach which can improve our understanding of processes on the microscopic level, although applications to dynamical processes are still very limited.

A further common approximation concerns the concept of local equilibrium-local thermodynamic equilibrium between the growing film and the bulk (substrate). Growth is an intrinsically nonequilibrium process, but nevertheless, in the description (even of the far-from-equilibrium growth) it is often supposed that the local equilibrium exists. This assumption allows to introduce thermodynamics quantities, for example the temperature.

There are various physical situations which have to be treated in the theory in a different way and in which different approximations can or cannot be used (I shall explain these further approximations in detail in Section 2). Most of all, it is very different if the crystal is growing from a gas (vapor) or from a liquid (melt). The growth from the gas is simpler to describe since the gas can be modeled more easily, whereas the correct description of a liquid is not an easy task. There are also other specific aspects which should be taken into account: whether the growth is free or directed, whether the growing crystal contains one or more components, whether the growth is quasi two-dimensional or three-dimensional, what is the geometry, and so on. Although some of the statements in this paper will be of general validity, I am not going to cover all of these different situations, but I shall concentrate on the single-component[2] growth from gas. However, I shall discuss both near equilibrium and also far-from-equilibrium growth.

In this review I shall explain the methodological aspects of computer simulations of crystal growth illustrated by selected examples. I do not attempt to present a complete review of any particular physical problem, and I refer the reader to existing review articles on the simulation of molecular beam epitaxy growth [12-14,21], on kinetic roughening [15-19], or on adatom diffusion [22]. Due to the large variety of physical situations, some of which require a specific modification of the method, even the methodological part will not be complete and is biased by the author's interest; nevertheless, I shall attempt to describe the main ideas and to evaluate the applicability of different approaches.

The plan of the paper is as follows. First I shall describe the construction of discrete models which are used in KMC as well as further approximations which are made in this approach (Section 2). The method of KMC is then explained in Section 3. In the next section, examples of applications for three different problems are given: kinetic roughening (Subsection 4.1), growth near equilibrium (Subsection 4.2), and molecular beam epitaxy (Subsection 4.3). In Section 5, possibilities of employing MD simulation in the study of growth phenomena are discussed. Finally, Section 6 contains an evaluation of the applicability of different methods and conclusions.

2. Models of crystal growth

KMC simulations of growth are based on simplified growth models. In this section I shall explain the construction of these models. The strategy is, as usual, to concentrate on a few presumably important aspects (processes) and disregard other details. In principle MC can be applied to both continuous or discrete models, however, in most simulations *discrete models* are used and I shall consider only these models here. This simplifies things a lot but it is, of course, an approximation.

Growth models have two essential ingredients: a geometrical part and a dynamical part. In the case of discrete models both crystal and vapor are described in a crude approximation: particles can occupy only discrete positions on some lattice. The system of solid and vapor is in this way approximated by a lattice with some sites occupied by particles and some left empty (lattice gas). The regions of high concentration of atoms correspond to the solid and the regions of low concentration of atoms to the vapor (Fig. 1a). In this picture one is interested only in structural properties and many features of the real crystals are neglected. Atoms are treated as static classical objects[3], therefore mechanical, chemical, optical, and other properties have to be disregarded. The lattice gas model is a strong but acceptable approximation for a crystal, it is quite a good approximation for a (not very dense) gas phase; it is problematic for a liquid. The lattice gas model can be also justified for growth from solution if the concentration is not very high.

In a discrete model we describe the system of solid and vapor as a lattice gas. It is natural to use the lattice with the same symmetry as is the symmetry of the crystal, but in some simulations the approximation is even more crude: a simple cubic lattice is used instead of the real structure of the material. This simplifies technically the simulation and in the spirit of approximate modelling one can still expect to get useful results when explaining observed phenomena. However, some effects may be lost [23].

The schematization goes one step beyond assuming a lattice gas. One can suppose that the processes inside the fluid can be neglected and that the growth can be well described only by processes at the interface between the fluid and the solid (Fig. 1b). On the same level of approximation one can also neglect bulk diffusion inside the crystal. In this picture we are interested only in movements of atoms representing the solid and the growth proceeds by adding atoms at positions determined by growth rules (see below). This is a well-

---

[2] It does not mean that we have to restrict to pure monatomic materials. Growth of a multi-component crystal can be dominated by the dynamics of one component. It is, for example, the case in the growth of GaAs. Under normal growth conditions the growth of GaAs can be well described by the growth of Ga only [20].

[3] In consequence of this fact interactions between atoms in a discrete model are necessarily artificial and the interaction parameters introduced are only effective.

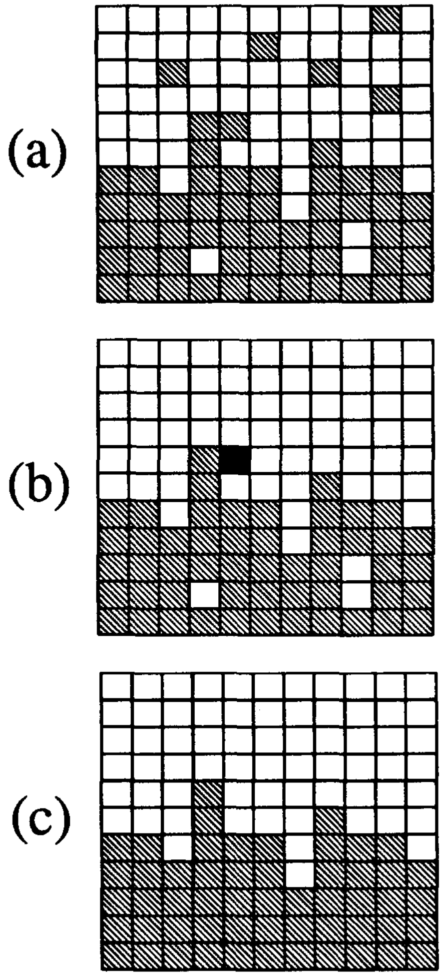

Fig. 1. Hierarchy of approximations in discrete growth models illustrated in the case of two dimensions (a) The configuration of lattice gas with the bottom region corresponding to solid and the top region corresponding to gas Atoms are represented by hatched squares. (b) Positions only of atoms of the solid are considered, new atoms are added by growth rules defined in a model. The darker square indicates the overhang. (c) Surface configurations in the SOS approximation.

justified approximation for ballistic growth when mutual interactions of particles in the fluid are negligible. An important example is MBE growth, where the surface is directly bombarded by atoms. Omission of processes inside the phases is problematic for growth from melt, and it may be also a quite crude approximation in the case of growth from vapor not far from equilibrium [24]. In these situations there are gradients of physical quantities (pressure, temperature) in the vicinity of the interface. Atoms inside the fluid are diffusing towards the interface where the growth process takes place. Again, one can hope that using appropriate growth rules a good qualitative model can be formulated, but the correct description of processes inside the phases may be crucial in some cases.

On top of these approximations, in the case of growth with planar interface and under conditions where very few vacancies and overhangs (cf. Fig. 1b) appear in the growing material, one can use the so-called solid-on-solid (SOS) approximation (Fig. 1c). It means that each atom is sitting on top of another atom: then the surface is described by a single-valued function, $h(x)$, of the substrate coordinate x. In all applications described below (Section 4) I shall deal with this situation.

Although the most interesting problem is the growth in three-dimensional space sometimes the growth in two-dimensional space is also of interest, one example being the growth of step edges. Let us introduce for further purposes some general notation. We denote by d the dimensionality of the physical space and by $d' = d - 1$ the dimensionality of the surface. The system size will be denoted by L.

The second ingredient of any growth model is the definition of dynamical growth rules. Also here some approximations are necessary. It is usually supposed that the motion of individual particles (atoms or molecules) take place instantaneously and that the motions are independent and Markovian. In order to develop a minimal model one selects only processes which are supposed to be relevant for phenomena to be studied, and other deemed inessential are ignored. Particles in the model are moved from site to site with a frequency proportional to the rates of processes. If we consider for simplicity the growth of a monatomic material, then the basic elementary processes (after omission of bulk diffusion) are the following: deposition of an atom on the surface, migration of an adatom on the surface and desorption of an atom from the surface. In the case of a multicomponent material, elementary processes for each component have to be considered separately. In principle quite complex rules, for example, for chemical reactions could be included.

Usually the rates of elementary processes are very little known and they are guessed with the use of all available experimental and theoretical information. They often depend on the local surroundings, in the crudest approximation dependence only on the occupation of nearest neighbors is considered (but again a quite complex dependence can be considered). I shall describe examples of SOS models with specific growth rules in Subsections 4.1, 4.2, and 4.3. I would like also to note that in the context of fractal growth a whole menagerie of growth models has been suggested [25,26,16,19] with applications ranging from crystal growth through aggregation phenomena to biological growth.

3. Kinetic Monte Carlo

Ordinary MC is a method for the calculation of average values in a given *equilibrium* thermodynamical ensemble. States in a space of configurations are generated and used for the calculation of quantities of interest [27-29]. The focus is on the convergence of series for the calculated quantities, and one is not interested in the generation of a sequence of states which properly corresponds to the dynamics of a system (in many cases the opposite is true [30]). Kinetic MC is a procedure for solving kinetic equations. The aim of KMC is to reproduce faithfully *nonequilibrium*, or *relaxation* processes. This time the emphasis is on the correctness of time evolution in the simulation. Before describing the methods of KMC, I shall first briefly recall the basic idea of thermodynamical MC.

3.1. Thermodynamical Monte Carlo

Let us denote the space of all possible configurations, C, in a statistical-mechanical model by $\mathcal{S} = \{C\}$, and by $P(C)$ a time independent distribution (for example, the canonical distribution) on this space. Let A be a quantity of interest (magnetization, energy, and so on). We want to calculate the average value $\langle A\rangle = \sum_C A(C)P(C)$. In MC a sequence of configurations, C_k, $k = 1,...,M$, is generated in such way that they form a Markovian chain with a distribution converging to the desired distribution $P(C)$. This chain is then used for the construction of series for the quantities to be calculated. In order to generate the Markovian chain one needs a matrix of *transition probabilities*, $W(C \to C')$, between two states. The transition probabilities in the standard thermodynamical MC do not need to have any relation to the dynamics of the system. They are not considered as given a priori but they are constructed in a way that guarantees that the distribution of generated states converges to $P(C)$.

At each MC step a trial configuration is generated, which is then either accepted or rejected. The inner loop of the algorithm in the kth time step is as follows.

Algorithm 1

```
(i) Generate a new configuration $C'$ from the original configuration $C_k$.
(ii) Calculate the transition probability $W(C \to C')$.
(iii) Generate a random number $r \in [0,1)$, with a uniform distribution.
(iv) Compare $r$ with $W(C \to C')$, if $W(C \to C') > r$ then accept the new configuration, $C_{k+1} = C'$, or else reject it, $C_{k+1} = C$.
```

This is repeated until some convergence criterion is fulfilled, and the calculation stops.

The condition of *detailed balance*,

$$W(C \to C')P(C) = W(C' \to C)P(C'), \qquad (1)$$

is a sufficient (but not necessary) condition for the convergence of the generated Markov chain[4]. There is freedom in the choice of the form of W's, provided the convergence is guaranteed. The most common choice is that of Metropolis et al. [31] which can be formally written as

$$W^{(M)}(C \to C') = \min\left(1, \frac{V(C' \to C)P(C')}{V(C \to C')P(C)}\right), \qquad (2)$$

where $V(C \to C')$ is some "underlying ", or "trial", stochastic matrix specifying possible transitions. For example, in the case of the Ising model, when the trial to generate a new configuration consists in flipping of one randomly selected spin we have $V(C \to C') = 1/\mathcal{N}$ ($\mathcal{N}$ being the number of sites) when C' differs from C just by one spin, and $V(C \to C')$ is zero otherwise. (In the case of a cluster algorithm [32] V has a different form.) If $P(C)$ is the canonical distribution, $P(C) = e^{-\beta E_C}/Z$ (β being the inverse temperature and E_C an energy of the configuration C), one recovers the popular form of $W^{(M)}(C \to C')$: a possible new configuration C' is accepted with certainty if it has a lower energy than the initial configuration C, and

---

[4] More precisely, it is one of the conditions together with other assumptions which are ergodicity, $\forall_{C,C'} W(C \to C') \geq 0$, and $\forall_C \sum_{C'} W(C \to C') = 1$.

with the probability $e^{-\beta(E_{C'}-E_C)}$ if $E_{C'} \geq E_C$. Notice that W's are normalized between zero and one. It is easy to check that the detailed balance is satisfied for the Metropolis choice. There are also other possibilities for the choice of the transition matrix [33,34], but one can expect that the Metropolis form is more efficient than alternatives, since it makes the acceptance rate as high as possible.

The Monte Carlo technique can be also viewed as a method of solving the master equation associated with the transition probabilities W,

$$\frac{\partial P(C,t)}{\partial t} = -\sum_{C'} W(C \to C')P(C,t) + \sum_{C'} W(C' \to C)P(C',t), \qquad (3)$$

which describes a stochastic process in the Markovian approximation [35]. Here, $P(C,t)$ is the probability distribution of configurations at time t.

It should be clear that a straightforward application of the algorithm 1 cannot be expected, in general, to describe correctly the dynamic properties. In the calculation of static quantities, the configurational changes do not need to correspond to physical events. It is only important that the transition probabilities which are used produce the correct equilibrium solution of the master equation (3). Note that for $P(C,t) = P(C)$, both sums on the r.h.s. of (3) exactly cancel due to the detailed balance condition (1).

3.2. *Principle of kinetic Monte Carlo*

About 20 years ago MC started to be used also for the study of kinetic processes [36,37]. In this case the configurational changes have to correspond to real events. Each of the events can happen with some probability per unit time (rate). To be specific, let N be the number of possible events in a given configuration C; in the case of crystal growth they are, for example, the hopping of an adatom, the adsorption of an atom, and so on. The rates of these event are R_a, $a = 1,...,N$. Both N and the set $\{R_a\}$ depend on the configuration C. Let us define the total rate

$$Q = Q(C) = \sum_{a=1}^{N} R_a. \qquad (4)$$

The transition probabilities can now be formally written as

$$W(C \to C') = \sum_{a=1}^{N} R_a V^a(C \to C'), \qquad (5)$$

where $V^a(C \to C')$ is again an "underlying" stochastic matrix for an event a, specifying whether the transition $C \to C'$ is possible by this event. The stochastic evolution of the system is again described by the master equation (3) with transition probabilities (5). KMC is a method of solving this equation. The way of solving is similar as in the thermodynamical MC: making random choices a Markov chain is generated. However, now this chain has to represent a possible evolution of the simulated system. In the simulation event a should occur with probability $R_a/Q(C)$. It is realized in a way that possible events are selected with probabilities proportional to their physical rates[5]. In principle, transition probabilities in KMC do not have to obey the detailed balance condition (1), but it was observed [38] that in the case of diffusion it is advantageous to use models with rules which satisfy this condition.

A simple, straightforward way to implement the idea of KMC is the following. Select the largest rate $R_{\max}$ of all rates of possible events in a model, calculate the relative probabilities $P_a = R_a/R_{\max}$ and create the list of possible events in the starting configuration. Then in each time step use the algorithm 2[6]:

Algorithm 2

(i) Select a possible event which can be realized in the starting configuration C_k.
(ii) Generate a uniform random number, $r \in [0,1)$.
(iii) Compare r with the probability of event P_e, if $r \leq P_e$ then carry out this event leading to a new state $C_{k+1} = C'$, if not stay in the same state.

However, this algorithm is not used in practice because in many cases, in particular in the problems of

---

[5] Also here some approximation enters, since usually in the simulations white noise is used and the real situation may be more complicated. In principle one can use in the simulation also other kinds of noise but this will be still only an attempt to model the reality.

[6] Several other algorithms were suggested in [36]. Probabilities P_a can also be calculated from the fraction $R_a/Q(C)$. Then they are, however, depending on the configuration and have to be updated at each time step.

crystal growth, it can be quite slow. The reason is that there could be a large difference (many orders of magnitude) in rates for different events. The low probability events are then selected and often rejected. For example, in the simulation of diffusion, the program would select the movement of a highly coordinated atom and a low coordinated atom with the same frequency, but the atom with high coordination moves very little in comparison to the low coordinated atom. The ratio of both rates is proportional to $e^{\beta \Delta E}$, where ΔE is a difference in the binding energy of both atoms. This procedure leads to many unsuccessful attempts especially for low temperatures. Sometimes the low-rate processes can be disregarded and not included in the model, but in some situations the low-rate events have to be necessarily performed during the evolution because the system has to pass through states where these events are dominant. An example of this situation is the nucleation of an island on a flat surface in the onset of layer-by-layer growth close to equilibrium. In this case the probability of condensation of an adatom on the flat surface is much smaller than the probability of desorption of that atom. In reality a critical island is formed after many fluctuations, and it is difficult to simulate these fluctuations by the simple algorithm described above.

A much faster algorithm without unsuccessful attempts (also called N-fold way algorithm) was formulated by Bortz, Kalos, and Lebowitz (BKL) [39] for the Ising model, and it is often used in KMC simulations of crystal growth [40,41]. I shall describe first the simplest variant of this algorithm. Let us consider again the kth time step, and use the same notation as before.

Algorithm 3 (BKL algorithm)

```
(i)   Choose a random number $r$ with uniform distribution in the range $[0,Q(\mathcal{C}_k))$.
(ii)  Find the corresponding event. This is done by the choice of the first index $s$ for which $\sum_{a=1}^{s} R_a(\mathcal{C}) \geq r$.
(iii) Carry out event $s$ leading to a new configuration, $\mathcal{C}_{k+1}$.
(iv)  Update those $R_a$ that have changed as a result of event $s$, update $Q$ and any data structure being used.
```

The whole procedure is repeated in the next time step and so on, until the simulation is complete.

This algorithm shows how to circumvent the problem of small acceptance probabilities, but it is usually not applied in this form but in a modified more effective form (cf. Algorithm 4 below). Let us consider the dependence of the computer time needed on N, which is related to the system size. Steps (i) and (iii) take a time independent of N, but step (ii) is time consuming. If the linear search is used the search time is $\mathcal{O}(N)$. Since the growth rules are usually local the updating in (iv) does not have to cost too much computer time, although careful programming is needed. One has to identify events which are not possible any more in a new configuration, they have to be removed from the list, and new events which become possible have to be added to the list. Depending on the data structure used, the time needed in step (iv) is $\mathcal{O}(N)$ at the most.

A faster algorithm according to Maksym [40] can be obtained if one considers, instead of individual events, groups of events. Let us group events into n groups, labeled by $\alpha = 1, \ldots, n$. This can be done either formally forming groups with the same number of events, which allows maximal effectivity of the algorithm, or in a way which keeps physics clear, forming groups of the same kind of events, corresponding to a certain kind of process (diffusion of an adatom over the specific energy barrier, desorption of an atom with the specific binding energy, and so on). Let us consider explicitly the second case: each group will represent a certain kind of process, all processes in a group have the same rate ρ_α.

In a given configuration, $\mathcal{C}$, there are some possible processes, and each kind of a possible process can be realized in one or more ways, by one or more events. Let that a process α can be realized in $n_\alpha(\mathcal{C})$ ways, in the configuration $\mathcal{C}$. I shall call quantities $n_\alpha(\mathcal{C})$ multiplicities. For example, there may be $n_{\mathrm{adat}}(\mathcal{C})$ adatoms with the same surroundings which can diffuse, or there are $n_{\mathrm{dep}}(\mathcal{C})$ sites where a new particle can be deposited. Some particles can take part in more processes, and some processes may not be possible in the given configuration. To each kind of process we assign a partial rate, $q_\alpha(\mathcal{C}) = n_\alpha(\mathcal{C})\rho_\alpha$, and a relative probability, $p_\alpha(\mathcal{C}) = q_\alpha(\mathcal{C})/Q(\mathcal{C})$, which are conditional to the given configuration. The total transition rate in a configuration $\mathcal{C}$ is now $Q(\mathcal{C}) = \sum_{\alpha=1}^{n} n_\alpha(\mathcal{C})\rho_\alpha$. In each step of the simulation (in the given configuration) the multiplicities of processes are known. The algorithm in the kth step of the simulation proceeds as follows.

Algorithm 4

(i) Choose a random number r_1 in the range $[0,Q(\mathcal{C}_k))$.

(ii) Decide which kind of process will take place choosing the first index σ for which $\sum_{\alpha=1}^{\sigma} q_\alpha(\mathcal{C}) \geq r_1$.

(iii) Select a realization of the process σ. Technically this can be done with the help of a list of coordinates for each kind of movement, and an integer random number r_2 in the range $[1,n_\sigma(\mathcal{C}_k)]$; r_2 is generated and the corresponding member from the list is selected.

(iv) Perform the selected movement.

(v) Update multiplicities n_α, relative rates q_α, the total rate Q and any data structure being used.

To estimate computer time demands let us suppose that the multiplicities are approximately the same, $n_\alpha \approx N/n$. The search has two parts: searching for the group, which takes time $\mathcal{O}(N/n)$, and searching within the group, which takes time $\mathcal{O}(n)$. Minimizing the total time leads to an optimal number of groups $n \propto N^{1/2}$, and the computer time then scales as $\mathcal{O}(N^{1/2})$.

An even faster algorithm for large N can be obtained if we instead of the two level search scheme, use a $K > 2$ level search scheme [42], i.e., if we divide the groups into subgroups, and these subgroups again into smaller subgroups, and so on down to the level K. Then the total search time scales as $\mathcal{O}(KN^{1/K})$. The best asymptotic behavior $\mathcal{O}(\ln_2 N)$ is obtained by using the largest possible K, for which there are only two events in the lowest level subgroups. In practice, for typical simulation sizes, $K = 4$, or $K = 5$, can give a faster scheme than the $\mathcal{O}(\ln_2 N)$ method [42].

I shall conclude this subsection with several comments:

(a) In kinetic Monte Carlo simulations one has to take care about similar sources of possible errors (defects in pseudorandom number generators, finite size effects, and so on) as in the thermodynamical MC. Also similar techniques (periodic boundary conditions, finite size scaling, and so on) are used. Since these simulations are usually very long, it is useful to write the code in a way allowing to restart the calculation from a checkpoint in the case of system failures.

(b) The same algorithm can be applied also to other problems (both equilibrium and nonequilibrium) where there are large differences in rates for different events, or in other words, where during the dynamical evolution the system is mostly trapped in deep local minima (as it happens for example in glasses).

(c) The advantage of the BKL algorithm is that in each time step a configuration is generated. But even with this algorithm the system can be trapped in isolated deep minima. We force it to make a transition out of them, but very shortly after having escaped a minimal configuration, the system simply falls back into it. Recently Krauth and Pluchery [43] suggested an algorithm in which in each step a *new* configuration, different from the previous, is selected. They showed that this gives an improvement of several orders of magnitude in computational speed with respect to the BKL algorithm. This modification is especially useful for "tough" optimalization problems [43] but it is not expected to be convenient for the study of growth.

(d) Another nice feature is that the BKL algorithm allows to take into account easily additional constraints on possible configurations as, for example, restrictions on the difference of height between nearest neighbours in the restricted SOS model; ($|h_i - h_j| \leq K$, i, j being nearest-neighbour sites, K is some integer). One consider only those processes which conserve the constraint, and does not have to check explicitly whether the constraint is satisfied.

(e) It has been found [30] that dynamical quantities measured in MC depend on the choice of transition probabilities, and that neither Metropolis (although it is the most effective in respect of the convergence), nor Kawasaki dynamics can be expected, in general, to describe correctly thermally excited, time dependent phenomena. The form of the transition probabilities should be chosen in agreement with physical processes.

3.3. Time in kinetic Monte Carlo

Now I would like to discuss the calculation of time in MC simulations. There is no real time in thermodynamical MC, and usually the number of steps, or better the number of steps per site (number of sweeps) is used as "time". But we need to know the real time in the simulation of dynamical processes in order to calculate correctly time dependent physical quantities, or time derivatives like rates of growth, and so on. Hence, we need to find some relation to the real physical time t. The number of MC steps, which I denote by t_{MC}, is clearly not the correct measure, since it does not take into account that different processes last different time intervals. Nevertheless, in some cases in a good approximation one can take $t \propto t_{\mathrm{MC}}$. This is true, for example, when the system evolves periodically in the space of states and the time interval is sufficiently long. This is the case of more or less perfect layer-by-layer growth. Or we can find a quantity which is easy to measure is the simulation and which is proportional to the real time. This is the case of far-from-equilibrium growth when there is a constant flux of particles falling on the surface, and when all particles are incorporated. Then the number of layers grown is proportional to the real time. In this case the kinetics is trivial (constant velocity), but one can look at the dependence of geometrical properties as a function of t_{MC}.

It the situation when we cannot justify proportionality $t \propto t_{\mathrm{MC}}$ we need to introduce somehow the physical time into a KMC simulation. This can be done provided some assumptions are justified [44]. Suppose that all physical processes can be separated so that in any time instance only one event takes place, and that the events are Poisson processes [35]. Let us have again N processes with rates R_a, $a = 1, \ldots, N$ as before. Then the probability that in time t (measured from zero) there were p events is $P(p) = [(Qt)^p/p!]e^{-Qt}$, where Q is again $Q = Q(C) = \sum_{a=1}^{N} R_a$. The time interval between two successive events (waiting time), τ, is a random variable with the distribution $P(\tau) = Qe^{-Q\tau}$, and the average value $\langle\tau\rangle = 1/Q$. This consideration allows us to generate a time increment between two events in KMC. In point (iv) of the above-described Algorithm 4 we will also generate another random number, r_3, uniformly distributed between 0 and 1 and calculate a time interval, $\Delta t_k = -[1/Q(C_k)] \ln r_3$, spent before the passage to a new configuration C_{k+1}. Note that $Q(C_k)$ depends on the configuration C_k. In an approximation one can only suppose that the system stays in the state C_k for a time inversely proportional to the total transition rate $Q(C_k)$ [45].

Mean quantities during the growth are then calculated as time averages over M time points,

$$\langle A\rangle = t^{-1}\sum_{k=1}^{M} \Delta t_k A(C_k), \tag{6}$$

where the total time is $t = \sum_{k=1}^{M} \Delta t_k$. It was tested that this procedure agrees with the results of the exact solution of master equations [45].

4. Applications of MC method

4.1. Kinetic roughening

The study of kinetic roughening is connected with previous activity on fractal growth [25,46]. In kinetic roughening one is interested in the evolution of roughness during growth. A remarkable fact is that there is a scaling with the time and the system size (self-affine scaling) [47], which is characterized by two independent exponents, called the dynamic (z) and the roughness (ζ) exponent. This allows to classify different kinds of growth from the statistical-mechanical point of view. In fact, it has been observed that asymptotic values (values for very large system size and long time) of the exponents z and ζ can take only some definite values corresponding to different universality classes.

There has been much interest in the study of kinetic roughening in various growth models, which were motivated by different physical situations; for reviews see Refs. [15-19]. There are two approaches in this field: (i) investigation of stochastic continuous equations describing growth, and (ii) numerical simulation of discrete models. Here I shall discuss only the simulation of discrete models. These models are usually much simpler than models used in qualitative, or semi-quantitative studies of growth (see the two following subsections). The reason is that it is believed that the scaling behavior is universal, i.e., that it is the same in a simple (toy) model as in a more realistic but also more complicated model of the same physical situation provided that both capture the same essential features of a growth process.

Several universality classes have been found. Two most important are the Edwards-Wilkinson [48] (EW) class and the Kardar-Parisi-Zhang [49] (KPZ) class. In many growth models (ballistic deposition, restricted SOS model, Eden model) the KPZ behavior was observed and the results agreed with the

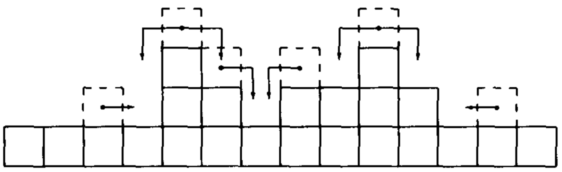

Fig. 2. Growth rules for the Wolf-Villain model in 1+1 dimension. Arrows indicate all possible jumps which can happen after incidence of a new particle (dashed box).

concept of universality - a small change in the growth rules did not caused a change of exponents. Physically this behavior is observed in situations where lateral correlations are important; this kind of growth is not volume conserving. The EW class corresponds to simple conserved growth leading to a relatively smooth surface. An example of the physical situation is the process of sedimentation of small material particles in a liquid caused by gravity.

Recently, much effort has been devoted to the identification of a possible universal behavior of MBE growth in which the dominant physical mechanism is surface diffusion. Several simple discrete models have been suggested [50-54] in which a particle relaxes only immediately after deposition and then remains immobile for the rest of the simulation. Because of this unrealistic feature these models are called "toy" models with surface diffusion. The Wolf-Villain (WV) model [50], which I present as the first example (Fig. 3), is one of them. A particle arriving at a randomly selected site moves to a site which provides the highest coordination (number of bonds to nearest-neighbors). Although the WV model looks very simple it turned out that finding a universal behavior for models with surface diffusion was not easy and very extensive numerical simulation were needed [55].

In the earlier works on toy models with surface diffusion different exponents were measured [50-54]. These results did not allow a clear identification of the universality class. Later it was found that this is due to the fact that such models have a complicated structure of slow crossovers [56,57]. Hence, to observe the true asymptotic behavior more extensive simulations were needed. In Fig. 2 I show the time evolution of the surface width (roughness) in the WV model in 1+1 dimensions. The crossover to slope 0.25, corresponding to the EW class, can be seen at a long time after more than $\approx 10^6$ deposited layers. Another peculiar feature of these models is that they show an anomaly in the scaling [58,56]. Moreover, in some cases growth turned out to be unstable [59,55].

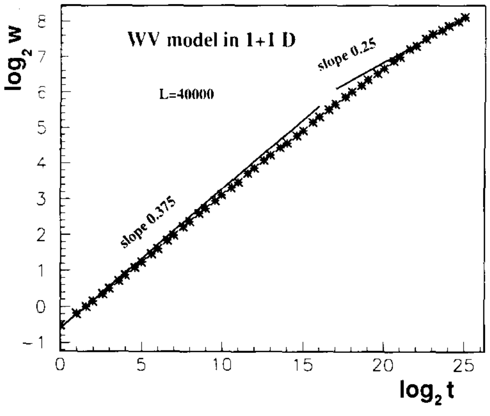

Fig. 3. The time evolution of the surface width in the Wolf-Villain model in 1+1 dimensions. The time is measured in terms of the number of deposited layers.

Kinetic roughening in more realistic full diffusion models have been studied simultaneously [51,60,61,55]. At present the situation can be summarized as follows [15,55]. There are two generic situations: either the growing surface is relatively smooth and the growth process belongs to the Edwards-Wilkinson class, or there is instability. The usefulness of some models for the study of universal behavior, however, has to be questioned since their asymptotic behavior switches between the Edwards-Wilkinson type and the morphologically unstable type following a change of space dimensionality, lattice coordination, or minor modification of its relaxation rules [55].

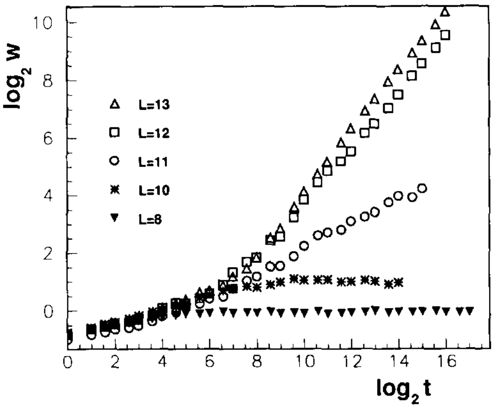

Fig. 4. Surface width vs time in the Wolf-Villain model with biased move up [53] in 2+1 dimensions for different system sizes.

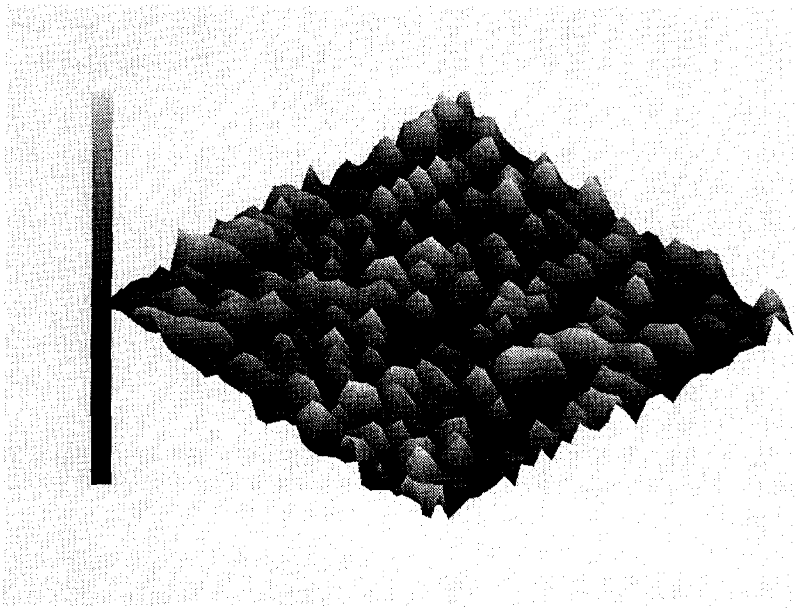

Fig. 5. Example of the surface morphology in the (2+1)-dimensional Wolf-Villain model with biased move up on a 160 × 160 lattice after 2^{16} monolayers were deposited.

The problem of instabilities is of great interest, and it is presently a subject of detailed study [62,63]. Unstable growth is not compatible with the traditional self-affine scaling. As an example I show strong unstable growth in a modification of the Wolf-Villain model, in which moves in the upward direction are positively biased, in 2+1 dimensions [53]. Fig. 4 shows the time evolution of the roughness for different system sizes. There is a critical system size L_c = 10 (the value of L_c depends on growth rules, and can be quite large when the amount of additional upward moves is small) below which the growth is stable - in the long time limit the roughness saturates to a finite value. The self-affine scaling is valid up to this critical size L_c. If the system size is larger than L_c the instability appears. The roughness is still increasing as a power law but the exponent (slope of the time dependence of the roughness) is much larger than at the beginning of the regime of stable growth. Hence, the self-affine scaling breaks down in this model. To understand better this instability it is useful to look at surface configurations. Fig. 5 shows an example of the morphology in the same model on a 160 × 160 lattice at time 2^{16}. The surface is very rough and the lateral size of instabilities corresponds to the critical size found in the time evolution of the roughness.

At the end of this subsection I would like to comment briefly some specific feature of kinetic roughening simulations. Typically these simulations are quite long (cf. Fig. 3), much longer then the simulations in which one is interested only in properties in the initial stages of the growth; however, often also much simpler models are used. To write a program for the simulation of a simple model is usually also simple. However, the *analysis* of the simulation results is far from being simple, requiring special care due to finite size and finite time effects, crossover behavior, and other complications which can cause deviation of the measured exponents from the real exponents. There are several methods for measuring the exponents and I refer the interested reader, for example, to Appendix A in Ref. [16].

4.2. Near equilibrium growth

The simulations of crystal growth originated in the study of near equilibrium growth [3]. In this situation in principle all three basic processes (deposition, desorption, and diffusion) have to be considered. Although the diffusion is certainly an important process it was not considered in some simulations [3]. This is a serious drawback but it is not completely wrong, since a condensation–evaporation process can be viewed as containing some effective diffusion; an adatom is evaporated from one position but later another adatom will stick again in the vicinity of this position. Hence, one can hope to obtain qualitatively correct results even without an explicit diffusion process. Of course, quantitatively the results will be different, for example, when the diffusion is included growth rate is several times larger [4]. When the diffusion is not considered the simulation greatly simplifies and speeds up. In this subsection I shall restrict to this simpler case.

At the beginning of crystal growth simulations the kinetic SOS model was developed [6,3]. I shall describe it here as the second example. It assumes many approximations discussed in Section 2. In the original model the simple cubic lattice was used and the dynamics was introduced by the condensation rate in the form [7]

$$C = C_{\mathrm{eq}} e^{\beta \Delta\mu}, \quad \Delta\mu = \mu - \mu_{\mathrm{eq}}, \tag{7}$$

and the evaporation rate

$$E = \nu e^{\beta E_b}, \quad E_b = m\epsilon, \tag{8}$$

where m is a number of lateral neighbors ($0 \leq m \leq 4$ in the simple cubic lattice), ϵ is energy per bond - the parameter of the kinetic SOS model, and $\beta = 1/k_B T$ is the inverse temperature (T being the substrate temperature, k_B is the Boltzmann constant).

In Fig. 6 I show surface configurations for different processes. Notice that in this variant of the model the evaporation rate naturally depends on a local configuration but not so the condensation rate. In this simple model without diffusion there is only one parameter, ϵ, which can be related to a specific material, and everything can be described by only two dimensionless variables $\beta\Delta\mu$ and $\beta\epsilon$.

The prescription for the condensation and the evaporation rates is not unique. Another possibility is to use rates in the form of the Glauber kinetics

$$C = \frac{e^{\beta\Delta\mu}}{e^{\beta\Delta E} + 1}, \quad E = \frac{1}{e^{\beta\Delta E} + 1}, \tag{9}$$

ΔE is a change of the energy of surface configuration for the elementary process considered. We have applied this form in the case of the kinetic BCSOS model [45], which is a modification of the kinetic SOS model for the bcc lattice

A typical problem which is solved using these models is the calculation of the rate of growth as a function of the temperature T and the disequilibria $\beta\Delta\mu$. The rate of growth in the configuration C is

$$G(C) = \frac{1}{L^{d'}} \left(\sum_a C_a n_a^C(C) - \sum_b E_b n_b^E(C) \right), \tag{10}$$

where a and b label different condensation and evaporation processes, $n_a^C(C)$ and $n_b^E(C)$ are multiplicities of these processes, and $1/L^{d'}$ is the normalization per site. In the simulation the average value is calculated using time averaging (6) and/or averaging over independent runs. As an example I show in Fig. 7 recent results [64] for the dependence of the mobility, $K(T, \beta\Delta\mu) = G(T, \beta\Delta\mu)/\beta\Delta\mu$ on the temperature, in the vicinity of the equilibrium thermal roughening transition, for three values of $\beta\Delta\mu$. These results explain an enhancement of the mobility below the roughening temperature, T_R, observed in the experiment on helium [65]. The numerical simulation allows a detailed study of the surface morphology, and it was found that the enhancement of mobility is connected with a change of the growth mode from layer-by-layer to the continuous, 3-dimensional, mode of growth. The driving force causes the surface to be rough even below T_R, and this in turn results in a different growth mode and kinetics.

Models of this kind are somewhat simplified, nevertheless they provide a qualitative explanation of many effects observed in experiments. To my knowledge there is not very much done on the simulation of concrete materials [8].

4.3. MBE growth

There is an extensive original literature as well as several review articles [12–14,66] on MC simulations

---

[7] The probability of condensation is proportional to the pressure of the gas. If we use the statistical-mechanical expression relating the pressure, p, and the chemical potential, μ ($\mu = f(T) + k_B T \ln p$, $f(T)$ being a function only of the temperature T), we arrive at (7).

[8] An attempt to find parameters for some materials was done in Ref. [10].

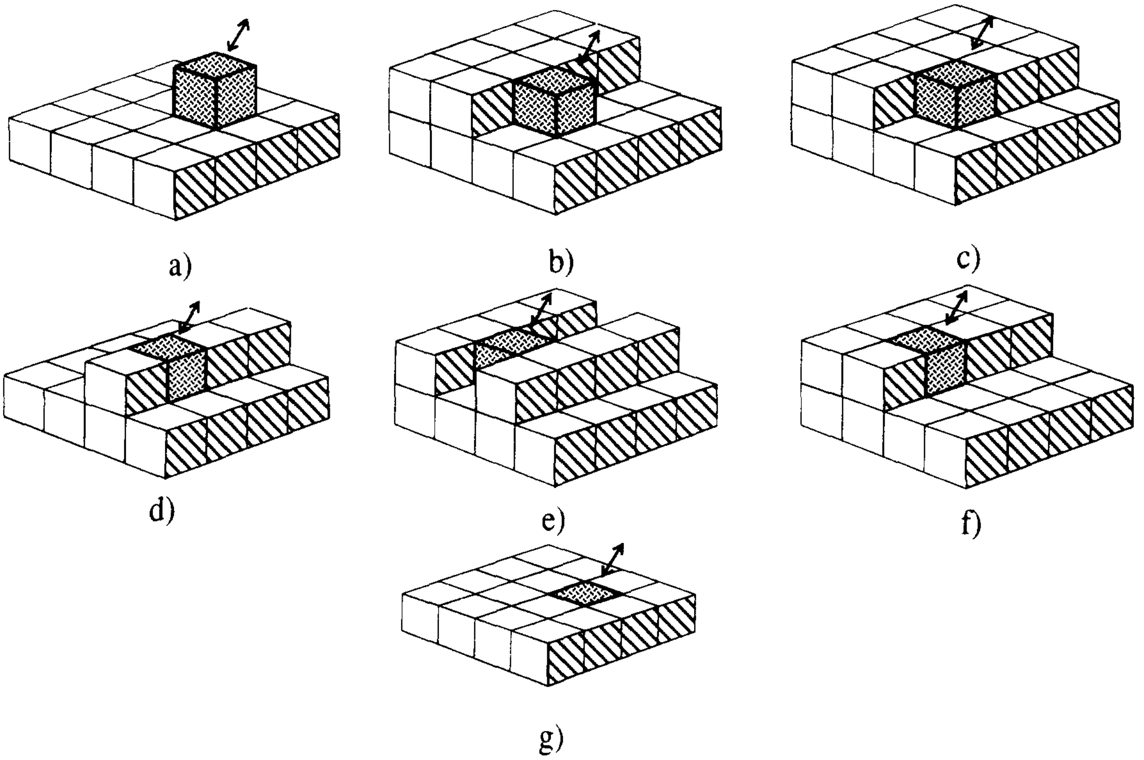

Fig. 6. The different kinds of growth-evaporation process on the surface of the simple cubic lattice.

of MBE growth. The dominant mechanism here is surface diffusion. Particles are falling down on the surface and then migrate. At not very high temperatures desorption can be neglected. In this subsection I shall restrict to one example, I shall describe the so-called full diffusion (FD) SOS model with the simple cubic lattice [66] which has been successfully used for the study of MBE growth [41,20,67].

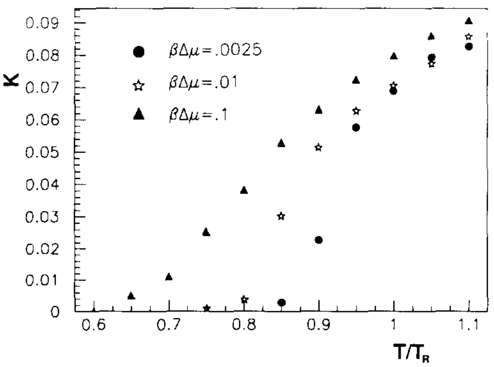

Fig. 7. Interface mobility K, as a function of reduced temperature T/T_R in the vicinity of roughening transition for the kinetic BCSOS model. The curves correspond to different values of disequilibria $\beta\Delta\mu$.

I shall first describe the simplest variant of the FD model: a model with Arrhenius dynamics and random deposition without additional relaxation. In the FD model *any* particle on the surface can diffuse during the whole simulation; usually jumps only to nearest-neighbors are considered. In the model with Arrhenius dynamics the hopping rate depends only on the bonding energy at the initial position (before a hop). The hopping rate of a surface adatom is $k_0 \exp(-\beta E)$, where k_0 is the vibration frequency of a surface adatom (of the order of $10^{13}\mathrm{s}^{-1}$), and E is the energy barrier to hopping. The energy barrier, E, is a sum of two contributions, a site-independent surface term E_S and a term given by the number m of lateral nearest-neighbors, mE_N, where E_N is the in-plane bond energy. There are two basic rates in this model, one for the deposition of new particles F, and another for the surface diffusion of a free adatom, $D = k_0 \exp(-\beta E_S)$. New arriving particles are deposited at randomly selected sites.

If we define the energy function, $H = \sum_{\langle i,j\rangle} |h_i -$

$h_j|$, which is simply the number of unsaturated lateral bonds, we can check that the transition probabilities for diffusion, $W_{i \to j} \propto e^{-\beta E}$, obey the detailed balance condition

$$\frac{W_{i \to j}}{W_{j \to i}} = \exp\{-\beta(m_i - m_j)\}. \qquad (11)$$

There are different modifications of the model described above, and one can modify both the rules for deposition and the rules for diffusion. Instead of purely random deposition one can consider some mechanism for the incorporation of arriving particles. Similar rules as in the case of toy models with surface diffusion were used (cf. the rules in the Wolf-Villain model described in Section 4.1). In this case the incoming particle searches the "best" site for deposition in some region (for computational simplicity a square of size $2S+1$, centered upon the site initially chosen, is used [41]). A possibility which was used [41] for the best choice is that the particle searches the site which provides the highest nearest-neighbor coordination, and in the case of conflict the closest site to the arrival site. Recently the FD model has been modified by introducing additional interaction to next-nearest-neighbors in planes below and above the hopping atom [67,68], in order to mimic the Ehrlich-Schwoebel effect [69].

In the simulations of the FD model [66,41], the two level BKL algorithm has been used (cf., however, Ref. [42]). Selection of the site for deposition is very simple, one of the $L^{d'}$ sites is chosen in random. The diffusion event is selected using a look up table with a special randomizing procedure [41].

The FD model has been successfully applied to the study of growth of different materials: Si [41], GaAs [20], Pt [67], in spite of the fact that it uses a simple cubic lattice instead of the proper structure of the material. I shall not review numerous applications of the FD model in the study of MBE growth, but I present the nice result by Šmilauer and Vvedensky [70] (Fig. 8) demonstrating that good *semi-quantitative* agreement between measured RHEED intensity and the step density of simulated surfaces for the GaAs(001) can be achieved.

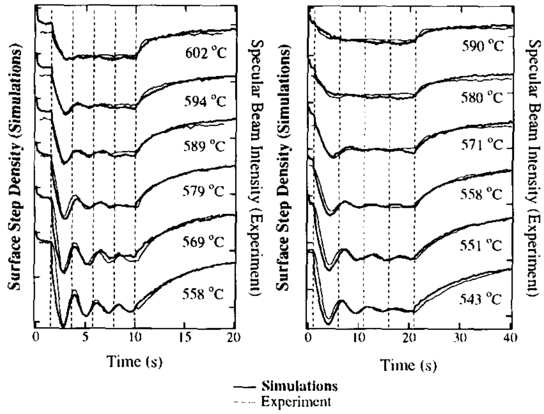

Fig. 8. Direct comparison between measured RHEED intensity and the step density of simulated surfaces for a GaAs(001) vicinal surface misoriented by 2° degrees toward [010] direction at a growth rate of 0.47 ML/s (left panel) and 0.20 ML/s (right panel) [70]. The step density increases downward and data at different temperatures has been scaled by the same factor to facilitate comparisons with the RHEED. Courtesy of Pavel Šmilauer.

The advantage of the described FD model is its simplicity and flexibility in contrast to previous modelling work on the growth of III-V compounds [12] which took into account the structural and compositional complexity of the growing system. I want to stress that the energy parameters determining the rates which are found in the modelling of growth by discrete models are only effective and should not be identified with energy barriers for diffusion even if very good agreement with experiment is obtained.

5. Molecular dynamics

In molecular dynamics [71] the evolution of a system of N mutually interacting particles is calculated by numerical integration of the equations of motion (Newton's, Hamilton's, or Lagrange's equations). The method of MD is explained in many textbooks [28,71,72] and I shall not repeat it here, but I shall discuss possible applications of MD in the case of crystal growth.

MD allows in principle to describe the true dynamics of a system and therefore it is the attractive method for the investigation of growth phenomena. However, there are two obstructions to the practical application of MD in the study of crystal growth. The first impediment concerns the time scale of the simulation. The time interval in which MD simulation can be performed is determined by the time step in the integration of the equations of motion and by the number of computational steps which can be calculated on present-day computers. The demands on computer power for the simulation of crystal growth are beyond today's possibilities. In the MD method all the dynamical processes should be described: from the atomic vibration ($10^{-13}s$) over adatom diffusion ($10^{-9}s$) to the growth of several monolayers (order of s!). The time step in integration is of the order $10^{-14}s$ or less, and it is set by an integration procedure. The number of steps in the simulation for systems of 1000 particles is about 10^6. Clearly a realistic MD simulation of crystal growth is not possible and it is unlikely that a computer will soon be available that can move thousands of atoms for 10^{15} time steps.

A second impediment is the reliability of potentials. In classical MD all of the physics is contained in the forces which are determined by the interatomic potentials. Because of computer demands simple pair potentials like Lennard-Jones, or modified Lennard-Jones are preferable; however, they may be inadequate (for example for semiconductors three body forces are important and more complicated potential such as the Stillinger-Weber potential [73] should be used). Better quality potentials could be obtained from first principle calculations; however, a simulation of the growth on this level is nowadays not possible at all. An alternative approach is the development of phenomenological potentials for different materials, which is, however, a time-consuming task.

In spite of these difficulties some authors have tried to perform MD simulation of growth [74-80]. Necessarily they have had to use unrealistically high growth rates in order to deposit a significant amount of material during the simulation. Mostly simple model potentials were used. These studies are instructive and could reveal some qualitative features. However, one has to be careful in the evaluation of their importance.

On the other side, MD can be well applied, and can be very useful in detailed studies of elementary processes as the relaxation of an atom on the surface after deposition, or adatom diffusion. Many simulations of surface diffusion have been performed (for a review, see Ref. [22]), and there are also some studies of impact phenomena [81,82]. Most of these studies were devoted to processes on flat surfaces with different crystallographic orientations. Only very recently some works for imperfect surfaces with steps appeared [83,84].

Using MD one can estimate the rates for different moves of an adatom on the surface. By following the trajectories of migrating particles one can calculate a diffusion constant from the time dependence of the mean-square distance from initial position. If this is done for several temperatures then one can extract an energy barrier for diffusion from the Arrhenius plot. Energy barriers can also be calculated directly using molecular statics at zero temperature. A very simple, naive way is to calculate the energy profile of a surface adatom as the superposition of potentials from individual particles in a model of the surface. Doing this along the path connecting two local minima over a saddle point, one can extract a barrier. However, the interaction of the adatom with the surface is neglected in this procedure. In reality, atoms can relax and this significantly changes the energy barriers. Hence, a more correct but also more computer time demanding procedure is to allow for this relaxation. One looks for a minimum of the potential energy of the adatom with its position in the plane parallel with the surface fixed, allowing relaxation of all substrate atoms and relaxation of the adatom in the direction perpendicular to the surface, instead of calculating directly the potential energy. I show an example of the surface energy profile obtained in this way in Fig. 9. It is an energy map for an A-step (a step with a (100) microfacet) on the fcc(111) surface with kink, which was calculated using a modified Lennard-Jones potential for iridium [85]. One can again extract energy barriers.

To have a complete energy map is nice but its calculation is quite costly. In order to obtain energy barriers it is sufficient to perform the calculation only at points along a path connecting initial and final points for diffusion. It is a straightforward task, provided the precise positions of the minima and the saddle point are known (this is the case for a flat surface), but a more sophisticated procedure is needed to find correct barriers (diffusion path) if these positions are not a priori known. In Fig. 10 an example of the result of such calculation is shown. It is a profile of the potential in the direction perpendicular to an A-step on the fcc(111) surface calculated again using a modified Lennard-Jones potential for iridium [85]. An Ehrlich-Schwoebel barrier and deep minima near the step edge can be seen. Energy barriers obtained in this way are lower than those obtained from a naive calculation without relaxation, but they are still not quite correct, since they are obtained for zero temperature and entropy effects are neglected. Nevertheless, such

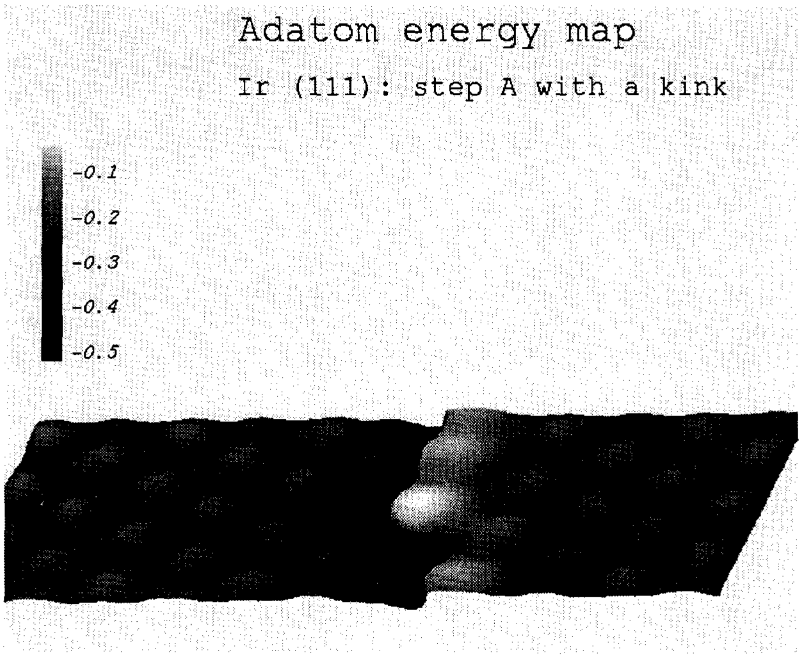

Fig. 9. The energy map of a fcc(111) surface with a kink on an A-step (a step with (100) microfacet) calculated using a modified Lennard-Jones potential for iridium. The different shades of grey correspond to different levels of the energy measured in Rydbergs. Courtesy of O.S. Trushin.

results are useful for qualitative considerations.

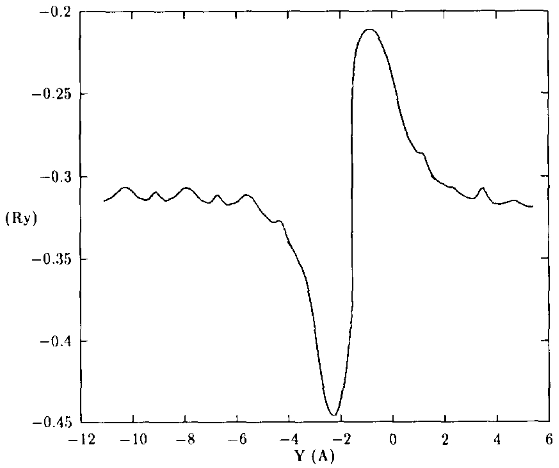

Fig. 10. The profile of potential along a diffusion path of an Ir atom over a (100) faceted step on Ir(111) [85]. The y-axis is parallel to the surface and perpendicular to the step, with the zero at the center of a step-edge atom obtained for configuration without an adatom.

6. Summary and outlook

In this paper I have discussed the methods of numerical simulation of crystal growth. The two basic methods, kinetic Monte Carlo and molecular dynamics, are complementary (see Table 1 where both methods are compared). In the first approach, kinetic Monte Carlo simulations, simplified models with a few elementary processes are built, and investigated on a long time scale. This is a flexible method allowing qualitative and also semi-quantitative explanation of phenomena observed in experiments. By varying rates of processes and comparing the results of the simulations with experimental data and possibly also with other theoretical predictions, we can identify the atomic processes which are essential for the phenomena under study. In general there is no guarantee that the model is correct, and only after careful testing of the model we can hope that it will have also some predictive power. Nevertheless, this modelling procedure turned out to be quite successful in the explanation of MBE growth of semiconductors [41,20,13] (both of the IV and of the III-V groups), and also metals [67] as well as

Table 1
Comparison of methods used in numerical simulations of crystal growth

Methods	Monte Carlo	Classical molecular dynamics	First principle molecular dynamics
Characteristics	stochastic lattice models a few fitted parameters	deterministic continuous space simple potentials	deterministic electronic structure ab initio
Results	evolution of morphology kinetics of growth scaling exponents	growth mechanism rates of processes energy barriers	static morphology energy barriers potentials
Stages of growth	early to asymptotic	a few layers	submonolayer
Time scales	1-1000 s	$\approx$10 ns	10-100 ps
Length scales[a]	10-1000	10-100	$\approx$ 10
Computer demands	mainly CPU time	both CPU time + memory	huge on both CPU time + memory

[a] Atomic distances.

near equilibrium growth [64,86].

As far as applications of molecular dynamics for crystal growth are concerned, they are not numerous because of principle and technical problems. The main difficulty is that the simulated growth is by many orders of magnitude faster than in the reality. However, molecular dynamics is a useful complementary tool for the study of elementary processes, energy barriers, impact phenomena, diffusion pathways, and so on. Results obtained by molecular dynamics can help to develop further discrete models used in Monte Carlo simulations. One can perform also ab initio calculations for the same purpose hoping to get a better understanding of elementary processes than using classical molecular dynamics simulations with model, or pseudoempirical potentials. However, up to now calculations of this kind are quite rare [87].

There are different kinds of applications differing by the level of abstraction.

(i) Academic statistical-mechanical studies of growth processes. Besides the problem of kinetic roughening (briefly discussed above) to this group belong also measurements of the fractality of grown objects, determination of dynamical exponent for evolution of instabilities, and so on. Monte Carlo methods are used here.

(ii) Qualitative studies based on simplified models for Monte Carlo with parameters not fixed by the comparison with experimental data or studies based on simple model potentials in classical molecular dynamics. On this level general rules predicted by phenomenological theories can be tested, and the importance of various microscopic processes can be evaluated. Either kinetic Monte Carlo or molecular dynamics is employed.

(iii) Material oriented research aiming to quantitative explanation of experiments and endeavouring for development of models with predictive power. Combined application of both Monte Carlo and molecular dynamics is desirable here.

All these applications have mutual influence and contribute to our understanding of crystal growth on the microscopic level. A combination of molecular dynamics simulation and kinetics Monte Carlo approach offers a promising avenue for further studies. However, in order to explain more complex phenomena, or the growth of more complex, composite materials a generalization and an extension of the present models are required. Also advances in algorithms for both kinetic Monte Carlo and molecular dynamics are desirable. One aim is to develop an effective parallel code for kinetic Monte Carlo [88].

Acknowledgements

I would like to thank P. Šmilauer for many discussions, for the possibility to show the Fig. 8, and for critical reading of the manuscript, O.S. Trushin for sharing his results, A.C. Levi for comments on the text, and J. Turner for help with application of the BIBTEX. The work was supported in part by grant No. 202/93/0512 of the Grant Agency of the Czech Republic, and in part by grant No. A 1010513 of the GA AV ČR.

References

[1] H. Müller-Krumbhaar, in: Current Topics in Material Science, Vol. 1, ed. E. Kaldis (North-Holland, Amsterdam, 1978) p. 1.
[2] A.A. Chernov, Contemporary Phys. 30 (1981) 251.
[3] J.D. Weeks and G.H. Gilmer, Adv. Chem. Phys. 40 (1978) 157.
[4] G.H. Gilmer and K.A. Jackson, in: Crystal growth and Materials, eds. E. Kaldis and H.J. Sheel (North-Holland, Amsterdam, 1977) p. 79.
[5] H.J. Leamy and G.H. Gilmer, J. Crystal Growth 24/25 (1974) 499.
[6] G.H. Gilmer and P. Bennema, J. App. Phys. 43 (1972) 1347.
[7] G.H. Gilmer, J. Crystal Growth 42 (1977) 3.
[8] J.P. van der Eerden, C. van Leeuwen, P. Bennema, W.L. van der Kruk, B.P. Th. Veltman, J. App. Phys. 48 (1977) 2124.
[9] V.O. Esin, L.P. Tarabaev, V.N. Porozkov and I.A. Vdovina, J. Crystal Growth 66 (1984) 459.
[10] V.O. Esin and L.P. Tarabuev, Phys. Stat. Sol. a 90 (1985) 425.
[11] G.H. Gilmer, J. Crystal Growth 35 (1976) 15.
[12] A. Madhukar and S.V. Ghaisas, CRC Crit. Rev. Sol. State and Mater. Sci. 14 (1988) 1.
[13] H. Metiu, Y.T. Lu and Z. Zhang, Science 255 (1992) 1088.
[14] D.D. Vvedensky, in: Semiconductor Interfaces at the Sub-Nanometer Scale, eds. H.W.M. Salemink and M.D. Pashley (Kluwer Academic Publisher, Dordrecht, 1993) p. 45.
[15] J. Krug, KFA Preprint No. 3031/1995, unpublished.
[16] A.-L. Barabási and H.E. Stanley, Fractal concepts in surface growth (Cambridge University Press, Cambridge, 1995).
[17] T. Halpin-Healy and Y.-C. Zhang, Phys. Rep. 254 (1995) 216.
[18] P. Meakin, Phys. Rep. 235 (1993) 189.
[19] M. Kotrla, Czech. J. Phys. 42 (1992) 449.
[20] T. Shitara, D.D. Vvedensky, M.R. Wilby, J. Zhang, J.H. Neave and B.A. Joyce, Phys. Rev. B 46 (1992) 6815; 46 (1992) 6825.
[21] D.E. Wolf, in: Scale Invariance, Interfaces and Non-Equilibrium Dynamics, NATO-ASI Series, eds. A. Mc Kane, M. Droz, J. Vannimenius and D.E. Wolf (Plenum, New York, 1995) p. 215.
[22] C.-L. Liu, Int. J. Mod. Phys. B 9 (1995) 1.
[23] J.W. Evans, Phys. Rev. B 43 (1991) 3897.
[24] R.F. Xiao, J.D. Alexander and F. Rosenberger, Phys. Rev. A 43 (1991) 2977.
[25] H.J. Herrmann, Phys. Rep. 136 (1986) 153.
[26] A. Bunde and S. Havlin, eds., Fractals in Science (Springer, Berlin, 1994).
[27] K. Binder and D.W. Heermann, Monte Carlo Simulations in Statistical Physics. An Introduction, Springer Series in Solid-State Sciences, Vol. 80 (Springer, Berlin, 1988).
[28] D.W. Heermann, Computer Simulation Methods in Theoretical Physics, 2nd ed. (Springer, Berlin, 1990).
[29] J.P. Valleau, in: Computer Simulations in Material Science: Interatomic Potentials, Simulation Techniques and Applications, NATO ASI, Series E: Applied Science, No. 205, eds. M. Meyer and V. Pontikis (Kluwer Academic Publishers, Dordrecht, 1991) p. 67.
[30] H.C. Kang and W.H. Weinberg, J. Chem. Phys. 90 (1989) 2824.
[31] N.C. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth and E. Teller, J. Chem. Phys. 21 (1953) 1087.
[32] R.H. Swendsen, J.S. Wang and A.M. Ferrenberg, in: Monte Carlo Methods in Condensed Matter Physics, Topics in Applied Physics, Vol. 71, ed. K. Binder (Springer, Berlin, 1992) p. 75.
[33] R.J. Glauber, J. Math. Phys. 4 (1963) 294.
[34] K. Kawasaki, Phys. Rev. 145 (1966) 224; 148 (1966) 375; 150 (1966) 285.
[35] N.G. Van Kampen, Stochastic Processes in Physics and Chemistry (North-Holland, Amsterdam, 1981).
[36] K. Binder, in: Monte Carlo Methods in Statistical Physics, Topics in Current Physics, Vol. 7, ed. K. Binder (Springer, Berlin, 1979) p. 1; 2nd ed. (1986).
[37] K. Binder and M.H. Kalos, in: Monte Carlo Methods in Statistical Physics, Topics in Current Physics, Vol. 7, ed. K. Binder (Springer, Berlin, 1979) p. 225; 2nd ed. (1986).
[38] Z. Racz, M. Siegert, D. Liu and M. Plischke, Phys. Rev. A 43 (1991) 5275.
[39] A.B. Bortz, M.H. Kalos and J.L. Lebowitz, J. Comp. Phys. 17 (1975) 10.
[40] P.A. Maksym, Semicon. Sci. Technol. 3 (1988) 594.
[41] S. Clarke, M. Wilby and D. Vvedensky, Surf. Sci. 255 (1991) 91.
[42] J.L. Blue, I. Beichl and F. Sullivan, Phys. Rev. E 51 (1995) R867.
[43] W. Krauth and O. Pluchery, J. Phys. A 27 (1994) L715.
[44] K.A. Fichthorn and W.H. Weinberg, J. Chem. Phys. 95 (1991) 1090.
[45] M. Kotrla and A.C. Levi, J. Stat. Phys. 64 (1991) 579.
[46] T. Vicsek, Fractal Growth Phenomena (World Scientific, Singapore, 1989).
[47] F. Family and T. Vicsek, J. Phys. A 18 (1985) L75.
[48] S.F. Edwards and D.R. Wilkinson, Proc. Roy. Soc. London Ser. A 381 (1982) 17.
[49] M. Kardar, G. Parisi and Y. Zhang, Phys. Rev. Lett. 56 (1986) 889.
[50] D.E. Wolf and J. Villain, Europhys. Lett. 13 (1990) 389.

[51] S. Das Sarma and P. Tamborenea, Phys. Rev. Lett. 66 (1991) 325.

[52] Z.-W. Lai and S. Das Sarma, Phys. Rev. Lett. 66 (1991) 2348.

[53] M. Kotrla, A. Levi and P. Šmilauer, Europhys. Lett. 20 (1992) 25.

[54] S. Das Sarma and S. Ghaisas, Phys. Rev. Lett. 69 (1992) 3762.

[55] M. Kotrla and P. Šmilauer, Phys. Rev. B, submitted.

[56] P. Šmilauer and M. Kotrla, Phys. Rev. B 49 (1994) 5769.

[57] M. Kotrla and P. Šmilauer, Acta Physica Slovaca 44 (1994) 237.

[58] M. Schroeder, M. Siegert, D.E. Wolf, J.D. Shore and M. Plischke, Europhys. Lett. 24 (1993) 563.

[59] P. Šmilauer and M. Kotrla, Europhys. Lett. 27 (1994) 261.

[60] M.R. Wilby, D.D. Vvedensky and A. Zangwill, Phys. Rev. B 46 (1992) 12896; errata 47 (1993) 16068.

[61] P. Tamborenea and S. Das Sarma, Phys. Rev. E 48 (1993) 2575.

[62] M. Siegert and M. Plischke, Phys. Rev. Lett. 73 (1994) 1517.

[63] P. Šmilauer and D.D. Vvedensky, Phys. Rev. B, in press.

[64] M. Kotrla and A.C. Levi, Surf. Sci. 317 (1994) 183.

[65] F. Gallet, S. Balibar and E. Rolley, J. Physique 48 (1987) 369.

[66] D.D. Vvedensky, S. Clarke, K.J. Hugill, A.K. Myers-Beaghton and M.R. Wilby, in: Kinetics of Ordering and Growth at Surfaces, ed. M.G. Lagally (Plenum Press, New York, 1990) pp. 297-311.

[67] P. Šmilauer, M.R. Wilby and D.D. Vvedensky, Phys. Rev. B 47 (1993) 4119.

[68] P. Šmilauer, M. Wilby and D.D. Vvedensky, Surf. Sci. Lett. 291 (1993) L733.

[69] G. Ehrlich and F.G. Hunda, J. Chem. Phys. 44 (1966) 1039; R.L. Schwoebel and E.J. Shipsey, Appl. Phys. 37 (1966) 3682;
R.L. Schwoebel, J. Appl. Phys. 40 (1969) 614.

[70] P. Šmilauer and D.D. Vvedensky, Phys. Rev. B 48 (1993) 17603.

[71] J.M. Haile, Molecular Dynamics Simulations. Elementary methods (Wiley, New York, 1992).

[72] F. Yonezawa, ed., Molecular Dynamics Simulations, Springer Series in Solid-State Sciences, Vol. 103 (Springer, Berlin, 1992).

[73] F.H. Stillinger and T.A. Weber, Phys. Rev. B 31 (1985) 5262.

[74] S.M. Paik, S.M. Kim and I.K. Schuller, Phys. Rev. B 43 (1991) 1843.

[75] C.M. Gilmore and J.A. Sprague, Phys. Rev. B 44 (1993) 8950.

[76] W.D. Luedtke and U. Landman, Phys. Rev. B 44 (1991) 5970.

[77] B.W. Dodson, CRC Crit. Rev. Sol. State and Mater. Sci. 16 (1990) 115.

[78] M.F. Crowley, D. Srivastava and B.J. Garrison, Surf. Sci. 284 (1993) 91.

[79] E. Aubin and L.J. Lewis, Phys. Rev. B 47 (1993) 6780.

[80] T.J. Moran and I.K. Schuller, Phys. Rev. B 49 (1994) 5729.

[81] D.E. Sanders and A.E. De Pristo, Surf. Sci. 254 (1991) 341.

[82] G. De Lorenzi and G. Ehrlich, Surf. Sci. 293 (1993) L900.

[83] P. Stoltze and J.K. Norskov, Phys. Rev. B 48 (1993) 5607.

[84] C.-L. Liu, Mod. Phys. Lett. B 8 (1994) 823.

[85] O.S. Trushin, M. Kotrla and F. Maca, unpublished.

[86] Z. Jiang and C. Ebner, Phys. Rev. B 40 (1989) 4833.

[87] R. Stumpf and M. Scheffler, Phys. Rev. Lett. 72 (1994) 254.

[88] N. Haider, S.A. Khaddaj, M. Wilby and D.D. Vvedensky, Comp. Phys. 9 (1995) 85.