Theory and simulation of crystal growth

REVIEW ARTICLE

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Andrea C Levi† and Miroslav Kotrla‡

† Università di Genova, Dipartimento di Fisica and INFM, Via Dodecaneso 33, 16146 Genova, Italy
‡ Institute of Physics, Academy of Sciences of the Czech Republic, Na Slovance 2, 180 40 Prague 8, Czech Republic

Abstract. Crystal growth phenomena are discussed with special reference to growth from vapour. The basic concepts of crystal growth are recalled, including the different growth modes, the dependence of the growth rate on disequilibrium and temperature, and the atomic processes relevant for growth. The methods used in crystal growth simulations are reviewed, with special reference to kinetic Monte Carlo methods. The roughness of growing surfaces, and the roughness properties of the discrete and continuum growth models (the latter being described via stochastic differential equations) are discussed, together with the special phenomena occurring in the vicinity of the roughening temperature. A number of simulations based on the six-vertex model and on kinetic counterparts of the BCSOS model are reviewed. Finally, the instabilities arising during growth are considered, including a discussion of phenomena such as dendritic growth and ramified cluster growth and reviewing the recent, extensive studies concerning unstable MBE growth.

Contents

1. Introduction

Science has become more and more interested in evolution phenomena. Probably most sciences study at first static, or equilibrium phenomena (the two concepts not being necessarily synonymous)†, not because they are more interesting, but because they are simpler and—even more important—more uniquely defined. Evolution depends on the initial conditions, but often leads to some equilibrium (or at least steady) state, independent of those conditions. No wonder that the scientists are tempted to focus their attention on this steady state rather than on the myriad evolution processes leading to it. In recent times, however, the evolution processes have ultimately become a central object of scientific study in many fields.

Crystal growth is special in that it was studied in detail, because of its practical importance, much before the present fashion (for a comprehensive review of crystal growth see Hurle (1993)). Recently, however, it has become clear that crystal growth is part of a much wider field of growth phenomena which is being intensively investigated, forming the subject of something which may be loosely called *growth science*, to which e.g. the books by Vicsek (1989) and Barabási and Stanley (1995) are devoted.

A vast variety of phenomena are studied by growth science, ranging from the spread of a forest fire to the sedimentation of sand on the bottom of a water basin. These growth phenomena have been recently reviewed e.g. in a beautiful article by Halpin-Healy and Zhang (1995); another important review was published by Evans (1993) dealing with what he calls *sequential adsorption*. Very recently, an interesting book by Villain and Pimpinelli (in French) appeared, dealing with many aspects of crystal growth (Villain and Pimpinelli 1995). The present article, for lack of space and competence, and also in order to avoid repetition, will not cover many subjects discussed in the above-mentioned reviews, and will rather discuss alternative topics. Thus, in comparison to Halpin-Healy and Zhang, we will try to remain closer to a microscopic picture and, in comparison to Evans, to remain closer to the equilibrium situation (this, in our opinion, determines a very interesting range of physical parameters). The physics thus obtained, notwithstanding the simplicity of the models, will hardly be simple, with the unpleasant consequence that very little that is exact will be said, most results being obtained from simulations. In spite of the title, there will be very little mathematics in this review.

To put the situation in perspective we must from the beginning distinguish two scenarios: stable versus unstable growth. Somewhat surprisingly, the scientists studying instability and ramifications have often ignored the (usually more microscopic) problems arising in stable growth, and vice versa. We think, in contrast, that very interesting, although complex, phenomena occur at the boundary between the two fields, such as the onset of ramifications near equilibrium. According to tradition, however, we shall treat first the stable, then the unstable scenario, stressing, whenever possible, such boundary phenomena.

More than 15 years ago, the stable- and unstable-growth phenomena were treated,

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† An exception is linguistics: *diachronic linguistics* (i.e., the study of the evolution of languages) is, in a certain sense, older than *synchronic linguistics*. But, in the case of linguistics, no equilibrium is in sight.

respectively, in two famous review articles by Weeks and Gilmer (1979) and by Langer (1980). The overlap between those two papers was remarkably vanishing, as if they treated completely different fields of science. This situation was unsatisfactory: it was clearly necessary to feed an atomistic picture into the theory of unstable growth, or to allow for non-trivial boundary conditions and shapes in the dynamics of crystal growth. This has happened subsequently, but not in the most direct way, since some remarkable discoveries have led the scientific fashion in unsuspected directions. The first such discovery was diffusion-limited aggregation (DLA), proposed by Witten and Sander (1981); the second were the stochastic differential equations for growth, which, after a relatively timid beginning by Edwards and Wilkinson (1982) (but the work of Chui and Weeks (1978) is even older) achieved explosive fame especially after Kardar *et al* (1986) proposed their non-linear equation. These developments have led to the vast field of fractal growth phenomena, to which books have been devoted (Vicsek 1989, Barabási and Stanley 1995). How is one to describe this enormous field? Completeness is out of the question; describing only our own work, and work related to it, would be incredibly limited. Something in between is clearly possible, but a condition is to keep clearly in mind the physical problems to be solved.

When dealing with crystal growth, many possibilities are to be considered, according to the nature of the fluid phase (melt, solution, vapour), to the stable or unstable nature of the growth process, to the growth mode (layer by layer, continuous, step flow, spiral, ...), to the growth rate (linear versus non-linear in the *disequilibrium* $\Delta\mu$), etc. In some cases, the anisotropy is so strong that the growth effectively takes place in two dimensions. It is also important whether the growth occurs at a reasonably well defined surface (hence predominantly in the direction normal to it) or in all directions. It is easily understood that these varying conditions lead to very different scenarios; yet it is not hopeless to treat some of such scenarios in a unified way, and indeed to find the values of the parameters where the process crosses over from one scenario to another. This will in many cases be our goal. In the following, we will focus attention on growth from vapour, unless otherwise stated. A preliminary, shorter account of some of the subjects discussed here was presented some time ago at the CMD/EPS Conference in Regensburg (Levi *et al* 1993) and some of the techniques were discussed elsewhere (Kotrla 1996a).

The paper is organized as follows. In section 2 we rapidly review some traditional notions of crystal growth (for further detail refer e.g. to the work of Weeks and Gilmer (1979)). In section 3 we describe the methodology of computer simulation for growth problems, and we give a short overview of the methods used in many simulations, of great applicational importance, related to molecular beam epitaxy. In section 4 we briefly discuss the very active field concerning the growth of rough surfaces (and the roughness of growing surfaces). In section 5 we describe work, mostly done by our research group, on growth models based on the six-vertex model: some of them (but not all) being kinetic counterparts of van Beijeren's BCSOS surface model and generalizations thereof. In section 6 we discuss dendritic growth, ramified cluster growth, and also recent results on a new type of unstable growth—pyramid-like growth observed (both experimentally and computationally) in epitaxy. Finally in section 7 we give a short outlook on future perspectives.

2. Traditional concepts of crystal growth

In this section we rapidly review some traditional notions on crystal growth. This is not of historical interest only, since the present-day research is still largely based on such notions. We restrict consideration here to the stable-growth scenario, and unstable growth will be discussed in section 6.

2.1. Surface growth

For stable growth the most widely considered geometry is that of a planar or quasi-planar surface, moving in the positive z-direction with (on average) constant velocity v. (For different geometries, see subsections 6.1 and 6.2.) Obviously if the crystal is in equilibrium with its vapour (i.e. they have the same chemical potential μ_{eq}), v vanishes. Otherwise, even if the chemical potential of the crystal may still be identified with the equilibrium chemical potential for sublimation μ_{eq}, the chemical potential μ of the vapour is higher. The difference $\Delta\mu = \mu - \mu_{eq}$ is the driving force for crystal growth.

Two basic and related questions are: what is the growth mode (see subsection 2.2 below) and what is the growth kinetics, i.e., how does the rate of growth G† depend on the driving force $\Delta\mu$ (see subsection 2.3)? Very different situations are encountered: linear growth versus highly non-linear nucleation; also: non-trivial space-time patterns (self-affine surfaces and fractal growth). Instabilities may arise, leading possibly to dendrite formation or to the non-existence of a steady rate G, but these will be considered later (see subsection 6.1).

An extreme but important case is when detachment (evaporation, desorption) is altogether negligible. This case is encountered in molecular beam epitaxy (MBE: see subsection 3.3), and is also the subject of the beautiful review article by Evans (1993), whose title (*Random and cooperative sequential adsorption*) indicates the irreversible deposition of new atoms (as opposed to the equilibrium situation where atoms stick at the surface and detach from it with the same probability). Much of the work done in recent years refers to this case; for us, however, MBE corresponds to high $\Delta\mu$ (not so high, however, that diffusion can be disregarded). We treat, as a rule, $\Delta\mu$ as finite and consider the $\Delta\mu = 0$ (equilibrium) and $\Delta\mu \to \infty$ (pure growth) cases as important limiting cases, useful, in particular, for purposes of checking. MBE is close, but not identical, to the latter case (and is of great importance for applications).

It should be noted that, as long as vapour growth is considered and the vapour may be treated as an ideal gas, the vapour density and pressure will be proportional to the *absolute activity* $z = \exp(\beta\mu)$ (where $\beta = 1/k_BT$, k_B being the Boltzmann constant, and T the temperature), so changing $\Delta\mu$ is equivalent to changing the vapour pressure (in excess of the equilibrium vapour pressure p_{eq}‡). In the case of MBE the vapour is replaced by a beam, whose directionality implies a more severe sort of disequilibrium than that given by $\Delta\mu$ only. If an appropriate average over beam directions is taken, the MBE case becomes identical to the vapour case (with $\Delta\mu$ very large). This averaged situation will be taken in the following as the MBE limit, unless stated otherwise.

2.2. Growth modes

Over many decades, it has become customary to distinguish the growth modes into broad categories, which preserve their importance even now, although some definitions have to be somewhat modified.

First of all, we have the *layer-by-layer* (or Frank–van der Merwe) growth mode (briefly: layer growth). Preferentially a crystal layer tends to be completed before a new layer is started above it (figure 1(a)). Near equilibrium, there is a bottleneck strictly related to *two-*

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† G is proportional to v, but is more loosely defined: its physical dimensions may vary according to convenience, e.g. G may represent the number of new atoms added to the crystal per unit time and area, etc.

‡ Of course the vapour pressure might be less than p_{eq}, but this *unsaturated-vapour* situation implies that the crystal sublimates (albeit possibly slowly) and disappears instead of growing. The extreme case is removing of material in far-from-equilibrium conditions: sputtering or ablation.
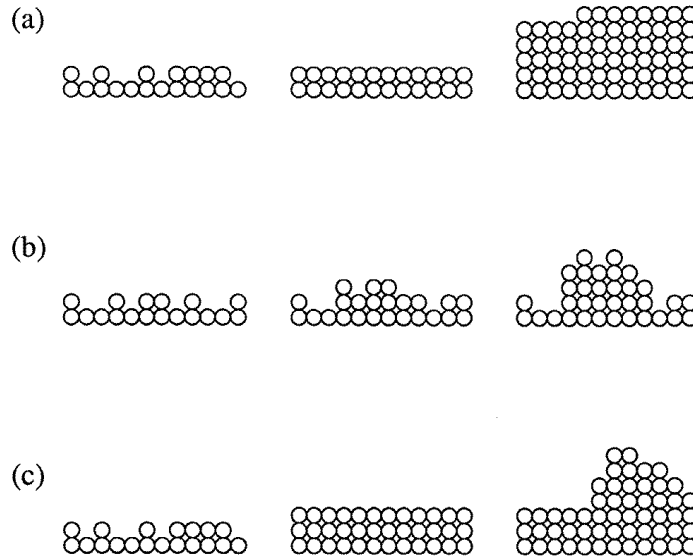
(a)

(b)

(c)

Figure 1. Modes of growth: (a) Frank–van der Merwe, (b) Volmer–Weber, (c) Stranski–Krastanov.

dimensional nucleation of clusters (*islands*) and as a consequence the kinetics in this mode is highly non-linear (see below). This mode is also called *two-dimensional growth*. Notice, however, that although in MBE two-dimensional nucleation and layer-by-layer growth are possible, there is no bottleneck: atoms are fed in from the beam (or gas) at such a high rate that no barrier to nucleation can affect the kinetics.

　　Then we have the opposite situation: the Volmer–Weber, or *three-dimensional* growth mode. Many crystal layers grow at the same time: the atoms, depositing over relatively high layers, cause the surface to form hillocks and cavities (see figure 1(b)).

　　The mode of growth can change with the substrate temperature, or with the strength of the disequilibrium. In far-from-equilibrium MBE growth, usually the growth mode changes from three-dimensional growth at low temperature to layer-by-layer growth at higher temperature. This transition, as we shall see, is due to the fact that at sufficiently high temperature the adatoms on the surface become so mobile that they can jump over local energy barriers, including the barriers at step edges which at low temperature prevent an atom from jumping *down* a step (a necessary process for layer growth). Sufficient inter-layer transport causes the surface to be smooth and to grow according to a two-dimensional mode. Under some conditions, when the adatoms are mobile but the barriers at step edges suppress the inter-layer transport, three-dimensional growth can proceed in a special way resulting in the creation of large, ordered, e.g. pyramid-like features on the surface (see subsection 6.3).

　　Different scenarios have to be considered for growth near equilibrium (see section 5) below). Typically, a two-dimensional surface in equilibrium undergoes a roughening transition at a temperature T_R: the surface is smooth below T_R but rough above. Growing surfaces are even *rougher* than in equilibrium, because in addition to the thermal fluctuations there are also stochastic fluctuations due to the growth process. Hence, above T_R a crystal surface should never grow in the layer-by-layer mode, although it can grow in this mode below T_R. At these high temperatures we have thus a reversal transition, from the layer-by-

layer mode to the three-dimensional mode with increasing temperature. This was studied in detail by simulations (see e.g. Kotrla and Levi (1991)) as well as being observed in experiments (Bennema 1993). Actually, Bennema observed a more complicated effect: with increasing $\Delta\mu$ and decreasing T the growth mode changed from 3D to layer by layer to 3D again, due to the non-linear nature of the boundary between modes.

On a certain crystal, the *substrate*, a crystal of different chemical composition may grow. If the crystal structure of the substrate is retained (up to a certain thickness of the growing deposit) we have the phenomenon of *epitaxy* (sometimes called *heteroepitaxy*, as opposed to *homoepitaxy* indicating the growth of a deposit having the same chemical nature as the substrate). In epitaxy, between the Frank–van der Merwe and the Volmer–Weber growth modes, an intermediate case is possible: the Stranski–Krastanov growth mode, where the deposit first grows layer by layer on the substrate and then, beyond a few layers, the growth becomes three dimensional (see figure 1(c)).

Another important case (which implies the surface to be a vicinal surface, either globally, with a well defined miscut with respect to a surface with low Miller indices, or at least, if there is no miscut, locally, at the slopes of a gentle hillock) is the *step-flow* growth mode: the surface is characterized by a step array, and the crystal grows as a step advances over the lower terrace. In a steady-step-flow situation, all steps move at the same velocity u in the direction down the step array. The step velocity u is proportional to $\Delta\mu$ and the growth velocity is $v = au/l$, where a is the step height and l the mean distance between two successive step edges.

2.3. Kinetics

2.3.1. The Wilson–Frenkel limit.
The three-dimensional mode of growth is fast, and v is approximately linear in $\Delta\mu$, so a *kinetic coefficient* may be defined:

$$\tilde{K}(T) = \lim_{\Delta\mu \to 0} \frac{G(\Delta\mu, T)}{\Delta\mu}. \tag{1}$$

We can simply estimate the growth rate (or more precisely, an upper bound to it). Let S be the *sticking rate*, E the *evaporation rate*. Then $G = S - E$. At equilibrium, $S_{eq} = E_{eq}$. S is proportional to the vapour *pressure*, i.e. to†

$$S = S_{eq} e^{\beta \Delta\mu}. \tag{2}$$

The growing surface is rougher than the equilibrium surface, so it has more *evaporation sites*:

$$E > E_{eq}. \tag{3}$$

Thus the Wilson–Frenkel (WF) (Hertz 1882, Wilson 1900, Frenkel 1932) *upper bound* to the growth rate is obtained: $G < G_{WF}$, where

$$G_{WF} = S_{eq}(e^{\beta \Delta\mu} - 1). \tag{4}$$

At *high T* and relatively *large* $\Delta\mu$ there are no bottlenecks and the WF limit is approached. Extrapolating back to vanishing disequilibrium, the corresponding kinetic coefficient is found to be

$$\tilde{K}_{WF} = \frac{S_{eq}}{k_B T}. \tag{5}$$

G/S_{eq} in the WF limit (more generally, in the continuous-growth mode) *decreases* with increasing T.

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† This relation can be directly derived if we use the statistical-mechanical expression relating the pressure, p, and the chemical potential, μ: $\mu = f(T) + k_B T \ln p$, where $f(T)$ is a function of the temperature T only.

2.3.2. Two-dimensional nucleation. In layer-by-layer growth the surface is supposed to be a smooth plane covered by a sparse population of two-dimensional clusters, or *nuclei*, or *islands*†. Crystal growth takes place via the formation (*nucleation*) and growth of such nuclei.

Let us consider growth near equilibrium. Islands nucleate from adatoms on the surface, while at the same time adatoms are exchanged with atoms of the gas.

The *promotion rate I* is the rate at which a new atom is added to an island, more precisely the number (divided by the total number of sites) of islands of size n that are *promoted* to size $n + 1$ per unit time (under steady conditions I is independent of n). The promotion rate was calculated in the 1930s by Becker and Döring (1935), following pioneering work by Volmer and others (reviewed in Volmer (1939))‡ as

$$I = A S_{eq} \sqrt{p} e^{p-q} \tag{6}$$

(the main factor is e^{-q}), where $p = \beta \Delta\mu$, $q = \beta \epsilon^2 / \Delta\mu$, and A depends only weakly on q, decreasing from $\sqrt{\pi}$ to $\sqrt{\pi}/2$ as q varies from 0 to ∞. q is an important parameter of the problem. In a first approximation ϵ equals the bond energy ϵ_0, but in a better approximation it is the *step free energy* per unit length. Thus ϵ and q vanish at T_R (there is no barrier to nucleation on a rough surface).

The growth rate G is not proportional to I, but to $I^{1/3}$! This was found by Kolmogorov (1937) and his followers of the Soviet school (see Zeldovič (1942) and others), studying the statistics of how surface points are reached by growing islands. Assume a certain velocity u of island expansion. For any point P the probability of growth having taken place at P is

$$\text{prob[covered]} = 1 - \text{prob[uncovered]}. \tag{7}$$

prob[uncovered] is the probability of P *not* getting covered at time t by islands nucleated at *any* previous time t', which can reach P only if nucleated within a distance $u(t - t')$:

$$P(t) = 1 - \exp\left(-\pi I \rho u^2 \int_0^t (t - t')^2 \, dt'\right) = 1 - \exp(-(\pi/3)\tau^3) \tag{8}$$

where ρ is the number of atoms per unit area (e.g. for a square lattice, if a is the lattice spacing, $\rho = a^{-2}$), and $\tau = (I\rho u^2)^{1/3} t$.

The deposition rate on an *initially ideal surface* is

$$\frac{dP}{dt} = (I\rho u^2)^{1/3} e^{-(\pi/3)\tau^3} \pi \tau^2. \tag{9}$$

dP/dt increases, then decreases (because the initial surface disappears). A rough estimate of the growth rate is (Weeks and Gilmer 1979)

$$G = \max \frac{dP}{dt} = 1.194 (I\rho u^2)^{1/3}. \tag{10}$$

Other estimates of the coefficient include: 1.015 (Nielsen 1994), 1.137 (Rangarajan 1973), …. But u is proportional to $\Delta\mu$ (e.g. $u = (1 - e^{-p})u_0$ where u_0 is the velocity in the *absence* of evaporation (according to some sort of 'Wilson–Frenkel law' in two dimensions); but $u_0 \approx aS = ae^p S_{eq}$—thus $u = a(e^p - 1)S_{eq} \approx ap S_{eq}$, for p small).

Moreover $e^{(1/3)p} \approx 1$. Therefore

$$G \sim p^{5/6} e^{-(1/3)q} S_{eq}. \tag{11}$$

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† Some people use the terms *islands, island growth* to characterize three-dimensional growth. We do not use such (rather confusing) nomenclature in this paper.

‡ A short, but nice historical account of the origins of crystal growth theory was recently given by one of his founders, Rostislav Kaischew, on his 85th birthday (Kaischew 1994).

$p^{5/6}$ is called the *Zeldovič factor*. But the main factor is of course

$$\exp\left(-\frac{1}{3}q\right) = \exp\left(-\frac{\epsilon^2}{3kT\,\Delta\mu}\right).$$

Layer growth corresponds to a *smooth surface* and relation (11) describes the kinetics of this growth. In principle it should take place at relatively low T. At T_R, ϵ vanishes, and *three-dimensional growth* should take over (cf. also section 5). Actually, this scheme is well verified experimentally *not* for growth from vapour (see, however, Bennema (1993)), *but* for growth of solid ^{4}He from the *superfluid*! (as established by experiments by Balibar and collaborators (Balibar and Castaing 1980)).

The kinetics of layer-by-layer growth in MBE is trivial. For temperatures that are not very high, evaporation can be neglected and any atom from the beam sticks to the surface; hence the growth rate is given by the flux of incoming particles.

The growth rate G/S_{eq} in equation (11) *increases* with temperature for fixed $\Delta\mu$ (at least if $\Delta\mu < 2\beta\epsilon^2$). This behaviour is characteristic of layer growth, and *opposite* to what happens for continuous growth, where G/S_{eq} *decreases* with increasing T. Thus the *maximum* of G/S_{eq} marks the passage from layer-by-layer to continuous growth (Kotrla and Levi 1991).

2.3.3. Spiral growth.

At low T, $\Delta\mu$ where nucleation is impossible, the reasonably fast growth of crystals (as carefully measured e.g. by Volmer and Schultz for iodine (Volmer and Schultz 1931)) was a mystery in the 1930s and 1940s, until Frank explained it as *spiral growth* around a pre-existing *screw dislocation* (Frank 1949). The dislocation produces a step and crystal growth proceeds by rotation of the step, which is wound in a spiral. Thus nucleation is replaced by step flow! The spirals were subsequently observed by electron microscopy. The growth rate is

$$G \sim (\Delta\mu)^2 \tag{12}$$

since $G = ua/l$ (u is the step velocity, a is now the step height, and l is the step spacing) and l is proportional to the radius ρ_c of the *critical nucleus* for nucleation, which is of the order of $\epsilon/\Delta\mu$, and thus $l \sim \Delta\mu^{-1}$; on the other hand, $u \sim \Delta\mu$. At lower temperatures, circular spirals are replaced by *polygonal spirals*, exhibiting the lattice symmetry (Budevski *et al* 1975, Swendsen *et al* 1976).

2.4. Atomic processes during growth

In order to understand crystal growth phenomena it is important to have in mind the different atomic processes that can take place during growth. Venables (1994) published a lucid discussion of these some time ago. Here only a sketchy survey will be given (see also Ricciardi (1996)).

The surface topography shows sequences of terraces and steps; sometimes hillocks (or cavities) are formed. Accordingly, in deposition new adatoms may stick on terraces or at steps; terraces and steps, in turn, may be located in a flat area or belong to a hillock or cavity. Similarly, in desorption adatoms may leave from terraces or from steps (atoms well inserted in a flat portion can seldom or never detach from the surface).

Adatoms move on the surface, diffusing either on a terrace, or along (usually below) a step edge. When in its wanderings on a terrace an adatom reaches a descending step, it encounters the above-mentioned energy barrier, the *Schwoebel*, or more correctly the *Ehrlich–Schwoebel (ES) barrier* (Ehrlich and Hunda 1966, Schwoebel and Shipsey 1966,

Schwoebel 1969), due to the fact that, when at the upper step edge, it is quite poorly bound to the substrate atoms. In order for layer-by-layer growth to be possible, the adatoms must be able to descend the steps and stick at the lower edge; if the ES barrier is too high, or the temperature is too low, they tend to remain on the upper terrace and the growth is three dimensional.

Two adatoms may associate (bind to each other), forming the two-particle embryo of a cluster. A growing cluster can capture a new adatom, or it may lose an adatom to the surrounding terrace. Two clusters can coalesce, forming a larger cluster, or a cluster can split into two. Finally, there can be an interchange between adatoms and substrate atoms: such interchange lies at the origin of segregation phenomena, favoured by low surface tension of the segregating species. The latter remains at the surface during growth and may tend to act as a *surfactant*, favouring layer growth†.

If the vapour can be treated as an ideal gas at temperature T_0 and pressure p_0 (as is usually the case), the number of atoms of mass m falling on the surface per unit area and time is

$$R = p_0(2\pi m k T_0)^{-1/2} \tag{13}$$

of which, if s is the *sticking coefficient*‡, sR remain on the surface. The latter gets covered by single adatoms, whose density n_1 increases initially as $n_1 = sRt$. Adatoms, however, may redesorb (with a permanence time on the surface proportional to $\exp(E_a/kT)$, E_a being the energy barrier, and the surface temperature T being not necessarily equal to the gas temperature T_0) or may associate in pairs. Before desorption or association they migrate on the surface with a diffusion coefficient D, given in a first approximation (neglecting long jumps (Ferrando *et al* 1994)) by

$$D = D_0 e^{-E_d/kT} \tag{14}$$

where E_d is an energy barrier to diffusion (considerably lower than E_a) and, neglecting long jumps, the prefactor D_0 for jump diffusion has the form

$$D_0 = \frac{1}{4}\nu l^2 \tag{15}$$

where ν is an oscillation frequency within the well at a site and l is the length of a diffusion step. E_d varies widely: on Rh(111) it is only 0.16 eV but on W(111) (tungsten is bcc) it is 1.78 eV, more than ten times larger (Kellogg 1994). D_0 also varies widely, but is of the order of 10^{-7} m^2 s^{-1}. Knowing the permanence time and the diffusion coefficient one can estimate the path length of an adatom on a surface, which can be quite long. The dynamics governed by equation (14) is often called *Arrhenius dynamics*.

In some systems, as mentioned above, the adatom may exchange positions with the underlying lattice. A good example is Pt(011). Generally speaking, on the (011) surfaces of fcc crystals, single-particle diffusion can take place easily only along the grooves (in the $\langle 1\bar{1}0\rangle$ direction); diffusion *across* the rows, however, may take place, but is not single particle: the adatom, instead, moves to a row displacing a row atom which becomes an adatom in the next groove. Similar exchange phenomena occur on the (001) surface.

Not only single adatoms but also clusters can diffuse. Usually this diffusion is much slower but in rare cases it is comparable: small rhenium clusters, e.g., diffuse as easily on W(112) as single rhenium atoms.

† Genuine interchanges between the bulk and surface, leading to segregation (Tréglia 1992, 1994) and surfactant effects (Vegt *et al* 1992, Oppo *et al* 1993), can be quite important, but are outside the scope of the present review.
‡ For metal atoms on metals s is 1, but for, say, rare-gas atoms on Au(111) (but also on alkali metal surfaces) s can be very small. Also, s is an average: in each individual collision, the sticking probability actually depends on the local environment.

(a) Incorporation by hopping
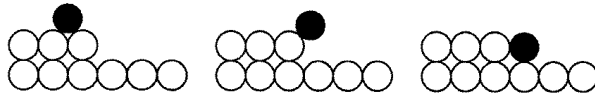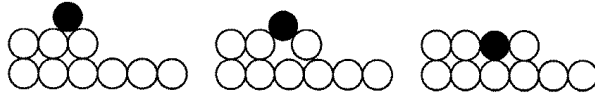

(b) Incorporation by exchange

Figure 2. Descent of a step by direct motion (a) and by atomic exchange (b).

The ES barrier, mentioned above, hinders the descent of an adatom from a step, favouring three-dimensional growth. The situation, however, is not always so simple. At steps, there are not only energy maxima, but minima as well: in some cases, the latter may be more important than the former. In other cases the ES barrier is very high for single-atom diffusion, but can be circumvented by exchange (the adatom incorporates into the upper terrace, whose former last atom remains as such, but moves one space on top of the lower terrace: see figure 2(b)). Finally, the phenomenon of re-entrant layer growth (found by Kunkel *et al* (1990) at low temperatures) shows that the ES barrier effect does not simply cause a transition in the growth mode from three dimensional at low temperatures (where the adatoms cannot descend the steps) to layer by layer at high T (where they have enough energy to overcome the barrier). Re-entrant layer growth has been widely discussed: presumably at very low T the islands are very small (which implies low barriers) and more or less dendritic (which implies no barriers at concavities). But a role may also be played by genuine kinetic effects, such as detachment by hitting (knockout) (Šmilauer *et al* 1993b) or funnelling (Evans 1991).

2.5. Diffusion bias

When a diffusing atom reaches the upper edge of a step, it finds itself in an environment corresponding to a maximum of energy, due to the reduced number of bonds available (see figure 2). This implies a diffusion barrier preventing the atom from *descending* the step. As we have seen, such an *Ehrlich–Schwoebel effect* or *diffusion bias* (Villain 1991) has a roughening effect on a high-symmetry surface, by preventing layer-by-layer growth at low temperatures, and can lead to unstable growth (see subsection 6.3). It can have, in contrast, in $1 + 1$ dimensions, a *smoothing* effect on a vicinal surface, where the growth takes place by step flow. As noted by Villain (1991), the atoms falling on a terrace will accumulate at the upper step; if a terrace happens to be wider than average, more atoms than average will deposit on it, and the upper step will move in more quickly, thereby reducing the area of the terrace. Thus the steps will tend to be equally spaced†.

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† In $2 + 1$ dimensions the situation is more complicated; see subsection 6.3.

Let us study the *recovery* of a vicinal surface from a sinusoidal perturbation, assuming perfect diffusion bias. In the following simple calculation island formation is neglected; otherwise, as shown by Krug and Schimschak (1995) an instability arises, similar to what happens on singular surfaces: see subsection 6.3. If l is the average step spacing and u the average step velocity, and if when moving from left to right the steps are *down*, the equation of motion of the nth step is

$$\frac{\mathrm{d}x_n}{\mathrm{d}t} = \frac{u}{l}(x_{n+1} - x_n). \tag{16}$$

Introducing the perturbation $\xi_n = x_n - nl - vt$, the ξs obey the same equations as the xs, but with different initial conditions: let us choose provisionally

$$\xi_n(0) = \delta \cos(pn). \tag{17}$$

The solution is (Levi *et al* 1993)

$$\xi_n(t) == \delta \mathrm{e}^{-(ut/l)(1-\cos p)} \cos\left(pn + \frac{ut}{l}\sin p\right). \tag{18}$$

For small (macroscopic) $p = 2\pi l/\Lambda$ this reduces to

$$\xi_n(t) = \delta \mathrm{e}^{-up^2 t/2l} \cos\left[p\left(n + \frac{ut}{l}\right)\right] \tag{19}$$

showing that recovery takes place with a characteristic time

$$\tau = \frac{2l}{up^2} = \frac{\Lambda^2}{2\pi^2 lu} \tag{20}$$

(where Λ is the wavelength of the perturbation), to be compared, e.g., with $\tau \approx \Lambda^2/\lambda w$ for the KPZ equation (Kardar *et al* 1986) (see below), where λ is the KPZ parameter and w is the surface width (if a is the step height, $w = (a/l)\delta$ in our case), and with $\tau \approx \Lambda^2/4\pi^2 \nu$ for a pseudo-diffusion equation of the EW type (Edwards and Wilkinson 1982), where ν is the coefficient of the Laplacian (see below, section 4). That is, the present model resembles the latter, with a pseudo-diffusion coefficient $\nu = \frac{1}{2}lu$.

The treatment above is only correct for small δ. If δ is *large*, on the other hand, the evolution leads to a wave whose *shape* changes (while the amplitude decreases) (Levi *et al* 1993).

3. Crystal growth simulations

Except for exceedingly idealized models, the crystal growth processes (several of which have just been described above) are too complex for a completely analytic description. It is sometimes possible and useful to write a *master equation* (including the relevant elementary processes), whose solution is the set of probabilities for the possible surface configurations (see subsection 3.2 and section 5); even so, such an equation is in general too difficult to solve exactly, and it is necessary to resort to *simulations*.

In *classical* condensed-matter physics, two kinds of simulation have proved useful: molecular dynamics (MD) and Monte Carlo (MC) simulations. In crystal growth, however, the relevant processes are so slow (the time required to form a new crystal layer is so long) in comparison to the motion of individual atoms under the action of mutual forces, that MD simulation is essentially not feasible (with very few exceptions: the interesting work of Villarba and Jónsson (1994) is one of these; for other references see Kotrla (1996a)). MD simulation is very useful for exploring possible processes and setting the parameters

(e.g. the barriers to diffusion, the desorption energies, the most probable paths followed by the system in phase space) which are relevant for growth, but to simulate growth itself MC simulation is often the only realistic procedure. As we shall see, MC simulations, however, cannot be very accurate and their results must usually be treated with caution.

One of the oldest Monte Carlo simulations of this kind was presented by Gilmer and Bennema (1972a), without taking into account surface diffusion; a little later the same authors performed a similar simulation including diffusion (Gilmer and Bennema 1972b). This work was quite interesting; nowadays, however, due to progress both in statistical mechanics and in computer science, it is possible to seek much more definite answers.

3.1. Models of crystal growth

MC simulations of growth are based on simplified growth models. In this subsection we shall explain the construction of these models. The strategy is, as usual, to concentrate on a few presumably important aspects (and processes) and disregard other details. In principle MC simulation can be applied to both continuum and discrete models; however, in most simulations *discrete models* are used and we shall consider only these models here. This simplifies things a lot but 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 vapour are described in a crude approximation: particles can occupy only discrete positions on some lattice. The system of solid and vapour is approximated in this way 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 vapour (figure 3(a)). In this picture many features of the real crystals are neglected: as a consequence, interactions between atoms in a discrete model are necessarily artificial and the interaction parameters introduced are only effective. 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 also be justified for growth from solution if the concentration is not very high.

It is natural to use the lattice gas model with a lattice whose symmetry is the same as that 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 the simulation technically, and in the spirit of approximate modelling one can still expect to get useful results when explaining the phenomena observed; some effects, however, may be lost (Evans 1991).

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 (figure 3(b)). On the same level of approximation one can also neglect bulk diffusion inside the crystal. In this picture we are interested only in the motion of the atoms forming the solid, and the growth proceeds by adding atoms at positions determined by growth rules (see below). This is a well justified approximation for ballistic growth where 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 the melt, and it may also be quite a crude approximation in the case of growth from vapour not far from equilibrium (Xiao *et al* 1991). 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
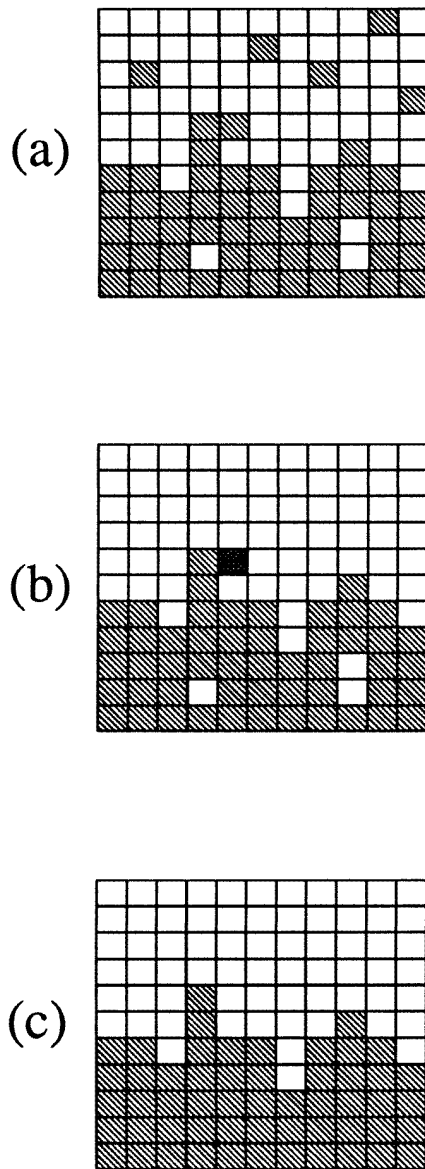
Figure 3. A hierarchy of approximations in discrete growth models illustrated in the case of two dimensions. (a) The configuration of the lattice gas with the bottom region corresponding to solid and the top region corresponding to gas. Atoms are represented by hatched squares. (b) Only positions of 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.

can hope that, using appropriate growth rules, a good qualitative model can be formulated even here, 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 a planar interface and under conditions where very few vacancies and overhangs (cf. figure 3(b)) appear in the growing material, one can use the so-called solid-on-solid (SOS) approximation (figure 3(c)). The latter means that each atom is sitting on top of another atom: then the surface is described by a single-valued function, $h(x, y)$, of the substrate coordinates (x, y).

The second ingredient of any growth model is the definition of dynamical growth rules. Here also some approximations are necessary. It is usually supposed that the motion of individual particles (atoms or molecules) takes 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 the phenomena to be studied, and others deemed inessential are ignored. Particles 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 only on the occupation of nearest-neighbour sites (but again quite complex dependence can be considered). We shall describe examples of SOS models with specific growth rules in sections 5 and 6. We would like also to note that in the context of fractal growth a whole menagerie of growth models has been suggested (Herrmann 1986, Vicsek 1989, Kotrla 1992, Bunde and Havlin 1994, Barabási and Stanley 1995) with applications ranging from crystal growth through aggregation phenomena to biological growth.

3.2. Kinetic Monte Carlo simulation

Standard thermodynamical MC simulation 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 (Binder and Heermann 1988, Heermann 1990, Valleau 1991). The focus is on the convergence of series for the quantities calculated, 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 (Kang and Weinberg 1989)).

About 20 years ago MC simulation started to be used also for the study of kinetic processes (Binder 1979, Binder and Kalos 1979). The aim of kinetic Monte Carlo (KMC) simulation is to reproduce faithfully *nonequilibrium*, or *relaxation* processes. This time the emphasis is on the correctness of time evolution in the simulation.

In order to fix ideas, let us denote the space of all possible configurations, $\mathcal{C}$, in a statistical-mechanical model by $\mathcal{S} = \{\mathcal{C}\}$, and a time-dependent distribution of configurations at time t by $P(\mathcal{C}, t)$.

The MC technique can be also viewed as a method of solving the master equation

$$\frac{\partial P(\mathcal{C}, t)}{\partial t} = -\sum_{\mathcal{C}'} W(\mathcal{C} \rightarrow \mathcal{C}') P(\mathcal{C}, t) + \sum_{\mathcal{C}'} W(\mathcal{C}' \rightarrow \mathcal{C}) P(\mathcal{C}', t) \qquad (21)$$

† Real processes are often much more complex: they may contain different time and space correlations.

associated with a matrix of *transition probabilities*, $W(\mathcal{C} \to \mathcal{C}')$, connecting two states. Equation (21) describes a stochastic process in the Markovian approximation (van Kampen 1981).

The transition probabilities in standard thermodynamical MC simulation do not need to have any relationship to the dynamics of the system. They are not considered as given *a priori* but they are constructed in a way which guarantees that the distribution of the states generated converges as fast as possible to the desired static distribution $P(\mathcal{C})$. At each MC step a trial configuration is generated, which is then either accepted or rejected. A sequence of configurations, $\mathcal{C}_k$, $k = 1, \ldots, M$ form a Markovian chain, which is used for the construction of series for the quantities to be calculated. The condition of *detailed balance*

$$W(\mathcal{C} \to \mathcal{C}')P(\mathcal{C}) = W(\mathcal{C}' \to \mathcal{C})P(\mathcal{C}') \tag{22}$$

is a sufficient (but not necessary) condition for the convergence of the Markov chain†. There is freedom in the choice of the form of the Ws, provided that the convergence is guaranteed. The most common choice is that of Metropolis *et al* (1953) which can be formally written as

$$W^{(M)}(\mathcal{C} \to \mathcal{C}') = \min\left(1, \frac{V(\mathcal{C}' \to \mathcal{C})P(\mathcal{C}')}{V(\mathcal{C} \to \mathcal{C}')P(\mathcal{C})}\right) \tag{23}$$

where $V(\mathcal{C} \to \mathcal{C}')$ is some 'underlying', or 'trial', stochastic matrix specifying possible transitions. If $P(\mathcal{C})$ is the canonical distribution, $P(\mathcal{C}) = (1/Z)\mathrm{e}^{-\beta E_\mathcal{C}}$ (β being the inverse temperature and $E_\mathcal{C}$ an energy of the configuration $\mathcal{C}$), one recovers the popular form of $W^{(M)}(\mathcal{C} \to \mathcal{C}')$: a possible new configuration $\mathcal{C}'$ is accepted with certainty if it has lower energy than the initial configuration $\mathcal{C}$, and with the probability $\mathrm{e}^{-\beta \Delta E}$, with $\Delta E = E_{\mathcal{C}'} - E_\mathcal{C}$ if $E_{\mathcal{C}'} \geqslant E_\mathcal{C}$. It is easy to check that the detailed balance is satisfied in this case. There are also other possibilities for the choice of the transition matrix, for example, the Glauber form (Glauber 1963):

$$W^{(G)}(\mathcal{C} \to \mathcal{C}') = \frac{1}{1 + \mathrm{e}^{\beta \Delta E}} \tag{24}$$

but one can expect the Metropolis form to be often more efficient with respect to convergence than the alternatives, since it makes the acceptance rate as high as possible.

Let us now describe the principle of kinetic Monte Carlo simulation. KMC simulation is a method for solving the master equation (21) describing the stochastic evolution of the system. The method for solving it is similar to that used in thermodynamical MC simulation: making random choices a Markov chain is generated. Now, however, in contrast to the procedure for standard thermodynamical MC simulation this chain has to represent a possible evolution of the system simulated. Configuration changes have to correspond to real events in the stochastic system. Each of the events in the real system can happen with some probability per unit time (rate). To be specific, let N be the number of possible events in a given configuration $\mathcal{C}$; in the case of crystal growth they are, for example, the hopping of an adatom, the adsorption of an atom, and so on. Let the rates of these events be R_a, $a = 1, \ldots, N$. Both N and the set $\{R_a\}$ depend on the configuration $\mathcal{C}$. Let us define the total rate

$$Q = Q(\mathcal{C}) = \sum_{a=1}^{N} R_a. \tag{25}$$

† More precisely, it is a member of the set of sufficient conditions together with other assumptions which are: ergodicity, $\forall_{\mathcal{C},\mathcal{C}'} W(\mathcal{C} \to \mathcal{C}') \geqslant 0$, and $\forall_\mathcal{C} \sum_{\mathcal{C}'} W(\mathcal{C} \to \mathcal{C}') = 1$.

The transition probabilities can now be formally written as

$$W(\mathcal{C} \to \mathcal{C}') = \sum_{a=1}^{N} R_a V^a(\mathcal{C} \to \mathcal{C}') \tag{26}$$

where $V^a(\mathcal{C} \to \mathcal{C}')$ is again an 'underlying' stochastic matrix for an event a, specifying whether the transition $\mathcal{C} \to \mathcal{C}'$ is possible by this event. In the simulation event a should occur with probability $R_a/Q(\mathcal{C})$. It is realized by selecting possible events with probabilities proportional to their physical rates. In principle, transition probabilities in KMC simulation do not have to obey the detailed-balance condition (22), but it was observed (Rácz *et al* 1991) that in the case of diffusion it is advantageous to use models with rules satisfying this condition. The detailed-balance condition should be satisfied if we are studying relaxation towards the equilibrium because then the convergence to the equilibrium distribution is guaranteed.

A simple, straightforward way to implement the idea of KMC simulation 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 the inner loop of the algorithm in the kth time step is as follows†.

Algorithm 1.

(i) Select a possible event which can be realized in the configuration $\mathcal{C}_k$.

(ii) Generate a random number within a uniform distribution of random numbers, $r \in [0, 1)$.

(iii) Compare r with the probability of the selected event P_e: if $r \leqslant P_e$, proceed with this event leading to a new state $\mathcal{C}_{k+1} = \mathcal{C}'$ and update the list of possible events; if not, stay in the same state.

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

This algorithm is very seldom used in practice because in many cases, in particular in the problems of 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 often selected and rejected. For example, in the simulation of diffusion with probability given by Arrhenius's law, the programme would select the movement of a highly coordinated atom and a poorly coordinated atom with the same frequency, but the atom with high coordination moves very little in comparison to the poorly coordinated atom. The ratio of the two rates is proportional to $e^{\beta \Delta E}$, where ΔE is a difference between the binding energies of the two 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 necessarily to be 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: it is difficult to simulate these fluctuations by the simple algorithm described above.

A much faster algorithm without unsuccessful attempts (also called the N-fold method algorithm) was formulated by Bortz *et al* (1975) (BKL) for the Ising model, and is often

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† Several other algorithms were suggested in Binder (1979). Probabilities P_a can also be calculated from the fraction $R_a/Q(\mathcal{C})$; then they are, however, configuration dependent and have to be updated at each time step.

used in KMC simulations of crystal growth (Clarke *et al* 1991). The basic idea is that at each MC step one process is selected with its corresponding probability and then also realized, instead of attempting a generic process (whose probability may be much lower). We 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 2 (the 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 choosing the first index s for which $\sum_{a=1}^{s} R_a(\mathcal{C}) \geqslant r$.

(iii) Proceed with the 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.

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 3 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 that is independent of N, but step (ii) is time consuming. If linear searching 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 no longer possible 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, can be obtained if one considers, instead of individual events, groups of events (Maksym 1988). Let us group events into n groups, labelled by $\alpha = 1, \ldots, n$. This can be done either formally by forming groups with the same number of events, which allows maximal effectiveness of the algorithm, or in a way which keeps the physics clear: forming groups of the same kinds of event, 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, and 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 possible process can be realized in one or more ways, by one or more event. Assume that a process α can be realized in $n_\alpha(\mathcal{C})$ ways, in the configuration $\mathcal{C}$. We shall call the quantities $n_\alpha(\mathcal{C})$ *multiplicities*. For example, there may be $n_{adat}(\mathcal{C})$ adatoms with the same surroundings which can diffuse, or there are $n_{dep}(\mathcal{C})$ 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 3.

(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 $\sum_{\alpha=1}^{\sigma} q_\alpha(\mathcal{C}) \geqslant r_1$.

(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 the multiplicities n_α, relative rates q_α, 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 a 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 $\mathcal{O}(N^{1/2})$. The time for step (v) may still be $\mathcal{O}(N)$ at the most, but it is quite short in many cases.

An even faster algorithm for large N can be obtained if we instead of the two-level search scheme, use a search scheme with $K > 2$ levels (Blue *et al* 1995), 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 $\mathcal{O}(K N^{1/K})$. The best asymptotic behaviour $\mathcal{O}(\ln_2 N)$ 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 (Blue *et al* 1995).

We shall conclude this subsection with a comment on time in KMC simulation. There is no real time in thermodynamical MC simulation, and usually the number of steps, or better the number of steps per site (number of sweeps) is used as 'time'. The number of MC steps, which we denote by t_{MC}, is clearly not the correct measure, since it does not take into account that different processes last for different time intervals. Nevertheless, in some cases it is a good approximation to take $t \propto t_{MC}$†. 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 in 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 of the 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}.

In the situations where we cannot justify a proportionality $t \propto t_{MC}$ we need to introduce somehow the physical time into the KMC simulation. This can be done (Fichthorn and Weinberg 1991, Kotrla and Levi 1991) provided that all physical processes can be separated so that in any time instance only one event takes place, and the events are Poisson processes. The time interval between two successive events (waiting time), τ, is a random variable with the distribution $P(\tau) = Q e^{-Q\tau}$, and the average value is $\langle \tau \rangle = 1/Q$ (van Kampen 1981), Q being the total rate as defined before. In the algorithms described above another random number, r_3, uniformly distributed between 0 and 1, will be generated, thus giving the time interval, $\Delta t_k = -(1/Q(\mathcal{C}_k)) \ln r_3$, spent before the passage to a new configuration $\mathcal{C}_{k+1}$. Note that $Q(\mathcal{C}_k)$ depends on the configuration $\mathcal{C}_k$. In an approximation one can only suppose that the system stays in the state $\mathcal{C}_k$ for a time inversely proportional to the total transition rate $Q(\mathcal{C}_k)$ (Kotrla and Levi 1991). Mean quantities during the growth are then

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† A coefficient of proportionality may exist, depending on model parameters.

calculated as time averages over M time points:

$$\langle A \rangle = t^{-1} \sum_{k=1}^{M} \Delta t_k \, A(\mathcal{C}_k) \tag{27}$$

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 the master equations (Kotrla and Levi 1991).

3.3. Methods for MBE simulations

MBE is a practically important problem with many applications in modern technology. We do not attempt to review this vast subject which includes morphological studies, submonolayer growth, recovery and even the removal of atoms during processes such as sputtering and etching, but we rather restrict consideration to methodological aspects.

The dominant mechanism here is surface diffusion. Particles fall down onto the surface and then migrate; at not very high temperatures desorption can be neglected. However, the details of the growth process and the chemistry are complex and largely unknown. Many results for semiconductors as well as for metals have been obtained by simulations with simplified models. There is an extensive original literature as well as several review articles (Madhukar and Ghaisas 1988, Vvedensky *et al* 1990, Metiu *et al* 1992, Vvedensky 1993, Haider *et al* 1995, Wolf 1995) on MC simulations of MBE growth. We shall describe here the so-called full-diffusion (FD) SOS model with the simple cubic lattice (Vvedensky *et al* 1990) which has been successfully used for the study of MBE growth—see e.g. Clarke *et al* (1991), Shitara *et al* (1992), Šmilauer *et al* (1993b) and other references.

We 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 neighbours are considered. In the model with Arrhenius dynamics the hopping rate does not depend on the bonding energy at the final position (after the 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} 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 neighbours, $m E_N$, 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, $D = k_0 \exp(-\beta E_S)$. Newly arriving particles are deposited at randomly selected sites.

If we define an 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, $W_{i \rightarrow j} \propto e^{-\beta E}$, obey the detailed-balance condition:

$$\frac{W_{i \rightarrow j}}{W_{j \rightarrow i}} = \exp\{-\beta(m_i - m_j)\}. \tag{28}$$

Different modifications of the model described above are possible: 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 (Clarke *et al* 1991). In this case the incoming particle searches for the 'best' site for deposition in some region. A possibility which was used (Clarke *et al* 1991) for the best choice is that the particle searches for the site which provides the highest nearest-neighbour coordination within a square with a side of $2R_i + 1$ lattice constants centred upon the incidence site (in the case of conflict the nearest site to the arrival site is chosen).

Recently the FD model has been modified by introducing additional interaction with next-nearest neighbours in planes below and above the hopping atom (Šmilauer *et al* 1993b, 1993a) in order to mimic the Ehrlich–Schwoebel effect.

In the simulations of the FD model (Vvedensky *et al* 1990, Clarke *et al* 1991) the two-level BKL algorithm has been used (cf., however, Blue *et al* (1995)). Selection of the site for deposition is very simple, one of the $L^{d'}$ sites is chosen at random. The diffusion event is selected using a look-up table with a special randomizing procedure (Clarke *et al* 1991).

The FD model has been successfully applied to the study of growth of different materials: Si (Clarke *et al* 1991), GaAs (Shitara *et al* 1992), Pt (Šmilauer *et al* 1993b), in spite of the fact that it uses a simple cubic lattice instead of the proper structure of the material. A practical advantage of the FD model described is its simplicity and flexibility, in contrast to previous modelling work on the growth of III–V compounds (Madhukar and Ghaisas 1988) which took into account the structural and compositional complexity of the growing system. We want to stress that the energy parameters determining the rates which are found in modelling growth by discrete models are only effective parameters, and should not be identified with the energy barriers for diffusion, even if very good agreement with experiment is obtained. For instabilities arising in MBE growth, see subsection 6.3.

4. Growth of rough surfaces

4.1. Kinetic roughness

In recent years, the kinetic roughening of surfaces under the action of a driving force has become a field of increasing interest. Several review articles (Meakin 1993, Halpin-Healy and Zhang 1995, Krug 1996) and books (Vicsek 1989, Barabási and Stanley 1995) have recently appeared on this subject and we will not review this extended field in the present paper, but we explain some basic notions and very briefly describe the present state of the art.

4.1.1. Scaling. The study of kinetic roughness† is connected with previous activity on fractal growth (Herrmann 1986, Vicsek 1989). Here the focus is on the way in which the surface becomes rough during far-from-equilibrium growth. Quantitatively, the surface roughness is described by the surface width w. Let us consider a surface in a d-dimensional space given by a single-valued function $h(x, t)$ of a d'-dimensional ($d = d' + 1$) substrate coordinate x. Then for a discrete model the surface width w is given by $w^2 = \langle N^{-1} \sum_i (h_i - \overline{h})^2 \rangle$, where $\overline{h} = N^{-1} \sum_i h_i$ is the average height, $h_i = h(x_i)$, $N = L^{d'}$, L is a linear size of the system, the index i labels lattice sites, and $\langle \ldots \rangle$ denotes a statistical average (in simulations an average over different runs).

A remarkable fact is the existence of self-affine scaling. Surface fluctuations exhibit universal behaviour leading to scaling in both time and space with two characteristic scaling exponents: a *roughness exponent* ζ and a *dynamic exponent* z. The surface profile and its properties are statistically invariant if the length in a direction parallel to the surface is scaled by a factor b and simultaneously the length in the perpendicular direction and the time t by factors b^ζ and b^z, respectively. Starting from an initially flat substrate, the surface

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† The phenomenon is called *kinetic roughening* by several authors. We prefer *kinetic roughness*, however, since generally speaking no transition is implied here. Also, the genuine dynamic roughening proposed by Nozières and Gallet (1987) is a very different effect (see the next subsection).

width w obeys the dynamical scaling law (Family and Vicsek 1985)

$$w(t, L) \propto L^\zeta f(t/L^z) \tag{29}$$

where the scaling function $f(x)$ has the properties: $f(x) = $ constant, $x \gg 1$ and $f(x) \propto x^\beta$, $x \ll 1$ ($\beta = \zeta/z$). Therefore, w grows according to a power law, $w \propto t^\beta$, until a steady state characterized by a constant value of the width is reached after a time t_{sat} proportional to L^z. The value of the saturated width w_{sat} varies with the system size according to $w_{\text{sat}} \propto L^\zeta$. The scaling is valid also for other quantities; for example for the height–height correlation function, or structure factor, it allows one to obtain more reliable results.

The exponents ζ and z (or ζ and β) characterize the scaling behaviour of the surface width for a particular model. This allows one to classify different kinds of growth from the statistical-mechanical point of view, in analogy with the theory of critical phenomena. In fact, it has been observed that asymptotic values (values for very large system size and long time) of the exponents z and ζ in many cases can take only certain definite values corresponding to different universality classes.

There are two approaches in this field: (i) investigation of stochastic continuum equations describing growth (see below) and (ii) numerical simulation of discrete models†. Both the discrete models and the stochastic equations are usually much simpler than more realistic models used in qualitative, or semi-quantitative studies of growth, the reason being that the scaling behaviour is believed to be 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.

The universal behaviour has been observed in a wide variety of growth models and there has been considerable effort put into finding different possible universality classes, several of which have been found. The universality classes are denoted according to the names of the corresponding stochastic equations.

4.1.2. Stochastic differential equations. The simplest time-dependent description of a stochastic surface is afforded by the Edwards–Wilkinson (EW) equation (Edwards and Wilkinson 1982):

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \eta \tag{30}$$

where ν has the dimensions of a diffusion coefficient, and η is a noise term. This equation can also describe a *growing* surface if considered as written in the *comoving frame*. It was originally proposed (as an approximation to a more complicated equation) for *sedimentation*. The EW equation, being linear, can be exactly solved; the scaling exponents are $\zeta = (3 - d)/2$, $z = 2$.

In $2 + 1$ dimensions (the critical dimension) the solutions of the EW equation give rise to a *mean square height difference*

$$g(\boldsymbol{x}) = \langle [h(\boldsymbol{x}) - h(\boldsymbol{0})]^2 \rangle \tag{31}$$

behaving asymptotically as $\ln r$, $x = |\boldsymbol{x}|$. This *logarithmic roughness* is quite similar to that of a surface *in equilibrium* (above the roughening temperature T_R).

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† The relationship of the two approaches is not obvious; usually it is based only on comparison of results for scaling exponents, but in particular cases a continuum equation can be obtained from a master equation for discrete models (see Předota and Kotrla (1996) and references therein).

A non-linear perturbation of the EW equation is the Kardar–Parisi–Zhang (KPZ) equation (Kardar *et al* 1986):

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \lambda (\nabla h)^2 + \eta. \tag{32}$$

The KPZ equation generates surfaces whose roughness may be stronger than logarithmic, i.e. of *power-law* form. In $1 + 1$ dimensions the scaling exponents of this equation have been exactly calculated by Kardar *et al* using the renormalization group approach ($\zeta = 1/2$, $z = 3/2$). In higher dimensions exact values of the exponents are not known but there are numerical results (see e.g. Barabási and Stanley (1995)); what the upper critical dimension is remains an open question.

If the EW equation is perturbed by a *periodic force* favouring the *integer levels* (i.e. if the crystal structure is taken into account) the Chui–Weeks (CW) equation is obtained (Chui and Weeks 1978)):

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + y_0 \sin 2\pi h + \eta \tag{33}$$

and the surface tends to become *smoother*. Thus a surface obeying the CW equation either is smooth, or if it is rough cannot be more than logarithmically rough†.

An important class of equations are the *conserving* equations of the form

$$\frac{\partial h(\boldsymbol{x}, t)}{\partial t} = -\boldsymbol{\nabla} \cdot \boldsymbol{J}[\nabla h(\boldsymbol{x}, t)] + \eta(\boldsymbol{x}, t). \tag{34}$$

$\boldsymbol{J}$ is the surface current depending on the derivatives of h and possibly on h itself. The EW equation is conserving but the KPZ equation is not. A linear diffusion equation is obtained for $\boldsymbol{J} = -K \boldsymbol{\nabla} \nabla^2 h(\boldsymbol{x}, t)$. It can be exactly solved and exponents are $\zeta = (5-d)/2$, $z = 4$.

With the particular choice

$$\boldsymbol{J} = -K \boldsymbol{\nabla} \nabla^2 h(\boldsymbol{x}, t) + \lambda \boldsymbol{\nabla}(\nabla h)^2 \tag{35}$$

where J is the gradient of the right-hand side of the KPZ equation, we obtain the so-called *conserved KPZ equation*. This equation has been recently studied (Tu 1992, Krug 1996), but its properties are still not completely known.

Very interesting developments have been presented by Maritan *et al* (1992). They write stochastic equations in surface coordinates (instead of Cartesian coordinates): this allows the study of a more general surface, involving overhangs.

4.1.3. Discrete models.   There has been much interest in the study of kinetic roughness in various discrete growth models, which were motivated by different physical situations. The pertinence of various models to universality classes has been identified.

The simplest model belonging to the EW class was formulated by Family (1986). In many growth models (ballistic deposition, the restricted SOS model, the Eden model surface) the KPZ behaviour was observed and the results agreed with the concept of universality—a small change in the growth rules did not cause a change of exponents. Physically this behaviour is observed in situations where lateral correlations are important; this kind of growth is not volume conserving. The EW class, in contrast, corresponds to simple conserved growth, leading to a relatively smooth surface. The original example of this physical situation is the process of sedimentation of small material particles in a liquid caused by gravity (Edwards and Wilkinson 1982).

† However, Rost and Spohn (1994) showed that a KPZ term can be generated by the interplay of the periodic potential and the driving force. There appears to be an open problem here.
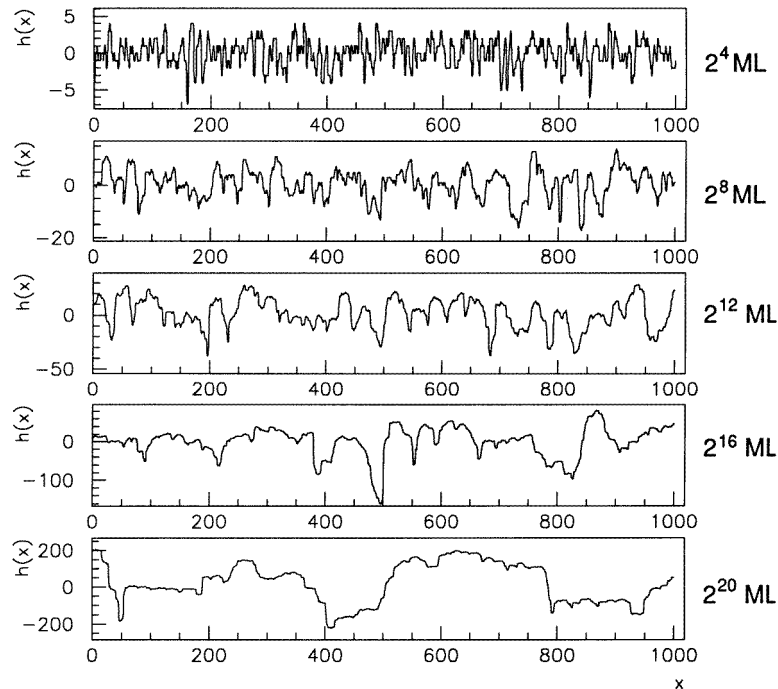
Figure 4. The example of time evolution of the surface profile in the one-dimensional Wolf–Villain model.

Recently much effort has been devoted to the identification of a possible universal behaviour of MBE growth (where surface diffusion is a central phenomenon). Several simple discrete models have been suggested (Wolf and Villain 1990, Das Sarma and Tamborenea 1991, Lai and Das Sarma 1991, Kotrla *et al* 1992, Das Sarma and Ghaisas 1992), in which a particle relaxes only immediately after deposition and then remains immobile for the rest of the simulation. Surfaces in these models may be very rough or even unstable. An unrealistic feature of these models is that surface profiles with very large local slope can develop. The example of evolution of the surface profile in one of them, in the Wolf–Villain model (Wolf and Villain 1990), is shown in figure 4.

The asymptotic behaviour in models for MBE was puzzling; now the situation can be summarized as follows (Siegert and Plischke 1994a, Krug 1996, Kotrla and Šmilauer 1996). There are two generic situations: either the growing surface is relatively smooth and the growth process belongs to the EW class, or there is instability. A new feature which has been found in these models is anomalous scaling, in which a new independent exponent appears, and in some models also multiscaling has beem observed (for more details see e.g. Krug (1996)). What the real explanation of these effects is and how generic they are remain to be understood.

Another interesting problem is the interface motion in a disordered medium, and the depinning transition caused by the driving force (for review see e.g. Barabási and Stanley (1995)). The universal behaviour of growth in systems with two or more species (e.g. systems with 'ferromagnetic' or 'antiferromagnetic' interactions) is at the moment an open problem (Předota 1995).

4.2. Dynamic roughening

In the context of the Chui–Weeks equation, Nozières and Gallet presented a theory which in principle solves the growth problem in the neighbourhood of the thermal roughening transition (Nozières and Gallet 1987). The Nozières–Gallet theory is based on a renormalization scheme (applied to the CW equation and stopped at the appropriate stage, depending on the strength of the disequilibrium $\Delta\mu$) in the treatment of fluctuations at the crystal–fluid interface. Such a theory was immediately applied to the special case of the solid–superfluid interface in ^{4}He, whose roughening, discovered independently by Israeli, French and Russian groups (Avron *et al* 1980, Balibar and Castaing 1980, Keshishev *et al* 1981), was experimentally studied, in the non-equilibrium case, by Gallet *et al* (1987). Further (theoretical) contributions on this subject were presented by us (Levi and Kotrla 1993, Kotrla and Levi 1994) and by Giorgini and Bowley (1995).

Let us briefly describe the physical situation near the roughening transition (for further details, see Levi and Kotrla (1993)). In the CW equation the term $\nu\nabla^2 h$ describes propagation over the surface of the information concerning the local level h. A new layer is completed in the time $\tau = a_z/v$, and in this time the information is propagated to a distance $l \sim \sqrt{2\nu\tau}$. As long as this distance is large enough—in fact, as long as it is larger than ξ, the *equilibrium* correlation length on the surface—the surface grows layer by layer, according to the same *Becker–Döring laws* as hold at lower temperatures. But near roughening (as well as above), ξ diverges and, as soon as it is larger than l, the information can no longer travel as far as ξ before a new layer is created; everything occurs as if ξ were infinite: the surface roughens (*dynamic roughening*) and the growth law becomes similar to the Wilson–Frenkel law; in particular, the growth velocity becomes linear in $\Delta\mu$. The result is an effective *lowering* of the roughening temperature as a function of $\Delta\mu$.

Here we present an elementary treatment of this effect, even simpler than that given in our previous work (Levi and Kotrla 1993). According to classical nucleation theory (as applied to crystal growth by Becker and Döring (1935)) a growth nucleus, or island, of N adatoms has a (Gibbs) free energy G made up of two terms: a negative term $-N\,\Delta\mu$ and a positive term, related to the energy cost of building the step that serves as island boundary, given by $N_b\varepsilon_s$, where N_b is the number of boundary atoms and ε_s is the step free energy per atom. If the island is convex, N_b is of the form $N_b = c\sqrt{N}$†, where e.g. $c = 4$ for a square island. G is maximal for the *critical nucleus*, i.e. for $N = N^* = [c\varepsilon_s/(2\,\Delta\mu)]^2$, and the maximum, the *nucleation barrier*, is $G^* = c^2\varepsilon^2/(4\,\Delta\mu)$. If, however, l is relatively small, the surface behaves as if it had a finite size l and, in particular, if l is less than the size of the critical nucleus, the latter does not form: the area of the largest islands is of order l^2, which also implies a *lowering* of the nucleation barrier. This is irrelevant at low temperatures, where $\xi \ll l$, but becomes important just below T_R (above T_R the effect is irrelevant again, since in the absence of a nucleation barrier the surface grows linearly in $\Delta\mu$, as if it were rough: this is irrelevant if it is indeed rough even at equilibrium). It should be recalled that ξ and ε_s are inversely proportional to each other (see e.g. Mazzeo *et al* (1992)), so no explicit reference to ξ is really necessary‡: the relevant quantities in our problem are $x = \beta\varepsilon_s$, $y = \beta\,\Delta\mu$. The growth velocity may be written as the 'rough' (or Wilson–Frenkel) growth velocity v_0 divided by a factor, $\omega > 1$, related to the nucleation barrier, which, in

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† The islands tend to be convex in order to reduce both the step free energy, by reducing the boundary length, and the kink free energy, by reducing the number of kinks. As a consequence, we shall disregard the kink contribution altogether. At high disequilibria this may not be correct, since the island does not live undisturbed long enough to optimize its shape.

‡ It will turn out that the critical value of ξ is relatively small, $\xi/a = \sqrt{2}e^{3/2}/3 = 2.11$.

the presence of this 'dynamic roughening' effect, is not fixed but depends, in turn, on the size of the effective critical nucleus, i.e. on the growth velocity, i.e. on $\omega = v_0/v$. The characteristic length l (which may be identified with the size of the relevant island) can be found from the Edwards–Wilkinson or Chui–Weeks equations as $l = \sqrt{(2\nu\tau)}$, where ν, the coefficient of the Laplacian term in the stochastic equations, is of the order of av_0, and τ is the time for growing one layer, a/v. Then $l/a = \sqrt{(2\omega)}$.
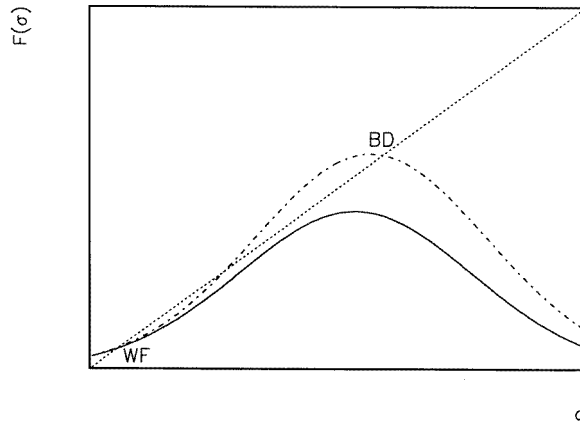

Figure 5. Dynamic roughening as a first-order transition described by equation (36), for a dimensionless disequilibrium $y = 0.03$. Chain curve ($x = 0.36$): the equation has three solutions, of which the physical one, marked BD, corresponds to slow, Becker–Döring-like growth. Solid curve ($x = 0.34$): the slow solution has disappeared altogether and the growth takes place according to a small σ-value, i.e. to fast, Wilson–Frenkel-like growth, corresponding to the point marked WF.

This leads to a self-consistency equation of the type

$$\sigma = e^{px\sigma - qy\sigma^2}. \tag{36}$$

Here $\omega = \sigma^2$ and (using the famous 'Kolmogorov cubic root'—see above—and taking $c = 4$) $p = 2\sqrt{2}/3, q = 1/3$. This equation always has solutions, but it is physically interesting only if the solution σ is *less* than the value, $\sigma^* = \sqrt{(2x/y)}$, corresponding to the maximum of the right-hand side (meaning an effective reduction of the critical nucleus size). Let us fix y (i.e. essentially the disequilibrium). Then for large x there is only one (Becker–Döring-like) solution, but below a certain value of x (provided that y is less than a critical value $y_c = 3e^{-3}/2 = 0.0747$) there are two more solutions (corresponding to faster growth). Finally, beyond another x-value $x = x_{NG}$ the slow mode disappears altogether and a jump is unavoidable to a faster (Wilson–Frenkel-like) growth mode. We take this as an indication that the Nozières–Gallet effect has set in (see figure 5). $x_{NG} < x_c$, where the critical value x_c equals $x_c = 3e^{-3/2}/\sqrt{2} = 0.473$, and for the correlation length the critical value is the inverse, $\xi_c/a = 2.11$ (corresponding to a rather low temperature $T \sim 0.55T_R$). Since this critical ξ is not very long, the jump in growth rate should really take place in the interesting cases. If, on the other hand, $y > y_c$, the growth should go to a faster regime smoothly, 'supercritically' (this is understandable since at such strong disequilibria the critical nucleus† is small anyway and even the Becker–Döring growth is

† The occurrence of the word *critical* with two different meanings is unfortunate, but unavoidable here.

already fast). The possibility of genuine critical phenomena in the neighbourhood of such a *growth critical point* is worth investigating.

5. Kinetic BCSOS and related growth models

Our research group has tried, whenever possible, to use the well known *six-vertex model* of statistical mechanics, which was exactly solved, around 1967, by Lieb and others (see the review of Lieb and Wu (1972)), and has proven so useful (via *van Beijeren's mapping* (van Beijeren 1977)) for studying the statistical mechanics of surfaces. Our first study, however, did not make use of van Beijeren's mapping: we used a different mapping, where the *lines* appearing in Lieb's representation of the six-vertex problem (where in each vertex only the downward and leftward arrows are marked) are directly identified with *surface steps* (see below (Garrod *et al* 1990)), and, by this representation, we treated an extremely simple case of growth by step flow. Subsequently, however, we reverted to van Beijeren's mapping in order to have a somewhat richer growth model (see below).

5.1. Mapping of crystal growth onto the six-vertex model

The six-vertex model (Pauling 1935) is the best model to describe *roughening* in equilibrium. Indeed, van Beijeren in 1977 was able to map his BCSOS (body-centred solid-on-solid) model (van Beijeren 1977) onto the six-vertex model, which had been exactly solved by Lieb *et al* ten years earlier. The roughening transition exists and corresponds in the mapping to the antiferroelectric transition of the six-vertex model (a very weak, ∞-order transition).

The six-vertex model is exactly solvable (Lieb and Wu 1972). The partition function is obtained from the transfer matrix, whose eigenfunctions are given by the *Bethe ansatz*.

The model is isomorphic to the Heisenberg–Ising chain (Yang and Yang 1966).

The properties of the model depend on six parameters, the energies of the six vertices, ϵ_j, $j = 1, \ldots, 6$, and on $\beta = (kT)^{-1}$. A considerable simplification occurs in the *symmetric* case, where $\epsilon_2 = \epsilon_1$, $\epsilon_4 = \epsilon_3$, $\epsilon_6 = \epsilon_5$. Then all properties depend only on two parameters:

$$x = \mathrm{e}^{\beta(\epsilon_5 - \epsilon_1)} \qquad y = \mathrm{e}^{\beta(\epsilon_5 - \epsilon_3)}. \tag{37}$$

In the (x, y) plane four phases are present:

(a) two ferroelectric phases, one for $x > 1$, $y < x - 1$ and the other for $y > x + 1$;
(b) an antiferroelectric phase for $x < 1$, $y < 1 - x$; and
(c) a disordered phase at high temperature ($|x - 1| < y < x + 1$).

Important special cases are:

(i) the KDP model ($\epsilon_3 = \epsilon_5 = \epsilon > 0$, $\epsilon_1 = 0$) (*ferroelectric*) (Slater 1941); and
(ii) the F model ($\epsilon_1 = \epsilon_3 = \epsilon > 0$, $\epsilon_5 = 0$) (*antiferroelectric*) (Rys 1963).

In *both* cases $kT_c = \epsilon/(\ln 2)$ (but the transition is of *first order* for KDP, of *infinite order* for F).

Here the six-vertex model is used out of equilibrium, to describe growth, according to two different mappings:

(1) the line mapping (model I);
(2) van Beijeren's mapping (models II and III).

These mappings are explicitly shown in figure 6. (Still other mappings were presented in the literature (Gwa and Spohn 1992a, b, Hontinfinde and Touzani 1995), but they refer to growth in $1 + 1$ dimensions, and are therefore very different.)
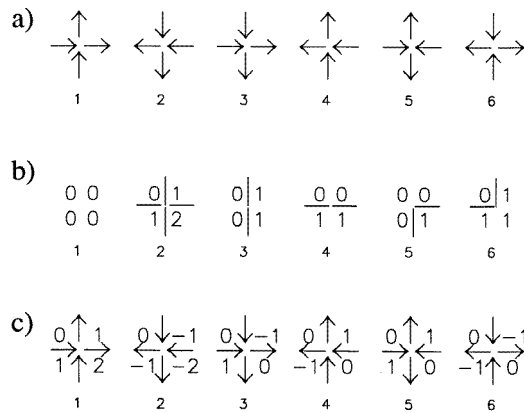
Figure 6. Mappings of surface levels onto the six-vertex model. (a) The vertices. (b) Line mapping: only the arrows pointing down and to the left survive; the lines thus arising are interpreted as surface steps. (c) van Beijeren's mapping: the levels are such that, for any pair of atoms, the higher-level atom is found to the right of the arrow.

5.2. Model I: step flow

Line mapping. The usual representation of the six-vertex model (*arrow representation*) places arrows on the bonds of a square lattice, in such a way that at each lattice point two arrows enter, and two arrows exit (*the ice rule*). There are six ways to satisfy the ice rule, and thus the six vertices are formed.

However, an equivalent (and in many cases more useful) representation is the *line representation*, where only the arrows pointing down and to the left are marked. The union of such arrows forms *lines* that go across the plane in the south-west direction.

In the *line mapping* these lines, occurring in the line representation of the six-vertex model, are directly identified with *steps on a surface* (Garrod *et al* 1990). These steps are all of the same sign: the resulting surface is thus a *vicinal surface*, whose growth takes place by *step flow*. The level of the surface increases in the south-east direction. When a step moves in the north-west direction, the upper terrace widens at the expense of the lower terrace, and the crystal grows.

In order for the mapping to be one to one, only one type of step (single steps) are permitted. Double and multiple steps are eliminated by sliding the crystal layers in the south-east direction by an amount proportional to their level. This procedure, however, also eliminates *step crossing* (corresponding to vertex 2 in the line mapping). So only vertices 1, 3, 4, 5, 6 survive and the six-vertex model becomes a *five-vertex model* (Garrod 1991, Gulácsi *et al* 1993, 1994)!

Conservation rules. Consider a square table of side N. Let A be the total length of horizontal line segments, B that of vertical line segments, and let N_i be the number of vertices of type i. Then during the growth process A and B are conserved, and

$$N_4 + N_5 = A \tag{38}$$

$$N_3 + N_5 = B \tag{39}$$

$$N_1 = L^2 - A - B. \tag{40}$$

Master equation. (A, B, N_1) define a *class* of configurations.
Configurations differing from each other only by translation (with cyclic boundary

conditions) form a *subclass*. During the growth process the class is conserved, but the subclass is not.

Let P_m be the probability for the system to be in a configuration belonging to subclass m within a class. Then the *master equation*

$$\frac{\mathrm{d}P_m}{\mathrm{d}t} = -(p_m C + q_m E)P_m + \sum_n (C M_{mn} + E M'_{mn})P_n \tag{41}$$

holds, where C, E are the *condensation (sticking)* and *evaporation coefficients*, p_m, q_m are the numbers of condensation and evaporation sites in the m-configurations, and M_{mn}, M'_{mn} the numbers of ways m-configurations are obtained from n-configurations by sticking and evaporation processes respectively.

The main results (obtained either by solving the master equation directly, or by Monte Carlo simulations) are as follows. After a *transient* phase, a *steady* situation is established. Starting from an *equilibrium* situation (i.e. from a situation where all configurations in a class are *equiprobable*), under growth conditions $(C > E)$ the growth rate *decreases*, so the steady-state growth rate is slower than the initial, equilibrium growth rate. This is due to the fact that the configurations corresponding to fast growth grow themselves out of the picture, leaving a prevalence of evaporation configurations.

5.3. Model II: deposition and desorption

van Beijeren's mapping. Model II (Kotrla and Levi 1991, 1992) is similar in some respects to model I, but it makes use of a different mapping onto the six-vertex model.

The line mapping is limited, because growth takes place solely by *step flow*. We are also interested in the *nucleation* of *new* steps. To study this it is better to revert to van Beijeren's mapping (for the (001) face of a bcc crystal), where an arrow indicates a level difference between two neighbouring atoms, the *higher* atom lying to the *right* of the arrow (van Beijeren 1977). *Temperature T* and *disequilibrium* $\Delta\mu$ were explicitly introduced, letting the system evolve according to a generalized *Glauber kinetics*:

$$C = \frac{\mathrm{e}^{\beta\,\Delta\mu}}{\mathrm{e}^{\beta\,\Delta E} + 1} \qquad E = \frac{1}{\mathrm{e}^{\beta\,\Delta E} + 1} \tag{42}$$

where ΔE is the change in surface energy.

On a finite, square table of side N, the model was solved by Monte Carlo simulation (or even analytically, for extremely small sizes). The boundary between (two-dimensional) *layer growth* and (three-dimensional) *continuous growth* is sought finding the *maximal growth rate* as T varies. For increasing $\Delta\mu$ it bends to the *left* (Kotrla and Levi 1991). This means that increasing disequilibrium favours three-dimensional growth. Indeed, for $T < T_R$ and $\Delta\mu$ small, plotting the surface level h as a function of time t the successive layers are well recognized as plateaus; but as $\Delta\mu$ is increased, the plateaus become progressively smeared out and $h(t)$ tends to become a straight line, indicating continuous growth. For large disequilibrium and high T the growth rate approaches the Wilson–Frenkel limit (4).

The surface roughness in this growth model was investigated. The results indicate the following (Kotrla and Levi 1992).

(1) For *any T* and *any* $\Delta\mu > 0$ the surface is *rough* (i.e. $\langle\Delta h^2\rangle$ *diverges* with L).
(2) For $\Delta\mu$ small (and for all $\Delta\mu$ if T is low) the roughness is logarithmic.
(3) For $T < T_R$ this behaviour *tends to a universal limit* as $\Delta\mu \to \infty$; see figure 7.
(4) For $T > T_R$ a crossover occurs from logarithmic to *power-law* roughness:

$$\langle\Delta h^2\rangle \sim L^\zeta \tag{43}$$

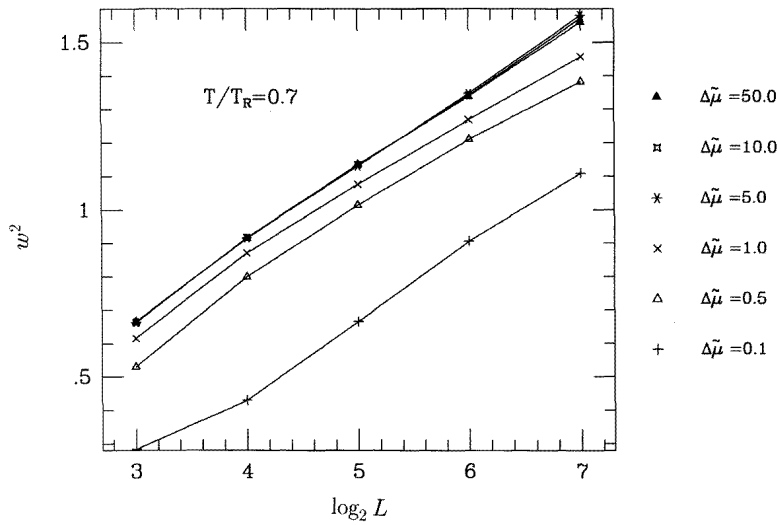**Figure 7.** The dependence of the roughness on the size L and $\Delta\mu$ at the temperature $T = 0.7T_R$ in model II.
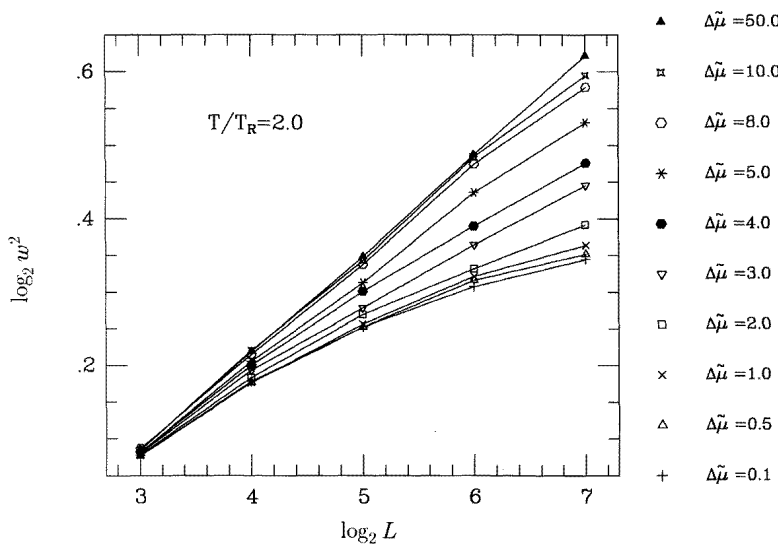

Figure 8. As the previous figure, but at the temperature $T = 2T_R$.

(see figure 8; for large $\Delta\mu$, ζ depends only on T (not on $\Delta\mu$), increases with T and tends to ≈ 0.35 as $T \to \infty$: this value appears to agree with the value of ζ for the KPZ universality class).

(5) For any value of $\Delta\mu$ (except $\Delta\mu \to \infty$) the power-law behaviour reverts to logarithmic for large L. The values of L at which this happens increase with $\Delta\mu$: this behaviour obeys a *scaling law*.

5.4. Model III: growth with diffusion

Crystal growth in the kinetic BCSOS model was considered in the above-mentioned studies (Kotrla and Levi 1991, 1992, Hontinfinde *et al* 1996) without diffusion, i.e. in an oversimplified version of the model where the growth process is reduced to a competition between sticking and desorption. Many of the most relevant effects which have recently attracted the attention of experimentalists and theoreticians alike are, however, related to diffusion and to barriers hindering it (Schwoebel and Shipsey 1966, Kunkel *et al* 1990). It is necessary, therefore, to include diffusion in the treatment (as was done many years ago in a simpler context by Gilmer and Bennema (1972b)): this was done most recently in Genova for the BCSOS model (Levi and Tartaglino 1996). The main advantages, with respect to older work, are the availability of present-day, faster computers and the use of the six-vertex model, which ensures e.g. an exact knowledge of the roughening temperature T_R.

In model III, diffusion is introduced explicitly in the description of the growth process. Actually, it is important to introduce at least two diffusion moves, with different activation energies: in the former the mobile atom remains at the same level; in the latter the atom descends (or climbs) a step (in the BCSOS model this move is similar to the knight's move in chess).

We recall the structure of the BCSOS model (van Beijeren 1977). The (001) surface of a body-centred cubic lattice is considered. The lattice comprises two sublattices (corner atoms and centre atoms), so the nearest neighbours of every atom belong to the other sublattice, with a very strong interaction J_0 which, in order to enforce the SOS condition exactly, is actually taken to be infinite in van Beijeren's theory. The next-nearest neighbours, on the other hand, belong to the same sublattice: the corresponding interaction J is the relevant energy scale for the model.

Model II above was a simple extension of van Beijeren's BCSOS model to non-equilibrium situations. Model III is a further extension where diffusion is taken into account; with model III we shall be forced, however, to relax van Beijeren's condition $J_0 \to \infty$: we shall take J_0 larger than J, but finite. This is necessary, since for $J_0 \to \infty$ no evaporation is possible; moreover, equilibrium takes place at a chemical potential $\mu \to -\infty$, i.e. for zero vapour pressure, so the vapour is replaced by a vacuum, and no deposition is possible. But if J_0 is finite, the level difference between neighbouring sites is no longer strictly forced to be 1: level differences of 3, e.g., become possible. Although such level differences are not considered here, they have been studied elsewhere, leading to a 14-vertex model (Barbero *et al* 1996).

A Monte Carlo simulation is performed. Two regimes are considered: in regime I, at low disequilibria $\Delta\mu$, diffusions are far more frequent than either depositions or desorptions; in regime II, corresponding to high disequilibria, on the other hand, desorption may be neglected altogether and the growth behaviour results from the competition between deposition and diffusion.

Here we focus the attention predominantly on regime I. Although in such a regime, because of their rarity, the adsorption–desorption processes cannot be directly simulated (between two such events something like 10^8 or 10^9 diffusion events may take place, which would lead to impossibly long simulation times), it is possible, nonetheless, to estimate the adsorption and desorption rates by counting the sites active for each process. This leads to an interesting and to some extent unexpected result: regime I splits into two rather different subregimes (Ia and Ib). The analysis of the physical situation is best conducted in terms of the *coverage* Θ: the diffusion processes drive the surface to *partial equilibrium*, without

changing Θ.

At complete equilibrium the desorption and adsorption rates are such that the surface tends to adsorb or lose atoms depending on Θ. A *partial growth rate* $G_p(\Theta) = S(\Theta) - E(\Theta)$ is defined, different from zero even at equilibrium. For low coverages, since the surface is essentially flat with a few atoms or small clusters weakly bonded on it, evaporation is favoured over deposition, so $G_p < 0$. When the coverage is close to 1, on the other hand, the interface looks like a flat surface with a few holes on it. Sticking is favoured: in fact, when more than half a layer is deposited ($\Theta > 1/2$), $G_p(\Theta) > 0$.

The effect of switching on the disequilibrium is to multiply the adsorption probability by $\exp(\Delta\mu/kT)$, where T is the temperature, while the desorption probability (at least for the moderate disequilibria corresponding to regime I) remains essentially unchanged. In subregime Ia, next to equilibrium, there are still ranges of Θ for which desorption remains more probable than adsorption. This fact creates a *bottleneck*, which blocks the growth until an important fluctuation overcomes the block: in other words, there exists a nucleation barrier. In subregime Ib, on the other hand, the disequilibrium is so great that for any coverage Θ the adsorption probability is larger than the desorption probability: in this case the growth becomes continuous in time (although still layer by layer).
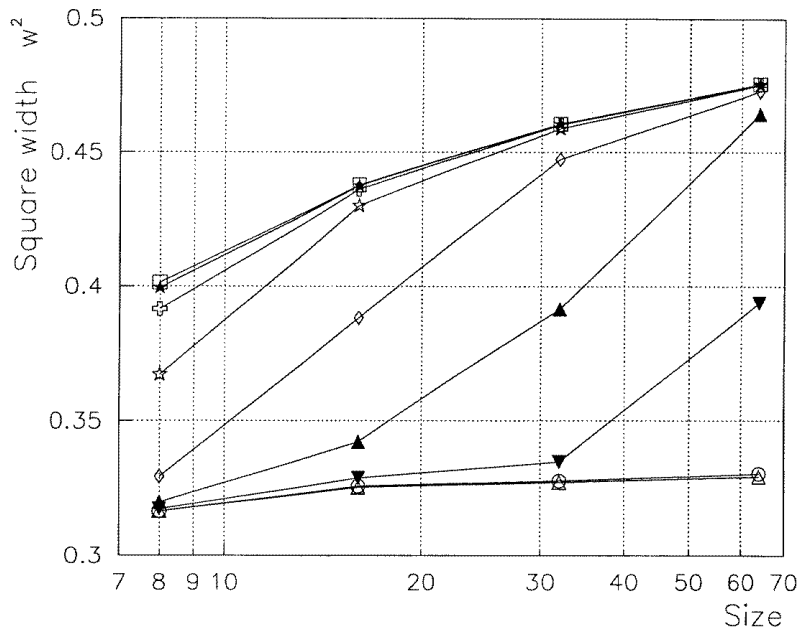

Figure 9. The roughness behaviour of model III, From the bottom to the top the graphs correspond to increasing disequilibria: $\Delta\mu/\epsilon = 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2$ and 5 respectively.

In contrast to that of model II, the roughness behaviour of model III is rather complicated, and cannot be represented by a simple functional dependence of w^2 on size. There is a crossover, instead (see figure 9), from a small-scale to a large-scale behaviour, this crossover occurring earlier for larger disequilibria.

6. Unstable growth

6.1. Dendritic growth

The *Mullins–Sekerka instability* (Mullins and Sekerka 1964, Langer 1980) arises whenever a *protuberance* of the crystal, extending into fluid regions where T is lower, grows faster than the rest. (For growth from vapour the protuberance must be bigger than a mean free path!) Then planar growth is disrupted and a needle crystal is formed (the latter is called a *dendrite* (from Greek $\delta\acute{\epsilon}\nu\delta\rho o\nu$, *tree*) because side branching nearly always occurs).

The instability is fought against by the *surface tension* γ which favours planar shapes; but γ is only sensitive to *local* disturbances and cannot stop the growth of *broad* protuberances.

Continuous theory. Needle crystals are treated as approximate paraboloids. Ivantsov (1947), neglecting γ and solving the heat equation in *parabolic coordinates*, found a simple functional relation between dimensionless *disequilibrium* $\Delta = \Delta\mu/\Delta\mu_c$ and *Péclet's number* $Pe = c\rho v/2\lambda$ where: ρ is the radius of curvature at the tip, c and λ are the specific heat and the thermal conductivity of the fluid, and where the critical disequilibrium $\Delta\mu_c$ equals Λ^2/cT (Λ being the latent heat), and e.g. reduces, for vapour growth from a monatomic gas, to $72/5\beta\epsilon^2$: i.e. $\Delta = 5/72q$.

For $\Delta > 1$ (*hypercooling*) there is no solution: no *stationary* freezing is possible. This is because the fluid is so cold at infinity that the release of latent heat is not sufficient to keep the interface at the melting temperature[†].

For $\Delta < 1$, Pe is found by inverting Ivantsov's law:

$$\Delta(Pe) = Pe \, e^{Pe} \int_{Pe}^{\infty} \frac{e^{-y}}{y} \, dy. \tag{44}$$

For small Pe, Δ, we have $\Delta \approx Pe(|\ln Pe| - C)$ (C is Euler's constant); for $\Delta \to 1$, Pe diverges as $(1 - \Delta)^{-1}$. But Pe contains the *product* ρ times v.

Introducing the surface tension γ changes the dependence of Pe on Δ somewhat; these changes, however, occur at rather low Pe values, which are seldom of interest experimentally. In the most interesting range, Ivantsov's law is well verified. There is another problem, however: Ivantsov's law is incomplete, in the sense that it gives only Pe (i.e. the product ρv) while a complete solution of the problem requires calculating both ρ and v, not only their product!

To obtain ρ and v separately we need another condition: the first formulation of a condition of this kind, due to Langer, may be written (Langer 1980) as

$$\sigma = \frac{\gamma}{n \, \Delta\mu_c \, \rho \, Pe} = \text{constant}.$$

Subsequently, more careful analysis showed that σ is not a universal constant, but depends only on the *anisotropy* α. For small Δ and for a square lattice, $\sigma \sim \alpha^{7/4}$ (Ben Amar and Pomeau 1986, Barbieri *et al* 1987)[‡] and $v \sim [Pe(\Delta)]^2$. Thus the velocity v is roughly quadratic in $\Delta\mu$.

The latter results have been obtained in the last fifteen years or so via very subtle mathematical analysis of the growth process. In the beautiful book *Solids Far From Equilibrium* (Godrèche 1991)[§] two chapters, one by the Caroli *et al* (1991), and most

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[†] Notice that nucleation requires approximately $q^{-1} > \frac{1}{3}$, while hypercooling occurs if $q^{-1} > \frac{72}{5}$, i.e. at a disequilibrium more than 40 times larger.

[‡] For a triangular lattice 7/4 becomes 7/6 (Gliozzi *et al* 1994).

[§] In general, the reader of the present article may find useful to consult that book, where many of the subjects considered here are discussed in depth.
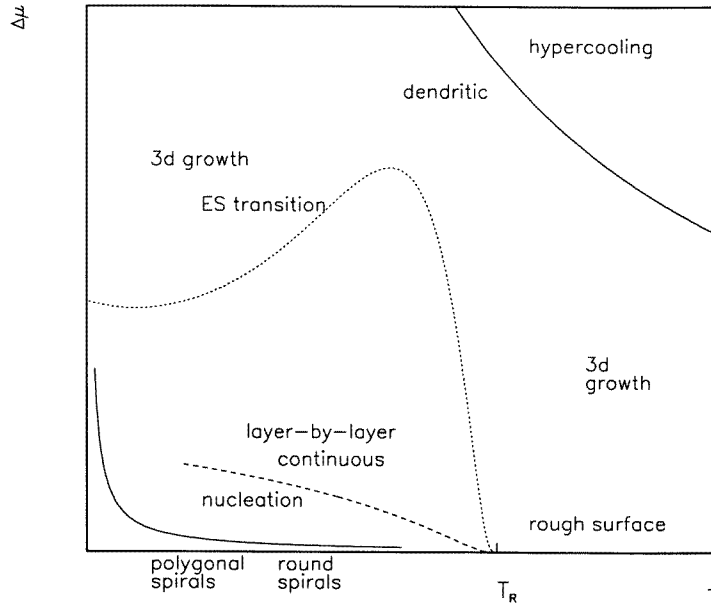
Figure 10. A schematic phase diagram in the $(T, \Delta\mu)$-plane. In this figure the transitions between layer-by-layer growth with and without a bottleneck for nucleation and between layer-by-layer and three-dimensional growth are evident. Two hyperbolae, $q_0 = $ constant (where q_0 is an approximation for q obtained by replacing the step energy per atom ε by a constant ε_0), mark the onset of nucleation and hypercooling respectively. The Ehrlich–Schwoebel transition from three-dimensional growth at low T to layer growth at higher T is also shown. The dendritic and hypercooling modes actually depend not only on T and $\Delta\mu$, but also on the boundary conditions.

especially one by Pomeau and Ben Amar (1991) deal extensively with these problems. In the presence of diffusion or heat transport (in the fluid, or in the crystal, or in both), the growth of a non-planar surface is a highly non-linear problem, as already stressed in the nineteenth century by Gibbs and Thomson. The non-linearity comes from the presence of a term containing the *total curvature* $\mathcal{K} = \rho_1^{-1} + \rho_2^{-1}$ (where ρ_1 and ρ_2 are the two principal radii of curvature), a notoriously non-linear object in geometry†. The Gibbs–Thomson equation gives the interface temperature as

$$T_{int} = T_M - \frac{\gamma T_M}{\rho_s \Lambda} \mathcal{K} \tag{45}$$

where ρ_s is the crystal density, γ is the interface free energy and Λ is the latent heat.

It is appropriate to sketch at this point an overall, schematic phase diagram for growth (figure 10).

6.2. Cluster growth

Since Witten and Sander introduced their fortunate diffusion-limited aggregation (DLA) model (Witten and Sander 1981), the literature on the subject has developed enormously. The main reason for this is that the DLA model is the simplest tool for generating random

† Similarly, the presence of non-linear space-time curvature makes general relativity such a difficult theory, although the scalar curvature reduces in two dimensions to the Gaussian curvature, not to the total curvature.

fractals: of course deterministic fractals, such as the Sierpiński gasket, had been known of for a long time, but, however elegant, were uninteresting as models of the physical world. The Sierpiński gasket, e.g., is too simple; the Mandelbrot set, on the other hand, has a fascinating chaotic nature, but is too complicated, and at the same time too deterministic, to afford a hope of describing 'natural' fractals, from the leaves of a tree to the affluents of a large river. Random fractals offered such a hope. Important connections were also discovered with clusters occurring in critical phenomena or percolation problems (although the properties were different in each case). The more important contribution of the DLA model was probably that of furnishing a *paradigm*, within which the fractal properties of natural or computer-generated objects could be studied, from the relatively simple overall fractal dimension to quantities obtainable only via much subtler analysis.

It is out of question to discuss these problems here (see, for example, Vicsek (1989) or Meakin (1988) for a thorough treatment). We wish, however, to consider cluster growth from the same point of view as we have considered crystal growth in the remainder of this paper: i.e. in terms of physical (thermodynamical) parameters—temperature T and disequilibrium $\Delta\mu$ in the first place. The clusters which we are going to consider, therefore, must in some limiting case ($\Delta\mu = 0$) be in equilibrium with the environment; hence they must be able to compensate growth by evaporation or dissolution, and hence a double DLA-like process must be involved. Such a double DLA process was first introduced (as were many other things in statistical mechanics) by Kadanoff (1985).

Let us first recall ordinary DLA, as was first proposed by Witten and Sander (1981). DLA is a growth process, taking place in a computer. The growth starts from a pre-existing *germ*, placed at the origin. In the simplest case the simulation is two dimensional. *Atoms* are sent in sequentially from the circumference of a large circle, having the germ at its centre. Each atom performs a *random walk* in the plane; finally either it reaches a site neighbouring the growing cluster, in which case it sticks irreversibly to the cluster, or it reaches the outer circumference again, in which case it is lost. In this way clusters are generated, possessing a characteristically ramified appearance: the fractal dimension of DLA clusters, as obtained numerically, is 1.71 ± 0.01 (Meakin 1983)†.

DLA growth is irreversible and, from our point of view, corresponds to $\Delta\mu \to \infty$. In order to allow for finite disequilibria, Kadanoff introduced a very simple modification of DLA, which he calls a *pedestrian model*. Two competing processes are taking place: one process is ordinary DLA, while in the other process atoms detach from the cluster, perform again a random walk and either stick to the cluster at another point or are lost. A modified version of this model was studied in detail by Gliozzi *et al* (1994). The work of Gliozzi *et al* was addressed to studying the temperature and disequilibrium dependence of the *growth morphology* of two-dimensional clusters (see figure 11).

As pointed out by Shochet *et al* (1992a, b), the problem of interfacial pattern formation is not yet solved. It turns out that the so-called *dense-branching morphology* (DBM), characterized by *tip splitting*, is the generic growth mode when the interfacial tension is isotropic, whereas anisotropy is necessary to stabilize dendrites (Ben-Jacob and Garik 1990, Ben Amar and Brener 1993) (see above). However, the DBM can appear even if anisotropy is present (Saito and Ueta 1989, Ben-Jacob and Garik 1990, Shochet *et al* 1992b).

In a very interesting article, Saito and Ueta (1989) described the morphology of growing two-dimensional clusters by means of a simulation, where the solid was surrounded by an actual vapour. They started from the equilibrium shape of a little two-dimensional crystal,

† Theories trying to prove that it must be $5/3 = 1.67$ (Turkevich and Scher 1986) were not accurate enough; more precise and convincing results have been obtained more recently by Erzan *et al* (1995).
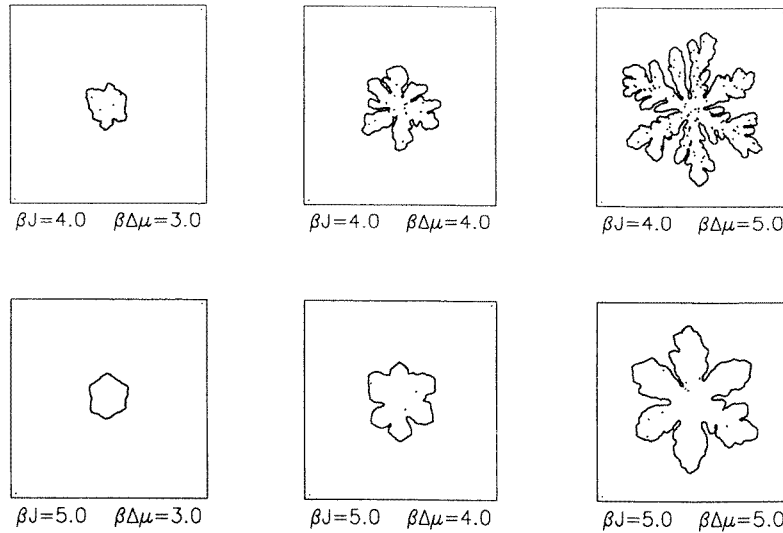
Figure 11. Clusters grown according to the procedure of Gliozzi *et al* for different temperatures and disequilibria. J = strength of the molecular bond; $\beta = 1/k_B T$. A tip-splitting transition takes place, for temperatures between $0.25 J/k_B$ and $0.33 J/k_B$, from the dendritic to the dense-branching morphology.

which for the square lattice geometry is known, in terms of the exact ϕ-dependence of the boundary tension γ, from work by Rottman and Wortis (1981) (for an extension to the triangular lattice see Zia (1986)). Using an actual vapour instead of the random walk of single atoms allows one to study collective effects, in particular the depletion zone in the immediate environment of the growing cluster.

Shochet *et al* studied the growth morphologies in terms of physically significant parameters (Shochet *et al* 1992b). The same was done by Gliozzi *et al* (1994), who specifically applied the analysis to the growth of clusters of the gel phase at the expense of the fluid phase in Langmuir monolayers. In these works the physical parameters are T and $\Delta\mu$. The role of disequilibrium is obvious; temperature, on the other hand, occurs indirectly, via the T-dependence of *anisotropy*. Gliozzi *et al* found, at a rather well defined temperature (or anisotropy), a morphology transition of the tip-splitting type, from the dendritic to the dense-branching morphology. Interestingly, even for large disequilibria and (relatively) high temperatures, the clusters generated in this way (contrary to what happens for simple DLA) are not ordinary fractals. Rather, they belong to the typology of *fat fractals* (Vicsek 1989), i.e. their measure, when measured with rulers of length l, is given by

$$M(l) = M(0) + Al^\gamma \tag{46}$$

(for ordinary, or *thin* fractals, $M(0)$ vanishes). A further development in terms of the description of cluster growth in Langmuir monolayers took into account the important effects of long-range interactions (Indiveri *et al* 1996a, b, Pastor-Satorras and Rubí 1995), which have a destabilizing influence even in thermodynamic equilibrium (McConnell 1991, Vanderlick and Möhwald 1989).

A fairly complete analysis of morphology transitions in the (disequilibrium, anisotropy)-plane was presented by Brener *et al* (1992), leading to the identification of four distinct morphologies which they call compact dendrite, fractal dendrite, compact seaweed, and

fractal seaweed (where *seaweed* indicates the DBMs).

In Langmuir monolayers, clusters of the gel phase are seen to grow with peculiar asymmetries, whenever the molecules possess chiral properties (Rietz *et al* 1993) (which affect both the diffusion process through the fluid and the process of attachment, especially when impurities are present (Pomeau 1987)). Other asymmetries may arise simply from the ordering of the hydrophobic tails in one direction, which determines in that direction a weaker dipolar repulsion or even an attraction. These problems are currently under study. However, even more important potentially will be the application of the above-mentioned methods to the growth of metal clusters on metals: such clusters exhibit very diverse forms, from compact to ramified, fat-fractal shapes (Hwang *et al* 1991), depending, as Bartelt and Evans (1994) have shown in an interesting paper, on the ratio between the rate of arrival of new atoms from the outside and the rate of diffusion along the periphery of the cluster. An intermediate case between Langmuir monolayers and metal adsorbates is that of self-assembled structures of, e.g., thiols on gold (Camillone *et al* 1994), which have recently been the object of very interesting studies.

6.3. Unstable MBE growth

It was found recently that MBE growth on a singular surface (i.e. a high-symmetry crystal face) is unstable. The three-dimensional growth in this case has a special form: pyramid-like structures (mounds) are formed on the surface and as time proceeds they increase and merge; the average size of mounds continues to grow all the time. This unstable-growth mode was first predicted by Villain (1991), and later was seen in computer simulations of a simple SOS model with Glauber dynamics governed by a Hamiltonian with a term $\sum_{\langle i,j \rangle} |h_i - h_j|^4$ (Siegert and Plischke 1992, 1994a), of the Wolf–Villain model (cf. subsection 4.1) in higher dimensions (Šmilauer and Kotrla 1994), and of the full diffusion model with the Ehrlich–Schwoebel barrier (Johnson *et al* 1994, Šmilauer and Vvedensky 1995, Siegert and Plischke 1996) as well as in numerical solutions of the Langevin equations (Johnson *et al* 1994, Siegert and Plischke 1994b, Stroscio *et al* 1995). This growth mode has been recently observed experimentally in various systems: GaAs/GaAs(001) (Johnson *et al* 1994), Cu/Cu(001) (Ernst *et al* 1994), Ge/Ge(001) (van Nostrand *et al* 1995), Fe/MgO(001) (Thürmer *et al* 1995), Fe/Fe(001) (Stroscio *et al* 1995), Rh(111) (Tsui *et al* 1996).

The existence of the instability observed in the above-mentioned experiments is attributed to the Ehrlich–Schwoebel (ES) barrier which suppresses interlayer transport see above. Let us recall the argument for that (Villain 1991, Johnson *et al* 1994). In MBE the surface height (measured in the comoving frame of reference) obeys a conserving equation (34) where $\boldsymbol{J}$ is the surface current which is a function of the derivatives of height and η is the shot noise due to the fluctuations in the incoming particle beam. The current can be written in the form

$$\boldsymbol{J}(\boldsymbol{x}, t) = \boldsymbol{j}[\boldsymbol{\nabla} h(\boldsymbol{x}, t)] + K \, \boldsymbol{\nabla} \nabla^2 h(\boldsymbol{x}, t). \tag{47}$$

Here the K-term represents the leading contribution to the equilibrium diffusion current (Mullins 1957, Herring 1957) and tends to smoothen the surface, and $\boldsymbol{j}$ is a non-equilibrium tilt-dependent contribution. In the case of a high-symmetry surface for small fluctuations of $\boldsymbol{\nabla} h(\boldsymbol{x}, t)$ one can assume (Villain 1991) $\boldsymbol{j}(\boldsymbol{x}, t) = C \, \boldsymbol{\nabla} h(\boldsymbol{x}, t)$. Let us assume for the moment that the ES barrier is infinitely high, i.e., no adatom can jump downwards at the step edge and all adatoms remain on the upper terrace. Then an adatom on a terrace preferentially sticks at the ascending step. This means that the current has the same direction and sense as $\boldsymbol{\nabla} h$, i.e., the coefficient C is positive and equation (34) is unstable.

Let us consider the growth of a vicinal surface with the tilt m, formed by a sequence of steps. The traditional picture is that growth proceeds in the step-flow mode (Burton *et al* 1951). If nucleation is neglected, a train of steps proceeds uniformly across the surface when atoms from the incoming beam land on adjacent terraces and diffuse to be trapped at the step edges. It can be expected that in the presence of the ES barrier the instability described above will be present, up to some value of the tilt.

A simple intuitive argument is as follows (the ES barrier being still infinite). If the terrace size l is smaller than the diffusion length l_d, then all of the adatoms reach the step edge of the upper terrace where they are incorporated. The surface current is uphill with the dependence $j(m) \propto 1/m$ on the tilt $m = 1/l$ of the surface, and the growth proceeds in the step-flow mode. If the terrace size is larger than l_d (the slope is lower than $1/l_d$) only some of the adatoms will reach the step edge of the upper terrace. This fraction is approximately l_d/l; thus the current is $j(m) \propto l_d/l = l_d m$. The current has a positive derivative $j'(m)$ for small m and this leads to instability (a negative Laplacian in equation (34); see also Krug *et al* (1993)).

Let us consider the question somewhat more closely. As was shown by Bales and Zangwill (1990) in $2 + 1$ dimensions a *meandering instability* of the steps arises (because atoms are more likely to attach to already advanced parts of the step): the surface, although stable across the steps, is unstable along them. Moreover, recently it was shown that even in $1 + 1$ dimensions the step-flow regime is really destabilized by island formation via fluctuations (Krug and Schimschak 1995). This leads to metastability: the growth behaves as stable for a time t_2 that increases with increasing slope m ($t_2 \propto m^2$). In $2+1$ dimensions, on the other hand, mounds indistinguishable from those obtained on singular surfaces evolve (Rost *et al* 1996). Thus, the instability is present also on vicinal surfaces.

One is interested here not only in the existence of instability, but also in its temporal evolution, which can also be measured experimentally. Two important quantities to follow are the average mound size and the average slope of a mound. These characteristics can be either measured directly or extracted from various correlation functions. The slope of mounds in experiments is usually found to be approximately constant (Ernst *et al* 1994, Johnson *et al* 1994, Thürmer *et al* 1995, Stroscio *et al* 1995) but in some cases has been observed to increase: the mounds become steeper (van Nostrand *et al* 1995, Ammer *et al* 1994, Albrecht *et al* 1993). The mound size increases with time according to a power law with an exponent n, i.e., $\propto (\text{time})^n$; different values of the exponent n have been measured ranging from 0.16 (Stroscio *et al* 1995) to 0.5 (Ernst *et al* 1994).

Johnson *et al* (1994) suggested a differential equation with the current interpolating between the step-flow and unstable regimes

$$j(m) \propto \frac{m l_d^2}{1 + (m l_d)^2} \tag{48}$$

where $m = \nabla h(x, t)$ and $m = |m|$. However, in this choice j always has the same sense as m and all slopes are unstable, and deeper and deeper grooves are expected to evolve. Hunt *et al* (1994) studied the one-dimensional form of the equation (48) and found coarsening (i.e. an increase of the lateral size R of perturbations), $R \propto t^n$, with $n \approx 0.22$.

Siegert and Plischke have argued that, due to the lattice symmetry, the function $j_\alpha(m)$ (α labels surface directions) should become negative beyond some characteristic value m^* of the slope. Then $j_\alpha(m^*) = 0$, $(\partial j_\alpha/\partial m)|_m = m^* < 0$ and the slope m^* would be stable against small perturbations (Siegert and Plischke 1994b). For example, if the growing surface has average orientation {001}, then local high-symmetry surfaces like {110} or {111} cannot be consistently described as vicinal surfaces; rather the symmetry requires the current to be

zero for such orientations. Siegert and Plischke generalized equation (48) to the form

$$j(m) = \frac{Dm(1 - m^2)}{(1 - m^2)^2 + (ml_d)^2}.\tag{49}$$

This current is properly equal to zero on the two high-symmetry surfaces $m = 0$ and $m = \infty$ and is also zero at the intermediate inclination $m = 1$. Integrating this equation in $(2+1)$D they found slope selection and observed that pyramids continue to grow until only a single pyramid remains in a finite-size system, and concluded that there is no scale selection in the problem. In this situation the roughness exponent is $\zeta = 1$, and there is only one exponent z ($\beta = 1/z$) and only one relevant length in contrast to the case for conventional theories of kinetic roughness (cf. subsection 4.1). They measured the coarsening exponent n using a slope–slope correlation function, and for equation (49) as well as for its anisotropic modification they obtained $n \approx 1/4$ although they expected Lifshitz–Slyozov–Wagner-like behaviour with $n = 1/3$ (Lifshitz and Slyozov 1961, Wagner 1961). They attributed this difference to the importance of the constraint $\nabla \times m = 0$. They also suggested that this coarsening process is similar to the domain growth problem and that the slope corresponds to the order parameter in the domain growth problem. The current (49) is only a prototype for the slope-selection mechanism, the current may have more zeros (the first one is stable, the next can again be unstable). In reality the value of the selected slope can be much lower—in fact in experiments with GaAs (Johnson *et al* 1994) the angle was of the order of degrees.

In order to explain the low value of the exponent $n \approx 0.16$ observed for growth in the Fe/Fe(001) system, Stroscio *et al* (1995) suggested that near equilibrium the Mullins–Herring term $K \nabla \nabla^2 h(x, t)$ is absent and replaced it by a higher-order term $B \nabla \nabla^2 \nabla^2 h(x, t)$. They have no special reason for including the sixth-order term, except that it is the next-lowest-order linear term after the Mullins–Herring term. By numerical integration of the Langevin equation (34) with

$$J = -B \nabla \nabla^2 (\nabla \cdot m) + Cm - \lambda m^2 m + \sigma \nabla(m^2)\tag{50}$$

in $(2+1)$D they obtained $n = 0.18 \pm 0.02$. The second term in equation (50) is a destabilizing uphill current, the third is the term suggested by Siegert and Plischke, and the last term was included in order to break up–down reflection symmetry. They argued that the exponent n is insensitive to the presence or absence of the symmetry-breaking term but that this term is essential for the agreement of the calculated morphologies with the experimental data. It is clear that when both the Mullins–Herring term and the sixth-order term are present a crossover from $n = 1/6$ to $n = 1/4$ is expected with the crossover time given by the values of corresponding coefficients.

A complementary approach to the study of Langevin equations is the study of microscopic models by MC simulations. This allows the investigation of microscopical mechanisms and of the dependence of growth on material and physical parameters. Johnson *et al* (1994) observed the formation of mounds in simulations using the full diffusion model with next-nearest-neighbour interaction (cf. subsection 3.3), which allows one to incorporate the ES barrier (Šmilauer *et al* 1993b). They noted that the instability is quite different from the large instabilities seen in earlier theoretical work (Siegert and Plischke 1992) where the slope of the structure increases without bounds, whereas for the FD model with the ES barrier it was constant or possibly only slowly increasing in time. The surface profile in earlier models contained deep grooves and the exponent for the time evolution of the roughness was sometimes very high, $\beta \approx 1$ (Kotrla and Šmilauer 1996).

Šmilauer and Vvedensky (1995) presented simulations of the full diffusion model with the ES barrier and a transient mobility just after deposition of an atom, for various material
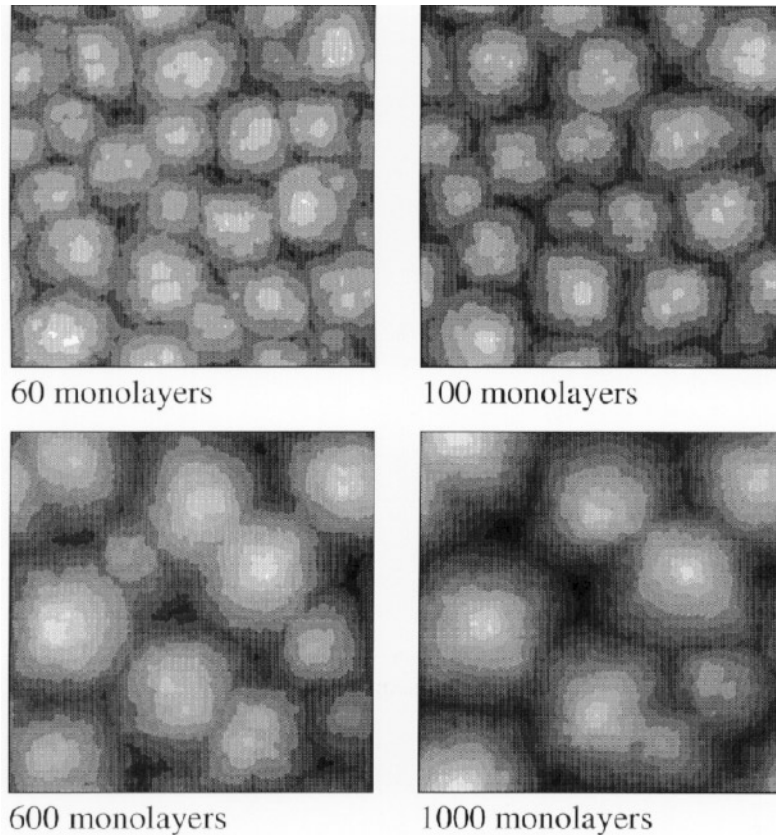
60 monolayers
100 monolayers

600 monolayers
1000 monolayers

Figure 12. Evolution of the surface morphology in a simulation of unstable epitaxial growth (1000 monolayers on a 300×300 lattice). Courtesy of Pavel Šmilauer.

(E_B, E_N and E_B) and physical (T, F) parameters (cf. subsection 3.3), with the emphasis on the early-time regime which is seen in experiments (see figure 12). Transient mobility was modelled by an incorporation process (see subsection 3.3). Note that in this formulation incorporation does not depend on the value of the ES barrier. They found that the average mound size increases with time as a power law with the exponent $n \approx 0.19$ to 0.26, and depending on the model parameters the slope stays approximately constant or increases according to a power law. They pointed out that there is competition between coarsening and steepening of the mounds.

They also observed that the slope of the mounds is strongly affected by changing the parameter R_i. For $R_i = 0$ the slope was higher and was increasing with time. On increasing R_i, both the rate of steepening and the absolute value of the slope decreased. The dependence on R_i is actually the result of a combination of two effects. An incorporation mechanism with large R_i reduces the number of atoms deposited on terraces, so the uphill current due to the ES effect becomes significantly smaller. The incorporation mechanism also directly contributes to the surface current. This partial current may be uphill (cf. Kotrla and Šmilauer (1996)) or downhill depending on the local configuration. Statistically it leads to contributions which change the observed slope. The absolute value of the slope increases as the height of the step-edge barrier increases. Although Šmilauer and Vvedensky did

not observe any significant change of the slope with the temperature in their simulation, the slope should also increase with decreasing temperature, as observed in experiments on Cu(001) (Ernst *et al* 1994). Finally, their data also showed that the exponent n is larger for lower step-edge barriers.

If there was only a sufficiently strong ES effect and nothing else, it would lead to structures whose slopes would increase up to a very large value, where the SOS approximation is not justified any longer. In order to have slope selection a counterbalancing mechanism is needed. Such a mechanism can be introduced directly into the model in different ways. An incorporation mechanism with parameter R_i from the previous model restricts the slope to the maximal value $1/R_i$ (a surface with a larger slope grows in a step-flow-like mode already during deposition). The restricted SOS model (representing constraints by lattice structure) could also be used, in order to limit the slope. Another mechanism was considered by Siegert and Plischke (1996). In contrast to the work of Šmilauer and Vvedensky (1995), they concentrated on the asymptotic behaviour in a similar model (also in $(2+1)$D). They use the same representation for the ES barrier, but instead of a transient mobility they introduce a slope-dependent downhill current generated during deposition. They allow a fraction p of the deposited particles to immediately hop to a nearest-neighbour column of lower height, if it exists. They use parameters which are far from being realistic for real materials, but which were optimized in order to use small system sizes ($L \leqslant 128$) and still observe instability with a slope consistent with the SOS approximation†. To have small system size is important from the numerical point of view in order to reach the steady state in a reasonably short time, because the dynamical exponent of these systems is large ($z \approx 4$). Measuring the dependence of the surface current on the tilt they found that the current has a zero even for $p = 0$, but for rather large slope $m \approx 1.6$. This is due to the particular implementation of the ES barrier in which a step of height 2 leads to downhill current (Siegert and Plischke 1996). For $p > 0$ the selected slope was about 0.5. They found a coarsening exponent $n \approx 0.25$, and for anisotropic diffusion $n \approx 0.18$.

A different approach was applied by Elkinani and Villain (1994). They proposed a simplified quasi-deterministic model in $(1+1)$D. An advantage of this model is that the computational time is greatly reduced and a systematic investigation of the effect of different parameters is possible. These authors found that deep cracks form even for a small ES barrier, but they form after a time which is very long if the ES barrier is small. They also observed that in certain cases the roughness increases proportionally to time. The model of Elkinani and Villain was further studied by Politi and Villain (1996). They found the coarsening to become extremely slow after mounds reached a critical radius. The same results have been obtained in a simple growth model with only post-deposition relaxation instead of full diffusion (Kotrla 1996b). In this model coarsening is evident and there is competition between coarsening and steepening. The coarsening behaviour strongly depends on the probability of passing the ES barrier. For any finite value of the barrier there is a crossover to slow coarsening and fast steepening. An example of the evolution of the surface profile is shown in figure 13. Wavelength selection was found also in a different model by Lanczycki and Das Sarma (1996).

At present, the situation can be summarized as follows. Pyramid-like growth is a non-equilibrium effect due to a combination of the microscopic ES barriers and the breaking of detailed balance by the pure deposition process (without desorption). During the growth

† As pointed out by Krug *et al* (1993) the Mullins–Herring term, $\nabla^2 \nabla^2 m$, suppresses the instability for small enough system sizes. In the linear approximation equation (34) takes the form $\partial h / \partial t = -\nu \nabla^2 h - K \nabla^2 \nabla^2 h + \eta$ and by Fourier transform it is easy to see that the growth process is stable for wavelengths smaller than $2\pi \sqrt{K/\nu}$.
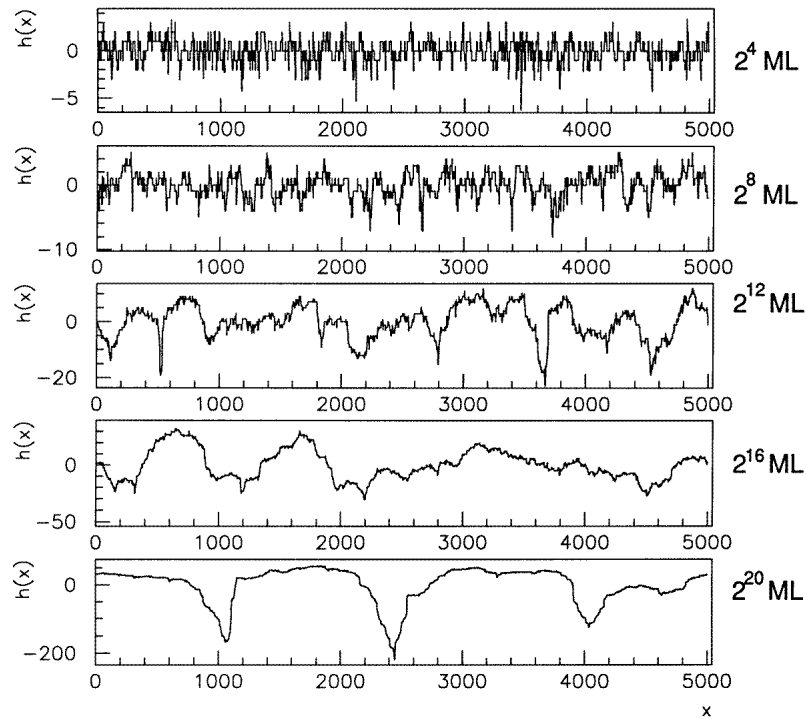
Figure 13. Coarsening and steepening of the surface profile in a simple relaxation model for a small ES barrier.

three-dimensional features on the surface coarsen with a power-law dependence of size on time. Various exponents have been measured in both experiment and simulation. The large interval of observed exponents is probably due to crossover effects which necessarily appear and may extend to rather long times, depending on the physical and material parameters. Initially the tilt of the mounds is much smaller than the possible finally selected slope. Thus, there will be a crossover regime with increasing slope. Since the steepening is related to the coarsening, one can expect a crossover in the exponent for coarsening as well.

The study of very long times is difficult in both experiments and simulations; thus it is not possible to draw firm conclusions yet. There are several things which remain to be explained. At present it is not clear what determines the value of the exponent n nor why the asymptotic value of the exponent n in theory is close to $1/4$ (instead of $1/3$ as in the case of domain growth in magnets). No fundamental understanding of the qualitative difference between domain growth in magnets and in MBE exists. It is also not clear whether the asymptotic behaviour is always the same ($t^{1/4}$?) or whether several 'classes' exist, as well as what the explanation is of large values of the exponent n observed at intermediate times—for example, $n = 1/2$ in an experiment on Cu(001) (Ernst *et al* 1994) or $n = 1/3$ in an experiment on Rh(111) (Tsui *et al* 1996). Finally, there are questions about the dependence on physical and material parameters which are only partially clarified—in particular, that of how to optimize the growth conditions in order to reach the slope-selection regime as fast as possible.

In order to understand the growth of real materials more information on material parameters—in particular, on the values of the ES barrier—is needed. These quantities

are difficult to measure, but they can be obtained from MD simulations. For some materials such studies have already been started† but clearly much more work is needed for materials for which pyramid-like growth was observed. MD calculations can also help one to evaluate the importance of post-deposition processes, such as transient mobility, the knockout process and other elementary processes.

7. Outlook

Much progress has been made in the understanding of crystal growth, but much remains to be done. The subject is extremely varied, and the method valid for one problem may not be useful for another.

In terms of theory, one of the most important problems is still the roughness of a growing surface, especially when $\Delta\mu$ is finite. For $\Delta\mu \to \infty$ the surface is usually extremely rough (and self-affine), and it can be adequately described in terms of the Family–Vicsek parametrization (29); but for finite $\Delta\mu$ the situation is quite different. In the absence of diffusion, the process resembles that described by the Edwards–Wilkinson equation and, indeed, if $\Delta\mu$ is small the simulations (Kotrla and Levi 1992) show logarithmic roughness (although at higher $\Delta\mu$ a transition to power-law roughness may take place (Kotrla and Levi 1992)), but in the presence of diffusion the situation is more complex (Levi and Tartaglino 1996). A true theoretical analysis of these problems is still lacking. The behaviour near T_R is quite important and not completely understood, although the ideas proposed by Nozières and Gallet (1987) are clearly correct. Elementary discussions such as were given by Levi and Kotrla (1993), as well as in the present paper, are not sufficient, but point to interesting developments.

Turning to Monte Carlo simulations, the warnings of Müller-Krumbhaar (1979) are still partly valid (indeed, the situation has not changed so much from his review to ours). 'Most of the models', he wrote, 'only give a representation of the interface, not of the bulk properties in the solid and nonsolid phases'. Indeed, this is still a limitation of many Monte Carlo studies.

Nowadays, however, progress in both statistical mechanics (e.g., the application to a wide class of surface systems of exact roughening theory) and computer science makes the study of the growth of real systems feasible. This is the more urgent task. The ingredients (such as the diffusion barriers) may be calculated using classical molecular dynamics— see for example Ferrando and Tréglia (1996), Ferrando *et al* (1996), Trushin *et al* (1996) and references therein—or from first principles (e.g. by the Car–Parrinello (1985) method) (Stumpf and Scheffler 1994). These data may then be used as input for a Monte Carlo simulation of growth. This programme is now being implemented by several research groups worldwide (including that of one of the authors in Genova), with good hopes of success.

The cases of homoepitaxy and heteroepitaxy should be distinguished: the latter, although more important for many applications, is more difficult, due to the elastic strains developing because of lattice parameter (or crystal symmetry) mismatch, and, although some interesting calculations are already available (Blandin *et al* 1994), will probably wait longer for more thorough study. A typical characteristic of heteroepitaxy is the smallness of the islands forming during growth, since large islands cannot form because of their high energetic cost, determined by elastic strains. There are many additional complications

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† We cannot review these calculations here, and we refer the interested reader to a recent review article by Liu (1995) and references therein.

such as polycrystallinity of the sample, surface reconstruction, and defects, which should be incorporated into existing models.

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