

Diffusion and relaxation kinetics in stochastic models for crystal growth

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The combined influence of relaxation and diffusion processes on the dynamic behavior of stochastic models for crystal growth is systematically investigated. The models are the kinetic Ising model, the discrete Gaussian model, and the SOS-Kossel model. The relaxation kinetics are introduced by single-site transition probabilities to account for adsorption and evaporation. The diffusion kinetics are introduced by two-site transition probabilities to account for nearest-neighbor exchange. The kinetic equations are studied by Monte Carlo simulation, quasichemical(pair) approximation (QCA), and high temperature expansion. The diffusion is found to generally enhance the growth rate of the crystal. In the range of validity of the QCA, i.e., outside the nucleation regime, the results are in very good quantitative agreement with previous Monte Carlo simulations. In the limit of infinite diffusion speed the growth rate approaches the Wilson-Frenkel rate. The local roughness or surface energy is reduced if surface diffusion occurs. The relative influence of diffusion on the response of the system to a chemical potential difference between the two phases depends significantly upon the particular type of transition probability. For the homogeneous Glauber-Ising chain no influence of the diffusion upon the dynamic behavior could be detected.

I. INTRODUCTION

Kinetic Ising models¹⁻³ and generalizations⁴⁻⁹ with so-called solid-on-solid (SOS) restrictions have been used for a long time as models for crystal growth from the vapor.⁴⁻⁹ Analytically, these models were always studied with either pure relaxation kinetics (single-site processes¹⁻³), or pure diffusion kinetics (two- or more-site processes^{3,10}). In crystal growth it is well known,^{11,12} that in addition to the basic adsorption- and evaporation mechanism (relaxation kinetics), surface diffusion is also very important in order to explain observed growth rates and surface structures. Various phenomenological studies^{11,12} and computer simulations⁷⁻⁹ were performed in recent years for a better understanding of this additional mechanism.

Since so far there exist no analytical investigations of microscopic models which *simultaneously* consider relaxation and diffusion, we present here a number of results for these combined kinetics, starting from the simplest one-dimensional kinetic Ising chain¹ and going to a multilayer solid-on-solid model.^{4,5}

Because of the many parameters involved in those models we restrict ourselves to certain characteristic cases, from which one can easily make quantitative predictions for other parameter values. A major problem will be the predicted existence of two temperature regimes associated with qualitatively different static and dynamic properties of the crystal surface.^{13,14} At low temperatures the surface in equilibrium is localized and growth is hampered by a nucleation barrier. At higher temperatures above a roughening temperature T_R the surface fluctuates freely and the growth rate is proportional to the chemical potential difference $\Delta\mu$ between the solid and the vapor. Available dynamic theories so far fail to give a satisfactory treatment of the growth rate below T_R for arbitrary values of $\Delta\mu$.

Our main approximation scheme, the quasichemical¹⁵ (QC) approximation, also produces unphysical metastable states with infinite lifetime for small $\Delta\mu < \Delta\mu_c$.

But outside this region ($\Delta\mu > \Delta\mu_c$) the scheme should give reliable results at all temperatures. The only approach which so far seems to allow for a complete quantitative treatment of dynamics in the two-phase regime is a cluster-reaction theory.¹⁶ But since it has not yet been applied to multilayer models of crystal growth it is not clear whether it would work near the roughening point.

The outline of the paper is as follows. Section II gives an analysis of the one-dimensional Ising chain using Monte Carlo methods and direct numerical integration techniques. The results are also compared with recent calculations of the cluster-reaction theory for the case without diffusion.¹⁷ In Sec. III the discrete Gaussian model^{14,18} is studied using a high temperature expansion, which should be valid for one and two dimensions. Section IV describes the QCA treatment of a (two-dimensional) Ising-lattice-gas system as a model for the adsorption of a monolayer on a substrate. This section mainly serves as a first step in the direction of studying diffusional effects in a metastable region. The main application to crystal growth then is given in Sec. V, where a multilayer SOS model is analyzed in QCA. There the influence of surface diffusion on the growth rate and local surface roughness is studied in some detail and compared to previous computer simulation results.¹⁹ Finally an approximate formula for the growth rate as a function of the diffusion speed is derived. The last section, Sec. VI, contains a summary and concluding remarks.

The basic master equation formalism used in these investigations is described in Sec. II. Certain modifications necessary for the other models then are outlined in each section separately.

II. ONE-DIMENSIONAL KINETIC ISING MODEL

The simplest model system, which exhibits the basic features of the interplay between relaxation and diffu-

sion, is the kinetic Ising model in one space dimension.¹ Because of the absence of a phase transition in one dimension, effects associated with first-order phase transitions cannot be studied on this system, but will be discussed in the following sections.

The Hamiltonian of the system is given by

$$\mathcal{H} = -\frac{J}{2} \sum_i S_i S_{i+1} - \frac{H}{2} \sum_i S_i, \quad (2.1)$$

where the local variables (spins) S_i are restricted to the values $S_i = \pm 1$.

Kinetics are introduced in the usual way^{1,2} by a master equation

$$\begin{aligned} \frac{d}{dt} P(\{S_i\}; t) = & - \sum_j \{ W_R(S_j \rightarrow -S_j) P(S_1, \dots, S_j, \dots; t) - W_R(-S_j \rightarrow S_j) P(S_1, \dots, -S_j, \dots; t) \\ & + W_D(S_j, S_{j+1} \rightarrow S'_j, S'_{j+1}) P(S_1, \dots, S_j, S_{j+1}, \dots; t) - W_D(S'_j, S'_{j+1} \rightarrow S_j, S_{j+1}) P(S_1, \dots, S'_j, S'_{j+1}, \dots; t) \}; \end{aligned} \quad (2.2)$$

where

$$S'_j = S_{j+1}, \quad S'_{j+1} = S_j.$$

Here $P(\{S_i\}; t)$ is the probability that a state $\{S_i\}$ is realized at time t . $W_R(S_j \rightarrow -S_j)$ is the transition probability for a relaxation process, namely that a change of a single site variable (spin) S_j into $-S_j$ occurs. $W_D(S_j, S_{j+1} \rightarrow S'_j, S'_{j+1})$ with $S'_j = S_{j+1}, S'_{j+1} = S_j$ is the transition probability for a diffusional process,¹⁰ namely, that two neighboring spins S_j and S_{j+1} are exchanged. Obviously the diffusional process W_D conserves the order parameter $m \equiv N^{-1} \sum_j S_j$, while the relaxation W_R changes it.

These transition probabilities as usual are required to fulfill a detailed balance condition which allows the system to reach the thermodynamic equilibrium $P_0(\{S_i\})$ for long times $t \rightarrow \infty$. There is then still an infinite number of possibilities to define such probabilities. We have studied two frequently used types of transition probabilities.

The first one, which we will call "symmetric," has already been used by Glauber for the purely relaxational case^{1,2}:

$$W_\alpha = \frac{1}{2\tau_\alpha} (1 - \tanh(\frac{1}{2} \Delta E_\alpha)). \quad (2.3)$$

The subscript α stands for either R or D ; τ_α is a characteristic time scale for the specific process; and ΔE_α is the change of energy in the system (divided by temperature) due to a single relaxation or diffusion process. Equation (2.3) is written explicitly as

$$W_R(S_i \rightarrow -S_i) = \frac{1}{2\tau_R} \left\{ 1 - S_i \tanh \left[\frac{K}{2} (S_{i-1} + S_{i+1}) + \frac{L}{2} \right] \right\}, \quad (2.4)$$

and

$$\begin{aligned} W_D(S_i, S_{i+1} \rightarrow S'_i, S'_{i+1}) \\ = \frac{1}{2\tau_D} \left\{ 1 - \frac{1}{4} (S_i - S_{i+1})(S_{i-1} - S_{i+2}) \tanh K \right\}, \end{aligned} \quad (2.5)$$

with

$$S'_i = S_{i+1}, \quad S'_{i+1} = S_i, \quad K \equiv J/k_B T, \quad L \equiv H/k_B T. \quad (2.6)$$

The second choice, which we will call "nonsymmetric," has been used in stochastic models of crystal growth.^{3,6} For those applications the spin variables $S_i = \pm 1$ are replaced by concentration variables $C_i = \{0, 1\}$ through the identity

$$C_i \equiv (1 + S_i)/2. \quad (2.7)$$

($C_i = 1$ then means that a certain site is occupied by an atom, $C_i = 0$ indicates an empty site.) The asymmetry for the transition probabilities for adsorption ($C_i = 0 \rightarrow C_i = 1$) and evaporation ($C_i = 1 \rightarrow C_i = 0$) has its physical grounds in the assumption that molecules impinge on a crystal surface at random from the vapor, i.e., irrespective of the local structure of the surface. Consequently, the adsorption rates $C_i = 0 \rightarrow 1$ (or $S_i = -1 \rightarrow +1$) are assumed to be independent of the position " i ," while only the evaporation rates depend upon i . This consideration becomes physically more relevant in the two- and three-dimensional systems, which are studied in the next sections, but the basic influence of different transition probabilities already shows up in the one-dimensional chain.

This nonsymmetric transition probability then is given explicitly as

$$W_R(S_i \rightarrow -S_i) = \frac{1}{2\tau_R} \{ (1 - S_i) e^L + (1 + S_i) e^{-K(S_{i+1} + S_{i-1})} \} \quad (2.8)$$

and

$$\begin{aligned} W_D(S_i, S_{i+1} \rightarrow S'_i, S'_{i+1}) = \frac{1}{4\tau_D} \{ (1 + S_i)(1 - S_{i+1}) e^{-K(S_{i-1} + 1)} \\ + (1 - S_i)(1 + S_{i+1}) e^{-K(S_{i+2} + 1)} \}, \end{aligned} \quad (2.9)$$

$$S'_i = S_{i+1}, \quad S'_{i+1} = S_i.$$

The evolution equation for the order parameter $m(t) = N^{-1} \sum_{i=1}^N \langle S_i \rangle$ is obtained from the master equation, Eq. (2.2), as

$$\begin{aligned} \frac{d}{dt} m(t) = N^{-1} \sum_{i=1}^N \langle 2 S_i W_R(S_i \rightarrow -S_i) \rangle \\ = -\frac{1}{\tau_R} \left\{ x - (1 - 2y)m(t) - \frac{z}{N} \sum_{i=1}^N \langle S_{i-1} S_{i+1} \rangle \right\} \end{aligned} \quad (2.10)$$

for the symmetric case, Eqs. (2.3), (2.4), and (2.5), where²

$$\begin{aligned}x &= \frac{1}{4} \{ \tanh(\frac{1}{2} L + K) + \tanh(\frac{1}{2} L - K) + 2 \tanh \frac{1}{2} L \}, \\y &= \frac{1}{4} \{ \tanh(\frac{1}{2} L + K) + \tanh(\frac{1}{2} L - K) \}, \\z &= \frac{1}{4} \{ \tanh(\frac{1}{2} L + K) + \tanh(\frac{1}{2} L - K) - 2 \tanh \frac{1}{2} L \}. \quad (2.11)\end{aligned}$$

The brackets $\langle \cdots \rangle$ denote averages taken with the probability distribution $P(\{S_i\}; t)$ at time t .

In the nonsymmetric case the order parameter evolves as

$$\begin{aligned}\frac{d}{dt} m(t) &= -\frac{1}{\tau_R} \left\{ (m(t) - 1)e^L + N^{-1} \right. \\&\quad \times \sum_{i=1}^N \langle (S_i + 1)e^{-K(S_{i-1} + S_{i+1})} \rangle \left. \right\}. \quad (2.12)\end{aligned}$$

Note that the diffusion process W_D does not appear explicitly in either Eq. (2.10) or Eq. (2.12). The equations are not closed but form only the first equation of a hierarchy, containing up to N -point correlations. But these correlations now are affected by the diffusion process.

The different sensitivity of the two cases, Eqs. (2.10) and (2.12), to diffusion produced by the transition probabilities W_D is already seen in the structure of the equations. For a process where the external "field" H is switched off at a certain time t_0 , the correlation term in Eq. (2.10) drops out, since $H=0$ implies $x=z=0$ [Eqs. (2.6), (2.11)]. This is the original Glauber model,¹ where $m(t)$ shows the simple exponential relaxation. In the nonsymmetric equation (2.12) the correlations are always present, independent of the external field.

The fact that the diffusion part W_D does not enter explicitly in the evolution equation for the total order parameter $m(t)$ can be used to treat a physically interesting limit without further approximation. In the case of very fast diffusion [Eqs. (2.4), (2.5) and Eqs. (2.8), (2.9), $\tau_D/\tau_R \rightarrow 0$] the evolution equations for the correlations (which are not shown here explicitly) contain a very rapidly varying part due to the diffusion process and a very slowly varying part due to the slow relaxation of the order parameter. The correlations thus evolve via the diffusion process very rapidly to a state, which is only controlled by the practically time-independent value of the order parameter. We call this state where the correlations are in thermodynamic equilibrium with a given fixed value of the order parameter the "instantaneous equilibrium" approximation. An arbitrary n -point correlation function $\langle S_{i_1} S_{i_2} \cdots S_{i_n} \rangle_{\text{eq}}$ accordingly is given as a nonlinear function Q of the order parameter m at time t :

$$\langle S_{i_1} S_{i_2} \cdots S_{i_n} \rangle_{\text{eq}} = Q_{i_1, \dots, i_n}(m(t)). \quad (2.13)$$

In this limit of infinite diffusion speed the equations of motion, Eqs. (2.10) and (2.12), accordingly are closed and can be integrated directly: Equation (2.10) becomes

$$\frac{d}{dt} m(t) = -\frac{1}{\tau_R} ((x - \tilde{x}) - 2(y - \tilde{y})m(t)), \quad (2.14)$$

and Eq. (2.12) becomes

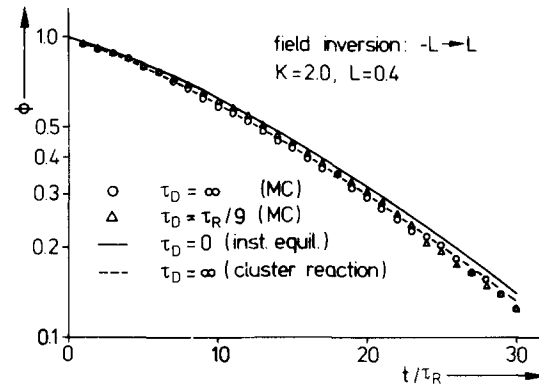


FIG. 1. Ising-Glauber chain. Time dependence of the relaxation function ϕ after field inversion ($-L \rightarrow L$) with symmetric transition probability, Eq. (2.3). Comparison of Monte Carlo simulation, instantaneous equilibrium approximation, and cluster reaction theory.¹⁷ No dependence upon diffusion time τ_D can be detected within numerical accuracy.

$$\frac{d}{dt} m(t) = -\frac{1}{\tau_R} (m(t) - 1)(e^L - e^{\tilde{L}}), \quad (2.15)$$

where \tilde{x} and \tilde{y} are defined by Eq. (2.11) with the field L being replaced by an "effective" field \tilde{L} ,

$$\tilde{L} = \ln \frac{[m + \sqrt{(1-m^2)e^{2K} + m^2}]^2}{(1-m^2)e^{2K}}. \quad (2.16)$$

Since the equations are nonlinear one cannot generally give the solution in closed form but has to resort to an expansion technique or to numerical integration.

We have studied the two cases Eqs. (2.10) and (2.12) with a standard Monte Carlo (MC) simulation procedure and compared the results with the limiting equations (2.14) and (2.15) for $\tau_D/\tau_R \rightarrow 0$ (numerically integrated) and with recent numerical cluster expansions¹⁷ of Eq. (2.10) (which only exists for a purely relaxational system so far). We have used various types of initial conditions, making a sudden change of the temperature T or the external field H at time $t=0$. Characteristic results are discussed in the following.

In Fig. 1 we plot the relaxation function for the order parameter

$$\phi(t) \equiv \frac{m(t) - m(\infty)}{m(0) - m(\infty)} \quad (2.17)$$

for the case of symmetric transition probabilities Eq. (2.10). Initially the field is kept in equilibrium with a field $H/k_B T = -0.4$ at a temperature $J/k_B T = 2$. At time $t=0$ the field is inverted to $H/k_B T = +0.4$. MC simulations on a chain of $N=10\,000$ sites do not show any observable difference in $\phi(t)$ between the case with and without diffusion ($\tau_D = \tau_R/9$). Note that $\tau_D = \tau_R$ means that there is one attempt to make an exchange process per every attempt to make a relaxation (spin flip, or evaporation-adsorption) process. For comparison relaxation functions are also plotted which were obtained from numerical integration of the "instantaneous equilibrium" approximation Eq. (2.14)—which is exact in the limit of infinite diffusion speed (apart from numerical rounding errors)—and also the results from a clus-

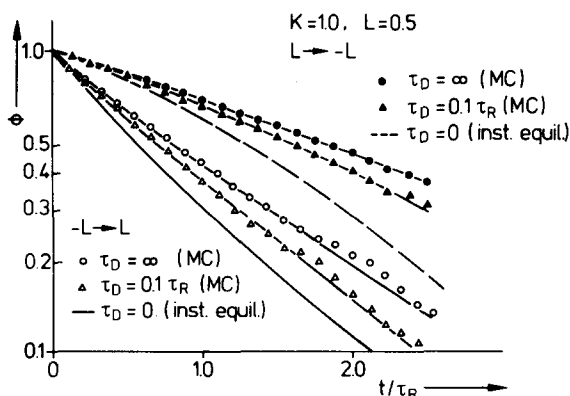


FIG. 2. The same analysis as in Fig. 1, but with nonsymmetric transition probability equations (2.8) and (2.9). The relaxation clearly depends upon diffusion time and the direction of the field inversion ($\pm L \rightarrow \mp L$).

ter-reaction method¹⁷ (for the other limit with no diffusion). Within the numerical accuracies there is no clear indication of any effect of the diffusion upon the relaxation function $\phi(t)$, even though the parameters chosen for the initial and final conditions are in the regime, where one would expect the strongest influence of the diffusion upon the time evolution: The final value of H should clearly be nonzero, the temperature should clearly be not zero (critical point!), nor infinite.

The results for the case of nonsymmetric transition probability [Eq. (2.12)] is plotted in Fig. 2, in the form of a relaxation function as Eq. (2.17). Two types of initial-final conditions are shown, starting at negative and at positive values of the field. In both cases the diffusion ($\tau_D = 0.1 \tau_R$) is clearly seen to lead to a faster relaxation. Again the limit of infinite diffusion speed is given. The two different initial conditions lead to different relaxational behavior.

The difference of the relaxation functions for the two different initial conditions in the nonsymmetric case (Fig. 2), the acceleration of the relaxation due to the diffusion process, and the different behavior for the symmetric and the nonsymmetric case can be understood in the following way. Because of the later application to crystal growth problems we will use the terminology of the lattice gas, where $S_i = 1$ ($C_i = 1$) means "adsorbed atom" and $S_i = -1$ ($C_i = 0$) "vacancy."

Consider first an essentially empty system ($\langle C_i \rangle \ll 1$) with nonsymmetric transition probability, where the order parameter in the final state has a larger value than in the initial state. The site-independent adsorption rate creates many uncorrelated isolated atoms. The system becomes rough and is driven into a state far from equilibrium with little correlation between particles. In the absence of diffusion, the correlations are brought towards equilibrium by the evaporation process only, which re-evaporates the excess of isolated atoms. The total number of adsorbed atoms thus is reduced. The diffusion process opens a new channel for the correlations to approach thermodynamic equilibrium, without reducing the number of adsorbed atoms. The dif-

fusion therefore leads to an acceleration of the total relaxation process. For the opposite case of evaporation ($H \rightarrow -H$), where the order parameter of the initial state has a larger value than in the final state, the argument has to be reversed. There will be very few additionally adsorbed isolated atoms and they are easily re-evaporated. The evolution of the system, therefore, is mainly determined by the rather slow evaporation of clustered atoms, which are energetically more stable than isolated atoms. The total evaporation rate thus is slower than the corresponding adsorption rate as seen in Fig. 2. When diffusion is included it tends to establish a balance between isolated and clustered atoms. Diffusion maintains a certain number of isolated atoms in spite of the evaporation process, and therefore helps to break the clusters up. The resulting isolated spins then are the most likely candidates for evaporation and in this way diffusion again leads to an acceleration of the total evaporation rate.

These arguments now do not work in a straightforward manner for the case of symmetric transition probabilities [Eq. (2.4)]. Since both the adsorption and the evaporation process depend on the local environment of each site the deviation of the short-range correlations from equilibrium should always be smaller than in the nonsymmetric case. Diffusion therefore cannot be as important as in the nonsymmetric case.

Since the nonsymmetric case is probably a good assumption for models of crystal growth we will restrict our attention to this case in the next sections.

III. DISCRETE GAUSSIAN MODEL

The discrete Gaussian model (DG)^{14,18,20,21} is a model for the solid-vapor interface of a crystal. In this section we will consider the effect of surface diffusion upon the steady state evolution of the system which then is always kept away from thermodynamic equilibrium. We will here restrict ourselves to the calculation of the growth rate in the limit of high temperatures, i.e., above the roughening transition, and give a more complete treatment for the whole temperature range in Sec. V, resorting to numerical techniques.

The discrete Gaussian model for a crystal surface is one of the so-called "solid-on-solid" models, where the local height of the interface above some reference plane is given by h_i . h_i can take on all integer values between $\pm\infty$, the index i for an interface in a d -dimensional system runs over all lattice sites in the $(d-1)$ -dimensional subsystem. The position of the interface between crystal and vapor is then defined as $\langle h_i \rangle$. The Hamiltonian of the system is written as

$$\mathcal{H} = J \sum_{\langle i,j \rangle} |h_i - h_j|^p - H \sum_i h_i, \quad J > 0, \quad (3.1)$$

where the summation is taken over pairs of nearest neighbors and H is the difference of chemical potentials between crystal and vapor phases. The exponent p is 1 for the usual SOS model or Kossel model; $p=2$ corresponds to the discrete Gaussian model. For mathematical convenience we restrict our attention to the latter case.

For the description of kinetic processes we use a master equation formulation²⁰ as in the previous section, II. In equilibrium, the probability is given by a canonical form

$$P_{eq}(\{h_i\}) \propto \exp[-\mathcal{H}(\{h_i\})/k_B T]. \quad (3.2)$$

The time-dependent probability distribution P changes according to the following master equation:

$$\begin{aligned} \frac{dP(h_1 \cdots h_i \cdots h_N, t)}{dt} = & - \sum_{i=1}^N \sum_{h'_i=h_i \pm 1} [W_R(h_i \rightarrow h'_i)P(\cdots h_i; t) - W_R(h'_i \rightarrow h_i)P(\cdots h'_i; t)] \\ & - \sum_{i=1}^N \sum_j^{(i)} \sum_{h'_j=h_j \pm 1} [W_D(h_i h_j \rightarrow h'_i h'_j)P(\cdots h_i, h_j, \cdots, t) - W_D(h'_i h'_j \rightarrow h_i h_j)P(\cdots, t)], \end{aligned} \quad (3.3)$$

where $W_R(h_i \rightarrow h'_i)$ represents the single-site transition rate such as adsorption ($h'_i = h_i + 1$) and evaporation ($h'_i = h_i - 1$), and W_D represents the two-site transition rate or exchange rate. The summation $\sum_j^{(i)}$ runs over the nearest neighbor sites with respect to site i . The expectation value of a quantity $A(h_i)$ is given by

$$\langle A(h_i) \rangle_t = \sum_{\{h_j\}} A(h_i) P(\{h_j\}, t). \quad (3.4)$$

From the master equation (3.3), we obtain the evolution of the averaged quantity as

$$\frac{d\langle A(h_i) \rangle}{dt} = - \left\langle \sum_r \{A(h_i) - A(h_i + r)\} W(h_i \rightarrow h_i + r) \right\rangle, \quad (3.5)$$

where the total transition rate W is given by

$$\begin{aligned} W(h_i \rightarrow h_i + r) = & W_R(h_i \rightarrow h_i + r) \\ & + \sum_j^{(i)} W_D(h_i, h_j \rightarrow h_i + r, h_j - r). \end{aligned} \quad (3.6)$$

We will now consider the concrete form of the single- and double-site transition rate, and investigate the diffusional effect on the growth of the system.

A. Adsorption and evaporation

First we consider the single-site processes of adsorption and evaporation of crystal atoms on the interface. The adsorption of a crystal atom is assumed to depend only on the temperature T and the vapor pressure (or the chemical potential difference H), and to be independent of the interfacial configuration.¹⁹ Then the adsorption rate at site i is given by

$$W_R(h_i \rightarrow h_i + 1) = \frac{1}{\tau_R} e^L \equiv k_0^*, \quad (3.7)$$

where τ_R is the appropriate relaxation time, and L is defined by Eq. (2.6). This rate k_0^* represents the asymptotic growth rate of the crystal, when H is very large and evaporation or other processes become negligible.

The transition probabilities are required to satisfy the detailed balance condition between evaporation ($h_i \rightarrow h_i - 1$) and adsorption ($h_i \rightarrow h_i + 1$),

$$\frac{W_R(h_i \rightarrow h_i - 1)}{W_R(h_i - 1 \rightarrow h_i)} = \frac{P_{eq}(\cdots, h_i - 1, \cdots)}{P_{eq}(\cdots, h_i, \cdots)} = e^{\Delta E_i / k_B T - H / k_B T}, \quad (3.8)$$

where the energy difference ΔE_i is given by

$$\begin{aligned} \Delta E_i = & \mathcal{H}(\cdots h_i \cdots) - \mathcal{H}(\cdots h_i - 1 \cdots) \\ = & 2J \sum_j^{(i)} (h_i - h_j) - zJ. \end{aligned} \quad (3.9)$$

z is the coordination number of the $(d-1)$ -dimensional lattice. The evaporation rate then is given as

$$W_R(h_i \rightarrow h_i - 1) = \frac{1}{\tau_R} \exp \left(2K \sum_j^{(i)} (h_i - h_j) - Kz \right), \quad (3.10)$$

with K from Eq. (2.6).

If there is an isolated crystal atom at the i th site or $h_j = h_i - 1$ for all the neighboring sites j , the evaporation rate is given by

$$k_0 = \frac{1}{\tau_R} e^{Kz}. \quad (3.11)$$

This will serve as a characteristic evaporation rate.

B. Interface diffusion

As well as the above single-site transition, the configuration of the crystal surface changes due to the diffusion of crystal atoms to the nearest neighboring sites, but maintaining the SOS restriction where overhangs are excluded. The exchange rate is assumed to depend only on the energy changes associated with the migration of the crystal atom. It is given by

$$W_D(h_i, h_j \rightarrow h_i - 1, h_j + 1) = \frac{1}{\tau_D} \exp \left(2K \sum_k^{(i)} (h_i - h_k) - Kz \right). \quad (3.12)$$

Here τ_D represents the proper time constant of atomic exchange, j is one of the z nearest neighbor sites of the i th site.

When there is an isolated atom on the i th site where the heights of all the neighboring sites are lower by unit height, the hopping rate to a neighboring site is given by

$$k_{00} = z \frac{1}{\tau_D} e^{Kz}. \quad (3.13)$$

Such an isolated atom diffuses a distance x_s in its lifetime k_0^{-1} ;

$$x_s = \sqrt{k_{00}/k_0} = \sqrt{z\tau_R/\tau_D}. \quad (3.14)$$

This diffusion length x_s is a measure of the effect of interfacial migration relative to the evaporation. The

characteristic rates of the various kinetic processes are given by Eqs. (3.7), (3.10), and (3.12). In order to investigate the growth rate of the crystal, we have to consider the change of the average height $\langle h_i(t) \rangle$. In the next subsection, we will consider this in a high temperature limit, and investigate the influence of surface diffusion on the growth rate of the crystal.

1. Crystal growth: High temperature approximation

The expectation value of the interface position is defined as

$$h(t) = \frac{1}{N} \sum_{i=1}^N \langle h_i \rangle_t, \quad (3.15)$$

and the growth rate of the interface R is given by

$$R = dh/dt. \quad (3.16)$$

The equation of motion for the local interface position is obtained from the master equation (3.5) as

$$\begin{aligned} \frac{d\langle h_i \rangle}{dt} &= \sum_{r=\pm 1} \langle rW(h_i \rightarrow h_i + r) \rangle \\ &= \frac{1}{\tau_R} \left[e^L - e^{-K} \left\langle \exp \left\{ 2K \sum_k^{(i)} (h_i - h_k) \right\} \right\rangle_t \right] \\ &\quad + \frac{e^{-K}}{\tau_D} \sum_j^{(i)} \left\langle \exp \left\{ 2K \sum_k^{(j)} (h_j - h_k) \right\} \right. \\ &\quad \left. - \exp \left\{ 2K \sum_k^{(j)} (h_i - h_k) \right\} \right\rangle_t. \end{aligned} \quad (3.17)$$

Combining this with Eq. (3.15), one obtains the growth rate

$$R = \frac{1}{\tau_R} \left[e^L - e^{-K} \frac{1}{N} \sum_{i=1}^N \left\langle \exp \left\{ 2K \sum_k^{(i)} (h_i - h_k) \right\} \right\rangle_t \right]. \quad (3.18)$$

It does not directly depend on the exchange process, which is only implicitly included in the nonlinear part.

Assuming the interface profile (i. e., the configuration of the model system) to be in equilibrium configuration [$H=0$, Eq. (3.18)]:

$$e^{-K} \left\langle \exp \left\{ 2K \sum_k^{(i)} (h_i - h_k) \right\} \right\rangle_{H=0, \text{eq}} = 1, \quad (3.19)$$

we obtain the "Wilson-Frenkel" value²² for the growth rate,

$$R_{WF} = \frac{1}{\tau_R} (e^L - 1). \quad (3.20)$$

In reality, the interface structure in a nonequilibrium situation is different from the equilibrium profile, and the growth rate is different from R_{WF} . The nonlinear equation (3.18) contains expectation values for a hierarchy of correlations. An explicit expression for the growth rate can be derived in a high temperature expansion for small K . Using Eq. (3.19), the growth rate (3.18) can be expanded as

$$\begin{aligned} R &= R_{WF} - \frac{1}{\tau_R} e^{-K} \frac{1}{N} \sum_{i=1}^N \left\langle \exp \left\{ 2K \sum_k^{(i)} (h_i - h_k) \right\} \right\rangle_D \\ &= R_{WF} - \frac{1}{\tau_R} e^{-K} \frac{1}{N} \sum_{i=1}^N \frac{(2K)^2}{2} \left\langle \left(\sum_k^{(i)} (h_i - h_k) \right)^2 \right\rangle_D + \dots, \end{aligned} \quad (3.21)$$

where $\langle \dots \rangle_D$ represents the difference of the expectation value from the equilibrium value without field;

$$\langle \dots \rangle_D = \langle \dots \rangle_t - \langle \dots \rangle_{H=0, \text{eq}}. \quad (3.22)$$

For the spatially homogeneous system, i. e., $\langle h_i \rangle_t = h(t)$, the growth rate is given by the correlation of the height deviation

$$\delta h_i = h_i - \langle h_i \rangle_t = h_i - h(t) \quad (3.23)$$

to be

$$R = R_{WF} - \frac{1}{\tau_R} e^{-K} 2K^2 \left\langle \left(\sum_k^{(i)} (\delta h_i - \delta h_k) \right)^2 \right\rangle_D. \quad (3.24)$$

The difference of this growth rate with respect to the Wilson-Frenkel rate is contained in the correlations

$$\begin{aligned} \langle \delta h_i \delta h_k \rangle_D &= \langle (h_i - h(t))(h_k - h(t)) \rangle_t \\ &\quad - \langle (h_i - \langle h_i \rangle_{H=0, \text{eq}})(h_k - \langle h_k \rangle_{H=0, \text{eq}}) \rangle_{H=0, \text{eq}}. \end{aligned} \quad (3.25)$$

We now investigate the diffusional effect on this height correlation.

The evolution of the height correlation $\langle h_i h_j \rangle_t$ is governed by

$$d\langle h_i h_j \rangle_t / dt = \sum_{r=\pm 1} \{ \langle h_i \cdot rW(h_j - h_j + r) + rW(h_i - h_i + r) \cdot h_j \rangle_t + \delta_{ij} \langle W(h_i - h_i + r) \rangle_t - \delta_{i,j+\delta} \langle W_D(h_i h_j - h_i + r, h_j - r) \rangle_t \}, \quad (3.26)$$

where the term containing δ_{ij} gives the contribution to the equal-site correlation and the last term gives the contribution for i and j being nearest neighbor sites. From this expression follows the kinetic equation:

$$d\langle \delta h_i \delta h_j \rangle_D / dt = \sum_{r=\pm 1} [\langle \delta h_i \cdot rW(h_j - h_j + r) + rW(h_i - h_i + r) \cdot \delta h_j \rangle_D + \delta_{ij} \langle W(h_i - h_i + r) \rangle_D - \delta_{i,j+\delta} \langle W_D(h_i, h_j - h_i + r, h_j - r) \rangle_D]. \quad (3.27)$$

Using the explicit form of W and expanding to the lowest order of inverse temperature K , we obtain

$$\begin{aligned} d\langle \delta h_i \delta h_j \rangle_D / dt &= \frac{1}{\tau_R} e^{-K} \cdot 2K \left\langle \delta h_i \cdot \sum_j^{(i)} (\delta h_j - \delta h_i) + \sum_k^{(i)} (\delta h_i - \delta h_k) \cdot \delta h_j \right\rangle_D + \frac{1}{\tau_D} e^{-K} \cdot 2K \left\langle \delta h_i \cdot \sum_r^{(i)} \left\{ \sum_m^{(r)} (\delta h_i - \delta h_m) \right. \right. \\ &\quad \left. \left. - \sum_n^{(j)} (\delta h_j - \delta h_n) \right\} + \sum_k^{(i)} \left\{ \sum_m^{(k)} (\delta h_k - \delta h_m) - \sum_n^{(i)} (\delta h_i - \delta h_n) \right\} \cdot \delta h_j \right\rangle_D + \frac{1}{\tau_R} \delta_{ij} \cdot (e^L - 1) + O(K^2). \end{aligned} \quad (3.28)$$

Equation (3.28) is a closed equation for the pair correlation $\langle \delta h_i \delta h_j \rangle$, and can be solved exactly. In the Fourier transformed form

$$\langle \delta h_q \delta h_{-q} \rangle_D = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \exp[-iq(R_i - R_j)] \langle \delta h_i \delta h_j \rangle_D, \quad (3.29)$$

the evolution equation (3.28) is rewritten as

$$d\langle \delta h_q \delta h_{-q} \rangle_D / dt = -\frac{1}{\tau_R} e^{-Kz} 4Kz(1 - \gamma(q)) \langle \delta h_q \delta h_{-q} \rangle_D - \frac{1}{\tau_D} e^{-Kz} 4Kz^2(1 - \gamma(q))^2 \langle \delta h_q \delta h_{-q} \rangle_D + \frac{1}{\tau_R} (e^L - 1), \quad (3.30)$$

where

$$\gamma(q) = \frac{1}{z} \sum_j e^{iq(R_i - R_j)}. \quad (3.31)$$

By solving (3.30), we obtain the time-dependent solution of the correlation function, and then from (3.24) we can obtain the relaxation of the growth rate to the steady value. We are now mainly interested in the steady rate R of crystal growth, where the interface is moving with constant velocity without changing the interface configuration. In this steady state, the height correlation is directly given from Eq. (3.30) as

$$\langle \delta h_q \delta h_{-q} \rangle_D = \frac{e^L - 1}{4Kz(1 - \gamma(q))} \times \frac{1}{1 + X_s^2(1 - \gamma(q))}, \quad (3.32)$$

where the diffusion length X_s is given in (3.14).

Since the growth rate R is given by (3.24) or

$$R = R_{WF} - \frac{2K^2 z^2}{\tau_R} \frac{1}{N} \sum_q (1 - \gamma(q))^2 \langle \delta h_q \delta h_{-q} \rangle_D, \quad (3.33)$$

where the q summation is taken for the first Brillouin zone, R is expressed in the high temperature case as

$$R = R_{WF} \left[1 - \frac{Kz}{2} \times \frac{1}{(2\pi)^d} \int_0^{2\pi} d^d q \frac{1 - \gamma(q)}{1 + X_s^2(1 - \gamma(q))} \right], \quad (3.34)$$

$$\rightarrow \begin{cases} R_{WF}[1 - Kz/2] & : X_s^2 \rightarrow 0 \\ R_{WF}[1 - Kz/2X_s^2] & : X_s^2 \rightarrow \infty. \end{cases} \quad (3.35)$$

As shown in Eq. (3.34), the growth rate is lower than the Wilson-Frenkel law if there is no diffusion. The suggestive interpretation that the temperature at which R goes to zero in Eqs. (3.34) and (3.35) corresponds to a mean-field treatment of the roughening point is not useful here. For small enough driving forces L the roughening temperature T_R cannot depend upon diffusion, since it is a static limit. The high temperature expansion equation (3.34) therefore is only valid at temperatures sufficiently far above T_R . (For dynamics without diffusion, see Refs. 20 and 21).

For large diffusion length $X_s \rightarrow \infty$, the growth rate asymptotically increases to the Wilson-Frenkel value. The local roughness⁹ of the surface may be expressed by the internal energy of the model:

$$U = \frac{1}{N} J \sum_{\langle ij \rangle} (h_i - h_j)^2. \quad (3.36)$$

The increase of the internal energy from the equilibrium value without field is given by

$$\begin{aligned} \langle U \rangle_D &= 2JZ \frac{1}{N} \sum_q (1 - \gamma(q)) \langle \delta h_q \delta h_{-q} \rangle_D \\ &\simeq \frac{k_B T}{2} (e^L - 1) \int_0^{2\pi} \frac{d^d q}{(2\pi)^d} \frac{1}{1 + X_s^2(1 - \gamma(q))} \end{aligned}$$

$$\rightarrow \begin{cases} k_B T(e^L - 1)/2 & : X_s^2 \rightarrow 0 \\ \frac{k_B T(e^L - 1)}{2X_s^2} \int_0^{2\pi} \frac{d^d q}{(2\pi)^d} \frac{1}{1 - \gamma(q)} & : X_s^2 \rightarrow \infty. \end{cases} \quad (3.37)$$

The energy difference $\langle U \rangle_D$ is positive for arbitrary diffusion length X_s and goes to zero for $X_s \rightarrow \infty$. It depends upon the driving force L in the same way as the Wilson-Frenkel growth rate, i. e., $\langle U \rangle_D \sim L$ for $L \rightarrow 0$. The decrease of $\langle U \rangle_D$, i. e., the decrease of local roughness, with increasing importance of the diffusion process leads to a faster growth of the crystal, since the randomly adsorbed atoms are incorporated more easily into stable clusters.

IV. TWO-DIMENSIONAL ISING SYSTEM

A. General method

In the following two sections (IV and V) we will treat the dynamics of crystal-growth models in the quasi-chemical approximation.¹⁵ We will use a formulation in "macrovariables" of the system^{23,24} right from the beginning rather than developing the approximation formulas from the microscopic master equation for both cases separately.

The macroscopic state of a system can be described in terms of extensive quantities X_i , the absolute values of which increase with the system size N . X_i , for example, are the total number of adatoms on the crystal surface or the energy, etc.

As before, we may describe the adsorption or evaporation of atoms at the surface of a crystal by a Markovian master equation

$$\begin{aligned} \frac{\partial P(\{X_i\}, t)}{\partial t} &= - \sum_{\{r_i\}} [W(\{X_i\} \rightarrow \{X_i + r_i\}) P(\{X_i\}, t) \\ &\quad - W(\{X_i - r_i\} \rightarrow \{X_i\}) P(\{X_i - r_i\}, t)], \end{aligned} \quad (4.1)$$

where $P(\{X_i\}, t)$ is the probability distribution that the system is found in a macrostate $\{X_i\}$ at time t , and $W(\{X_i\} \rightarrow \{X_i + r_i\})$ is the transition probability per unit time from a macrostate $\{X_i\}$ to $\{X_i + r_i\}$ with changes $\{r_i\}$. We may normalize the instantaneous changes r_i to order unity. Since various microscopic transition processes induce changes of the macrovariables X_i , the transition probability W is proportional to the system size N :

$$W(\{X_i\} \rightarrow \{X_i + r_i\}) \equiv N w(\{x_i\}; \{r_i\}), \quad (4.2)$$

where x_i is the intensive quantity of order unity

$$x_i \equiv X_i / N. \quad (4.3)$$

With these two definitions, (4.2) and (4.3), one can derive the phenomenological equations of motion²⁵ for the expectation values $x_i(t)$,

$$\frac{dx_i(t)}{dt} = \sum_{\{r_j\}} r_i w(\{x_j(t)\}, \{r_j\}), \quad (4.4)$$

from the master equation (4.1). This kind of phenomenological description is commonly used in the chemical reaction theories. We will now apply this formalism to the surface adsorption in this section, and the crystal growth for SOS model in the next section.

B. Monolayer-adsorption model

We use a two-dimensional kinetic Ising system with nearest neighbor interaction and with both relaxation and exchange kinetics as a model for the adsorption of a monolayer of atoms on a given planar substrate.²⁶ The lattice structure, therefore, is assumed to be given; long ranged elastic forces are not taken into account. The local concentration of adatoms then is defined by C_i , where $C_i = 1$ stands for an occupied site and $C_i = 0$ for a vacancy.

The Hamiltonian then is given as

$$\mathcal{H} = -2J \sum_{\langle ij \rangle} C_i C_j - \Delta\mu \sum_i C_i, \quad (4.5)$$

where the first sum goes over nearest neighbor sites, and $\Delta\mu$ is the chemical potential difference between the solid and the vapor (or solution).

The macroscopic state of the system can be described by the total number of adatoms on the surface N_A . The intensive variable $C \equiv N_A/N$ then is just the coverage. $N_V = N - N_A$ is the number of vacant sites. The number of adatom-adatom bonds is denoted by N_{AA} , the number of vacancy-vacancy bonds by N_{VV} , and the number of adatom-vacancy bonds by Q . The latter corresponds to the energy of the system and is also a measure for the local roughness. These quantities are related by

$$N_{AA} = \frac{1}{2} z N_A - \frac{1}{2} Q, \quad N_{VV} = \frac{1}{2} z N_V - \frac{1}{2} Q, \quad (4.6)$$

where z is the configuration number of the lattice.

The Hamiltonian equation (4.5) then is rewritten in terms of these macrovariables N_A and Q as

$$\mathcal{H} = JQ - H \cdot N_A, \quad (4.7)$$

where

$$H = zJ + \Delta\mu. \quad (4.8)$$

The time dependence of the macrovariables Q and N_A is now the subject of the kinetic quasichemical (Bethe-Peierls) approximation, QCA.

The two types of kinetic processes, relaxation (corresponding to adsorption and evaporation) and diffusion, are now discussed in the following paragraphs.

1. Adsorption and evaporation

The adsorption is assumed to be determined by the chemical potential difference $\Delta\mu$ or the external "field" H and to be independent of the environment of the adsorbing site. The adsorption rate of atoms onto a vacant site, surrounded by k vacant sites and $z-k$ occupied sites, is given by²⁷

$$W_R(N_A, Q \rightarrow N_A + 1, Q + 2k - z) = \frac{1}{\tau_R} e^{L \cdot \bar{N}_V}, \quad (4.9)$$

where τ_R is a characteristic time constant and L is defined in Eq. (2.6).

The effective number of vacant sites $\bar{N}_V(k)$ contains the information about the configuration of the environment and is given by

$$\bar{N}_V = N_V \frac{\binom{N_{VV}}{k} \binom{\frac{1}{2} Q}{z-k}}{\binom{\frac{1}{2} z N_V}{z}} \quad (4.10)$$

in QC approximation.¹⁵ Here the distribution of N_{VV} - and Q bonds in the lattice is assumed to be random.

Inversely, the evaporation rate depends on the local configuration. When an adatom surrounded by k adatoms and $z-k$ vacancies is evaporated, the k bonds to the neighboring atoms have to be broken at the cost of the corresponding bond energy. The evaporation rate then is defined as

$$W_R(N_A, Q \rightarrow N_A - 1, Q + 2k - z) = \frac{1}{\tau_R} e^{K(\pi-2k)\bar{N}_A} \quad (4.11)$$

with K from Eq. (2.6).

The factor \bar{N}_A correspondingly represents the number of adatom sites with the appropriate configuration in QC approximation:

$$\bar{N}_A = N_A \frac{\binom{N_{AA}}{k} \binom{\frac{1}{2} Q}{z-k}}{\binom{\frac{1}{2} z N_A}{z}}. \quad (4.12)$$

Note that this choice of the transition probability equations (4.9) and (4.11) corresponds to the nonsymmetric case being discussed in Sec. II, Eqs. (2.8) and (2.9).

Since the effective numbers \bar{N}_A and \bar{N}_V are of macroscopic order, the adsorption or evaporation rate is proportional to the system size N , and we can use the relations of Sec. IV.A. The evolution of the coverage $c = N_A/N$ is governed by the phenomenological equation (4.4) as

$$\begin{aligned} \frac{dc(t)}{dt_R} &= \sum_{k=1}^z \{W_R(c, q; 1, 2k-z) - W_R(c, q; -1, 2k-z)\} \\ &= \frac{1}{\tau_R} \left\{ c_V e^L \sum_{k=1}^z \binom{z}{k} \frac{\tilde{N}_{VV}^k (\frac{1}{2} q)^{z-k}}{(\frac{1}{2} z c_V)^z} \right. \\ &\quad \left. - c \sum_{k=1}^z \binom{z}{k} \frac{\tilde{N}_{AA}^k (\frac{1}{2} q)^{z-k}}{(\frac{1}{2} z c)^z} e^{K(\pi-2k)} \right\} \\ &= \frac{1}{\tau_R} \left\{ c_V e^L - c \left[\frac{\tilde{N}_{AA} e^{-K} + \frac{1}{2} q e^K}{\frac{1}{2} z c} \right]^z \right\}. \end{aligned} \quad (4.13)$$

Here d/dt_R means the single-atom contribution to time change. c_V is the density of vacant sites

$$c_V = N_V/N. \quad (4.14)$$

In deriving (4.13), we have used the relations between the bond densities

$$\begin{aligned} q &\equiv Q/N, \quad \tilde{N}_{AA} \equiv N_{AA}/N = \frac{1}{2} z c - \frac{1}{2} q, \\ \tilde{N}_{VV} &\equiv N_{VV}/N = \frac{1}{2} z c_V - \frac{1}{2} q. \end{aligned} \quad (4.15)$$

The evolution of the density of adatom-vapor bonds q ,

which is proportional to the exchange energy density $e = Jq$, is given by

$$\begin{aligned} \frac{dq}{dt_R} &= \sum_{r=1}^z \sum_{k=1}^r (2k-z) W_R(c, q; r, 2k-z) \\ &= \frac{z}{\tau_R} \left\{ c_V e^L \left[\frac{\tilde{N}_{VV} - \frac{1}{2} q}{\frac{1}{2} z c_V} \right] \right. \\ &\quad \left. + c \left[\frac{\tilde{N}_{AA} e^{-K} + \frac{1}{2} q e^K}{\frac{1}{2} z c} \right]^z \left[\frac{\tilde{N}_{AA} e^{-K} - \frac{1}{2} q e^K}{\tilde{N}_{AA} e^{-K} + \frac{1}{2} q e^K} \right] \right\}. \quad (4.16) \end{aligned}$$

The equilibrium solution of Eqs. (4.13) and (4.16) is given by

$$\begin{aligned} 4 \tilde{N}_{AA} \tilde{N}_{VV} &= q^2 e^{2K}, \\ \left(\frac{c_V}{c} \right)^{z-1} &= e^L \left(\frac{\tilde{N}_{VV}}{\tilde{N}_{AA}} \right)^{z/2}, \end{aligned} \quad (4.17)$$

which is identical to the equilibrium solution in the Bethe-Peierls approximation.²⁸ The critical temperature is given by

$$K_c = J/k_B T_c = \ln(z/z-2) \text{ and } L=0. \quad (4.18)$$

2. Surface migration

In addition to the pure relaxation processes of evaporation and adsorption we will now allow for surface diffusion. There an adsorbed atom may hop to one of its neighboring vacant sites. This exchange process then depends on the environment of both sites involved. For an adatom with k nearest neighbors which attempts to hop to a neighboring place surrounded by l vacant sites, the exchange rate is given as

$$W_D(N_A, Q \rightarrow N_A, Q+2k+2l+2-2z) = \frac{1}{\tau_D} e^{K(2k-2)} \bar{Q}. \quad (4.19)$$

τ_D here is a characteristic "diffusion" time and the probabilistic factor \bar{Q} in QC approximation is given as

$$\bar{Q} = Q \frac{\binom{N_{AA}}{k} \binom{\frac{1}{2} Q}{z-k-1} \binom{N_{VV}}{l} \binom{Q}{z-l-1}}{\binom{\frac{1}{2} z N_A}{z-1} \binom{\frac{1}{2} z N_V}{z-1}}. \quad (4.20)$$

Note that the exponential factor in Eq. (4.19) depends only on the initial state of the adatom. Physically this corresponds to a jump over an activation barrier, where the jumping atom initially does not know the state behind the barrier. In Eq. (4.20) we have included the fact that after the jump the atom always sees its previous position as a vacancy. For the remaining $z-1$ bonds the probability distribution was taken as random.

The evolution of the bond density q then is obtained in analogy to Eq. (4.16) as

$$\begin{aligned} \frac{dq}{dt_D} &= \sum_{k,l=1}^z (2k+2l+2-2z) W_D(c, q; 0, 2k+2l+2-2z) \\ &= \frac{z-1}{\tau_D} e^K \left[\frac{\tilde{N}_{AA} e^{-K} + \frac{1}{2} q e^K}{\frac{1}{2} z c} \right]^{z-1} \left[\frac{\tilde{N}_{AA} e^{-K} - \frac{1}{2} q e^K}{\tilde{N}_{AA} e^{-K} + \frac{1}{2} q e^K} + \frac{\tilde{N}_{VV} - \frac{1}{2} q}{\frac{1}{2} z c_V} \right], \end{aligned} \quad (4.21)$$

where dq/dt_D is the contribution from the diffusion process only. Of course, there is no direct contribution to the relaxation of the coverage dc/dt .

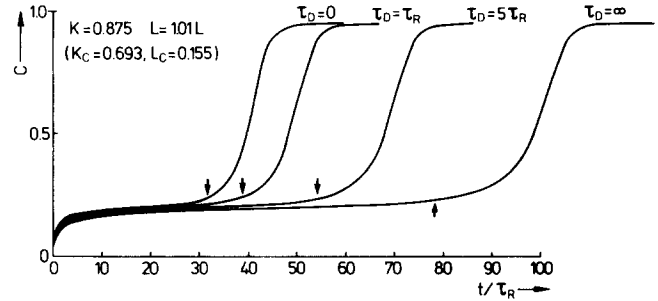


FIG. 3. Two-dimensional Ising model in QC approximation. The lifetime τ_{eff} of the metastable states outside the spinodal regime ($|L| > |L_c|$) decreases with decreasing diffusion speed τ_D^{-1} .

Combining Eqs. (4.21) and (4.16), the total change of correlations q becomes

$$\frac{dq}{dt} = \frac{dq}{dt_R} + \frac{dq}{dt_D}. \quad (4.22)$$

Equations (4.22) and (4.13) now form a closed set for the evolution of the system, which we have to study simultaneously. For this purpose we used a numerical integration technique.

3. Numerical results

We consider here the two-dimensional square lattice ($z=4$). In contrast to the one-dimensional Ising chain this two-dimensional Ising model has a phase transition at a critical temperature T_c . We cannot expect behavior significantly different from the case discussed in Sec. II in the one-phase region above T_c . Right at T_c we know from renormalization group treatments that the dynamics are ultimately controlled by the relaxational part only.²⁹ The most interesting region therefore is the low temperature range $T < T_c$.

The static QC approximation is known to show a spinodal line as limit for the existence of metastable states in the two-phase region. Of course this is an outcome of the approximation used, while the real system (without elastic forces) does not show a true spinodal line.^{18b, c, 30} The concept of the spinodal line, however, is useful as an estimate for the practical range of the nucleation regime. In our case the spinodal line is given by the critical "field"

$$L_c(z=4) = 2 \log\{(e^{2K} + 8)\sqrt{e^{2K} - 1} + (e^{2K} - 4)^{3/2}\} - 3 \ln 3 - 4K \quad (4.23)$$

if we start from an originally mostly vacant system. For $L \leq L_c$ the system will remain almost vacant. For $L > L_c$ the system will undergo a first order phase transition.^{28, 30} This behavior is shown in Fig. 3 ($K=0.875$; $K_c = \ln 2 = 0.693$, $L = 1.01L_c$; $L_c = 0.155$), where the time dependence of the coverage c is plotted for various ratios of the characteristic diffusion time τ_D and the relaxation time τ_R [Eqs. (4.9), (4.19)]. As the relative influence of diffusion increases (or τ_D becomes small), the relaxation of the coverage towards equilibrium becomes fast and the lifetime of the metastable region becomes short. For infinitely fast migration (diffusion) rate, τ_D

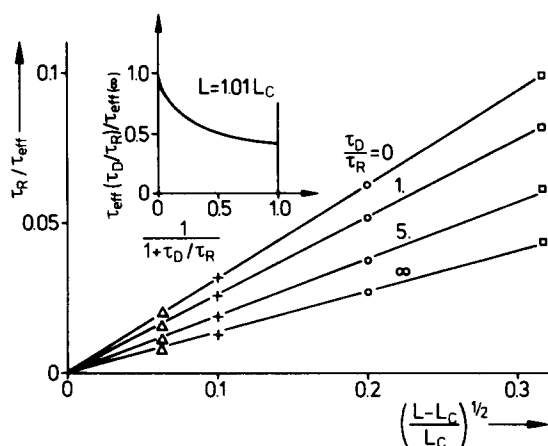


FIG. 4. Inverse lifetime τ_{eff}^{-1} vs scaled field $\sqrt{L-L_c}$ near the spinodal field L_c . The insert shows the dependence of the lifetime τ_{eff} of metastable states upon diffusion time τ_D . (model as in Fig. 4.)

$\rightarrow 0$, the surface configuration q takes on the “instantaneous” equilibrium form

$$q = \frac{z}{2} \frac{\sqrt{1 + 4(e^{2K} - 1)C_V C - 1}}{e^{2K} - 1} \quad (4.24)$$

for given C , as qualitatively discussed in Sec. II for the one-dimensional correlations.

A measure for the lifetime of the metastable states can be written as^{30,31}

$$\tau_{eff} = \int_0^\infty \frac{c(t) - c(\infty)}{c(0) - c(\infty)} dt. \quad (4.25)$$

Figure 4 shows the nonlinear relaxation time τ_{eff} as a function of the square root of the field differences $(L - L_c)^{1/2}$. This corresponds to the usual scaling behavior in mean-field-like approximations. Neither the values of the critical field L_c nor the exponent of τ_{eff} are influenced by the diffusion process. The amplitude and hence the actual relaxation time, however, may change by up to a factor of 2.

Of course there remains the basic difference between the metastable states produced by this mean-field-like approximation and the nucleation regime of a real system. In the latter the lifetime of metastable states is inversely proportional to the nucleation rate.³² The nucleation rate consists of an exponential which is independent of the time scales involved and a kinetic prefactor. It is the prefactor which depends on the kinetic processes and in fact it increases with diffusion length X_s in the usual formulation. The nucleation process thus becomes more probable with increasing diffusion speed and, therefore, the nucleation regime becomes narrower with increasing X_s . The quasichemical approximation, therefore, gives quantitatively meaningful results only for chemical potential differences sufficiently larger than the “spinodal” value. This is studied in the next section in comparison with computer simulations of crystal growth. The limit of infinite diffusion speed in nucleation theory will be discussed at the end of Sec. V.

V. SOLID-ON-SOLID MODEL

A. Layerwise quasichemical approximation

In this section we investigate the SOS model⁴⁻⁹ which is frequently used as a model for the solid-vapor interface, in an approximation, which can be applied on the whole temperature range. Alternatively, we have investigated the similar discrete Gaussian model (Sec. III) in a high-temperature expansion only.

The model is defined as a lattice which can be filled with atoms, but only such that in a given “upward” direction from solid to vapor there are no filled sites above a vacant site. This is the so-called solid-on-solid restriction (SOS), which excludes vacant sites inside the solid part and overhangs at the solid-vapor interface.

The Hamiltonian of the system is written as

$$\mathcal{H} = -2J \sum_{\langle ij \rangle} C_i C_j - \Delta \mu \sum_i C_i + V(\{C_i\}), \quad (5.1)$$

where the first sum runs over all neighboring pairs of sites in the lattice, $C_i = \{0, 1\}$ indicates whether the site is vacant or filled, and $V(\{C_i\})$ is a potential which provides the SOS restriction. It is infinite for a forbidden configuration and zero otherwise.

An interface originally introduced into the system then persists at all temperatures. The inhomogeneity of the system due to the interface suggests a layerwise QCA to be used.³³ There, one divides the system into layers parallel^{4,5} to the interface. In the n th layer there are N lattice sites, $N(n)$ of which are occupied by crystal atoms. Similarly to the preceding section, the macrostate of each layer is described by the number of crystal-atom-vacancy bonds $Q(n)$. The numbers of vacancies $N_v(n)$, crystal-crystal bonds $N_{cc}(n)$, and vacancy-vacancy bonds $N_{vv}(n)$ in the n th layer are determined from geometric considerations as

$$\begin{aligned} N_v(n) &= N - N(n), \\ N_{cc}(n) &= \frac{1}{2} z N(n) - \frac{1}{2} Q(n), \\ N_{vv}(n) &= \frac{1}{2} z N_v(n) - \frac{1}{2} Q(n). \end{aligned} \quad (5.2)$$

Here z is the coordination number in the layer. Because of the SOS restriction, the number of various bonds between adjacent layers are determined uniquely. Assuming that a site in the n th layer is connected with only a single site in the $(n+1)$ th layer, the numbers of crystal-crystal bonds $N_{cc}(n, n+1)$, crystal-vacancy bonds $N_{cv}(n, n+1)$, and vacancy-vacancy bonds $N_{vv}(n, n+1)$ between layers are given as

$$\begin{aligned} N_{cc}(n, n+1) &= N(n+1), \\ N_{cv}(n, n+1) &= N(n) - N(n+1), \\ N_{vv}(n, n+1) &= N_v(n). \end{aligned} \quad (5.3)$$

Owing to the SOS restriction there are no vacancy-crystal bonds between the n th and $n+1$ th layer: $N_{vc}(n, n+1) = 0$.

With these macrovariables $\{N(n), Q(n)\}$, the Hamiltonian is rewritten as

$$\mathcal{H} = J \sum_n Q(n) - H \sum_n N(n), \quad (5.4)$$

where

$$H = \Delta\mu + zJ. \quad (5.5)$$

There is no direct coupling between n th and $n+1$ th layer in the Hamiltonian (5.4). The coupling enters by the SOS restriction on the configuration.

When there is a difference of the chemical potentials $\Delta\mu$ (or H) the crystal grows or evaporates. The kinetic processes occurring at the interface are adsorption, evaporation, and interfacial migration of crystal atoms. The SOS restriction allows the kinetic processes to occur only at the interface between the crystal and vapor phase. As in the preceding section, we consider the single-site process (adsorption and evaporation) and the two-site process (interfacial migration) separately.

1. Adsorption and evaporation

As in the preceding section, the adsorption rate is assumed to be determined only by the difference of chemical potentials or H .^{19,22} Furthermore, we have to take care of the SOS restriction, where the adsorbing site in the n th layer must have an underlying crystal atom in the $(n-1)$ th layer. With these considerations, the adsorption rate of a vacant site in the n th layer, surrounded by k vapor atoms, is given by

$$W_R(N(n), Q(n) \rightarrow N(n)+1, Q(n)+2k-z) = \frac{1}{\tau_R} e^{L \cdot \overline{N_v(n)}}, \quad (5.6)$$

where τ_R is the characteristic relaxation time, and L is given by Eq. (2.6). {Again we use the nonsymmetric choice [Eq. (2.12)] of transition probabilities.} The factor $\overline{N_v(n)}$ stands for the active number of interfacial vapor atoms in the n th layer. Using the same random distribution assumption for the neighboring configuration as in the previous section we have

$$\overline{N_v(n)} = N_{cv}(n-1, n) \frac{\binom{N_{vv}(n)}{k} \binom{\frac{1}{2} Q(n)}{z-k}}{\binom{\frac{1}{2} z N_v(n)}{z}}. \quad (5.7)$$

The adsorption rate of a single isolated vacant site is given by $(1/\tau_R)e^L$, which corresponds to the rate k_0^* defined in Ref. 19 [see Eq. (3.7)].

The evaporation process is described in analogy to Eq. (4.12) by

$$W_R(N(n), Q(n) \rightarrow N(n)-1, Q(n)+2k-z) = \frac{1}{\tau_R} e^{-K(2k-z) \cdot \overline{N(n)}}, \quad (5.8)$$

where k is the number of crystal atoms surrounding the evaporating crystal atom in the n th layer, and K is given by Eq. (2.6).

The factor $\overline{N(n)}$ represents the active number of interfacial crystal atoms, which can evaporate and have the appropriate neighboring configuration:

$$\overline{N(n)} = N_{cv}(n, n+1) \frac{\binom{N_{cc}(n)}{k} \binom{\frac{1}{2} Q(n)}{z-k}}{\binom{\frac{1}{2} z N(n)}{z}}. \quad (5.9)$$

The evaporation rate of a single isolated crystal atom is given by $(1/\tau_R)e^{Kz}$, which corresponds to k_0 defined in Ref. 19 [see Eq. (3.11)].

Since the transition probabilities given above are of macroscopic order N and satisfy the condition (4.2), we can write down the phenomenological equation for the average concentration $c(n)$ and bond density $q(n)$:

$$c(n) \equiv N(n)/N, \quad q(n) \equiv Q(n)/N. \quad (5.10)$$

The variation of concentration is given by

$$\begin{aligned} \frac{dc(n)}{dt_R} &= \sum_k \{W_R(c(n), q(n); 1, 2k-z) - W_R(c(n), q(n); -1, 2k-z)\} \\ &= \frac{1}{\tau_R} \left\{ [c(n-1) - c(n)] e^L - [c(n) - c(n+1)] \left[\frac{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K}{\frac{1}{2} z c(n)} \right]^z \right\}. \end{aligned} \quad (5.11)$$

Here we defined the crystal-crystal bond density $\tilde{N}_{cc}(n)$ as

$$\tilde{N}_{cc}(n) \equiv N_{cc}(n)/N, \quad (5.12)$$

and used the relations Eq. (5.3) together with the definitions

$$c_v(n) \equiv N_v(n)/N = 1 - c(n),$$

$$\tilde{N}_{vv}(n) \equiv N_{vv}(n)/N = \frac{1}{2} z c_v - \frac{1}{2} q(n). \quad (5.13)$$

The evolution of the crystal-vapor bond density $q(n)$ then is given by

$$\begin{aligned} \frac{dq(n)}{dt_R} &= \sum_{r=1} \sum_k (2k-z) W_R(c(n), q(n); r, 2k-z) \\ &= \frac{z}{\tau_R} \left\{ [c(n-1) - c(n)] e^L \left[\frac{\tilde{N}_{vv}(n) - \frac{1}{2} q(n)}{\frac{1}{2} z c_v(n)} \right] + [c(n) - c(n+1)] \left[\frac{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K}{\frac{1}{2} z c(n)} \right]^z \left[\frac{\tilde{N}_{cc}(n) e^{-K} - \frac{1}{2} q(n) e^K}{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K} \right] \right\}. \end{aligned} \quad (5.14)$$

The equilibrium profile of concentration is given by

$$4\tilde{N}_{cc}(n)\tilde{N}_{vv}(n) = q^2(n)e^{2K} \quad (5.15a)$$

and

$$e^L \left[\frac{c(n-1) - c(n)}{c(n) - c(n+1)} \right] = \left[\frac{\tilde{N}_{cc}(n)e^{-K} + \frac{1}{2}q(n)e^K}{\frac{1}{2}zc(n)} \right]^z. \quad (5.15b)$$

Equation (5.15a) can be rewritten as

$$q(n) = \frac{z}{2} \frac{\sqrt{1 + 4(e^{2K} - 1)c(n)c_v(n)} - 1}{e^{2K} - 1}. \quad (5.16)$$

If we make the instantaneous equilibrium approximation for $q(n)$ [i. e., Eq. (5.16)] and take the high temperature and long-range interaction limit ($K \rightarrow 0$, $z \rightarrow \infty$ and $Kz = \text{finite}$), then we obtain $q(n) = z c(n)c_v(n)$ and Temkin's⁴ mean field equation for the concentration $c(n)$:

$$\frac{dc(n)}{dt} = \frac{1}{\tau_R e^{-Kz}} \{ [c(n-1) - c(n)]e^{L-Kz} - [c(n) - c(n+1)]e^{-2Kz} \}. \quad (5.17)$$

Now we consider the two-site process or the interfacial migration of crystal atoms.

2. Interfacial migration (diffusion)

In the spirit of the layer-wise treatment interfacial migration of crystal atoms has two aspects; an intralayer exchange process within each layer where the number of crystal atoms in the layer is conserved, and the inter-layer exchange process between layers where the number of crystal atoms in each layer varies. In both cases, of course, the total number of crystal atoms in the whole system does not change. The intra-layer process changes the configuration or roughness in a single layer, and the inter-layer process affects the interfacial configuration or profile. We want to find the relation between the total growth of the crystalline system and its configuration or roughness.

a. *Intralayer migration.* First we consider the exchange process in a single layer. This process has a close similarity with the surface migration of the monolayer model of the preceding section. In the case when the crystal atom surrounded by k crystal atoms hops to one of the neighboring vacant site, which is surrounded by l vapor atoms, the change of the crystal-vapor bond number is $2k + 2l + 2 - 2z$, and the rate is given by

$$W_D^{\text{intra}}(N(n), Q(n) - N(n), Q(n) + 2k + 2l + 2 - 2z)$$

$$= \frac{1}{\tau_D^{\text{intra}}} e^{-K(2k+l)} \cdot \overline{Q(n)}. \quad (5.18)$$

τ_D^{intra} is the appropriate time constant of intralayer exchange, and the energy factor takes only the energy change due to the bond breaking of exchanging crystal atoms into account. Because of the SOS restriction, the vertical configuration of exchanging atoms should have a certain arrangement. There should be a vapor atom above the exchanging crystal atom, and a crystal atom under the exchanging vapor site. So the effective number of crystal-vapor bonds $Q(n)$ with certain neighboring configurations is given by

$$\begin{aligned} \overline{Q(n)} = Q(n) & \frac{N_{cv}(n, n+1)}{N_{cv}(n, n+1) + N_{cc}(n, n+1)} \\ & \times \frac{N_{cv}(n-1, n)}{N_{cv}(n-1, n) + N_{vv}(n-1, n)} \\ & \times \frac{\binom{N_{cc}(n)}{k} \left(\frac{1}{2}Q(n)\right)}{\binom{\frac{1}{2}zN(n)}{z-1}} \frac{\binom{N_{vv}(n)}{l} \left(\frac{1}{2}Q(n)\right)}{\binom{\frac{1}{2}zN_v(n)}{z-1}}. \end{aligned} \quad (5.19)$$

Here we have used the same random distribution approximation for the surrounding configurations as was used in the preceding section or Eq. (4.20). The exchange rate of a single isolated crystal atom is given by $(1/\tau_D^{\text{intra}}) \cdot e^{Kz} \cdot z$, which corresponds to the rate k_{00} defined in Ref. 19:

$$\frac{1}{\tau_D^{\text{intra}}} e^{Kz} \cdot z = k_{00}. \quad (5.20)$$

The diffusion length of an isolated atom¹⁹ on a smooth interface is given by using Eqs. (3.11) and (5.20) as

$$X_2 = \sqrt{k_{00}/k_0} = \sqrt{z\tau_R/\tau_D^{\text{intra}}}, \quad (5.21)$$

which measures the relative significance of the exchange process relative to the single-site process. Here the lattice constant is set equal to unity.

Since the transition probability is of a macroscopic order N , we can write down the phenomenological equations for the averaged concentration $c(n)$ and bond density $q(n)$ as

$$dc(n)/dt_D^{\text{intra}} = 0 \quad (5.22)$$

and

$$\begin{aligned} \frac{dq(n)}{dt_D^{\text{intra}}} &= \sum_k \sum_l (2k + 2l + 2 - 2z) W_D^{\text{intra}}(c(n), q(n); 0, 2k + 2l + 2 - 2z) \\ &= \frac{z-1}{\tau_D^{\text{intra}}} e^K q(n) \frac{c(n) - c(n+1)}{c(n)} \frac{c(n-1) - c(n)}{c_v(n)} \left[\frac{\tilde{N}_{cc}(n)e^{-K} + \frac{1}{2}q(n)e^K}{\frac{1}{2}zc(n)} \right]^{-1} \\ &\quad \left[\frac{\tilde{N}_{cc}(n)e^{-K} - \frac{1}{2}q(n)e^K}{\tilde{N}_{cc}(n)e^{-K} + \frac{1}{2}q(n)e^K} + \frac{\tilde{N}_{vv}(n) - \frac{1}{2}q(n)}{\frac{1}{2}zc_v(n)} \right]. \end{aligned} \quad (5.23)$$

Because of the SOS restriction, Eq. (5.23) has an additional probabilistic factor in comparison with Eq. (4.20). When the intralayer diffusion is infinitely fast ($\tau_D^{\text{intra}} \rightarrow 0$), the local equilibrium for the bond density $q(n)$ [Eq. (5.16)] is attained.

b. *Interlayer migration.* Next we consider the ex-

change process of a crystal atom with a vacancy in different layers. This produces a change in the interfacial profile.

When the crystal atom in the n th layer, surrounded by k crystal atoms, exchanges sites with a vacancy in the n' th layer with l surrounding vapor atoms, the exchange

probability is given by

$$W_D^{\text{inter}}(N(n), N(n'), Q(n), Q(n') \rightarrow N(n) - 1, N(n') + 1, Q(n) + 2k$$

$$-z, Q(n') + 2l - z) = \frac{1}{\tau_D^{\text{inter}}} e^{-K(2k-z)} \overline{N_{cv}(n, n')}. \quad (5.24)$$

The effective number of crystal-vacancy pairs is obtained by considering the SOS restriction and the random distribution approximation of the neighboring configurations:

$$\overline{N_{cv}(n, n')} = \left(\frac{zN(n)N_v(n')}{N} \right) \frac{N_{cv}(n, n+1)}{N_{cv}(n, n+1) + N_{cc}(n, n+1)} \frac{N_{cv}(n'-1, n')}{N_{cv}(n'-1, n') + N_{vv}(n'-1, n')}$$

$$\times \frac{\binom{N_{cc}(n)}{k} \left(\frac{1}{2} Q(n) \right) \binom{N_{vv}(n')}{l} \left(\frac{1}{2} Q(n') \right)}{\left(\frac{1}{2} z N(n) \right) \left(\frac{1}{2} z N_v(n') \right)}; \quad n \neq n'. \quad (5.25)$$

This expression is very similar to Eq. (5.19), but instead of the correlation $Q(n)$ we here have the first term in parentheses on the rhs of Eq. (5.25). In this expression we allow for diffusional jumps between the topmost sites of neighboring solid columns. Since our QC approximation only considers correlations between directly neighboring sites explicitly we have to consider these exchanges between the topmost sites of various levels ($n \neq n'$) in the above mean-field-like approximation. The remaining terms in Eq. (5.25) of course take care of the correlations between the various solid columns in QC.

The evolution equation for the concentration $c(n)$ due to interlayer diffusion then is written as

$$\begin{aligned} \frac{dc(n)}{dt_D^{\text{inter}}} &= \sum_{r=\pm 1} \sum_k \sum_l \sum_{n'(\neq n)} r W_D^{\text{inter}}(c(n), c(n'), q(n), q(n'); r, -r, 2k-z, 2l-z) \\ &= \frac{z}{\tau_D^{\text{inter}}} \left\{ [c(n-1) - c(n)] e^{L_0} - [c(n) - c(n+1)] \left[\frac{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K}{\frac{1}{2} z c(n)} \right]^z \right\}, \end{aligned} \quad (5.26)$$

where the self-consistent field L_0 is given by

$$e^{L_0} = \sum_{n=-\infty}^{\infty} [c(n) - c(n+1)] \left[\frac{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K}{\frac{1}{2} z c(n)} \right]^z. \quad (5.27)$$

Deriving the above equation (5.26), we have used the SOS boundary condition

$$c(-\infty) = 1, \quad \text{and } c(\infty) = 0, \quad (5.28)$$

which means that the system is completely crystallized far below the interface, and completely noncrystalline far above the interface. From Eqs. (5.26), (5.27), and (5.28), it is evident that the total concentration, $\sum_{n=-\infty}^{\infty} c(n)$, does not change from this interlayer exchange process.

The density $q(n)$ of crystal-vacancy bonds is also governed by the phenomenological equation

$$\begin{aligned} \frac{dq(n)}{dt_D^{\text{inter}}} &= \sum_{r=\pm 1} \sum_k \sum_l \sum_{n'(\neq n)} (2k-z) W_D^{\text{inter}}(c(n), c(n'), q(n), q(n'); r, -r, 2k-z, 2l-z) \\ &= \frac{z^2}{\tau_D^{\text{inter}}} \left\{ [c(n-1) - c(n)] \left[\frac{\tilde{N}_{vv}(n) - \frac{1}{2} q(n)}{\frac{1}{2} z c_v(n)} \right] e^{L_0} + [c(n) - c(n+1)] \left[\frac{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K}{\frac{1}{2} z c(n)} \right]^z \left[\frac{\tilde{N}_{cc}(n) e^{-K} - \frac{1}{2} q(n) e^K}{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K} \right] \right\} \\ &\quad - \frac{z^2}{\tau_D^{\text{inter}}} [c(n-1) - c(n)] [c(n) - c(n+1)] \left[\frac{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K}{\frac{1}{2} z c(n)} \right]^z \left[\frac{\tilde{N}_{cc}(n) e^{-K} - \frac{1}{2} q(n) e^K}{\tilde{N}_{cc}(n) e^{-K} + \frac{1}{2} q(n) e^K} + \frac{\tilde{N}_{vv}(n) - \frac{1}{2} q(n)}{\frac{1}{2} z c_v(n)} \right]. \end{aligned} \quad (5.29)$$

The second term on the right hand side of Eq. (5.29) takes care of the overcounted layer $n' = n$.

Equations (5.11), (5.14), (5.22), (5.23), (5.26), and (5.29) are our fundamental evolution equations. When all processes, adsorption, evaporation, intra- and interlayer exchange processes, coexist, then the total variations of the concentration or bond density are described by

$$\begin{aligned} \frac{dc}{dt} &= \frac{dc}{dt_R} + \frac{dc}{dt_D^{\text{inter}}}, \\ \frac{dq}{dt} &= \frac{dq}{dt_R} + \frac{dq}{dt_D^{\text{intra}}} + \frac{dq}{dt_D^{\text{inter}}}. \end{aligned} \quad (5.30)$$

Of course the equilibrium structure (5.15) is not modified by the diffusional effect.

In order to investigate the dynamical properties, we have to solve the coupled nonlinear equations. Because of their complexity we resort to numerical integration.

3. Crystal growth: Numerical results

The growth rate of the crystal in our model is defined as

$$R = \frac{d}{dt} \sum_n c(n). \quad (5.31)$$

There is no direct contribution from the diffusion processes equations (5.22) and (5.26). These effects are contained in the correlations $q(n)$ within each layer and in the inhomogeneity, i. e., the concentration profile, across the interface.

The Wilson–Frenkel expression for the growth rate [Eq. (3.20)]

$$R_{WF} = \frac{1}{\tau_R} (e^L - 1) = k_0^* (1 - e^{-L}) \quad (5.32)$$

as before follows from the approximation that the interface profile and the correlations remain at their equilibrium value during the growth process. In reality the interfacial structure in the nonequilibrium steady state of growth is different from the equilibrium structure and even depends periodically^{4,5} upon the position of the interface in the lattice, at least for temperatures below the roughening temperature T_R . The high temperature expansion of Sec. III takes into account the modifications of interfacial structures due to the external driving force $\Delta\mu$ (or H or L), but neglects the periodic position dependence of the structures during growth. It therefore holds only sufficiently above T_R .

We have studied the case of a simple cubic system, the interface being oriented in the (100) direction. The coordination number z in a layer is $z = 4$ and the critical temperature for a two-dimensional layer in QC approximation $T_c^{(2d)}$ is given by

$$K_c^{(2d)} = J/k_B T_c^{(2d)} = \ln 2 = 0.693 \dots \quad (5.33)$$

For the numerical integration of Eq. (5.31) it turned out to be sufficient to consider some 20 coupled equations simultaneously (Fig. 5). The first layer was fixed to be completely crystalline, $c(1) = 1$, the last layer being completely vacant $c(22) = 0$. Figure 5 shows the propagation of the interface at a temperature slightly above $T_c^{(2d)}$ with a “field” $L = 0.5$ without diffusion. The width of the interface is small compared to the size of the system normal to the interface. The growth rate R shows an oscillation due to the localization of the interface at discrete positions normal to the growth direction (Fig. 6). One does not have full translational in-

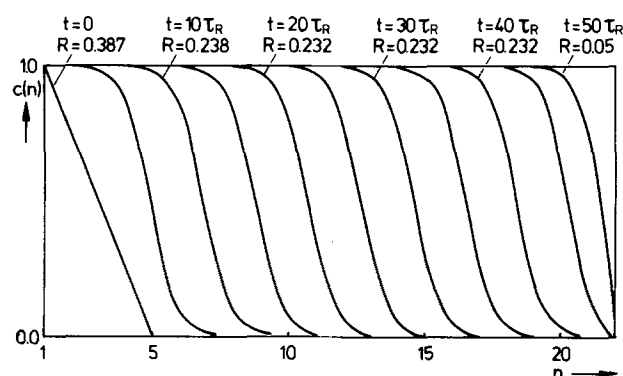


FIG. 5. SOS model interface in CC approximation, propagating over some 20 layers. The parameters for particle interaction and field were $K = 0.625$, $L = 0.5$; diffusion was not allowed. The small influence from the boundaries indicates that 20 layers are sufficient for the present analysis of dynamic properties.

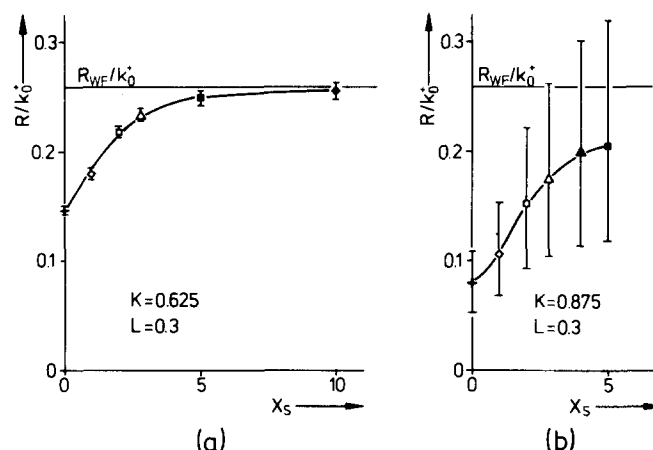


FIG. 6. SOS model. Dependence of the average growth rate R upon the diffusion length X_s at two temperatures a) $K = 0.625$, b) $K = 0.875$. The bars denote the maxima and minima of the oscillation of the growth rate.

variance normal to the interface and therefore does not observe a roughening transition in this approximation.

The averaged growth rate R divided by the adsorption k_0^* is shown in Fig. 7 as a function of the field L at a temperature ($K = 0.625$) above $T_c^{(2d)}$. Curve a represents the growth rate without the diffusion process. It is significantly below the Wilson–Frenkel value R_{WF}/k_0^* . When the intra- and interlayer diffusion process ($\tau_D^{inter} = \tau_D^{intra} = \tau_D$) is included, the growth rate is enhanced. Curves b and c represent the growth rate with diffusion, where the diffusion length $X_s = \sqrt{z\tau_R/\tau_D}$ is 1 and 2 lattice units, respectively. The curves A, B, and C are the corresponding growth rates obtained from Monte Carlo simulations (from Ref. 19). The agreement is very good down to fields $L = 0.02$.

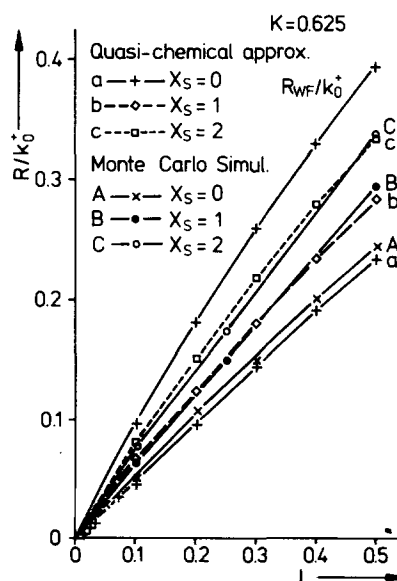


FIG. 7. Average growth rate R vs field L at a temperature $K = 0.625$ (above the two-dimensional critical temperature $K_c = 0.693$, in QCA). The agreement between our QCA and previous MC results is very good. There is no adjustable parameter in the calculation.

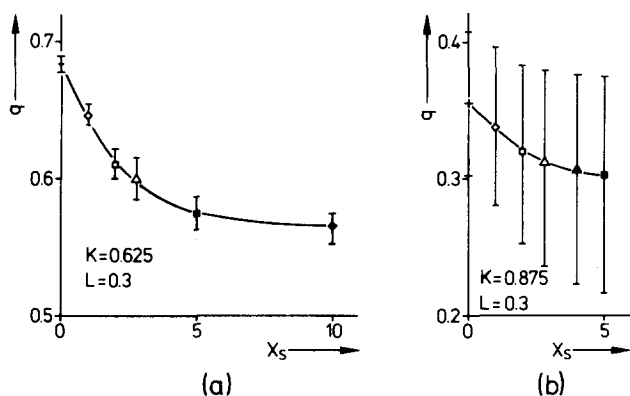


FIG. 8. Decrease of local roughness $q = \sum_n q(n)$ with increasing diffusion length X_s at a) $K=0.625$, and b) $K=0.875$. The bars denote the maxima and minima of the oscillating roughness during growth.

The internal energy or the local roughness $q = \sum_n q(n)$ is shown in Fig. 8 as a function of the diffusion length X_s for the field $L=0.3$, where the calculated growth rate agrees well with the MC simulations. Parallel to the periodic oscillation of the growth rate the local roughness also varies. Surface diffusion enhances the relative amplitude of oscillation, q_{\max}/q_{\min} , but decreases the maximum and the averaged values. The surface in the average becomes smoother.

At temperatures below the critical temperature $T_c^{(2d)}$ ($K=0.875$, see Fig. 9) the existence of metastable regions with infinite lifetime at small fields becomes obvious. This is a nonphysical result of the QC approximation and also persists in the high temperature range.³⁰ But there the critical field L_c is so small (Fig. 7) that it is numerically hard to detect. At the lower temperature $K=0.875$ (Fig. 9) the critical "spinodal" field is

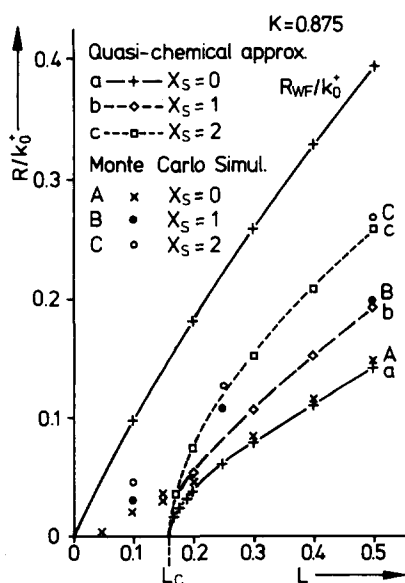


FIG. 9. Average growth rate R vs field L for $K=0.875$ (below the roughening temperature). For fields outside the spinodal regime ($L > 1.5 L_c$) the calculation agrees well with the MC simulations.

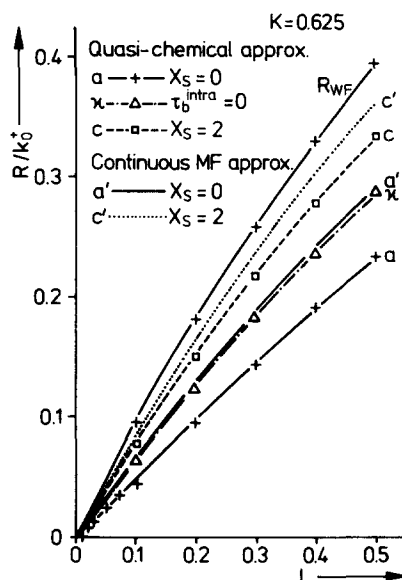


FIG. 10. Growth rate calculated in "continuous" mean-field approximation ($K=0.625$). Curve x represents the result of QCA with infinitely fast intra-layer diffusion and lies very close to the MC results (Fig. 7, curve B) for both inter- and intralayer diffusion at $X_s=1$. The agreement between the approximate formula equation (5.49) and the computer simulations is good for $X_s > 2$.

already almost equal to the critical field $L_c^{(2d)}$ of the two-dimensional system [Eq. (4.23)].

For larger driving forces $L > L_c$ the influence of the diffusion upon the growth rate is qualitatively equivalent to the case at higher temperature. For values $L > 1.5 L_c$ the Monte Carlo simulations again are very well reproduced.

The growth rate again varies periodically as the interface proceeds layer by layer. In Fig. 6(b) the maximum and minimum values of R as well as the averaged rate are plotted as a function of the diffusion length X_s . The enhancement of the growth rate due to surface diffusion is mainly contained in the maximum value of the instantaneous growth rate. The local roughness also oscillated with time. The extremal values are shown in Fig. 8(b) as a function of the diffusion length.

We will now turn to the question whether one can give an analytic formula that approximately describes the influence of surface diffusion upon the growth rate in closed form. For this purpose we first discuss the question whether the diffusion within a layer or the molecular exchange between different layers gives the main contribution from the diffusion to the growth rate. In our QCA formulas, Eq. (5.30), it is easy to suppress any particular process separately. Excluding interlayer diffusion ($\tau_D^{\text{inter}} = \infty$) and letting the intralayer diffusion speed go to infinity ($\tau_D^{\text{intra}} = 0$) (i. e., instantaneous equilibrium within a layer), we only find a moderate enhancement of the growth rate as compared to the case with no diffusion (Figs. 10, 11). The remaining difference to the Wilson-Frenkel rate therefore has to be attributed to interlayer diffusion or to the adjustment of the interface profile.

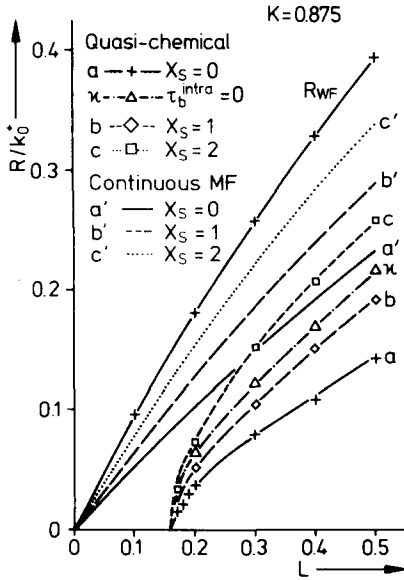


FIG. 11. The same as Fig. 10, but now at $K=0.875$. As is clear from the setup of Eq. (5.49), the continuous mean-field approximation ceases to be good below the roughening temperature, where nucleation becomes important.

This behavior suggests the approximation to treat each layer in a homogeneous mean-field approximation, which by definition always represents a kind of instantaneous equilibrium. Then we allow for diffusion between the layers and give an analytic approximation for the interface profile. This is explained in the following subsection.

B. Continuous mean-field approximation

Assuming infinite intralayer diffusion speed we can make an “instantaneous-equilibrium” approximation for the pair correlations $q(n)$ in the n th layer. Similar to Eq. (5.17) we use the mean-field limit $q(n) = z \cdot c(n) \cdot c_v(n)$. Our previous system of equations (5.30) with Eqs. (5.11), (5.14), (5.22), (5.23), (5.26), and (5.29) can then be reduced to a single equation of the Temkin type⁴:

$$\frac{dc(n)}{dt} = \frac{1}{\tau_R} \{ [c(n-1) - c(n)](e^L + X_s^2 e^{L_0}) - [c(n) - c(n+1)]e^{K\pi(1-2c(n))}(1 + X_s^2) \}, \quad (5.34)$$

where the diffusion length is defined here by

$$X_s^2 = z\tau_R/\tau_D^{\text{inter}} \quad (5.35)$$

and the self-consistent field L_0 reduces to

$$e^{L_0} = \sum_n [c(n) - c(n+1)]e^{K\pi(1-2c(n))}. \quad (5.36)$$

In order to integrate this in closed form we assume the concentration profile to vary smoothly across the interface. This corresponds to sufficiently high temperatures above T_R . Then we can expand the difference of concentrations in differential form³⁴:

$$c(n) - c(n+1) = \left[-\frac{\partial}{\partial x} - \frac{1}{2} \frac{\partial^2}{\partial x^2} \right] c(x). \quad (5.37)$$

In the steady state with the growth rate R

$$R = \frac{d}{dt} \int_{-\infty}^{\infty} c(x) dx = \frac{1}{\tau_R} (e^L - e^{L_0}), \quad (5.38)$$

the system moves with constant velocity R or the concentration is only a function of η ³⁴

$$\eta = X - Rt. \quad (5.39)$$

Using these continuous and steady state approximation, (5.37) and (5.39), to the mean field equation (5.34), we obtain the following differential equation for the concentration $c(\eta)$:

$$-R \frac{dc}{d\eta} = \frac{1}{\tau_R} \left[\left(-\frac{dc}{d\eta} + \frac{1}{2} \frac{d^2c}{d\eta^2} \right) (e^L + X_s^2 e^{L_0}) + \left(\frac{dc}{d\eta} + \frac{1}{2} \frac{d^2c}{d\eta^2} \right) e^{K\pi(1-2c)} (1 + X_s^2) \right]. \quad (5.40)$$

This equation is rearranged as

$$\frac{d^2c}{d\eta^2} = 2 \frac{-R\tau_R + (e^L + X_s^2 e^{L_0}) - e^{K\pi(1-2c)}(1 + X_s^2)}{(e^L + X_s^2 e^{L_0}) + e^{K\pi(1-2c)}(1 + X_s^2)} \frac{dc}{d\eta} \quad (5.41)$$

and integrated to be

$$\frac{dc}{d\eta} = I_0 + 2 \left(\frac{-R\tau_R}{e^L + X_s^2 e^{L_0}} + 1 \right) c(\eta) + \frac{1}{Kz} \left(\frac{-R\tau_R}{e^L + X_s^2 e^{L_0}} + 2 \right) \times \log[(e^L + X_s^2 e^{L_0}) + (1 + X_s^2)e^{K\pi(1-2c)}]. \quad (5.42)$$

The integration constant I_0 and the growth rate R are determined from the SOS boundary condition:

$$\begin{cases} c = 1, & dc/d\eta = 0 & \text{as } \eta \rightarrow -\infty \\ c = 0, & dc/d\eta = 0 & \text{as } \eta \rightarrow \infty. \end{cases} \quad (5.43)$$

The results are

$$I_0 = \frac{1}{Kz} \left(\frac{R\tau_R}{e^L + X_s^2 e^{L_0}} - 2 \right) \log[(e^L + X_s^2 e^{L_0}) + (1 + X_s^2)e^{K\pi}] \quad (5.44)$$

and

$$\frac{R\tau_R - (e^L + X_s^2 e^{L_0})}{R\tau_R - 2(e^L + X_s^2 e^{L_0})} = \frac{1}{2Kz} \log \frac{(e^L + X_s^2 e^{L_0}) + (1 + X_s^2)e^{K\pi}}{(e^L + X_s^2 e^{L_0}) + (1 + X_s^2)e^{-K\pi}}, \quad (5.45)$$

where $R\tau_R$ and e^{L_0} satisfy the relation (5.38). From Eqs. (5.45) and (5.38), the growth rate R is determined implicitly.

We obtain the limiting values of the growth rate for $X_s^2 \rightarrow 0$ or $X_s^2 \rightarrow \infty$. For $X_s^2 = 0$ the growth rate reduces to the known mean field value^{34b}

$$\frac{R}{k_0^*} = 2 - \frac{1}{1 - (1/2Kz) \log(e^L + e^{K\pi})/(e^L + e^{-K\pi})}. \quad (5.46)$$

For infinitely fast diffusion ($X_s^2 \gg 1$) the growth rate is given as

$$\frac{R}{k_0^*} = (1 - e^{-L}) \left[1 - \frac{1}{X_s^2} \left(\frac{Kz/2}{\ln(Kz/2)} - 1 \right) + O\left(\frac{1}{X_s^4}\right) \right], \quad (5.47)$$

which converges for $X_s^2 \rightarrow \infty$ to the Wilson-Frenkel law from below. Note that metastable states here are excluded by the approximation equation (5.37).

For intermediate values of X_s^2 , we have to evaluate Eqs. (5.45) and (5.38) numerically. Because we have used the approximation of infinitely fast intralayer dif-

fusion, the rates obtained in this subsection are always larger than the quasichemical values (Figs. 10 and 11).

At low temperatures the approximation equation (5.37) of course is not good owing to the neglect of a nucleation regime. But with increasing temperature (Fig. 10), i. e., above the roughening temperature, this approximation becomes systematically better.

C. Two-dimensional nucleation with infinite diffusion speed

For completeness we summarize here arguments about the asymptotic growth rate in the limit of infinite diffusion speed ($X_s \rightarrow \infty$) for temperatures below T_R . (For references see the review article by Venables, Ref. 35).

In QC approximation the growth rate R vanishes for driving forces L below the spinodal value L_c . For sufficiently strong fields the Wilson-Frenkel rate R_{WF} is reached asymptotically ($L \gg L_c$, Fig. 9). In reality, however, the nucleation mechanism allows for nonvanishing growth rates for arbitrarily small values of L . A semiphenomenological expression used by Gilmer and Bennema¹⁹ describes the influence of diffusion for small diffusion lengths. The formula, however, has to be fitted to the $X_s = 0$ case and predicts infinite growth rate for infinite surface diffusion speed which is clearly unphysical.

This problem arises owing to the implicit assumption that a two-dimensional "nucleation rate" is well defined even in this limit. Denoting the number of critical nuclei in a system of N sites by n , we may write down an evolution equation for the number of nuclei (see, e. g., Refs. 35–38):

$$\frac{dn}{dt} = N[1 - q] \cdot [k_0^2(1 + c_0 X_s^2)] \cdot \exp(-\gamma^2 c_1/L), \dots, \quad (5.48)$$

where we assumed the radius of the critical nucleus to be small compared with X_s . Here the last (exponential) term represents the nucleation barrier, the second term is the kinetic prefactor or the frequency of attachment of atoms to the surface of a supercritical cluster, and the first term accounts for the excluded area, which is already covered by supercritical clusters. This is single-layer representation for the moment. The constants c_0, c_1 are some positive system dependent quantities; k_0^2 is the net impingement frequency of atoms onto the surface; and γ is the edge free energy of a surface step. The excluded volume factor $(1 - q)$ has been discussed in various papers; here we need only the simplest approximation, which gives a lower limit on the rate of change dn/dt . We therefore set for $X_s \gg 1$

$$q \approx X_s^2 n/N, \quad (5.49)$$

which assumes that there is only one cluster generated within an area X_s^2 on a surface of N sites. Equations (5.48) and (5.49) are readily integrated to give

$$n(t) = \frac{N}{X_s^2} \{1 - \exp[-t X_s^2 k_0^2 (1 + c_0 X_s^2) e^{-\gamma^2 c_1/L}]\} \dots \quad (5.50)$$

Taking now the limit $X_s \sim \sqrt{N} \rightarrow \infty$, Eq. (5.50) reduces to a step function, i. e., immediately after the potential

difference L has been switched on, a finite number $n = N/X_s^2$ of supercritical clusters has appeared in the (infinite) system. The nucleation rate dn/dt immediately drops to zero and the few isolated nuclei serve as ideal sinks for all excess atoms on the surface in the limit of infinite diffusion speed ($X_s \rightarrow \infty$). The surface then has equilibrium structure everywhere except near the perimeter of the nuclei: This latter effect gives no contribution to the macroscopic thermodynamics of the system and, therefore, the Wilson-Frenkel rate holds also below T_R for $X_s \rightarrow \infty$.

VI. CONCLUSION

We have compared the influence of diffusion on the relaxation of the order parameter in various kinetic models. In the particular application of these models to crystal growth, the relaxation of the order parameter corresponds to the growth rate.

We have found that the diffusion leads to a faster response of the systems (a higher growth rate) in practically all cases considered here. An exception is the one-dimensional Ising chain with "symmetric" transition probabilities. If both the adsorption and evaporation of atoms depend on the local environment of the respective site, the correlations in the system are always closer to their equilibrium values than in the case of nonsymmetric transition probabilities, where the adsorption is assumed to be independent of the local environment in the lattice. In the second case, therefore, diffusion has a significantly more pronounced effect than in the first case, since it tends to bring the correlations closer to their equilibrium value at given order parameter.

For the other systems, higher-dimensional Ising model, discrete Gaussian and SOS model, we have restricted our attention to the nonsymmetric transition probabilities. In the Ising model below the critical temperature quasichemical approximation produces an (unphysical) regime of metastable states with infinite lifetime. Outside this region we find a reduction of the relaxation time due to diffusion by up to a factor of 2.

The Ising-type models always converge to thermodynamic equilibrium for sufficiently long times. Since both the initial relaxation of the order parameter and the final relaxation in linear response theory become independent of the diffusion process the diffusion is important in the intermediate nonlinear regime only. Diffusion therefore is very important in the nucleation regime which we did not consider explicitly, since the QC approximation does not work there.

In the discrete Gaussian and SOS model, on the other hand, one can maintain a nonequilibrium situation for arbitrary times, which corresponds to continuous growth of a crystal. The diffusion process there leads to an enhancement of the growth rate, since clustering of isolated impinging atoms then is supported and reevaporation is reduced. The results of the QCA are in very satisfactory agreement with previous computer simulations of combined relaxation and diffusion. In the high temperature expansion of the discrete Gaussian model,

being appropriate for the "rough" surface phase ($T > T_R$), we obtain the Wilson-Frenkel growth rate as an upper limit at infinite diffusion speed. In the QC approximation for the SOS model we obtain this rate as a limit for infinite diffusion speed and for driving forces (chemical potential differences) $\Delta\mu$ large compared to the spinodal value $\Delta\mu_c$ below which the system is in metastable states of infinite lifetime. The above mentioned clustering of adsorbed atoms due to diffusion is seen in the reduction of the (interface-) energy of the system (SOS model). A mean-field type approximation within the layers parallel to the interface and continuum approximation normal to the interface finally allows us to give an analytic expression for the growth rate as a function of the diffusion length in closed form, which agrees quantitatively with the computer simulations above T_R within about 20%.

We have thus obtained a fairly clear picture for the influence of surface diffusion upon growth rates of dislocation-free crystals, starting from a microscopic description. The remaining uncertainty for small growth rates below and around the roughening point due to the breakdown of the QC approximation may eventually be overcome by using an appropriately adjusted cluster-reaction theory, which also works in the nucleation regime.

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