

Model for growth of binary alloys with fast surface equilibration

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We study a simple growth model for $(d+1)$ -dimensional films of binary alloys in which atoms are allowed to interact and equilibrate at the surface, but are frozen in the bulk. The resulting crystal is highly *anisotropic*: Correlations perpendicular to the growth direction are identical to a d -dimensional *two-layer system in equilibrium*, while parallel correlations generally reflect the dynamics of an Ising system. For stronger in-plane interactions, the correlation volumes change from oblate to highly prolate shapes near a critical demixing or ordering transition. In $d=1$, the critical exponent z relating the scaling of the two correlation lengths varies continuously with the chemical interactions. [S1063-651X(97)04504-2]

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I. INTRODUCTION

Growth by vapor deposition is a highly effective process for producing high quality materials. The resulting films can show properties that are very different from systems in bulk equilibrium [1,2]. For example, in some binary alloys [2], the deposited atoms are highly mobile as long as on the surface, but relatively immobile once incorporated in the bulk. As a result, the surface fluctuations that are formed during the growth process are frozen into the bulk. A characteristic signature of such (metastable) phases is *anisotropic* correlations that are related to the growth direction, and are absent in bulk equilibrium.

A number of models for composite film growth have been introduced in the past [3–8]. Generally in these models, the probability that an incoming atom sticks to a given surface site depends on the state of neighboring sites in the layer below. Once a site is occupied, its state does not change any more, and thus the surface configuration becomes frozen in the bulk. Such growth rules are equivalent to (stochastic) cellular automata, where each site is updated in parallel as a function of the states of its neighbors. Subsequent states of the cellular automaton correspond to successive layers in the crystal.

It is in general not possible to calculate exact correlation functions for such (nonequilibrium) growth processes. The exception occurs in special cases where the growth rules satisfy a detailed balance condition, relating their stationary behavior to an equilibrium system of one lower dimension [9]. However, it can be shown that if d -dimensional probabilistic cellular automata with two states, and up-down symmetry, undergo a symmetry breaking, their critical behavior is identical to the corresponding Ising model in equilibrium [9]. Correlations in time are then equivalent to those generated by Glauber dynamics of the Ising system. In *Glauber dynamics* the local states evolve with probabilities consistent with the changes of the Boltzmann weight. However, no local conservation law of particle number is imposed in such dynamics. $(d+1)$ -dimensional crystals grown according to the rules of these cellular automata, therefore, have an order-disorder phase transition with correlations perpendicular to the growth direction characterized by the critical exponent ν , and those parallel to the growth direction by the exponent

νz of the d -dimensional Ising model (z being the appropriate dynamical critical exponent).

Since in the above models the local adsorption probabilities depend on the surface states, some form of fast redistribution of atoms is implied. One possibility is the mixing of particles in the gas phase prior to adsorption. However, it is easy to envision conditions where the local adsorption probabilities are determined by densities in the gas phase (e.g., in ballistic deposition). In such cases, rapid desorption from unfavorable locations on the surface may provide the appropriate redistribution mechanism. However, given the high mobility of particles on the surface, surface diffusion is another important process. In this case, it is essential to also include the interactions between the diffusing surface particles which eventually leads to formation of domains and islands.

In this paper, we include the interactions between atoms on the top layer, which is assumed to equilibrate completely (by surface diffusion *or* desorption-resorption mechanisms) before another layer is added. Such an assumption is realistic only if the growth rate is much slower than characteristic equilibration times of the surface layer. Its limits of validity are discussed in the conclusion; in particular, it is likely to break down in the vicinity of a critical point, where the system undergoes a continuous phase transition from chemically disordered to either phase separated (for attractive interactions), or sublattice ordered (for repulsive interactions). We show that this model satisfies detailed balance, and can therefore be analyzed with methods from equilibrium statistical physics. While the resulting critical behavior is similar to the previously studied (cellular automata) models, the “temporal” correlations in $1+1$ dimension are very different from those obtained from the corresponding (particle non-conserving or Glauber) dynamical Ising model [10]: On approaching zero temperature [i.e., the critical temperature of the $(1+1)$ -dimensional system], the diverging vertical and horizontal correlation lengths are related by an exponent z that is, in general, larger than the Glauber value of 2, and varies continuously with the ratio of the perpendicular and parallel coupling constants. In all dimensions, if the ratio between the two coupling constants is larger than unity, the two correlation lengths cross at some temperature, changing the shapes of typical correlated clusters from oblate (at high growth temperatures) to prolate (near the critical point).

II. MODEL

The model is defined as follows. We consider a $(d+1)$ -dimensional hypercubic lattice and two kinds of atoms A and B . Let ϵ_{AA} , ϵ_{AB} , and ϵ_{BB} be the interaction energies between neighboring atoms of types AA , AB , and BB , respectively. When each layer has N sites, there are 2^N possible configurations for a layer. The energy cost for adding a layer of configuration γ on top of one with configuration α is the sum of the internal energy E_γ of the new layer and of the interaction energy $V_{\alpha\gamma}$ with the previous layer. These energies are just the sums of all local bonds ϵ_{ij} between nearest neighbors ij within the new layer and between the two layers, respectively. In addition, E_γ contains a chemical potential $\mu_A N_A + \mu_B N_B$ that is related to the partial pressures of A and B atoms in the gas phase.

Since we assume that the top layer is in thermodynamic equilibrium, the conditional probability that it is in configuration γ , given configuration α for the layer below, is

$$W_{\gamma\alpha} = \frac{\exp[-\beta(E_\gamma + V_{\alpha\gamma})]}{\sum_{\delta} \exp[-\beta(E_\delta + V_{\alpha\delta})]}, \quad (1)$$

where $\beta = 1/k_B T$; T is the temperature at which the crystal is grown, and k_B is the Boltzmann constant. After adding many layers, the probability for finding a given configuration γ is determined by the stationarity condition

$$P_\gamma = \sum_{\alpha} W_{\gamma\alpha} P_\alpha, \quad (2)$$

which has the solution

$$P_\alpha = \frac{\sum_{\gamma} \exp[-\beta(E_\alpha + E_\gamma + V_{\alpha\gamma})]}{\sum_{\delta,\nu} \exp[-\beta(E_\delta + E_\nu + V_{\delta\nu})]} \equiv \frac{\sum_{\gamma} \exp[-\beta H_{\alpha\gamma}]}{\sum_{\delta,\nu} \exp[-\beta H_{\delta\nu}]}. \quad (3)$$

The above expression is the equilibrium probability for the top layer of a two-layer system, obtained after summing over the states of the bottom layer. Transverse correlation functions (i.e., perpendicular to the growth direction) are therefore exactly the same as correlation functions in a two-layer system.

In fact, from Eqs. (1) and (3) it easily follows that the system satisfies detailed balance, i.e.,

$$W_{\alpha\gamma} P_\gamma = W_{\gamma\alpha} P_\alpha. \quad (4)$$

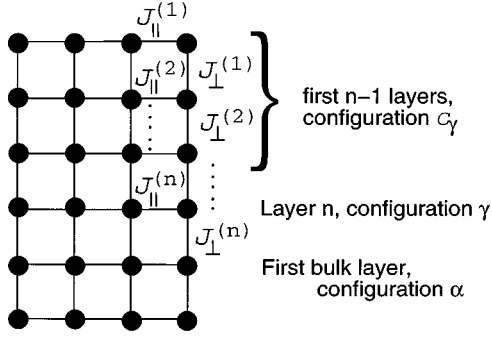
This means that (beyond a transient thickness) the crystal looks the same along or against the growth direction, and that the sequence of layers corresponds to time evolution of thermodynamic equilibrium states. This generalizes the previous results for cellular automata, which are obtained by setting the in-plane interactions E_α to zero. As in such cellular automata, the $(d+1)$ -dimensional system has transverse properties like d -dimensional models. In particular, we expect phase transitions to occur at the same temperature as for a d -dimensional two-layer system.

The two-layer Hamiltonian occurring in Eq. (3) can be rewritten in terms of Ising variables by introducing the spin states $\sigma = +1$ for an A atom, and $\sigma = -1$ for a B atom. Using $J = (\epsilon_{AA} - 2\epsilon_{AB} + \epsilon_{BB})/4$ and $h = 3(\epsilon_{AA} - \epsilon_{BB})/4 + (\mu_A - \mu_B)/2$, and neglecting an additive constant, the two-layer Hamiltonian becomes

$$H_{\alpha\gamma} = J_{\perp} \sum_{\langle i,j \rangle} (\sigma_i^{(\alpha)} \sigma_j^{(\alpha)} + \sigma_i^{(\gamma)} \sigma_j^{(\gamma)}) + J_{\parallel} \sum_{i=1}^N \sigma_i^{(\alpha)} \sigma_i^{(\gamma)} + h \sum_{i=1}^N (\sigma_i^{(\alpha)} + \sigma_i^{(\gamma)}), \quad (5)$$

where we have also allowed for the possibility of anisotropic couplings parallel and perpendicular to the growth direction. $\langle i,j \rangle$ denotes a pair of nearest-neighbor sites within a layer. As a function of the ‘‘field’’ h , there is a first-order transition between A and B rich phases. Here, we focus on the coexistence line at $h=0$, which terminates at a critical point, where the correlation lengths diverge both parallel and perpendicular to the growth direction. For $h=0$, the Hamiltonian is invariant under the reversal of the signs of all spins. This means that on an average an equal number of A and B atoms are deposited. If the coupling constants J_{\perp} and J_{\parallel} are positive, atoms of the same kind attract each other, and the two types of atoms phase separate below the critical temperature. If J_{\perp} and J_{\parallel} are both negative, and if the lattice structure allows a unique ground state, the low-temperature phase is ‘‘antiferromagnetic’’ with A and B atoms sitting on different sublattices. These two cases can be mapped onto each other by reversing the sign of the coupling constants, and of the spins on one of the sublattices. If $J_{\parallel} < 0$ and $J_{\perp} > 0$, the low-temperature phase alternates between A and B layers. Since the composition of the layers is only determined on average by the deposited flux, our model allows this form of ‘‘superlattice ordering transition.’’ However, in realistic growth situations, the ordered phase will have different domains, leading to approximately the same numbers of A and B particles, even within a single layer. In the opposite case ($J_{\parallel} > 0$ and $J_{\perp} < 0$), all layers have an antiferromagnetic occupation in the ground state, with sublattices for the same type of atoms laying on top of each other. These situations can also be mapped to the ferromagnet by reversing the sign of the negative coupling constant, and simultaneously of the spins on one of the sublattices. We shall therefore focus on $J_{\parallel}, J_{\perp} > 0$ from now on.

Generalizing our model, by allowing several layers at the surface to equilibrate, is straightforward. To mimic the large energy of the impinging particles, as well as their modified environment, we can assign each of the top n layers from the surface a different temperature, depending on its depth. Equivalently, we can give to each layer different interaction parameters (see Fig. 1). The probability that a layer with configuration γ follows one in configuration α in the bulk is obtained by considering the layer at the moment when it is the n th layer from the top, i.e., immediately before its configuration is frozen. Denoting the configuration of the first $n-1$ layers by \mathcal{C}_γ and their energy (including the coupling to

FIG. 1. System where the top n layers equilibrate.

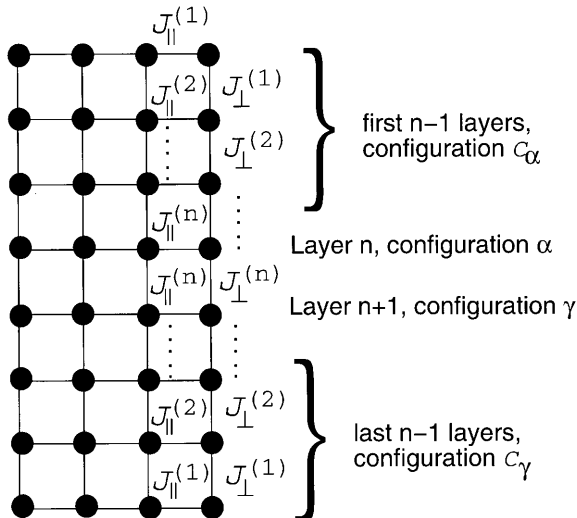
the n th layer, and different interaction constants in the different layers) by $E(C_\gamma)$, the conditional probabilities $W_{\gamma\alpha}$ can be written as

$$W_{\gamma\alpha} = \frac{\sum_{C_\gamma} \exp\{-\beta[E_\gamma + V_{\alpha\gamma} + E(C_\gamma)]\}}{\sum_{\delta, C_\delta} \exp\{-\beta[E_\delta + V_{\alpha\delta} + E(C_\delta)]\}}.$$

Following the approach for the case $n=1$, we can show that the set of weights

$$P_\alpha = \frac{\sum_{\gamma, C_\gamma, C_\alpha} \exp\{-\beta[E_\alpha + E_\gamma + V_{\alpha\gamma} + E(C_\gamma) + E(C_\alpha)]\}}{\sum_{\delta, \nu, C_\delta, C_\nu} \exp\{-\beta[E_\delta + E_\nu + V_{\delta\nu} + E(C_\delta) + E(C_\nu)]\}}$$

describes a stationary state. It is easy to verify that this stationary solution satisfies detailed balance. The stationary state corresponds to an equilibrium Hamiltonian with $2n$ layers, and interactions which depend on the distance from the closest surface (see Fig. 2). In this symmetric system, configurations of the layers n and $n+1$ have the same probabil-

FIG. 2. Graphical illustration of the stationary distribution P_γ .

ity distribution. Layer n of Fig. 2 therefore sees exactly the same environment as layer n of Fig. 1 in a grown bulk (beyond a transient thickness). The top (and also the bottom) layer of Fig. 2 describe the equilibrium at the top surface layer, while the n th layer describes the transverse correlations in the bulk. While the correlations parallel to the growth direction will be more complicated, the general conclusions derived below for the case $n=1$ should remain valid. In the following, we restrict our discussion to the case $n=1$.

III. ONE DIMENSION

The $(1+1)$ -dimensional model can in fact be solved exactly, and displays interesting critical properties. In the preceding section, we have found that correlations perpendicular to the growth direction are identical to those of a two-layer system, giving the two-spin correlation function

$$g_\perp(l) \equiv \langle \sigma_i^{(\alpha)} \sigma_{i+l}^{(\alpha)} \rangle = \sum_\alpha \sigma_i^{(\alpha)} \sigma_{i+l}^{(\alpha)} \frac{\sum_\gamma \exp[-\beta H_{\alpha\gamma}]}{\sum_{\delta, \nu} \exp[-\beta H_{\delta\nu}]} \propto \left(\frac{\lambda_2}{\lambda_1} \right)^l, \quad (6)$$

where λ_1 and λ_2 are the largest and next largest eigenvalues of the 4×4 transfer matrix. Explicit diagonalization of the matrix gives

$$\begin{aligned} \lambda_1 &= \exp(\beta J_\parallel + 2\beta J_\perp) + \exp(\beta J_\parallel - 2\beta J_\perp) \\ &\quad + O(\exp(-\beta J_\parallel - 2\beta J_\perp)), \\ \lambda_2 &= \exp(\beta J_\parallel + 2\beta J_\perp) - \exp(\beta J_\parallel - 2\beta J_\perp). \end{aligned} \quad (7)$$

It is then easy to check that in the limit of zero temperature ($\beta \rightarrow \infty$), the correlations decay exponentially with a correlation length ξ_\perp which diverges as

$$\xi_\perp \simeq \exp(4\beta J_\perp)/2. \quad (8)$$

The following argument provides a better physical understanding for the form of ξ_\perp . At low temperatures, the energy of the two-layer system is only slightly above its ground state, and consequently most of the spins are parallel. The lowest-energy excitations of the ground state that destroy long-range correlations are straight domain walls that cost an energy of $4J_\perp$ and occur with a probability $2 \exp(-4\beta J_\perp)$ (see Fig. 3). The factor 2 is included since either the left part or the right part of the system can flip in order to create a domain wall at a given location. More complicated excitations like domain walls with steps cost at least an energy of $4J_\perp + 2J_\parallel$ and occur with probabilities smaller by a factor of $\exp(-2\beta J_\parallel)$ than straight domain walls. The transverse correlation length is given by the inverse density of domain walls, leading to Eq. (8).

The correlation length parallel to the growth direction can be obtained by similar considerations. Parallel correlations are destroyed by the motion of domain walls. The probability that a domain wall moves by one lattice site to the right or to the left when a new layer is added is $\exp(-2\beta J_\parallel)$ (see Fig. 3).

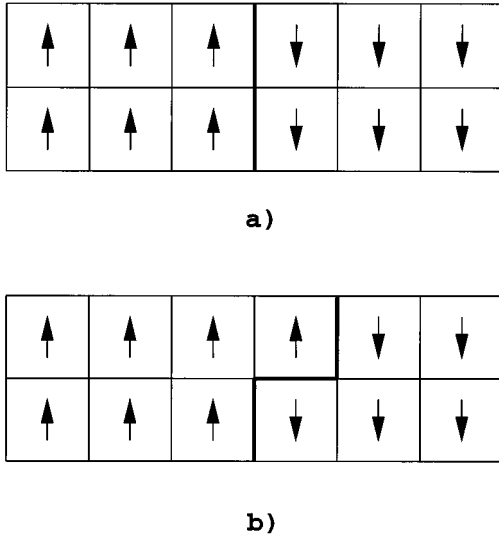


FIG. 3. (a) Straight domain walls are the lowest-energy excitations of a two layer system. (b) A kink in the domain wall costs additional energy.

Since these steps in the domain wall are independent from each other, it takes ξ_{\perp}^2 steps to move over the distance of the perpendicular correlation length. This mechanism destroys correlations of the order ξ_{\perp} in the spin orientation after $\xi_{\perp}^2 \exp(2\beta J_{\parallel})$ layers. We conclude

$$\xi_{\parallel} \propto \exp(8\beta J_{\perp} + 2\beta J_{\parallel}) \propto \xi_{\perp}^{2+J_{\parallel}/2J_{\perp}}, \quad (9)$$

leading to $z = 2 + J_{\parallel}/2J_{\perp}$. Since we have assumed that domain walls move by single steps, our result is only valid for sufficiently low temperatures, $\beta^{-1} \ll J_{\parallel}$. Depending on the ratio between the two coupling constants, the critical exponent z can assume any value larger than two. Since z is larger than one, the parallel correlation length becomes much larger than the perpendicular correlation length when the temperature is low. On the other hand, we can expect that for high temperatures the direction that has the stronger coupling has the larger correlation length, as shown explicitly in Sec. IV. Thus, if $J_{\parallel} < J_{\perp}$, the two correlations lengths must cross at some temperature.

The above intuitive argument (see also [11] for a similar argument in the context of one-dimensional Ising models) does not consider the creation and annihilation of pairs of domain walls, which play an important role in the dynamics of the system. In the following, we therefore derive the exponent z from the complete dynamics of the domain walls. We will see that models with different J_{\parallel} but the same J_{\perp} are equivalent, apart from an overall time scale proportional to $\exp(-2\beta J_{\parallel})$. We will also see that these models are closely related to the Glauber model [10] describing the dynamics of a one-dimensional Ising spin chain that is known to have a dynamical critical exponent $z=2$. In the Glauber model, it does not cost any energy to move a domain wall and therefore this motion does not become slower with decreasing temperature.

The domain wall dynamics consist of three different elementary processes: motion to the right or left by one site,

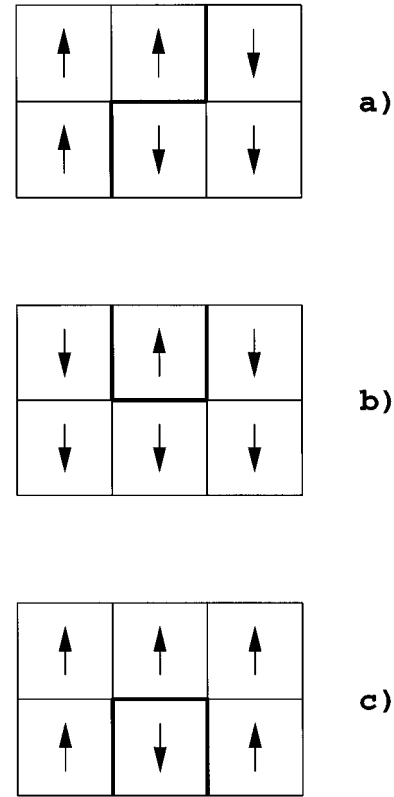


FIG. 4. Three elementary processes in domain wall dynamics: (a) motion of a wall, (b) creation of a pair of walls, and (c) annihilation of a pair of walls.

creation of a pair of neighboring domain walls, and annihilation of a pair of neighboring domain walls (see Fig. 4), occurring with probabilities $\exp(-2\beta J_{\parallel})$, $\exp[-2\beta(2J_{\perp} + J_{\parallel})]$, and $\exp(-2\beta J_{\parallel}) / [\exp(-2\beta J_{\parallel}) + \exp(-4\beta J_{\perp})]$, respectively. These probabilities are obtained by dividing the Boltzmann factor for the considered event by the sum of the Boltzmann factors of all possible events at that place, and retaining only the leading contributions. The neglected terms become vanishingly small compared to the leading terms in the limit of zero temperature. In the denominator of the third expression, the Boltzmann factor for domain wall annihilation can be larger or smaller than the Boltzmann factor for the two domains walls staying at their place, depending on the values of the coupling constants. We therefore keep both contributions. For $J_{\parallel} > 2J_{\perp}$, the three probabilities are all very small and can therefore be interpreted as rates. If we extract a time scale $\exp(-2\beta J_{\parallel})$, these rates become 1, $\exp(-4\beta J_{\perp})$, and $\exp(4\beta J_{\perp})$, independently of the value of J_{\parallel} , showing that models with different J_{\parallel} differ only by the overall time scale. For $J_{\parallel} < 2J_{\perp}$, the situation is slightly different: A pair of neighboring domain walls is annihilated almost with probability one during a single time step, while this process occurs for $J_{\parallel} > 2J_{\perp}$ on an average only after $\exp[2\beta(J_{\parallel} - 2J_{\perp})]$ time steps. However, in both cases this process is very fast compared to the time it takes to move a domain wall or to create a pair of domain walls. Additionally, the probability that a pair of neighboring domain walls ultimately escapes annihilation by increasing their distance to two is $2 \exp(-4\beta J_{\perp})$ in both cases. This

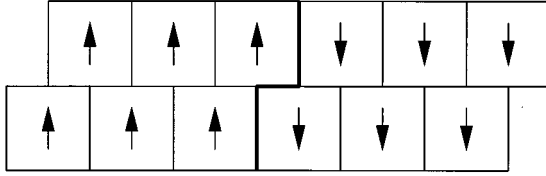


FIG. 5. Different lattice structure that allows domain wall motion at no additional energy.

shows that (apart from the overall time scale) models with $J_{\parallel} < 2J_{\perp}$ are equivalent to those with $J_{\parallel} > 2J_{\perp}$. (A short calculation shows that they are also equivalent to models with $J_{\parallel} = 2J_{\perp}$.) This equivalence becomes even more obvious when we describe the model in terms of creation and annihilation of pairs of domain walls at distance two, and of domain wall motion. Domain walls at distance two are created by first flipping one spin (creating a pair at distance one) and then flipping one of its neighbors, which happens in all cases with a rate $2 \exp(-2\beta J_{\parallel} - 8\beta J_{\perp})$. [Strictly speaking, the pair at distance one cannot only be generated by flipping a spin in a homogeneous domain, but also by the encounter of two domain walls that have been further apart before. However, it can easily be calculated that the number of pairs at distance one generated by this process is smaller by a factor of $\exp(-4\beta J_{\perp})$ than the number of those generated by flipping a spin in a homogeneous domain.] Domain walls at distance two decrease their distance to one with a rate $2 \exp(-2\beta J_{\parallel})$, from where they annihilate almost certainly. If we extract a factor $\exp(-2\beta J_{\parallel})$ from the time scale, the motion of domain walls, the creation of pairs of domain walls at distance two, and the annihilation of pairs of domain walls at distance two, occur with the rates 1, $2 \exp(-8\beta J_{\perp}) = \xi_{\perp}^{-2}/2$, and 2, irrespective of the value of J_{\parallel} . Since we can neglect the interference of pairs of domain walls at distance one with any of these three processes, the dynamics of the model is completely described by these three rates.

To complete this discussion, we show that the dynamics of our model are essentially equivalent to the dynamics of the Glauber model. In the Glauber model, the rate with which a spin at site i flips is given by [10]

$$W(\sigma_i) = \frac{\alpha}{2} \left[1 - \frac{\gamma}{2} \sigma_i (\sigma_{i+1} + \sigma_{i-1}) \right], \quad (10)$$

with $\gamma = \tanh(2\beta J) \approx 1 - 2 \exp(-4\beta J) \approx 1 - \xi^{-2}/2$ at low temperatures. The parameter α sets the time scale and is independent of temperature. Motion of a domain wall, creation of a pair of neighboring domains walls, and annihilation of a pair of neighboring domain walls occur with the rates $\alpha/2$, $\alpha \xi^{-2}/4$, and α respectively. If we set $\alpha = 2 \exp(-2\beta J_{\parallel})$, we find the same rates as for our model, with the only difference being that creation and annihilation of pairs of domain walls happens at distance one instead of distance two. This difference is obviously irrelevant at low temperatures, where domain walls must diffuse over large distances of the order of the correlation length before they encounter each other. Reducing this distance by one has no noticeable effect on the dynamics of the system. Combining the critical exponent

$z=2$ of the Glauber model with the temperature dependence of the time scale in our model, we find Eq. (9).

Nonuniversal dynamical critical exponents are also known from other one-dimensional Ising systems. An Ising spin chain with two different coupling constants J_1 and J_2 , with $J_1 < J_2$, has an exponent $z = 1 + J_2/J_1$ [12,13]. Finally, we note that the result Eq. (9) depends strongly on the lattice structure of the system. When the cells of the lattice do not lay on top of each other but are shifted by half a lattice constant, as in Fig. 5, the motion of a domain wall does not cost any energy, and we retrieve the exponent $z = 2$.

IV. GENERAL DIMENSIONS

In contrast to the previous discussions of 1+1 dimension, in the physically more relevant case of (2+1)-dimensional growth (and more generally for the case of $d+1$ dimensions), critical demixing and ordering transitions generically occur at *finite growth temperature*. The anomalies due to vanishing mobilities are no longer present, and the mobility of a domain wall should be finite in the neighborhood of the critical point. We therefore cannot use the method of the preceding section in order to obtain the relation between the transverse and parallel correlation lengths close to the critical point. However, we can derive the critical exponent z using general arguments. As before, correlations perpendicular to the growth direction are identical to those of a two-layer system and diverge at a critical point with the exponent ν of a d -dimensional Ising system. A sequence of layers can be regarded as successive snapshots of configurations in time. Since our model satisfies detailed balance, this time sequence corresponds to an equilibrium system. The critical behavior of equilibrium systems falls into several universality classes that are determined by symmetries and conservation laws. Since there is no local conservation of spins from one layer to the next, we expect our model to be in the universality class of an Ising system with relaxational (model A or Glauber) dynamics. Therefore, correlations parallel the growth direction diverge with an exponent $z\nu$, where z is the (Glauber) dynamic exponent of the d -dimensional Ising model. Since z is larger than one, correlation volumes are prolate near the critical point. This is also true just below the critical point, where the system has established long-range correlations. There, one usually defines correlation volumes for the deviation from the mean ‘‘magnetization’’ (i.e., difference between A and B concentrations) within a domain.

Next, we derive the high- and low-temperature behaviors of our model in general dimensions. The overall probability for encountering a particular sequence of layers is given by

$$P(\alpha_N, \alpha_{N-1}, \dots, \alpha_1) = W_{\alpha_N \alpha_{N-1}} W_{\alpha_{N-1} \alpha_{N-2}} \dots W_{\alpha_2 \alpha_1}. \quad (11)$$

Substituting from Eq. (1), it follows that the numerator of the above expression is simply the Boltzmann weight for a regular ferromagnetic nearest neighbor Ising model. The denominator is the product of factors

$$\begin{aligned}
Z_\alpha &\equiv \exp(+\beta\tilde{E}_\alpha) \\
&= \sum_\gamma \exp[-\beta(V_{\alpha\gamma} + E_\gamma)] \\
&= \sum_\gamma \exp\left[\beta J_\parallel \sum_i \sigma_i^{(\alpha)} \sigma_i^{(\gamma)} + \beta J_\perp \sum_{\langle ij \rangle} \sigma_i^{(\gamma)} \sigma_j^{(\gamma)}\right],
\end{aligned} \tag{12}$$

one for each layer. After the summation is performed, \tilde{E}_α introduces additional interactions within layer α . These interactions are in general nonlocal, and involve multiple spins, rendering the problem highly anisotropic, and non-trivial.

We first estimate \tilde{E}_α by a high-temperature expansion. For each Ising bond appearing in Eq. (12), we can write

$$\exp(\beta J \sigma_i \sigma_j) = c(1 + t \sigma_i \sigma_j), \tag{13}$$

where $c = \cosh(\beta J)$ and $t = \tanh(\beta J)$ is the small parameter for the high-temperature expansion. After summing over the spins in layer γ , the surviving contributions to Z_α are represented graphically by paths connecting pairs of spins in layer α . For hypercubic layers of coordination number $2d$,

$$\begin{aligned}
Z_\alpha &= (c_\parallel c_\perp^d)^N \sum_{\{\sigma^{(\gamma)}\}} \prod_i (1 + t_\parallel \sigma_i^{(\alpha)} \sigma_i^{(\gamma)}) \prod_{\langle ij \rangle} (1 + t_\perp \sigma_i^{(\gamma)} \sigma_j^{(\gamma)}) \\
&= (c_\parallel c_\perp^d)^N \left[1 + \sum_{\langle ij \rangle} t_\parallel^2 t_\perp \sigma_i^{(\alpha)} \sigma_j^{(\alpha)} + \dots \right] \\
&\approx (c_\parallel c_\perp^d)^N \exp\left(+ t_\parallel^2 t_\perp \sum_{\langle ij \rangle} \sigma_i^{(\alpha)} \sigma_j^{(\alpha)} + \dots \right).
\end{aligned}$$

After inversion, the leading effect of the denominators is to *reduce* the in-plane couplings to $\beta J_\perp - t_\parallel^2 t_\perp$. At higher orders, antiferromagnetic bonds of strength $t_\parallel^2 t_\perp^s$, for spins at a distance s , and multiple spin interactions are also generated.

A similar high temperature expansion results in the perpendicular and parallel correlation functions for a pair of spins at a distance l within the same plane or column,

$$g_\perp(l) \approx t_\perp^l \left\{ 1 + \frac{l(l+1)}{2} [2(d-1)t_\perp^2 + t_\parallel^2] + \dots \right\}$$

and

$$g_\parallel(l) \approx t_\parallel^l [1 + dl(l+1)t_\perp^2 + \dots].$$

When $J_\parallel \neq J_\perp$, these two correlation functions differ already in the first term, leading to stronger correlations in the direction that has the stronger coupling. When $J_\parallel < J_\perp$, correlation volumes are oblate at high temperatures and must change their shape to prolate when the temperature is decreased and the critical point is approached.

Due to the weakening of the in-plane bonds, the two correlation functions differ even for $J_\parallel = J_\perp$, resulting in a reduced correlation length perpendicular to the growth direction. In fact, such a weakening is precisely what is needed to make the correlations within each layer appear as d dimensional, despite the $(d+1)$ -dimensional connectivity of the

overall system of spins. The anisotropy in correlations is amplified at lower temperatures, and ultimately they diverge with different exponents at the critical point.

At very low temperatures, there are typically few unaligned neighbors, and in a low-temperature expansion, Eq. (12) is evaluated as

$$Z_\alpha \approx \exp\left(N\beta J_\parallel + \beta J_\perp \sum_{\langle ij \rangle} \sigma_i^{(\alpha)} \sigma_j^{(\alpha)}\right). \tag{14}$$

(The spins in layer γ are assumed to be completely aligned to those in layer α in the configuration of lowest energy.) Thus at this order, the effective in-plane couplings are $\beta J_\perp - \beta J_\parallel \approx 0$. The physical meaning of this result is that at low temperatures each new layer essentially repeats the configuration of the previous layer. The boundaries between different domains have very small mobility [of order of $\exp(-\beta J_\parallel)$]. It is this reduced mobility that leads to the unusual critical properties of the $(1+1)$ -dimensional model discussed earlier.

V. CONCLUSIONS

In summary, we have studied a model for thin film growth of $(d+1)$ -dimensional binary alloys that explicitly includes the relaxation and diffusion of the atoms on the top surface. Since there is no further equilibration inside the film, the bulk configuration reflects the time history of fluctuations at the surface. The resulting correlations are highly anisotropic: within each layer, they correspond to the equilibrium on a d -dimensional system, while the behavior parallel to the growth direction reflects the dynamics of a d -dimensional Ising system with no conservation laws. These results are similar to previous (cellular automata inspired) models which include no surface equilibration. This suggests that a wider universality is present: As long as equilibration stops after a finite number of layers from the top surface, the above conclusions should hold. One exception is for $(1+1)$ -dimensional systems, which due to the vanishing mobility of domains at zero temperature, exhibit nonuniversal behavior.

A crucial assumption of the model is that the surface layer has sufficient time to equilibrate, before it is completed and incorporated in the bulk. This requires that any surface equilibration times τ_R should be less than the time for the growth of a layer τ_G . The latter is controlled by the speed of deposition. The former time, however, depends on the actual dynamics at the surface. It is important to emphasize that τ_R has nothing to do with the ‘‘dynamics’’ that determine the correlations in growth direction. If the main equilibration mechanism is diffusion of particles on the surface, τ_R will be quite long, and diverge close to a critical point, where the system performs a continuous phase transition from a chemically disordered state to phase separation. Thus, $\tau_R \propto \xi_\perp^{z_c}$, where $z_c > z$ is the exponent for conservative (model B) dynamics. On the other hand, τ_R can be considerably reduced if the surface particles are allowed to desorb into the gas. By fast mixing of the vapor, it is then possible to achieve a τ_R that is independent of the dynamics at the surface.

If the inequality $\tau_R < \tau_G$ is violated, the most likely scenario is that in-plane equilibrations are frozen at some scale,

resulting in configurations similar to those obtained in a rapid quench. The situation is further complicated in the low-temperature phase. Phase separation during deposition results in the coarsening of domains, as observed in experiments on Al-Ge [14]. Computer simulations of this process generate at low growth speed domains that extend into filaments along the growth direction [14], a result also obtained from analytical calculations [15], and in agreement with our observation in Sec. IV that each new layer essentially repeats the previous layer at low temperatures.

A similar study for systems that have a continuous phase transition from a chemically disordered to an ordered (“antiferromagnetic”) phase has not yet been performed to our knowledge. Since the dynamics for antiferromagnetic ordering do not require long-range transport of particles, large correlated domains can be formed during finite time, given large correlations in the layer below. We therefore expect that a small finite growth velocity does not destroy the phase transition of ordering systems, but only shifts the critical temperature to a lower value.

All considerations so far are based on the assumption that the surface of the film is flat. It is likely that surface roughness and formation of domains will affect each other. It is thus quite interesting to explore the interconnections between roughness and phase transitions in composite film growth. Another complication that exists in recent experiments on growth of Co-Pt alloys [2], is that one of the two components is magnetic. The additional magnetic interactions provide yet another twist to this interesting problem.

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- [1] S. Froyen and A. Zunger, *Phys. Rev. Lett.* **66**, 2132 (1991).
[2] P. W. Rooney, A. L. Shapiro, M. Q. Tran, and F. Hellman, *Phys. Rev. Lett.* **75**, 1843 (1995).
[3] T. R. Welberry and R. Galbraith, *J. Appl. Crystallogr.* **6**, 87 (1973).
[4] I. G. Enting, *J. Phys. C* **10**, 1379 (1977).
[5] K. Kim and E. A. Stern, *Phys. Rev. B* **32**, 1019 (1985).
[6] L. C. Davis and H. Holloway, *Phys. Rev. B* **35**, 2767 (1987).
[7] Y. Bar-Yam, D. Kandel, and E. Domany, *Phys. Rev. B* **41**, 12 869 (1990).
[8] P. W. Rooney and F. Hellman, *Phys. Rev. B* **48**, 3079 (1993).
[9] G. Grinstein, C. Jayaprakash, and Y. He, *Phys. Rev. Lett.* **55**, 2527 (1985).
[10] R. J. Glauber, *J. Math. Phys.* **4**, 294 (1963).
[11] R. Cordery, S. Sarker, and J. Tobochnik, *Phys. Rev. B* **24**, 5402 (1981).
[12] M. Droz, J. Kamphorst Leal Da Silva, and A. Malaspinas, *Phys. Lett. A* **115**, 448 (1986).
[13] M. Droz, J. Kamphorst Leal Da Silva, A. Malaspinas, and A. L. Stella, *J. Phys. A* **20**, L387 (1987).
[14] C. D. Adams, D. J. Srolovitz, and M. Atzmon, *J. Appl. Phys.* **74**, 1707 (1993).
[15] M. Atzmon, D. A. Kessler, and D. J. Srolovitz, *J. Appl. Phys.* **72**, 442 (1992).