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Kinetics of precursor-mediated ordering of two-dimensional domains

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Monte Carlo simulations have been carried out to study the kinetics of precursor-mediated ordering of a lattice gas with nearest- and next-nearest-neighbor repulsive interactions. We find that the growth exponent x is affected strongly by the rate at which a precursor is deexcited into a chemisorbed state. If this rate is high, x is close to the value obtained for conservation of density. If this rate is low, x is close to the value for nonconserved density even though the total number of particles is actually conserved. We conclude that the length of precursor "hops" influences the growth exponent.

When an adsorbed system is quenched below an order-disorder transition temperature, ordered *domains* begin to form. If the ground state is degenerate, the local configurations at the boundaries between domains are not those with the lowest free energy. To reduce the total free energy of the system, the lengths of these boundaries are reduced, and the domain sizes become larger. In Monte Carlo studies of the kinetics of domain growth with lattice-gas models, two types of dynamics have been used widely: Kawasaki dynamics and Glauber dynamics.[1-3] In Kawasaki dynamics, which simulate closed systems, particles migrate from one lattice site to a vacant nearest-neighbor lattice site. Glauber dynamics, which simulate open systems, allow exchange of particles with an external reservoir.

By analogy to static critical phenomena, it has been proposed[4,5] and observed[6-9] that at late stages of growth, when the domain sizes are much larger than all microscopic lengths, the growth law has a power law form $l \sim t^x$, where l is the length scale of the domains. The physics of domain growth is governed by only one length scale: the size of the domains. One of the main goals in the study of kinetics of domain growth is to determine the value of the growth exponent x and to establish the factors that affect its magnitude.

For a square lattice gas that orders into a $c(2\times2)$ structure, the degeneracy is $p=2$, and the growth exponent is $x=\frac{1}{2}$, independent of whether Kawasaki or Glauber dynamics are used.[10-20] The situation, however, is not so clear for $p>2$. This occurs, for example, in the case of a lattice gas with equal repulsive nearest- and next-nearest-neighbor interactions on a square lattice. In this case, a (2×1) structure with $p=4$ occurs when the lattice gas is quenched below the transition temperature. For a fractional coverage of 0.5, this transition temperature is $1/\beta_t\phi=0.525$ (Ref. 21), where ϕ is the lateral interaction strength. Sadiq and Binder[22] have studied this system in detail, showing that $x \sim 0.35$ for Kawasaki dynamics and $x \sim \frac{1}{2}$ for Glauber dynamics. In the case of Kawasaki dynamics, they argued that domain growth is governed by the diffusion of an excess (or deficit) fractional coverage at the domain walls. It was suggested that diffusion of the adsorbed particles from regions of excess to regions of deficit fractional coverage is necessary for domain growth, and that such a mechanism gives rise to $x \sim \frac{1}{3}$.[23] An investigation by Vinals and Gunton[24] of a lattice-gas model for hydrogen chemisorbed on Fe(110) was not able, however, to verify this conjecture.[22] This system has both a (2×1) and a (3×1) phase. The (2×1) phase has degeneracy $p=2$, and the (3×1) phase has degeneracy $p=3$. Although domain walls with excess fractional coverage exist for both phases, it was found that $x=\frac{1}{2}$ for the (2×1) phase, whereas the value of x ranged from ~ 0.14 to ~ 0.25 for the (3×1) phase. Hence, for $p>2$, domain growth is not well understood. Indeed, a recent Monte Carlo study even suggested that the Sadiq-Binder result of $x \sim 0.35$ is due to crossover from zero to the true asymptotic value which is $\frac{1}{2}$.[25]

These dynamical models have not heretofore considered the possibility of a precursor state. In many real systems, however, precursor states are important intermediates for surface diffusion,[26] adsorption, and surface reactions.[27,28] The preexponential factor for diffusion D_0 of hydrogen adatoms on the Pt(111) surface has been found experimentally[26] to be 1.0 $\mathrm{cm}^2\,\mathrm{s}^{-1}$ (at a fractional coverage of 0.24). If we take the lattice constant λ to be 3.0 Å and the vibrational frequency parallel to the surface ν to be $10^{13}\ \mathrm{s}^{-1}$, then the value of the preexponential for a random walk between sites is $D_0=\lambda^2\nu/4=2.25\times10^{-3}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$. The high experimental value is strong evidence for the existence of a stable precursor particle that executes many "hops" before it is deexcited into a chemisorption state. Therefore, we have investigated a lattice-gas model with both a strongly bound chemisorption state and a weakly bound, mobile precursor state. We consider a square lattice gas with identical and repulsive nearest- and next-nearest-neighbor interactions in order to compare with previous results that did not include a precursor state.[22] Here two possible adsorption states exist at each site on the lattice, a strongly bound chemisorption state and a weakly bound precursor state. A particle in the chemisorbed state can only be excited into the precursor state at the same site. On the other hand, a particle in the precursor state can experience one of the four following fates: (1) it can be deexcited into the chemisorbed state at the same site (if there is not another particle chemisorbed there already); (2) it can desorb from the lattice (if the system is open); (3) it can migrate into the precursor state of a nearest-neighbor site; or (4) it can remain in the precursor state at the same site. We allow adsorption from the gas phase into the precursor state at any site when an open system is being modeled.

There are five microscopic processes, the rates of which we have to consider: excitation, deexcitation, migration, desorption, and adsorption. The excitation-deexcitation potential is modeled by two intersecting parabolae, as illustrated in Fig. 1, where

$$E_1 = k_1\zeta^2/2+\alpha_1$$

and

$$E_2 = k_2(\zeta-\zeta_0)^2/2+\alpha_2 \ ,$$

and the variable ζ is the excitation coordinate with origin at the equilibrium position of the chemisorbed particle. The model parameters are k_1 k_2, α_1, α_2, and ζ_0. The zero of energy is the bottom of the chemisorption well of an isolated particle. The bottom of the precursor well is α_2, and the bottom of the chemisorption well is given by $\alpha_1 = \phi_{\text{NN}} N_{\text{NN}} + \phi_{\text{NNN}} N_{\text{NNN}}$, where the subscripts indicate nearest- and next-nearest-neighbor sites, N is the number of occupied sites, and ϕ is the strength of the lateral interaction. The top of the barrier is the point of intersection of the two parabolae. The barrier heights for excitation E_{exc} and deexcitation E_{dex} are therefore functions of the local configuration of chemisorbed particles. We investigate only cases where the precursor density is vanishingly small and hence need not consider the interaction between precursor particles. We assume there is no interaction between a chemisorbed particle and a precursor particle.[28] Thus, α_2 is independent of the local configuration of adsorbed particles. The migration and desorption barriers of the precursor, E_{mig} and E_{des}, are also assumed to be constants, independent of the local configuration.[28] If we take the "attempt frequency" to be τ^{-1} for each of the microscopic processes, the probabilities of success in each attempt is the appropriate Boltzmann factor. The probability of adsorption p_{ads} is assumed to be constant and is chosen according to the value of the probability of desorption and the constraint of constant average fractional coverage.

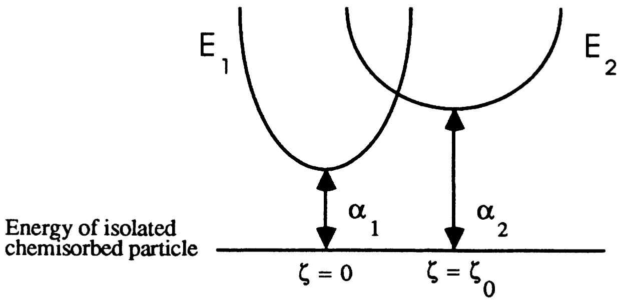

FIG. 1. Model for excitation-deexcitation potential.

The method we use differs from those used by previous investigators in two ways. First, the probability of success of a microscopic event is calculated using the *proper energy barrier* which has to be surmounted to go from the initial state to the final state. This is in contrast to Kawasaki and Glauber dynamics where the probability of success of an event is calculated using the *difference in energy of the initial and final states.* It can be shown that the Kawasaki probability is in general not equivalent to the probability calculated using the proper energy barrier, and hence *Kawasaki dynamics do not correctly* describe the kinetics of barrier crossing.[29]

Second, the probabilities of success of the various microscopic processes vary over many orders of magnitude. To carry out the simulation, we divide the microscopic processes into a "fast" group and a "slow" group. The "fast" group consists of processes that a precursor particle undergoes, i.e., deexcitation into a chemisorption state, migration to a nearest-neighbor precursor state, and, in the case of open systems, desorption into the external reservoir. The choice of which event in the slow group to pick during the simulation is made similarly to the "n-fold" way.[30] We group the slow excitation and adsorption events into classes i, each corresponding to a probability p_i of a successful attempt, and m_i is the number of potential events in each class i. For instance, if there were a total of n_i chemisorbed particles with a particular environment such that the probability of successful excitation were p_i, then $m_i = n_i$. An event in class i is chosen with relative probability $R_i = m_i p_i / \sum_i m_i p_i$. Having chosen an event in class i, the time is increased by $6\tau/p_i$. The factor of 6 is due to the assumption of equipartition of energy, i.e., the heat bath excites a chemisorbed particle with equal probability in six directions, and only one of these can produce a precursor particle. Once a precursor particle is produced, it can either migrate, deexcite, desorb, or remain where it is. Again, the attempt frequency in each of the six directions is the same, and the time increment for each attempt is τ. The time is incremented by τ even if the precursor remains in its original location. The unitarity condition is

$$(p_{\text{dex}}+p_{\text{des}}+4p_{\text{mig}}+p_0)/6=1 \ ,$$

where p_{dex} is the conditional probability for successful deexcitation given that the precursor is excited towards the surface, and p_{des} is the conditional probability for successful desorption given that the precursor is excited away from the surface. Similarly, p_{mig} is the conditional probability for successful migration in one of the four possible directions for migration, given that the precursor is excited in that direction. p_0 is the sum of the six conditional probabilities of failure. When the precursor either

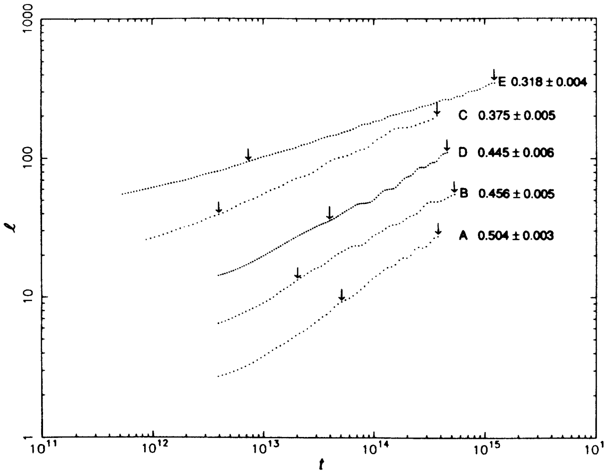

FIG. 2. $l(t)$ for each set has been multiplied by an offset factor, f for clarity. f is 1, 2, 8, 4, 16 for sets A, B, C, D, E, respectively. For sets A, B, and C, $k_1\zeta_0^2/\phi=20$, and $k_2\zeta_0^2/\phi=10$. For set D, $k_1\zeta_0^2/\phi=40$, and $k_2\zeta_0^2/\phi=10$. For set E, $k_1\zeta_0^2/\phi=20$, and $k_2\zeta_0^2/\phi=1$.

deexcites or desorbs, we go to the slow events again and either excite or adsorb another particle into the precursor state.

The values of the parameters used are summarized in the caption for Fig. 2. Table I shows the probabilities of successful excitation of the chemisorbed particle and deexcitation of the precursor particle for the extreme cases of zero and eight repulsive interactions. We used the same temperature as Sadiq and Binder,[22] $1/\beta\phi=0.3325$; and we constrained α_2/ϕ to be equal to 10. If we assume a value of 1.5 kcal/mole for the lateral repulsion, then the system has a temperature of 251 K, and the excitation energy of an isolated chemisorbed particle is 15.0 kcal/mole. The probability of successful desorption is set equal to 0.3 for simulations in set A and 0.06 for simulations in set B. The value of p_{ads} is 4.32×10^{-9} for set A and 8.64×10^{-10} for set B. Sets C, D, and E are closed systems. Each of the sets of parameters shown in Table I utilized 20 runs each with a lattice size of 100×100 and five runs each with a lattice size of 120×120. We did not detect any finite-size effects although this could be due to the similarity in size of the lattices. The domain sizes were calculated by evaluating the area of each individual domain and taking the average. The length scale as a function of time $l(t)$ was then obtained by taking the square root of the average area, and we did not let $l(t)$ exceed $\sim L/3$. Since our lattice sizes are only 100×100 and 120×120, there is a possibility of our not having reached the asymptotic regime. However, our domain sizes are comparable to those attained in[22] which we take as a benchmark. Initial random configurations with a fractional coverage of 0.5, and periodic boundary conditions were used. The growth exponents are shown in Fig. 2. These were obtained by least-squares fitting of all the data points between the arrows. If $1/\tau\sim10^{13}\,\text{s}^{-1}$, this corresponds to domain growth at $0.5<t<200$ s.

TABLE I. Probabilities of success for excitation and deexcitation of an isolated particle and a particle with eight nearest- and next-nearest neighbor repulsive interactions.

Set	α_1/ϕ	p_{exc}	p_{dex}
A,B,C	0	$8.679\,8448\times10^{-14}$	1.000 0000
	8	$1.149\,4297\times10^{-4}$	0.047 0738
D	0	$2.687\,0601\times10^{-14}$	0.309 5745
	8	$1.745\,2212\times10^{-5}$	0.007 1473
E	0	$8.679\,8448\times10^{-14}$	1.000 0000
	8	$1.582\,7465\times10^{-3}$	0.648 1999

In Kawasaki dynamics, a particle that hops successfully then occupies one of the nearest neighbor sites to the original site. In Glauber dynamics, a particle that desorbs from the lattice has a uniform probability of *attempting* to readsorb on each site of the lattice, thus allowing a more efficient search for domain configurations of lowest free energy. In the precursor-mediated ordering described here, a chemisorbed particle is first excited into the precursor state, after which it may either deexcite into its original site, migrate to a neighboring site, or (in the case of an open system) desorb. In the limit of *strong coupling* of the precursor to the lattice, the distribution of sites into which it attempts to deexcite will be peaked sharply at its original site. In this case, the search for the lowest free-energy configurations is even less efficient than with Kawasaki dynamics (where the distribution of sites is composed of δ functions at the nearest-neighbor sites). In the opposite limit of *weak coupling* of the precursor to the lattice where the probability of deexcitation is low, the distribution of sites into which the precursor attempts to deexcite will be more uniform over the lattice. When $p_{\text{mig}}\gg p_{\text{dex}}$, the precursor particle can be excited or deexcited into a site on the lattice at any distance from its original chemisorption site. There is no constraint for deexcitation (readsorption) into the nearest-neighbor site. Thus, the range for particle "hops" becomes similar to what it is when using Glauber dynamics, although the total density is still conserved.

This discussion can be quantified by considering the results for sets C, D, and E of Table I which are closed systems. The growth exponent obtained for this system by Sadiq and Binder[22] using Kawasaki dynamics is ~0.35. In set E, p_{dex} is high (cf. Table I) and x *is less than the value obtained using Kawasaki dynamics.* This is the case in the experimentally obtained growth exponent of 0.28 ± 0.05 for O on W(110) which orders into (2×1) domains and may have a degeneracy of $p=4$.[31] More stable precursors in sets C and D (cf. Table I) increase the growth exponent to *values higher than expected for a closed system described by Kawasaki dynamics.* Sets A and B of Table I simulate open systems in which all parameters except for the probabilities of adsorption and desorption are the same [and also equal to those of the closed system of set C (cf. Table I)]. The contribution of particle exchange via adsorption and desorption is greater in set A and $x\sim0.5$. With a lower rate of desorption and adsorption, set B has a growth exponent that is smaller than that expected for open systems (cf. set A) but greater than that of an otherwise identical closed system (cf. set C).

To summarize, we have presented a description of precursor-mediated ordering at surfaces, a situation that is expected to obtain in "real" systems.[26–29] Hence, experimental values of the growth exponent can be used as a qualitative assessment of the stability of the precursor state. For systems in which both surface migration and particle exchange via desorption and adsorption occur, the experimental growth exponent can be used to gauge the relative rates of these processes.

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