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Diffusive disordering kinetics in one dimension

M. C. Tringides,[a,b]* J. H. Luscombe,[b]† and M. G. Lagally[a]
[a]*University of Wisconsin, Madison, Wisconsin 53706*
[b]*Ames Laboratory, Iowa State University, Ames, Iowa 50011*
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The growth laws that characterize the nonequilibrium kinetics of one-dimensional models with conserved dynamics as they are quenched from a low to a high temperature are examined. Exact results are obtained for the antiferromagnetic Ising model at infinite final temperature. Finite final temperature quenches and models with two competing interactions are studied with Monte Carlo simulations. In all cases, exponential decay of the peak intensity and invariance of the full width at half maximum of the structure factor $S(q,t)$ is found, contrary to results applicable to similar processes in two dimensions. A possible experimental realization of the above models is the disordering of the Si(100)-$2\times n$ metastable state.

I. INTRODUCTION

The time evolution of systems that are far from thermodynamic equilibrium is a fundamental problem in nonequilibrium statistical mechanics, as well as being of practical importance in a variety of materials processing applications.[1] In recent years there has been intense interest[1,2] in the kinetics of domain growth in systems quenched from a high-temperature disordered phase to a point inside a coexistence region. Of particular interest is that, in analogy with critical phenomena, the kinetics of such growth processes appear to be governed by a few universal parameters that are independent of the specific details of the system. There are two key quantities entering a universal description of growth kinetics. The first is a time-dependent length, $L(t) \gg \xi$, characteristic of the growing domains and larger than the correlation length of equilibrium fluctuations, ξ. It is generally observed that growth occurs with a power-law time dependence,[3]

$$L(t) \propto t^a, \quad (t > t_0), \tag{1}$$

where t_0 is an initial time that is system dependent and where the exponent specifies a growth class. Second, it is generally found that the fundamental experimental probe of strongly nonequilibrium systems, the elastic-scattering structure factor, $S(q,t)$, can be scaled with a single length parameter such that

$$S(q,t) = L^d(t) F(q/K), \quad (t > t_0), \tag{2}$$

where d is the dimensionality of the system, F is a universal scaling function independent of time, and K is the full width at half maximum (FWHM). $S(q,t)$ is defined in Eq. (8). Equation (2) implies self-similar growth: there is a distribution of domain sizes that remains invariant in units of $L(t)$. In this regime, the evolution of the system is controlled by the motions of domain walls; efforts to understand the growth exponent and scaling function have therefore concentrated on the mechanisms that drive interfacial motions. Domain growth kinetics is thus characterized by (1) power-law growth of the average domain size and (2) scaling of $S(q,t)$.

In this paper we consider the disordering of a system after a rapid increase in temperature, such that the system equilibrates in a disordered phase at the new temperature. In particular, owing to a possible connection with experiment (see below), we are interested in the disordering kinetics of a one-dimensional system in which the number of disordering entities is conserved in time. We study a lattice-gas system initially in equilibrium at temperature $T = T_I$, both for the case of nearest-neighbor (repulsive) interactions but also for the case where competing interactions stabilize various superstructures. The temperature is then instantaneously set to a new value, $T = T_F > T_I$, at which point the system has a degree of order inconsistent with what could be maintained at T_F. We compute the evolution of the structure factor between the initial and final states for the case of Kawasaki[4] stochastic particle-hole exchange dynamics, first in an exact analytic calculation for $T_F = \infty$ (random hopping), and then with Monte Carlo (MC) methods for $T_F < \infty$.

Our main results are as follows. Irrespective of the initial state, we find (1) an exponential decay of the Bragg peak associated with the initial superstructure and (2) a constant width of the structure factor as the peak decays exponentially. Hence, for the one-dimensional problem considered here there is no scaling of $S(q,t)$ for disordering kinetics. Our results indicate that disordering occurs randomly, i.e., without correlations among the motions of the disordering atoms. We attribute the lack of scaling to the well-known fact that in one dimension a system with short-range interactions cannot maintain long-range order for any temperature. Thus, the correlated regions associated with the initial state will not shrink in an organized manner, but will instead be randomly disrupted due to thermal agitations.

These results for $S(q,t)$ have also been observed experimentally in the disordering kinetics of the Si(100)-($2\times$n) ordered-defect state.[5] This is a system prepared by quenching the Si crystal from $T = 1200\,^\circ\mathrm{C}$ at a rate of $200\,^\circ\mathrm{C}$/sec. It is well known that the Si(100) surface atoms dimerize to minimize the energy of the free Si bonds. However, depending on preparation, there is also an abundance of dimer vacancies in the reconstructed surface. It has been observed[5] that following the quench, the vacancies order in the direction orthogonal to the dimerization direction, with every n spacings a missing dimer, where typically $6<n<10$. This ordered-defect superlattice, however, is not the equilibrium defect configuration and is metastable. There is evidence[5] that the density of vacancies remains constant as they disorder. The disordering presumably occurs diffusively, with the dimer vacancies interchanging with dimers. We will present arguments that the disordering of this system is also one dimensional.

The organization of the paper is as follows. In the next section we present the analytic solution for $S(q,t)$ when $T_F=\infty$ and the initial state is governed by near-neighbor interactions. In Sec. III we present Monte Carlo results for simulations involving competing interactions and for finite final temperatures. In Sec. IV we discuss our results and the connection with the Si(100)-(2×n) system.

II. EXACT SOLUTION FOR $T_F=\infty$

In this section we outline an analytic solution of the nonequilibrium structure factor for a one-dimensional system driven by random nearest-neighbor hopping. We consider a lattice-gas system initially in equilibrium, governed by the nearest-neighbor Hamiltonian

$$H[c]=-V\sum_i c_i-J\sum_i c_i c_{i+1}\ , \tag{3}$$

where $c_i=0,1$ are occupation variables, V is the adsorption energy per site, and J is the adatom interaction energy. We are interested in the case of repulsive interactions, $J<0$. The equilibrium probability distribution is given by

$$P[c]=Z^{-1}\exp\{-\beta(H[c]-\mu N)\}\ , \tag{4}$$

where $\beta=(k_B T)^{-1}$, Z is the partition function, and μ is the chemical potential. We choose $\mu=V+J$ such that the coverage $\Theta=\langle c_i\rangle=\frac{1}{2}$, where the angular brackets here denote an average with respect to $P[c]$. The system therefore has particle-hole symmetry and is equivalent to the Ising model in zero magnetic field. Exchange dynamics is governed through detailed balance by the difference in energy environments that would result from an interchange of nearest neighbors[4] and therefore is not influenced by a uniform distribution of single-site energies. Dynamically, then, we are unconcerned with the one-body terms in Eq. (3). The particular choice of half coverage is merely to facilitate the calculation.

We define the equilibrium structure factor at a momentum q as

$$\chi_q=\sum_n e^{inqa}\langle\delta c_0\delta c_n\rangle\ , \tag{5}$$

where $\delta c_i=c_i-\langle c_i\rangle$ and a is the lattice constant. The structure factor χ_q is related to the angular profile of a diffracted beam in a diffraction experiment from an ordered overlayer, at a momentum transfer q by

$$I_q=\chi_q+\delta(q)/4\ , \tag{6}$$

where $\delta(q)$ is a δ function. In one dimension χ_q can be evaluated exactly. At $\Theta=\frac{1}{2}$ it is given by

$$\chi_q=\frac{1-u^2}{4[1-2u\cos(qa)+u^2]}\ , \tag{7}$$

where $u\equiv\tanh(\beta J/4)$. Thus, for $J<0$ and $T\to 0$, χ_q develops a strong peak at the boundary of the Brillouin zone, $qa=\pi$, which corresponds to the antiferromagnetic structure shown in Fig. 1(a). The δ-function term in (6) has no contribution. For $T=\infty$, $\chi_q=\Theta(1-\Theta)=\frac{1}{4}$ and the system is structureless. We are interested in the evolution of the structure factor between these two extremes at constant coverage.

The elastic-scattering structure factor for the nonequilibrium system is the generalization of Eq. (5),

$$S(q,t)=\sum_n e^{inqa}\langle\delta c_0\delta c_n\rangle_t\ , \tag{8}$$

where the subscript t denotes a nonequilibrium average. We note here that $S(q,t)$ satisfies a sum rule such that the angular profile integrated over all directions is independent of time. The initial condition is given by $S(q,0)=\chi_q(T=T_I)$. We assume that in the absence of interactions, i.e., $T_F=\infty$, particles obey a simple near-neighbor random hopping dynamics

$$\frac{dc_i}{dt}=-\alpha(2c_i-c_{i+1}-c_{i-1})\ , \tag{9}$$

where α is the diffusion coefficient and is taken as a parameter of the model. Note that hopping is prevented when neighboring sites have the same occupation. Equation (9) conserves the coverage, as can be seen by summing over all lattice sites. It is then straightforward to show, utilizing an equation of motion (presented elsewhere[6(a)]) for the product $c_i c_j$ analogous to Eq. (9),

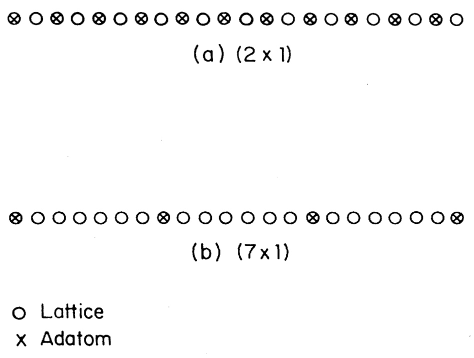

FIG. 1. (a) Low-temperature antiferromagnetic (2×1) state. ○ denotes lattice sites and × denotes adatoms. (b) 7×1 low-temperature state: ○ denotes lattice sites and × adatoms. For the Si(100)-2×n ordered state, the chain corresponds to a row normal to the dimerization direction, with ○ corresponding to dimers and × missing ones.

that for $T_F=\infty$ and $\Theta=\frac{1}{2}$,

$$S(q,t)=\tfrac{1}{4}+(\chi_q-\tfrac{1}{4})e^{-2\lambda_q t}-2\lambda_q\int_0^t dt' e^{-2\lambda_q(t-t')}\epsilon(t')\ , \tag{10}$$

where

$$\lambda_q=4\alpha\sin^2(qa/2)\ , \tag{11a}$$

$$\epsilon(t)\equiv\langle\delta c_0\delta c_1\rangle_t\ , \tag{11b}$$

and where χ_q is evaluated at the initial temperature. $\epsilon(t)$ is the nonequilibrium near-neighbor correlation function, which is seen to act as a "source" for the evolution of $S(q,t)$ via near-neighbor exchange dynamics.

We omit the specifics of solving for $\epsilon(t)$ in Eq. (10) and for evaluating the integral, for which an exact solution can be obtained.[6(a)] The dominant role of the integral in Eq. (10) is in governing the long-time decay of $S(q,t)$ and also in guaranteeing that the sum rule is obeyed for all times. Utilizing our solution for $S(q,t)$, we show in Fig. 2 a semilog plot of the relaxation of the Bragg peak, $S(\pi/a,t)$ for initial temperature, $K_BT_I=-J/8$ and $T_F=\infty$. The initial decay is exponential in accord with Eq. (10). The exponential decay persists for longer times the smaller the initial temperature. At very long times, there is a crossover to a power-law decay $t^{-d/2}$, where d is the dimensionality of the system. This long-time decay could have been a definite signature of the dimensionality of a physical process. Unfortunately, the intensity at the crossover point is less than 1% of its peak value and therefore too small to be detected experimentally or even to be seen in the simulations. In Fig. 3 we present $S(q,t)$ for $k_BT_I=-J/8$ for the portion of the Brillouin zone $qa=0.95\pi$ to $qa=\pi$ for several times. It is seen that for $0<\alpha t<0.2$ (which, from Fig. 2, is well within the exponential regime), $S(q,t)$ decays while preserving its shape: The FWHM at zero time is essentially that for the subsequent times shown. As can be seen from Eq. (10), each wave-vector component of $S(q,t)$ relaxes with its own relaxation rate. In the initial state considered here, the peak intensity is associated with a relatively narrow range of wave vectors, and thus the peak decays while preserving its shape. There is a slight broadening in the width at late times to satisfy the sum rule as the peak intensity is eventually redistributed to all wave vectors.

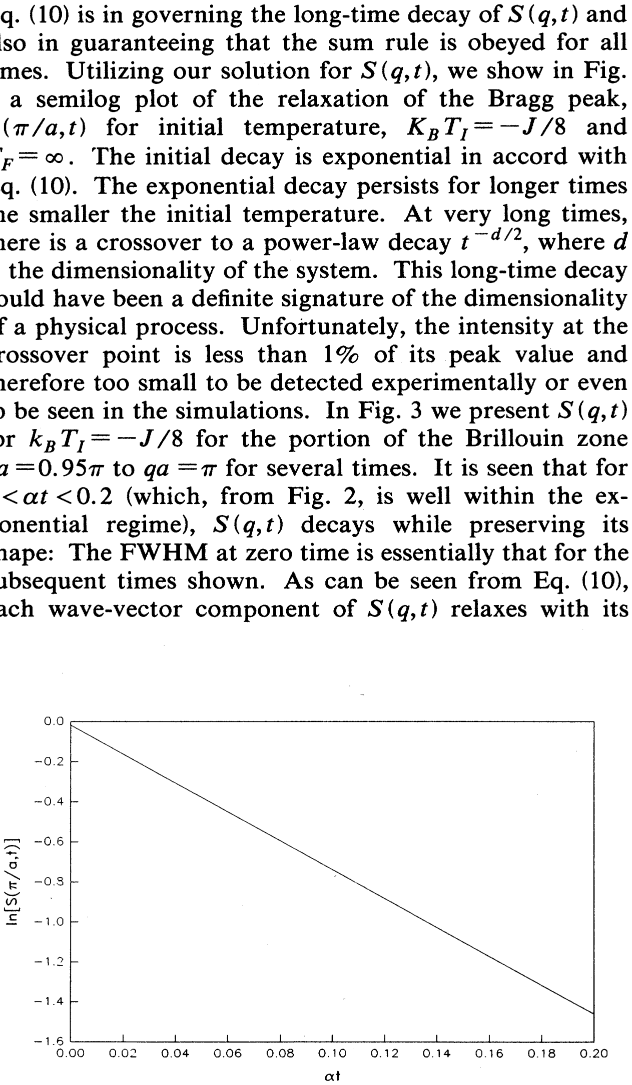

FIG. 2. Semilog plot of the decay of the peak intensity $S(\pi/a,t)$ vs time for the antiferromagnetic Ising model with initial temperature $J/K_BT_i=-8$ and infinite final temperature $J/K_BT_f=0$. The result is from an exact solution. The decay obeys first-order kinetics.

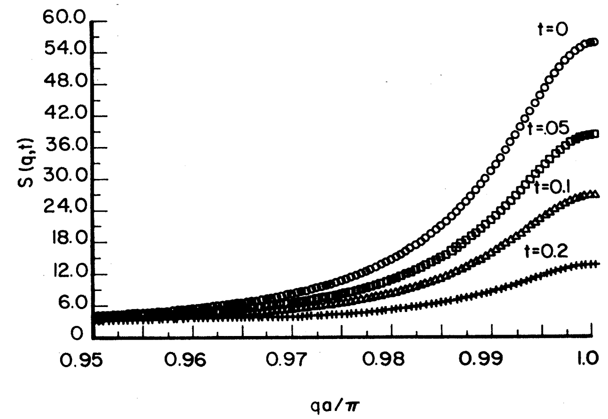

FIG. 3. The structure factor $S(q,t)$ calculated exactly for the one-dimensional antiferromagnetic Ising model with infinite final temperature. The full width at half maximum (FWHM) is invariant with time, implying the absence of scaling. Similar results are obtained with the Monte Carlo studies.

III. MONTE CARLO SIMULATIONS

In this section we examine the decay of $S(q,t)$ for the system prepared in an ordered state and for a finite final temperature. We use simulations because analytic results are not possible. The system was prepared in two initial conditions, in the antiferromagnetic state to compare with our previous analytic result and in the (1×7) state shown in Fig. 1(b), which is representative of the disordering kinetics experiment on Si(100). We emphasize that our model system is one dimensional, but as we will argue later, it is related to the disordering of the Si(100)-$(2\times n)$ ordered defect state, where $n=6,7,8$, or 9 depending on preparation. The $(2\times n)$ state consists of dimer vacancies aligned every "n" spacings. Evidence will be presented below that these ordered defects disorder one dimensionally. For the purposes of the simulation, the $(2\times n)$ phase is denoted as $(1\times n)$. The occupants c_i in our model represent not the actual atoms or dimers but the missing dimers. We run the simulation at $n=7$ but similar results are expected for other values of n.

The (1×7) structure requires competing further-neighbor interactions for stabilization. Thus, we consider a more general Hamiltonian than that of Eq. (3):

$$H[c]=-V\sum_i c_i-J_{n,n}\sum_{\langle n,n\rangle}c_ic_j-J_{n,d}\sum_{\langle n,d\rangle}c_ic_j\ , \tag{12}$$

where the second term refers to a sum over nearest-neighbor interactions as in Eq. (3), and where there is as well a sum over d-neighbor interactions. For the antiferromagnetic Ising model $J_{n,d}=0$. For the (1×7) state we assume $J_{n,7}=-J_{n,n}/4$, as is suggested from experiment (see below), with $J_{n,n}$ repulsive.

We simulate the disordering kinetics utilizing a standard MC algorithm.[6(b)] At $t=0$ the system is prepared in a perfectly ordered state corresponding to zero temperature. The exact number of missing dimers is difficult to quantify experimentally. As the simplest approximation, we have taken a perfect (1×7) structure. Similar results are obtained, however, if an excess of dimer vacancies is assumed as long as this excess is less than 20% of the ones in ordered sites. Kawasaki dynamics of exchanging a particle with a hole were followed with the Monte Carlo algorithm.

We monitor the evolution of $S(q,t)$, which is evaluated at discrete points in reciprocal space, $q_n=2\pi n/N$, imposed by periodic boundary conditions, where N is the size of the lattice. We have calculated $S(q,t)$ about the Bragg wave vector $q_B=2\pi/7$ for the (1×7) structure. The MC routine was repeated M times to collect the necessary statistics. M was varied between 100 and 200 without appreciable change in the results. Also, the size of the system N was varied between 100 and 500 to check for finite-size effects. No differences were observed. Similar results were obtained for both initial structures. Figure 4 shows the decay of the Bragg peak for the (1×7) initial state at two final structures. The decay is described by an exponential for at least 1 order of magnitude drop in intensity. Eventually the decay levels off as the configuration of scatterers becomes random. Finite-temperature runs were made with various sets of interactions; again the results are similar for the antiferromagnetic and (1×7) initial states. For the (1×7) arrangement, $J_{n,n}$ was chosen always repulsive and stronger than the d'th-neighbor interaction to model the Si(100)-$(2\times n)$ phase. The strength of these interactions is not known but their ratio is suggested by electronic calculations,[7] and their magnitude can be estimated from the disordering temperatures. In Fig. 4, $(\times)$ shows the result at $T_F=\infty$ and (o) show the results for $J_{n,n}/kT=-4J_{n,d}/kT$ with the negative sign denoting repulsion.

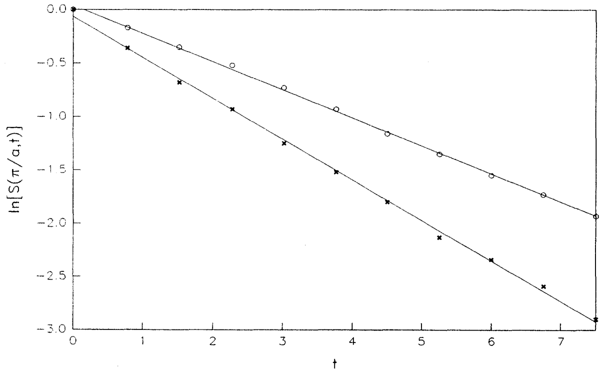

FIG. 4. Semilog plot of the decay of the peak intensity $S(2\pi/7a,t)$ vs time for the one-dimensional model that has a perfect (7×1) initial state and (i) infinite-temperature final state $(\times)$; (ii) $J_{n,n}/KT_f=-2=-4J_{n,d}/KT_f$ final temperature (○). The decay obeys first-order kinetics. Results are from Monte Carlo simulations.

Because the initial configuration is always perfectly ordered, $S(q,t)$ is a δ function broadened only by the finite size of the system. No change in the FWHM is observed for the whole range of the intensity drop when there is nearest-neighbor interaction. When d-neighbor interactions are included $(d>6)$, only after the intensity has dropped by a factor of 10 does the structure factor start to broaden. Similar behavior is seen for various finite sizes suggesting that the finite size of the system is not important.

The exponential decay of Bragg peaks in the disordering of one-dimensional systems without change in width can be seen essentially as a nonequilibrium analog of the Debye-Waller factor. For a system in equilibrium the effect of lattice vibrations is to diminish elastic scattering with an overall (wave-vector-independent) attenuation that is exponential with increasing temperature, a consequence of thermal displacements about lattice sites being uncorrelated. It is therefore as though, upon letting $T_I\rightarrow T_F$, we have taken our system in time through a series of equilibrium states of increasing temperature. We have, of course, obtained the system's nonequilibrium response to a large and discontinuous change in temperature. However, the reason we can make this analogy is that the system is one dimensional: The system remains "disordered" for all temperatures and hence, the motions of the disordering particles are uncorrelated. It is known that thermal fluctuations are always sufficiently strong compared to interparticle interactions that the initial domains are randomly disrupted, without regard to their structure, i.e., without a progressive inward shrinkage from the boundaries that would presumably result in a scaling of $S(q,t)$ for disordering. In contrast, we note that in two dimensions for an initial state in an ordered phase with long-range order, disordering evolution occurs at domains boundaries and hence, is correlated. In this latter case, then, one would not expect "Debye-Waller" behavior of the structure factor, and scaling of $S(q,t)$ is observed. Because the two main results of the disordering, i.e., the exponential decay of the peak and the invariance of the FWHM, are also present in the Debye-Waller effect, it is interesting to ask if they are related. For the latter, the FWHM does not change because all the wave vectors are losing intensity at the same rate. The initial one-dimensional ordered state disorders also by uncorrelated displacements of the scatterers. It is a first-order process because the decay rate is proportional to the number of scatterers still present in ordered domains, which leads to exponential decay of the peak intensity. The random displacement of scatterers will very quickly create many monomers, because motion is uncorrelated, and intensity will be moved away from the peak of the structure factor to the "wings." All the wave vectors around the peak are losing intensity at the same rate because the disordering of scatterers is independent of the domain size. The FWHM, therefore, will not change.

IV. DISORDERING OF Si(100)-$(1\times n)$ PHASES

Both an exponential intensity decay and a constant FWHM during the decay have been observed experimentally[5] in the disordering kinetics of the Si(100)-$(2\times n)$ ordered-defect state, as described in the introduction. Figure 5 shows the decay at three different temperatures of the intensity of the satellite peak corresponding to the (2×7) ordered state. All three curves can be fitted very well with an exponential decay. The initial intensity is smaller at the higher temperature because of the true Debye-Waller effect. Figure 6 shows the satellite Bragg peak at early times superimposed on one obtained later, after normalizing the peaks. It is clear that there is no change in the FWHM of the peak.

Because, in principle, this is a two-dimensional system, both of these results are incompatible with the expected power-law "growth" (decay) and scaling of the structure factor. As mentioned in the Introduction, power-law growth and scaling have been observed[8,9] in several experimental and many model system studies[2] for quenches from disordered to ordered states. It would be expected also for the disordering kinetics from an initial ordered state, unless the final temperature is higher than the transition temperature that destroys the effect of correlations. Although we do not have a phase diagram for the Si(100) surface, it is rather likely that the disordering temperatures ($T=600-700$ K) of the $(2\times n)$ phases are not large compared to the interaction energies governing the kinetics, and so correlations are still present. It would be very difficult to determine a phase diagram for such a surface because many ordered states are known to exist,[10] depending on the preparation method. It is also difficult to determine the phase diagram theoretically because electronic calculations[10] of the minimum-energy configuration give states that are very close to each other, so it is difficult to distinguish the true minimum. The $(2\times n)$ structure is not a true low-temperature equilibrium ordered state but a metastable one locked in by the rapid quench.[5,11] We believe, however, that the nonequilibrium behavior of a true equilibrium state is also applicable to metastable states. The disordering is between the $(2\times n)$ phase and the (2×1) phase with randomly positioned dimer vacancies, which is the equilibrium state. If this disordering were a two-dimensional process it would have high degeneracy $p=n$, because n equivalent sublattices can support the ordered configurations. This would lead to a power-law dependence for the average domain size of the $(2\times n)$ phase, with growth (decay) exponent less than $\frac{1}{2}$ and scaling of the structure factor.

Experimentally, an intensity decay consistent with 1D ordering is observed. The anisotropy of the Si(100) surface that leads to the $(2\times n)$ structure in the first place suggests that the disordering might be one dimensional. The ordered state is made out of missing dimers every "n" spacings, orthogonal to the dimerization direction. Domains with $(2\times n)$ structure are of the order of 100 ordered dimers or more in diameter. It is likely that the motion of the dimer vacancies during the disordering is restricted to the dimer rows on which they are initially located, so effectively each row behaves independently as a one-dimensional system. Some degree of diffusion between rows can be allowed; if it is much less than the diffusion along each row, it will not affect the one dimensionality of the process. Both an exponential decay of the peak intensity and an invariance of the FWHM will then

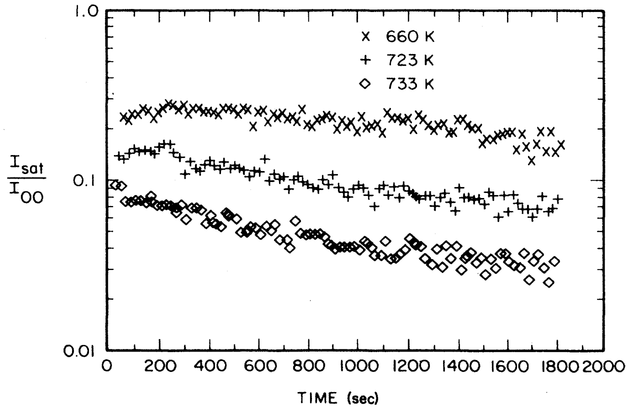

FIG. 5. Decay of the peak intensity of the satellite peak that corresponds to the Si(100)-(2×7) phase at three different temperatures. The decay obeys first-order kinetics.

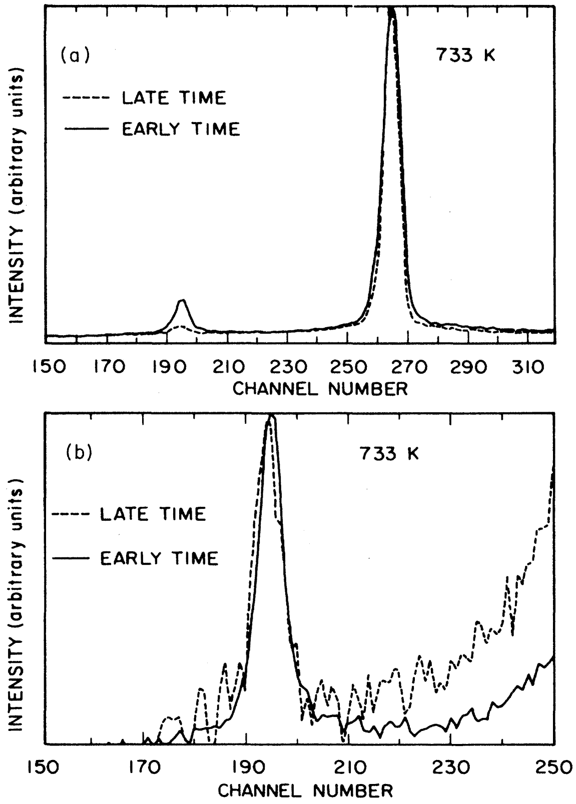

FIG. 6. Comparison of the shape of the satellite peaks of the Si(100)-(2×7) ordered state at early and late times after the peak heights have been normalized. The FWHM is constant.

be observed, as our model calculations have indicated.

Is there any other information supporting the above interpretation in terms of one-dimensional disordering? Calculations[7] on the energies of the electronic configurations have shown that there is strong repulsion between two nearest-neighbor defects (i.e., dimer vacancies) along the dimer rows. This strong repulsion forces the vacancies to be as widely separated along the rows as possible. A weak attractive interaction between dimer vacancies at the "n"-neighbor position will stabilize the $(2\times n)$ phase. In choosing the pairwise interactions in the Monte Carlo simulation $J_{n,n}=-4J_{n,7}$ we were motivated by these considerations. These interactions imply that once the system starts disordering, it is more favorable for a defect to continue diffusing within its row than to an adjacent one; otherwise it will become a nearest neighbor of another defect. The strong repulsion between neighboring defects prohibits this. The one-dimensional character of the disordering process is therefore suggested by the highly anisotropic interactions between defects. The system, of course, is two dimensional, and the anisotropy of the interactions is expected to be less important at higher temperatures. As stated before, however, the disordering temperatures (600–700 K) are smaller than typical interaction energies in semiconductors, so correlations between defects are expected to persist and the anisotropy to be important.

It has been suggested[12] recently and subsequently corroborated[13] that the formation of the Si(100)-$2\times n$ phase is a result of the presence of small amounts of Ni impurities on the surface (the Ni Auger peak is between 0.3%–0.8% of the Si peak). The experiments suggest that the $(2\times n)$ is not formed if the Ni level is below the lower of the above values.

The formation of the $(2\times n)$ phase is correlated to the amount of Ni present as seen by AES. At high temperatures, no Ni is observable with AES. If the sample is slowly cooled, again no Ni is observed at low temperatures. If the sample is quenched, Ni is observed, its concentration depends on the quench rate (a faster rate gives a higher "surface" concentration), and the value of n in the $(2\times n)$ phase appears to be correlated with the Ni concentration (a higher concentration leading to lower n).[12] It is difficult to see how this situation can come about with generally accepted concepts of solubility and cooling curves. Nevertheless, if one accepts that Ni, by whatever means, stabilizes the $(2\times n)$ structure, then one may ask if the observed disordering behavior can be ascribed to the behavior of Ni.

One can construct a scenario in which Ni is the cause of the disordering behavior. In order to observe exponential decay of the intensity of the "n" Bragg peaks, two conditions must be met. Ni must "disappear" in a mode identical to radioactive decay, and all the resulting dimer vacancies must spontaneously disorder as the holding potential provided by the Ni atom disappears. A decrease in Ni concentration with time is suggested,[12] but its decay rate is not given.[14] We first discuss how the concentration of Ni could decrease in a "radioactive decay" mode, i.e., without memory of its history. If one postulates that the Ni atoms important for the formation of the $(2\times n)$ structure reside in a thin subsurface layer (two to three atoms thick), and furthermore, that as soon as a Ni atom moves anywhere out of this layer it is "lost" for the purpose of forming the $(2\times n)$ phase, then one has the analog of radioactive decay and correspondingly first-order kinetics for the disappearance of the relevant Ni atoms. This process is straightforward to envision if Ni were simply to pop up from the subsurface layer to the surface (where it can accumulate to any concentration), but this behavior is inconsistent with experiment,[12,14] which shows the observable Ni concentration to decrease with annealing time. Therefore, Ni must be diffusing into the crystal, or possibly precipitating.[15] In either case, it would appear that a concentration gradient and a diffusion mechanism are required, causing deviations[14] from first-order kinetics for the disappearance of Ni. The only way that first-order kinetics could be obeyed for inward motion of Ni is if there exists an extreme supersaturation of Ni that is confined to one or two layers, with the concentration of Ni in the rest of the crystal below the solubility limit and with rapid diffusion of Ni. This is difficult to imagine.

We now address the second of the necessary conditions for observing Ni caused exponential decay of the "n" Bragg peak intensity, namely that the dimer vacancies that are bound in the ordered array by a Ni atom spontaneously disorder as the holding potential of the Ni atom disappears. This requires first of all no activation barrier for this disordering (once the Ni potential is gone). Assuming that this is true, if there is one or less than one dimer vacancy associated with each Ni atom,[12] the Bragg intensity will show exponential decay if the Ni concentration does. The true Ni concentration is quite uncertain, however, depending on the assumed distribution of Ni impurity in depth, the mean free path, and the sensitivity factors. A value for the ratio of Si to Ni atoms ranging from 15 to 150 can be obtained from various assumptions using the data of Ref. 12. It is thus possible that a patch of up to 10 dimer vacancies is influenced by one Ni atom. The decay of Ni with first-order kinetics would, in the latter case, produce "droplets" of disorder in the $(2\times n)$ phase whose number would increase with first-order kinetics. The effect on the Bragg peak should be a broadening of the profile as the intensity decreases.[16] This is not observed.

Therefore, although it is possible and likely that Ni impurities provide the potential that orders the $(2\times n)$ phase, it is difficult to construct a scenario by which the disordering behavior is due to the disappearance of the Ni atoms. The major obstacle is a model for the diffusion of Ni into Si that obeys first-order kinetics. A more likely scenario is that the rate-limiting step in the decay of the $(2\times n)$ phase is the disordering of the dimer vacancies, and that these disorder one dimensionally, as described above. The decrease in the Ni surface or subsurface concentration can then proceed by whatever mechanism, as long as it is rapid compared to the disordering of the dimer vacancies. The values $J_{n,n}$ and $J_{n,d}$ in our modeling then refer to the interactions between the dimer vacancies themselves. It is physically reasonable that one-dimensional disordering occurs, given the nature of the dimerized surface and the fact that the defects are dimer vacancies. This one dimensionality of the Si(100) surface, which essentially results from the anisotropy in dimerization, has also been seen in EELS experiments[17] of potassium adsorption on Si(100). The measured plasmon dispersion curves can be explained by assuming decoupled one-dimensional potassium chains in the valleys between the dimers.

V. CONCLUSIONS

We have shown by analytic and Monte Carlo calculations that the disordering kinetics of one-dimensional systems with short-range interactions obey exponential decay of the peak intensity and invariance of the structure factor FWHM. This is contrary to what is observed for two-dimensional disordering. It should be a general result for systems ordering or disordering one dimensionally.

Experimental results of disorder of the metastable Si(100)-($2\times n$) phase display the above features, suggesting that the disordering in this system is one dimensional. Ni impurities may cause the formation of the ($2\times n$) phase; however, a one-dimensional disordering appears to be necessary to explain the diffraction measurements. Specific interactions used in the model give a qualitative picture of the behavior, but it should be clear from our treatment that microscopic information about the kinetic mechanisms can be obtained from the macroscopic time evolution of a system in a strongly nonequilibrium situation.

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*Present address: Ames Laboratory and Department of Physics, Iowa State University, Ames, IA 50011.

†Present address: Texas Instruments, Inc., Box 655936, MS154, Dallas, TX 75265.

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