Influence of Time-Dependent Rates of Mass Transfer on the Kinetics of Domain Growth

Kristen A. Fichthorn
Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802

W. Henry Weinberg
Department of Chemical Engineering, University of California, Santa Barbara, California 93106
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Although there is a growing consensus as to the universality of domain growth kinetics in quenched systems, discrepancies remain among theory, experiments, and simulations. We identify a major discrepancy between the three—the time dependence of mass transfer kinetics. We show that this discrepancy can be resolved in Monte Carlo simulations of domain growth. Our results strengthen the emerging consensus that systems having a nonconserved order parameter obey Lifschitz-Allen-Cahn growth kinetics in the asymptotic scaling limit.

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Growth and ordering processes are abundant in nature, underlying phenomena as diverse as snowflake and soot formation, crystal growth, and the evolution of the Universe. The search for universality and possible subclassifications in these apparently wide and varied phenomena is a significant fundamental problem in nonequilibrium statistical mechanics [1]. In thermally quenched systems, the development of long-range order is accomplished by the growth of ordered domains. It is becoming increasingly evident that domain growth in these systems exhibits universal behavior. That is, many systems which conserve the order parameter conform to the Lifschitz-Slyozov (LS) theory [2] of domain growth, while systems having a nonconserved order parameter generally exhibit Lifschitz-Allen-Cahn (LAC) [3] growth kinetics. Ordering kinetics in these theories are described by a power-law expression of the form $\langle l(t)\rangle \sim (At)^x$, where $\langle l(t)\rangle$ is a characteristic length of a domain at time t, A is a proportionality factor, and x is a growth exponent. In the LAC theory, $x=\frac{1}{2}$, while $x=\frac{1}{3}$ in the LS theory. Although the current understanding of domain growth has emerged with considerable controversy, these theories remain the most widely accepted descriptions of domain growth.

The contribution of computer simulations to the understanding of ordering kinetics in thermally quenched systems has been significant. The essential physics of experimental systems can be captured in Monte Carlo simulations of model systems, which can be understood in great detail. It has been well established, however, that the interpretation of Monte Carlo simulations of domain growth is fraught with subtleties. Finite-size effects, poor quality of random numbers, and the existence of "initial transients" have marred many conclusions in this field. As a result, there is a disturbing disparity between the assertion that the physics of domain growth are universal and a host of contradicting Monte Carlo results. The influences of finite-size effects [4–6] and inadequate random numbers [6] have been addressed in sufficient detail that it is possible to identify and alleviate these sources of error in Monte Carlo simulations of domain growth. The effect of initial transients, however, has been understood, heretofore, only qualitatively.

When a disordered system is quenched below its phase-transition temperature, there is a time period during which small domains form. Once domains have formed, it is the assumption of the LAC theory that they are self-similar and that growth should obey a power-law scaling. Both simulations [7] and experiments [8] in systems with nonconserved order parameters have verified that this time period is generally short compared to the time scale of a typical domain-growth study. However, although self-similarity is attained relatively quickly, LAC scaling is not. In several Monte Carlo studies of domain growth [9–11], low values of calculated growth exponents have been attributed, retrospectively, to the influence of initial transients. When simulations are run on larger lattices and to longer times, the value of the growth exponent increases [9,10]. This phenomenon has been termed "crossover" [12]. Qualitatively, it is understood that simulations must be run "long enough" that asymptotic scaling is achieved. However, there has been no quantitative means of discerning when the asymptotic limit has been reached. In certain systems, the amount of computational time required to reach the asymptotic regime may be prohibitive. The possible inexactitude of results in these systems prevents a clear and decisive resolution of true asymptotic domain growth.

In this Letter, we identify the primary source of initial transients in Monte Carlo simulations of domain growth and we show that their influence can be quantified. We demonstrate, in Monte Carlo simulations of two model systems with nonconserved order parameters, that these initial transients can be long lived and significant enough to lead to an apparent growth law of the LS form when the actual growth law is of the LAC form. We discuss the relevance of our findings to the interpretation of experimental studies of domain growth and to the resolution of other outstanding theoretical issues in this field.

In the LAC theory, the time scale of domain growth is determined primarily by the rate of mass transfer in the system. The rate of mass transfer is contained in the pro-

portionality factor of the scaling relation and is assumed to be constant and independent of time. Although this assumption may be reasonable for the asymptotic stages of domain growth, when the system is close to thermal equilibrium, it is untenable for the early stages following the quench. Instead, it is reasonable to expect a transient decrease in the rate of mass transfer during the early stages of domain growth. In these initial stages, when the rate of mass transfer is decreasing with time, low growth exponents will arise when scaling is measured with the assumption that the rate of mass transfer is constant. This transient decrease in the rate of mass transfer is the origin of the initial transients in domain growth and can be demonstrated in a Monte Carlo simulation.

We consider a model of a two-dimensional chemisorbed overlayer in which mass transfer is accomplished by surface diffusion. Specifically, our model is a two-dimensional square-lattice gas with equal and repulsive nearest- and next-nearest-neighbor interactions. At a fractional coverage of $\theta=\frac{1}{2}$, this system undergoes an order-disorder phase transition below a critical temperature of $k_BT_c=0.525\phi$ [13], where ϕ is the lateral interaction strength, to a ground state having a fourfold-degenerate (2×1) superstructure. Although the order parameter in this system is nonconserved (indicating, from theory, LAC growth), there has been controversy as to whether LAC or LS growth kinetics exist. In previous Monte Carlo studies of this system, growth exponents of $x=\frac{1}{2}$ were observed when occupancy exchange was accomplished via Glauber dynamics [5], an algorithm allowing both nearest- and next-nearest-neighbor exchange [12], and when exchange was accomplished by simulated precursor-mediated surface diffusion [10]. Growth exponents close to $\frac{1}{3}$ were observed in a Monte Carlo model utilizing Kawasaki dynamics [5] to accomplish nearest-neighbor exchange and a model incorporating proper barrier-crossing dynamics [14]. A possible experimental analog of this lattice-gas system is the low-temperature adsorption of atomic oxygen on W(110) at a fractional surface coverage, $\theta=\frac{1}{2}$ [8]. In experimental low-energy electron-diffraction studies [8] of domain growth in this system, growth exponents consistent with the LS theory have been measured.

At low temperatures, below the order-disorder phase-transition temperature, adsorption is localized, and it is likely that surface diffusion occurs through adatom "hopping." We consider two models of adatom hopping which are possible mechanisms of surface diffusion for chemisorbed species influenced by adsorbate lateral interactions [14,15]. In the first of these, we simulate vacancy-mediated surface diffusion, in which the exchange of vacant-occupied, nearest-neighbor sites is taken to be representative of an event of thermally activated barrier crossing. Vacancy-mediated diffusion was modeled with seven rates given by

$$\tau_{c,i}^{-1}=\nu e^{-E_b(i)/k_BT},\quad i=-3,\ldots,3, \tag{1}$$

where $E_b(i)=E_{r,0}+i\phi/2$ is the activation barrier for the diffusion of a chemisorbed particle whose number of neighbors changes by i upon relocation. In a second model, we simulate precursor-mediated diffusion [10]. In this mechanism, a chemisorbed particle is thermally excited into a short-lived physically adsorbed state, in which it executes a series of nearest-neighbor hops over both vacant and occupied lattice sites before deexciting into a vacant site. The dynamics of precursor-mediated surface diffusion were modeled by eleven time scales of which nine characterize the excitation rates of a chemisorbed species to the physically adsorbed state:

$$\tau_{\mathrm{ex},j}^{-1}=\nu_{\perp,\mathrm{ex}}e^{-E_c(j)/k_BT},\quad j=0,\ldots,8, \tag{2}$$

where $E_c(j)=E_{p,0}-j\phi$ is the activation energy to excite a particle with j neighbors. In addition, there are two time scales, one characterizing the deexcitation rate from the physically adsorbed state to the chemisorbed state, $\tau_{\mathrm{dex}}^{-1}=\nu_{\perp,\mathrm{dex}}e^{-E_{\mathrm{dex}}/k_BT}$, and the other characterizing the rate of migration of a physically adsorbed precursor, $t_{\mathrm{mig}}^{-1}=\frac{1}{4}\nu_{\parallel}e^{-E_{\mathrm{mig}}/k_BT}$. Since these physically adsorbed species are short lived, their concentration is low and their mutual interaction can be omitted.

We simulated domain growth with a dynamical Monte Carlo algorithm designed to maintain correctly the passage of real time [16] for these mechanisms. Our simulation algorithm is essentially the same as the "N-fold way" algorithm [17] except that, on trial i, time is incremented by τ_i utilizing the mean interevent time in a collection of superimposed Poisson processes, given by [16]

$$\tau_i=\frac{f}{\sum_k m_k r_k}. \tag{3}$$

Here m_k is the number of particles having a rate r_k $(=\tau_k^{-1})$, $f=4$ for vacancy-mediated diffusion, and $f=6$ for the precursor mechanism. The average rate of adatom hopping on trial i, Γ_i, is given by

$$\Gamma_i=\frac{1}{f\theta N}\sum_k m_k r_k, \tag{4}$$

where N is the number of sites in the system. It is evident, as the systems evolve from a high to a low energy, that the rate of adatom hopping must decrease [cf. Eqs. (1) and (2)]. To study this decrease, we utilized a second method for incrementing time—the "uniform interevent step" (UIS). During a simulation run, time was incremented, upon the successful execution of an event, in both "real-time" units [i.e., as given by Eq. (3)], and in units of UIS, where 1 UIS$=1/\theta N$. By incrementing time in UIS and only upon the realization of an event, we simulate a diffusion coefficient which is constant and independent of time. Thus, we obtain two sets of results from the same simulation: a set which is consistent with a reasonable experimental study of domain growth (real-time increments), and a set which is strictly consistent with the assumption of both the LS and LAC theories that the rate of mass transfer is constant and independent

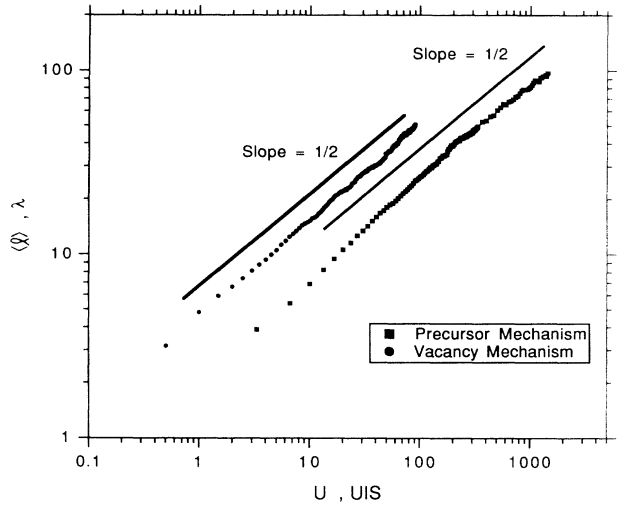

FIG. 1. Plots of the average domain size, in units of the lattice constant, λ, vs time, in units of UIS, for both vacancy-mediated and precursor-mediated diffusion. Lines with slopes of $\frac{1}{2}$ are included for comparison.

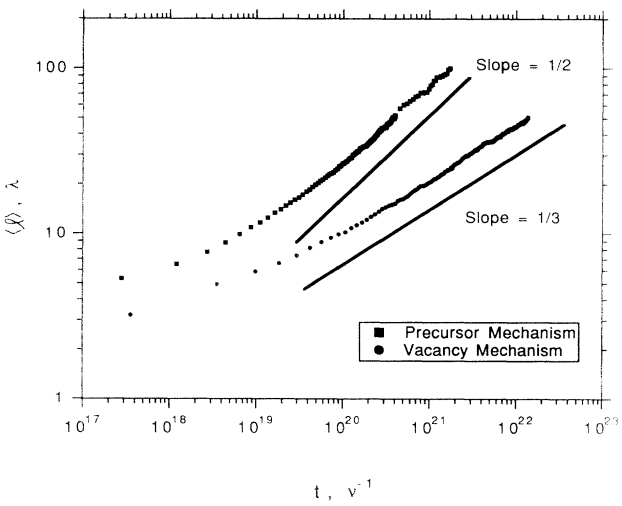

FIG. 2. A plot of the average domain size, in units of the lattice constant, λ, vs real time, in units of ν^{-1}, for both precursor-mediated and vacancy-mediated diffusion. Lines with slopes of $\frac{1}{3}$ and $\frac{1}{2}$ are included for comparison.

of time (UIS increment). The relationship between a UIS on trial i, U_i, and a real-time increment is $U_i = \Gamma_i \tau_i$, or, in the continuum limit, $dU = \Gamma(t)dt$. The time dependence of the rate of adatom hopping can thus be obtained from a plot of the derivative of UIS time with respect to real time as a function of real time.

Relevant parameters in these models are the activation energies and preexponential factors, which were chosen to be $E_{p,0} = 8\phi$, $E_{v,0} = 5.5\phi$, $E_{\text{dex}} = \phi = E_{\text{mig}}$, and $\nu = \nu_{\perp,\text{ex}} = \nu_{\perp,\text{dex}} = \nu_{\parallel}$. We report here the results of simulations that were run at a temperature of $k_B T = 0.1\phi$. A more detailed study of the effects of temperature will be reported elsewhere [18]. For each mechanism, 15 to 20 simulations were conducted on initially random lattices of 350^2 (vacancy mechanism) and 512^2 (precursor mechanism) sites with periodic boundary conditions. As will be discussed elsewhere [18], we ascertained that the results reported here were not influenced by finite-size effects or inadequately random numbers.

Figure 1 shows the average linear dimension of a domain, $\langle l \rangle$, as a function of UIS time U for representative results of all runs for both the vacancy and precursor mechanisms. It can be seen in Fig. 1 that, when the rate of adatom hopping is modeled as being independent of time, domain growth is consistent with the LAC theory for both mechanisms. However, it would appear from examination of Fig. 2, which shows $\langle l \rangle$ as a function of real time, that precursor-mediated domain growth is consistent with the LAC theory at long times, while the vacancy mechanism leads to LS growth. The apparently low growth exponent found with the vacancy mechanism arises from the time dependence of the hopping rate. The simulated hopping rate as a function of time is shown in Fig. 3 for both mechanisms. It can be seen in Fig. 3 that, while the hopping rate relaxes to an apparently constant value for the precursor mechanism, it is continually decreasing with vacancy-mediated diffusion. Strictly speaking, $\Gamma(t)$ will continually decrease in both systems until thermal equilibrium is achieved because it is only at equilibrium that a static situation is maintained. However, Fig. 3 indicates that it is possible that $\Gamma(t)$ changes very slowly in the late stages of growth and is effectively constant. Figures 1–3 show, for the precursor mechanism, that when this occurs, the asymptotic regime is reached and domain growth is consistent with the LAC theory.

The phenomenon of relaxation should be a general one in quenched systems and not unique to this study. Since our model includes the essential features of an experimental system, we expect that a similar decrease in the

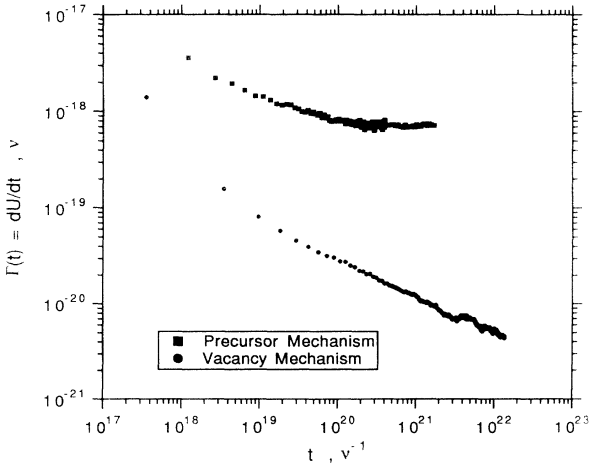

FIG. 3. A plot of dU/dt [$=\Gamma(t)$], in units of ν, vs t, in units of ν^{-1}, for both precursor-mediated and vacancy-mediated diffusion.

rate of adatom hopping will occur in experimental systems, where low growth exponents have been measured [8]. A time dependence of simulated mass transfer should also be present in other Monte Carlo studies of domain growth. Time in most of these studies is measured in Monte Carlo steps, or attempted transitions. Hence, the number of attempted transitions between two successful events defines the time scale. Initially, there will be more successful transitions per attempt than in the final stages of domain growth because transition probabilities must satisfy the detailed-balance criterion for thermal equilibrium, which links them to the energy of the system. This general phenomenon has been noted by others [5,17] because conventional Monte Carlo algorithms proceed very slowly in the late stages of domain growth compared to the early stages. We have shown that this relaxation should be interpreted as time-dependent mass transfer and that it is inconsistent with the LAC theory.

In summary, we have clarified the primary source of "initial transients" in domain growth and shown that these can be quantified in Monte Carlo simulations. Our uniform interevent step methodology proved to be extremely useful in this regard. We believe that this methodology will have many useful future applications [18] because it removes a significant impediment to the interpretation of Monte Carlo simulations. Perhaps it is finally possible to attain a unified consensus as to the universality of domain growth.

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