Modeling the Kinetics of Heterogeneous Catalysis

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Contents

1. Introduction

A variety of microscopic processes occurring at the gas–solid interface (for example, adsorption, desorption, diffusion, reaction, surface reconstruction, and adsorbed layer ordering) play essential roles in heterogeneous catalysis. Much of the work devoted to studying these phenomena involves determining their *kinetics*.[1] In this paper we provide a review of how the kinetics of these processes can be modeled. The methods which have been used to treat the kinetics of surface rate processes can be broadly divided into two categories, analytical and numerical. In the analytical approach, rate equations describing the time dependence of the fractional surface coverages, for instance, are written down. Generally, various approximations need to be made before these equations can be solved. In the numerical approach, which depends largely upon Monte Carlo techniques, the properties of various lattice gas models are studied using computer simulations. We focus on the numerical approach in this paper.

It should be noted at the outset that a major problem to be resolved in modeling the kinetics of heterogeneous catalytic systems is that the total reaction rate does not necessarily have a simple mass–action dependence. In a Langmuir–Hinshelwood reaction between two adsorbed species A and B, it is normal to write the reaction rate as proportional to the product of the fractional coverages of A and B on the surface. If the reactants are randomly distributed on the catalyst surface, this mass–action formulation of the reaction rate would be adequate. Generally, however, correlations arise between the positions of the adsorbates even if they were initially distributed randomly. This can be a consequence of, for instance, lateral interactions between adsorbed molecules, or reconstructions of the catalyst surface, or simply the reaction between otherwise noninteracting adsorbed nearest-neighbor pairs of molecules.

In the absence of such correlations, the kinetics of the microscopic processes can be easily modeled using only rate equations that describe the time dependence of the fractional coverages θ_A and θ_B on the surface.[2] In the presence of correlations, it becomes necessary to include additional rate equations that account for the time dependence of, for instance, the probability θ_{AB} of finding unlike nearest-neighbor pairs of adsorbed reactants.[3] The types of pairs which must be considered depend upon the range of the correlations. It may also be necessary to consider, for instance, the probability θ_{ABA} of occurrence of like-triplets of neighboring ABA adsorbates. Generally, a hierarchy of coupled rate equations can be formulated for quantities such as θ_x, θ_{xy}, and θ_{xyz}. This introduces mathematical difficulties in solving for the time-dependent behavior of the system. Generally, even for nonreacting systems, the solutions can be obtained analytically only for special cases.[4] Approximations have to be made in order to uncouple, for instance, the rate equations describing quantities such as θ_{xy} and θ_{xyz} from the rate equations for the fractional (site) coverages θ_x.

This is a serious drawback because a realistic heterogeneous catalytic system can be quite complicated. It can include two or more interacting adsorbed species, the lateral interactions between the adsorbates may not be isotropic, the surface may reconstruct, and the occurrence of reaction itself may cause nontrivial correlations to arise in the distribution of the adsorbed species. It can, thus, be expected that the rate equations describing a heterogeneous catalytic system are rather involved to formulate and quite difficult to solve.

In the analytical approach we surmount such problems by either pretending that the correlations do not exist, when we assume a random distribution of adsorbed particles, or by employing mean field approximations which treat only the short-range (pair) correlations, described by the θ_{xy}'s, exactly.[5–13] However, such mean field approximations may not provide quantitatively accurate results and, even worse, may not even provide qualitatively correct descriptions of the phenomena, particularly when long-range correlations cannot be neglected.[14]

In the numerical approach no approximations need to be made in dealing with the distribution of adsorbed particles on the surface because this issue, in principle, can be treated exactly using Monte Carlo simulations. It is also comparatively easy to gain
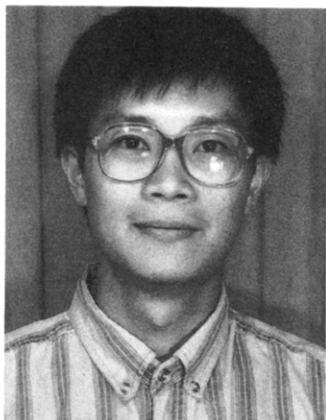
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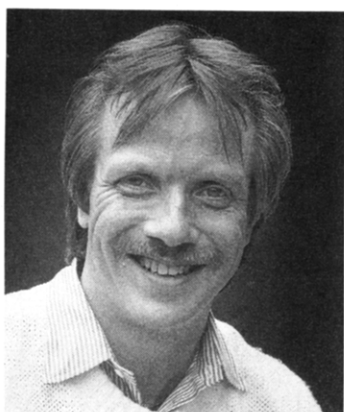
W. Henry Weinberg was born December 5, 1944 in Columbia, SC. He received a B.S. in Chemical Engineering from the University of South Carolina, Columbia (June 1966) and his Ph.D in Chemical Engineering (NSF Fellow) from the University of California, Berkeley (December 1970). He was a NATO Postdoctoral Fellow at the University of Cambridge, England, from January 1971 to March 1972. He joined the faculty of the California Institute of Technology as an Assistant Professor of Chemical Engineering in March 1972 and became an Associate Professor of Chemical Engineering in July 1974, Professor of Chemical Engineering in July 1977, and Professor of Chemical Engineering and Chemical Physics in December 1977. In 1989, he accepted his present position as Professor of Chemical Engineering and Chemistry at the University of California, Santa Barabara. Professor Weinberg has been a Visiting Professor at Harvard University (1980), University of Pittsburgh (1987–1988), and University of Oxford (Wolfson College), England (1991). He was also the Chevron Professor of Chemical Engineering and Professor of Chemical Physics at the California Institute of Technology from March 1981 to March 1986. Professor Weinberg is affiliated with the American Association for the Advancement of Science, the American Chemical Society, the American Institute of Chemical Engineers, the American Physical Society (Fellow), the American Vacuum Society (Fellow), California Catalysis Society, North American Catalysis Society, Phi Beta Kappa, Sigma Xi, and the National Academy of Engineering (USA). Professor Weinberg has received numerous honors and awards over the course of his career; most recently he was given the Arthur W. Adamson Award of the American Chemical Society (1995) and named Distinguished Lecturer, College of Engineering, Hong Kong University of Science and Technology (1994). He has given over 200 presentations at various academic, industrial, and governmental organizations and over 125 invited or contributed presentations at various conferences during the past 15 years.

microscopic insight from Monte Carlo simulations even for relatively complicated lattice gas models. It is, for instance, straightforward to incorporate precursor states,[15] and surface reconstructions[16] are naturally described by allowing the surface atoms to relax.

We will first discuss the basic principles involved in performing Monte Carlo simulations. Simulating equilibrium situations merely involves the sampling of configurations which are distributed according to the correct distribution. However, simulating time-dependent systems requires a consideration of the relationship between each step in the simulation and the real time in which the system is evolving. We will discuss this issue in some depth. Following this description of how Monte Carlo simulations can be performed, we will discuss some applications.

2. Monte Carlo Simulations of Equilibrium Phenomena

The crux of Monte Carlo simulations is the important sampling procedures which allow configurations C of the system which is simulated to be generated according to some distribution $P(C)$.[17] For surface rate processes which are thermally driven, the required equilibrium distribution is the Boltzmann distribution, which is given by

$$P(C_i) = \exp(-H[C_i]/k_B T)/\sum_j \exp(-H[C_j]/k_B T) \quad (1)$$

where H is the Hamiltonian for the system and the sum is over all configurations of the system. The configuration C of a lattice gas is dictated by the positions of filled and empty lattice sites. We allow transitions from an initial configuration C_i to a final configuration C_f to occur with a probability of $\omega(C_i, C_f)$. Detailed balance requires that at equilibrium the distribution of configurations satisfies

$$\omega(C_i, C_f)P_{eq}(C_i) = \omega(C_f, C_i)P_{eq}(C_f) \quad (2)$$

where $P_{eq}(C)$ is the Boltzmann distribution.

A standard way to perform this importance sampling procedure is the Metropolis algorithm.[18] Starting from an initial configuration C_i, the probability of a transition to another configuration C_f is given by

$$\omega(C_i, C_f) = 1 \qquad \text{for } \Delta E_{if} \leq 0$$
$$= \exp(-\Delta E_{if}/k_B T) \qquad \text{for } \Delta E_{if} > 0 \quad (3)$$

where $\Delta E_{if} = E_f - E_i$ is the change in energy if the configuration changes from C_i to C_f. Another important sampling algorithm that generates configurations according to a Boltzmann distribution is the Kawasaki algorithm[19] for which the transition probability is given by

$$\omega(C_i, C_f) = \exp(-\Delta E_{if}/2k_B T)/[\exp(-\Delta E_{if}/2k_B T) + \exp(\Delta E_{if}/2k_B T)] \quad (4)$$

Each of these algorithms obviously satisfies detailed balance and generates a distribution of configurations suitable for computing the properties of a system at thermal equilibrium. This has been exploited in calculating the phase diagrams for various models

of nonreacting adsorbed overlayers.[14] The square lattice gas with nearest-neighbor and next-nearest-neighbor repulsive interactions has, for example, been studied very intensively using Monte Carlo simulations.[20]

These algorithms for computing the transition probabilities $\omega(C_i,C_f)$ can be used in the following straightforward fashion. Beginning with a lattice on which the lattice gas particles are randomly distributed, a pair of lattice sites is selected at random. If either both sites are occupied or both sites are vacant, the iteration is ended and a new pair of sites is selected. If one of the selected sites is occupied and the other is vacant, the change in energy ΔE that occurs if the particle is moved from the former site to the latter is computed. This change in the configuration is accepted or rejected according to one of the above prescriptions. Equilibrium properties can be calculated by sampling the configurations that are generated using this procedure. Although some technical difficulties arise from the use of a lattice of finite size to model a system in the thermodynamic limit, finite-size scaling procedures can be used to overcome these problems.[21]

3. Simulation of Time-Dependent Phenomena

Besides being used merely as an algorithm for constructing equilibrium ensembles of configurations, the Monte Carlo procedure of generating a new configuration from a previous configuration can itself be regarded as a simulation of the physical process by which the configuration of a lattice gas relaxes toward equilibrium.[14] In the simulation procedure described above, the hopping of lattice gas particles from one site to a vacant nearest-neighbor site can be simulated by choosing nearest-neighbor pairs of sites. Frequently, time is then measured in terms of the number of Monte Carlo steps per site, that is the number of attempts per site which are made to change the configuration of the system. This measure of simulation time is often assumed to be linearly related to real time. Clearly, when such a dynamical interpretation is attached to the simulations, it becomes critically important to convert correctly from simulation time to real time.[22] If we consider an arbitrary distribution in configuration space, it has been shown that the frequently assumed linear relationship between these two times is *generally incorrect* for nonequilibrium situations, although the deviation from the linear relationship may not be large when the *distribution* of the configurations is not changing rapidly.[23,24]

Consider eq 4 for the transition probabilities in the Kawasaki algorithm. For a pair of configurations C_i and C_f, it can be seen that the probabilities $\omega(C_i,C_f)$ and $\omega(C_f,C_i)$ sum to unity. It is also possible to formulate the transition probabilities between these configurations in terms of the *activation energies* E_{if} and E_{fi} for transitions $C_i \rightarrow C_f$ and $C_f \rightarrow C_i$, respectively. This formulation is particularly relevant because, for thermally activated processes, the rate is determined by the magnitude of the energy barrier at the saddle point and not by the energy difference between the initial and final states.[25] The forward transition probability in such a formulation would be

given by

$$\omega(C_i,C_f) = \exp(-E_{if}/k_B T) \qquad (5)$$

and a similar expression holds for the reverse transition. Since the difference in the energy of the configurations ΔE_{if} is equal to $E_{if} - E_{fi}$, it is apparent that this "activation energy formulation" also satisfies detailed balance. Note that E_{if} and E_{fi} are the activation energies for the forward and reverse transitions, and the difference of these two barriers is also equal to the difference in energy of the two configurations. However, it is likewise clear that the sum of the transition probabilities $[\omega(C_i,C_f) + \omega(C_f,C_i)]$ is not equal to unity, and indeed, each pair of configurations C_i and C_f will, in general, have a different value for this sum. Thus, the Kawasaki algorithm speeds up each pair of transitions by normalizing the sum of its transition probabilities to unity. This, however, means that different pairs of transitions are speeded up by different amounts.[23]

To summarize, eq 1 does not apply for nonequilibrium situations. For such situations transition probabilities must be chosen carefully, and in particular, eq 5 must be used rather than eqs 3 or 4. All three choices of transition probabilities will lead to a distribution of equilibrium configurations which satisfy eq 1, but only eq 5, which correctly describes thermally activated microscopic events, will be valid in nonequilibrium situations. If a system is at a nonequilibrium steady state, for example, a surface reaction in which reactants are constantly supplied to the gas phase and products constantly removed from the gas phase, eq 5 can be used to describe the rates of surface reaction, surface diffusion, and product desorption. Equation 1 will *not* describe the distribution of surface configurations in such a case. If the system, however, is allowed to go to equilibrium by stopping the supply of new reactants to the gas phase, by not removing the products from the gas phase, by allowing adsorption of the product molecules, and by allowing the reverse surface reaction to occur, then both eqs 5 and 1 produce the same equilibrium distribution.

What does all this imply about the relationship between simulation time and real time? If we are performing Monte Carlo sampling, using the Kawasaki algorithm, upon a stationary distribution of configurations, the distribution of the types of transitions that are attempted is also stationary and simulation time will be linearly related to real time. However, if the distribution of configurations is changing during the simulation, the distribution of the types of transitions which are attempted is also changing. Therefore, on average, the transitions at the beginning of the simulations will be speeded up by a different amount from the transitions later in the simulation. The relationship between real time and simulation time clearly cannot be linear if we take the number of Monte Carlo steps as a measure of the simulation time. Depending upon how fast the distribution of attempted configurations is changing, this deviation from linearity may or may not be large.

This nonlinear relationship is demonstrated most clearly in Figure 1, which is reproduced from ref 26, in which the effect of time-dependent adatom hopping
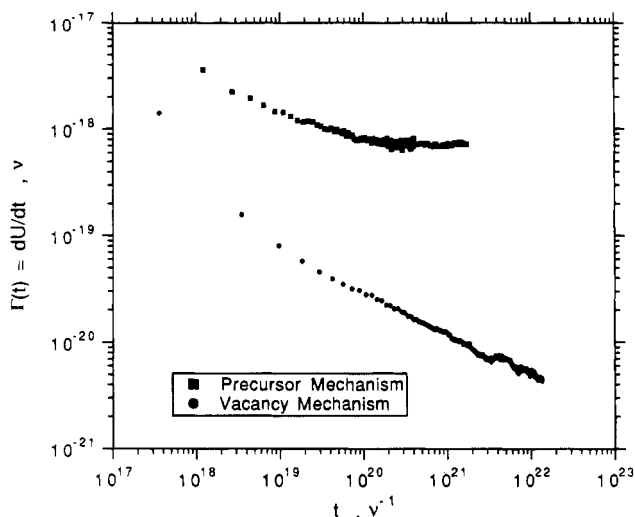
Figure 1. A plot of dU/dt as a function of t for a simulation of domain growth. The quantity U is proportional to the number of Monte Carlo steps in the simulation and t is a measure of time obtained using the time increment given by eq 8 in the text. Both t and U are given in units of the preexponential factor ν. This plot illustrates the nonlinear relationship between U and t, and the typically approximate linearity in the late stages of domain-growth simulations. (Reprinted from ref 26. Copyright 1992 American Institute of Physics.)

rates upon domain growth kinetics is investigated. In Figure 1, t denotes a measure of time obtained from an activation energy formulation of the transition probabilities. The details will be discussed in section 6 in connection with eq 8. The quantity U is another measure of time which is simply proportional to the number of Monte Carlo steps which have been executed in the simulations. Such a measure of time, in effect, rescales the rate of all transitions for each configuration by fixing the average transition rate to a value which is independent of the configuration, i.e., a procedure analogous to the Kawasaki algorithm. It can be seen that t and U are not linearly related. Also note that as the domains coarsen (at long "times"), the nonlinearity decreases since the distribution of configurations changes more slowly when the domains are larger. This latter effect is necessary for the validity of simulations aimed at obtaining growth exponents using computationally efficient, but perhaps not very physical, prescriptions for the transition probabilities.

The same conclusion was also reached in a study in which the self-diffusion coefficient for a lattice gas was calculated. By using different prescriptions to compute the jump rates, different self-diffusion coefficients were obtained, although the equilibrium behaviors were the same.[27] Although we have discussed this issue in terms of only the activation energy formulation and the Kawasaki algorithm, the same considerations also apply to other formulations of the transition probabilities.

Somewhat relevant to the issue of relating real time to simulation time is the technical consideration of the efficiency of a simulation. In the activation energy formulation, the transition probabilities can be extremely small in the case of large barriers and low temperatures. If the simulations were to be performed by addressing each possible transition at

random, the number of successful moves would be very small compared to the total number of attempts. Thus, the simulation would be quite inefficient. Of course, the Kawasaki transition probabilities alleviate this problem because these probabilities are normalized to unity for each pair of transitions regardless of the configurations involved. The remedy for the activation energy formulation is not new and was proposed by Bortz et al.[28] The basic idea is to make a list of all possible transitions which a configuration C can undergo. One of these transitions is selected according to its probability, the configuration is changed accordingly, and the list of possible transitions is updated. The time increment is then equal to the mean interevent time computed according to the distribution of possible transitions for the configuration C. This procedure is iterated. The details and the relevant equations for such a procedure, which has been used in several applications, will be discussed below in section 6.

4. Adsorbate Aggregation

We have emphasized that, in general, correlations exist between the adsorbed species. This leads to ordering or aggregation, the effects of which upon the kinetics of surface reactions have been widely studied using Monte Carlo techniques. In this section we will discuss some of the results that have been obtained. Consider the reaction between two adsorbates A and B, the distribution of B on the surface being random. If we consider the adsorbate distribution of A to be random also, we would expect the reaction rate to be proportional to the fractional coverage θ_A. On the other hand, if adsorbate A is distributed in the form of compact islands on the surface, the reaction rate would be expected to be proportional to the length of the perimeter of these islands, and, hence, proportional to $\theta_A^{1/2}$. Using Monte Carlo simulations this simple model has been investigated by Silverberg, et al.[29] They found that the reaction rate scales neither as θ_A nor as $\theta_A^{1/2}$. Rather, from their simulations it was found that the exponent ranges between 0.59 and 0.7.[29] While the actual value of the exponent might contain information concerning the fractal dimension of the perimeter, it is clear that neither assuming the adsorbate to be distributed randomly nor assuming the adsorbate to be in the form of compact islands on the surface is adequate for the model which was studied. A similar result was obtained earlier by Stiles and Metiu[30] who showed that the reaction rate between adsorbates A and B cannot be expressed in terms of the simple mass–action form, $k_r\theta_A\theta_B$.

Adsorbate aggregation in the form of ($\sqrt{3} \times \sqrt{3}$)-R30° domains of molecularly adsorbed nitrogen has also been investigated using Monte Carlo simulations.[31] A hexagonal lattice was used to simulate the Ru(001) surface, and the nitrogen molecules were modeled as lattice gas particles which have nearest-neighbor and next-nearest-neighbor lateral interactions. The strengths of these interactions were obtained by fitting the simulation results to experimental data. The Monte Carlo simulations clearly show that adsorbate aggregation in this system occurs in four stages: nucleation of domains; growth

of isolated domains; simultaneous growth at isolated domain boundaries and at antiphase domain boundaries; and growth of antiphase domains.[31] Figure 2 shows snapshots of the simulation which illustrate these issues in an unambiguous fashion. Such work demonstrates the possibility of gaining microscopic insight into complex physical phenomena via simulations.

In the simulations discussed above, the extent of aggregation is controlled by the strength of the lateral interaction between the lattice gas particles. However, Monte Carlo studies of *reacting* lattice gas models have shown that reactant aggregation can also occur in the absence of any lateral interaction. This is a consequence of the reaction and removal from the lattice of nearest-neighbor AB pairs of particles. Indeed, this source of correlation can lead to kinetic phase transitions, as shown by Ziff, Gulari, and Barshad.[32] In the so-called monomer–dimer model

$$A(g) \rightarrow A(a)$$

$$B_2(g) \rightarrow 2B(a)$$

$$A(a) + B(a) \rightarrow AB(g)$$
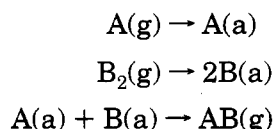
where (g) and (a) denote gas-phase and adsorbed particles, respectively, the system exhibits three possible phases. When the relative probability of adsorption p_A of A is lower than approximately 0.391, the surface is poisoned by adsorbate B, and when p_A is greater than approximately 0.525, the surface is poisoned by adsorbate A. Only for intermediate values of p_A does a reactive steady state exist.

Recently, there has been much interest in this system, and Monte Carlo simulations have been used to study the kinetics.[32-38] In addition, the effects of desorption,[38] surface diffusion,[39,40] lateral interactions,[41] and a hot-dimer adsorption mechanism[42] upon the behavior of this system have each been investigated using Monte Carlo simulations. In addition to Monte Carlo methods, mean-field approximations at the site and at the pair level have been used to study the monomer–dimer model.[43] The mean-field approximation at the pair level gave good agreement with Monte Carlo simulations for the first-order kinetic phase transition to surface poisoning by A. The agreement with Monte Carlo simulations is not so good for the second-order transition to surface poisoning by B, tending to indicate that only the first-order transition is mean field in nature.[43]

There has also been some interest[44,45] in the so-called monomer-monomer model:

$$A(g) \rightarrow A(a)$$

$$B(g) \rightarrow B(a)$$

$$A(a) + B(a) \rightarrow AB(g)$$
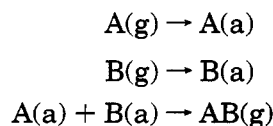
first studied by Wicke et al.,[46] and for which exact solutions for the fluctuations in the saturation coverage and reaction rates exist.[47] In particular, relating the roughening of the interface of the aggregates of adsorbed molecules which are formed to the reaction rate is relevant to heterogeneous catalysis.[48,49] In the monomer–monomer model, the reaction rate decreases with time as a result of segregation of the A and B adparticles for lattices of dimension less than or equal to two.[47] It has been postulated that the exponent α for the time dependence of the reaction rate ($R \sim t^\alpha$) is related to the exponent β for the time dependence of the roughness ($\sigma \sim t^\beta$) of an initially flat interface between semiinfinite domains of A and B. By performing Monte Carlo simulations in which the initial configuration consists of half a monolayer of A particles and half a monolayer of B particles, both randomly distributed on the lattice, Kang and Weinberg[49] found the value of α to be approximately equal to 0.916. Then, by performing simulations in which the initial configuration consists of semiinfinite domains of A and B separated by a straight interface, the roughening exponent for the interface was found to be 0.455. These results show very good agreement with the postulated relationship, namely, $\alpha = 2\beta$. For these simulations, the simulation time is linearly related to the real time, and the latter can be measured simply by the number of Monte Carlo steps per site.[23]

5. Precursor-Mediated Adsorption

One of the advantages of using Monte Carlo simulations to study models of adsorbed systems is the ease with which relatively involved models may be simulated. To illustrate this, we review here an investigation of the probability of precursor-mediated physical adsorption of ethane, from a supersonic molecular beam, onto the reconstructed Ir(110) surface.[15] Since the adsorption is precursor mediated, in the model each site on the lattice can be in one of three possible states: vacant, occupied by a physically adsorbed particle, or occupied by a physically adsorbed particle and a particle trapped in the precursor state in a second layer. Each iteration in the simulations is begun by selecting a lattice site at random. If the site is occupied by a precursor particle, then the particle attempts either to hop to one of its four nearest-neighbor sites or to desorb, each of the five possibilities being selected with equal probability. The probability for success of a hop is given by p_m and that for desorption is given by p_d. A hop is allowed only if the nearest-neighbor site which is selected is not already occupied by a precursor particle, and if a hop occurs into a vacant site, the precursor particle becomes physically adsorbed. If the site selected at the beginning of the iteration is vacant or is occupied by only a physically adsorbed particle, then a gas-phase particle is allowed to impinge upon it with a probability of p_f. The impinging particle is adsorbed with a probability of p_0 if the site is vacant and with a probability of p_1 if the site is occupied by a physically adsorbed particle.

The simulation, thus, requires an input of five parameters; p_0 and p_1 depend upon the experimental molecular beam energy, while p_d and p_m do not, and p_f depends upon the beam flux. Of these parameters the value of p_0 can be obtained from experimental data for a clean surface. The values of p_1 and p_f are obtained from fitting the simulation results to the data. We can take p_m to be equal to unity and vary the ratio p_d/p_m to obtain the best fit. Since p_d and p_m do not depend on the beam energy, it should be
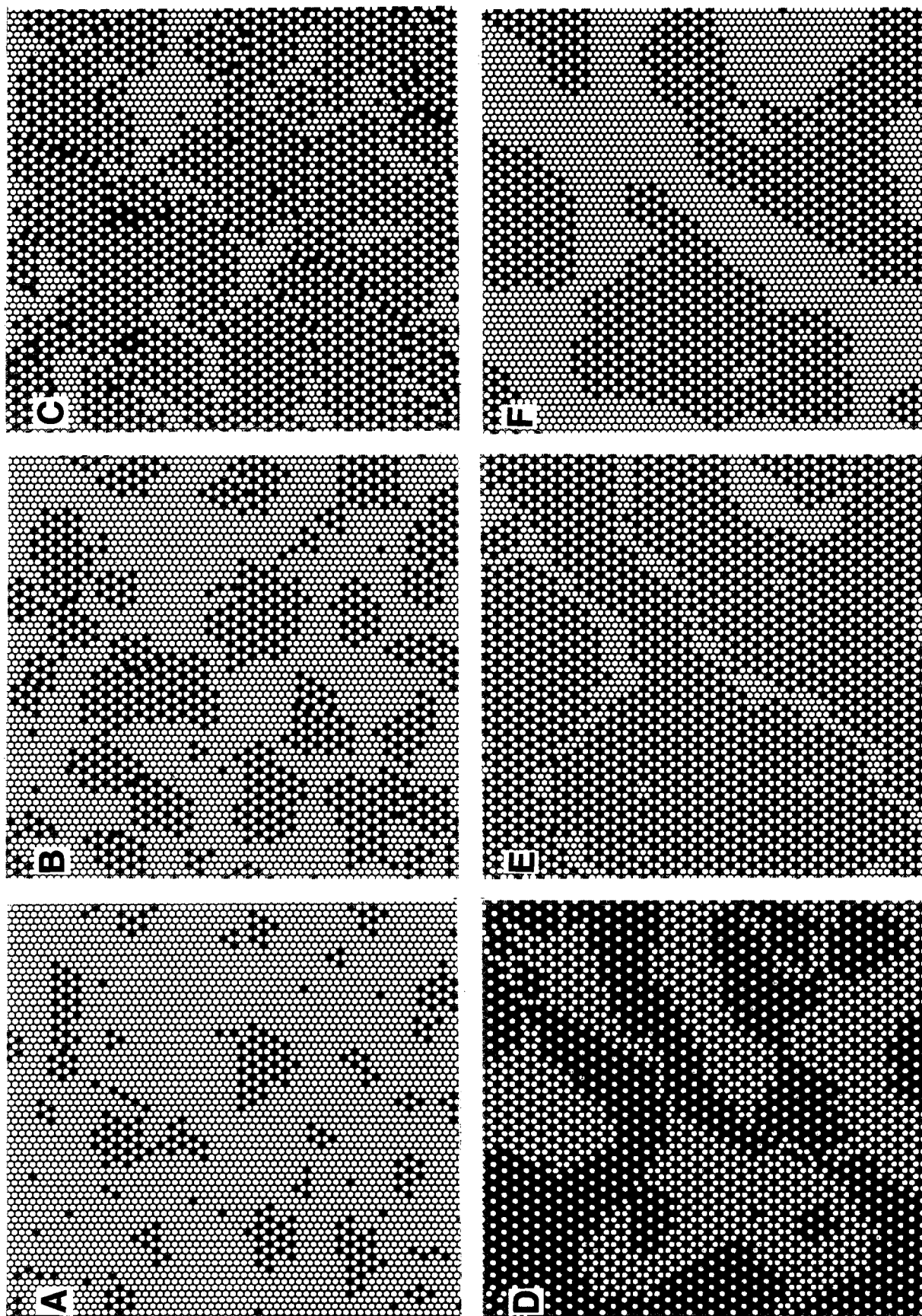
Figure 2. Snapshots of Monte Carlo simulations of the nucleation and coarsening of $(\sqrt{3} \times \sqrt{3})R30°$ domains. Microscopic insight into the ordering of N_2 on Ru(001) is provided from such simulation results. (Reprinted from ref 31. Copyright 1985 American Institute of Physics.)
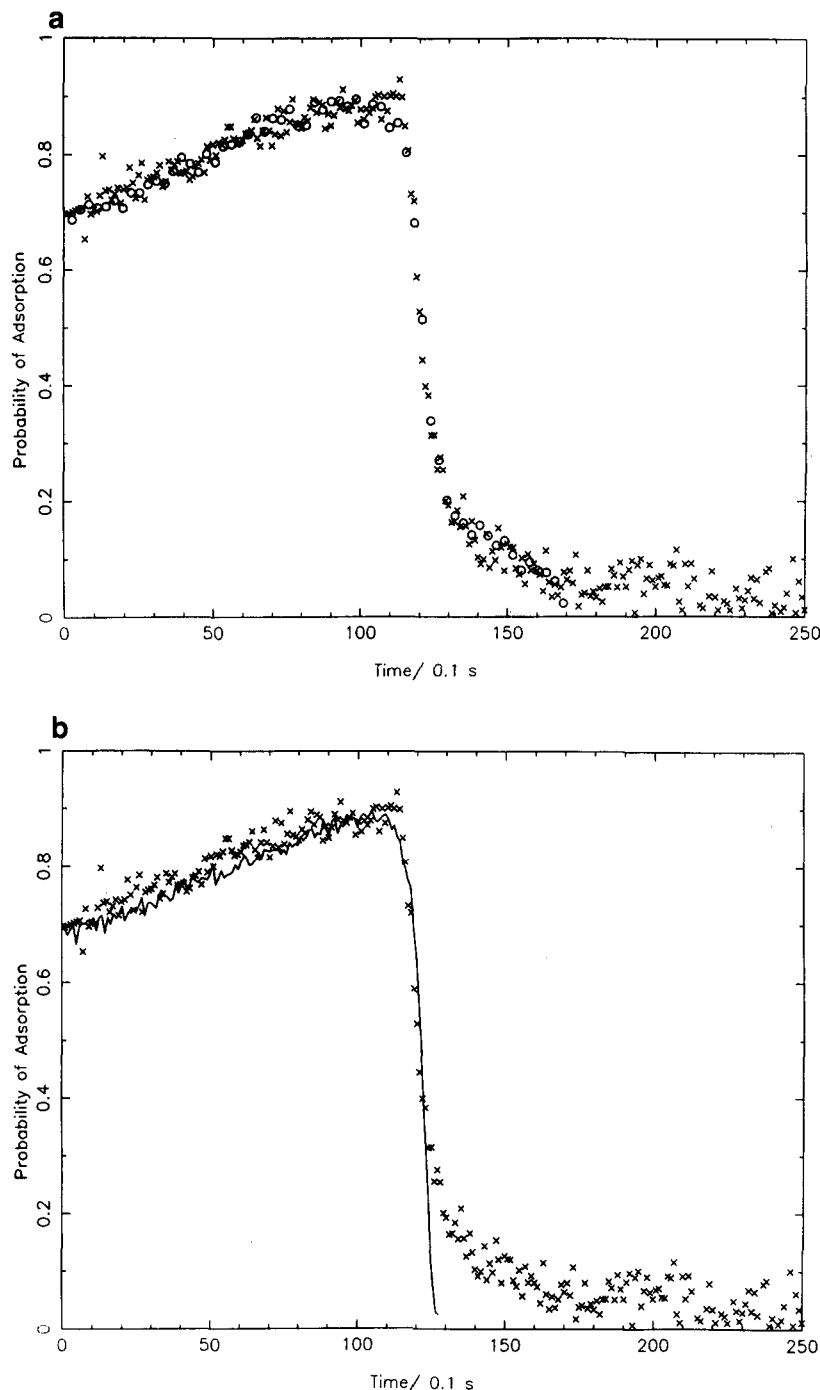
Figure 3. Results from simulations of the precursor-mediated physical adsorption of ethane on the reconstructed Ir(110) surface. a: The crosses indicate experimental results and the circles are the simulation results. These results are for a molecular beam energy of 6.6 kcal/mol. b: The crosses indicate experimental results and the line indicates simulation results for an infinitesimal molecular beam flux. Note the absence of the "tail" seen in the experimental results and the simulation results of part a. (Reprinted from ref 15. Copyright 1990 American Institute of Physics.)

noted that the simulation results for the best values of these parameters must fit the experimental data at all beam energies in order to be physically consistent.

Some of the results from the Monte Carlo simulations performed by Kang, Mullins, and Weinberg,[15] using the procedure described above, are shown in Figure 3a. The crosses are experimental data and the circles are results obtained from simulations for a beam energy of 6.6 kcal/mol. The agreement between the two is very good indeed. In addition to this type of simulation, by modifying the procedure slightly, it was possible to simulate the limiting

situation in which the beam flux tends to zero. This is achieved by following the trajectory of each impinging gas-phase particle until it either desorbs or becomes physically adsorbed at a vacant site before introducing another gas-phase particle into the system. Results from simulations using this modified procedure do not exhibit the "tail" which is observed in the experimental beam reflectivity measurements, as may be seen in Figure 3b. By making use of this piece of information, it was possible to extract from the simulation results, particularly from the magnitude of the "tail" in the reflectivity measurements, values for the desorption barrier and migration

barrier for a precursor molecule. These physical quantities are not readily amenable to direct measurement. Thus, the possibility of extracting them from experimental data clearly shows the utility of Monte Carlo simulations in dealing with a somewhat involved physical model.

When a gas molecule impinges upon a site in which there is already a trapped precursor, the situation becomes more complicated than when it impinges upon either a vacant site or on top of a layer of already adsorbed molecules. The trapped molecule may gain sufficient energy to desorb along with the impinging molecule, or the impinging molecule may be scattered from the trapped molecule and become trapped itself while desorbing the previously trapped molecule. Such events were justifiably neglected in the simulations discussed above beause it was found that the fractional coverage of the precursor was in all cases smaller than approximately 0.06. Intrinsic precursor states were also quite rightly not considered in these simulations which modeled *physical* adsorption. However, it is not difficult to incorporate such mechanisms into the simulation procedure for systems in which they play important roles.

6. Temperature-Programmed Desorption

One of the most widely used experimental techniques for studying the binding energies of adsorbed species is temperature-programmed desorption. Experimental results have traditionally been analyzed using the Arrhenius (or Polanyi–Wigner) expression for the dependence of the desorption rate coefficient upon fractional surface coverage θ and temperature T, i.e.

$$R_d = k_d^{(0)}(\theta) \exp(-E_d(\theta)/k_B T)\theta^n \qquad (6)$$

where $k_d^{(0)}(\theta)$ and $E_d(\theta)$ are, respectively, the preexponential factor and activation energy of the desorption rate coefficient, and n is the order of the desorption reaction.[50-57] If the adsorbed atoms or molecules are randomly distributed on the surface at all times, and $k_d^{(0)}$ and E_d do not depend upon θ, the TPD spectrum can be obtained trivially by integrating the rate expression. However, such conditions are generally not satisfied for most systems of interest in heterogeneous catalysis. The activation energy E_d and the preexponential factor $k_d^{(0)}$ frequently depend upon the coverage, and indeed may show kinetic compensation.[58,59] In addition, as we have seen above, even the occurrence of reaction between nearest-neighbor pairs of adsorbates produces correlations between the adsorbed species. We can formulate rate equations which take such effects into account, but, as noted above, the hierarchy of equations that results requires some approximation for closure. Mean-field approximations are often used to provide closure and are qualitatively useful. However, since Monte Carlo simulations can provide exact answers and are readily performed even for complicated lattice gas models, they are now widely used to analyze experimental TPD spectra. Several workers have published algorithms for such analyses.[13,60-62]

Clearly, in simulating temperature-programmed desorption, it is essential to use the correct measure of time in the simulations. In a recent algorithm employed by Meng and Weinberg to simulate first-order desorption, particular attention is paid to this issue.[63] The correct relationship between simulation time and real time is obtained by calculating the time increment directly from the total rate of desorption from the surface using a relationship that is easily derived from the rate equation. Since this algorithm is very useful and can be extended in a straight-forward fashion to higher order desorption,[64] we will describe the main features here.

The basic idea is to write the rate of desorption from the surface in the form

$$-dN/dt = \sum_i N_i k_{d,i}^{(0)} \exp(-E_{d,i}/k_B T) \qquad (7)$$

where N is the total number of adsorbed molecules and N_i is the number of adsorbed molecules for which the local configuration of the adsorbed layer is denoted by the subscript i. Generally, $E_{d,i}$, the activation barrier for a molecule with local configuration i, is dependent upon its local configuration via lateral interactions. However, the corresponding preexponential factor $k_{d,i}^{(0)}$ can frequently be assumed to be a constant $k_d^{(0)}$ independent of the local configuration.[65] At any time, the average time increment for the desorption of a molecule from the surface is, thus, given by

$$\tau(N) = 1/\sum_i N_i k_d^{(0)} \exp(-E_{d,i}/k_B T) \qquad (8)$$

Similarly, the probability that a particular molecule with a local configuration j desorbs in an interval of time equal to τ is given by

$$P_j = N_j k_d^{(0)} \exp(-E_{d,j}/k_B T)/\sum_i N_i k_d^{(0)} \exp(-E_{d,i}/k_B T) \qquad (9)$$

Hence, for any configuration occurring in the course of a simulation, we compute τ, and this will then be the time increment for the successful desorption of any one molecule from the surface. After each molecule is desorbed, the configuration is changed and the list of transitions is updated. The quantity denoted by t in Figure 1 is the measure of time obtained using the time increment τ for each Monte Carlo step. The nonlinearity of τ and the number of Monte Carlo steps has been noted above. In simulating temperature-programmed desorption experiments, the temperature of the surface is also updated using this time increment and the imposed temperature ramp. In addition, thermal equilibrium is reestablished via surface diffusion of the adsorbed molecules. Minimization of the total energy is frequently used as a criterion for deciding when the configuration is representative of thermal equilibrium.

In order to treat higher-order desorption, or reaction, the procedure described above only needs to be modified slightly.[64] For example, to treat the temperature-programmed reaction between adsorbates

A and B, we need to keep track of a list of all nearest-neighbor AB pairs, assuming that reaction occurs between nearest-neighbor pairs. Each pair will have a particular local configuration which affects its reaction probability. Simultaneous desorption, reaction, and diffusion can obviously be simulated in the same manner if the rates for all these processes are comparable. If the diffusion rate is very much faster, we can always allow the surface configuration to relax completely to equilibrium before simulating the slower processes using the procedure outlined above. This relaxation to equilibrium can be achieved by simulating surface diffusion, as was done by Meng and Weinberg,[63,64] or by using a mean-field approximation to populate the sites of a lattice.[29] The latter would be more efficient since it involves fewer steps, but it may not be satisfactory if the correlation length is large.

7. Conclusions

We have reviewed the use of Monte Carlo simulations in modeling the kinetics of the elementary processes important in heterogeneous catalysis. The review deals principally with the importance of using the correct measure of time in simulations of time-dependent phenomena. We have also discussed the important sampling procedure that is basic to Monte Carlo simulations, whether for equilibrium or nonequilibrium situations. The extension of the simulations to time-dependent problems was treated in detail and it was shown that, in general, the relationship between real time and the number of Monte Carlo steps is not linear. The latter quantity should, therefore, be used only with great care as a measure of simulation time.

In addition to the discussion of the basic issues involved in performing Monte Carlo simulations, we have also described some previous work. This was done to illustrate the usefulness of the technique when confronted with modeling a heterogeneous catalytic system which may be rather complicated in terms of the elementary processes involved. A temperature-programmed desorption simulation procedure which incorporates the correct measure of time and is computationally efficient was reviewed in some detail. Although methods such as mean field approximations can allow an analytical treatment of some simple lattice gases, the use of numerical simulation methods is unavoidable for quantitatively accurate modeling of typical surface reaction systems. This is because, typically, the statistics of the adsorbed layer can only be treated approximately using analytical methods. However, the use of Monte Carlo simulations can, in principle, treat the statistics of the adsorbed layer exactly. With increasing computational power, Monte Carlo simulations have rapidly become an important tool for investigating complex systems and should play an increasingly important role in elucidating heterogeneous catalysis.

References

(1) Weinberg, W. H. In *Kinetics of Interface Reactions*; Kreuzer, H. J., Grunze, M., Eds.; Springer: Berlin, 1987; p 94.
(2) Razon, L. F.; Schmidt, R. A. *Catal. Rev. Eng. Sci.* **1986**, *28*, 89. Imbihl, R. *Optimal Structures in Heterogeneous Reaction Systems*; Plath, P. J., Ed.; Springer: Heidelberg, 1989. Ertl, G. *Adv. Catal.* **1990**, *37*, 213.
(3) Evans, J. W. *Langmuir* **1991**, 7, 2514. Pak, H.; Evans, J. W. *Surf. Sci.* **1987**, *186*, 550. Evans, J. W.; Hoffman, K. K.; Pak, H. *Surf. Sci.* **1987**, *192*, 475.
(4) Baxter, R. J. *Exactly Solved Models in Statistical Mechanics*; Academic: London, 1982.
(5) Cordoba, A.; Luque, J. J. *Phys. Rev. B* **1982**, *26*, 4028.
(6) Zhdanov, V. P. *Surf. Sci.* **1981**, *102*, L35; **1981**, *111*, L662; **1983**, *123*, 106; **1984**, *133*, 469; **1986**, *137*, 515; **1986**, *169*, 1; **1987**, *179*, L57.
(7) Hellsing, B.; Zhdanov, V. P. *Chem. Phys. Lett.* **1988**, *147*, 613.
(8) Kreuzer, H. J.; Payne, H. S. *Surf. Sci.* **1988**, *198*, 235; **1988**, *200*, L433; **1988**, *205*, 153; **1989**, *222*, 404.
(9) Benziger, J. B.; Schoofs, G. R. *J. Phys. Chem.* **1984**, *88*, 4439.
(10) Sundaresan, S.; Kaza, K. R. *Surf. Sci.* **1985**, *160*, 103; *Chem. Eng. Commun.* **1985**, *32*, 333; **1985**, *35*, 1.
(11) Asada, H.; Masuda, M. *Surf. Sci.* **1989**, *207*, 517.
(12) Surda, A.; Karasova, I. *Surf. Sci.* **1981**, *109*, 605.
(13) Sales, J. L.; Zgrablich, G.; Zhdanov, V. P. *Surf. Sci.* **1989**, *209*, 208.
(14) *Monte Carlo Methods in Statistical Physics*; Binder, K., Ed.; Topics in Current Physics, Vol. 7; Springer: Berlin, 1986. *Applications of Monte Carlo Methods in Statistical Physics*; Binder, K., Ed.; Topics in Current Physics, Vol. 36; Springer: Berlin, 1987.
(15) Kang, H. C.; Mullins, C. B.; Weinberg, W. H. *J. Chem. Phys.* **1990**, *92*, 1397.
(16) Masseo, G.; Jug, G.; Levi, A. C.; Tosatti, E. *Surf. Sci.* **1992**, *273*, 237.
(17) Kalos, M. H.; Whitlock, P. A. *Monte Carlo Methods*; Wiley-Interscience: New York, 1986; Vol. I (Basics).
(18) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(19) Kawasaki, K. *Phys. Rev.* **1966**, *145*, 224; **1966**, *150*, 285.
(20) Sadiq, S.; Binder, K. *J. Stat. Phys.* **1984**, *35*, 517.
(21) Barber, M. N. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic Press: London, 1983; Vol. 8.
(22) Kang, H. C.; Weinberg, W. H. *Acc. Chem. Res.* **1992**, *25*, 253; *Surf. Sci.* **1994**, *299/300*, 755.
(23) Kang, H. C.; Weinberg, W. H. *J. Chem. Phys.* **1989**, *90*, 2824.
(24) Fichthorn, K. A.; Weinberg, W. H. *J. Chem. Phys.* **1991**, *95*, 1090.
(25) Gomer, R. *Rep. Prog. Phys.* **1990**, *53*, 917. Ala-Nissila, T.; Ying, S. C. *Prog. Surf. Sci.* **1992**, *39*, 227.
(26) Fichthorn, K. A.; Weinberg, W. H. *Phys. Rev. Lett.* **1992**, *68*, 604.
(27) Ferrando, R.; Scalas, E. *Surf. Sci.* **1993**, *281*, 178.
(28) Bortz, A. B.; Kalos, M. H.; Lebowitz, J. L. *J. Comput. Phys.* **1975**, *17*, 10.
(29) Silverberg, M.; Ben-Shaul, A.; Robentrost, F. *J. Chem. Phys.* **1985**, *83*, 6501. Silverberg, M.; Ben-Shaul, A. *Chem. Phys. Lett.* **1987**, *134*, 491; *Surf. Sci.* **1989**, *214*, 17.
(30) Stiles, M.; Metiu, H. *Chem. Phys. Lett.* **1986**, *128*, 337.
(31) Hood, E. S.; Toby, B. H.; Weinberg, W. H. *Phys. Rev. Lett.* **1985**, *55*, 2437.
(32) Ziff, R. M.; Gulari, E.; Barshad, Y. *Phys. Rev. Lett.* **1986**, *50*, 2553.
(33) Razon, L. F.; Schmitz, R. A. *Catal. Rev. Sci. Eng.* **1986**, *28*, 89.
(34) Dumont, M.; Dufour, P.; Sente, B.; Dagonnier, R. *J. Catal.* **1990**, *122*, 95.
(35) Evans, J. W.; Miesch, M. S. *Phys. Rev. Lett.* **1991**, *66*, 833.
(36) Meakin, P.; Scalapino, D. J. *J. Chem. Phys.* **1987**, *87*, 731.
(37) Jensen, I.; Fogedby, H. C.; Dickman, R. *Phys. Rev. A* **1990**, *41*, 3411.
(38) Deem, M. W.; Weinberg, W. H.; Kang, H. C. *Surf. Sci.* **1992**, *276*, 99.
(39) Evans, J. W. *J. Chem. Phys.* **1993**, *98*, 2463.
(40) Jensen, I.; Fogedby, H. C. *Phys. Rev. A* **1990**, *42*, 1969.
(41) Silverberg, M.; Ben-Shaul, A. *J. Chem. Phys.* **1987**, *87*, 3178; *J. Stat. Phys.* **1988**, *52*, 1179.
(42) Pereyra, V. D.; Albano, E. V. *Appl. Phys. A – Solids and Surfaces* **1993**, *57*, 291.
(43) Dickman, R. *Phys. Rev. A* **1986**, *34*, 4246.
(44) Fichthorn, K.; Gulari, E.; Ziff, R. *Phys. Rev. Lett.* **1989**, *63*, 1527.
(45) Considine, D.; Redner, S.; Takayasu, H. *Phys. Rev. Lett.* **1989**, *63*, 2857.
(46) Wicke, E.; Kumman, P.; Keil, W.; Scheifler, J. *Ber. Bunsen-Ges. Phys. Chem.* **1980**, *4*, 315.
(47) Clement, E.; Leroux-Hugon, P.; Sander, L. M. *Phys. Rev. Lett.* **1991**, *67*, 1661.
(48) Kang, H. C.; Weinberg, W. H. *Phys. Rev. E* **1993**, *47*, 1604; *48*, 3464.
(49) Kang, H. C.; Weinberg, W. H. *J. Chem. Phys.* **1994**, *100*, 1630.
(50) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(51) de Jond, A. M.; Niemantsverdriet, J. W. *Surf. Sci.* **1990**, *233*, 355.

(52) Tronconi, E.; Lietti, L. *Surf. Sci.* **1988**, *199*, 43.

(53) King, D. A.; Madey, T. E.; Yates, J. T. *J. Chem. Phys.* **1971**, *55*, 3236.

(54) Bauer, E.; Poppa, H.; Todd, G.; Bonczek, F. *J. Appl. Phys.* **1974**, *45*, 5164.

(55) Falconer, J. L.; Madix, R. J. *J. Catal.* **1977**, *48*, 262.

(56) Chan, C. M.; Aris, R.; Weinberg, W. H. *Appl. Surf. Sci.* **1978**, *1*, 360.

(57) Taylor, J. L.; Weinberg, W. H. *Surf. Sci.* **1978**, *78*, 259.

(58) Kang, H. C.; Jachimowski, T. A.; Weinberg, W. H. *J. Chem. Phys.* **1990**, *93*, 1418.

(59) Fichthorn, K. A.; Weinberg, W. H. *Langmuir* **1991**, *7*, 2539.

(60) Lombardo, S. J.; Bell, A. T. *Surf. Sci.* **1988**, *206*, 101; **1989**, *224*, 451; *Surf. Sci. Rep.* **1991**, *13*, 1.

(61) Lutsevich, L. V.; Tkachenko, O. A.; Zhdanov, V. P. *Langmuir* **1991**, *7*, 1225; **1992**, *8*, 1757.

(62) Heras, J. M.; Velasco, A. P.; Viscido, L.; Zgrablich, G. *Langmuir* **1991**, *7*, 1124.

(63) Meng, B.; Weinberg, W. H. *J. Chem. Phys.* **1994**, *100*, 5280.

(64) Meng, B.; Weinberg, W. H. *J. Chem. Phys.* **1995**, *102*, 1003.

(65) Weinberg, W. H. In *Dynamics of Gas-Surface Interactions*; Rettner, C. T., Ashfold, M. N. R., Eds.; Royal Society of Chemistry: Cambridge, 1991; p 171.