

Dynamical Monte Carlo simulation of surface atomic recombination

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Abstract

We present a dynamical Monte Carlo model for heterogeneous atomic recombination in terms of the theory developed by Fichthorn and Weinberg (1991 *J. Chem. Phys.* **95** 1090) to simulate a Poisson process. The transient and steady-state solutions for the fractional surface coverage of reversible and irreversible sites, which hold physisorbed and chemisorbed atoms, respectively, are compared with the results from a phenomenological mean field model. The effects of low and high activation energies for desorption are investigated. It is observed that the results from the Monte Carlo simulation are in excellent agreement with those obtained from the phenomenological model in the limit of low occupation of adsorption sites.

1. Introduction

The study of the surface kinetics of atomic species, such as N and O atoms, and in particular of the elementary processes leading to heterogeneous recombination, is nowadays an important field of research, since many of the characteristics of plasma reactors are in fact controlled by wall reactions. The need to address the role of surface processes to understand the behaviour of different gas discharges is therefore an issue strongly felt by the plasma physics community. Among many other possible examples, this has been recently pointed out in [1, 2], respectively, for the cases of ECR and DC discharges, and in [3] for the nitrogen afterglow. Consequently, different studies have been realized in the last few years with the purpose of providing a physical insight into the various elementary mechanisms that occur on the surface, while the rates of atomic recombination on various surfaces have been studied in many works using a variety of experimental procedures. The recombination probability, γ , has been measured for the most common atomic species, N, O and H, and different surfaces such as pure silica, Pyrex glass and metal. Due to the large number of papers appeared on the subject, any reference given here would be merely indicative. Nevertheless, the reader may consult, for example, the experimental study [4] and the phenomenological papers [5, 6], which cover most of significant aspects of this subject.

The classic approach to studying surface processes is based upon a deterministic formulation that considers only

average concentrations of the adsorbed species. In this mean field approximation, the various concentrations are represented by continuous functions of time that are ruled by a system of differential equations. Although this method should give an accurate solution in many situations, in some cases a microscopic picture is desirable, in particular by including the effects of fluctuations in density or the spatial correlations between the positions of adsorbed species. For example, mechanisms such as dissociative adsorption of a diatomic molecule on a surface or the reaction rate of a bimolecular surface reaction have an explicit dependence on the local configuration of the surface that cannot be achieved using a classical approach. Monte Carlo methods on a lattice representing the adsorption sites of the different species stand as an obvious alternative to the classical description. Many problems related to surface kinetics have been studied using Monte Carlo methods as computational tools, such as, e.g. dissociative adsorption [7], surface abstraction [8] or the simplest case of adsorption–desorption equilibrium [9].

In most of the Monte Carlo methods the time-evolution of the system is described by a single differential-difference equation for a grand probability function, in which time and the populations of the different species appear all as independent variables. This equation is usually called the master equation and is the one to be solved by the usual Monte Carlo simulations. The first class of Monte Carlo algorithms for surface reactions was introduced by Ziff *et al* [10]. This method is a null-event one, since a site or a pair of sites on the lattice is randomly chosen and then it is assumed that an event may occur or not.

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In order to eliminate null events, another class of algorithms has been developed, the continuous-time Monte Carlo methods. In these methods a specific microprocess is chosen randomly first, and then a site or a pair of sites is chosen only among the group of sites that are in a condition to perform the chosen microprocess. The original algorithm of this type was proposed by Bortz *et al* [11] for spin prediction of an Ising model. A recent application of this formulation to surface reactions has been presented in [12], where a good review of the available literature related to the Monte Carlo treatment of surface kinetics is given as well.

One delicate issue in Monte Carlo algorithms is the connection of Monte Carlo events with real time. This is not an important drawback when the purpose of the study is to obtain the equilibrium properties of a certain system, but of course the situation changes when the method is to be utilized in the study of dynamical phenomena. The usual procedures to consider time in Monte Carlo methods have been tested in different situations, but the question of their accuracy is finally answered empirically on a case-by-case basis. Real-time Monte Carlo methods were introduced in the 1970s by Gillespie [13, 14], for the case of spatially homogeneous reactions. This method does not include any approximations or assumptions, with the exception of the very fundamental definition of the reaction parameters in terms of the transition probabilities. The procedure does not try to solve numerically the master equation, which is never explicitly used, and instead simulates the elementary processes that the master equation describes analytically.

Following this, Fichthorn and Weinberg have presented in [9] the theoretical basis for a dynamical Monte Carlo method able to be utilized in the study of dynamical phenomena, provided a set of conditions are satisfied. In what concerns the treatment of time, the method presented in [9] is similar to that developed in [13, 14], by directly simulating the Markov process and establishing a direct relationship between Monte Carlo time and real time. On the other hand, this approach is a null-event algorithm in the sense of [10], with a similar way of selecting the microprocess to occur and the surface sites involved in it. This dynamical Monte Carlo method furnishes a simple and easy way to implement the description of surface kinetics, as in [10], but with an exact treatment of time. One of the main advantages of this method is precisely that it ensures *a priori* a correct description of the time-evolution of the system and not only of its stationary solution. As long as the definition of the reaction parameters is accepted, the principal source of inaccuracy is simply related to the quality and resolution of the random number generator.

Although the dynamical Monte Carlo method presented in [9] constitutes a powerful tool to study surface kinetics, the system under analysis in that work was very simple, the attainment of an adsorption–desorption equilibrium in a lattice–gas interaction. In this paper, we develop a kinetic model of surface reactions to investigate the application of the dynamical Monte Carlo scheme [9] to surface atomic recombination. Here, we will consider as the working system the recombination of ground-state nitrogen atoms $N(^4S)$ on silica surfaces. As before, the theoretical basis for the dynamical Monte Carlo method is the theory of Poisson processes, in which the time is advanced using a stochastic

algorithm in such a way that no two events may occur simultaneously. Therefore, the method initially developed in [9] is applied here to a much more complicated system, by considering all elementary microscopic processes involved in surface atomic recombination and keeping in mind the various constraints associated with the application of the method. As largely discussed in [9], the dynamical Monte Carlo method is consistent with the master equation if (i) the transition probabilities of the various microscopic events are formulated in such a way that a dynamical hierarchy of transition rates is established with the probabilities satisfying the detailed-balance criterion, (ii) the time increments upon successful events are calculated appropriately in a way that only trials in which an event occurs are considered and (iii) the system is sufficiently large to assure that there exists an effective independence between the various events. In these conditions, an unambiguous correspondence between Monte Carlo time and real time is established and both static and dynamic properties of the system may be obtained.

For the sake of clarity this paper is organized as follows. In section 2, we present the structure of the kinetic model used to study the surface atomic recombination. A phenomenological model for heterogeneous recombination is presented in section 2.1, whereas in section 2.2 the rates of the various elementary processes involved in atomic recombination are derived for the case of recombination of $N(^4S)$ atoms on silica-base surfaces. The applicability of the dynamical Monte Carlo method to atomic recombination is analysed and discussed in section 3. The predicted results obtained from this method are discussed in section 4. Finally, in section 5, we summarize the main conclusions of this paper.

2. Modelling of surface atomic recombination

2.1. Phenomenological description of heterogeneous recombination

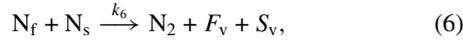
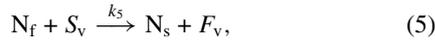
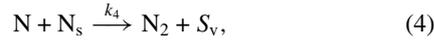
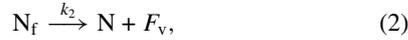
Let us start by analysing the scheme of microscopic events involved in heterogeneous atomic recombination and the kinetic rate balance equations able to describe these phenomena under a phenomenological approach.

It is assumed that the surface is totally covered with adsorption sites, which can hold atoms either reversibly or irreversibly, so that the surface can be regarded as a lattice of adsorption cells. Adsorption in a reversible site is usually associated with physisorption [15, 16], in which the bond between surface and gas particles is due to van der Waals forces, with relatively low particle–surface bond energies (typically $10\text{--}50\text{ kJ mole}^{-1}$), so that the bond is important only at low temperatures ($\sim 100\text{--}300\text{ K}$). As the temperature rises the gas is removed more or less completely from the surface through a mechanism usually termed thermal desorption. In contrast, adsorption in an irreversible site occurs as a result of chemisorption [15, 16] and in this case the bond formed between the atom and the solid surface is a true chemical bond, usually covalent. The atom remains trapped in the potential well of the irreversible site until it may be removed by atomic recombination.

We assume here $a \sim 10^{-8}\text{ cm}$ as a typical radius of an adsorption site, valid for either metal or silica surfaces [6, 17],

which corresponds to a surface density of reversible sites $[F] = 10^{16} \text{ cm}^{-2}$, and that on silica 0.2% of the surface is covered by irreversible sites [4]. We have therefore that the fraction, φ , of the surface covered by irreversible sites is $\varphi = [S]/([F]+[S]) = 2 \times 10^{-3}$, with $[S]$ denoting the surface density of irreversible sites, also termed in [4] as active sites due to the fact that they are the only sites where recombination may occur. Half the distance between two irreversible sites is hence $b \sim a/\sqrt{2} \times 10^{-3} \sim 2 \times 10^{-7} \text{ cm}$.

Our phenomenological model takes into account the following surface mechanisms: physical adsorption and desorption of atoms at reversible sites (1, 2); chemisorption on irreversible sites (3); recombination of chemisorbed atoms with gas-phase atoms (Eley–Rideal (E–R) recombination—(4)); surface diffusion of physisorbed atoms (5); recombination between a physisorbed and a chemisorbed atom, when the first atom after diffusion arrives at an occupied irreversible site (Langmuir–Hinshelwood (L–H) recombination—(6)). The complete list of reactions leading to surface recombination of nitrogen atoms on silica may be written as follows:



where F_v and S_v denote vacant physisorption and chemisorption sites, N_f and N_s physisorbed and chemisorbed nitrogen atoms, and N and N_2 gas-phase atoms and molecules, respectively. We have therefore $[F] = [F_v] + [\text{N}_f]$ and $[S] = [S_v] + [\text{N}_s]$ for the total surface density of each type of sites, either vacant or occupied.

The appropriate rate balance equations for the fractional surface coverage of physisorbed and chemisorbed sites, i.e. $\theta_f = [\text{N}_f]/[F]$ and $\theta_s = [\text{N}_s]/[S]$, dictated by the conjoint playing of reactions (1)–(6), take the form:

$$\frac{d\theta_f}{dt} = (1 - \theta_f)[N]k_1 - \theta_f k_2 - \theta_f(1 - \theta_s)[S]k_5 - \theta_f\theta_s[S]k_6, \quad (7)$$

$$\frac{d\theta_s}{dt} = (1 - \theta_s)[N]k_3 - \theta_s[N]k_4 + \theta_f(1 - \theta_s)[F]k_5 - \theta_f\theta_s[F]k_6, \quad (8)$$

with $[N]$ denoting the atomic gas-phase concentration in cm^{-3} .

In the case where reactions (5) and (6) are ignored, equations (7) and (8) are decoupled and they just express the time-evolution of the fractional coverage of physisorbed and chemisorbed sites by the attainment of adsorption–desorption and chemisorption–recombination equilibria, respectively.

In this simplest case, we get with the initial conditions $\theta_f^0 = \theta_s^0 = 0$ at $t = 0$,

$$\theta_f(t) = \frac{r_1}{r_1 + r_2}(1 - e^{-(r_1+r_2)t}) \quad (9)$$

and

$$\theta_s(t) = \frac{r_3}{r_3 + r_4}(1 - e^{-(r_3+r_4)t}), \quad (10)$$

where $r_1 = [N]k_1$, $r_2 = k_2$, $r_3 = [N]k_3$ and $r_4 = [N]k_4$ denote the corresponding populating and depopulating rates in $\text{site}^{-1} \text{ s}^{-1}$. In [9], only equation (7) with processes (1, 2) has been considered in the discussion of the theoretical foundations of dynamical Monte Carlo simulations in terms of Poisson processes, while in this paper the validity of the same approach is evaluated in a much more complex context.

2.2. Rates of elementary processes

Although the results shown in this paper have been obtained using in certain cases modified rates for reactions (1)–(6), in order to speed up the attainment of a steady-state equilibrium by the dynamical Monte Carlo method, we will discuss here the actual rates usually employed in a DC or HF nitrogen discharge for atomic recombination of $\text{N}(^4\text{S})$ atoms on silica-base surfaces. In fact, the aim of this paper is to discuss the application of the dynamical Monte Carlo simulations to surface recombination, while in a future publication the probabilities, γ , for recombination of $\text{N}(^4\text{S})$ atoms will be quantitatively evaluated and compared with experimental data [2, 4, 5].

The sticking probabilities for adsorption in reversible or irreversible sites are usually expressed as

$$k_i^{0'} = k_i^0 \exp\left(-\frac{E_i}{k_B T_g}\right), \quad (11)$$

with $i = 1$ for physisorption and $i = 3$ for chemisorption, k_i^0 are the steric factors for surface processes involving gas-phase particles, E_i are the activation energies and T_g is the gas temperature near the wall, which we assume here to be equal to the wall temperature, T_w . Once $k_1^{0'}$ and $k_3^{0'}$ are known, the rates r_1 and r_3 , in $\text{site}^{-1} \text{ s}^{-1}$, are simply given by

$$r_1 = [N]k_1 = \frac{k_1' \phi_N}{[F]} \quad (12)$$

and

$$r_3 = [N]k_3 = \frac{k_3' \phi_N}{[S]}, \quad (13)$$

where $\phi_N = \langle v_N \rangle [N]/4$, with $\langle v_N \rangle = \sqrt{8KT_g/\pi M_N}$, denotes the flux of $\text{N}(^4\text{S})$ atoms to the surface, and $k_1' = k_1^{0'}(1 - \varphi)$ and $k_3' = k_3^{0'}\varphi$ are the sticking probabilities corrected for the fractions of the surface covered by physisorption and chemisorption sites, respectively. Here, for the sake of simplicity we assume as in [4] that $k_i^0 = 1$ and $E_i = 0$, both for reversible and irreversible sites, so that $k_1^{0'} = k_3^{0'} = 1$. Note that in this case we have $r_1 = r_3$.

On the other hand, for thermal desorption of reversible sites, we use

$$r_2 = k_2 = \nu_d \exp\left(-\frac{E_d}{k_B T_w}\right), \quad (14)$$

where $\nu_d = 10^{15} \text{ s}^{-1}$ denotes the frequency factor and $E_d = 51 \text{ kJ mole}^{-1}$ the activation energy for desorption of physisorbed N atoms from pure silica [4]. As stated before the desorption from irreversible sites does not occur.

The gas-phase atoms impinging on an occupied irreversible site with a chemisorbed atom may react, resulting in a recombined molecule. This is the so-called E–R mechanism, whose rate, per second and occupied irreversible site, is given by

$$r_4 = [N]k_4 = r_3 k'_4, \quad (15)$$

where r_3 is the rate for chemisorption and k'_4 is the recombination probability,

$$k'_4 = k_4^0 \exp\left(-\frac{E_r}{k_B T_w}\right), \quad (16)$$

with $k_4^0 = 1$ and $E_r = 14 \text{ kJ mole}^{-1}$ [4] denoting, respectively, the steric factor and the activation energy for recombination of $\text{N}(^4\text{S})$ atoms. It is worth noting at this point that according to [4] and using the model proposed in [18], the activation energy for desorption of a chemisorbed atom is roughly given by $\sim E_r/0.055 \simeq 290 \text{ kJ mole}^{-1}$, with E_r denoting the activation energy for recombination and $E_r/0.055$ the energy of the atom–surface bond. With this binding energy the chemisorbed atoms can desorb only at relatively high temperatures $T_w \sim 1000 \text{ K}$ [4], so that here we will assume that these atoms are held irreversibly on the surface and they may be removed only by recombination.

Let us consider now the diffusion of physisorbed atoms on the surface under a phenomenological approach. As is well known, if the diffusion coefficient, D_s , is independent of the concentration, the solution to Fick's second law is a Gaussian. With the initial condition that at $t = 0$ all particles N_T are located at $x = y = 0$ on the surface [19], the particle density assumes the form

$$n(x, y, t) = \frac{N_T}{4\pi D_s t} \exp\left(-\frac{x^2 + y^2}{4D_s t}\right). \quad (17)$$

The mean-square displacement of an atom in time t is therefore given by $\Lambda^2 = \langle x^2 \rangle + \langle y^2 \rangle = 4D_s t$. Since the distance between two neighbouring reversible adsorption sites is twice the radius of the cell, $a \sim 10^{-8} \text{ cm}$, we obtain with $\Lambda = 2a$ the characteristic time for surface diffusion, $\tau_D = a^2/D_s$. Using as in [4, 17] the surface diffusion coefficient obtained from an Arrhenius plot, τ_D may be written as follows:

$$\tau_D = \nu_D^{-1} \exp\left(\frac{E_D}{k_B T_w}\right) \quad (18)$$

with $\nu_D = 10^{13} \text{ s}^{-1}$ and $E_D = 0.5E_d$ denoting the frequency factor and the activation energy for surface diffusion of N atoms on silica [4].

The rate of surface diffusion to an adjacent cell that should be used in Monte Carlo simulation is simply given by τ_D^{-1} ; however, this rate does not correspond to the rate of reaction (5) that must be considered in the set of rate balance equations (7) and (8). Reaction (5) describes, in fact, the conjoint action of two distinct events: (i) surface diffusion of a physisorbed atom into an irreversible site localized at a farther distance; (ii) possibility of the occurrence of recombination in the case of occupancy of the site with a chemisorbed atom. $k_5[S_v]$ being the rate of occupancy of a vacant irreversible site due to diffusion, per second and physisorbed atom, the probability of an atom being chemisorbed on an irreversible site, before being desorbed back to the gas-phase, or recombining, is given by $k'_5 = k_5[S_v]\tau_N$, where

$$\tau_N = (k_2 + k_5[S_v] + k_6[N_s])^{-1} \quad (19)$$

denotes the mean residence time of physically adsorbed atoms ($\tau_N \sim k_2^{-1}$, for $T_w > 300 \text{ K}$). Defining the rate of populating an irreversible site, in $\text{site}^{-1} \text{ s}^{-1}$, due to surface diffusion as $r_5 = k_5[F]$, and therefore the rate for depopulating a reversible site as $k'_5[S] = r_5[S]/[F]$ (see equations (7) and (8)), we get

$$r_5 = \frac{k'_5 [F]}{\tau_N [S_v]}. \quad (20)$$

Setting k'_D as the probability that a physisorbed atom will diffuse to a vacant or occupied irreversible site, $k'_D = k'_5[S]/[S_v]$, we can still write (20) in the form

$$r_5 = \frac{k'_D [F]}{\tau_N [S]}. \quad (21)$$

As a result of the Gaussian profile for the density, the mean surface diffusion distance of a physically adsorbed atom before desorption is given by $\Lambda_D = \sqrt{4D_s \tau_N}$, with $D_s = a^2/\tau_D$ and $\tau_N \sim k_2^{-1}$ being the mean residence time of atoms on the surface, so that using equations (14) and (18) one obtains

$$\Lambda_D^2 = 4 \frac{\nu_D}{\nu_d} a^2 \exp\left(\frac{E_d - E_D}{k_B T_w}\right). \quad (22)$$

The probability that atoms will reach an irreversible site by diffusion is evaluated in [20] by solving the diffusion equation. Here, as in [4] we may assume that each irreversible site is surrounded by a collection zone of radius $\Lambda_D < b$, with $b \sim 2 \times 10^{-7} \text{ cm}$ denoting half the distance between two irreversible sites, and that one-fourth of the atoms impinging on the surface within the collection zones reach irreversible sites before desorption. The other three-fourths of the atoms migrate towards farther distances. We may write therefore the probability that a physisorbed atom will diffuse to an irreversible site as

$$k'_D = \frac{1}{4} \frac{\Lambda_D^2 - a^2}{b^2 - a^2}, \quad (23)$$

where $(\Lambda_D^2 - a^2)/(b^2 - a^2)$ is the probability that a physisorbed atom has been physisorbed within the collection zone. When $\Lambda_D \gg a$, we may still write (23) using (22) in the form

$$k'_D \simeq \frac{\nu_D [S]}{\nu_d [F]} \exp\left(\frac{E_d - E_D}{k_B T_w}\right). \quad (24)$$

Once k'_D is known, r_5 may be then calculated using equation (21).

The rate of recombination due to the L–H mechanism, which should be used in the set of rate balance equations (7) and (8), can be calculated in a way similar to the calculation of r_5 . The rate of arrival of physisorbed atoms at an occupied irreversible site, per second and physisorbed atom, and there recombining, is $k_6[N_s]$, so that the probability of this occurrence is $k'_6 = k_6[N_s]\tau_N$. The rate $r_6 = k_6[F]$, defined in this form for the same reasons as r_5 , is given by

$$r_6 = \frac{k'_6 [F]}{\tau_N [N_s]}. \quad (25)$$

Since the probability k'_6 is equal to the product of the probability that a physically adsorbed atom will diffuse to an occupied irreversible site and the recombination probability,

$$k'_6 = k'_D \frac{[N_s]}{[S]} k'_4, \quad (26)$$

we still have

$$r_6 = \frac{k'_D [F]}{\tau_N [S]} k'_4. \quad (27)$$

We note that r_5 and r_6 have been defined as $k_5[F]$ and $k_6[F]$, respectively, and not making use of similar expressions with the total surface density of irreversible sites $[S]$, so that the rates of time-evolution of θ_f are in fact $r_5[S]/[F]$ and $r_6[S]/[F]$ (see equation (7)).

Finally, the mean residence time of physisorbed atoms on the surface is a function of the partial coverage of chemisorbed sites, θ_s . Using equations (21) and (27) in equation (19), we obtain

$$\tau_N = \left(k_2 + \frac{k'_D}{\tau_N} (1 - \theta_s) + \frac{k'_D k'_4 \theta_s}{\tau_N} \right)^{-1} \quad (28)$$

and therefore

$$\tau_N = \frac{1 - k'_D + k'_D (1 - k'_4) \theta_s}{k_2}. \quad (29)$$

τ_N has its minimum and maximum values at $\theta_s = 0$ and $\theta_s = 1$, respectively, and it is of the order $\sim k_2^{-1}$.

3. Dynamical Monte Carlo method applied to heterogeneous recombination

As discussed in [9], the dynamical Monte Carlo method provides a description of both the static and dynamic properties of the system. Further, a relationship between Monte Carlo time and real time is clearly established in the framework of this method. In order that a consistent simulation and time correspondence are achieved, the Monte Carlo time step must be derived from the transition probabilities of the various microscopic events, with these probabilities formulated as rates with physical meaning. The time-evolution is accomplished then in a scale at which no two events occur simultaneously and the algorithm used must be consistent with the theory of Poisson processes.

In a Poisson process, any particular event that becomes possible at time t can potentially occur at any later time

$t + \Delta t$, with a uniform probability based on its rate and independent of the events before time t . Consequently, in the dynamical Monte Carlo approach a chronological sequence of distinct events, $\mathbf{E} = \{e_1, e_2, \dots, e_k\}$, separated by certain interevent times should be created. Both the chain of events and the corresponding inter-event times should be obtained from probability distributions $\mathbf{W} = \{w_1, w_2, \dots, w_k\}$ weighting appropriately all possible outcomes. The transition probabilities should be constructed in terms of the average transition rates, $\mathbf{R} = \{r_1, r_2, \dots, r_k\}$, by creating a dynamical hierarchy of transition probabilities, as $w_i = r_i/\xi_{\max}$, with $\xi_{\max} \geq \sup\{r_i\}$. If the system consists of N_T species, they must be partitioned among the various possible transition events as $N_T = \{n_1, n_2, \dots, n_k\}$, where n_i is the number of species capable of undergoing a given event e_i with probability w_i . The Monte Carlo algorithm should be able to select randomly a certain event, among the various possible events available at each time.

If a sufficiently large system is utilized to ensure that the independence of various events is achieved, the Monte Carlo algorithm effectively simulates a Poisson process. The correspondence between Monte Carlo time and real time is fully achieved, provided that at each trial j at which an event is realized, the time is updated with an increment τ_j selected from an exponential distribution of the type

$$\tau_j = -\frac{1}{\lambda} \ln(U), \quad (30)$$

where U is a uniform random number between 0 and 1, and $\lambda = \sum_i n_i r_i$ is the total rate, in s^{-1} , for the occurrence of an event of any type for the total ensemble of sites, either occupied or vacant. It is worth remembering at this point that equation (30) is consistent with the fact that the probability of an event of frequency ν occurring after a time t is given by $P(t) = \exp(-\nu t)$. The time advance defined by equation (30) is similar to the one proposed in [13, 14] for the case of homogeneous volume chemical reactions. The present algorithm is different though, in keeping track of the local configuration of the surface, as well as in the way the events taking place are selected. In this respect, the method used in this study is close to the null-event algorithms developed from [10], as will be seen below.

Let us consider now the system under analysis in this paper. The various microscopic events to be considered are: (i) physical adsorption at reversible sites with the rate r_1 given by equation (12); (ii) desorption of physisorbed atoms with the rate r_2 given by equation (14); (iii) chemical adsorption at irreversible sites with the rate r_3 given by equation (13); (iv) recombination E–R between a gas-phase atom and a chemisorbed atom with the rate r_4 given by equation (15); (v) diffusion of physisorbed atoms to one of the four nearest-neighbouring sites with the rate $r_D = \tau_D^{-1}$ given by equation (18); (vi) recombination L–H between a diffusing atom and an adsorbed atom, either chemisorbed or physisorbed, in the case where the first atom diffuses to an occupied site, with the probability k'_4 given by equation (16).

The last two steps are not considered here in exactly the same manner as in the phenomenological model (i.e. through the rates r_5 and r_6). In the set of rate balance equations, we assume that the L–H recombination occurs when a physisorbed

atom, after diffusion, arrives at an occupied irreversible site, i.e. near a chemisorbed atom, whereas in Monte Carlo simulation the recombination L–H may occur either with a chemisorbed or a physisorbed atom. In the Monte Carlo simulation two physisorbed atoms may recombine, depending on the probability k'_4 , and if the recombination does not take place the diffusing atom is desorbed from the surface. There exists, therefore, a reduction of the average time spent by the physisorbed atoms on the surface, which leads to an underestimation of the surface coverage of physisorbed atoms, θ_f , relative to the phenomenological model. As a result of the overall surface kinetics, θ_s may be underestimated as well. However, the differences between the results from the two models are vanishingly small for low surface coverage.

We should note however that the probability k'_4 for L–H recombination on reversible sites is assumed here to be the same as for irreversible sites, which probably leads to an underestimation of the effects of recombination between two physisorbed atoms and, consequently, to a diminution of the magnitude of the differences between the two models. For an activation energy of desorption, $E_d = 51 \text{ kJ mole}^{-1}$ (see equation (14)), the corresponding activation energy for recombination may be assumed to be of the order $E_r^* \simeq 0.055 \times 51 = 2.8 \text{ kJ mole}^{-1}$ [18], which makes the recombination probability given by equation (16) in this case much larger than that for recombination on irreversible sites. In contrast to L–H recombination, the E–R mechanism of recombination is considered between gas-phase and chemisorbed atoms only in both models.

Figure 1 shows the flow diagram of the algorithm used for simulating the surface recombination of $\text{N}(^4\text{S})$ atoms with a two-dimensional lattice of $l \times l$ sites. A trial in this algorithm begins when one site (i, j) and a uniform number s between 0 and 1 are generated randomly. First, it is verified if the site is occupied or vacant. If the site is vacant, the character of the site is analysed. In the case of a reversible site, physical adsorption occurs if $s \leq w_1$, with w_1 denoting the probability this occurrence, whereas in the case of an irreversible site chemisorption may occur if $s \leq w_3$, w_3 now being the probability of chemisorption.

Let us consider now the right branch of the flow diagram. When the site is occupied, we must start by analysing if the site holds a physisorbed or a chemisorbed atom. In the first case, the atom is removed if $s \leq w_2$, with w_2 denoting the probability of thermal desorption of a physisorbed atom. In the opposite case, $s > w_2$, we must check if the atom may diffuse to one of the four nearest-neighbouring sites by regarding if $s \leq (w_2 + w_D)$, where w_D denotes now the probability of diffusion obtained from the rate $r_D = \tau_D^{-1}$ given by equation (18). In the favourable case, the atom is removed from the site (i, j) and added to one of the four nearest-neighbouring sites (i', j') randomly chosen. Now, we need to check if this new site is occupied or vacant. In the case of vacancy, the atom passes to occupy the new site, whereas in the case of occupancy of the site (i', j') , either with a physisorbed or a chemisorbed atom, we must check if L–H recombination may occur. For this purpose, a second random number, r , between 0 and 1 is generated and compared with the probability k'_4 given by equation (16). L–H recombination occurs and both atoms are removed from the surface if $r \leq k'_4$. In contrast, only one atom is desorbed and the other remains on the site if $r > k'_4$.

Finally, in the case of occupancy of the site (i, j) with a chemisorbed atom, E–R recombination occurs if $s \leq w_4$, with w_4 denoting the probability of E–R recombination between a gas-phase and a chemisorbed atom obtained from r_4 given by equation (15).

In the algorithm of figure 1, the transition probabilities are created from a dynamical hierarchy of transition probabilities, as $w_i = r_i / \xi_{\max}$, with $\xi_{\max} \geq \sup\{r_1, r_3, r_4, r_2 + r_D\}$. After successful realization of an event at trial j the time is advanced by an increment τ_j selected from the exponential distribution (30), with the total rate, λ , for time advancing, in s^{-1} , given by

$$\lambda = (l \times l)[(1 - \theta_f)r_1 + (1 - \theta_s)r_3 + \theta_s r_4 + \theta_f(r_2 + r_D)]. \quad (31)$$

It is worth remembering here that the populating and depopulating rates, r_i , are expressed in $\text{site}^{-1} \text{s}^{-1}$, while $l \times l$ is the total number of sites in the two-dimensional lattice.

The procedure just described provides just one possible realization of the stochastic time-evolution of the system. In order to get a statistically complete picture, it should be desirable to carry out several independent realizations of the temporal evolution of the system, each starting with the same initial conditions and proceeding to the same time t . The results of the different runs should then be averaged in a proper way [12]. However, if the lattice used is big enough, then the results will be significant even for a single run [13].

Let us still mention that, as a first test of the dynamical Monte Carlo method, we have calculated the time-evolution of the fractional coverages θ_f and θ_s in the absence of diffusion, $r_D = 0$. In this limit case, $\theta_f(t)$ and $\theta_s(t)$ are given by equations (9) and (10), respectively. The dynamical Monte Carlo results obtained matched perfectly these two expressions.

4. Results and discussion

For the input parameters given in section 2 and assuming $T_g = 500 \text{ K}$ and $T_w = 350 \text{ K}$ for the gas and wall temperatures, respectively, and a gas-phase atomic density $[N] = 10^{15} \text{ cm}^3 \text{ s}^{-1}$, we have $r_1 = 2.17 \times 10^3 \text{ site}^{-1} \text{ s}^{-1}$, $r_2 = 2.45 \times 10^7 \text{ site}^{-1} \text{ s}^{-1}$, $r_3 = 2.17 \times 10^3 \text{ site}^{-1} \text{ s}^{-1}$, $r_4 = 1.76 \times 10^1 \text{ site}^{-1} \text{ s}^{-1}$ and $r_D = 1.56 \times 10^9 \text{ site}^{-1} \text{ s}^{-1}$, while the recombination probability of the L–H mechanism is $k'_4 = 8.14 \times 10^{-3}$. Unfortunately, this set of input parameters corresponds to a low surface coverage of the reversible sites. Even when diffusion is ignored, the fractional coverage of reversible sites as $t \rightarrow \infty$ is of the order $\theta_f = r_1 / (r_1 + r_2) \simeq 8.86 \times 10^{-5}$ (see equation (9)), so that either a huge lattice, $l \times l$, or the average over different realizations of the system becomes necessary to avoid significant fluctuations in the results, which produces an increase in computational time. Due to this fact and keeping in mind that the purpose of this paper is to discuss the applicability of the dynamical Monte Carlo method to the task of heterogeneous atomic recombination, the determination of actual probabilities for recombination being left to a forthcoming paper, we will present here results for a simulation in which certain rates have been modified in order to shorten the attainment of a steady-state equilibrium.

Accordingly, figures 2(a) and (b) show the fractional surface coverage of both reversible θ_f and irreversible θ_s sites,

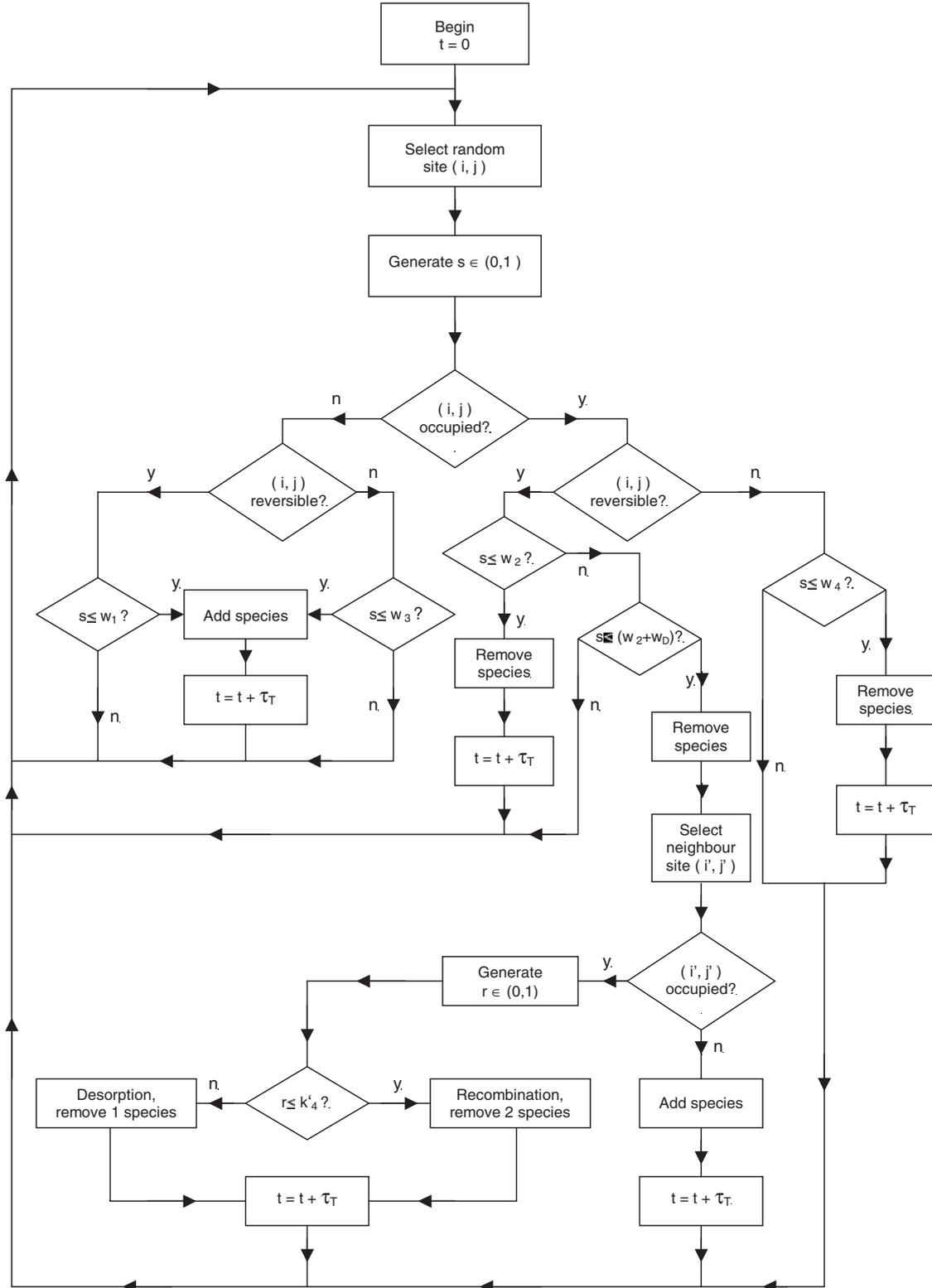


Figure 1. Flow diagram for simulating the approach to and the attainment of equilibrium for the surface coverages of reversible and irreversible sites in heterogeneous atomic recombination.

as a function of real time, starting from an empty surface at time $t = 0$, as the following changes in the input parameters are considered: $E_d = 51 \times 1.3 = 66.3 \text{ kJ mole}^{-1}$; $E_D = 0.5 \times 66.3 = 33.2 \text{ kJ mole}^{-1}$; $\nu_D = 10^{11} \text{ s}^{-1}$. The corresponding modified rates are $r_2 = 1.27 \times 10^5 \text{ site}^{-1} \text{ s}^{-1}$ and $r_D =$

$1.13 \times 10^6 \text{ site}^{-1} \text{ s}^{-1}$, while r_1, r_3, r_4 and k'_4 are not changed. In this case a 750×750 lattice may be used in the calculations. The coverages θ_f and θ_s are defined with respect to the total number of sites of each type. The dashed curves correspond to the results of the phenomenological model. The differences

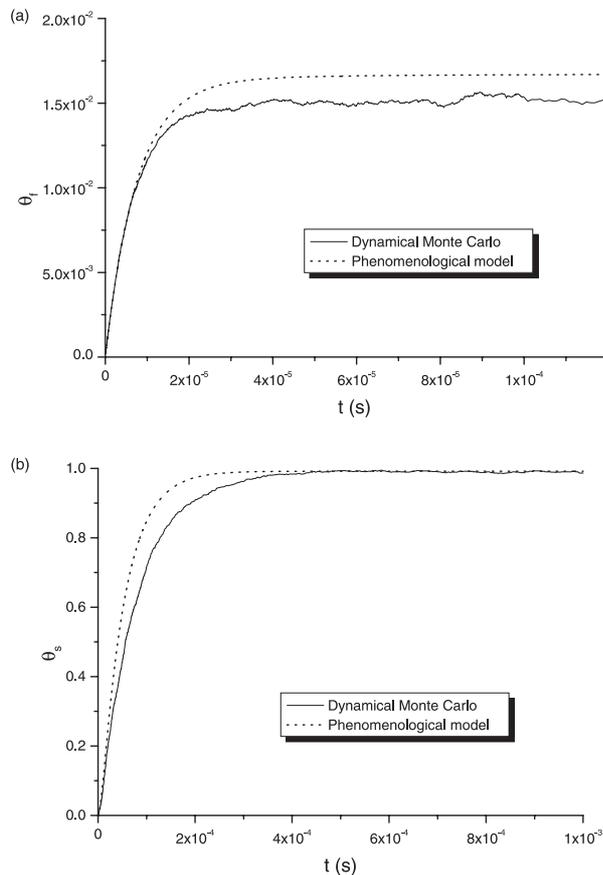


Figure 2. Fractional surface coverage of reversible (a) and irreversible (b) sites, termed here as θ_f and θ_s , respectively, as a function of time, using a dynamical Monte Carlo simulation (—) and a phenomenological model (---), assuming a desorption energy $E_d = 66.3 \text{ kJ mole}^{-1}$.

between the results of both models are due to the hypothesis made concerning the interactions between two physisorbed atoms. We recall here that in the phenomenological model two physisorbed atoms do not interact with each other, while in Monte Carlo when a physisorbed atom arrives to a reversible site already occupied, either the two physisorbed atoms may recombine or one is desorbed, the other sticking on the surface. The interactions between physisorbed atoms have the effect of reducing the average time spent by these particles at the surface. This is why the phenomenological model overestimates the coverage θ_f (and, in some cases, θ_s as well).

The differences between the results from the two models become vanishingly small in the case of lower coverage of physisorbed atoms, which may be obtained by increasing the rate, r_2 , of thermal desorption. Figures 3(a) and (b) show the fractional coverage θ_f and θ_s for the same conditions as in figures 2(a) and (b), except that E_d is now $62.2 \text{ kJ mole}^{-1}$ and E_D is also modified accordingly ($r_2 = 5.18 \times 10^5 \text{ site}^{-1} \text{ s}^{-1}$ and $r_D = 2.28 \times 10^6 \text{ site}^{-1} \text{ s}^{-1}$). In the case of a lower energy for desorption, θ_f is lower and encounters between two physisorbed atoms are more scarce, so that the inclusion or ignoring of such processes has only a very small effect on the results.

Through the example shown here, we verify that Monte Carlo simulations may be utilized to simulate the

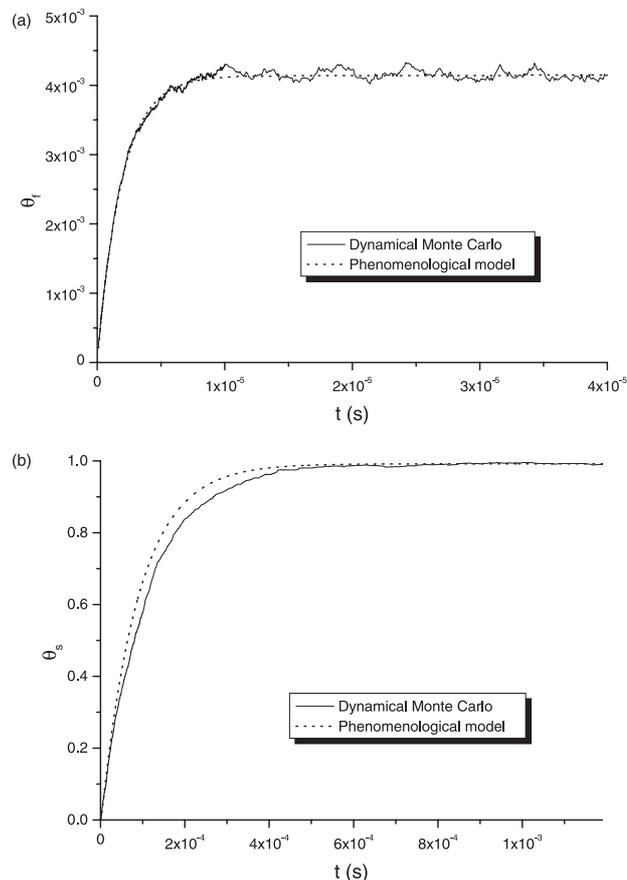


Figure 3. As in figure 2 but with $E_d = 62.2 \text{ kJ mole}^{-1}$.

dynamical evolution of a lattice-gas system associated with heterogeneous atomic recombination. There is an excellent agreement between the results from the Monte Carlo and phenomenological models, both in the approach to equilibrium and in the steady-state fractional surfaces coverage, in spite of a number of minor differences between them. The amplitude of the fluctuations depends on the number of events averaged, so that the dimension of the lattice should be determined by the steady-state surface coverage that will be attained. For the present example, the fractional surface coverage of reversible sites is $\theta_f(\infty) \sim 1.5 \times 10^{-2}$ and $\sim 7 \times 10^{-3}$ in figures 2(a) and 3(a), respectively, and may be obtained using a 750×750 two-dimensional lattice.

The algorithm used for Monte Carlo simulation considers that a physisorbed atom may diffuse to one of the four nearest-neighbouring sites and, in the case of occupancy of this new site, the diffusing atom may either recombine or desorb, depending on the probability k'_4 . This assumption leads to an underestimation of the surface coverage θ_f , since in the case where recombination does not take place the physisorbed atom cannot continue sticking on the surface. In order to evaluate the effects of such an assumption, figures 4(a) and (b) show the fractional coverage θ_f and θ_s calculated for the same input parameters as in figures 3(a) and (b) but supposing now that a physisorbed atom that does not recombine is not immediately lost to the gas-phase. The physisorbed atom will remain on the surface, diffusing to a neighbouring site. If this new site is occupied, the diffusing atom will attempt recombination

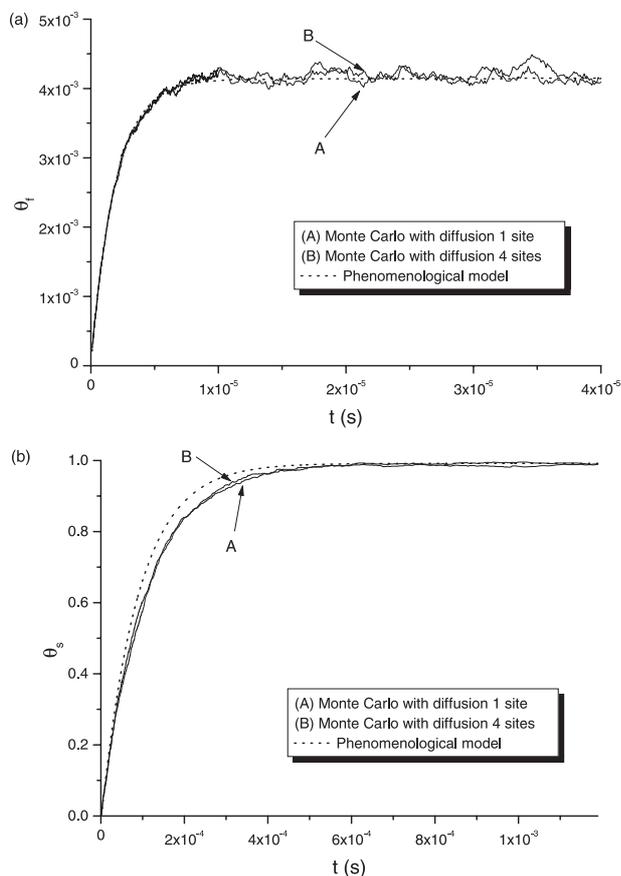


Figure 4. Fractional surface coverage of reversible (a) and irreversible (b) sites, θ_f and θ_s , respectively, as a function of time, using a dynamical Monte Carlo simulation assuming that one attempt (curve A) and four attempts (curve B) are made for recombination (see text). The broken curve is our phenomenological model. The results are obtained for $E_d = 62.2 \text{ kJ mole}^{-1}$.

a second time. The scheme is repeated for a maximum of four attempts, at which point it definitively desorbs if the recombination has not occurred.

Figure 4(a) shows that no significant effects are observed when we pass from our standard model with only one attempt for recombination to the four-attempts case. However, larger differences are obtained if we decrease the rates for thermal desorption, since in this case the mean residence time for physisorbed atoms on the surface is controlled by diffusion rather than by desorption; that is, we have no more $\tau_N \sim k_2^{-1}$ in equation (29). Figures 5(a) and (b) show the fractional surface coverages θ_f and θ_s assuming, for comparison, one, two and four attempts for recombination before a physisorbed atom is definitively desorbed, in the case of a relatively high desorption energy, $E_d = 76.5 \text{ kJ mole}^{-1}$, with E_D modified accordingly. In this case we have a low desorption rate, $r_2 = 3.83 \times 10^3 \text{ site}^{-1} \text{ s}^{-1}$. With such a low r_2 rate, $\theta_f(\infty) \sim 0.10$, ~ 0.19 and ~ 0.28 when we assume one, two and four attempts, respectively, for recombination. For these high values of the surface coverage θ_f , ‘collisions’ between two physisorbed atoms are likely to occur. These encounters between two physisorbed atoms, which in the Monte Carlo formulation lead to the loss of one or two physisorbed atoms to the gas-phase, are not taken into account in the phenomenological model.

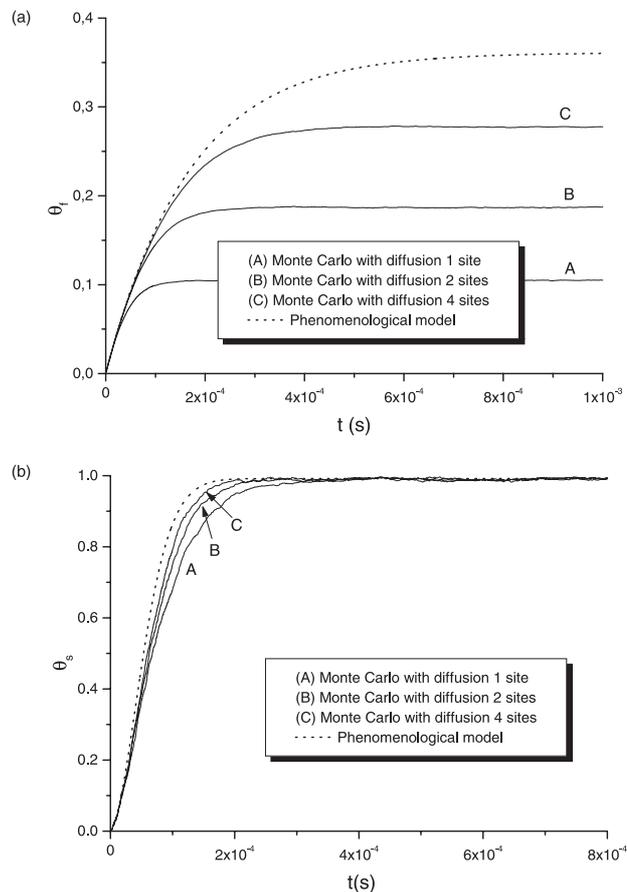


Figure 5. Fractional surface coverages of reversible (a) and irreversible (b) sites, θ_f and θ_s , respectively, as a function of time, using a dynamical Monte Carlo simulation assuming that one (curve A), two (curve B) and four attempts (curve C) are made for recombination (see text). The broken curve is our phenomenological model. The results are obtained for $E_d = 76.5 \text{ kJ mole}^{-1}$.

This is why the latter model presents now appreciably higher values for the fractional coverage θ_f .

5. Conclusions

We have shown that a Monte Carlo method of the same type as that formulated by Fichthorn and Weinberg [9] may be used to simulate the sequence of elementary surface processes involved in heterogeneous atomic recombination. Both the transient and stationary solutions for the surface coverage of two types of adsorption sites, holding physisorbed and chemisorbed atoms on the surface, are well described in the present Monte Carlo formulation. The Monte Carlo results are compared with those from a phenomenological model. In spite of a number of conceptual differences concerning the diffusion and recombination of physisorbed atoms, only minor differences are found in the results, with the exception of the limit of a very high occupation of physisorption sites.

The effect of varying the mean residence time of physisorbed atoms has been investigated by changing the activation energy for desorption, from a relatively low value in which the residence time is mainly determined by thermal desorption, until the opposite situation of a high activation

energy where the permanence of the atoms on the wall is determined by the hypotheses made for diffusion.

The dynamical Monte Carlo method presented in this work is a real-time, exact way of treating time-dependent surface kinetics. It stands as an alternative to the traditional procedure of numerically solving the deterministic reaction rate equations. Even if the differences between the classic and stochastic formulations are in many cases purely academic, the stochastic approach is superior, since it is always valid whenever the deterministic approach is, and it is sometimes valid when the deterministic approach is not.

The purpose of this paper has been fully achieved since we have shown that a dynamical Monte Carlo method can be used to describe surface atomic recombination, provided a certain number of conditions are satisfied. In particular, this is true if: the transition probabilities are formulated appropriately in terms of the transition rates; the time increments correspond to a scale where no two events occur simultaneously; and the system is sufficiently large so that the various events are independent. Although a specific working system has been considered for illustration of the method, namely the recombination of ground-state nitrogen atoms $N(^4S)$ on silica-base surfaces, the results shown here are merely indicative because some of the rates have been modified in order to speed up the attainment of computational convergence.

Future work will concentrate on the derivation of actual probabilities, γ , of recombination in the same system, and a comparison with experiment will be carried out. The advantage of using a Monte Carlo formulation will be explored, for instance by taking into account the influence of the surface configuration on the choice of microprocess. Nevertheless, the description of the various elementary processes playing a role in heterogeneous recombination as well as the validity of the method is already satisfactory as it stands in this paper.

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