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# Influence of surface stress on reconstruction processes: analytical study and simulation by the Monte Carlo method

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**Abstract.** A model is developed to study the effect of site–site and adsorbate–site interactions on a substrate with spontaneous and adsorbate-induced surface reconstruction. The analytical results obtained by the application of the mean field approximation are compared with those obtained by Monte Carlo simulation. The behaviour of the adsorbate–substrate system is analysed as a function of the interaction between sites and that between a site and the adsorbate in its surroundings as a measure of surface stress.

## 1. Introduction

The effects of substrate re-accommodation during surface reconstruction on surface processes, particularly those related to catalytic processes such as adsorption and diffusion, reaction and desorption of adsorbed species, have given rise to several models for the study of surface reconstruction [1–9]. The application of modern experimental techniques and the development of novel theories for the analysis of results have contributed to the understanding of this highly complex phenomenon [10–16].

In recent years, attention has been focused on adsorbate-induced reconstruction, which seems to have direct implications on the kinetics of other surface processes [17–21]. A large amount of experimental evidence supports the existence of a close relationship between adsorptivity, surface roughness and catalytic activity. Numerous efforts have been made to satisfactorily account for these phenomena.

Somorjai has summarized as follows what he calls the ‘three enigmas of surface science’:

- (a) Sites of strong chemisorption are also sites with strong catalytic activity.
- (b) The breaking of chemical bonds in adsorbed species takes place within a very narrow temperature range which is typical of the adsorbate–substrate system.
- (c) This range changes at low temperatures in the presence of highly adsorptive sites or very rough surfaces.

In this respect, Somorjai and Levine have proposed a model of chemisorption-induced substrate reconstruction (CISRM) [22, 23]. This model has been studied by other researchers by means of the Monte Carlo simulation technique [24, 25] and results have been compared with Somorjai’s conclusions.

The present work develops a model for the study of surface reconstruction focusing on phenomena taking place at microscopic level on the surface. The model will be described in general and the ‘stress effect’ on both spontaneous and adsorbate-induced reconstruction

will be analysed. Such an effect is caused by the fact that sites on a reconstructing surface do not behave independently from each other. Rather, their state depend on the situation of the adsorbate–substrate system in their surroundings.

Two situations in which a site reconstruction process is affected by its surroundings will be discussed:

- (a) the state of a site is strongly influenced by the state of neighbouring sites;
- (b) the state of a site is affected by the presence of adsorbed species on neighbouring sites.

Analytical solutions will be proposed by means of a mean field approximation and compared to Monte Carlo simulation. The latter method is widely used in surface physical chemistry and is being increasingly employed for the study of surface reconstruction in particular.

## 2. Description of the model

The model here presented is based on the assumption that surface reconstruction is an activated process by which every site in the crystalline lattice can reversibly pass from an initial state  $S_1$  to a final state  $S_2$ . The initial state corresponds to a site of the normal surface and the final one to a site of the reconstructed surface.

This ‘reaction’ of the surface sites has an activation energy  $E_{12}$  for reaction  $S_1 \rightarrow S_2$  and  $E_{21}$  for reaction  $S_2 \rightarrow S_1$ . The transition from one state to the other may involve a geometrical and/or energetical change of the surface site. For instance, the change of state may involve a shift or change of the site adsorptive potential or catalytic activity.

According to this model, the reconstruction kinetics is governed by a first order reversible process:



where  $k_{12}$  and  $k_{21}$  are the rates of both reactions, expressed as:

$$k_{12} = v_{12} \exp(-E_{12}/RT) \quad (2)$$

$$k_{21} = v_{21} \exp(-E_{21}/RT) \quad (3)$$

where  $v_{ij}$  is a frequency factor or pre-exponential coefficient,  $R$  is the universal constant of gases and  $T$  is the temperature of the system.

If it is assumed that a site reconstruction process is induced by the adsorbate and depends on its surroundings, the activation energy of both reactions will depend on the site and its occupation state, as well as on the neighbouring sites and their occupation state. Therefore, the total activation energy for the reconstruction process of a particular site is expressed as:

$$E_{12} = E_{12(0)} + E_{12ad} + E_{12sur} + E_{12adsur} \quad (4)$$

where  $E_{12(0)}$  is the activation energy for the spontaneous reconstruction of the empty site without considering its surroundings.  $E_{12ad}$  is the contribution by the presence of an adsorbed species. If negative it means that the adsorbate favours the site reconstruction, and if positive it implies that the adsorbate stabilizes the initial state.  $E_{12sur}$  is the contribution by the site surroundings and depends on the reconstruction state of the neighbouring sites, with the same sign convention as in the previous case.  $E_{12adsur}$  is the contribution by adsorbed species on the site surroundings; this is to say, the sum of the interactions between the site and the adsorbates on neighbouring sites. The same sign convention applies here too.

A similar analysis can be done for the reverse reaction:

$$E_{21} = E_{21(0)} + E_{21ad} + E_{21sur} + E_{21adsur} \quad (5)$$

with similar interpretations for each term.

### 3. Case 1: spontaneous reconstruction without adsorbate influence

If the reconstruction is not induced by the adsorbate and if the sites are independent from their surroundings, we have:

$$\begin{aligned} E_{12} &= E_{12(0)} \\ E_{21} &= E_{21(0)}. \end{aligned}$$

Under these conditions the rate at which the surface is reconstructed is determined by the following expression:

$$dF_2/dt = -dF_1/dt = k_{12}F_1 - k_{21}F_2 \quad (6)$$

where  $F_1$  is the fraction of the lattice sites which have not been reconstructed yet (state S1) and  $F_2$  is the fraction of the reconstructed sites (state S2).

For a given temperature, the fraction of reconstructed sites is taken from the expression corresponding to equilibrium:

$$k_{12}F_{1eq} = k_{21}F_{2eq}. \quad (7)$$

Since

$$F_{1eq} = 1 - F_{2eq} \quad (8)$$

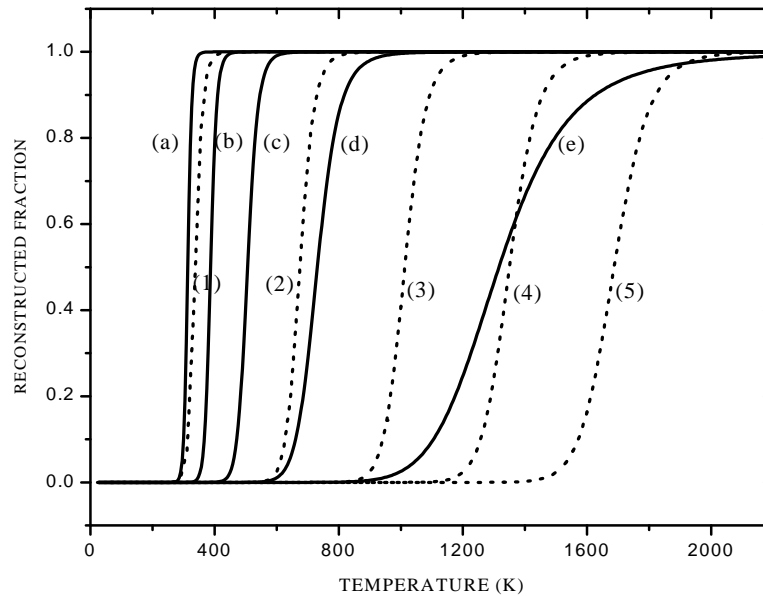
we obtain

$$(1 - F_{2eq})/F_{2eq} = k_{12}/k_{21} = K_{eq} = \nu_{12}/\nu_{21} \exp(\Delta E/RT) \quad (9)$$

with

$$\Delta E = E_{21} - E_{12}. \quad (10)$$

Figure 1 shows the evolution of the surface as a function of temperature, for different values of  $\Delta E$  and  $\nu_{12}/\nu_{21}$ .



**Figure 1.** Evolution of the system equilibrium for sites with no interaction with their surroundings without adsorbed species on the surface. The solid curves show the behaviour of surfaces for different  $\nu_{12}/\nu_{21}$  ((a)  $10^{20}$ ; (b)  $10^{16}$ ; (c)  $10^{12}$ ; (d)  $10^8$ ; (e)  $10^4$ ), values for which  $\Delta E$  is kept constant at 30 kcal. The dotted curves correspond to different surfaces with  $\nu_{12}/\nu_{21} = 10^{12}$  and for different  $\Delta E$  values ((1) 20 kcal; (2) 40 kcal; (3) 60 kcal; (4) 80 kcal; (5) 100 kcal).

#### 4. Case 2: independent sites with adsorbate-induced reconstruction

For those cases in which reconstruction is induced by the adsorbate, our model assumes that if different species are adsorbed on the surface, the total activation energies are expressed as:

$$E_{12} = E_{12(0)} + E_{12adj} \quad (11)$$

$$E_{21} = E_{21(0)} + E_{21adj} \quad (12)$$

where  $E_{12adj}$  stands for the contribution by a species  $j$  adsorbed on the site during the reconstruction process.

If the surface is not completely occupied, for each free site, that is to say, without an adsorbed species, we have:

$$E_{12} = E_{12(0)} \quad (13)$$

$$E_{21} = E_{21(0)}. \quad (14)$$

In this case, the equilibrium state cannot be deduced from expression (9) since it does not depend only on the temperature but also on the surface coverage of each adsorbed species,  $\Theta_j$ .

If two zones are distinguished on the surface, one with occupied sites and another one with empty sites, it is possible to propose the following system for the equilibrium state:

$$\sum_j \Phi_{1o\phi} + F_{1v} + \sum_j \Phi_{2o\phi} + F_{2v} = 1 \quad (15)$$

$$\sum_j F_{1oj} + \sum_j F_{2oj} = \sum_j \Theta_j \quad (16)$$

$$\sum_j F_{2oj} + F_{2v} = F_2 \quad (17)$$

$$k_{12}F_{1v} = k_{21}F_{2v} \quad (18)$$

$$k_{12j}F_{1oj} = k_{21j}F_{2oj} \quad (19)$$

where  $F_{1oj}$  is the fraction of sites occupied by species  $j$  in state S1,  $F_{1v}$  is the fraction of empty sites in state S1,  $F_{2oj}$  is the fraction of sites occupied by species  $j$  in state S2 (reconstructed),  $F_{2v}$  is the fraction of sites in state S2 (reconstructed) and  $F_2$  is the fraction of sites in state S2 (reconstructed). Equation (18) is the equilibrium condition for the empty sites, with:

$$k_{12} = v_{12} \exp(-E_{12(0)}/RT) \quad (20)$$

$$k_{21} = v_{21} \exp(-E_{21(0)}/RT). \quad (21)$$

Expression (19) represents  $j$  equations corresponding to sets of sites occupied by species  $j$ , for which

$$k_{12j} = v_{12} \exp(-(E_{12(0)} + E_{12adj})/RT) \quad (22)$$

$$k_{21j} = v_{21} \exp(-(E_{21(0)} + E_{21adj})/RT) \quad (23)$$

where  $E_{12adj}$  and  $E_{21adj}$  are the contributions of a  $j$  species adsorbed on the site to both rates of surface transformation.

The solution of the system is straightforward. To illustrate this, for the particular case of a single adsorbed species, the solution will be:

$$F_{2o} = G'\Theta \quad (24)$$

$$F_{1o} = \Theta/(1 + f') \quad (25)$$

$$F_{1v} = (1 - \Theta)/(1 + f) \quad (26)$$

$$F_{2v} = G(1 - \Theta) \quad (27)$$

$$F_2 = (G' - G)\Theta + G \quad (28)$$

where

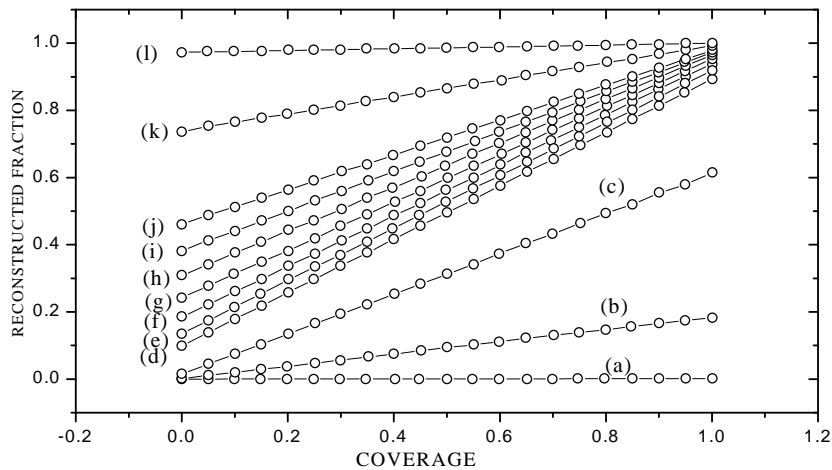
$$f = k_{12}/k_{21} = K_{eq} \quad (29)$$

$$f' = k'_{12}/k'_{21} = K'_{eq} \quad (30)$$

$$G = f/(1 + f) \quad (31)$$

$$G' = f'/(1 + f'). \quad (32)$$

Figure 2 shows the equilibrium state of the system for  $E_{21ad} = -E_{12ad}$  and clearly exhibits the linear variation of the reconstructed fraction with the coverage and the variation of the slopes with the system temperature.



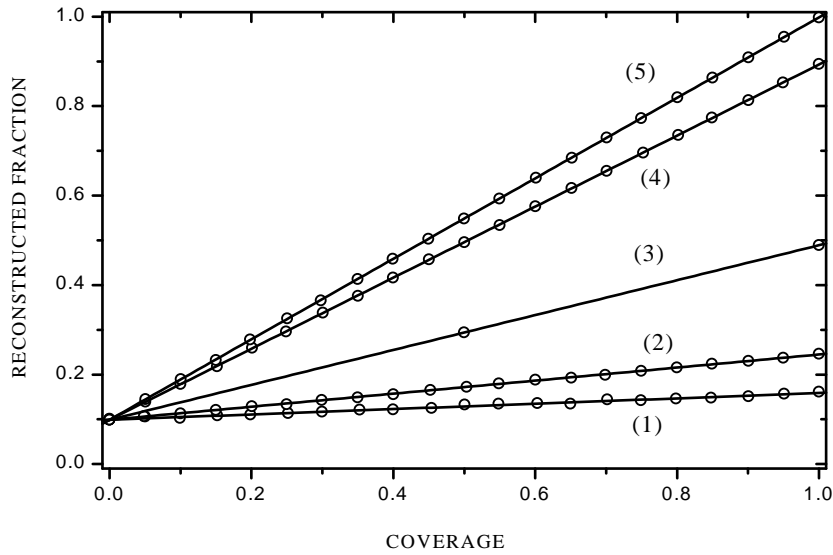
**Figure 2.** Variation of the reconstructed surface fraction with coverage. The slope of the straight lines changes with variations in the system temperature ((a) 500 K; (b) 600 K; (c) 650 K; (d) 700 K; (e) 710 K; (f) 720 K; (g) 730 K; (h) 740 K; (i) 750 K; (j) 760 K; (k) 800 K; (l) 900 K). The system exhibits adsorbate-induced reconstruction but the sites do not interact with their surroundings. The lines stand for the analytical solution and the symbols represent the results obtained by Monte Carlo simulation. In all the cases considered here we use the following values for the parameters:  $\Delta E = 36$  kcal;  $E_{12ad} = -E_{21ad}$ ;  $\nu_{12} = \nu_{21} = 2.1 \times 10^{10}$  seg $^{-1}$ .

Figure 3 shows the system equilibrium state as a function of the coverage for different values of the adsorbate interaction for a constant temperature. Again, it can be seen that the slope of the straight line varies with the contribution of the adsorbate to the reconstruction process.

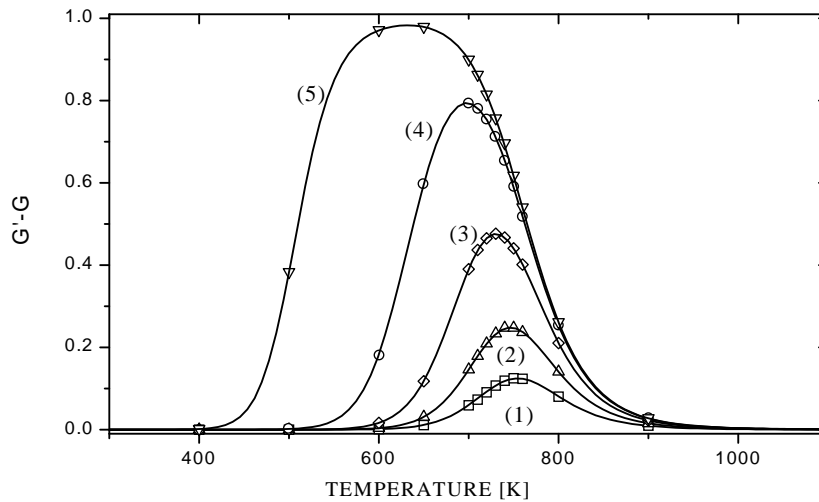
From expression (28) it follows that the slope of the straight lines is determined by the expression  $(G' - G)$ , which depends on the temperature, on  $\Delta E$  and on the adsorbate–site interaction energy.

Figure 4 shows the dependency of  $(G' - G)$  on the temperature for different values of the adsorbate–site interaction.

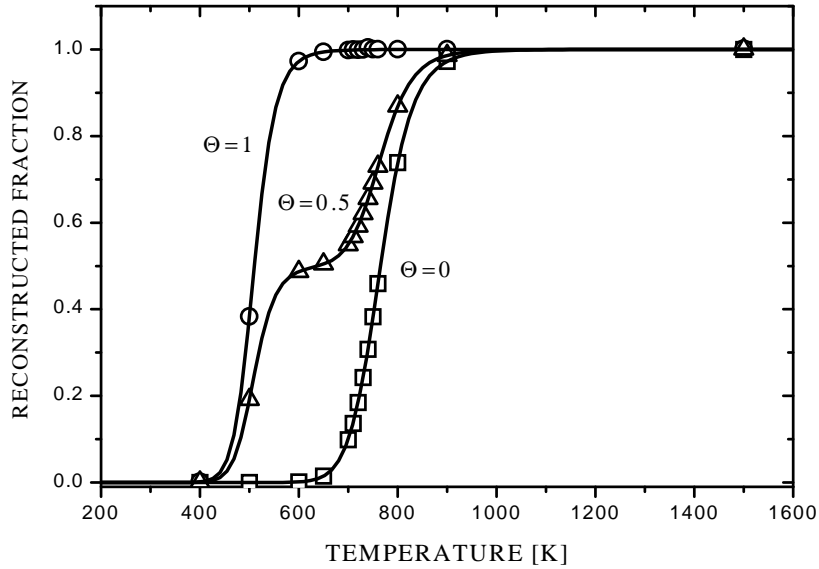
Figure 5 shows the evolution of the substrate–adsorbate system as a function of the temperature for three different coverage values ( $\Theta = 0, 0.5$  and  $1$ ).



**Figure 3.** Variation of the reconstructed surface fraction with coverage. The system temperature remains constant (700 K) and the slopes change with variations of the adsorbate–site interaction ((1) 0.375 kcal; (2) 0.75 kcal; (3) 1.5 kcal; (4) 3 kcal; (5) 6 kcal). The system exhibits adsorbate-induced reconstruction but the sites do not interact with their surroundings. The lines stand for the analytical solution and the symbols represent the results obtained by Monte Carlo simulation. In all the cases considered here we use the following values for the parameters:  $\Delta E = 36$  kcal;  $E_{12ad} = -E_{21ad}$ ;  $\nu_{12} = \nu_{21} = 2.1 \times 10^{10}$   $\text{seg}^{-1}$ .



**Figure 4.** Variation of the  $(G' - G)$  difference with temperature for different values of adsorbate–site interaction ((1) 0.375 kcal; (2) 0.75 kcal; (3) 1.5 kcal; (4) 3 kcal; (5) 6 kcal).  $(G' - G)$  stands for the slope of the straight lines in figures 2 and 3 in a system with adsorbate-induced interaction in which sites do not interact with their surroundings. The lines stand for the analytical solution and the symbols represent the results obtained by Monte Carlo simulation. In all the cases considered here we use the following values for the parameters:  $\Delta E = 36$  kcal;  $E_{12ad} = -E_{21ad}$ ;  $\nu_{12} = \nu_{21} = 2.1 \times 10^{10}$   $\text{seg}^{-1}$ .



**Figure 5.** Evolution with temperature of a surface with adsorbate-induced reconstruction for different coverage values. The lines stand for the analytical solution and the symbols represent the results obtained by Monte Carlo simulation. In all the cases considered here we use the following values for the parameters:  $\Delta E = 36$  kcal and  $\nu_{12} = \nu_{21} = 2.1 \times 10^{10}$  seg $^{-1}$ .

### 5. Case 3: induced reconstruction affected by the surroundings

#### 5.1. Case 3(a): there only exists interaction between sites

In this case it is assumed that only the last term in expression (5) is null and therefore

$$E_{12adsur} = E_{21adsur} = 0 \quad (33)$$

that is to say

$$E_{12} = E_{12(0)} + E_{12ad} + E_{12sur} \quad (34)$$

$$E_{21} = E_{21(0)} + E_{21ad} + E_{21sur} \quad (35)$$

where  $E_{12sur}$  and  $E_{21sur}$  stand for the influence of the state of neighbouring sites on the reconstruction process of one site.

Under this assumption the solution for the system is not straightforward, since equations (20), (21), (22) and (23) depend, through the activation energies, on the instantaneous state of the sites while the reconstruction process of all the surface is in progress.

In order to analytically solve the system, the mean field approximation method can be applied. By this method, considering only the nearest-neighbour and the next-nearest-neighbour interactions and separating empty and occupied sites, the rates can be expressed as follows:

for empty sites

$$k_{12} = \nu_{12} \exp(-(E_{12(0)} + \Delta E_{12sur})/RT) \quad (36)$$

$$k_{21} = \nu_{21} \exp(-(E_{21(0)} + \Delta E_{21sur})/RT) \quad (37)$$

for sites occupied by species  $j$

$$k_{12j} = \nu_{12} \exp(-(E_{12(0)} + E_{12adj} + \Delta E_{12sur})/RT) \quad (38)$$

$$k_{21j} = \nu_{21} \exp(-(E_{21(0)} + E_{21adj} + \Delta E_{21sur})/RT) \quad (39)$$



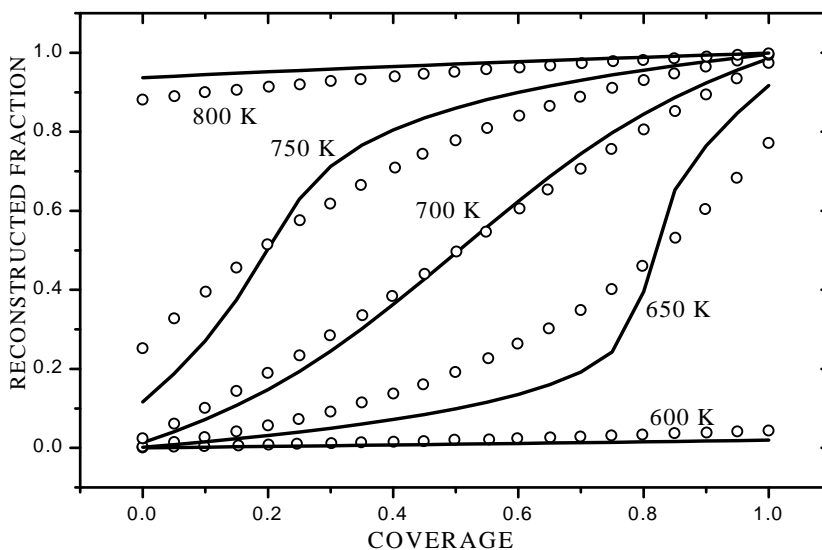
with

$$\Delta E_{12sur} = F_2(z_1 E_{12R1} + z_2 E_{12R2}) + (1 - F_2)(z_1 E_{12N1} + z_2 E_{12N2}) \quad (40)$$

$$\Delta E_{21sur} = F_2(z_1 E_{21R1} + z_2 E_{21R2}) + (1 - F_2)(z_1 E_{21N1} + z_2 E_{21N2}) \quad (41)$$

$F_2$  is the fraction of reconstructed sites.  $Z_1$  is the number of first neighbours.  $Z_2$  is the number of second neighbours.  $E_{12R1}$  is the effect of the interaction with reconstructed nearest neighbour on reaction  $S1 \rightarrow S2$  of the site.  $E_{12R2}$  is the effect of the interaction with reconstructed next nearest neighbour on reaction  $S1 \rightarrow S2$  of the site.  $E_{21R1}$  is the effect of the interaction with a reconstructed nearest neighbour on reaction  $S2 \rightarrow S1$  of the site.  $E_{21R2}$  is the effect of the interaction with a reconstructed next nearest neighbour on reaction  $S2 \rightarrow S1$  of the site.  $E_{12N1}$  is the effect of the interaction with an unreconstructed nearest neighbour on reaction  $S1 \rightarrow S2$  of the site.  $E_{12N2}$  is the effect of the interaction with an unreconstructed next nearest neighbour on reaction  $S1 \rightarrow S2$  of the site.  $E_{21N1}$  is the effect of the interaction with an unreconstructed nearest neighbour on reaction  $S2 \rightarrow S1$  of the site.  $E_{21N2}$  is the effect of the interaction with an unreconstructed next nearest neighbour on reaction  $S2 \rightarrow S1$  of the site.

Figure 6 shows the results of the analytical solution considering only the interaction between nearest-neighbouring sites.



**Figure 6.** Evolution with coverage of a surface with adsorbate-induced reconstruction and interaction between neighbouring sites; the curves are labelled with their corresponding temperature as indicated. In all the cases considered here we use the following values for the parameters:  $\Delta E = 36$  kcal;  $E_{12ad} = -E_{21ad} = 3$  kcal;  $E_{12adsur} = E_{21adsur} = 0$ ;  $E_{12sur} = E_{21sur} = 0.375$  kcal and  $\nu_{12} = \nu_{21} = 2.1 \times 10^{10}$   $\text{seg}^{-1}$ . The lines stand for the analytical solution and the symbols represent the results obtained by Monte Carlo simulation.

### 5.2. Case 3(b): the reconstruction is induced by the adsorbate and there only exists interaction between a site and adsorbed species in neighbouring sites

In this case it is assumed that

$$E_{12sur} = E_{12sur} = 0. \quad (42)$$

Then, expression (5) becomes

$$E_{12} = E_{12(0)} + E_{12ad} + E_{12adsur} \quad (43)$$

and for the reverse reaction:

$$E_{21} = E_{21(0)} + E_{21ad} + E_{21adsur} \quad (44)$$

where  $E_{12adsur}$  and  $E_{21adsur}$  stand for the influence on the reconstruction process of a site from the occupation state of neighbouring sites.

Under this assumption, the solution is not straightforward, since equations (20), (21), (22) and (23) depend, through the activation energy, on the presence of adsorbate in the neighbouring sites.

By applying again the mean field approximation for the analytical solution of the system and considering interactions of first and second neighbours, the rates are expressed as follows.

For empty sites

$$k_{12} = \nu_{12} \exp(-(E_{12(0)} + \Delta E_{12adsur})/RT) \quad (45)$$

$$k_{21} = \nu_{21} \exp(-(E_{21(0)} + \Delta E_{21adsur})/RT) \quad (46)$$

and for occupied sites of species  $j$ :

$$k_{12j} = \nu_{12} \exp(-(E_{12(0)} + E_{12adj} + \Delta E_{12adsur})/RT) \quad (47)$$

$$k_{21j} = \nu_{21} \exp(-(E_{21(0)} + E_{21adj} + \Delta E_{21adsur})/RT) \quad (48)$$

where

$$\Delta E_{12adsur} = \sum_j \{\Theta_j (z_1 E_{1j12} + z_2 E_{2j12})\} \quad (49)$$

$$\Delta E_{21adsur} = \sum_j \{\Theta_j (z_1 E_{1j21} + z_2 E_{2j21})\} \quad (50)$$

$\Theta_j$  is the surface coverage of species  $j$ .  $z_1$  is the number of first neighbours.  $z_2$  is the number of second neighbours.  $E_{1j12}$  is the effect of the interaction with a nearest neighbour occupied by species  $j$  on reaction  $S1 \rightarrow S2$  of the site.  $E_{2j12}$  is the effect of the interaction with a next nearest neighbour occupied by species  $j$  on reaction  $S1 \rightarrow S2$  of the site.  $E_{1j21}$  is the effect of the interaction with a nearest neighbour occupied by species  $j$  on reaction  $S2 \rightarrow S1$  of the site.  $E_{2j21}$  is the effect of the interaction with a next nearest neighbour occupied by species  $j$  on reaction  $S2 \rightarrow S1$  of the site. The results of the application of the model considering only one adsorbed species and interactions with first neighbours are shown in figure 7.

### 5.3. Case 3(c): the reconstruction is induced by the adsorbate and there are both site–site and site–adsorbate interactions

This is the most general case and the one closest to experimental evidence. The sites interact with each other and the presence of adsorbed species affects the process both locally and on the neighbouring sites.

Experimental data show that small amounts of adsorbate can cause the total reconstruction of the surface.

For this case, equations (20)–(23) become for the empty sites

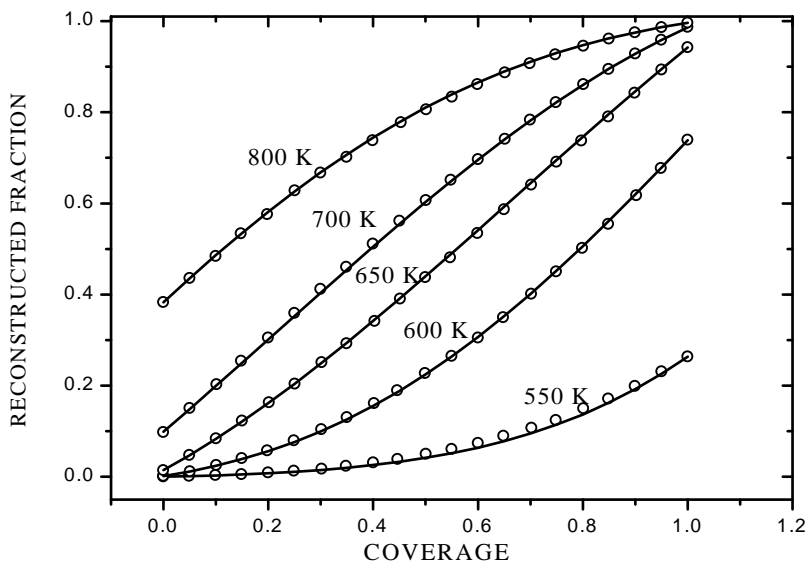
$$k_{12} = \nu_{12} \exp(-(E_{12(0)} + \Delta E_{12adsur} + \Delta E_{12sur})/RT) \quad (51)$$

$$k_{21} = \nu_{21} \exp(-(E_{21(0)} + \Delta E_{21adsur} + \Delta E_{21sur})/RT) \quad (52)$$

and for sites occupied by species  $j$

$$k_{12j} = \nu_{12} \exp(-(E_{12(0)} + E_{12adj} + \Delta E_{12adsur} + \Delta E_{12sur})/RT) \quad (53)$$

$$k_{21j} = \nu_{21} \exp(-(E_{21(0)} + E_{21adj} + \Delta E_{21adsur} + \Delta E_{21sur})/RT). \quad (54)$$



**Figure 7.** Evolution with coverage of a surface with adsorbate-induced reconstruction and interaction between sites and species adsorbed in neighbouring sites. The curves are labelled with their corresponding temperature as indicated. In all the cases considered here we use the following values for the parameters:  $\Delta E = 36$  kcal;  $E_{12ad} = -E_{21ad} = 3$  kcal;  $E_{12adsur} = E_{21adsur} = 0.375$  kcal;  $E_{12sur} = E_{21sur} = 0$  and  $\nu_{12} = \nu_{21} = 2.1 \times 10^{10}$   $\text{seg}^{-1}$ . The lines stand for the analytical solution and the symbols represent the results obtained by Monte Carlo simulation.

## 6. Monte Carlo simulation

Monte Carlo simulation has proved to be a powerful technique for studying processes such as those occurring in surfaces, which are difficult to handle with traditional techniques [26–29].

In order to apply Monte Carlo simulation it must be taken into account that the probability of a site  $i$  passing from state  $S1$  to state  $S2$  in a sufficiently short time  $\Delta t$  is determined by the following expression:

$$P_{12}(\Delta t) = \nu_{12} \exp(-E_{12}^i/RT)\Delta t \quad (55)$$

where  $E_{12}^i$  is the activation energy taken as a barrier of positive energy;  $R$  is the gas constant;  $T$  is the absolute temperature and  $\nu_{12}$  is a pre-exponential factor. For the most general case, according to the model and assuming only one type of adsorbate, the following expression is obtained for a site  $i$

$$E_{12}^i = E_{e12}^i + s_i E_{ad12} + E_{1ad12} \sum_{jNNi} s_j + E_{2ad12} \sum_{jNNNi} s_j + E_{1R12} \sum_{jNNi} r_j + E_{2R12} \sum_{jNNNi} r_j + E_{1N12} \sum_{jNNi} n_j + E_{2N12} \sum_{jNNNi} n_j \quad (56)$$

where  $E_{e12}^i$  is the activation energy for the spontaneous reconstruction of site  $i$ ,  $E_{ad12}$  is the contribution from the species adsorbed on the site,  $E_{1ad12}$  is the interaction with a species adsorbed on a nearest neighbour,  $E_{2ad12}$  is the interaction with a species adsorbed on a next nearest neighbour,  $E_{1R12}$  is the interaction with a reconstructed nearest-neighbouring site,  $E_{2R12}$  is the interaction with a reconstructed next-nearest-neighbouring site,  $E_{1N12}$  is the interaction with an unreconstructed nearest-neighbouring site,  $E_{2N12}$  is

the interaction with an unreconstructed next-nearest-neighbouring site,  $s_i$  is the occupation number of site  $i$  (1 occupied, 0 empty),  $n_j$  is the unreconstructed state number of site  $i$  (1 unreconstructed, 0 reconstructed),  $r_j$  is the reconstructed state number of site  $i$  (1 reconstructed, 0 unreconstructed),  $\sum_{jNNi}$  is the sum for all the nearest neighbours of site  $i$  and  $\sum_{jNNNi}$  is the sum for all the next nearest neighbours of site  $i$ . Similarly, the possibility of a site  $i$  passing from state S2 to S1 in time  $\Delta t$  is given by the following expression:

$$P_{21}(\Delta t) = v_{12} \exp(-E_{21}^i/RT)\Delta t \quad (57)$$

where

$$E_{21}^i = E_{e21}^i + s_i E_{ad21} + E_{1ad21} \sum_{jNNi} s_j + E_{2ad21} \sum_{jNNNi} s_j + E_{1R21} \sum_{jNNi} r_j + E_{2R21} \sum_{jNNNi} r_j + E_{1N21} \sum_{jNNi} n_j + E_{2N21} \sum_{jNNNi} n_j \quad (58)$$

with similar meanings for each term but in reference to the reverse reaction.

Our statistical set is given by a bidimensional array of  $N$  sites, which satisfies periodic boundary conditions.

The simulation scheme is thus determined by the following steps:

- A surface with  $N$  unreconstructed sites ( $est(i) = 1$ ) and with a random occupation state ( $ocup(i) = 1$  or  $0$ ) is prepared according to a pre-established coverage. The temperature  $T$  and  $\Delta t$  of the system are set so that they do not take values above 1 under any of the probability conditions obtained by expressions (55) and (57).
- A site is randomly chosen and the reaction probability is calculated by expression (55) if the site is unreconstructed or by (57) if it is reconstructed.
- The probability obtained above is compared with a random number RND between 0 and 1. If the probability turns out to be lower than RND, it is inferred that the site state has changed. If the site was not initially reconstructed ( $est(i)$ ) it is inferred that it has been reconstructed (from  $est(i) = 1$  to  $est(i) = 0$ ). If the site was initially reconstructed, the inverse occurs (from  $est(i) = 0$  to  $est(i) = 1$ ). If RND is lower than the probability, it is inferred that the site does not participate in the reaction and no changes in its initial state occur.
- Every  $10N$  times of running steps (2) and (3), the fraction of reconstructed sites is calculated and we observe whether this value tends to remain constant. If it does, it is inferred that the system has achieved equilibrium, and the process comes to an end. If not, step (2) is repeated until the equilibrium state is reached.

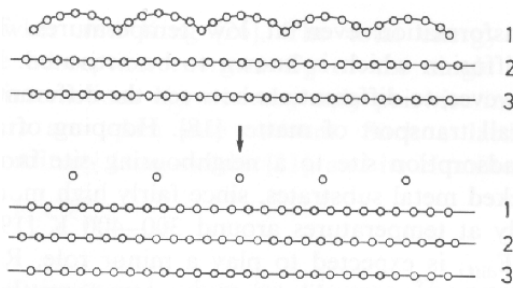
The simulations were performed on a surface of  $10^6$  sites, and a reproducibility of results within 0.1% was obtained. The results for the different situations are presented in the figures already mentioned and compared with analytical results.

## 7. An application example

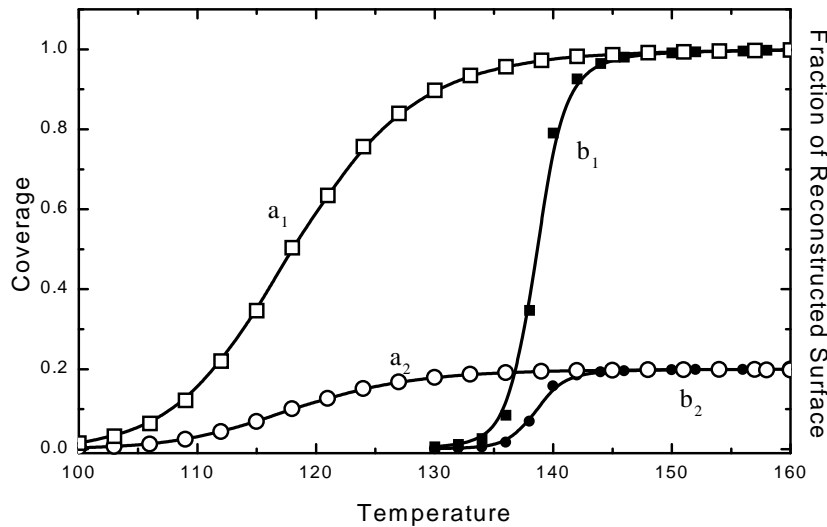
It will be very useful to show a simple application of our model to the analysis of the adsorbate-induced hex  $\rightarrow 1 \times 1$  transformation of the Pt(100) surface structure. This system was exhaustively studied by several authors [30–37].

Particularly, Reynolds *et al* [38] have studied, by means of the Monte Carlo simulation technique, the evolution of the size of the island formed by the surplus atoms segregating on top of the  $1 \times 1$  plane during the reconstruction process.

In figure 8 we have shown a schematic representation of the reconstruction mechanism proposed by the authors. As one can observe, the number of surplus atoms is a measure of



**Figure 8.** Schematics of the mechanism proposed for the adsorbate-induced structural transformation hex reconstructed  $\rightarrow 1 \times 1$  on Pt(100). Lines indicate layers of Pt atoms; circles represent single Pt atoms.



**Figure 9.**  $a_1$  represents the evolution of the surface when spontaneous reconstruction occurs;  $a_2$  represents the evolution of the coverage of segregate surplus atoms when spontaneous reconstruction occurs.  $b_1$  represents the evolution of the surface when induced reconstruction is affected by the surroundings;  $b_2$  represents the evolution of the coverage of segregate surplus atoms when induced reconstruction is affected by the surroundings.

the degree of the reconstruction. When the surface is completely reconstructed, the number of surplus atoms is equivalent to  $\Theta = 0.2$  of the coverage in the topmost layer.

The evolution of the system can be reproduced by our model (case 1), with the following values of the parameter:  $\Delta E = 5.5$  kcal and  $K_{eq} = \nu_{12}/\nu_{21} = 2 \times 10^{10}$ , figure 9 (curves  $a_1$  and  $a_2$ ).

In figure 9 (curves  $b_1$  and  $b_2$ ) we show the evolution of the system if we consider that the evolution of the surroundings affects the behaviour of a given site (case 3). The curve has been obtained considering that the interactions between atoms which belong to the same row of the square substrate lattice are only to nearest neighbours. The interaction energy was taken as  $E_{int} = 1$  kcal. In this case, the transition is reached in a small range of temperature, a product of the cooperative effect between the atoms in the topmost layer.

In both cases the results are in agreement with the experimental data, which indicate that the total reconstruction occurs at 150 K.

## 8. Conclusions

The model has proved to have an excellent capacity to study surface reconstruction in situations similar to those observed experimentally. It also offers an accurate analytical solution for spontaneous and induced reconstruction when site interaction with the surroundings is absent. In this case, the results match those obtained by Monte Carlo simulation.

For those systems presenting lateral interactions, the analytical solution is not straightforward. As expected, the results obtained by applying the mean field approximation differ from those obtained by Monte Carlo when interaction energies increase.

A better agreement between analytical and simulation results is obtained for interaction between sites and neighbouring adsorbate than for site–site interaction. This is due to the fact that the random distribution of the adsorbate on the surface exhibits a better match with the mean field approximation.

This is not the case for the distribution of reconstructed sites during the reconstruction process. In the case here analysed, the presence of site–site interactions forces the reconstructed sites to prefer a distribution into islands on the surface, rather than a random distribution. The latter would be desirable for the application of the mean field approximation.

The Monte Carlo simulation technique allows us to use the model in other situations that cannot be analytically solved, such as the reconstruction process on a heterogeneous surface, long-range interactions, the presence of more than one adsorbed species, adsorption of species occupying more than one site on the surface, the presence of surface impurities and others. Also, Monte Carlo simulation allows the study of the surface reconstruction kinetics and its effect on the kinetics of other process simultaneously taking place on the surface.

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