Collective diffusion in a twin-spin model of $O/W(110)$

Magdalena A. Załuska-Kotur

Institute of Physics Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

Stanisław Krukowski

High Pressure Research Center Polish Academy of Sciences, Sokołowska 29/37, 01-142 Warsaw, Poland

Łukasz A. Turski

Center for Theoretical Physics Polish Academy of Sciences & College of Science, Al. Lotników 32/46, 02-668 Warsaw, Poland

Following our previously developed twin-spin model description of the equilibrium properties of the $O/W(110)$ system we study its collective diffusion by means of a Monte Carlo dynamics. It is shown that the collective diffusion coefficient for our model has a different density dependence than this following from other models known in the subject literature. The essential feature of the model, responsible for its different dynamics, are the state dependent interactions. Further assumptions concerning interaction dependent barriers make our results comparable to the experimental data.

I. INTRODUCTION

The growing interest in various nanotechnological processes and technologies stimulates extensive analysis of the surface diffusion processes, particularly in those cases in which the diffusing particles interactions are of importance. It is well known that lateral interactions between particles adsorbed at the solid surface modify the adsorbate dynamics and, among other things, may change the diffusion coefficient even by several orders of magnitude.[1-5] Repulsive interactions, in general, cause the increase of the collective diffusion coefficient as a function of coverage, whereas attractive interactions have usually the opposite effect. The adlayer of O at $W(110)$ surface is an example of a system, whose main static properties can be described by a relatively simple lattice gas model with competing, attractive and repulsive interactions of comparable strength.[6] How those interaction influence the dynamical behavior of such system is an important question, which, so far, has not been satisfactory answered. In this work we try to shed some light on that problem constructing a new model for surface diffusion based on our, previously proposed, twin-spin model of the $O/W(110)$.[7] The salient feature of that model is the double-well structure of the single adsorption center. It has been shown that the dynamics of particles in the double-well potential has many interesting properties.[3] Particles in our model can occupy three different positions within the double-well structure. The interparticle interactions strongly depend on the particle state, which decides about the character of the collective dynamics. It turns out that the dynamical properties of such a twin-spin model, different from these of a conventional lattice gas, appear to be in reasonable agreement with observed behavior of the real system.

In the conventional lattice gas model, to describe adlayer of $O/W(110)$ at the coverage higher then 0.5, i.e., to account for all the existing phases of this system, it was claimed that three-body O atoms interactions are necessary.[8,9] In order to reproduce all the phases properly, these three-body interac-

tions have to have the strength comparable with that of the basic two-particle interactions. We have recently proposed an alternative model of the $O/W(110)$ system.[7] In our model the double-well structure of an adsorption site binding potential is represented by three-states of a single particle. In addition, the local potential felt by a particle and interparticle interactions are state dependent. Our model leads to the results that agree with existing experimental data.

To describe the $O/W(110)$ dynamics we need to know more than just the energies of the various states of that system and how they influence the many particle arrangements resulting in macroscopically observed phases. Indeed, we need the transition rates between different particle configurations. In so far proposed models of the lattice gas $O/W(110)$ dynamics it was assumed that the essential kinetics is given by the single particle jumps between neighboring sites, with rates inversely proportional to the equilibrium occupation probability of the initial state. Even though the statics of the system is then properly reproduced by the constructed model, dynamical properties are not necessarily in agreement with experiments.[10-15] It would be useful to have such a model of the surface layer, that reproduces both static, and dynamic properties correctly. We shall show in what follows that our twin spin model is a good candidate of such a description for $O/W(110)$.

The $O/W(110)$ adlayer is known to have very interesting dynamical properties.[10-13,16-18] The diffusion coefficient in this system increases with coverage, up to the coverage $\rho \approx 0.3$, by more than one order of magnitude and then decreases. Careful analysis of experimental data shows that the activation barrier for the equilibrium collective diffusion coefficient E_A increases by about 0.4 eV when the coverage grows up from 0.2 to 0.4, whereas no change is observed for the activation barrier of the nonequilibrium diffusion.[12,13] It has been shown in Ref. 14 that the diffusion obtained from the simplest version of $O/W(110)$ model differs substantially from the experimental results.[11] The collective diffusion coefficient following from the conventional models does

not show any specific shift in the activation energy.[14] It varies rather slowly with increasing coverage or temperature. The activation barrier of collective diffusion increases also very little,[15] when system is described by the model with three-body interactions included. In this last model the behavior of the activation energy becomes closer to the experimentally obtained data, when not the total, collective, but the center of mass diffusion coefficient is taken into account. These two quantities differ only by so called thermodynamical factor, which is inversely proportional to the equilibrium compressibility of the surface layer. The questions one obviously has to ask are which of those quantities is really measured in experiment and is it possible that the theoretical models used in data analysis are inadequate, for they miss some of the essential physics?

In order to address these two questions we have studied dynamical properties of $O/W(110)$ within our twin-spin model using Monte Carlo (MC) dynamics with two different types of transition rates. Our first and simplest choice is that the rates depend only on the interactions between particles located in their equilibrium positions. The second choice of the transition rates is such, that the transition rates are determined by interactions between particles located not only at their equilibrium sites but also at the saddle points between them. These saddle points have to be visited by particles undergoing a "jump" from one equilibrium site to another.

It turns out that the first choice result is the diffusion coefficient $D=D(\varrho)$, which still changes rather slowly when the coverage is increased from 0 to 0.5. Its qualitative behavior is, however, akin to that observed in experiments; situation never found in analysis based on conventional lattice gas models. Dynamics resulting from the model with second type of transition rates results in much higher peak of the diffusion coefficient around the coverage $\rho\sim0.3$. Such effect has not been obtained within anyone of the previous models. The activation barrier inferred from this result increases at this coverage by around 0.4 eV, and we do not observe any jump for nonequilibrium diffusion. These results agree with the best experimental estimates.[11–13]

II. THE MODEL

A. Statics

The twin-spin model, or the triple state model, describing the oxygen O adatoms at $W(110)$ surface is build around the notion of the double-well structure of the adsorption center binding energy. Once trapped in an adsorption site a single adatom finds itself in one of the two equivalent positions inside a double-well potential associated with that site. Only one out of the two energy-equivalent positions in that well can be occupied by the adatom. The isolated adatom, in the saddle point energy state separating two sides of the well, has higher local energy, but for some configurations of neighboring adatoms this third state can be energetically favored. The double-well structure can be described by three variables $n_i^A, n_i^B, n_i^C = 0,1$ that is particle occupation of the A, B, and C states. Because none two of these states can be occupied at the same time, the variables fulfill a local constrain $n_i^A + n_i^B + n_i^C = 1$. These occupation variables can,

therefore, be considered as *three states* of a single variable n_i. In the analysis of static properties we founded it more convenient to ascribe two independent two-state spins to each adsorption site. These two-spins encode together four different states: A, B, C, and an empty site.[7] When the dynamical properties of such a system are analyzed, it is more convenient to use conventional occupation number representation.

The Hamiltonian for our model of lattice gas, described in greater detail in Ref. 7, now written in terms of the occupation number variables n_i assumes the form

$$H = -J \sum_{(NN)} (n_i^A - n_i^B)(n_j^A - n_j^B)$$

$$+ J_2 \sum_{(NNN)} (n_i^A + n_i^B)(n_j^A + n_j^B)$$

$$+ 4J \sum_{(NN)} n_i^C n_j^C - 2J' \sum_{(3NN)} n_i^C n_j^C$$

$$- J' \sum_{(3NN)} (n_i^A + n_i^B)(n_j^A + n_j^B)$$

$$+ V \sum_i n_i^C - \mu \sum_i (n_i^A + n_i^B + n_i^C), \tag{1}$$

where μ is the chemical potential, (NN) denotes the sum over all nearest neighbor sites i,j, (NNN) denotes the sum over all next-nearest neighbors, and (3NN) over third-neighbor pairs.

We have shown in our previous publication[7] that with the choice for the interaction parameters $J \approx 0.1$ eV, $J_2 = 1.5J$, $J' = 0.1J$, and $V = J$, our model reproduces pretty well all known static properties of the $O/W(110)$ system. We shall use the same values for these interaction constants in the following analysis of the dynamics properties for the same system.

B. Dynamics

Adsorption sites for the O at the $W(110)$ surface form a two dimensional lattice with centered, rectangular symmetry. At each site [see Fig. 1(a)] the adatom can be in one of three states A, B, or C. From the state A this adatom can jumps either left, into an empty neighboring adsorption site, or right into state B or C. When particle occupies state B the situation is mirrored. From the state C particle can jump to one of positions A or B, or to any one of the states in one of the neighboring sites. All these possible particle transfer processes creates quite a complex "elementary unit" for a single diffusion step. Note, that the rates for the particle jumps depend on the energy of the initial state and the energy of the saddle point. The values for the bare energy barriers, not modified by interaction between particles, between all these different particle positions-states have been evaluated in Ref. 7 using the density functional theory method. For jumps within each double well the barrier is equal to $V_2 = 0.2$ eV, whereas for jumps out of the adsorption well, particle needs to overcome higher $V_1 = 0.5$ eV barrier.
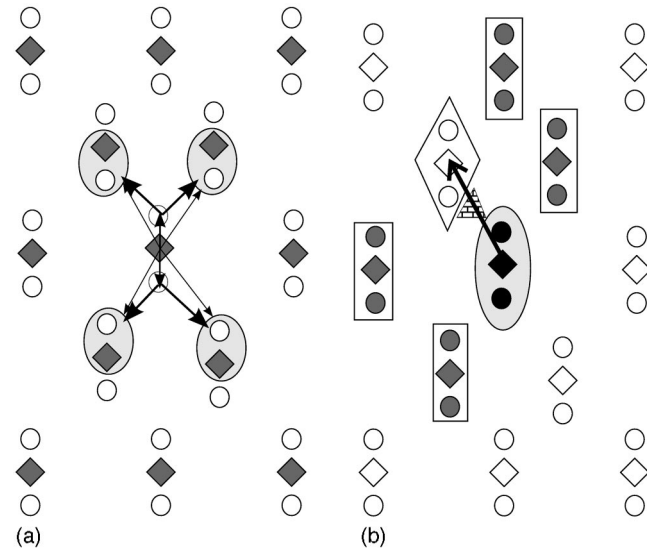
FIG. 1. Schematic picture of the adsorption sites. Circles represent A and B states, diamonds are for C states. (a) Adatoms jumps from single adsorption site. (b) Neighboring sites of the saddle point (denoted as triangle).

As discussed earlier the diffusing particle jumps between many local energy minima. When the particle does not interact with other particle in its neighborhood, it can jump between two minima of equal energy inside double-well adsorption site structure. The barrier for jumps between these two states is much smaller than the barrier to jump out of the adsorption center. The isolated adatom jumps from the position A to B and sometimes it receives enough energy to jump out, to one of the neighboring sites. The double-well structure of the adsorption site does not change much in the dynamics of the single adparticle, particularly when there is large difference in barrier height.[19]

The situation becomes different, when the diffusing particles do interact with each other, when they occupy different sites and when interactions differ between positions A and B, as in the situation described by Eq. (1). If that is the case the transition rates W_{ij}, for jumps from i to j sites are defined differently, depending on states from, and into which the particle jumps.

Rates, used by us in MC calculations are given by the following expressions:

$$W_{ij}^{\Delta} = \nu \exp\left[-\beta\left(V_{\alpha} - E_i - J_s^{\Delta} \sum_{\langle NN \rangle_s} n_i \right) \right],$$

$$W_{ij}^{C} = \nu \exp\left[-\beta\left(V_{\alpha} - E_i + J_s^{C} \sum_{\langle NN \rangle_s} n_i \right) \right]. \quad (2)$$

In these equations W_{ij}^{Δ} is the transition rate for a jump from the $\Delta = A$ or B state, at the site i, to any other state at a neighboring site j or from any of states into the A or B states. This formula describes also jumps within the same adsorption site, when $j = i$. The rate W_{ij}^{C} defines a C state to a C state jumps. $V_{\alpha} = V_1$ or V_2 depending on whether the jump is outside or inside the adsorption site. E_i is the energy, given

by the value of the Hamiltonian (1) at initial configuration of the system. As usually $\beta = 1/k_B T$. The sum in the exponents is over all saddle point sites $\langle NN \rangle_s$ that are the first neighbors of that saddle point which lies between sites from and into which the particle jumps [see Fig. 1(b)].

In Eq. (2) coefficients J_s^{Δ} and J_s^{C} measure the strength of the interactions of the particle, at the saddle point with its neighbors. In our first set of simulations we have assumed that these interactions are equal to zero and the dynamics depends only on the initial energy of the system, i.e., the adsorption site energy modified by the presence of other adatoms. The height of the intersite barrier remained the same. If both $J_s = 0$ transition rates along and out of the atomic lines differ by several orders of magnitude, essentially due to a huge difference in E_i. Setting nonzero values for J_s^{Δ} and J_s^{C} we can change the relative speed of both diffusion processes, along and across the ordered lines. Note, that in the transition rates (2), the positive interactions at the saddle point, defined as above, favor the probability of a jump out, and into the ordered line of adatoms. For a particle which is in between occupied rows those rates disfavor the jump probability along lines.

We have calculated collective diffusion coefficient for several values of the saddle point interactions. Below we show results for $J_s = J_s^{\Delta} = J_s^{C} = 1.5J$, i.e., these which lead to the collective diffusion coefficient with values closest to the experimental data. For this specific choice, both of two kinds of jumps are of comparable efficiency.

Our preliminary results shown in Ref. 20, indicated that the adsorbate dynamics governed by the state dependent transition rates looks quite different than this following from the usual lattice gas approach. In Ref. 20 we have already mentioned how strongly the coverage dependence of the collective diffusion coefficient is controlled by the definition of the transition rates.[21] The dynamics that has been discussed in Ref. 20 assumed instantaneous equilibration within each of the adsorption sites—no inside adsorption site jumps were allowed. In the results presented in the following section this constraint has been relaxed, which, as we believe, corresponds more closely to the real experimental situation.

III. DYNAMICAL SIMULATIONS

We have studied the system dynamics using the dynamical MC simulations. The mode of the dynamics is specified by the choice of the configuration dependent transition probabilities given in Eq. (2). Only single jumps of particles from site to the neighboring site are allowed. The collective diffusion coefficient is calculated by use of methods worked out by us in previous works.[22,23] The dynamical Monte Carlo analysis of the $O/W(110)$ adlayer is difficult due to reasons discussed in the previous section. There are the large differences in barrier energies, and many local equilibrium states that are separated from the other minima by very high barriers. Due to that the simulations have to be run for a very long time, provided we want to obtain results truly corresponding to the equilibrium situation. This is actually the reason why it is very difficult to reach sufficiently good precision using harmonic profile decay method,[22] and why the step-coverage

relaxation analysis,[23] for a wide coverage range turned out to be the more effective method to analyze diffusion in $O/W(110)$.

It is well known, that the step profile analysis gives results that can be far from equilibrium measurements, especially when the initial stages of evolution are taken into account.[23–25] We have discussed such situation extensively in Ref. 23, and we have shown, that the results of the diffusion coefficient eventually approach the equilibrium values, after long enough relaxation time. Below we compare results that were obtained after short and long relaxation time, and show that the results, in particular their scaling properties differ in an essential way.

In the profile evolution analysis method,[23] the initially steplike coverage profile is relaxed, and from its shape the coverage dependence of the diffusion coefficient is calculated using the Boltzmann-Matano method

$$D(\rho) = -\frac{1}{2t}\left(\frac{d\rho}{dx}\right)^{-1}\int_{\rho_0}^{\rho} x \, d\rho, \qquad (3)$$

where x is the position along the axis vertical to the step, $\rho(x)$ is local coverage at point x, and t is the simulation time. This method allows us to calculate the diffusion coefficient for a wide range of coverages. We have checked, for several coverages, that the value of the diffusion coefficient is the same, when the profile evolution method is used, with average over at least 1000 samples at one point.

In Fig. 2 we compare the coverage dependence of the diffusion coefficient, we have obtained using two modes of the dynamics described above. Figure 2(a) shows the diffusion coefficient in the first case when both interactions J_s are equal to 0. The figure presents results for $k_B T = 0.7J \approx 800$ K, which is slightly below the critical temperature $k_B T_C \approx 0.8J$. The diffusion coefficient reaches its local maximum close to the coverage 0.3, then slightly decreases, and then rapidly increases, starting from the coverage of half occupied system up to coverages around 0.8, where the squared phase changes back into the disordered one.[7] The most interesting part of this plot, which can be compared with the experimental data lies in the $0-0.5$ range of coverage. We can see that for these coverages the diffusion in our system behaves qualitatively as in the experimental system. It first increases, then decreases, and has the maximum around coverage 0.3. The increase of the diffusion coefficient, however, is twice too low, compared with more than one order of magnitude increase observed in experiments.[10,11] The diffusion coefficient slowly increases for low coverages, which is different from the behavior of the diffusion coefficient obtained on using the conventional models,[15] as well as for the twin spin model but with simplified dynamics.[21]

The qualitative and quantitative changes in the diffusion are more dramatic for the second choice of our transition rates, i.e., when both J_s are equal but nonvanishing [Fig. 2(b)]. The appropriate choice of interactions at the saddle point can make the probability of jumps in various directions equal. Note that scale of both plots in Fig. 2 is different. It can be seen that in that case the value of diffusion coefficient
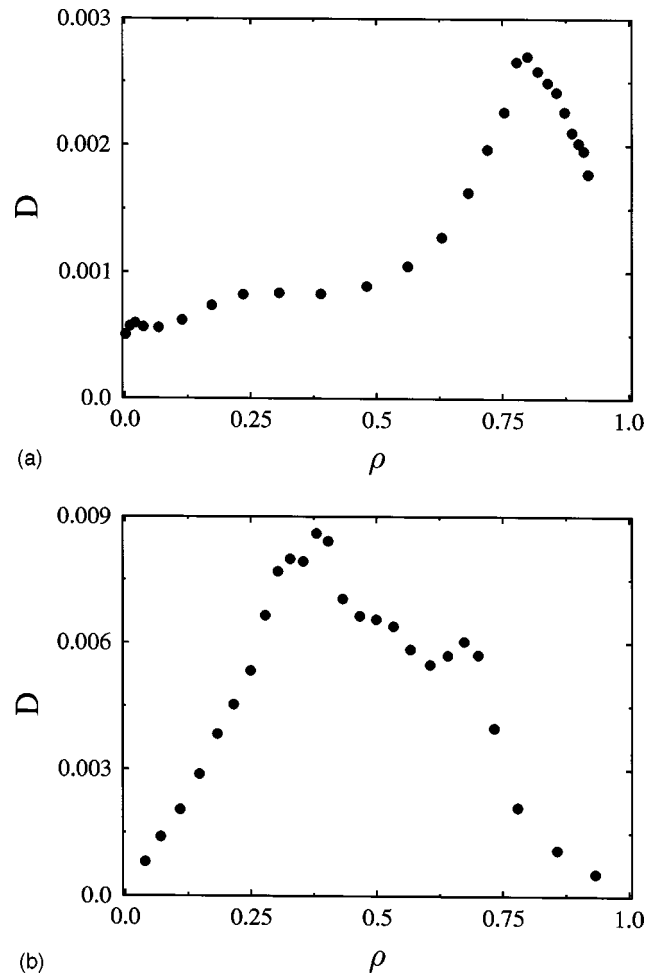

(a)

(b)

FIG. 2. Diffusion coefficient as a function of coverage at $T = 0.7J$ for a dynamics given by transition rates with (a) no interactions at the saddle point and (b) interactions with $J_s^A = J_s^C = 1.5J$.

for low coverages (below 0.5) increases by a factor 10, as compared to the first case, starting from the same value (which is just a single particle diffusion at given temperature). It can be also seen that diffusion drops down for the dense system.

More detailed analysis has been done for the lower coverages. The results for the diffusion coefficient, calculated from the profiles after long relaxation time, thus close to the equilibrium values, are presented in Fig. 3. Note that in Fig. 2(b) the diffusion coefficient at $\rho=0.5$ is much higher than that shown in Fig. 3. The difference stems from the shorter relaxation used in simulations presented in Fig. 2. Data presented in Fig. 3 were calculated by longer simulations and with lower values of the coverage change step (up to the coverage 0.5). Figure 3 shows more systematic data for several temperatures, all below the critical temperature. The kind of oscillations visible in the individual curves for ρ higher than 0.3 is due to quite large inaccuracy of calculations at such low temperatures, however the general tendency of the diffusion behavior is reproduced.

The values of the diffusion coefficient, presented in Fig. 3 contain the information of its temperature dependence. The
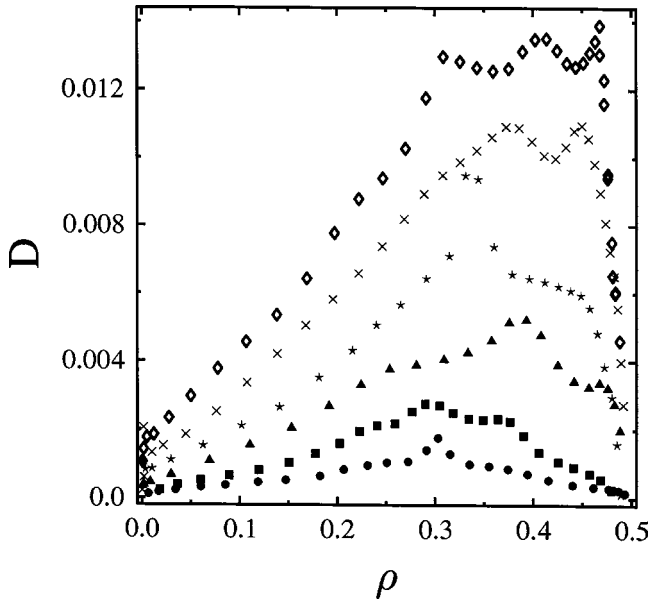
FIG. 3. Diffusion coefficient for dynamics given by the transition rates dependent on the interactions at the adsorption site and at the saddle point, for temperatures $k_T T = 0.8J, 0.75J, 0.7J, 0.65J, 0.6J, 0.55J$ subsequently from top to bottom. All temperatures are below $k_T T_c \approx 0.8J$. The relaxation time of dynamic process scales with the temperature, hence we changed the number of calculated MC steps as the temperature decreased. Subsequently 60 000, 80 000, 15 0000, 200 000, 300 000, 500 000 number of MC steps have been used.

usual experimental analysis of such data is based on the Arrhenius-like parametrization of the diffusion coefficient

$$D(\rho, T) = D_0(\rho) \exp[-E_A(\rho)/T]. \tag{4}$$

Note that the activation energy of the diffusion process $E_A(\rho)$ and the prefactor $D_0(\rho)$ are coverage dependent. The analysis of the experimental data shows that E_A obtained in equilibrium measurements changes with coverage rather slowly everywhere within $(0-0.5)$ coverage range, except one narrow region, around coverage $\rho = 0.3$, where it increases rapidly by 0.4 eV.[11–13] If there is only weak dependence of the activation energy on coverage in wide range of density, we can assume that it is almost constant in these region. Hence the temperature and coverage dependence of the diffusion coefficient should be separated each from the other, differently, however, in low and high coverage regimes of the phase diagram. For this reason we write

$$D(\rho, T) = D(\rho) f_c(T), \tag{5}$$

where $f_c(T)$ with $c = 1,2$, are the temperature dependent scaling functions in low and high coverage regions of the phase space, respectively.

From the plots in Fig. 4, it is evident, that one can identify $f_c(T) = \exp(-E_A^c/T)$, and that within quite a wide range of coverages, and for various temperatures the diffusion coefficient can be approximated by a single independent of the density activation barrier E_A^c parametrization. This single activation energy within wide range of temperatures should be
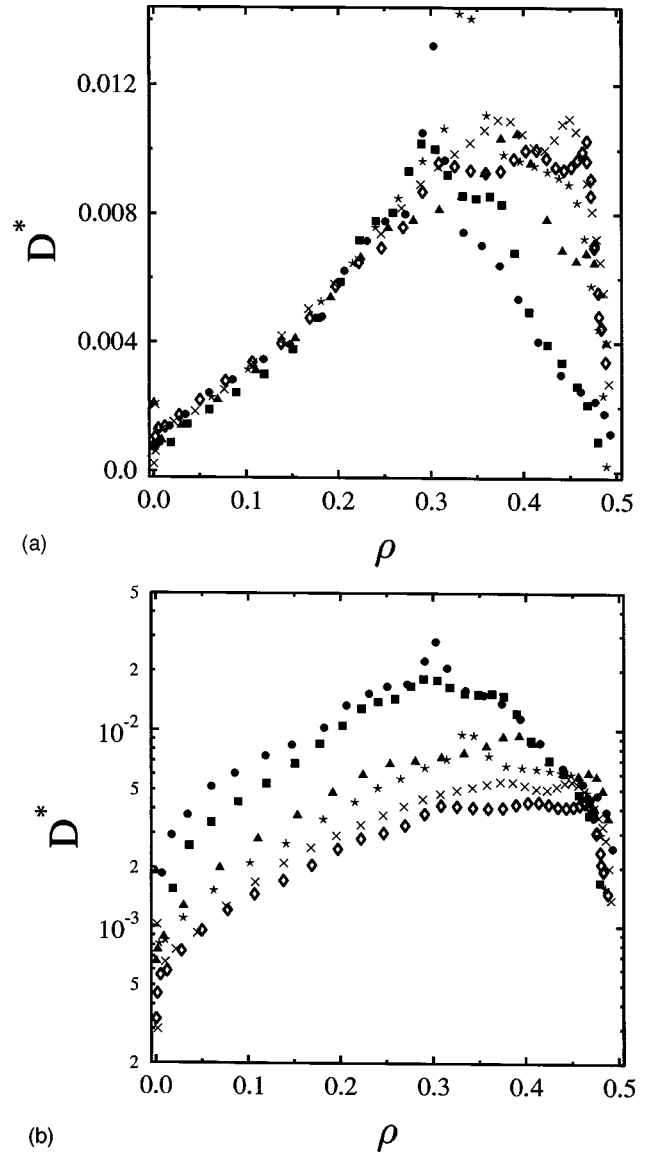

(a)

(b)

FIG. 4. The same data as in Fig. 3, divided by the scaling factor, in order to collect them into one line (a) for lower coverages $0-0.27$, $D^* = D/f_1(T)$ and (b) for higher coverages, above 0.45 $D^* = D/f_2(T)$.

understood here only as the mean value. We expect that the exact value of E_A changes with the coverage, however not much far from the E_A^c parameter. Functions $f_c(T)$ as a function of inverse temperature are plotted in Fig. 5. The activation barrier can be calculates from the slope of presented lines, and for the coverage from 0 to around 0.27 it is equal to $E_A^1 = 4.3J \approx 0.43$ eV and for the coverage above 0.4 or 0.45, depending on the temperature is $E_A^2 = 8.7J \approx 0.87$ eV. Note that for all temperatures plotted here we are below the critical temperature $k_T T_c \approx 0.8J$, and the phase transition between disordered and ordered 2×1 phase is present at coverages between between 0.27 and 0.4, depending on the temperature.

The strong change in the diffusion properties is caused by the change of the system ordering. The obtained values of the activation energies should be compared with experimen-
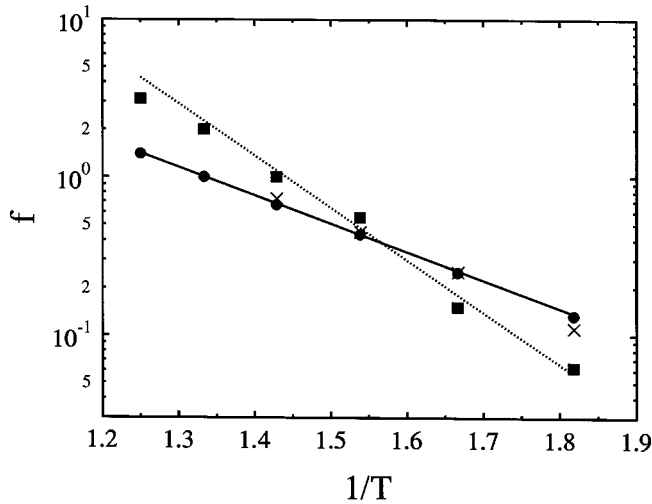
FIG. 5. The temperature dependence of scaling factors $f(T)$: circles for $f_1(T)$ at lower coverages, and squares for $f_2(T)$ at higher coverages. Crosses denote scaling factor for disordered system.
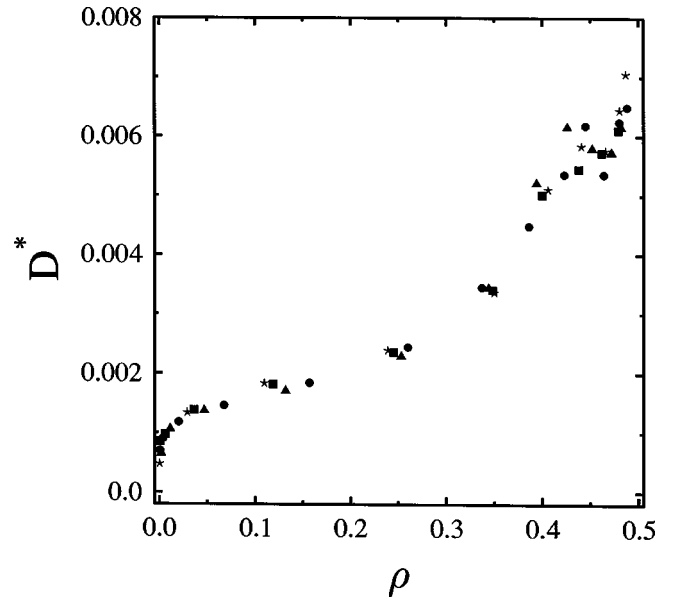

FIG. 6. Rescaled diffusion coefficient calculated from the step after short relaxation time. Dynamics is the same as in Fig. 3. The temperatures $k_T T = 0.7J$, after 150 MC steps (circles) $0.65J$ after 200 MC steps (stars) $0.6J$, after 300 MC steps (squares), and $0.55J$ after 500 MC steps (triangles). All temperatures are below $k_T T_c \approx 0.8J$.

tal 0.6 eV and, respectively, 1.04 eV as quoted in Refs. 11–13. The discrepancy between our calculations and the experimental data is around 0.15 eV, this can be traced to still not precise estimation of the interparticle interaction constant J, and the resulting inaccuracy in the scaling relation inferred from the numerical data. The difference between low and high coverage activation energies obtained by us is around 0.4 eV, very similar to the experiment. Note also, that the prefactor D_0 increases rapidly by almost four orders of magnitude within the same range of coverages, quite as the experimental situation.

The values of E_A discussed above are taken from equilibrium experiments. In the system that is far form equilibrium activation energy should be more or less the same value, around 0.6 eV, for coverages up to 0.5.[12,13] In Fig. 6 we show the scaling of the diffusion coefficient in highly disordered system. This diffusion coefficient has been calculated from the initial stages of the step evolution, when the local order within the system has not been developed yet. This initial relaxation time is 10^3 times shorter than the one we used calculating the curves presented in Figs. 3,4. We can see that the behavior of the nonequilibrium results is essentially different, especially in the close to coverage 0.5 part. It can be also seen that there is only one scaling function in the whole range of coverages, which suggests that the activation energy in the nonequilibrium situation stays at the same level for all these coverages. The scaling numbers have been plotted in Fig. 5 by cross marks. We can see that they all lie on the low coverage scaling function, which means that, the activation energy for the diffusion in disordered system is close to the ≈ 0.43 eV, although we expect that it slowly changes with the coverage.

IV. CONCLUSIONS

The crucial point in the discussed here dynamics of the $O/W(110)$ model is the difference between A and B states. According to the first term of Eq. (1) the particle attracts its

neighbors in the same state. Attractive interaction makes jumping out from the adsorption site more difficult. These interactions cause that the diffusion curves in Refs. 14,15 decrease with coverage for low values. The twin spin model $O/W(110)$ is closer to the conventional models if we assume that state A is equivalent to B, and that state C is excluded from the model. We checked that the diffusion coefficient for this special version of our model indeed leads to the same dynamical behavior like in Refs. 14,15. In the twin spin model (1) when two particles are nearest neighbors and both are in the same state, say A, they attract each other. The barrier between A and B state is quite low, so the particle can jump back and forth between them. When the particle is in the state B, its interaction with neighboring sites A becomes repulsive. The local energy of neighbor increases, and particle can more easily jump out from its place. The additional state B is for an adatomlike step that helps it to climb up. Thanks to the A-B repulsive interaction, the diffusion in our model grows when coverage increases, at low coverages. The difference between A and B states guarantees good qualitative tendency in the coverage dependence of the diffusion coefficient, but it is not sufficient to obtain good quantitative results for activation energy and for an increase of the diffusion coefficient.

Good quantitative results can be obtained, as follows from our work, by an additional dependence of the barrier height on the properly chosen interaction with neighboring sites. This interaction is defined in such a way that it removes discrepancy between movement along and vertically to the ordered oxygen lines. We have shown that such choice of interactions at the saddle point leads to a value close to the experimental activation energies and diffusion coefficient

functions.[11–13,16–18] We compared results obtained in highly nonequilibrium conditions, at the initial stages of the step relaxation process, with the diffusion calculated after three orders longer time. The results are qualitatively different, the activation energy for the diffusion process increases by 0.4 eV, coming from disorder to an ordered system.

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