



Sequential desorption of dimers from square lattices: A novel mechanism for phase transitions

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ABSTRACT

This work describes a novel mechanism for phase transitions during desorption, involving the formation of lattice size dependent intermediate states when there is enough adsorbate mobility. Monte Carlo simulations are performed to analyze the mechanism of the thermal desorption for adsorbed homonuclear dimers on two-dimensional square lattices. The lattice-gas model with nearest-neighbor repulsive interactions between particles is implemented to study the cases of mobile (with diffusion) and immobile desorption. The number of peaks for the immobile desorption spectra is related to the connectivity of the adsorbed species for both monomer and dimer molecules. However, for the case of mobile desorption, the spectra give information about the desorption mechanism, which differs significantly for monomers and dimers, particularly when the initial temperatures correspond to the critical region.

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1. Introduction

Temperature-programmed desorption (TPD) is one of the most widely used experimental techniques in surface science to get insight into the kinetics and thermodynamics of the adsorbed phase [1–3]. However, the phenomenon occurring at the molecular scale is hard to infer straightforwardly from the TPD spectra. For the case of simple molecules chemisorbed on single-crystal surfaces where there is a regular structure of the surface and bulk atoms, along with the strongly localized nature of chemisorption, it is possible to model the adlayer in terms of the lattice-gas approach [4–19]. The strong molecule-molecule interaction makes the equilibrium and dynamics of adlayers one of the most challenging problems to be addressed by classical statistical mechanics. This is true for analytical as well as for computer simulation approaches. In the framework of the lattice-gas model, the kinetics of desorption can be described by means of a simple expression for the desorption rate. However, it can only be solved exactly in some special cases [13].

Approximate solutions can be obtained by employing the mean-field [5] and quasi-chemical [4,7] approximation or transfer matrix technique [20]. The use of Monte Carlo (MC) simulations of TPD spectra is an alternative method to analyze the problem. Compared to the approaches mentioned above, MC simulations are much more versatile and powerful, allowing the description of the system with considerable physical detail. In particular, MC simulations facilitate the exact description of spatial correlations among adsorbed species and the accurate prediction of the behavior of the model, within statistical fluctuations [6,8,9,11,14–16]. In addition, MC simulations are particularly useful to directly visualize the configurational changes of the adsorbate during desorption. Furthermore, phase transitions can be easily studied as a function of coverage

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and temperature, and the results correlated with experimental observations given by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) to test the validity of the model.

In many cases the correct interpretation of TPD spectra needs additional information. For instance, the effect of adspecies mobility on desorption can change significantly the shape of the TPD curve adding multiple spurious desorption peaks, most of which are originated by metastable structures. Particularly, Meng and Weinberg [16], developed a Monte Carlo algorithm to simulate TPD spectra, in which non-equilibrium effects are taken into account. They demonstrated that multiple peaks in thermal desorption spectra may arise not only from lateral interactions between adsorbates, but also from limited adsorbate mobility. They analyzed in detail the case of unimolecular desorption from square lattices with repulsive nearest-neighbor interactions in which five peaks are observed in the TPD spectrum for an immobile adlayer, in contrast with the two peaks that appear for an adlayer in equilibrium. The case of finite hopping rate lies between those of an equilibrated and immobile adlayer. These intermediate peaks are originated by the desorption of molecules with i nearest neighbors ($i = 0, 1, 2, 3, 4$). The work shows clearly that a not well equilibrated adsorbed phase results in metastable structures which are responsible for spurious peaks in the TPD spectra. It is worth noting that these spurious peaks can be mistakenly attributed to additional adsorption states if the effects of mobility are not considered. Furthermore, the TPD experiment is inherently a dynamic measurement and therefore it is very difficult to know if the adlayer is well equilibrated or not.

The desorption of molecules with multisite occupation is more complicated than the single site desorption. The difficulty in the analysis of the multisite statistic arises from the non-equivalence between particles and vacancies, as well as the fact that the occupancy of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied. On the other hand, isolated vacancies cannot serve to determine whether that site can ever become occupied.

Although the multisite adsorption and desorption problem is less developed than the corresponding single-site problem, the adsorbed molecules consist in many cases of a number of single k components. Even simple gases, like nitrogen, carbon monoxide, oxygen, etc., are composed of more than one atom and can therefore, in principle, occupy more than one site, as has been reported experimentally [21,22]. More complicated molecules such as $C_mH_{2(m-1)}$ adsorbed on different solid surfaces represent a clear example of the multisite adsorption process.

The statistical aspect of molecules with multisite occupation is by now well understood [23–40]. In fact, among other results, it is well established that, for two-dimensional lattices, there is a finite number of ordered structures for dimers with nearest-neighbor repulsive interaction. On square lattices, dimers form a $c(2 \times 4)$ ordered phase at coverage $\theta = 1/2$ at temperatures below $k_B T_C/w = 0.331 \pm 0.0001$, and a zigzag ordered phase at $\theta = 2/3$ at temperatures below $k_B T_C/w = 0.1823 \pm 0.0007$, where w is the nearest-neighbor interaction constant [34,39].

Although the results obtained provide quantitative and qualitative understanding of the statistical and kinetic aspects of molecules with multiple occupancy of sites, the TPD spectra of these molecules are less analyzed. In this respect, a series of interesting papers related to the desorption of n -alkane has been published in recent years [41–44]. In particular, accelerated molecular dynamics of temperature-programmed desorption of n -pentane from the basal plane of graphite [44] has been recently implemented in order to elucidate the underlying kinetic phenomena that contrast the standard experimental interpretation.

A significant difficulty when interpreting TPD is that these macroscopic experiments offer a limited picture of the underlying microscopic kinetic events. In this regard, theory and simulation could be useful. However, modeling efforts have been limited to lattice-based approaches [4–17]. At temperatures where thermal desorption is significant, adsorption may not be localized to specific binding sites and therefore the validity of lattice models is questionable. This difficulty is evident for large molecules, whose various conformational states do not easily map the lattice. However, for small molecules, such as monomers and dimers, the lattice–gas approach has been successfully used to describe the desorption mechanism [20,18,19].

In this paper, desorption of dimers from two-dimensional square lattices is analyzed in order to understand the effect of the mobility on the shape of the TPD curves. Typical examples of square lattices are face centered cubic crystals that have been cut leaving the (100) face exposed for molecular adsorption. Even this simple surface shows some complexity considering that it offers three different adsorption sites that fit the square lattice model: (i) on top of an atom (atop), (ii) in between two atoms (bridge) and (iii) in between four atoms (fourfold).

Immobile and mobile TPD spectra are obtained by means of Monte Carlo simulations. It is observed that the number of peaks in the case of immobile desorption depends on the connectivity d of the molecules. The number of peaks is equal to $(d + 1)$, which gives, for the case of dimers in square lattices ($d = 6$), seven peaks. For the case of mobile desorption, the number of intermediate peaks depends on the size of the lattice. In this case, a simple mechanism for the desorption process is proposed.

Throughout the simulation, the system proceeds according to a kinetic algorithm [15,45]. This method has been successfully applied to rate processes in adlayers with strongly repulsive interactions at subcritical temperatures, where a second order phase transition occurs [45].

It is worth noting that this is a hypothetical experiment aimed to elucidate the desorption mechanism of molecules that occupy more than one site. Moreover, in real experiments the desorption temperatures are in general above the critical temperatures. However, it is interesting to analyze the desorption mechanism and how it is affected by the transient mobility and the lattice size.

The rest of the paper is organized as follows: in Section 2, we describe the model and the simulation scheme, in Section 3, we present the results and the discussions and finally in Section 4 we give our conclusions.

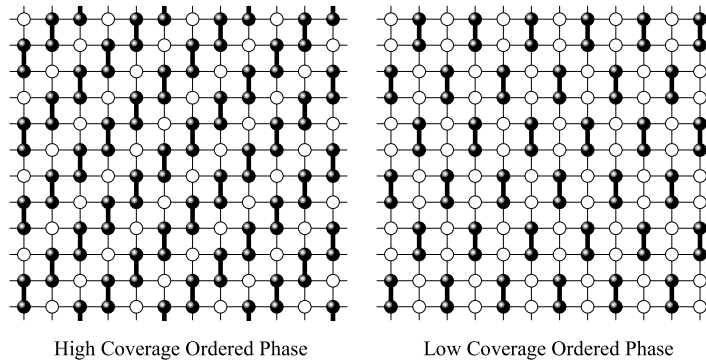


Fig. 1. High coverage ordered phase (HCOP) at $\theta = 2/3$ and low coverage ordered phase (LCOP) at $\theta = 1/2$.

2. The model and the desorption simulation scheme

In order to analyze TPD spectra by Monte Carlo simulations, we give a brief description of the equilibrium adsorbed phases. The adsorption of dimers on different lattices has already been treated in the past [24–27,32–40]. Here we describe the main characteristics of the ordered structures.

The adsorbate molecules are assumed to be composed of two identical units in a linear array with constant bond length equal to the lattice constant a . The dimers can only adsorb flat on the surface occupying two lattice sites (each lattice site can only be single occupied). The surface is represented as an array of $M = L \times L$ adsorption sites in a square lattice arrangement, where L is the linear size of the array. In order to define the Hamiltonian H of N dimers adsorbed on M sites at a given temperature T , let us introduce the spin variable $c_{i,j}$, which can take the following values: $c_{i,j} = 0$ if the corresponding site is empty or $c_{i,j} = 1$ if the site is occupied by a unit. Under this consideration, H is given by

$$H = w \sum_{\langle(i,j);(i',j')\rangle} c_{i,j} c_{i',j'} - Nw - \frac{\mu}{2} \sum_{i,j} c_{i,j} \quad (1)$$

where w is the nearest-neighbor interaction constant, which can be either repulsive (positive) or attractive (negative), $\langle(i,j);(i',j')\rangle$ represents pairs of neighboring sites and μ is the chemical potential. The first term of the right hand side of Eq. (1) is the interaction energy for all the possible pairs of units (bonds), including those belonging to the dimer; then, in the second term, we subtract the interactions corresponding to the N dimers (within the units of the dimer). Under the assumption that the surface is homogeneous, the interaction energy between the adsorbed dimer and the substrate is neglected for the sake of simplicity. It should be pointed out that any dissociation followed by re-bonding effect and exchange process which may occur in some experimental systems is not considered in our problem.

As it is mentioned in the introduction, dimers adsorbed at sub-monolayer coverage with nearest-neighbor repulsive lateral interactions form ordered structures at temperatures below the critical one. There are at least two well analyzed ordered structures. The first one is the so-called low coverage ordered phase (LCOP) or equivalently $c(4 \times 2)$ phase (see Fig. 1), with a critical coverage $\theta_c = 1/2$ and a reported critical temperature $k_B T_c / w = 0.331 \pm 0.0001$. The critical behavior of the system belongs to the Ising universality class as discussed in Ref. [34]. The second structure is the so-called zigzag ordered phase or high coverage ordered phase (HCOP) (see Fig. 1). This structure is formed by domains of parallel zigzag stripes one dimer wide at 45° to the lattice symmetry axes, separated from each other by single-site empty channels. The critical coverage and critical temperature are $\theta_c = 2/3$ and $k_B T_c / w = 0.1823 \pm 0.0007$, respectively. The critical behavior of the system suggests that the phase transition occurring for repulsive dimers on square lattices at $2/3$ monolayer coverage does not belong to the universality class of the two-dimensional Ising model and it is carefully classified by Romá et al. [39]. Fig. 2 shows the phase diagram (critical temperature vs. coverage) obtained from Ref. [25]. The continuous line corresponds to the TPD experiment and it will be explained below.

In order to develop a general model for describing the desorption processes on such a surface, let us define elementary transition probabilities per unit of time, W_{ij} , for a given molecule to make a transition from the initial state representing the molecule at site i to the final state j . To be specific, for monomolecular processes, the final state j could be the molecule in the gaseous state for desorption, or the molecule occupying one of the vacant nearest-neighbor (NN) sites for surface diffusion. Let

$$r_i = \sum_{j \neq i} W_{ij} \quad \text{and} \quad R = \sum_i r_i \quad (2)$$

be the total probability for a particle at site i and for the whole system, respectively, to change its state per unit of time. Then, the probability for the system to change its state at a time in the interval $(t, t + dt)$ is given by (Poisson process [45]):

$$P(t)dt = Re^{-Rt} dt. \quad (3)$$

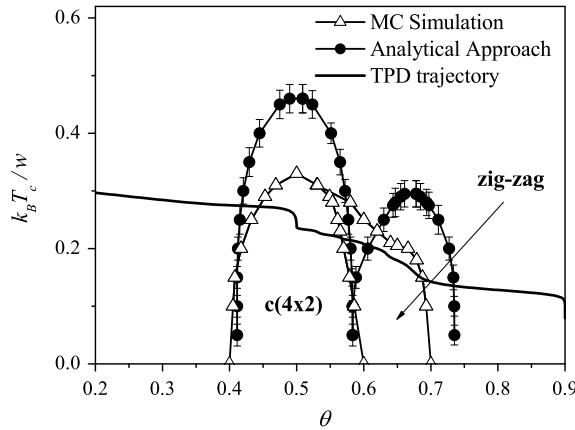


Fig. 2. The critical temperature calculated using an analytical approach and by means of Monte Carlo simulations, for adsorbed dimers with repulsive nearest neighbor lateral interaction, is shown. The continuous line is the trajectory of the TPD experiment in the (T, θ) -space, where the linear size of the system is $L = 60$.

This means that the time elapsed before the system makes a transition should be obtained as

$$\Delta t = -\frac{\ln(\xi)}{R} \quad (4)$$

where ξ is a random number uniformly distributed between 0 and 1. Note that Eq. (4) is applicable even if the system under consideration contains only a few particles. However, in the case of desorption, there is always a large number of molecules. Under such circumstances, one can in principle employ the average time increment

$$\langle \Delta t \rangle = -\frac{1}{R} \int_0^1 \ln(\xi) d\xi = \frac{1}{R}. \quad (5)$$

The latter approach has been used in Refs. [6,9,11,14].

It is easy to show that if an arbitrarily large probability R' is used instead of R , then the time elapsed before a transition has the correct distribution as long as each event is accepted with probability R/R' .

When surface diffusion is much faster than desorption, we can consider a unique desorption probability W_{id} for a molecule located in site i and apply a separate relaxation procedure to adsorbed molecules to keep the equilibrium distribution. The appropriate algorithm is:

- (i) Let $r \geq \max W_{id}$; $R' = N_a r$; $t = t_0$.
- (ii) Obtain a random number ξ ; $\Delta t = -\frac{1}{R'} \ln(\xi)$; $t = t + \Delta t$.
- (iii) Select at random an occupied site i .
- (iv) Obtain a random number ξ' ; if $\xi' < W_{id}/r$, then accept the desorption step at time t .
- (v) Relax the adsorbate through a Monte Carlo exchange process between adsorbed molecules and empty sites until equilibrium is reestablished.
- (vi) Repeat from step (ii).

Since we are interested in describing the general behavior of TPD spectra, it is sufficient to consider only NN interactions between adsorbed molecules and no interactions for the activated complex, so that the desorption probabilities W_{kd} , with $k = 1, \dots, N$, are calculated through

$$W_{kd} = \nu \exp \left[- \left(w \sum_{(i,j)} c_{i,j} + E_d \right) / k_B T \right], \quad (6)$$

where the sum runs over all nearest neighbor sites of dimer k , E_d is the desorption energy for the dimer k ($E_d = 10$ Kcal/mol), k_B is the Boltzmann constant and the pre-exponential factor is taken as $\nu = 10^{13} \text{ s}^{-1}$. The relation between time and temperature is given by the heating rate $\beta = dT/dt$ where ($\beta = 1 \text{ K s}^{-1}$).

The probabilities W_{kd} must be updated after every temperature change or every desorption event. Steps (i)–(vi) are repeated until exhaustion of the adsorbed molecules. This is a very efficient way to carry out thermal desorption simulations, which allows us to obtain accurate statistics. The simulated spectra are usually obtained by averaging over 2×10^3 different samples. From the variation of the coverage during the temperature interval of 0.5 K, the desorption rate is obtained by the ratio $\Delta\theta/\Delta T$.

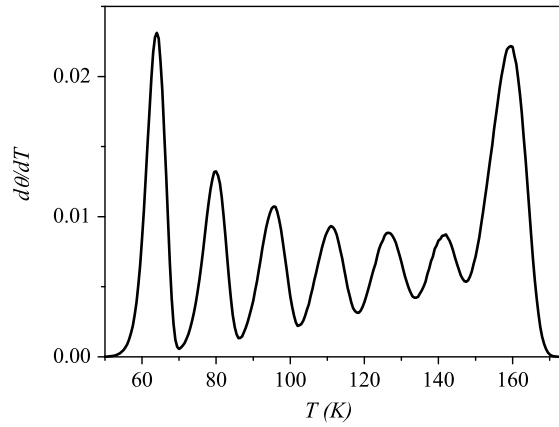


Fig. 3. TPD spectrum for immobile adsorbate. The initial coverage is $\theta_0 = 0.9$. The size of the system is $L = 96$ and the lateral interaction is $w = 1$ kcal/mol.

3. Results and discussion

In this section we present the results of our model and the discussions.

In Fig. 3, the TPD spectrum for immobile particles is shown (in all the TPD spectra $d\theta/dt$ is expressed in arbitrary units). For large enough nearest-neighbor lateral interactions ($w = 1$ kcal/mol in this case), the TPD corresponding to square lattices presents seven peaks originating from the interaction with n units from nearest neighbor dimers, $n = 0, \dots, 6$.

For mobile adsorbates, desorption and diffusion occur simultaneously. When diffusing, the molecules tend to arrange themselves so that the system seeks its lowest energy configuration. The question is: can the shape of the TPD spectra give some additional information about the desorption process, particularly, starting from temperatures below the critical one? To give a consistent answer, we proceed to analyze the effect of the size of the system on the TPD spectra. In what follows, the initial coverage will be taken as $\theta_0 = 0.9$. Throughout the experiment we consider that the initial temperature of the system is below the critical temperature. The temperature is increased following the path shown in Fig. 2. The sizes to be used are chosen to be compatible with the formation of the previously reported ordered phases, i.e. HCOP zigzag and LCOP $c(4 \times 2)$.

The desorption rate, $(d\theta/dT)$, the fraction of dimers with j nearest neighbors, F_j , the average number of dimers per row, $\langle N \rangle$, and its variance, σ^2 , defined as

$$\sigma^2 = \frac{1}{L} \sum_{i=1}^L (\langle N \rangle - N_i)^2 \quad (7)$$

(where N_i is the number of dimers in the i th row) are plotted as a function of temperature.

Fig. 4(a) shows the desorption curve for the $L = 12$ lattice. For the sake of simplicity in the explanation we are going to assume that the phases are formed with the dimer long axis oriented parallel to the direction of the rows in the lattice. Three well defined maxima can be observed at $T = 64$ K, $T = 108$ K and $T = 140$ K, respectively and the last peak is followed by a plateau that extends to $T = 158$ K. The valley between the first and second desorption peaks is located at $T = 90$ K while the second valley, i.e. between the second and third peaks, extends from $T = 116$ to $T = 130$ K with no desorption in this temperature range. The fraction of dimers F_j with j nearest neighbors as a function of temperature is plotted in Fig. 4(b) and shows that when the systems form the zigzag phase the dimers have, on average, two nearest neighbors. From the zigzag to $c(4 \times 2)$ phase transition the number of dimers with two neighbors decreases accompanied by an increase in the number of dimers with one neighbor and a slight increment in the number of dimers with three neighbors. The latter is due to the possibility of the dimers to rotate 90° when a vacancy is generated above them; this rotation increases the number of neighbors to three, which increases the repulsive energy and consequently produces most likely the desorption of this molecule. The sharp maximum at $T = 140$ K, corresponding to the desorption from the $c(4 \times 2)$ phase, is accompanied by a maximum in the number of dimers with one neighbor. This can be explained in the following way: when a dimer desorbs from the $c(4 \times 2)$ phase, the dimer in the bottom (top) row can then move sideways and contact the dimer beneath (above) increasing its energy and inducing its desorption. It is worth noting that for $L = 12$, four dimers per row are needed to form the zigzag phase and three dimers per row to form the $c(4 \times 2)$ phase. In order to illustrate this, Fig. 5 shows the average number of dimers per row $\langle N \rangle$ and its variance, σ^2 . In this figure it can be clearly observed that the number of dimers for the region corresponding to the zigzag phase is four, while the number of dimers for the region corresponding to the $c(4 \times 2)$ phase is three. The variance in each region is negligible. This proves that the system is perfectly aligned and that domains of phases with different alignments do not coexist. On the other hand, if the proposed desorption mechanism is the right one, the alignment given by the zigzag phase will be maintained for the $c(4 \times 2)$. Although it is observed that the dimers are adsorbed in an aligned fashion and in order to transition from the zigzag to the $c(4 \times 2)$ phase each row loses a dimer,

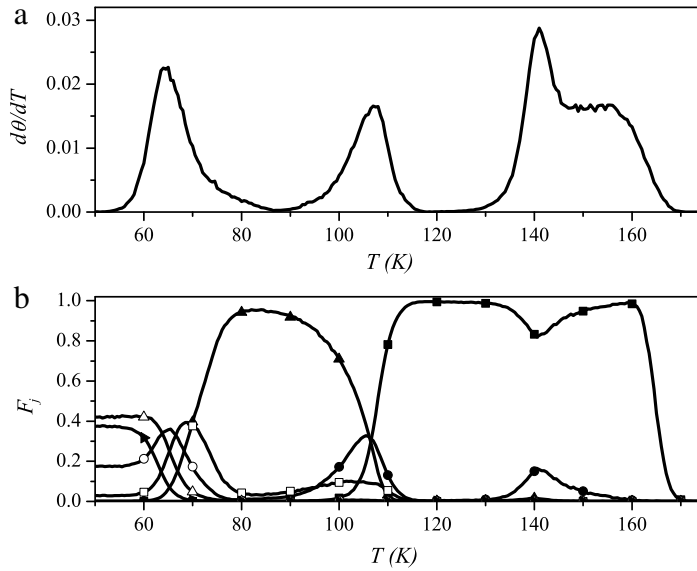


Fig. 4. (a) Mobile TPD and (b) fraction of dimers F_j with j nearest neighbors as a function of temperature T for $L = 12$. ($j = 0$: solid square; $j = 1$: solid circle; $j = 2$: solid up triangle; $j = 3$: open square; $j = 4$: open circle; $j = 5$: open up triangle; $j = 6$: solid right triangle.)

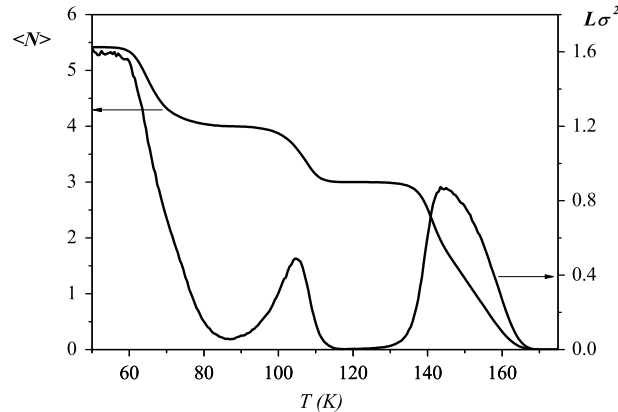


Fig. 5. The average number of dimers per row, $\langle N \rangle$, and its variance, σ^2 , as a function of temperature for $L = 12$.

the mechanism of desorption is not completely clear. There are two different ways to arrive at the same result. The first one is that a dimer desorbs from each row until all rows have the same number of dimers and the second one is that more than one dimer can desorb from a row and the transfer of dimers between rows allows all rows to reach the same number.

In order to discern between these two mechanisms it is necessary to also consider the next lattice size that is commensurate with the formed phases, i.e. $L = 24$. Fig. 6 shows the desorption curve for the $L = 24$ system. It can be observed that the maxima at low and high temperatures do not change. However, instead of one intermediate maximum, two maxima appear at $T = 100$ and $T = 117$ K along with a minimum at $T = 108$ K. As opposed to the previous case, the system goes from one ordered phase to the next one passing through an intermediate state at $T = 108$ K where the number of nearest neighbors per dimer fluctuates between 0, 1 and 2 as shown in Fig. 6(b).

Fig. 7 shows the number of dimers per row and its variance. For this lattice size eight dimers are needed per row to form the zigzag phase and six dimers per row to form the $c(4 \times 2)$ phase. The variance in both cases is close to zero, indicating that the dimers are aligned. On the other hand, at $T = 108$ K the system has seven dimers per row also with a variance close to zero. This indicates that the desorption occurs in a sequential fashion, i.e.: once the zigzag phase is formed with eight dimers per row, one dimer per row desorbs until all rows have seven dimers and then one dimer per row desorbs until each row has six dimers, thus forming the $c(4 \times 2)$ phase.

Clearly, if the proposed mechanism for desorption is the right one, the number of valleys that appear in the TPD spectrum is related to the number of dimers in a given row, in such a way that the low temperature valley corresponds to the zigzag phase, and the high temperature valley corresponds to the $c(4 \times 2)$ phase. The number of intermediate valleys is equal to the number of integers between the number of dimers per row necessary to form the zigzag phase and the number of

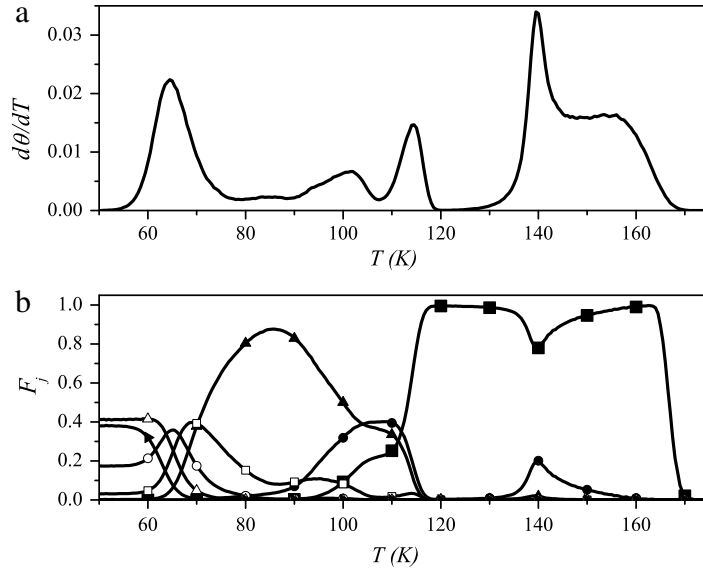


Fig. 6. (a) Mobile TPD and (b) fraction of dimers F_j with j nearest neighbors as a function of temperature T for $L = 24$. ($j = 0$: solid square; $j = 1$: solid circle; $j = 2$: solid up triangle; $j = 3$: open square; $j = 4$: open circle; $j = 5$: open up triangle; $j = 6$: solid right triangle.)

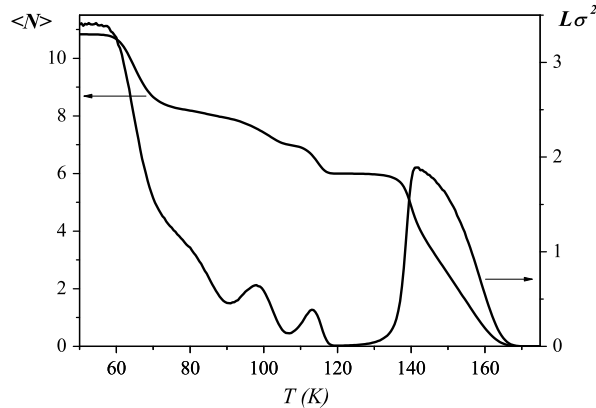


Fig. 7. The average number of dimers per row, $\langle N \rangle$, and its variance, σ^2 , as a function of temperature for $L = 24$.

dimers per row that are needed to form the $c(4 \times 2)$ phase. In order to confirm this hypothesis, Fig. 8 shows the cases for $L = 36, 48, 60, 72$ where 4000 MCS were performed to obtain the TPD curves. For instance, for $L = 36$ the number of valleys is four, in fact, 12 dimers per row are necessary to form the zigzag phase, while nine dimers per row are necessary to form the $c(4 \times 2)$ phase. The intermediate valleys are due to the desorption of molecules from the structures formed by 11 and 10 dimers per row, respectively. It is easy to see that this argument is still valid for the rest of the cases.

For large systems the relaxation (diffusion) process is computationally expensive. Fig. 9(a) shows the TPD spectrum for $L = 144$. In order to obtain this spectrum, 4000 MCS were performed for relaxation. The same case but with 40 MCS is shown in Fig. 9(b). In the latter case, the number of relaxation steps is not enough to equilibrate the system and the intermediate maxima cannot be distinguished from each other, resulting in only two intermediate maxima. A similar phenomenon can occur in the experimental cases when the heating rate is such that the system is not allowed to be in equilibrium along the experiment.

In all the cases, the fact that the number of dimers per row decreases in steps of one with variance close or equal to zero, describes the mechanism of the desorption process. In summary: first the dimers desorb and equilibrate to form the zigzag phase at temperatures between 80 and 90 K. Then, from the number of neighbors and the number of dimers per row it is found that the dimers are perfectly aligned (domains with perpendicular direction do not coexist). In order to illustrate this in Fig. 10 we show the snapshots corresponding to the evolution of the zigzag structures for different relaxation times for the $L = 48$ lattice. Once the zigzag structure is formed, the desorption occurs in a sequential fashion, in which each row (or column) loses a dimer until all rows (columns) have the same amount. This process is repeated until the $c(4 \times 2)$ phase is formed, having the same alignment of the the zigzag phase that originated it. The evolution of the systems is shown in Fig. 11.

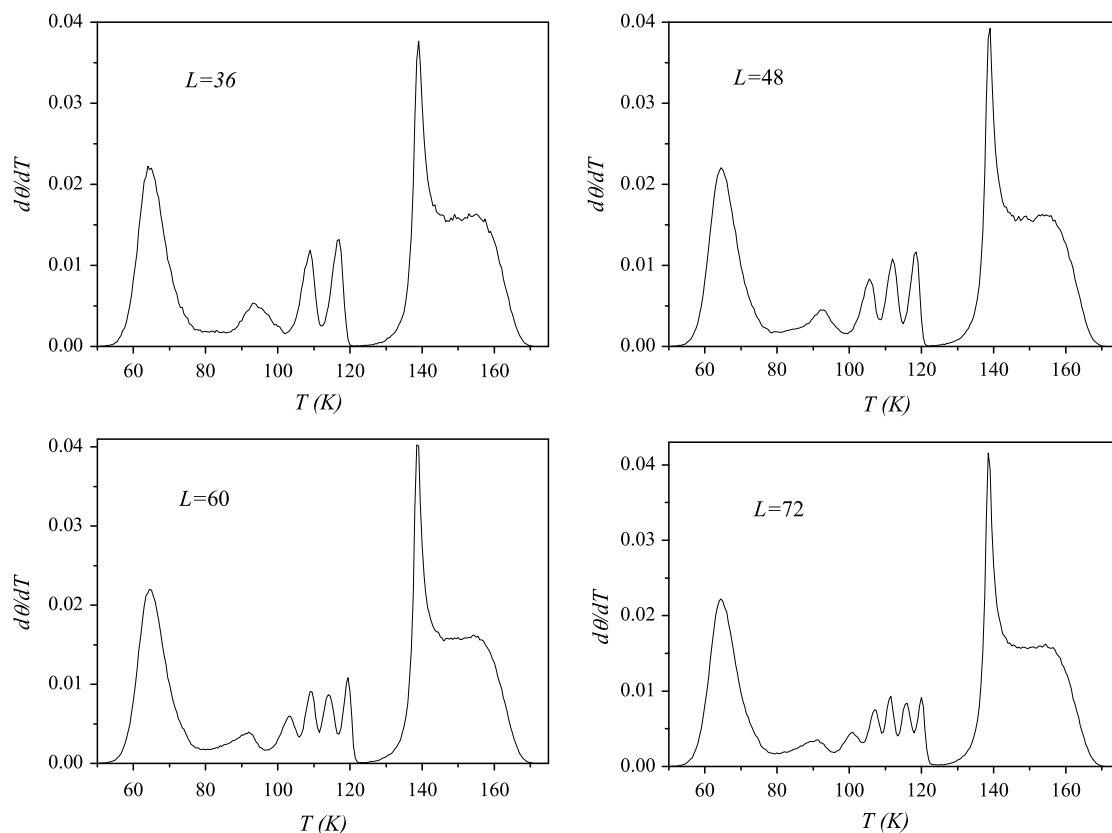


Fig. 8. Mobile TPDs for systems of different sizes.

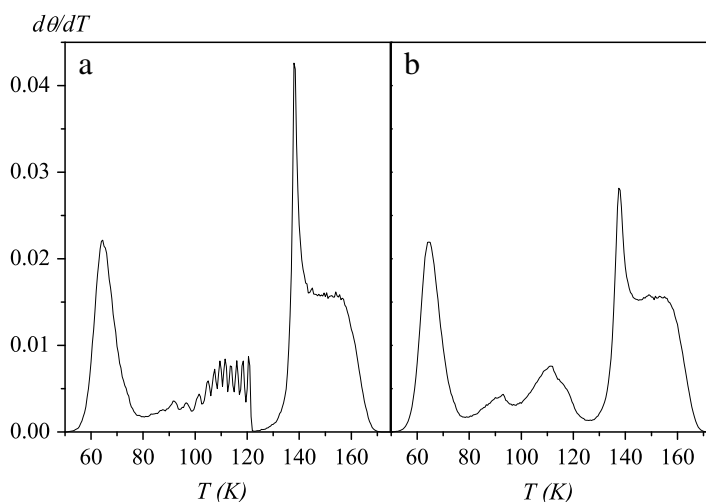


Fig. 9. Mobile TPD for $L = 144$ for (a) 4000 MCS and (b) 40 MCS.

This mechanism is completely different from the one observed for monomers. This type of mechanistic analysis accounting for the diffusion of molecules and its effect in the desorption phenomenon is impossible to perform experimentally and therefore the use of simulations to understand the events occurring at the nanoscale level is of major importance. Regarding the effect of the lattice size on the TPD spectra, it would be interesting to correlate the present study with size constrained systems, such as surfaces with high density of steps. Although an $L = 48$ lattice might seem small compared to real systems, it is actually very close to a typical terrace size in commonly used single crystals. Let us take the example of a Pd(100) surface. The interatomic distance is 2.75 Å, meaning that a region with $L = 48$ corresponds to 13.2 nm. A commercially available crystal can be purchased with different precisions in the cut angle, but a typical value is 1°; this angle would give

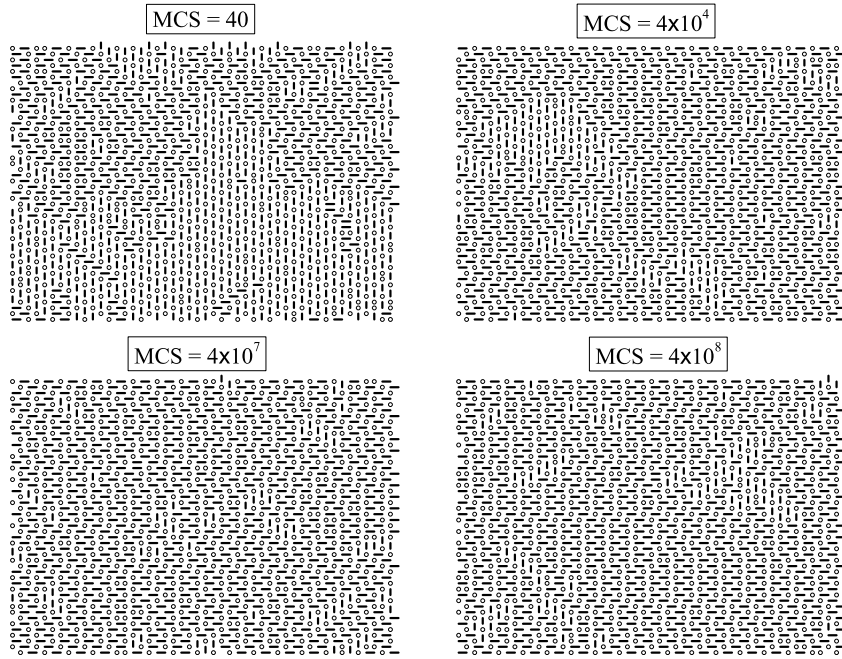


Fig. 10. Snapshots of the system for $T = 88$ K and $L = 48$ and different relaxation times.

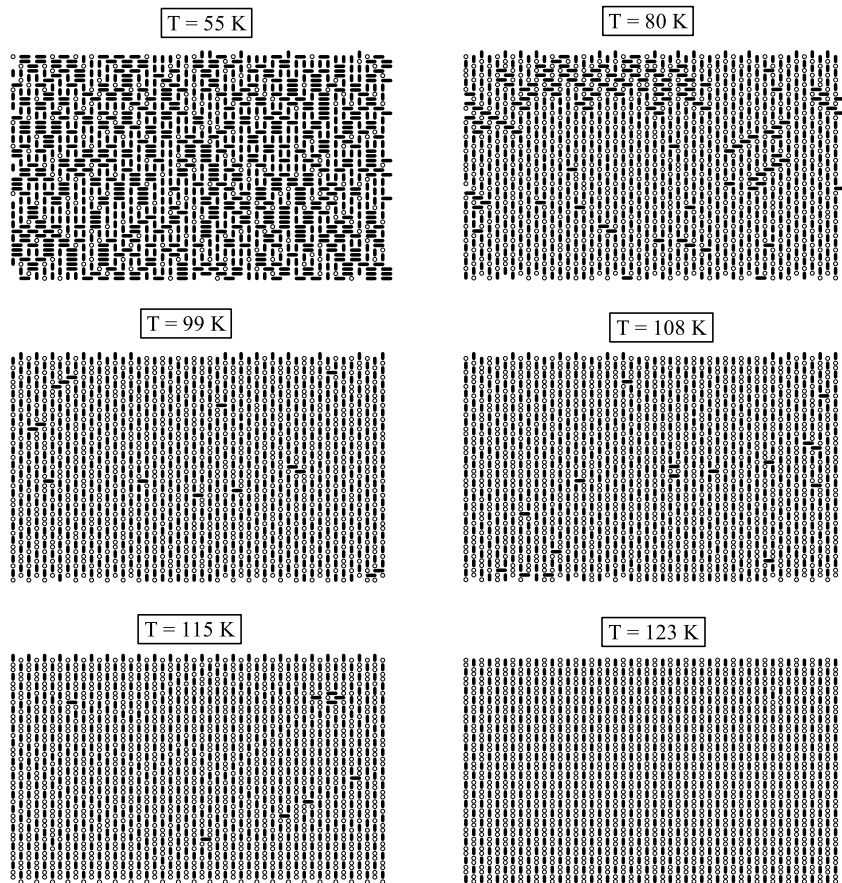


Fig. 11. Snapshots of the system for $L = 48$ and 4000 MCS and different temperatures.

terraces with a width of 11.5 nm, which is very close to the value of an $L = 48$ lattice. However, more than making a direct comparison with real systems, the main emphasis of this work is to describe a novel mechanism for phase transitions during the desorption process when there is enough surface mobility of the adsorbate.

4. Conclusions

In this work we have elucidated and explained the insights of the mechanism of desorption of homonuclear dimers with nearest-neighbor repulsive interaction from square lattices. The mechanism was inferred from the behavior of curves of thermal desorption, number of nearest neighbors and number of dimers per row and their variance as a function of the temperature. It is first observed that as the dimers desorb, the number of neighbors as a function of the temperature shows that the ordered phases formed are aligned with one of the lattice directions, discarding the possibility of domains with perpendicular directions. During the TPD experiment the orientation of the high coverage zigzag phase determines the orientation of the lower coverage $c(4 \times 2)$ phase. The desorption of dimers occurs in a sequential manner, in which at each step of the sequence the system loses one dimer per row until every row of the lattice has lost a dimer. This mechanism explains the observation of intermediate peaks and it is proven to be true by counting the average number of dimers per row and its variance.

Although this is a hypothetical experiment and has not been correlated with experimental data yet, it is of high interest to show this novel mechanism for the case of dimers, as it has not been described before and it is significantly different from the one that has been established for the desorption of monomers.

In fact, as it was shown by Weinberg and co-worker, the effect of the mobility on monomer desorption can change the shape of the TPD curve adding multiple spurious desorption peaks, most of which are originated by metastable structures. They analyzed the case of unimolecular desorption from square lattices with repulsive nearest-neighbor interactions in which five peaks are observed in the TPD spectrum for an immobile adlayer, in contrast with the two peaks that appear for an adlayer in equilibrium. Finite hopping rate originated intermediate peaks in the TPD spectrum.

For dimer desorption a not well equilibrated adsorbed phase results in two intermediate peaks in the TPD spectra in the case of large systems. However, when there is high mobility, a series of intermediate peaks appears depending on the size of the system. A detailed analysis of the events leading to appearance of these peaks shows a novel mechanism of phase transition during desorption.

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