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## Monte Carlo study of temperature-programmed desorption spectra with attractive lateral interactions

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We present results of a Monte Carlo study of temperature-programmed desorption in a model system with attractive lateral interactions. It is shown that even for weak interactions there are large shifts of the peak maximum temperatures with initial coverage. The system has a transition temperature below which the desorption has a negative order. An analytical expression for this temperature is derived. The relation between the model and real systems is discussed.

### I. INTRODUCTION

Many studies have been published on Monte Carlo (MC) simulation of desorption from single-crystal surfaces,<sup>1-8</sup> but little attention has been given to the effect of attractive lateral interactions. There may be three reasons for this. First, temperature-programmed desorption (TPD) spectra with attractive lateral interactions appear less interesting than TPD spectra with repulsive lateral interactions, which can show multiple peaks even with just one adsorbate. Second, repulsive lateral interactions are more common than attractive lateral interactions. This can be understood using the bond-order conservation principle.<sup>9</sup> Nearest-neighbor interactions are often repulsive, because nearest neighbors bond to the same substrate atom(s). Multiple bonds of a substrate atom are generally weaker than when a substrate atom bonds just to one adsorbate, so it is energetically more favorable for adsorbates to stay apart. Only when the direct adsorbate-adsorbate interaction is strong, with respect to the substrate-adsorbate interaction, then will one find attractive lateral interactions. This is the case for physisorbed adsorbates. Third, a good quantitative MC method is necessary to understand the effects of attractive lateral interactions. In particular, it is necessary to have an MC method with the correct real time, instead of MC time, dependence. Such methods have only recently been developed.<sup>8,10</sup> It is known that attractive lateral interactions cause peaks in TPD spectra to shift to higher temperature and to become smaller.<sup>1,2,5</sup> In this paper, we will concentrate on shifts of peaks with initial coverage.

### II. COMPUTATIONAL DETAILS

We have used MC modeling of the reactions based on the master equation

$$\frac{dP_\alpha}{dt} = \sum_{\beta} [W_{\alpha\beta}P_\beta - W_{\beta\alpha}P_\alpha], \quad (1)$$

where  $P_\alpha$  is the probability of having the adlayer in configuration  $\alpha$ . The  $W$ 's are transition probabilities per unit time corresponding to various reactions. The master equation is solved using the first-reaction method in which a time for each reaction to occur is generated from an appropriate probability distribution, and then the adlayer is modified according to the first reaction after which the procedure is repeated.<sup>11</sup> Details of this method can be found elsewhere.<sup>10</sup> The transition probabilities per unit time are given by

$$W_{\alpha\beta} = \nu_{\alpha\beta} \exp\left[-\frac{E_{\alpha\beta}}{k_B T}\right], \quad (2)$$

where  $E_{\alpha\beta}$  and  $\nu_{\alpha\beta}$  are the activation energy and prefactor, respectively, of the reaction  $\beta \rightarrow \alpha$  that transforms configuration  $\beta$  into configuration  $\alpha$ . The  $W$ 's may be time-dependent through the temperature. For the simulation of TPD spectra,

$$T = T_0 + Bt \quad (3)$$

holds, where  $T_0$  is the temperature at the beginning of the simulation,  $t$  is time, and  $B$  is the (constant) heating rate.

For all the desorption reactions, we have used the same prefactor  $\nu_{\alpha\beta} = \nu_0$ . The activation energy is given by

$$E_{\alpha\beta} = E_0(1 + \gamma N_{\alpha\beta}), \quad (4)$$

where  $E_0$  is the activation energy for an isolated adsorbate,  $N_{\alpha\beta}$  is the number of (nearest) neighbors of the desorbing adsorbate in the reaction  $\beta \rightarrow \alpha$ , and  $\gamma$  is a positive dimensionless parameter determining the strength of the interactions between the adsorbates. The linear dependence of the activation energy on the number of neighbors seems to be appropriate for the systems that are best known for attractive adsorbate-adsorbate interaction, namely, noble gas atoms, but we will also look at other dependencies on the number of neighbors later on.

Apart from desorption we also have diffusion. This is modeled by jumps of adsorbates to neighboring sites.

The diffusion should be fast with respect to desorption, because we want a thermally equilibrated adlayer before each desorption. We found that for values  $\gamma < 0.1$ , a prefactor for diffusion of  $\nu_{\alpha\beta} = 20\nu_0$  was sufficient. We used the same expression (4) for the activation energy as for the desorption. The number of neighbors in that expression refers to the situation prior to the jump of the adsorbate.

Most MC simulations were done on a square lattice of dimensions  $100 \times 100$ . This effectively models an infinite lattice. Although we did not do extensive simulations of lattices with different numbers of neighboring sites  $Z$ , we will present an analysis that holds for any value of  $Z$ . All simulations have been done with our code PIZAZZ.<sup>12</sup>

### III. RESULTS AND DISCUSSION

The MC simulations that have just been described depend on five parameters;  $\nu_0$ ,  $E_0$ ,  $\gamma$ ,  $B$ , and  $T_0$ . The last one is not very relevant; as long as it is chosen as a low temperature, where the desorption is negligible, the TPD spectra will be the same. We can remove two more parameters by scaling the time, and the temperature. Instead of time we use  $\nu_0 t$ , and instead of temperature, we use  $k_B T/E_0$ . The only remaining parameters are then  $\gamma$  and  $k_B B/\nu_0 E_0$ , the scaled version of  $B$ . The former is, of course, the more relevant one. We will also present results for desorption at constant temperature. These depend on just one parameter;  $k_B T/E_0 \gamma$ .

Figure 1 shows the TPD spectrum for  $\gamma = 0.05$  and  $k_B B/\nu_0 E_0 = 10^{-16}$ . [This is roughly the TPD spectrum one would get with  $\nu_0 = 10^{13} \text{ s}^{-1}$ ,  $E_0/k_B = 3000 \text{ K}$ ,  $E_0 \gamma/k_B = 150 \text{ K}$ , and  $B = 3 \text{ K s}^{-1}$ , values very similar to the Xe/Pt(111) system.<sup>13</sup>] Although  $\gamma$  is rather

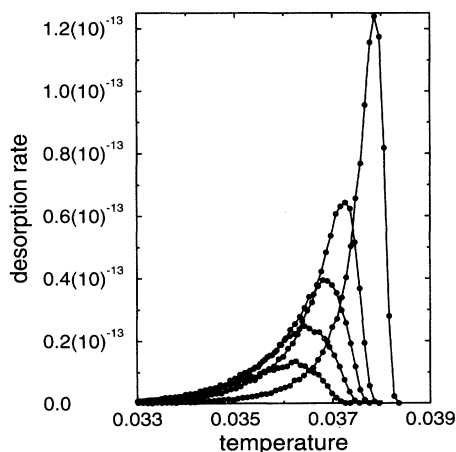


FIG. 1. TPD spectra showing the desorption rate  $-d\theta/d(\nu_0 t)$  as a function of the temperature  $k_B T/E_0$  for  $\gamma = 0.05$  and heating rate  $k_B B/\nu_0 E_0 = 10^{-16}$ . The dots are results directly from the MC simulations, and the lines connect MC results with the same initial coverage. The five curves are from left to right for initial coverage 0.262, 0.463, 0.644, 0.822, and 1.000.

small, we see a substantial shift of the peak maximum with decreasing initial coverage. Lower coverages may show larger desorption rates. This implies that the order of the desorption is negative, which has been observed in Xe/Pt(111) experimental spectra before.<sup>13,14</sup> Smaller values of the parameter  $\gamma$  show smaller distances between the peak maxima, but not until  $\gamma$  is clearly smaller than 0.01 do the curves of different initial coverages stop crossing. (We will derive a better estimate below.) Making  $\gamma$  larger spreads out the peak as far as we could check. However, for  $\gamma$  larger than about 0.1, we ran into convergence problems with the grid size and the diffusion rate. For really large values of  $\gamma$ , one expects island formation. Islands are one explanation for zero-order desorption,<sup>15</sup> so the trend towards more negative order should reverse for some  $\gamma$ .

As the interactions are attractive between the adsorbates, there is an order-disorder phase transition. Below the phase-transition temperature islands just mentioned are formed. This phase-transition temperature is about half  $E_0 \gamma/k_B$ . The negative-order TPD spectra have peaks well above this temperature, however. This implies that a model, which assumes that the adsorbates are randomly distributed over the substrate, might explain the peak shifts. To check this, it seems more convenient to look at desorption at a constant temperature, as this reduces the relevant parameters to just one;  $k_B T/E_0 \gamma$ . The results are shown in Fig. 2. The model and the MC results agree very well, except for the relatively low temperatures at intermediate coverages. At those temperatures, there is still some short-range order. The adsorbates tend to have somewhat more neighbors than in a random distribution, so that the desorption is smaller than in the model. The model and the MC sim-

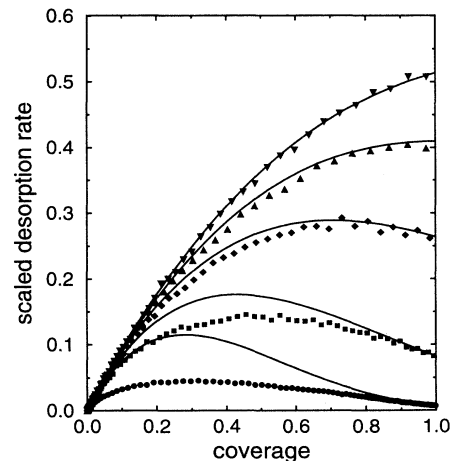


FIG. 2. Scaled desorption rate  $-\exp(E_0/k_B T) d\theta/d(\nu_0 t)$  as a function of coverage  $\theta$ . The symbols are results directly from the MC simulations, and the lines are from the model with random distribution of adsorbates. Results are shown for five temperatures from top to bottom  $k_B T/E_0 \gamma = 6, 4.48, 3, 1.6, \text{ and } 0.8$ . The value of  $k_B T/E_0 \gamma = 4.48$  corresponds to the transition temperature above which negative-order desorption is not possible.

ulation show that for desorption at low constant temperature starting with a high coverage the desorption rate increases, reaches a maximum, and then decreases. The initial increase implies a negative order. At higher temperatures the order is positive for all coverages, and so we have another transition temperature. This temperature can be defined as the temperature where the order is zero at  $\theta = 1$ .

We can derive this temperature from the model, or more generally, by assuming that for  $\theta \approx 1$  there are only adsorbates that still have all their neighbors or have only lost one. With  $N_\alpha$ , the number of adsorbates in configuration  $\alpha$  the master equation gives us the general result

$$\begin{aligned} \frac{d\langle N \rangle}{dt} &\equiv \frac{d}{dt} \sum_{\alpha} P_{\alpha} N_{\alpha} \\ &= \sum_{\alpha\beta} W_{\alpha\beta} P_{\beta} (N_{\alpha} - N_{\beta}) \\ &= - \sum_{\beta} P_{\beta} \sum_{n=0}^Z W_{\beta}^{(n)} N_{\beta}^{(n)}, \end{aligned} \quad (5)$$

where  $N_{\beta}^{(n)}$  is the number of adsorbates in configuration  $\beta$  with  $n$  neighbors, and  $W^{(n)}$  is the transition probability per unit time for such adsorbates. Dividing by the number of sites this gives us, for the desorption rate  $r$  at  $\theta \approx 1$ , the expression

$$\begin{aligned} r &\equiv - \frac{d\theta}{dt} \\ &= [1 - (1 + Z)(1 - \theta)] W^{(Z)} + Z(1 - \theta) W^{(Z-1)}, \end{aligned} \quad (6)$$

where  $Z$  is the number of neighboring sites. The coefficients of  $W^{(n)}$  are the fractions of all adsorbates with  $n$  neighbors. From this we can find when the negative-order desorption disappears by setting  $dr/dt = -d^2\theta/dt^2 = 0$  at  $\theta = 1$ , which gives us

$$\frac{W^{(Z)}}{W^{(Z-1)}} = \frac{Z}{Z+1}. \quad (7)$$

As  $W^{(n)} \propto \exp(-nE_0\gamma/k_B T)$ , this leads to

$$k_B T = \frac{E_0\gamma}{\ln(Z+1) - \ln Z}, \quad (8)$$

for the transition temperature. For  $Z = 4$ , we have  $k_B T \approx 4.48 E_0\gamma$ , which is indeed far above the order-disorder phase-transition temperature. It is also instructive to compute the order  $x$  at  $\theta = 1$ . We find that it equals for desorption at a constant temperature,

$$\begin{aligned} x &\equiv \frac{\theta}{r} \left( \frac{\partial r}{\partial \theta} \right)_T = \theta \frac{d^2\theta}{dt^2} \bigg/ \left( \frac{d\theta}{dt} \right)^2 \\ &= 1 - Z \left[ e^{E_0\gamma/k_B T} - 1 \right]. \end{aligned} \quad (9)$$

For the values used in Fig. 1 this becomes  $x = -9.96$  at the peak maximum temperature of  $k_B T/E_0 = 0.0379$ . Whether the negative order really shows up in a TPD

spectrum depends on the positions of the peaks. For normal heating rates, the peak maximum is at about  $k_B T/E_0 \approx 1/30$ . This value should be lower than the temperature at which the negative order disappears. Hence, for  $Z = 4$ , we find negative orders in TPD spectra if  $\gamma > 0.00744$ .

We would finally like to remark on the relevance of the results just presented to real systems. As has already been mentioned, negative orders in TPD have been seen for Xe/Pt(111).<sup>13,14</sup> As the effect seems to be large, it should be easy to find experimentally. However, this depends crucially on the dependence of the activation energy for the desorption on the number of neighbors. Above we have assumed that the activation energy was additive. If we assume a dependence  $E_0(1 + \gamma\sqrt{N_{\alpha\beta}})$ , then we find from Eq. (7)

$$k_B T = E_0\gamma \frac{\sqrt{Z} - \sqrt{Z-1}}{\ln(Z+1) - \ln Z} \quad (10)$$

for the transition temperature. For  $Z = 4$  this gives us  $k_B T = 1.20 E_0\gamma$ , and with the peak maximum at  $k_B T/E_0 \approx 1/30$ , we must have  $\gamma > 0.0278$  in order to get negative orders in TPD spectra. We see that the effects are much weaker than for additive interactions. As attractive interactions are primarily found for physisorption, the additive activation energy may seem to be a good approximation. However, substrate-mediated effects may give large nonadditive contributions.<sup>13</sup>

Nonadditivity need not be the only factor obscuring negative orders as we can demonstrate for Xe/Pt(111). Activation energies for this system as a function of the number of neighbors have been determined using molecular dynamics (MD).<sup>13</sup> They are well approximated by  $E_0/k_B = 2851$  K and  $\gamma = 0.031$ . As  $Z = 6$ , negative-order desorption should disappear only at 575 K, whereas peak maxima are found somewhat below 110 K. Large peak shifts as a function of initial coverage are expected. Indeed, if we use the same activation energies for the diffusion, we find spectra very similar to Fig. 1. However, such large shifts have neither been found experimentally,<sup>14</sup> nor with MD.<sup>13</sup> The reason for this is that the lateral interactions are larger than the activation energies suggest. A value of  $\gamma = 0.049$  is more appropriate for diffusion. This is found using the effective Xe-Xe potential of the MD study. If we use this value for the diffusion, we obtain the spectra in Fig. 3.

We see that the shifts are small. There is a reasonable agreement between Fig. 3 and the zero-order-like spectra of the MD study. Figure 3 still shows slight negative order, and there are no extra peaks or shoulders. We think that these latter features in the MD study are probably artifacts caused by fits and extrapolations. The same holds for the oscillations in the order and the prefactor (Fig. 7 of the MD study<sup>13</sup>), which are particularly sensitive to numerical errors.

It might seem contradictory that attractive lateral interactions, which in our model with randomly distributed adsorbates cause large peak shifts, reduce these shifts in Xe/Pt(111). The reason for this is that in the model, the lateral interactions only effect the desorption, whereas the effect in Xe/Pt(111) is dominantly on the structure

of the adlayer. For the model, the probability that an adsorbate has  $n$  neighbors equals  $\binom{Z}{n} \theta^n (1 - \theta)^{Z-n}$  (note that this does not depend explicitly on the temperature). For Xe/Pt(111), the fraction of Xe atoms with many neighbors is larger than according to this expression, as desorption takes place not far above the order-disorder transition. The probability of a Xe atom having  $n$  neighbors and the short-range order are similar to what was found in the MD study. Figure 2 already showed the consequence. The curves of the model are always above the results of the simulations. At low temperature this means, that starting at high coverage, the desorption rate in the model increases more than in the simulations, which implies a more negative order, and hence larger peak shifts.

#### IV. CONCLUSIONS

TPD spectra of systems with attractive lateral interactions may show large shifts of the peak maxima as a function of initial coverages. These shifts indicate negative-order desorption. A simple model with random occupation of sites can explain them qualitatively. The same model can also be used to derive an exact analytical expression for a transition temperature above which negative-order desorption is not possible. This transition temperature may be higher than the order-disorder phase-transition temperature by about an order of magnitude. Nonadditivity and the structure of the adlayer

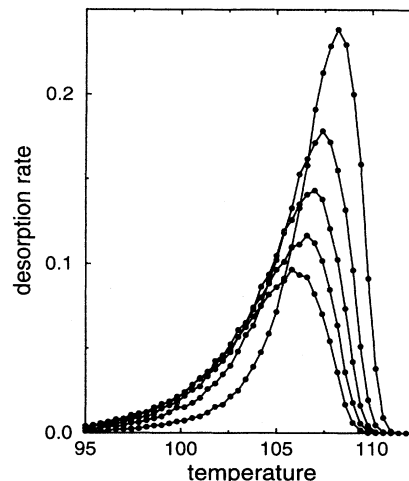


FIG. 3. TPD spectra showing the desorption rate  $-d\theta/dt$  (in number of Xe atoms per second per site), as a function of the temperature (in K) for heating rate  $B = 1 \text{ K s}^{-1}$ . The dots are results directly from the MC simulations, and the lines connect MC results with the same initial coverage. The five curves are from left to right for initial coverage 0.598, 0.698, 0.806, 0.906, and 1.000.

may decrease the peak shifts. Therefore, more experiments are necessary to see if the negative-order desorption that occurs in the model system described above also occurs in real systems.

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