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Thermal desorption of interacting molecules from heterogeneous surfaces

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The thermal desorption of interacting particles from heterogeneous surfaces is studied by means of a Monte Carlo simulation method. It is shown how desorption spectra are affected by site-energy heterogeneity, site structure, and adsorbate-adsorbate interactions.

I. INTRODUCTION

Thermal desorption of atoms and molecules from solid surfaces has been widely studied in the last two decades and it is well known that two effects are the principal causes of the complex dependence of spectra on surface coverage, namely lateral interactions of adsorbed particles and heterogeneity of adsorptive-site energies.

The first of these effects, adsorbate-adsorbate interactions, has received greater attention, and desorption rate equations have been solved using mean-field approximations to describe the adsorbed lattice gas.[1-6] Predictions for simple as well as for associative desorption are in fairly good agreement with experimental results for ideally prepared homogeneous surfaces.

Surfaces used in practical applications, such as catalysts for example, are strongly heterogeneous. However, not enough effort has been dedicated to the study of heterogeneity effects on thermal desorption curves and a number of calculations have been published which analyze the problem only superficially. In particular, Grant and Carter[7] assume a uniform probability density between two energy limits and find that the desorption rate should be constant over a temperature range. Czanderna *et al.*[8] show that the desorption curves for heterogeneous surfaces become broader as the range of allowed site energies increases. Tokoro *et al.*[9] analyze desorption from surfaces where heterogeneity is characterized by a nonlinear variation of activation energy with coverage. They find that a range of activation energy broadens the desorption peaks over a much wider range, and that multiple peaks could be seen under special circumstances.

More recently, Codoba and Luque[10] developed an interesting model to calculate thermal desorption curves from an heterogeneous linear chain of adsorbing sites, assuming site independence, and show that desorption spectra are strongly influenced by the structure of adsorbing site energies and by adsorbate-adsorbate interactions. This seems to be the first attempt to treat the general problem by taking into account both lateral interactions and heterogeneity. However, their site-independence hypothesis, made through the assumption of a Bragg-Williams approximation for the description of the lattice gas, is not appropriate since adsorption is strongly influenced by adsorptive energy correlations.[11]

As more-perfect lattice-gas models are not resoluble for heterogeneous surfaces, a more rigorous analysis can only be made by numerical methods. Our purpose here is to use Monte Carlo simulation to analyze joint effects of heterogeneity and adsorbate-adsorbate interactions. We shall first treat the case of two (or more) kinds of sites, with fixed adsorptive energies, arranged in different structures on a linear chain (in order to compare our results to those obtained in Ref. 10), and then generalize to two-dimensional lattices with a Gaussian energy distribution for each kind of site.

II. MONTE CARLO SIMULATION SCHEME

Our statistical ensemble will be composed by N sites, each with adsorptive energy ε_i $(i=1,\ldots,N)$. Adsorbate-adsorbate interaction energy is w_0 for nearest-neighbor (NN) occupied sites and w_1 for next-nearest-neighbor (NNN) occupied sites, and we assume that attractive interactions are given by positive energy. The desorption energy for a particular molecule at site i is then given by

$$E_d=\varepsilon_i+w_0\sum_{j(\mathrm{NN})\text{ to }i}S_j+w_1\sum_{j(\mathrm{NNN})\text{ to }i}S_j\;, \tag{1}$$

where $S_j=1$ if site j is occupied $(+)$ and $S_j=0$ if it is empty $(-)$, and its mean value will be a function of the coverage $\Theta=\sum_{j=1}^{N}S_j/N$.

Now, the residence time for an adsorbed molecule is

$$\tau=\tau_0\exp(E_d/R_gT)\;, \tag{2}$$

so that the probability for a molecule to desorb in a time interval Δt will be

$$P(\Delta t)=\Delta t/\tau\;. \tag{3}$$

If the temperature is raised at a constant rate $dT/dt=\mu$, then the probability for desorption in a temperature interval ΔT is

$$\begin{aligned}P(\Delta T)&=\Delta T/\tau\mu\\&=\beta\Delta T\exp(-E_d/R_gT)\;,\end{aligned} \tag{4}$$

where $\beta=(\tau_0u)^{-1}$.

With this, the simulation follows through the following steps.

(a) Fix a distribution for the adsorptive energies ε_i ($i=1,\ldots,N$), completely fill N sites with adsorbed molecules, and fix an initial temperature T_0.

(b) Increase the temperature by ΔT.

(c) For a given occupied site, obtain E_d and P according to (1) and (4), and generate a uniformly distributed random number $0<\xi<1$. If $\xi<P$ the molecule is desorbed, otherwise it is not.

(d) Repeat step (c) until the totality of the N sites have been tested and obtain the total number of molecules desorbed in the present temperature interval, the value of coverage Θ, the mean value for the desorption energy $E_d(\Theta)$, and the desorption rate $\Delta\Theta/\Delta T$.

(e) Test the N sites for reaccommodation through a jumping mechanism. If E_i and E_f are the initial and final energies of a molecule in a possible jump then the quantity $Q=\exp|(E_i-E_f)/R_g T|$ is evaluated and a random number ξ is generated. If $\xi<Q$ the jump is allowed, otherwise it is not.

(f) Repeat from step (b) on until all molecules have been desorbed.

Initial coverages other than $\Theta_i=1$ can be produced in two ways, namely by simulating the thermal desorption until the desired Θ_i is attained and then restarting the process at T_0, or by simulating the adsorption-desorption process until the equilibrium is reached at the desired Θ_i. We found no substantial differences between the two methods.

Lattice dimensionality and type could, in principle, be any one, though we used one-dimensional linear chains and two-dimensional square lattices with periodic boundary conditions.

In practice, we found that good statistics could be obtained with $N=10^4$ sites, and satisfactory curve smoothness with $\Delta T=10$ K. Moreover, in order to compare our results to those obtained in Ref. 10, we used $\beta=5\times10^6$ K^{-1}.

III. DISCRETE SITE-ENERGY DISTRIBUTION ON A LINEAR CHAIN

In order to compare Monte Carlo results to those obtained in Ref. 10, we start our analysis by considering a linear chain of sites with only NN interactions. As a first simple case to be treated, and to check the accuracy of our Monte Carlo method, we simulated an homogeneous linear chain for different values of the NN interaction energy w_0. The results, shown in Fig. 1, are encouraging: for $w_0>0$ (attractive interactions) and $w_0=0$ (no interactions) the spectra are similar to those of Cordoba and Luque,[10] and for $w_0=0$ there is also quantitative agreement, but for $w_0<0$ (repulsive interactions) our simulation results in a double peak in qualitative contrast to their predictions. This is a striking example of the drastic breakdown of kinetic models which suppose site independence or that all site configurations are equally probable. In fact, when desorption begins, the dominating configuration is $(+\;+\;+\;+\;+\;+)$ with $E_d=\varepsilon+2w_0$, which yields the first peak, while when $\Theta\simeq\frac{1}{2}$ the most probable configuration is $(+\;-\;+\;-\;+\;-)$ with $E_d=\varepsilon$ which corresponds to the second peak. Thus we see that, even for homogeneous surfaces, we can obtain double-peaked desorption spectra if adsorbate-adsorbate interactions are repulsive.

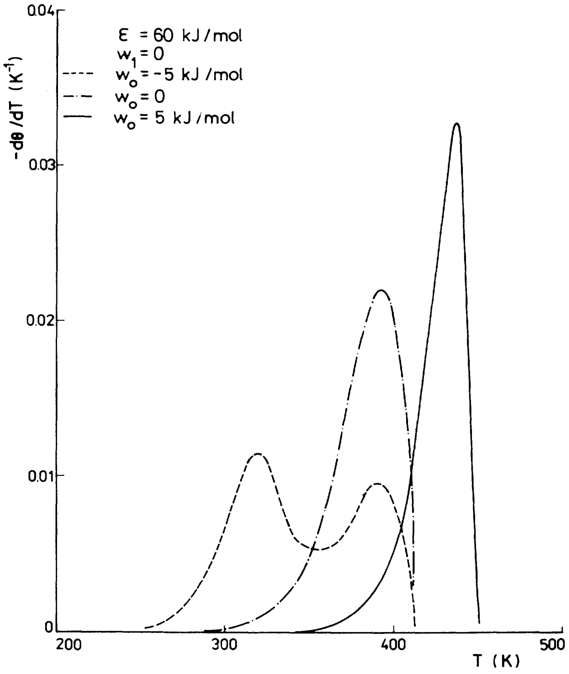

FIG. 1. Homogeneous linear chain, variation with NN interaction energy.

We shall now consider thermal desorption from heterogeneous surfaces. Figure 2 shows the effects of the adsorbate-adsorbate interaction energy for a linear chain with 50% of the sites with energy ε_1 and 50% with energy ε_2, distributed at random (heterogeneous random linear chain). We see that for $w_0>0$ the spectrum shows two peaks which overlap more and more as w_0 increases, and for sufficiently strong attractive interactions we obtain a single peak, while for $w_0<0$ each peak splits in two due to the effect discussed before. So, we can have from one to four peaks depending on the strength and sign of adsorbate-adsorbate interactions.

Now, heterogeneous surfaces can have a variety of structures. In Figs. 3 and 4 we present desorption spectra from heterogeneous linear chains all composed by two kinds of sites, of adsorptive energy ε_1 and ε_2, but having different structures: periodic chain, random chain, 10-site patches, and two macroscopic domains. For attractive NN interactions (Fig. 3) it is interesting to note that the periodic chain presents only one peak while 10-site patches and macroscopic domains give very similar spectra with well-separated peaks. For repulsive NN interactions (Fig. 4) a new interesting feature appears for the cases of patches and macroscopic domains, namely, a three-peak spectrum in which the central peak is the highest. This can be explained in terms of the following sequence of most probable configurations as desorption takes place:

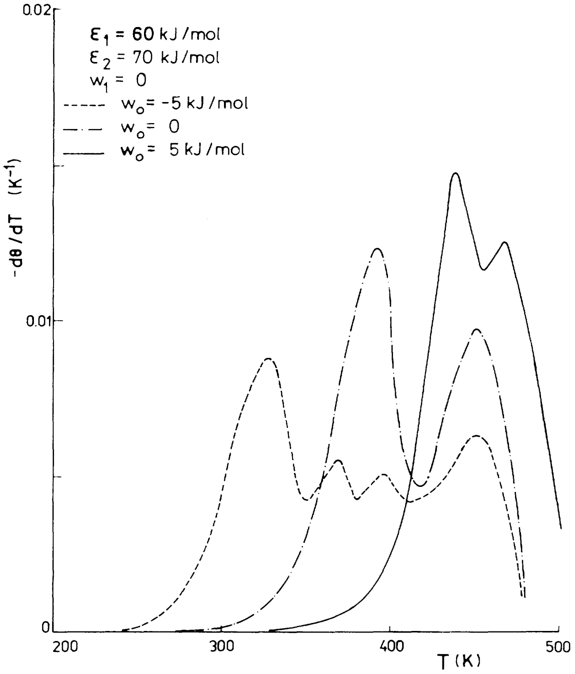

FIG. 2. Heterogeneous random linear chain, variation with NN interaction energy.

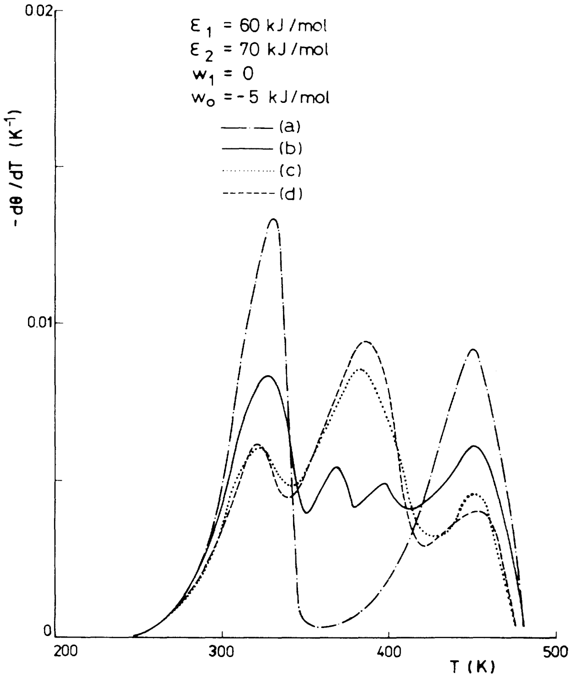

FIG. 4. The same as Fig. 3 for repulsive NN interactions.

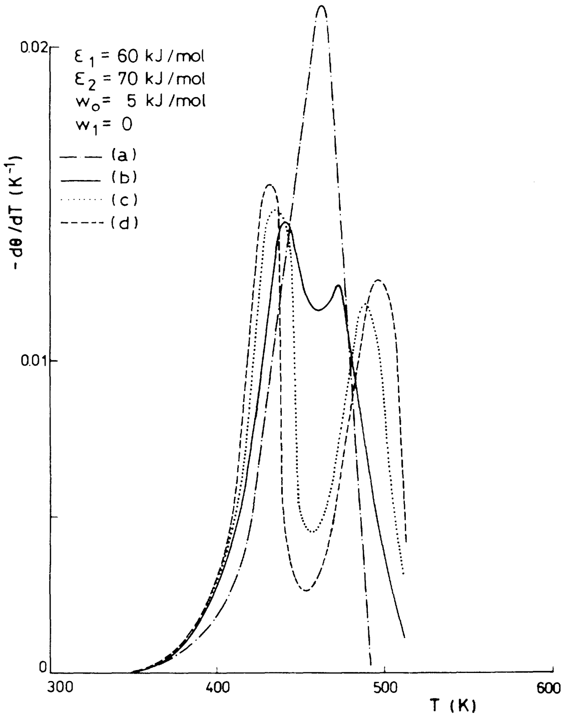

FIG. 3. Heterogeneous linear chain with attractive NN interactions, variation with site structure: (a) periodic chain, (b) random chain, (c) 10-site patches, (d) two macroscopic domains.

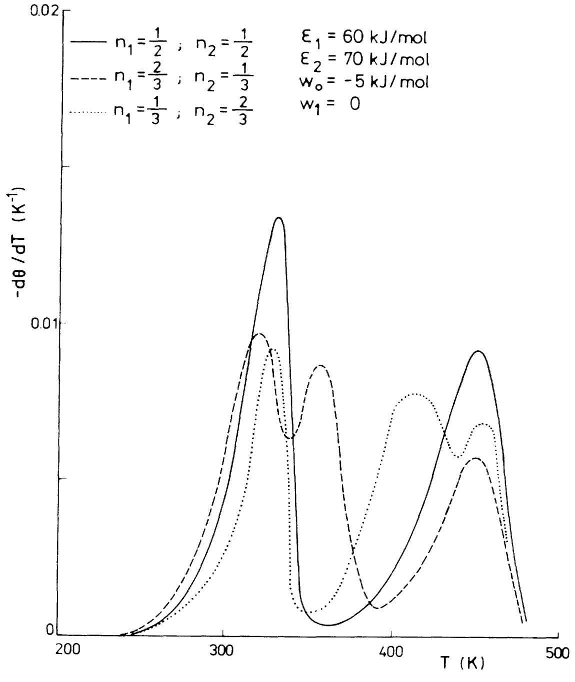

FIG. 5. Periodic chain with repulsive interactions, variation with the proportion of sites "1" and "2."

$$\underset{\varepsilon_1}{+\,+\,+\,+\,+\,+\,+\,+\,+\,+}\quad \underset{\varepsilon_2}{+\,+\,+\,+\,+\,+\,+\,+\,+\,+}\quad [E_d(1)],$$

$$\underset{\varepsilon_1}{+\,-\,+\,-\,+\,-\,+\,-\,+\,-}\quad \underset{\varepsilon_2}{+\,+\,+\,+\,+\,+\,+\,+\,+\,+}\quad [E_d(2)],$$

$$\underset{\varepsilon_1}{+\,-\,+\,-\,+\,-\,+\,-\,+\,-}\quad \underset{\varepsilon_2}{+\,-\,+\,-\,+\,-\,+\,-\,+\,-}\quad [E_d(3)].$$

Thus, we see that not only heterogeneity and interaction energy, but also the site structure can severely modify the desorption spectra. The general trend is that as the degree of mixing of sites of different energies increases the corresponding desorption peaks overlap more and more.

One more interesting feature appears in the case of the periodic chain for $w_0 < 0$ [Fig. 4(a)]: when the proportion of ε_1 sites to ε_2 sites is changed, the peak corresponding to the more abundant sites splits in two. This effect is shown in Fig. 5 and can be readily explained in terms of the most probable configurations. For other cases, changes in the proportions n_1 and n_2 of sites of energy ε_1 and ε_2 simply modify the peak height without producing splitting.

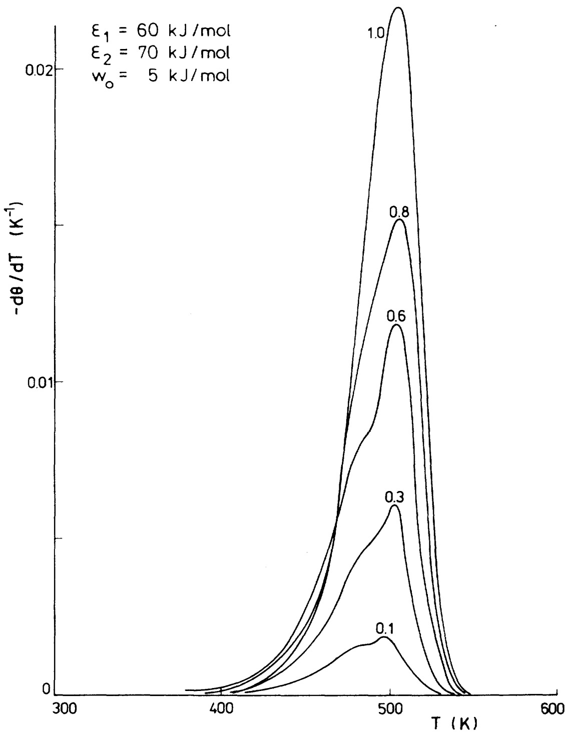

FIG. 6. Heterogeneous random lattice with attractive NN interactions, variation with initial coverage. Θ_i values are shown on the curves.

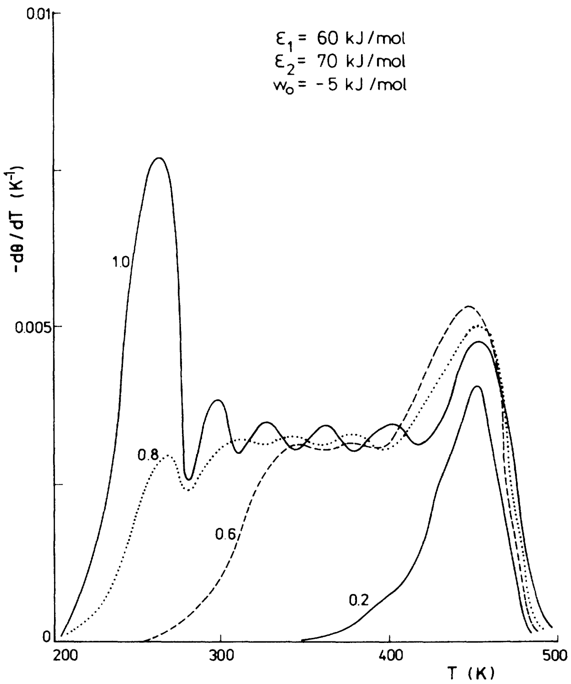

FIG. 7. The same as Fig. 6 for repulsive NN interactions.

It is usually accepted that the shift of desorption peaks to the right, when the desorption process is started at decreasing initial coverages Θ_i, is evidence for surface heterogeneity when no readsorption is present. However, this is true only when adsorbate-adsorbate interactions are negligible. In fact, attractive interactions can mask these effects or, if sufficiently strong, can even produce shifts to the left. On the other hand, repulsive interactions can produce shifts to the right even for homogeneous surfaces. Figures 6 and 7 show the variation with initial coverage for an heterogeneous random lattice with attractive and repulsive NN interactions, respectively, and the general features can be appreciated. In particular, for $w_0 < 0$ we see how the first peak disappears as Θ_i decreases while the second peak approximately remains constant. Contrary to this, for $w_0 > 0$ a two-peak structure develops as Θ_i decreases. This contrasting behavior suggests that the variation with Θ_i could be a way to get some idea about the type of adsorbate-adsorbate interactions present in a given system.

Extension of the analysis to more than two kinds of sites is straightforward and will not be given here. Instead, it is more important the situation where each kind of site does not have a definite adsorptive energy but is characterized by an energy distribution around a mean value. To get the main features of such a system we need to analyze the behavior of one kind of site with a continuous energy distribution.

IV. DESORPTION FROM A GAUSSIAN SURFACE

Mainly, two energy distribution functions have been widely used, in practice, to characterize heterogeneous surfaces: the normal, or Gaussian, and the log-normal, or skewed, distribution.

For our analysis we choose, for the sake of simplicity, the Gaussian distribution function:

$$f(\varepsilon)=\frac{1}{\sqrt{2\pi}\sigma_\varepsilon}\exp\left[-\frac{1}{2}\frac{(\varepsilon-\bar{\varepsilon})^2}{\sigma_\varepsilon^2}\right], \tag{5}$$

where $\bar{\varepsilon}$ and σ_ε are the mean value and standard deviation of the site adsorptive energy ε, respectively, and $f(\varepsilon)d\varepsilon$ is the fraction of sites with adsorptive energy in the interval $(\varepsilon, \varepsilon+d\varepsilon)$.

The dispersion σ_ε obviously represents the degree of heterogeneity of the surface and in the limit $\sigma_\varepsilon \to 0$ (Dirac's δ distribution) we have a homogeneous surface where all sites have the same adsorptive energy $\bar{\varepsilon}$. We can generate surfaces with different heterogeneity degrees by sampling site energies from the distribution (5) with different values of σ_ε. Then, by the Monte Carlo method we can simulate the desorption process obtaining the desorption rate $(-d\Theta/dT)$ as the coverage decreases while the temperature T is steadily increased at a constant rate μ.

Figure 8 shows desorption curves from Gaussian linear chains of sites with $\bar{\varepsilon}=60$ kJ/mol and different heterogeneity degrees for different NN interaction energies w_0. We see how the spreading of the peaks increases with σ_ε. In particular, a new qualitative feature is shown in the case of repulsive NN interactions, namely the production of a third peak in the middle of the two peaks expected to correspond to desorption energies $\bar{\varepsilon}$ and $\bar{\varepsilon}+2w_0$.

This third peak, which corresponds to a desorption energy $\bar{\varepsilon}+w_0$, indicates the presence of an intermediate surface phase composed by a random distribution of "holes" (isolated empty sites) embedded in a string of occupied sites:

$$++-+++-++-++++-+\ .$$

Such a phase develops from the very beginning of the desorption process when sites belonging to the low-energy tail of the Gaussian distribution of adsorptive energies are desorbed preferentially.

We turn now to two-dimensional lattices where other interesting features occur. Figure 9 shows the desorption spectra for a square lattice with repulsive NN interactions and attractive NNN interactions. This kind of situation occurs, for example, for adsorbed light-atom species on metal surfaces like the interesting case of oxygen on W(110) where, as an approximation to the more complex actual situation, a double phase transition appears in the adsorption isotherm as an ordered $c(2\times2)$ phase is entered and left.[12,13] This ordered phase corresponds to configurations of the type

$$\begin{array}{ccc} + & - & + \\ - & + & - \\ + & - & + \end{array}$$

and is responsible for the second high peak. The first peak corresponds to the configuration

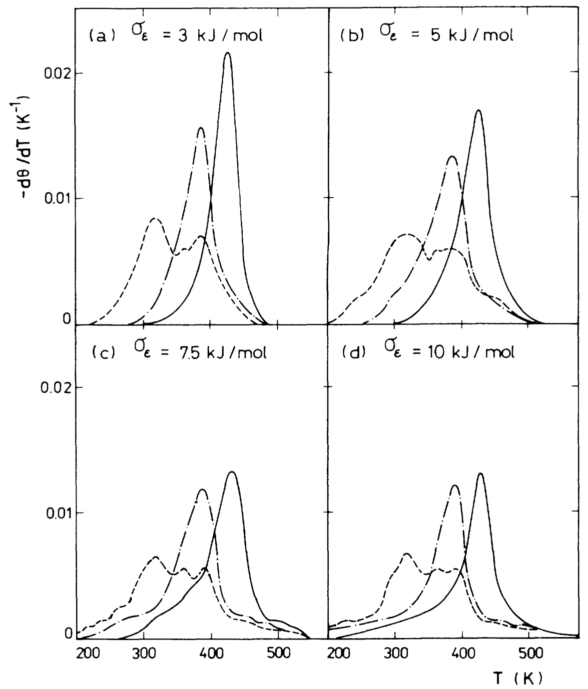

FIG. 8. Gaussian lineal chain with $\bar{\varepsilon}=60$ kJ/mol, variation with adsorptive energy dispersion for different NN interactions: — — —, $w_0=-5$ kJ/mol; —·—·—·, $w_0=0$ kJ/mol; ——, $w_0=5$ kJ/mol.

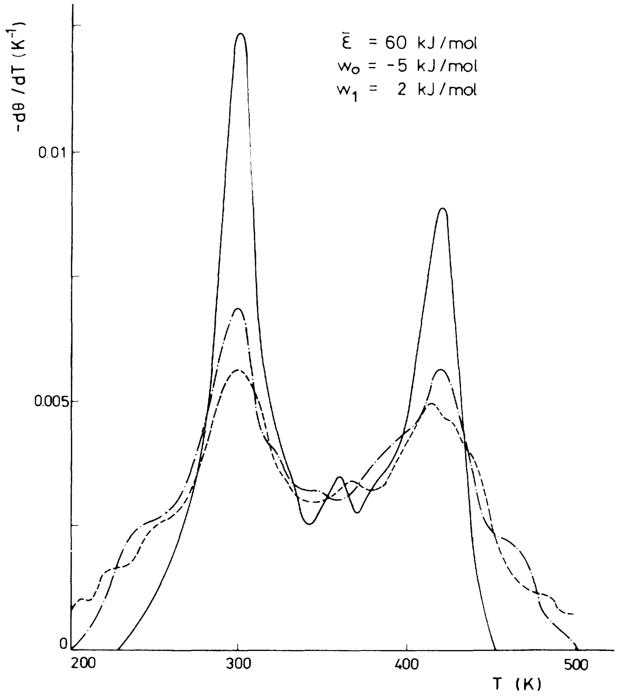

FIG. 9. Gaussian two-dimensional square lattice with repulsive NN and attractive NNN interactions, variation with adsorptive energy dispersion.

$$\begin{array}{ccc} + & + & + \\ + & + & + \\ + & + & + \end{array}$$

while the other small intermediate peaks are due to configurations like

$$\begin{array}{ccc} + & + & + \\ + & + & + \\ + & - & + \end{array}, \quad \begin{array}{ccc} + & + & + \\ + & + & - \\ + & - & + \end{array},$$

$$\begin{array}{ccc} + & + & + \\ - & + & - \\ + & - & + \end{array}.$$

We shall now see to what extent adsorbate-adsorbate interactions can compensate the shift to higher temperature (due to heterogeneity) as the initial coverage Θ_i decreases. Figure 10 shows the behavior of desorption curves from Gaussian square lattices with different heterogeneity degrees σ_ε. We see in Figs. 10(a) and 10(b) that for a value of $w_0 = 2$ kJ/mol for NN interactions, an heterogeneity of $\sigma_\varepsilon = 1$ kJ/mol does not compensate the shift to lower temperatures due to attractive adsorbate-adsorbate interac-

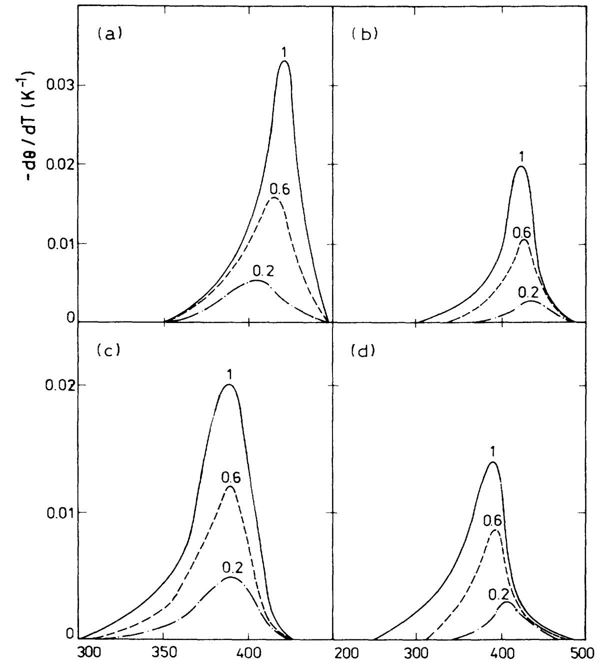

FIG. 10. Gaussian two-dimensional square lattice with attractive NN interactions; influence of NN interactions and adsorptive energy dispersion on the Θ_i shift: $\bar{\varepsilon} = 60$ kJ/mol; (a) $\sigma_\varepsilon = 1$ kJ/mol, $w_0 = 2$ kJ/mol; (b) $\sigma_\varepsilon = 5$ kJ/mol, $w_0 = 2$ kJ/mol; (c) $\sigma_\varepsilon = 1$ kJ/mol, $w_0 = 0$ kJ/mol; (d) $\sigma_\varepsilon = 5$ kJ/mol, $w_0 = 0$ kJ/mol. Θ_i values are shown on each curve.

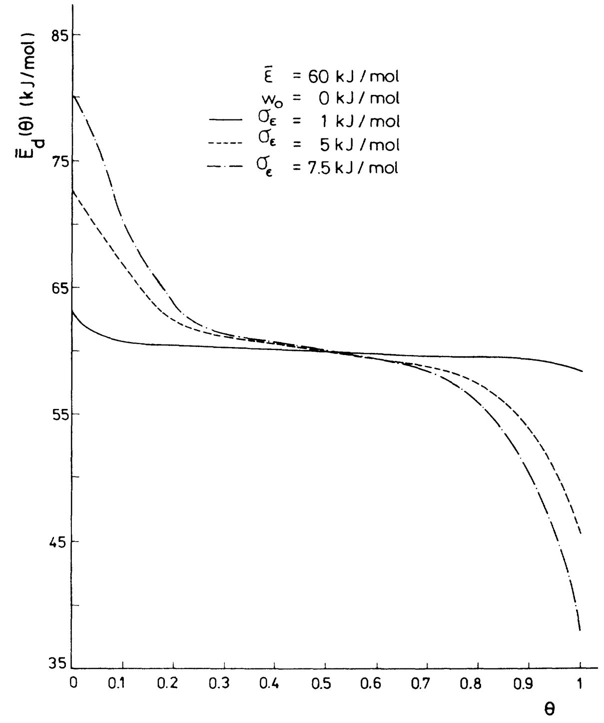

FIG. 11. Gaussian two-dimensional square lattice with no NN interactions; influence of adsorptive energy dispersion on the mean desorption energy.

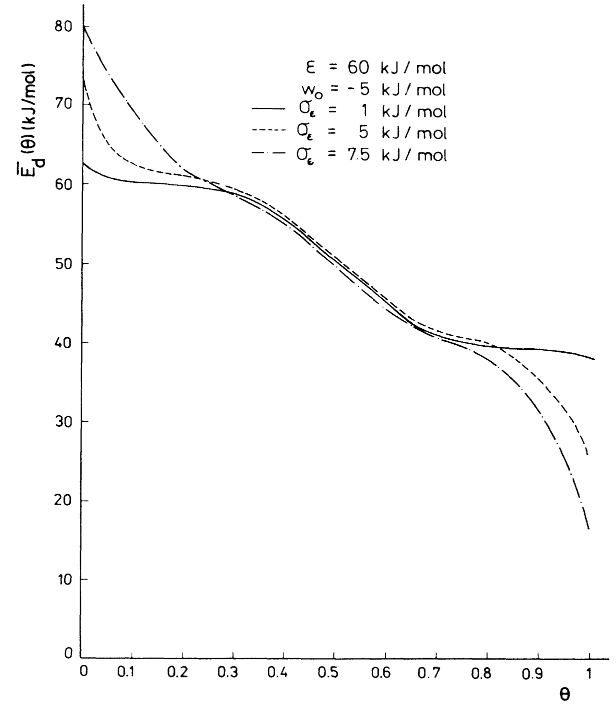

FIG. 12. The same as Fig. 11 for repulsive NN interactions.

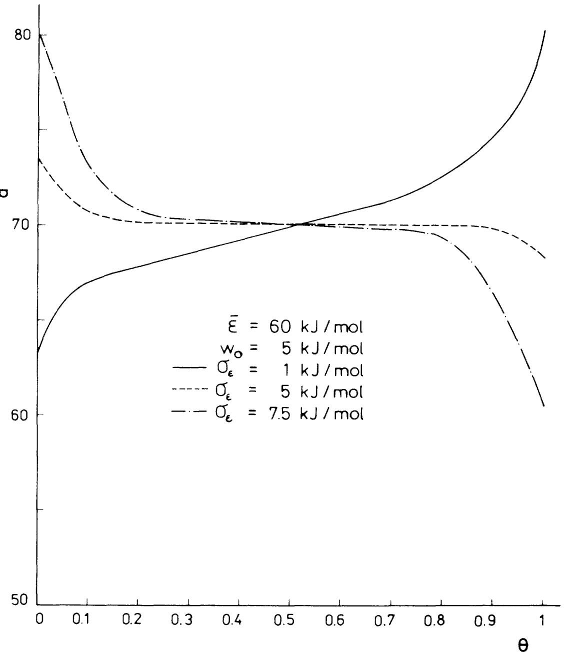

FIG. 13. The same as Fig. 11 for attractive NN interactions.

tions, and a value of $\sigma_\varepsilon = 5$ kJ/mol is necessary to produce an appreciable shift to higher temperatures. On the other hand, in Figs. 10(c) and 10(d), where no adsorbate-adsorbate interactions are present, even for $\sigma_\varepsilon = 1$ kJ/mol, we can already perceive a shift to the right and we have a much stronger shift for $\sigma_\varepsilon = 5$ kJ/mol.

One useful quantity that can be directly obtained in a Monte Carlo simulation is the mean desorption energy. Figures 11 to 13 show for a number of cases the variation with the coverage Θ of the mean desorption energy $\bar{E}_d(\Theta)$, obtained by averaging the binding energy over all desorbed molecules in a given interval ΔT. In particular, when no adsorbate-adsorbate interactions are present, Fig. 11, we find that Gaussian surfaces are characterized by descending sigmoidal curves for $\bar{E}_d(\Theta)$ with steeper branches to both sides of $\Theta = 0.5$ as σ_ε increases. Attractive interactions can invert the sigmoidal shape, making it ascending for sufficiently low σ_ε, as shown in Fig. 13. Repulsive interactions, on the other hand, while enhancing the descending character of the $\bar{E}_d(\Theta)$ curve, introduce an interesting double phase transition behavior as an ordered $c(2\times2)$ phase is entered and left, Fig. 12. As it would be expected, these phase transitions tend to smooth out as the surface heterogeneity increases.

V. DESORPTION SPECTRUM-SITE ENERGY DISPERSION RELATION

The stochastic character of the desorption process indicates that even for an homogeneous surface, which is given by a Dirac's δ distribution for the adsorptive energy ($\sigma_\varepsilon = 0$), the desorption peak has a dispersion $\sigma_T > 0$ which we could call the "natural dispersion" to distinguish it from the peak enhancement due to diffusive and readsorption effects.

For heterogeneous surfaces where the adsorptive energy distribution is given by a Gaussian with dispersion σ_ε, we found, as for the example in Fig. 8, that σ_T increases with σ_ε. If experimental conditions were such that diffusive and readsorption effects could be neglected so that only "natural dispersion" must be considered, then there should be a general relation between σ_T and σ_ε depending only on the adsorbate-adsorbate interaction energy. The discovery of such a relation should be useful because we could then immediately estimate surface heterogeneity from the desorption peak dispersion.

With this in mind we simulated a number of desorption spectra from square lattices with different adsorptive energy distributions and different values of adsorbate-adsorbate attractive interaction energy. We excluded repulsive interaction energy because the peak multiplicity makes the analysis of dispersion very difficult. We found, as shown in Figs. 14 and 15, that a general relation exists if the relative dispersions $\sigma_\varepsilon/\bar{\varepsilon}$ and σ_T/T_M, where T_M is the temperature of the peak maximum, are used. Such a relation can be expressed as

$$\sigma_T/T_M = C_1 + C_2\exp(-C_3\sigma_\varepsilon/\bar{\varepsilon}) , \quad (6)$$

where the coefficients $C_i(w_0)$ are given by

$$C_i(w_0) = a_{i1} + a_{i2}w_0 + a_{i3}w_0^2, \quad i = 1,2,3 . \quad (7)$$

The constants a_{ij} were fitted by least squares and their

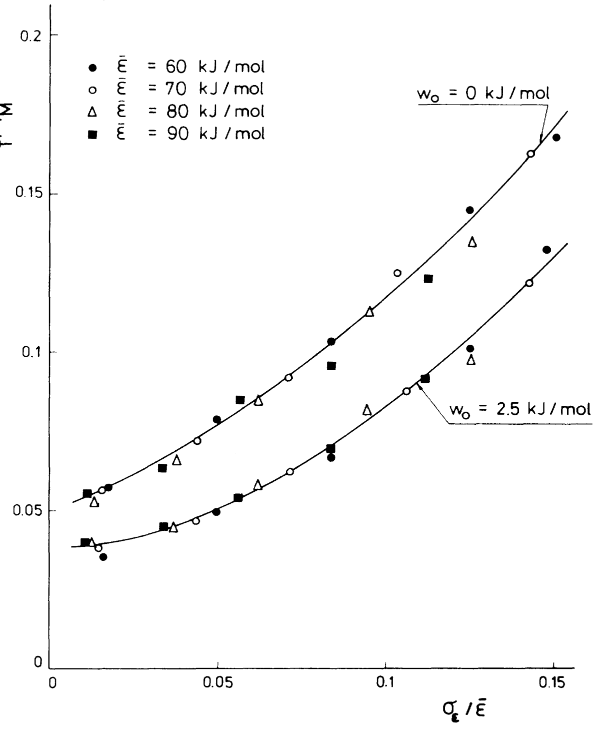

FIG. 14. Dispersion curves for $w_0 = 0$ and 2.5 kJ/mol.

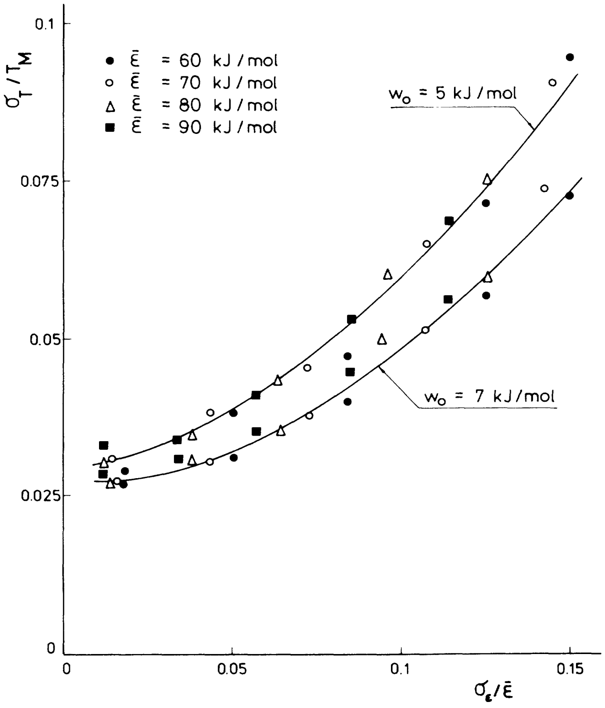

FIG. 15. Dispersion curves for $w_0 = 5$ and 7 kJ/mol.

TABLE I. Values for coefficients a_{ij} in Eq. (7).

j \ i	1	2	3
1	-3.04×10^{-3}	5.04×10^{-3}	-3.24×10^{-4}
2	5.21×10^{-2}	-1.19×10^{-2}	8.24×10^{-4}
3	8.27	7.60×10^{-1}	-1.61×10^{-2}

values are presented in Table I.

We can think of at least two ways in which such a quantitative relation between σ_T/T_M and $\sigma_\varepsilon/\bar{\varepsilon}$ could be used. One, as we already mentioned, is to obtain the surface heterogeneity $\sigma_\varepsilon/\bar{\varepsilon}$ from the desorption peak dispersion σ_T/T_M in experiments where we can assure that diffusive and readsorption effects are negligible. The other is to estimate the influence of diffusive and readsorption effects in experiments where we know $\sigma_\varepsilon/\bar{\varepsilon}$ and w_0 by independent measurements. If $\sigma_\varepsilon/\bar{\varepsilon}$ and w_0 are known then we can calculate the "natural dispersion" σ_T/T_M and compare it to the observed desorption peak dispersion. The amount by which the observed dispersion exceeds the natural dispersion will be a measure of the diffusive and readsorption effects.

VI. CONCLUSIONS

We have shown that Monte Carlo simulation is an appropriate method to discuss the general problem of thermal desorption of adsorbed molecules when both heterogeneity and adsorbate-adsorbate interactions are present. In particular, we conclude that models for heterogeneous surfaces which are based on the site-independence hypothesis lead to wrong predictions especially when repulsive adsorbate-adsorbate interactions are present.

Desorption spectra for heterogeneous surfaces can be strongly affected by energy heterogeneity, site structure, and adsorbate-adsorbate interactions, and we have seen the general effects produced by each one of these factors.

Attractive interactions can mask heterogeneity by mixing up different peaks and compensating their shift to higher temperatures as the initial coverage is decreased, while repulsive interactions can introduce spurious heterogeneity by splitting desorption peaks.

The site structure is another important factor in determining the shape of desorption spectra, since sites with different energies can be arranged in different ways on the surface. Macroscopic domains give, as expected, well-differentiated peaks for each site energy, and this is also true for relatively small patches (say about ten sites). As sites with different energies become more and more mixed up, the overlapping of different peaks increases and finally, for a periodic structure, there is only one peak.

When the site energy is characterized by a Gaussian distribution, desorption peaks broaden according to the empirical formula given in Eq. (6). Complex real situations where two or more kinds of sites are present, each one having a Gaussian energy distribution, can be analyzed by combining the results of Secs. III, IV, and V. Further developments will be given for the problem of studying the effects of readsorption on the thermal desorption curves.

ACKNOWLEDGMENT

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