

# Study of adsorption of binary mixtures on disordered substrates

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## Abstract

The adsorption of binary mixtures on solid heterogeneous substrates is studied by Monte Carlo simulation in the framework of the lattice gas model. The energy of the surface has been modeled by considering two kind of adsorption sites, deep and shallow traps, forming square homogeneous patches of different sizes; these adsorption domains have been distributed either at random or in chessboard-like lattice to obtain simple heterogeneous topographies. The adsorption process has been monitored through total and partial isotherms and differential heats of adsorption corresponding to both species of the mixture, for different values of the parameters involved in the model (lateral interactions, energy gap between deep and shallow patches) and different topographies. A rich variety of behaviors is found and analyzed in the context of the lattice gas theory. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Many molecular processes like adsorption, corrosion, diffusion, etc. involve the interaction of gases with solid surfaces [1–5]. Real solid surfaces are heterogeneous because of a large number of contributing factors that can be sorted in terms of geometrical (cracks, vacancies, etc.) and chemical (impurities, different adsorption sites, etc.) heterogeneity [6,7].

The energetic topography of real surfaces and the lateral interactions between adsorbed molecules can result in considerable deviations from a strictly ideal behavior of adsorbed phases on homogeneous surfaces.

The adsorption process of mixture gases on solid surfaces is a topic of great interest not only from

an intrinsic but also from the technological point of view, due to its importance for new developments in fields like gas separation and purification. Although this problem has been theoretically [8–10] and experimentally [10–13] studied for many years, some aspects are still unclear being necessary to reach a better understanding about the behavior of the adsorbate during the adsorption process of the mixture.

In order to describe real multicomponent adsorption systems, it is necessary to take into account three main effects on the calculation of the thermodynamic quantities: (i) lateral interactions between adsorbed particles, (ii) characteristics of the energetic surface, and (iii) relative molecular sizes of the components of the mixture. Most of the studies have only been focused on the first two aspects, considering equal sizes of the components [10,14]. Patchwise and random heterogeneous surfaces correspond to two different disordered topographies which have been extensively used in order to model the energetic substrate for the study of surface processes [15,16]. On the other hand,

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a correlated heterogeneous medium can be considered of an intermediate topography between random and patchwise cases, allowing to obtain a better description of real substrates [17]. In addition, the interaction between each species of the mixture and the surface could be very different [14].

In this paper, we present a Monte Carlo simulation study for the adsorption of interacting binary mixtures on simple highly correlated trap heterogeneous substrates [18], in the context of the lattice gas model [15,19,20]. The process was analyzed by following total and partial isotherms as well as differential heats of adsorption corresponding to both species of the mixture.

We have studied the simplest heterogeneous case, where the substrate is represented by a bivariate surface, corresponding to a bimodal site-energy distribution. According to this model, deep and shallow adsorption sites are grouped together, forming square patches; these regular adsorptive domains are distributed at random, or in a chessboard-like ordered topography. A more realistic model capable of reproducing in a statistical sense the main topographic features, would consider energy distributions for both sites and bonds (saddle point energy maxima existing between sites). Leading contributions to this subject have been presented by Mayagoitia and co-workers [21–23]. In this context, a substrate with two kind of energetic sites and all of the bonds having the

same constant energy, corresponds to an extreme case of a site-bond surface [23], called bivariate trap surface.

The work is organized as follows: in Section 2, the general basis of the Monte Carlo simulation of adsorption and the basic definitions of the thermodynamic functions are given. Results and discussions are presented in Section 3. Finally, the conclusions are given in Section 4.

## 2. Monte Carlo simulation and basic definitions

The adsorption of a binary mixture of gases on a heterogeneous solid surface was simulated by using the grand canonical ensemble Monte Carlo method (GCMC).

The substrate has been represented by a square lattice of  $M = L \times L$  adsorption sites with periodic boundary conditions. The heterogeneity was introduced by considering two kind of adsorptive sites, deep and shallow traps, according to a bimodal site-energy distribution (see Fig. 1(a)). The solid heterogeneous surface is modeled as a collection of finite homotatic patches where each patch is assumed to be a square domains of equal size  $M_p = l \times l$  sites. These adsorptive domains were used to generate two energy substrates, having different geometrical structures: (i) random distribution of patches, and

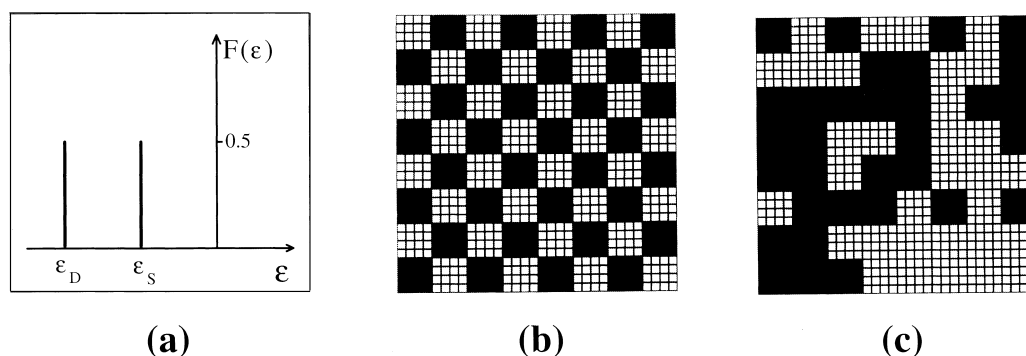


Fig. 1. The patchwise heterogeneous surface formed by only two kinds of square patch with different energies, i.e. deep and shallow patches with adsorption energies  $\epsilon_S$  (white sites) and  $\epsilon_D$  (black sites), respectively. Both types of sites are present with the same concentration. The energy frequency function corresponding to the site energy distribution is represented in (a). Two different topographies are shown, namely the chessboard-like ordered (b) and the random patches (c) distribution. The lattice size used here is  $L = 32$  and the patch size corresponds to  $l = 4$ .

(ii) chessboard-like array. These energetic topographies have been qualitatively represented in Fig. 1 for a patch size  $l = 4$  where black (white) squares correspond to deep (shallow) adsorption sites. Fig. 1(b) and (c) correspond to patchwise and random cases, respectively.

In order to write the Hamiltonian  $\mathcal{H}$  of the adsorbed phase, let us introduce the spin variable  $c_i$  which can take the following values:  $c_i = 0$  if the corresponding site  $i$  is empty,  $c_i = 1$  if the site  $i$  is occupied by an A-atom and  $c_i = -1$  if the site  $i$  is occupied by a B-atom. We used the discrete variable  $\alpha$  for distinguish the different sites:  $\alpha = 0$  ( $\alpha = 1$ ) represents a shallow (deep) site. The size of both components is the same and double occupancy of lattice sites is excluded. Under these considerations,  $\mathcal{H}$  is given by

$$\begin{aligned} \mathcal{H} = & \frac{1}{2} \sum_i^M \sum_{l_{m,i}} [w_{AA} \delta_{c_i, c_l, 1} + w_{BB} \delta_{c_i, c_l, -1} \\ & + w_{AB} (\delta_{c_i, 1} \delta_{c_l, -1} + \delta_{c_i, -1} \delta_{c_l, 1})] \\ & + \sum_i^M [\delta_{c_i, 1} (\epsilon_{AS} \delta_{\alpha, 0} + \epsilon_{AD} \delta_{\alpha, 1}) \\ & + \delta_{c_i, -1} (\epsilon_{BS} \delta_{\alpha, 0} + \epsilon_{BD} \delta_{\alpha, 1})] \\ & - \sum_i^M [\mu_A \delta_{c_i, 1} + \mu_B \delta_{c_i, -1}] \end{aligned} \quad (1)$$

where the symbol  $\delta$  represent the Kronecker delta;  $\mu_A$ ,  $\mu_B$  are the chemical potentials of both species, A and B, respectively;  $\epsilon_{AD}$  and  $\epsilon_{BD}$  ( $\epsilon_{AS}$  and  $\epsilon_{BS}$ ) denote the energy interactions between each component (A and B, respectively) and deep (D) (shallow (S)) sites.  $l_{m,i}$  means that for a given site  $i$ , the sum runs over the four nearest neighbor sites of  $i$ . The pairwise interactions,  $w_{AA}$ ,  $w_{BB}$ ,  $w_{AB}$  are assumed to occur between nearest neighbors only.

The grand partition function for an bicomponent mixture is defined as [19]

$$\begin{aligned} \mathcal{E}(\boldsymbol{\mu}, T, V) = & \sum_{N_A, N_B=0}^{\infty} \frac{\exp(\mathbf{N} \cdot \boldsymbol{\mu} / k_B T)}{\prod_{i=A,B} N_i! \Lambda_i^{3N_i}} \\ & \times \int_{\Omega} \exp\left[-\frac{U(\mathbf{x}_N)}{k_B T}\right] d\mathbf{x}_N \end{aligned} \quad (2)$$

where  $N_i$  denotes the number of molecules of component  $i$ ,  $\mathbf{N}$  the bicomponent vector of  $N_i$ 's,  $\boldsymbol{\mu}$  the

bicomponent vector of chemical potentials  $\mu_i$ 's,  $k_B$  the Boltzmann constant,  $V$  the system volume,  $T$  the temperature,  $U$  the total energy of  $\mathbf{N}$  particles with coordinates specified by the set  $\mathbf{x}_N = \{x_1, \dots, x_N\}$ ,  $\Omega$  is the phase space of the system, and  $\Lambda_i$  is the thermal wavelength of the species  $i$

$$\Lambda_i = \left( \frac{h^2}{2m_i k_B T} \right)^{1/2} \quad (3)$$

$m_i$  being the mass of the component  $i$  and  $h$  is the Planck's constant. The probability of finding the system in a state specified by  $\mathbf{x}_N$  is

$$P(\mathbf{x}_N) = \frac{\exp(\mathbf{N} \cdot \boldsymbol{\mu} / k_B T) \exp(-U(\mathbf{x}_N) / k_B T)}{\left[ \prod_{i=A,B} N_i! \Lambda_i^{3N_i} \right] \mathcal{E}} \quad (4)$$

Following the Metropolis scheme [24], the transition probability from a state  $\mathbf{x}_N$  to a new state  $\mathbf{x}'_N$ ,  $W(\mathbf{x}_N \rightarrow \mathbf{x}'_N)$ , is defined by

$$W(\mathbf{x}_N \rightarrow \mathbf{x}'_N) = \min \left\{ 1, \frac{P(\mathbf{x}'_N)}{P(\mathbf{x}_N)} \right\} \quad (5)$$

in order to satisfy the Principle of Microscopic Reversibility.

In adsorption–desorption equilibrium there are two elementary ways to perform a change of the system state, namely, adsorbing one molecule onto the surface (adding one molecule into the adsorbed phase volume  $V$ ), and desorbing one molecule from the adsorbed phase (removing one molecule from the volume  $V$ ). The corresponding transition probabilities are, respectively,

$$\begin{aligned} W_a(\mathbf{x}_N \rightarrow \mathbf{x}_{N+1}) \\ = \min \left\{ 1, \exp \left[ -\frac{\mathcal{H}(\mathbf{x}_{N+1}) - \mathcal{H}(\mathbf{x}_N)}{k_B T} \right] \right\} \end{aligned} \quad (6)$$

$$\begin{aligned} W_d(\mathbf{x}_N \rightarrow \mathbf{x}_{N-1}) \\ = \min \left\{ 1, \exp \left[ -\frac{\mathcal{H}(\mathbf{x}_{N-1}) - \mathcal{H}(\mathbf{x}_N)}{k_B T} \right] \right\} \end{aligned} \quad (7)$$

Given a square lattice of  $M$  adsorption sites with energies already assigned, the algorithm to carry out an elementary step in Monte Carlo simulation (1 MCS), is the following:

1. Set the value of  $\mu_A$ ,  $\mu_B$  and temperature  $T$ .

2. Set an initial state  $x_N$  by adsorbing  $N$  molecules onto the lattice.
3. One of the components of the mixture is chosen at random.
4. Choose randomly one of the  $M$  sites, and generate a random number  $\xi \in [0, 1]$ 
  - 4.1. if the site is empty then adsorb the molecule chosen in step 3 if  $\xi \leq W_a$ ;
  - 4.2. if the site is occupied then desorb the molecule if  $\xi \leq W_d$ .
5. Repeat from step 3  $M$  times.

In the present case, the equilibrium state could be well reproduced, after discarding the first  $n \approx 2 \times 10^5$  MCS. Then, averages were taken over  $n' \approx 2 \times 10^5$  successive configurations.

Statistically, the total and partial isotherms are obtained as simple averages:

$$\theta(\mu_A, \mu_B) = \frac{\langle N \rangle}{L^2}, \quad \theta_A(\mu_A, \mu_B) = \frac{\langle N_A \rangle}{L^2},$$

$$\theta_B(\mu_A, \mu_B) = \frac{\langle N_B \rangle}{L^2} \quad (8)$$

where  $\theta$ ,  $\theta_A$  and  $\theta_B$  are the total and partial surface coverages, defined, respectively, as  $\theta = N/L^2$ ,  $\theta_A = N_A/L^2$ ,  $\theta_B = N_B/L^2$ ; and the thermal average,  $\langle \dots \rangle$ , means the time average throughout the Monte Carlo simulation.

The differential heat of adsorption  $q_i$  for the  $i$ -species is defined as [25,26]

$$q_i = - \left( \frac{\partial U}{\partial N_i} \right)_{T, N_{j \neq i}} \quad (9)$$

where  $U$  is the energy of the adsorbed phase. The rhs part of the last equation can be written as

$$\left( \frac{\partial U}{\partial N_i} \right)_{T, N_{j \neq i}} = \sum_k \left\{ \left[ \frac{\partial U}{\partial (\mu_k/k_B T)} \right]_{T, \mu_{j \neq i}} \left[ \frac{\partial (\mu_k/k_B T)}{\partial N_i} \right]_{T, N_{j \neq i}} \right\} \quad (10)$$

By expressing both derivatives in the rhs of this equation as fluctuations in the grand canonical ensemble we finally obtain the following forms for the differen-

tial heats of adsorption [14]:

$$q_A = - \frac{\Phi(A)[\langle N_B \rangle - \langle N_B \rangle^2] - \Phi(B)[\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle]}{[\langle N_A^2 \rangle - \langle N_A \rangle^2][\langle N_B^2 \rangle - \langle N_B \rangle^2] - [\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle]^2} \quad (11)$$

$$q_B = - \frac{\Phi(B)[\langle N_A \rangle - \langle N_A \rangle^2] - \Phi(A)[\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle]}{[\langle N_A^2 \rangle - \langle N_A \rangle^2][\langle N_B^2 \rangle - \langle N_B \rangle^2] - [\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle]^2} \quad (12)$$

where

$$\Phi(\Omega) = \langle UN_\Omega \rangle - \langle U \rangle \langle N_\Omega \rangle \quad (13)$$

### 3. Results and discussion

In order to study the adsorption process of binary mixtures on heterogeneous substrates, the Monte Carlo simulations have been performed by considering the following statement: (i) the heterogeneity is associated only to the A species (the B particles do not interact with the substrate). (ii) There only exist nearest neighbor interactions between A particles ( $w_{AA} \neq 0$ ,  $w_{AB} = w_{BB} = 0$ ). (iii) The chemical potential associated to the B species is kept fixed ( $\mu_B = 0$ ). In addition, we have considered  $k_B T = 1$  for simplicity, without any loss of generality. The computational simulations have been developed for square  $L \times L$  lattices, with  $L = 200$ ; with this lattice size we verified that finite size effects are negligible.

In our simulations, the first  $2 \times 10^5$  Monte Carlo steps per site (MCS) were discarded to allow equilibrium, while the next  $2 \times 10^5$  MCS were used to compute averages.

Fig. 2 shows the results obtained for the adsorption of a binary mixture on a homogenous surface ( $\Delta\epsilon_A = \epsilon_{AD} - \epsilon_{AS} = 0$ ), in presence of lateral interactions between nearest neighbor adparticles.

In Fig. 2 we have plotted the A partial (a), B partial (b) and total (c) isotherms for the homogeneous problem, considering different energy interactions,  $w_{AA}/k_B T = -2$  (attractive case), 0 (noninteracting case), and 2 (repulsive case). It can be observed in Fig. 2(b) and (c), that the initial coverage takes the same value  $\theta = 0.5$  for the three isotherms; this

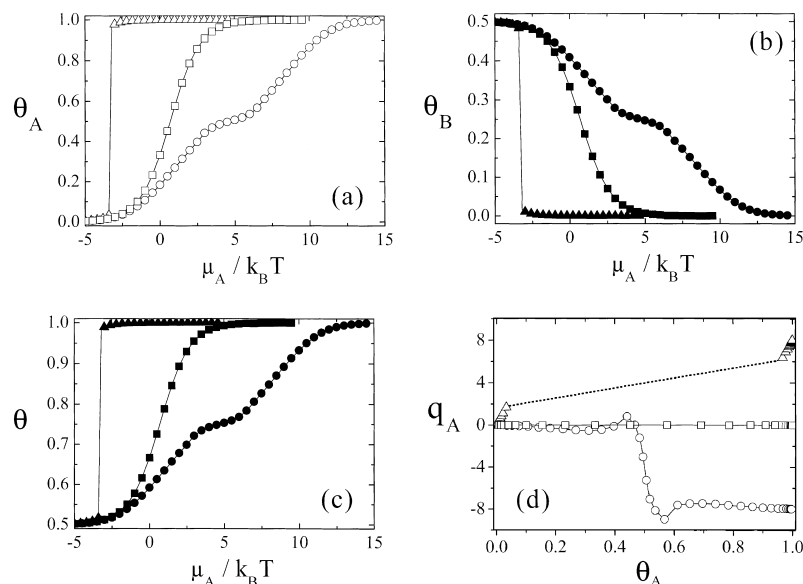


Fig. 2. Homogeneous case:  $\Delta\epsilon_A/k_B T = 0$ . (a) Partial A isotherm  $\theta_A$  vs.  $\mu_A/k_B T$ , (b) partial B isotherm  $\theta_B$  vs.  $\mu_A/k_B T$ , (c) total isotherm  $\theta = \theta_A + \theta_B$  vs.  $\mu_A/k_B T$  and (d) differential heat of adsorption  $q_A$  vs.  $\theta_A$ , for different values of energetic interaction between A particles:  $w_{AA}/k_B T = -2$  (triangles);  $w_{AA}/k_B T = 0$  (squares) and  $w_{AA}/k_B T = 2$  (circles). In all cases  $w_{BB} = w_{AB} = 0$ .

behavior can be explained as follows: for  $\mu_A \rightarrow -\infty$  the A particle coverage is zero while the B particles are randomly distributed on the lattice with  $\theta_B$  given by the Langmuir isotherm ( $\theta_B = \exp\{\mu_B/k_B T\}/[1 + \exp\{\mu_A/k_B T\} + \exp\{\mu_B/k_B T\}]$ ), which for  $\mu_B = 0$  is  $\theta = \theta_B = 0.5$ .

It is well known that for a lattice gas of interacting monomers adsorbed on a square surface, there exists a critical temperature (given by  $k_B T_C = 0.567|w|$ ) corresponding to a phase transition in the adsorbate. The nearest neighbor couplings,  $w$ , determine the character of the phase transition: (i) if  $w < 0$  (attractive case) the system exhibits a first-order phase transition, and (ii) for  $w > 0$  (repulsive case) a continuous order order phase transition occurs in the adsorbate.

We have considered both, attractive and repulsive cases: (I) in the attractive case (triangles), the total isotherm exhibits a discontinuity, which evidences the first-order phase transition in the adsorbate. This behavior is due to the interactions between A particles; it can be clearly observed in Fig. 2(a), where the partial A isotherm  $\theta_A$  versus  $\mu_A$  (open triangles) shows an abrupt change of coverage from  $\theta \approx 0$  to  $\theta \approx 1$ . This phenomenon induces an interesting behavior in the B isotherm (solid triangles in Fig. 2(b)), which

also exhibits a well-defined step although the B particles do not interact neither with B particles nor with A particles ( $w_{BB} = w_{AB} = 0$ ). (II) In the repulsive case (circles) the interaction between A molecules determine a  $c(2 \times 2)$  ordered phase for such particles. Therefore, the A isotherm presents a plateau at half coverage (open circles in Fig. 2(a)). At equilibrium, the B particles occupy half of the empty sites, and the corresponding B isotherm (solid circles in Fig. 2(b)) presents a plateau at  $\theta = 0.25$ ; this behavior is a consequence of the excluded volume but is not due to the interactions. The total isotherm (solid circles in Fig. 2(c)) is the sum of the partial isotherms, then the plateau appears at  $\theta = 0.75$ .

The Langmuir case (noninteracting case) presents the well known monotonic behavior in Fig. 2 (open and solid squares).

In Fig. 2(d), the differential heat of adsorption  $q_A$  corresponding to the A species is plotted versus  $\theta_A$ , for both attractive and repulsive cases. The differential heats  $q_B$  for the B species were not included in the figure because they are strictly zero over all the coverage range.

For  $w_{AA}/k_B T = -2$ ,  $q_A$  presents two different regimes corresponding to a first-order phase transi-

tion: at low coverage ( $0 \leq \theta_A \leq 0.05$ ),  $q_A$  varies from 0 to  $2k_B T$ , which corresponds to very diluted gas adsorbed phase, where an A particle has in average at most one neighbor site occupied by another A particle; in the second regime, between  $0.95 \leq \theta_A \leq 1$ ,  $q_A$  varies from  $6k_B T$  to  $8k_B T$  evidencing the existence of a condensed gas adsorbed phase.

For the repulsive case ( $w_{AA}/k_B T = 2$ ), the behavior of  $q_A$  can be explained by analyzing two different adsorption regimes: (i) for  $0 < \theta < 0.5$ , the ad-molecules avoid  $NN$  occupancy which produces  $q_d \approx 0$  (as for  $w_{AA} = 0$ ), and (ii) for  $0.5 < \theta < 1$ , the adsorption of one more molecule involves an increment  $cw_{AA}$  in the energy of the system, where  $c$  is the lattice connectivity. The maximum in  $q_A$  for  $\theta \rightarrow 0.5^-$  corresponds to the critical coverage at which a dramatic change of order takes place in the system (the system passes from the disordered to the ordered phase) [26]. A similar situation occurs for the minimum in  $q_A$  at  $\theta \rightarrow 0.5^+$ .

Let us now discuss the effect of the heterogeneity on the adsorption process. In order to do this we have considered two major contribution to the disorder: (i) the difference in the adsorption energies between

shallow and deep patches  $\Delta\epsilon_A = \epsilon_{AD} - \epsilon_{AS}$ , and (ii) the topological distribution of the patches.

Fig. 3 shows the A partial (a), B partial (b) and total (c) isotherms for a chessboard-like substrate of deep and shallow patches (with  $l = 4$ ), considering different values for the energetic parameter  $\Delta\epsilon_A$ , ( $\Delta\epsilon_A = 0, -16$  and  $-32$ , in  $k_B T$  units), keeping  $\epsilon_{AS} = 0$ . The lateral interaction is the same as for the homogenous case, i.e.  $w_{AA} = 4k_B T$ . Fig. 3(d) shows the differential heat of adsorption of A species corresponding to the above mentioned cases.

In the homogeneous case (circles), the A isotherms exhibits a plateau at half coverage due to the order-disorder phase transition in the adsorbate. In this regime, the A particles are forming a  $c(2 \times 2)$  structure, occupying half of the total number of sites ( $\theta_A = 0.5$ ); the remaining sites are found half covered by B particles ( $\theta_B = 0.25$ ). The total isotherm follows the same behavior, showing a plateau at  $\theta = \theta_A + \theta_B = 0.75$ . The differential heat  $q_A$  (Fig. 3(d)) presents a jump at half coverage which determine two different adsorption regimes; this behavior was discussed for Fig. 2(d).

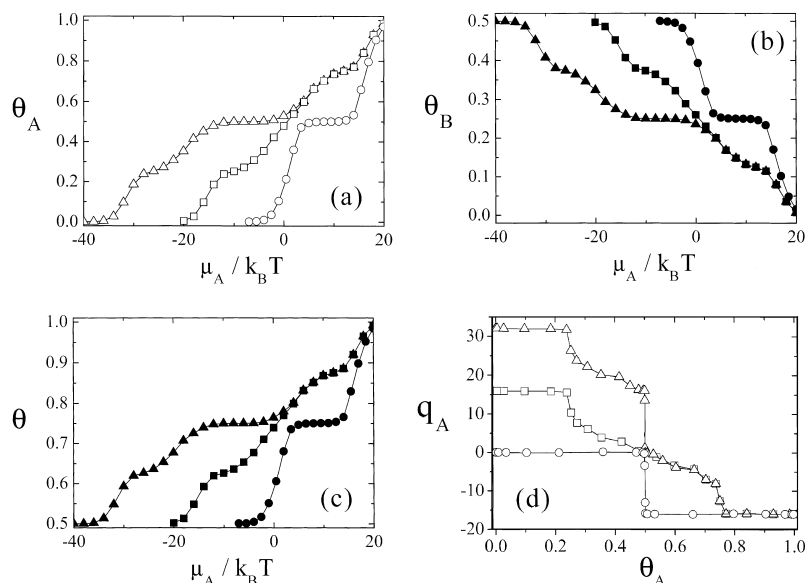


Fig. 3. Chessboard like heterogeneous substrate ( $l = 4$ ), and repulsive interaction between A particles. (a) Partial A isotherm  $\theta_A$  vs.  $\mu_A/k_B T$ , (b) partial B isotherm  $\theta_B$  vs.  $\mu_A/k_B T$ , (c) total isotherm  $\theta = \theta_A + \theta_B$  vs.  $\mu_A/k_B T$  and (d) differential heat of adsorption  $q_A$  vs.  $\theta_A$ , for different values of the energetic parameter  $\Delta\epsilon$ .  $\Delta\epsilon_A/k_B T = -32$  (triangles),  $\Delta\epsilon_A/k_B T = -16$  (squares), and  $\Delta\epsilon_A/k_B T = 0$  (circles). In all cases  $w_{AA}/k_B T = 4$  and  $w_{BB} = w_{AB} = 0$ .

For  $\Delta\epsilon_A = -16k_B T$ , three adsorption regimes can be observed:

1. At low coverages,  $0 < \theta_A \leq 0.25$ , the A particles are adsorbed on deep patches forming a  $c(2 \times 2)$  ordered structure, resulting in a plateau in the A isotherm at  $\theta_A = 0.25$ . In this regime the B particles occupy half of the remaining sites (75% of the lattice sites), and even though the B particles do not interact neither between them nor with A particles, a plateau appears in the B partial isotherm at  $\theta_B = 0.375$ . The total isotherm  $\theta(\mu_A)$  follows the behavior of the partial isotherms (see Fig. 3(a)–(c)). For this coverage range, the energy change involved in the adsorption (desorption) of an A particle corresponds to the adsorption energy of the strong sites, and the differential heat of adsorption is constant ( $q_A = 16k_B T$ ) (Fig. 3(d)).
2. For  $0.25 < \theta_A \leq 0.75$ , the incoming A particles can be adsorbed with equal probabilities in a deep patch, surrounded by four adparticles, or in a shallow patch forming a  $c(2 \times 2)$  structure. Therefore, there is no step in the A isotherm at half coverage. Then, there is no jump in  $q_A$  at half coverage.
3. For  $\theta_A > 0.75$ , the A particles are adsorbed on shallow patches, and a new plateau in the A isotherm appears due to the ordered phase  $c(2 \times 2)$  during the filling of these domains. The dependence of  $\theta_B$  and  $\theta$  with  $\mu_A$  can be explained by following a similar reasoning than for (1). In this regime,  $q_A = -cw_{AA}$  as for the homogeneous problem, because the adsorption process occurs on patches of energy  $\epsilon_{AS} = 0$ .

In Fig. 3 is also plotted the case  $\Delta\epsilon_A = -32k_B T$ , keeping unchanged the rest of the energetic parameters. At low coverages,  $0 < \theta_A \leq 0.25$ , the behavior is the same as in the previous case, that is A particles are adsorbed in deep patches forming a  $c(2 \times 2)$  phase. For  $0.25 < \theta_A \leq 0.5$ , the deep patches are filled by A particles. The filling of the shallow patches ( $0.5 < \theta_A \leq 1$ ) can be explained by similar argument. According to that, the differential heat of adsorption shows the corresponding values of energy involved in the adsorption and desorption of a particles during the different coverage regimes.

It should be noticed that there is an interesting behavior in the observed quantities at  $\theta_A = 0.5$ . In fact, partial and total isotherms exhibit a plateau at

coverage around 0.5, similarly as for the homogeneous case. In the same way, the differential heat of adsorption presents a very marked step at half coverage, instead of the smooth dependence observed for  $\Delta\epsilon_A = -16k_B T$ . In the homogeneous problem, the plateau in the A isotherm at  $\theta_A$  appears because of the repulsive interactions between A particles, when the  $c(2 \times 2)$  ordered structures in the adsorbate are found. This is precisely the origin of the plateaus at  $\theta_A = 0.25$  and  $0.75$  in the isotherms for the heterogeneous cases. However, for  $\Delta\epsilon_A = -32k_B T$ , the plateau at  $\theta_A = 0.5$  is a consequence of the energy difference between deep and shallow patches, and does not depend on  $w_{AA}$ . Under this regime, deep patches are found full covered by A particles, while shallow patches are half covered by B particles; then the B isotherm  $\theta_B(\mu_A)$  presents a plateau at  $\theta_B = 0.25$ . Finally, the total isotherm  $\theta(\mu_A)$  shows a plateau at coverage  $\theta = 0.75$ . Additionally, the differential heat of adsorption  $q_A(\theta_A)$  presents an abrupt change at  $\theta_A = 0.5$ . For  $\theta_A < 0.5$  ( $\theta < 0.75$ ), the A particles adsorb on deep patches surrounded by four occupied sites, which corresponds to an energy change of  $16k_B T$  in the system.

Simulations were also employed to study the effect of attractive lateral interactions on the adsorption process of a binary mixture. Isotherms and differential heats of adsorption corresponding to a fixed value of the interaction parameter  $w_{AA} = -3k_B T$  have been plotted in Fig. 4, considering three different values for the heterogeneity parameter,  $\Delta\epsilon_A = 0$  (circles),  $-16k_B T$  (squares), and  $-32k_B T$  (triangles).

In the homogeneous case, the A isotherm (open circles in Fig. 4(a)) shows the well known stepped behavior. For  $\mu_A < -5.0$  the surface is half covered by B particles ( $\theta_B = 0.5$ ) while  $\theta_A = 0$ ; if the chemical potential of the A species increases, the system suddenly reach a new equilibrium state with  $\theta_A = 1$  and  $\theta_B = 0$ ; the “A adsorbate” passes from a dilute to a condensed phase in a very narrow range of  $\mu_A$ . Simultaneously, the B isotherm (solid circles) experiments an abrupt change, from  $\theta_B = 0.5$  to  $\theta_B = 0$ . Consequently, there appears a very well-defined step in the total isotherm, where the total coverage change from  $\theta = 0.5$  to 1 at this value of the chemical potential (see Fig. 4(c)). In this case, the differential heat of adsorption corresponding to the A species (open circles in Fig. 4(d)) exhibits a simple behavior: at very low coverage,  $\theta_A \approx 0$ ,  $q_A \approx 0$  while for  $\theta_A \approx 1$ ,  $q_A \approx$

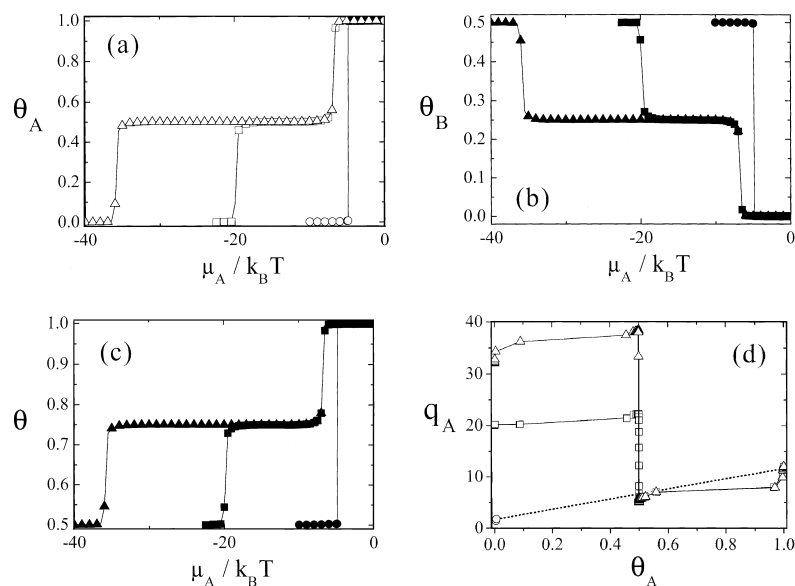


Fig. 4. Chessboard like heterogeneous substrate ( $l = 4$ ), and attractive interaction between A particles. (a) Partial A isotherm  $\theta_A$  vs.  $\mu_A/k_B T$ , (b) partial B isotherm  $\theta_B$  vs.  $\mu_A/k_B T$ , (c) total isotherm  $\theta = \theta_A + \theta_B$  vs.  $\mu_A/k_B T$  and (d) differential heat of adsorption  $q_A$  vs.  $\theta_A$ , for different values of the energetic parameter  $\Delta\varepsilon$ .  $\Delta\varepsilon_A/k_B T = -32$  (triangles),  $\Delta\varepsilon_A/k_B T = -16$  (squares), and  $\Delta\varepsilon_A/k_B T = 0$  (circles). In all cases  $w_{AA}/k_B T = -3$  and  $w_{BB} = w_{AB} = 0$ . The dot line is an eye guide.

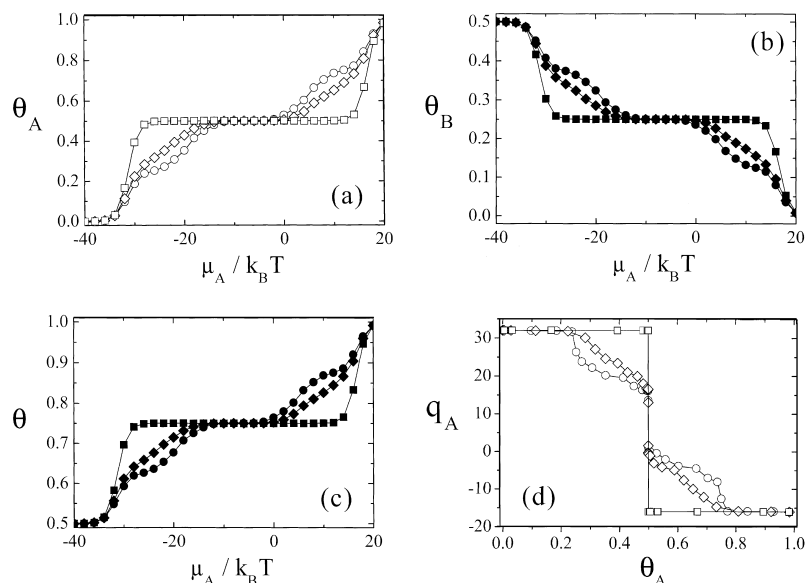


Fig. 5. Different heterogeneous topographies (with  $\Delta\varepsilon_A/k_B T = -32$ ), and repulsive interaction between A particles. chessboard  $1 \times 1$  (squares), random  $1 \times 1$  (diamonds) and chessboard  $4 \times 4$  (circles). (a) Partial A isotherm  $\theta_A$  vs.  $\mu_A/k_B T$ , (b) partial B isotherm  $\theta_B$  vs.  $\mu_A/k_B T$ , (c) total isotherm  $\theta = \theta_A + \theta_B$  vs.  $\mu_A/k_B T$  and (d) differential heat of adsorption  $q_A$  vs.  $\theta_A$ . In all cases  $w_{AA}/k_B T = 4$  and  $w_{BB} = w_{AB} = 0$ .



$12k_B T$  (which corresponds to the condensed phase).

For the heterogeneous problem, where the interacting A particles “see” a chessboard-like substrate, the A and B partial isotherms present two plateaus; the first one corresponds to the filling of the deep patches, and the second one appears when the shallow patches are covered. For very low values of  $\mu_A$ , the surface is half covered by the B species; if  $\mu_A$  is increased, the system experiments a fast change where the A particles displace the B particles from the deep patches resulting  $\theta_A = 0.5$  and  $\theta_B = 0.25$ . The same effect is observed at a higher value of  $\mu_A$ , corresponding to the filling of shallow patches by the A species. These abrupt transitions in the isotherms appear at two very well-defined energy values observable through the differential heat  $q_A$  (Fig. 4(d)) corresponding to the two adsorption regimes.

It is important to remark that, as for the repulsive case, the transition that occurs in the A adsorbate induces a similar behavior in the B adsorbate, even though there are no lateral interactions between B particles.

Let us discuss the effect of the different energetic topographies on the adsorption process. In Fig. 5 we

have plotted the A partial (a), B partial (b) and total (c) isotherms, and the differential heat of adsorption (d) for  $\Delta\epsilon_A = -32k_B T$  and different topographies: chessboard-like array of size  $1 \times 1$  (squares),  $4 \times 4$  (circles), and random distribution of  $1 \times 1$  patches (diamonds). The A (B) partial isotherm corresponding to the  $1 \times 1$  ordered substrate presents a well-marked plateau at coverage  $\theta_A = 0.5$  ( $\theta_B = 0.25$ ). This behavior is due to the effect of lateral interactions is reinforced by the effect of topography. This fact is shown in the differential heat  $q_A$  as a jump at half coverage (see Fig. 5(d)).

However, for a random distribution the behavior is quite different (see Fig. 5). The shapes of the isotherm and the differential heat are similar to the  $4 \times 4$  chessboard like substrate (which was previously discussed). This fact can be understood by considering that for the random distribution of deep and shallow sites (with equal concentration of each kind of site), the mean linear cluster size  $\langle l \rangle$  can be calculated from percolation theory to be  $\langle l \rangle \simeq 5.4$  for a square lattice at half coverage. Nevertheless, the shape of the clusters is quite irregular, which determines that the curves, particularly  $q_A$  present

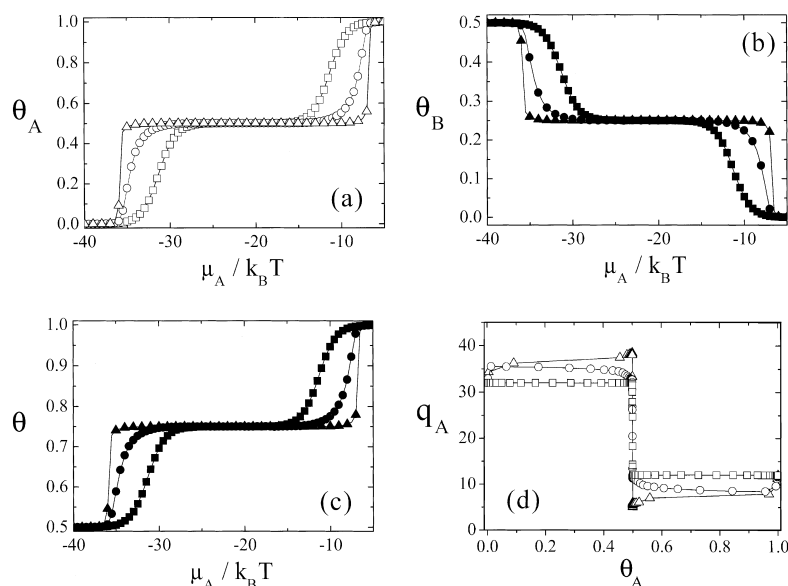


Fig. 6. Different heterogeneous topographies (with  $\Delta\epsilon_A/k_B T = -32$ ), and repulsive interaction between A particles. chessboard  $1 \times 1$  (squares), random  $1 \times 1$  (diamonds) and chessboard  $4 \times 4$  (circles). (a) Partial A isotherm  $\theta_A$  vs.  $\mu_A/k_B T$ , (b) partial B isotherm  $\theta_B$  vs.  $\mu_A/k_B T$ , (c) total isotherm  $\theta = \theta_A + \theta_B$  vs.  $\mu_A/k_B T$  and (d) differential heat of adsorption  $q_A$  vs.  $\theta_A$ . In all cases  $w_{AA}/k_B T = -3$  and  $w_{BB} = w_{AB} = 0$ .

rather different behavior in the range of coverage  $0.25 < \theta_A < 0.75$ .

Finally, we present in Fig. 6 the results corresponding to the attractive problem, by considering the same topographies discussed in Fig. 5. The results obtained for two different topographies, the  $1 \times 1$  and  $4 \times 4$  chessboard-like substrates, show an interesting behavior for both isotherms (Fig. 6(a)–(c)) and differential heats of adsorption (Fig. 6(d)). We have seen for the repulsive case that  $1 \times 1$  topography give place to a reinforcement in the tendency of lateral interactions to form a  $c(2 \times 2)$  ordered phase. However, in the attractive case the energetic topography compete with the lateral interactions, which attempt to produce a clustering in the A adsorbate. The result that emerges from this behavior is the inhibition of the stepped transition that appears in the  $4 \times 4$  case which is replaced by a continuous and smooth increasing. The random  $1 \times 1$  substrate case results in an intermediate case between the two topographies previously discussed. As before, the total isotherm  $\theta$  versus  $\theta_A$  in Fig. 6(c) follows the same behavior observed for the A and B partial isotherms.

#### 4. Concluding remarks

In this paper we have studied the effects of the lateral interactions (attractive or repulsive) and the surface heterogeneity on the adsorption of a binary mixture. The heterogeneous substrate has been modeled by considering two kind of adsorptive sites (deep and shallow), with energies  $\varepsilon_{AD}$  and  $\varepsilon_{AS}$  ( $\Delta\varepsilon_A = \varepsilon_{AD} - \varepsilon_{AS}$ ), forming  $l \times l$  patches distributed at random or chessboard-like ordered domains on a simple square lattice.

Several conclusions can be drawn from the present work.

We have observed that the adsorption process is strongly affected by the energetic topography. In fact, while for an homogeneous surface the repulsive (attractive) lateral interactions generate a order–disorder (a single step condensation) phase transition, the existence of a particular topography acts on the transition as follows: if the mean cluster size is small, the topography destroy the transition, and a plateau in the isotherm, or a step in the differential heat of adsorption, appears (in our case at half coverage) only due to

the difference between energies of deep and shallow sites; if the mean cluster size is considerable, a double transition (order–disorder or condensation) occurs in the system, first on patches of deep adsorptive sites and then on shallow adsorptive sites. This process is clearly shown in the isotherms and the differential heat of adsorption of the A species.

On the other hand, even though there are no interactions between B molecules, the partial B isotherms appears to be very sensitive to both, the topography and lateral interactions between A particles. This behavior, induced by the A species, is not observed through the differential heat of adsorption  $q_B$ .

In summary, the model presented in this paper represents a very important tool in order to study the main characteristics of the heterogeneous adsorption of a binary mixture, without any special requirement or time consuming computation.

#### References

- [1] W.A. Steele, *The Interaction of Gases with Solid Surfaces*, Pergamon Press, New York, 1974.
- [2] E.A. Flood (Ed.), *The Solid–Gas Interface*, Marcel Dekker, New York, 1967.
- [3] V.P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces*, Plenum Press, New York, 1991.
- [4] G. Zgrablich, V. Mayagoitia, F. Rojas, F. Bulnes, A. Gonzalez, M. Nazzarro, V. Pereyra, A.J. Ramirez-Pastor, J.L. Riccardo, K. Sapag, *Langmuir* 12 (1996) 129.
- [5] D.M. Ruthven, *Principles of Adsorption and Desorption Processes*, Wiley, New York, 1984.
- [6] W. Rudzinski, D.H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, New York, 1992.
- [7] W. Rudzinsky, W.A. Steele, G. Zgrablich, *Equilibria and Dynamics of Gas Adsorption on Heterogeneous Surfaces*, Elsevier, Amsterdam, 1996.
- [8] S. Sircar, *Langmuir* 7 (1991) 3065.
- [9] M. Heuchel, R.Q. Snurr, E. Buss, *Langmuir* 13 (1997) 6795.
- [10] A.L. Myers, *Molecular thermodynamics of adsorption of gas and liquid mixtures*, in: A.I. Liapis (Ed.), *Fundamental of Adsorption*, Engineering Foundation, 1987.
- [11] F. Gonzalez-Cavallero, M.L. Kerkeb, *Langmuir* 10 (1994) 1268.
- [12] J.A. Dunne, R. Mariwala, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, *Langmuir* 12 (1996) 5888.
- [13] J.A. Dunne, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, *Langmuir* 12 (1996) 5896.
- [14] F. Bulnes, A.J. Ramirez-Pastor, J.L. Riccardo, V. Pereyra, in: D.D. Do (Ed.), *Adsorption Science and Technology*, World Scientific, Singapore, 2000, p. 517.
- [15] A.J. Ramirez-Pastor, F. Bulnes, J.L. Riccardo, *Surf. Sci.* 426 (1999) 48.

- [16] A.J. Ramirez-Pastor, D. Stacchiola, M.S. Nazzarro, J.L. Riccardo, G. Zgrablich, *Surf. Sci.* 449 (2000) 43.
- [17] J.L. Riccardo, M.A. Chade, V.D. Pereyra, G. Zgrablich, *Langmuir* 8 (1992) 1518.
- [18] K. Sapag, F. Bulnes, J.L. Riccardo, V. Pereyra, G. Zgrablich, *Langmuir* 9 (1993) 2670.
- [19] T.L. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1962.
- [20] K. Binder (Ed.), *Monte Carlo Methods in Statistical Physics*, Springer, Berlin, 1979.
- [21] V. Mayagoitia, F. Rojas, V. Pereyra, G. Zgrablich, *Surf. Sci.* 22 (1989) 394.
- [22] V. Mayagoitia, F. Rojas, J.L. Riccardo, V. Pereyra, G. Zgrablich, *Phys. Rev. B* 41 (1990) 7150.
- [23] J.L. Riccardo, V. Pereyra, G. Zgrablich, F. Rojas, V. Mayagoitia, I. Kornhauser, *Langmuir* 9 (1993) 2730.
- [24] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller, *J. Chem. Phys.* 21 (1953) 1087.
- [25] V.A. Bakaev, W.A. Steele, *Langmuir* 8 (1992) 148.
- [26] A.J. Ramirez-Pastor, F. Bulnes, *Physica. A* 283 (2000) 198.