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## Quasi-chemical approach for adsorption of mixtures with non-additive lateral interactions

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## ABSTRACT

The statistical thermodynamics of binary mixtures with non-additive lateral interactions was developed on a generalization in the spirit of the lattice-gas model and the classical quasi-chemical approximation (QCA). The traditional assumption of a strictly pairwise additive nearest-neighbors interaction is replaced by a more general one, namely that the bond linking a certain atom with any of its neighbors depends considerably on how many of them are actually present (or absent) on the sites in the first coordination shell of the atom. The total and partial adsorption isotherms are given for both attractive and repulsive lateral interactions between the adsorbed species. Interesting behaviors are observed and discussed in terms of the low-temperature phases formed in the system. Comparisons with Monte Carlo simulations are performed in order to test the validity of the theoretical model.

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### 1. Introduction

The adsorption of gas mixtures on solid surfaces is a current and exciting topic of research in surface science due to its importance in many technological applications, especially gas separation and purification and catalysis [1–6]. As in any adsorption process, the interactions among the adsorbed species play an important role in the process of mixed-gas adsorption on solids. In fact, the study of the adsorbate–adsorbate interactions in adsorbed films on regular substrates has its own interest due, particularly, to the emerging adsorbate structures that arise on the surface. These structures have an effect on microelectronics fabrication, catalyst surfaces, chemical sensors and electrodes, surfaces undergoing corrosion, [7,8] etc.

Various theories have been proposed to describe monolayer adsorption of interacting particles [9,10]. Particularly, the lattice-gas approximation [9,10] is one of the most widely used and practically applicable. In this framework, the adsorption field is usually represented by a lattice of adsorption sites. Normally, these sites are occupied by one molecule at most, and only

nearest-neighbor interactions are considered. The introduction of intermolecular forces brings about the possibility of phase transitions [11,12]. Among the common types of phase transitions are, condensation of gases, melting of solids, transitions from paramagnet to ferromagnet and order-disorder transitions.

From a theoretical point of view, the lattice-gas model can be solved exactly for one-dimensional substrates, and in this case the model does not show a phase transition [13]. All other cases are expressed in terms of series solution [14], except for the special case of two-dimensional lattices at half-coverage, which was exactly solved by Onsager in 1944 [15]. Under these conditions, the model does show a phase transition. Close approximate solutions in dimensions higher than one can be obtained, and the two most important of these are the Bragg-Williams approximation (BWA) [9], and the quasi-chemical approximation (QCA) [9,16]. These leading models, along with much recent contributions, have played a central role in the study of adsorption systems in presence of lateral interactions between the adatoms.

In this context, valuable contributions have been made to the problem of mixture adsorption by the group of Y. K. Tovbin and co-workers, who studied pure and mixed adsorption in the presence of lateral interactions and surface heterogeneity [17–20]. On the basis of a new theoretical method (the so-called fragment cluster method), and by using BWA, QCA, and lattice-gas theory, the

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authors investigated the main adsorption functions (isotherms and heats of adsorption), and the effects of the phase transitions occurring in the system.

More recently, several papers from our group have focused on the study of binary gas adsorption by theory and Monte Carlo (MC) simulation method [21–27]. Simple lattice-gas models have been investigated, and the behavior of the adsorbed phase has been studied in dependence on lateral interactions between adsorbed molecules [21–25], surface heterogeneity [21,22], lattice geometry [23–25] and adsorbate structure [26–28]. In refs. [21–28], the chemical potential of one component was assumed a constant. Similar results were reported by Fefelov et al., [29] who analyzed the adsorption of binary mixtures with a simultaneous variation of the chemical potentials of the mixture components.

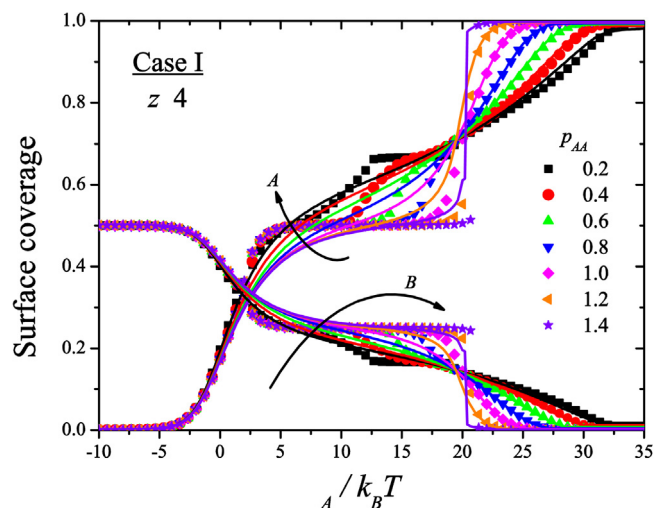
More complex adsorbate–adsorbate interactions can be introduced by considering non-pairwise interactions in terms of non additivity. The deviation from the additive behavior appears to be especially significant in the case of chemisorption. In this process, the valence electrons are either concentrated to form a single bond between two isolated atoms, or shared among all neighbors, which are occasionally occupying sites in the first coordination shell of the central atom. Non-additive lateral interactions have also been recognized in several experimental systems [30–36], and the consequences of such non-pairwise couplings in the adsorption thermodynamics have been studied for long time.

In fact, statistical mechanics of adsorbed monolayers with non-additive lateral interactions has been a subject of simulation and analytical treatment [37–45]. A seminal contribution was made by Milchev and Paunov [37], who studied, by means of MFA, the adsorption of monomers with non-additive interactions on two-dimensional lattices. Later, QCA [38] and MC simulations [39] were used to investigate the problem. In refs. [37–39], the study was restricted to some especial cases mainly including attractive interactions. The effect of repulsive interactions on the thermodynamics of non-additive monomers adsorbed on square lattices has also been analyzed [40,41]. Different low-temperature ordered phases were reported depending on the surface coverage, the value of the non-additivity parameter, and the magnitude of the lateral interactions. Similar results were found for substrates of different connectivity: triangular and hexagonal lattices [42], and nanotube bundles [43]. In all cases [37–43], single adsorbates have been considered to evaluate the effect of non-additive lateral interactions.

Recently, the adsorption of binary mixtures with non-additive lateral interactions has been studied by grand canonical MC simulations in the framework of the lattice-gas model [44]. The process was monitored through the adsorption isotherms and the differential heats of adsorption. Different combinations of both inter- and intra-species interactions were considered in the analysis. Novel ordered phases were observed, and their relationship with the behavior of the thermodynamic functions of the adsorbed monolayer was discussed.

In the case of multicomponent adsorbates with additive interactions, MC results have been backed up by theoretical analysis based on MFA, QCA and cluster-exact calculations [25]. The same has not happened in the case of multicomponent adsorbates with non-additive interactions and, consequently, the results predicted by MC techniques in ref. [44] have not been corroborated yet by analytical methods. The objective of this paper is to provide a thorough study in this direction. For this purpose, a new theoretical formalism is presented based on a generalization of the classical QCA, in which (i) the adsorbate is a binary mixture of species *A* and *B*, and (ii) non-additive interactions between the particles are considered. In addition, MC simulations are included in order to test the validity of the theoretical model.

QCA proved to be a very useful tool for the research of adsorption of binary mixtures with additive lateral interactions [25]. Here, the



**Fig. 1.** Partial adsorption isotherms for species *A* and *B* at different values of the non-additive parameter for case I. Symbols represent the MC data and solid lines the QCA. The same graphic scheme will be used throughout all the work.

scheme developed in ref. [25] is extended to include non-additive lateral interactions. It is expected that the present study, which is a natural extension of our previous work [21–28,40–44], will provide a starting point and valuable information about the applicability of a simple theoretical model to address a problem whose experimental realization is very complex. The paper is organized as follows. The model and the simulation scheme are described in Section 2. The theoretical approach is introduced in Section 3. The results are presented and discussed in Section 4. Finally, the conclusions are drawn in Section 5.

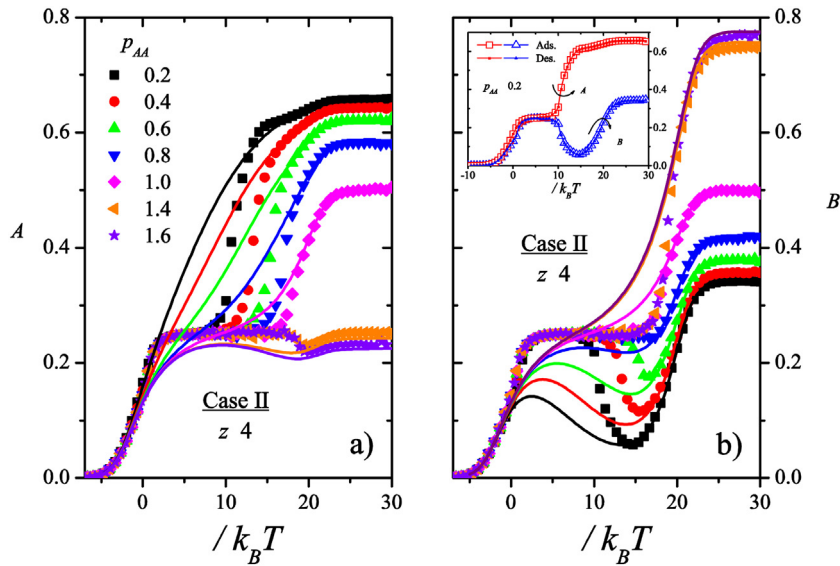
## 2. Non-additive model and Monte Carlo simulation in the grand canonical ensemble

The non-additivity refers to the binding energy between two atoms when this depends on the surrounding where those atoms are immersed. The dependence of the laterals interactions on the number of neighbors in experimental systems is hard to know. However, here we adopt the simplest rule, the linear dependence [see Eq. (1)]. To this a non-additive parameter  $p_{xx}$  is defined as a measure for the ratio of the strongest  $w_{xx}^z$  to the weakest  $w_{xx}^1$  possible bonds. The weakest correspond to a unique nearest neighbor (NN) and the strongest correspond to first sphere of coordination occupied, in the lattice-gas model this corresponds to  $z$ , NNs. In equations (37)–(39),  $p_{xx} = \frac{w_{xx}^z}{w_{xx}^1}$ , where  $xx$  stands for *AA*, *BB* or *AB*. For  $m$  particles in its NNs,  $w_{xx}^m$  varies linearly with  $m$ :

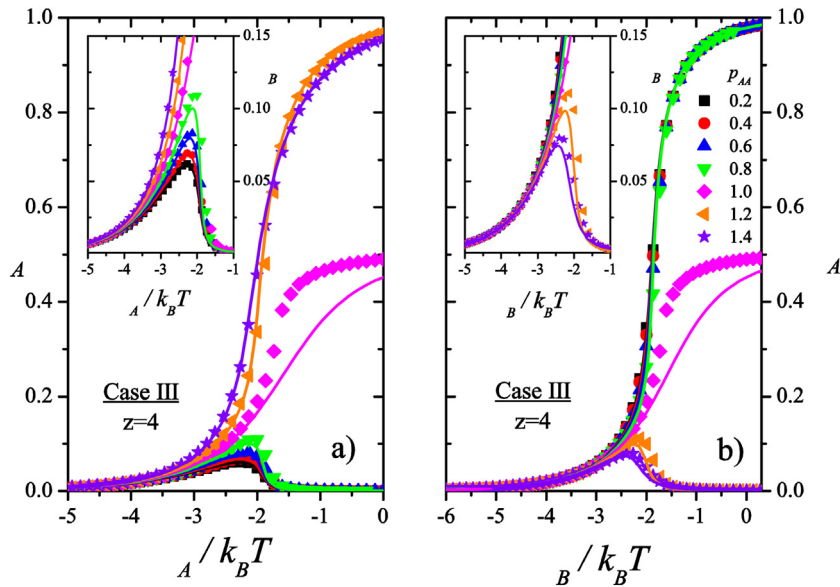
$$\frac{w_{xx}^m}{w_{xx}^1} = \frac{p_{xx}z - 1}{z - 1} - m \frac{p_{xx} - 1}{z - 1} \quad (1)$$

where  $w_{xx}$  becomes the energy parameter for the  $xx$  combination. In particular when,  $p_{AA} = p_{AB} = p_{BB} = 1$  the energies are additives, in accordance with previous results [24]. To emulate the adsorption process, the most adequate is lattice-gas model. With a lattice model is possible modeling surfaces [100] or [111]. These correspond with square and triangular lattice respectively. The main difference is the coordination ( $z$ ) of each adsorption site, for example: square lattice  $z = 4$  and triangular  $z = 6$ .

For the adsorption binary we consider two species *A* and *B* which can be deposited on a homogeneous two-dimensional surface consisting in  $M$  sites. To simplify the process, multi-deposition is prohibited and periodic boundary conditions have been considered. Different kinds of energies have been considered: adsorbate–adsorbent interaction,  $\varepsilon$ , and lateral interactions. The last



**Fig. 2.** Partial adsorption isotherms for species A and B at different values of the non-additive parameter for case II. The inset in part (b) shows the simulated isotherms, for the particular value  $p_{AA} = 0.2$ , during an adsorption (hollow symbols) and a desorption (small full symbol) sequence.



**Fig. 3.** Partial adsorption isotherms for species A and B at different values of the non-additive parameter for case III. The insets show a zoom of the isotherms before the symmetry breaking.

interactions can be interpreted by: inter-species,  $w_{AB}$ , and intra-species,  $w_{AA}$  and  $w_{BB}$ . Chemical potentials for each species were considered at temperature  $T$ ;  $\mu_A$  and  $\mu_B$  one for species A and B respectively. The adsorption in each site can be monitor by an occupation variable  $c_i$  can take the value zero if the site  $i$  is empty and equal to +1 (−1) if it is occupied with the species A (B). Thus, the Hamiltonian of the system can be written as:

$$H = \sum_i^M \sum_{l \in (NN,i)} [w_{AA} \delta_{c_i,l,1} + w_{BB} \delta_{c_l,i,-1} + w_{AB} (\delta_{c_i,1} \delta_{c_l,-1} + \delta_{c_l,-1} \delta_{c_i,1})] + \epsilon \sum_i^M (\delta_{c_i,1} + \delta_{c_i,-1}) - \sum_i^M (\mu_a \delta_{c_i,1} + \mu_b \delta_{c_i,-1}) \quad (2)$$

The process is simulated through MC simulations in the Grand Canonical Ensemble [45] The adsorption-desorption process is calculated following Metropolis rule [46]. A Monte Carlo step (MCs) is achieved when  $M$  sites have been tested to change its occupancy

state. The equilibrium state is reached after discarding  $10^6$  MCs, and averages are taken over the next  $10^6$  MCs. The partial and total adsorption isotherms are obtained as:

$$\theta_A(\mu_A, \mu_B) = \frac{\langle N_A \rangle}{M}, \theta_B(\mu_A, \mu_B) = \frac{\langle N_B \rangle}{M}, \quad (3)$$

and,

$$\theta(\mu_A, \mu_B) = \frac{\langle N_A + N_B \rangle}{M}, \quad (4)$$

where the brackets mean the time average over the MC simulation runs.  $N_A$  ( $N_B$ ) and  $N$  denote the number of adsorbed A (B) molecules and the total number of adsorbed particles, respectively. Accordingly,  $\theta_A$  ( $\theta_B$ ) and  $\theta$  represent the partial surface coverage of the species A (B) and the total surface coverage, respectively.

### 3. Quasi-chemical approximation for mixtures with non-additive interactions

The partition function of  $N_A$  atoms of species  $A$  and  $N_B$  atoms of species  $B$  on a regular substrate consisting of  $M$  sites and connectivity  $z$  is given in the quasi-chemical approximation (QCA) by the form [9],

$$Q = q_A^{N_A} q_B^{N_B} \sum_{N_{AA}} \sum_{N_{AB}} \sum_{N_{BB}} \Omega(N_A, N_B; N_{AA}, N_{AB}, N_{BB}; M) e^{-\beta H} \quad (5)$$

Here  $q_{A(B)}$  is the non-configurational partition function of a single particle,  $H$  is the configurational energy (Hamiltonian) of the system, and  $\beta$  is the inverse of temperature,  $k_B T$ , where  $k_B$  is the Boltzmann constant.  $\Omega(N_A, N_B; N_{AA}, N_{AB}, N_{BB}; M)$  gives, in the context of QCA, the number of configurations with a specified numbers of atoms ( $N_A, N_B$ ) and nearest-neighbor pairs ( $N_{AA}, N_{AB}, N_{BB}$ ) over a total number of pairs equal to  $zM/2$ . The different numbers of pairs must satisfy the following constrains:

$$\begin{cases} 2N_{AA} + N_{AB} + N_{A0} = zN_A \\ 2N_{BB} + N_{AB} + N_{B0} = zN_B \\ 2N_{00} + N_{A0} + N_{B0} = z(M - N_A - N_B) \end{cases} \quad (6)$$

where  $N_{x0}$  is the number of pairs consisting in an atom of species  $x$  and an adjacent empty site. Thus, only three of these numbers are independent (i.e.  $N_{AA}, N_{AB}$  and  $N_{BB}$ ).

In this formalism, the number  $\Omega$  is replaced by,

$$\tilde{\Omega}(N_A, N_B; N_{AA}, N_{AB}, N_{BB}; M) = \frac{\left[\frac{zM}{2}\right]!}{\left[\left(\frac{N_{A0}}{2}\right)!\right]^2 \left[\left(\frac{N_{B0}}{2}\right)!\right]^2 \left[\left(\frac{N_{00}}{2}\right)!\right]^2 N_{AA}! N_{BB}! N_{00}!} \quad (7)$$

This numbers over counts the number of configurations as it treats the pairs as independent entities.<sup>9</sup> To equal this to the actual number of configurations,  $\Omega$ , we must normalize  $\tilde{\Omega}$ ,

$$\Omega(N_A, N_B; N_{AA}, N_{AB}, N_{BB}; M) = C(N_A, N_B; M) \tilde{\Omega}(N_A, N_B; N_{AA}, N_{AB}, N_{BB}; M)$$

and  $\Omega(N_A, N_B; M) =$

$$C(N_A, N_B; M) \sum_{N_{AA}} \sum_{N_{AB}} \sum_{N_{BB}} \tilde{\Omega}(N_A, N_B; N_{AA}, N_{AB}, N_{BB}; M).$$

Here  $\Omega(N_A, N_B; M)$  is the number of ways to arrange  $N_A$  and  $N_B$  particles of species  $A$  and  $B$ , in  $M$  sites. In the present case of single site occupation (monomers), this number can be calculated in an exact way.

Within this approximation, the configurational energy accounting non-additive interactions,  $H_{cq}(N_A, N_B; N_{AA}, N_{AB}, N_{BB})$ , is readily written as, [38]

$$H_{cq} = \frac{1}{2} \sum_{m_A=0}^z \sum_{m_B=0}^{z-m_A} \left[ (m_A N_A w_{AA}^{m_A} + m_B N_B w_{AB}^{m_B}) P_A(m_A, m_B) + (m_A N_B w_{AB}^{m_A} + m_B N_B w_{BB}^{m_B}) P_B(m_A, m_B) \right] \quad (8)$$

This expression takes into account all the possible environments where particles of any species are immersed, here  $w_{AA}^{m_A}, w_{BB}^{m_B}, w_{AB}^{m_A}$  and  $w_{AB}^{m_B}$  are obtained from Eq. (1).  $P_{A(B)}(m_A, m_B)$  is the probability of occurrence of an environment consisting of  $m_A$  atoms of species  $A$  and  $m_B$  atoms of species  $B$  in the first coordination sphere around an atom of species  $A$  ( $B$ ), that is,

$$P_x(m_A, m_B) = \binom{z}{m_A} \binom{z-m_A}{m_B} \left[ \frac{N_{Ax}}{\frac{1}{2}zN_x} \right]^{m_A} \left[ \frac{\frac{1}{2}N_{xB}}{\frac{1}{2}zN_x} \right]^{m_B} \left[ \frac{\frac{1}{2}N_{x0}}{\frac{1}{2}zN_x} \right]^{z-m_A-m_B}, \quad (9)$$

where  $x$  stands for  $A$  or  $B$ .

From expressions (8) and (9) and taking into account the Eq. (6) we are able to strongly simplify the partition function (5) by the usual method of the maximum term, that is, taking only the largest term corresponding to the values  $N_{AA}^*, N_{AB}^*$  and  $N_{BB}^*$ , obtained from the Eq. [9],

$$\begin{cases} \frac{N_{A0}^2}{4N_{AA}N_{00}} = e^{-\beta \frac{\partial H}{\partial N_{AA}}} \\ \frac{N_{B0}^2}{4N_{BB}N_{00}} = e^{-\beta \frac{\partial H}{\partial N_{BB}}} \\ \frac{N_{A0}N_{B0}}{2N_{AB}N_{00}} = e^{-\beta \frac{\partial H}{\partial N_{AB}}} \end{cases} \quad (10)$$

The thermodynamic properties of the system, considering the numbers  $N_{xy}^*$ , independent of  $N_A, N_B$  and  $M$ , are given by the chemical potentials corresponding to each species,

$$\mu_A = -\frac{1}{\beta} \frac{\partial \ln Q}{\partial N_A}, \mu_B = -\frac{1}{\beta} \frac{\partial \ln Q}{\partial N_B}. \quad (11)$$

The complete set of Eqs. (10) and (11) can be solved to obtain, for example, the total and partial adsorption isotherms of the system.

### 4. Results

The main goal of the present work is to analyze the goodness of the QCA compared with the MC simulation data in different scenarios of adsorption. MC simulations were carried out on one-dimensional, square and triangular lattices. In the case of two-dimensional lattices, the total number of sites can be expressed by  $M = L^2$ , where  $L$  is the linear dimension. In these cases it was found that  $L = 128$  (square) and  $L = 120$  (triangular) were enough to avoid the occurrence of finite size effects. In the one-dimensional case,  $L = 1000$  was used under the same basis. In all the cases, periodic boundary conditions were included. For simplicity, the adsorbate–adsorbent interactions were taken equal to zero without any loss of generality. Throughout the study, the analysis will be divided into three cases:

Case I:  $\mu_B = 0, w_{AA} > 0, w_{AB} = w_{BB} = 0, p_{AB} = p_{BB} = 1.0$  and  $p_{AA} \neq 1.0$

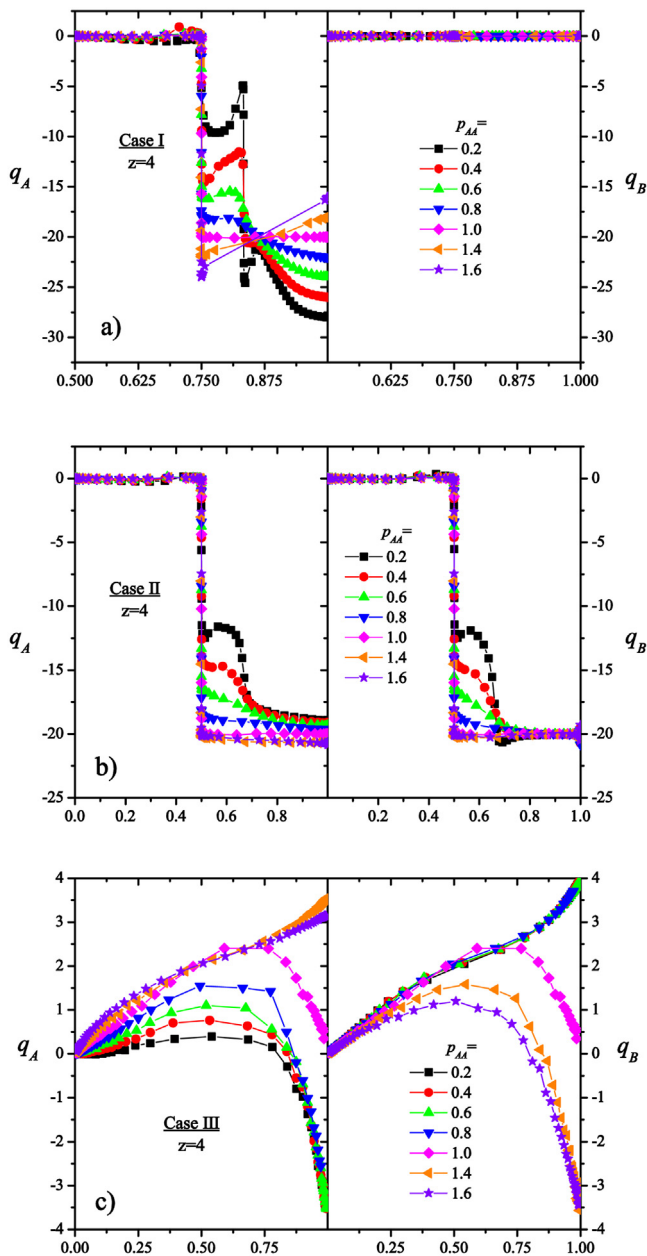
Case II:  $\mu_B = \mu_A, w_{AB} = w_{BB} = w_{AA} > 0.0, p_{AB} = p_{BB} = 1.0$  and  $p_{AA} \neq 1.0$ ,

Case III:  $\mu_B = \mu_A, w_{AB} > 0, w_{AA} = w_{BB} < 0.0, p_{AB} = p_{BB} = 1.0$  and  $p_{AA} \neq 1.0$

Case I is a typical situation frequently considered in literature [19,20], whereas cases II and III represent a more realistic situation from the experimental point of view, where the variation of the total pressure in the gas phase will lead to simultaneous changes in the chemical potential of each species.

We will start considering the square lattice with an intra-species interaction of  $w_{AA}/k_B T = 5.0$ . Starting from the initial condition  $\mu_B/k_B T = 0$  and  $\mu_A/k_B T \rightarrow -\infty$ , the particles of the species  $B$  covers half the substrate randomly and no particle of species  $A$  are deposited. For  $p_{AA} \leq 1.0$ , as the chemical potential  $\mu_A/k_B T$  is increased, the species  $A$  begins to adsorb. As has been observed in a previous work [44], different ordered structures appear in the substrate as a consequence of the non-additive interacting species. The broad plateaus in the isotherms are an evidence of this: the plateaus at  $\theta = 1/2$  and  $\theta = 2/3$  correspond to the  $c(2 \times 2)$  and zig-zag ordered structures, respectively. As the chemical potential increases, the species  $B$  is gradually expelled from the surface, until the species  $A$  are finally imposed covering the entire substrate. Fig. 1 shows the adsorption isotherms, i.e.  $\mu/k_B T$  versus the surface coverage, for several values of  $p_{AA}$ . At low and high coverage, the QCA

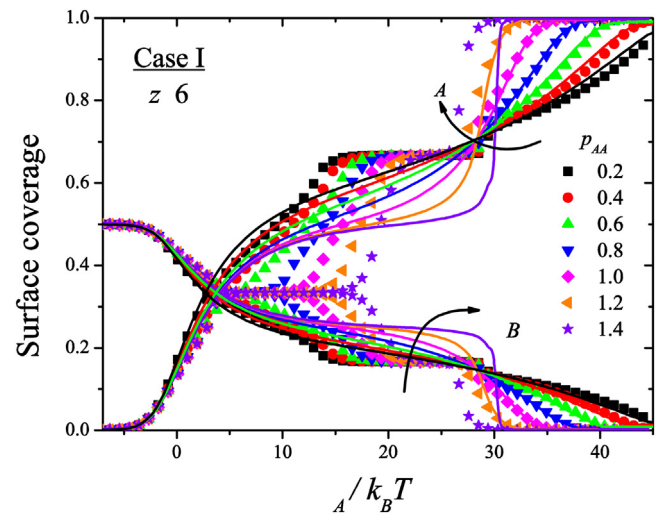




**Fig. 4.** Differential heat of adsorption for both species on square lattice, as indicated. Parts a), b) and c) correspond to case I, case II and case III, respectively.

shows a good concordance with the MC simulation for both species, as expected for this kind of approach. However, in the zone where the plateaus are present, CQ curves tend to smooth, and thus deviate from the simulation data. For  $p_{AA} > 1.0$ , from the MC simulation only one plateau is observed at  $\theta = 1/2$ , and a condensation indicated by a jump in the isotherms [44]. The chemical potentials obtained from the QCA, show an incipient Van der Waals loop at the same interval of discontinuity of the MC data.

Fig. 2 shows the isotherms corresponding to case II for  $w_{AB} = w_{BB} = w_{AA} = 5.0 k_B T$ . Fig. 2(a) corresponds to the partial isotherm for the species A. In the additive situation, the isotherm start showing a broad plateau corresponding to a  $c(2 \times 2)$  ordered structure. When  $p_{AA} < 1.0$ , a narrowing of the half coverage plateau for species A is observed followed by the formation of a new plateau corresponding to a zig-zag phase. At the same time, the species B is gradually expelled from the substrate reaching a minimum, coin-



**Fig. 5.** Idem to Fig. 1 for the triangular lattice.

ciding with the formation of the above mentioned second plateau in species A. Finally, species B is partially reinserted.

The QCA reproduces successfully the minimums, the dependence on  $p_{AA}$ , as well as the saturation coverages of species B. Concerning the species A, the theoretical approach has a similar behavior to that observed in case I.

The inset of Fig. 2(b) shows, for the particular value  $p_{AA} = 0.2$ , the partial isotherms obtained both by a sequence of adsorption (increasing chemical potential) as by one of desorption (decreasing chemical potential). As expected in this kind of systems, the equilibrium states do not depend on the history (initial conditions), and no difference is observed in the simulated isotherms between an adsorption and a desorption simulated sequences.

The case III is a combination of attractive and repulsive interactions between the adparticles. In particular, attractive intra-species interactions,  $w_{AA} = w_{BB} = -1.0 k_B T$ , and repulsive inter-species interactions,  $w_{AB} = 1.0 k_B T$ , were considered. Each species starts with the formation of clusters, where clusters of different species are separated by empty sites. The partial isotherms increase until both species reach a critical coverage of about  $\theta_A \simeq \theta_B \simeq 0.12$ . From this point, both species start a competition to enlarge its clusters. In the additive case,  $p_{AA} = 1$ , both species have the same probability to fill the substrate, fact that can be observed in the identical partial isotherms ending at half coverage. For  $p_{AA} < 1.0$ , the adsorption of species B (which is additive) is favored, since the configurational energy of clusters consisting of particles B is the lowest. The situation is reverted when  $p_{AA} > 1.0$ . It is clear that the symmetry breaking is a consequence of the no-additivity in this attractive case, however, no condensation is observed at any value of the non-additive parameter  $p_{AA}$ . Fig. 3 parts (a) and (b) shows the partial isotherms for this case. The inset shows a zoom of the isotherms before the symmetry breaking. The described behavior for both species is well reproduced by the QCA.

As a help to understand the energetic of the processes involved, Fig. 4 shows the differential heat of adsorption versus the total coverage of both species, obtained from Monte Carlo simulations.<sup>44</sup> In all the cases, the behavior of the differential heat is in accordance with the analysis conducted in the partial isotherms. Fig. 4(a), corresponding to case I, presents a behavior that can be explained by analyzing the same three regimes of Fig. 1, namely (i) for  $0.5 < \theta < 0.75$  ( $0 < \theta_A < 0.5$ ), (ii) for  $0.75 < \theta < 0.83$  ( $0.5 < \theta_A < 2/3$ ), and (iii) for  $0.83 < \theta < 1$  ( $2/3 < \theta_A < 1$ ). As can be seen, the plateaus in the adsorption isotherms correspond to marked jumps in the heat curves, signaling the formation of the different structures in

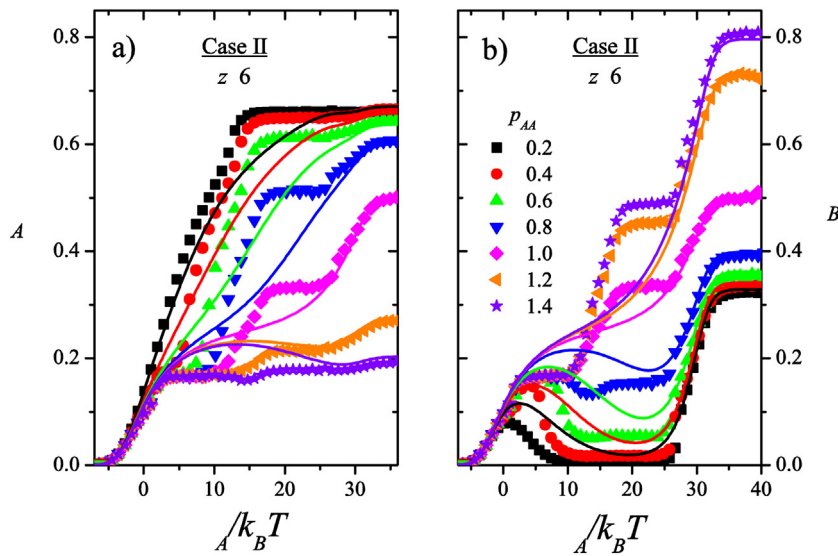


Fig. 6. Idem to Fig. 2 for the triangular lattice.

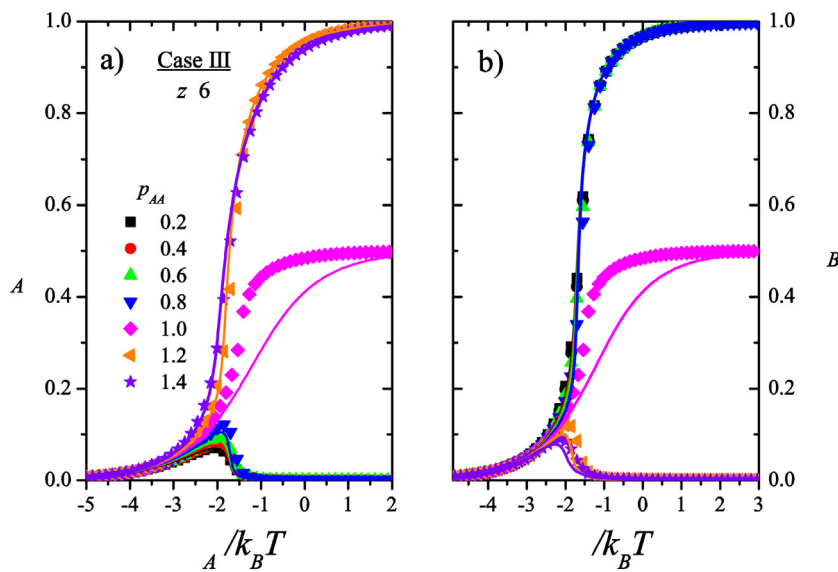


Fig. 7. Idem to Fig. 3 for the triangular lattice.

the substrate. A similar analysis can be done in Fig. 4 (b) for the case II. The behavior of smooth variations in the partial isotherms of Fig. 3, that corresponds to the case III, is observed now in the heat curves of Fig. 4(c), as a result of the processes of cluster formation and competition already discussed.

In order to complete the study, the performance of the QCA has been tested over different geometries. Figs. 5–7 show the partial adsorption isotherms on the triangular lattice (coordination number  $z=6$ ) for the cases already considered, whereas the same study on a one-dimensional system (coordination number  $z=2$ ) is considered in Fig. 8.

Fig. 5 shows the partial isotherms corresponding to the case I triangular lattice. As can be seen for species A, two broad plateaus are formed at  $\theta_A = 1/3$  and  $\theta_A = 2/3$  corresponding to the  $(\sqrt{3} \times \sqrt{3})$  and  $(\sqrt{3} \times \sqrt{3})^*$  ordered structures, respectively. On the other hand, species B starts at half coverage for low chemical potential, and then it is displaced as the other species is adsorbed. As in this case species B has no interaction at all, its adsorption isotherm curves are a consequence of particles B occupying ran-

domly half of the empty sites left by particles A. Thereby, when the  $(\sqrt{3} \times \sqrt{3})^*$  ordered structure is formed, species B presents a plateau at  $\theta_B = 1/6$ . After this, particles B are gradually expelled from substrate. The effect of non-additivity on species A as  $p_{AA} < 1$  ( $p_{AA} > 1$ ) is a narrowing of the first (second) plateau at expenses of the second (first). The results obtained from the QCA have a good agreement with the MC data at low and high coverages, although they are not able to reproduce in detail the different plateaus, as expected.

Fig. 6 shows the adsorption isotherms for the case II. In the additive situation,  $p_{AA} = 1.0$ , the partial isotherms are the same and the already described ordered structures at  $\theta_A = \theta_B = 1/6$  and  $\theta_A = \theta_B = 1/3$  are observed.

For non-additive interaction, the thermodynamic behavior is similar to the previously described for square lattice. When  $p_{AA} < 1.0$  the first plateau tends to disappear followed by a second plateau that increases toward  $\theta_A = 2/3$  as  $p_{AA}$  decreases, where a  $(\sqrt{3} \times \sqrt{3})^*$  ordered structure is formed. At the same time, during the formation of the above mentioned second plateau, particles

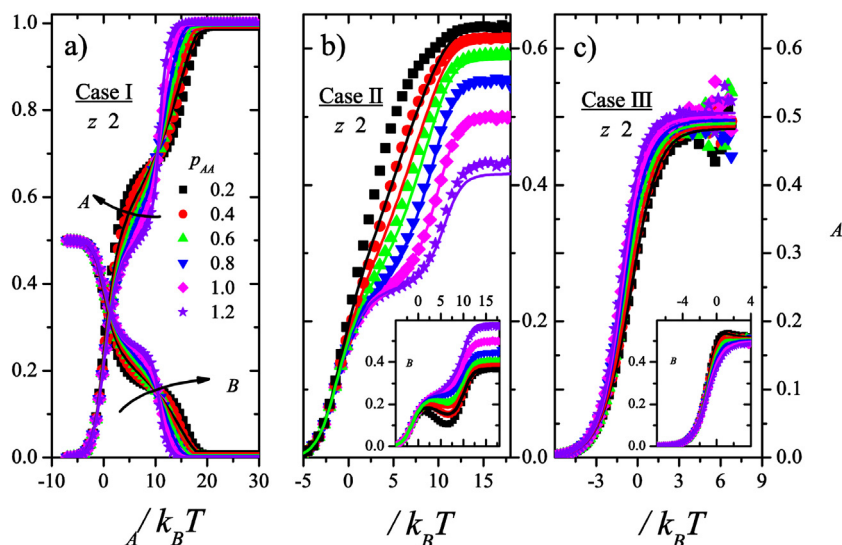


Fig. 8. Results in one-dimension: a) partial isotherms of both species for case I and different values of  $p_{AA}$ ; b) partial isotherm of species A and B (inset) for case II; c) idem for case III.

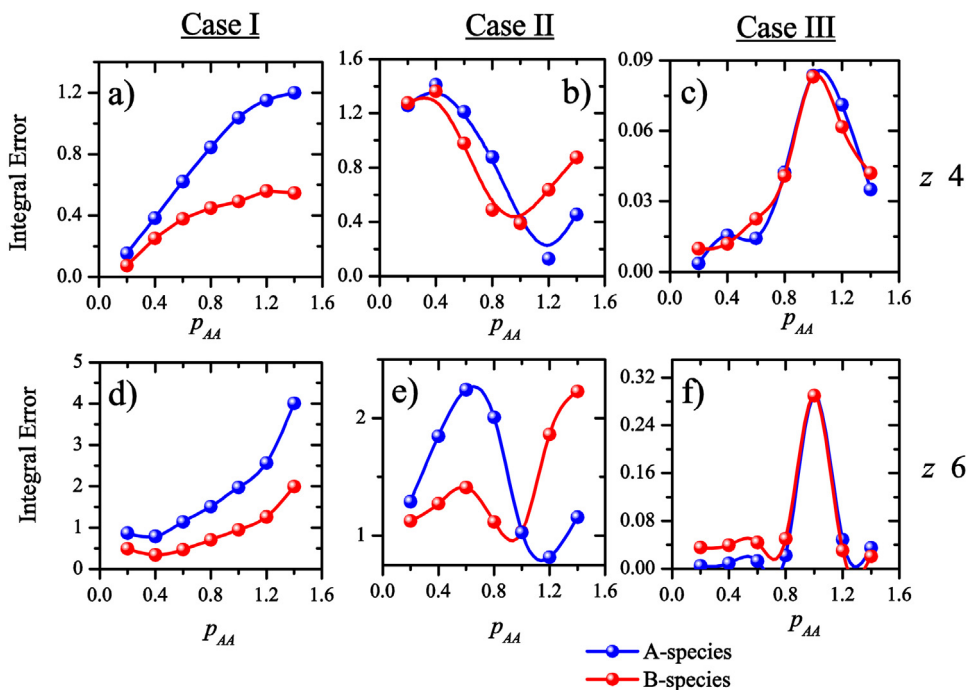


Fig. 9. Integral error, as defined in the text, versus various values of parameter  $p_{AA}$ , for the different cases and geometries, as indicated.

$B$  are partially expelled, which is manifested by a minimum in the corresponding isotherms. Thereafter, the species  $B$  is gradually adsorbed on the available sites until completion. The QCA reproduces the saturation coverages for both species as well as the minimum on the isotherm of species  $B$  but, as expected, fails in reproducing the plateaus.

When  $p_{AA} > 1.0$ , the situation is somewhat different. The first plateau in both species correspond to the formation of a  $(\sqrt{3} \times \sqrt{3})$  ordered structure at equal density,  $\theta_A = \theta_B = 1/6$ . For species  $A$ , the second plateau tends to disappear resulting in a widening of the first one. As the chemical potential increases, the partial isotherm of species  $B$  presents a new plateau at  $\theta_B \simeq 1/2$ . Here, a  $(\sqrt{3} \times \sqrt{3})^*$  ordered structure is formed by a combination of both species in an approximate ratio of  $\theta_B \simeq 3\theta_A \simeq 1/2$ , which is more pronounced as

$p_{AA}$  increases. The QCA reproduces well both the minimum and the saturation coverages.

Case III for the triangular lattice is shown in Fig. 7. As can be seen, the behavior is almost identical as for the square lattice. The QCA has a good agreement with the MC.

Let's consider now the adsorption on a one-dimensional system consisting in a lineal chain of  $L$  sites (coordination number  $z = 2$ ). The repulsive interactions induce the formation of an ordered structure at half coverage in the chain, where each particle adsorbed has its nearest neighbor empty.

Fig. 8(a) shows the isotherms for the case I. The QCA reproduces very well the isotherms in the complete range, except for very low parameter values,  $p_{AA} < 0.4$ .

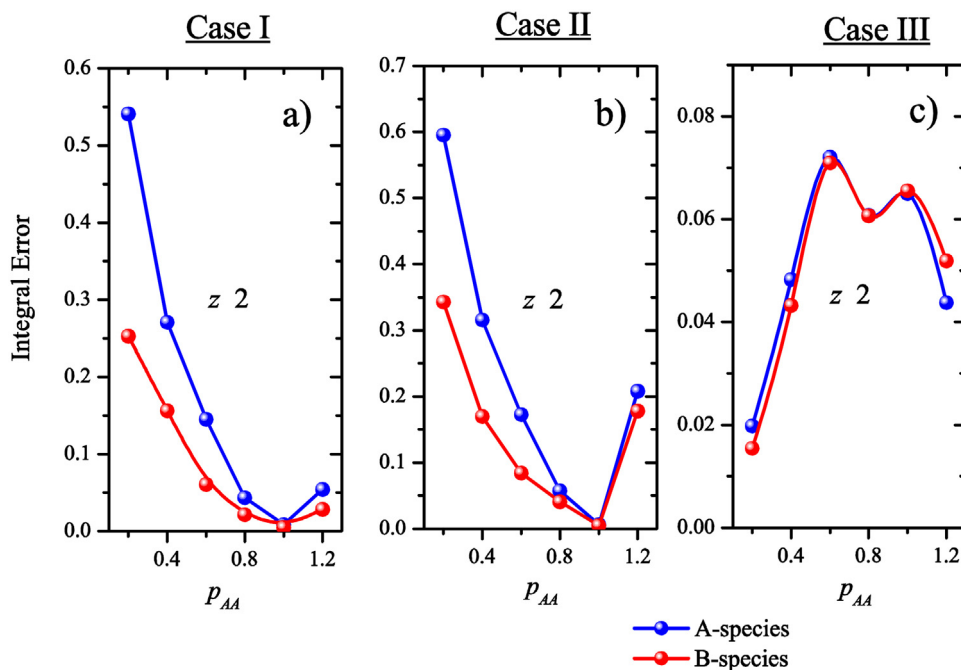


Fig. 10. Integral error versus the parameter  $p_{AA}$  in the one-dimensional lattice, for the different cases.

The case II is shown in Fig. 8(b). As in the previous case, the QCA reproduces well the MC data only near the additive situation. Finally, Fig. 8(c) corresponds to the case III. As can be seen there is a good agreement between the MC data and the QCA.

To quantify the performance of the QCA in the different situations analyzed, the integral error is defined as:

$$\text{IntegralError} = \int_0^{\theta_{\max}} |\beta\mu(\theta)_{\text{Theoretical}} - \beta\mu(\theta)_{\text{MC}}| d\theta \quad (12)$$

This quantity measures the area between the adsorption isotherm curves in the range  $0 \leq \theta \leq \theta_{\max}$ , where  $\theta_{\max}$  is the saturation coverage corresponding to each case.

Fig. 9 parts (a)–(f) show the integral error versus  $p_{AA}$  for the two-dimensional lattices previously analyzed. The upper panels correspond to the square lattice whereas the lower ones correspond to the triangular lattice. As can be seen, the different cases have a similar behavior in both geometries. Case I shows the error increasing monotonically with the parameter. Case II presents a minimum around the additive case ( $p_{AA} = 1$ ), whereas the case III shows a maximum in the same place. In addition, case II seems to show a maximum around  $p_{AA} \approx 0.4$ . The last case, that includes some attractive interactions, is the best reproduced by the QCA, as can be seen from the scales of the graphs.

Fig. 10 shows, for the one-dimensional system ( $z=2$ ), a somewhat different behavior. Case I presents a minimum around  $p_{AA} = 1$ , instead of the monotonic behavior observed in the two-dimensional systems. Case II also has a minimum around the additive case, but lacks the local maximum around  $p_{AA} \approx 0.4$ . Case III has similar characteristics as in the two-dimensional systems.

The behavior observed in Figs. 1–8 should change in the presence of surface heterogeneity. In fact, the existence of a very small quantity of defects (sites or bonds with different energy) breaks down the order of the low-temperature phases and, consequently, the characteristic plateaus in the adsorption isotherms tend to disappear [47,48].

## 5. Conclusions

In this work we have addressed the adsorption problem of a binary mixture of interacting monomers, following the quasi-chemical configuration counting approach and by comparing it with MC simulation results. The traditional assumption of a strictly pairwise additive nearest-neighbor interaction has been replaced by a more realistic one where the bond linking a certain atom with any of its neighbors depends on the occupation degree of the first coordination shell of the atom.

Different cases were analyzed, fixing the chemical potential of one species or by varying both potentials simultaneously, as well as different combinations of attractive and repulsive inter- and intra-species interactions. As a way to test further the performance of the theoretical approach, different geometries have been considered, from a one-dimensional system to the square and triangular two-dimensional cases.

The theoretical results present a very good qualitative and quantitative agreement with the MC simulation data in all the studied cases. From the integral error curves it can be observed that there is a monotonically increasing tendency with the non-additive parameter in most of the cases. With regard to case III, this tendency is inverted, although the corresponding errors are lower by a factor of 10 respect to the other cases.

Considering the complexity in the experimental study of these processes, it is important to note the usefulness of this theoretical approach as a first tool to predict the behavior of a system governed by a large number of parameters. Thus, the application of QCA allows (1) to identify and characterize the most prominent features of the process of adsorption of mixtures with inter- and intra-species non-additive interactions (i.e. systems in the presence of surface restructuring), (2) to draw general conclusions on the effects of the competition between two adsorbed species and (3) to provide a framework to consistently interpret experimental findings without heavy or time-consuming calculations. In this line, a comprehensive analysis of experimental data corresponding to adsorption of interacting mixtures is in progress.



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