# Critical behavior of repulsively interacting particles adsorbed on disordered triangular lattices

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A simple model for amorphous solids, consisting of a triangular lattice with a fraction of attenuated bonds randomly distributed (which simulate the presence of defects in the surface), is used here to find out, by using grand canonical Monte Carlo simulations, how the adsorption thermodynamics of repulsively interacting monomers is modified with respect to the same process in the regular lattice. The degree of disorder of the surface is tunable by selecting the values of (1) the fraction of attenuated bonds $\rho$ ($0 \leq \rho \leq 1$) and (2) the attenuation factor $r$ ($0 \leq r \leq 1$), where $r$ is defined as the ratio between the value of the lateral interaction associated to an attenuated bond and that corresponding to a regular bond. Adsorption isotherm and differential heat of adsorption calculations have been carried out showing and interpreting the effects of the disorder. A rich variety of behavior has been observed for different values of $\rho$ and $r$, varying between two limit cases: bond-diluted lattices ($r = 0$ and $\rho \neq 0$) and regular lattices ($r = 1$ and any value of $\rho$). In addition, the critical behavior of the system was studied, showing that the order–disorder phase transition observed for the regular lattice survives, though with modifications, above a critical curve ($\rho$–$r$–temperature).

## I. Introduction

For a very long time in the history of the studies of heterogeneous adsorbents, the adsorptive energy distribution was considered as the only important characteristic to be known in order to describe the behavior of adsorbed particles, and much effort was dedicated to the development of methods for its determination from experimental adsorption data.[1–4] However, most real solids surfaces present a combination of two types of heterogeneity:[5–7] (1) energetic heterogeneity, manifested through the variation of adsorption energy from one site to another, and (2) geometric heterogeneity, associated with the existence of irregularities in the lattice of adsorbing sites, whose effects on adsorption are manifested through adsorbate–adsorbate interactions. These heterogeneities may produce a complex spatial dependence of the solid–gas interaction potential, which can be denoted as adsorption energy topography.

The description of thermodynamic phenomena taking place on a substrate which presents the inherent complexity of geometric heterogeneities, is a challenging topic in modern surface science.[5,8,9] In this context, the amorphous solids[10] can be considered as the prototype of systems with quenched geometrical disorder and have been the object of many studies in the field of magnetism. Based on simple "site-diluted" or "bond-diluted" models like the Ising, Heisenberg and Potts models, the effect of the disorder on the nature of the phase transitions and their universality have been discussed and are still posing open problems.[11–14] As it is well known,[15,16] the lattice-gas model is isomorphic to the Ising model in a magnetic field, and one can apply the results known for the latter to analyze the adsorption thermodynamics of monomers on a lattice of sites. Despite this result, the main studies in magnetism have been developed in absence of an external field and, consequently, are not directly related to the adsorption problem. Due to this fact, and to the potential applications, it is of interest and of value to inquire how a geometric disorder influences the main thermodynamic properties of adsorbed particles.

In a previous article,[17] Quintana *et al.* studied the thermodynamics of adsorption of repulsively interacting monomers on disordered triangular lattices. Inspired by the problem of adsorption on amorphous solids, disorder was introduced by randomly deleting a fraction of bonds, representing interactions between particles adsorbed at nearest-neighbor (NN) sites. Thermodynamic quantities like adsorption isotherm, differential heat of adsorption and configurational entropy of the adlayer were obtained by Monte Carlo simulations and their behavior discussed. The results showed that as the fraction of diluted bonds increases, the order–disorder phase transitions observed for the ordered lattice at $\theta = 1/3$ and at $\theta = 2/3$ survive up to a critical disorder value, which is of the order of $10^{-3}$. In other words, the presence of a very small quantity of defects (diluted bonds) break down the order of the low-temperature phases.

In this paper, we extend the model in ref. 17 transforming the diluted bonds, leading to null interactions between particles adsorbed at NN sites, into attenuated bonds, associated to a NN interaction $rw$, where $r$ is the attenuation factor ($0 \leq r \leq 1$), and $w$ is the lateral coupling associated to a regular bond. Now, the degree of disorder of the surface is tunable by selecting the values of (1) the fraction of attenuated bonds $\rho$ ($0 \leq \rho \leq 1$) and (2) the attenuation factor $r$. In this framework, and by using grand canonical Monte Carlo

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simulations, a detailed ($\rho$–$r$–temperature) phase diagram was obtained, showing that regular lattices and bond-diluted lattices[17] appear as particular cases of the present model, along with a rich variety of intermediate states, where the phase transition observed for the regular lattice survives.

## II. Lattice–gas model and Monte Carlo simulation scheme

The surface of amorphous solids cannot be adequately described by a regular lattice of adsorbing sites. One of the main characteristics of such surfaces is the existence of irregularities in the lattice of adsorbing sites, like variable distance among neighboring sites, whose effects on adsorption are manifested through adsorbate–adsorbate interactions. In this line of thinking, a simplified statistical model for amorphous solids is presented in the following paragraphs.

We consider a triangular lattice (connectivity $z = 6$) with $M = L \times L$ sites, $m = 3M$ bonds, and periodic boundary conditions. The surface is built on the basis of two elements: sites and bonds. A site represents an adsorptive potential minimum, where particles from a gas phase will be allocated upon adsorption (only one particle is allowed at each site), while a bond represents the adsorbate–adsorbate interaction[18] between two particles adsorbed at the connected sites. Each bond can be either a regular bond, associated to a NN interaction $w$, or an attenuated bond, associated to a NN interaction $rw$, where the attenuation factor $r$ varies between 0 and 1. Attenuated and regular bonds are randomly distributed with concentration $\rho$ and $1 - \rho$, respectively. In this way, the degree of disorder of the surface is tunable by selecting the values of (1) the fraction of attenuated bonds $\rho$ and (2) the attenuation factor $r$. In the extreme cases where $r = 0$ (and $\rho \neq 0$) and $r = 1$ (and any value of $\rho$), the "disordered lattice" reduces to the well-known bond-diluted and regular lattices, respectively.

If the lattice is exposed to a gas phase of particles at temperature $T$ and chemical potential $\mu$, particles will adsorb in such a way that an equilibrium mean coverage, $\theta$, is achieved. The hamiltonian of the system can be written as

$$H = w \sum_{\langle i,j \rangle} b_{ij} c_i c_j - (\varepsilon_i - \mu) \sum_i c_i, \qquad (1)$$

where the sum in the first term is taken over all NN pairs of sites, $c_k$'s are site-occupation numbers (= 0 if site $k$ is empty, = 1 if occupied), $b_{ij}$'s are bond-occupation numbers (= 1 if the bond connecting sites $i$ and $j$ is a regular bond, = $r$ if the bond connecting sites $i$ and $j$ is an attenuated bond) and $\varepsilon_i$ is the adsorption energy at site $i$. In the case of an homogeneous surface of sites, as the one to be considered here, all $\varepsilon_i$ are the same and we can take them as equal to zero without loss of generality.

The problem has been studied by grand canonical MC simulations using a typical adsorption–desorption algorithm.[21] The procedure is as follows. Once the values of the temperature $T$ and the chemical potential $\mu$ are set, a site is randomly selected and its coordinates are established. Then, an attempt is made to interchange its occupancy state with probability given by the Metropolis rule:[22] $P = \min\{1, \exp(-\Delta H/k_BT)\}$, where $k_B$ is the Boltzmann constant and $\Delta H$ is the difference between the Hamiltonians of the final and initial states. A Monte Carlo step (MCS) is achieved when $M$ sites have been tested to change its occupancy state. Typically, the equilibrium state can be well reproduced after discarding the first $n' = 5 \times 10^5$ MCS. Then, the next $n = 5 \times 10^5$ MCS are used to compute averages.

Thermodynamic quantities, such as mean coverage, $\theta$, and configurational energy, $U$, are obtained by simple averages over $n$ configurations

$$\theta = \langle N \rangle / M; \; U = \langle H \rangle - \mu \langle N \rangle, \qquad (2)$$

where the brackets denote averages over statistically uncorrelated configurations.

In our Monte Carlo simulations, we varied the value of $\mu$ and monitored the density $\theta$. Apart from the isotherms ($\theta$ *vs.* $\mu$) and the configurational energy, other quantities are calculated such as the differential heat of adsorption $q_d$ which can be obtained from the simulation as:[23]

$$q_d = -\frac{\partial U}{\partial \langle N \rangle}. \qquad (3)$$

The ordered states in the adsorbed phase can be well described by decomposing the original lattice into three interpenetrating sublattices $\alpha = 1, 2, 3$. The $(\sqrt{3} \times \sqrt{3})$ ordered state[24] corresponds to one sublattice filled and the other two empty. In the $(\sqrt{3} \times \sqrt{3})^*$ state one sublattice is empty and the other two filled. In terms of the sublattice coverage

$$\theta_\alpha = \frac{3}{M} \sum_{i \in \alpha} c_i, \qquad (4)$$

we can define the order parameter $\Psi$ of the system as

$$\Psi = \frac{4}{\sqrt{6}} \left( \sum_\alpha \Psi_\alpha^2 \right)^{1/2} \qquad (5)$$

where $\Psi_\alpha = [\theta_\alpha - (\theta_\beta + \theta_\gamma)/2] \delta_{\alpha\beta\gamma}/2$ and the $\delta$ takes the value 1 for a cyclic permutation of subindexes (1, 2, 3) and the value 0 otherwise.

Given that our system is disordered, it is important to stress that all the above calculations are repeated over 100 replicas of the system for each fixed pair of values ($\rho$, $r$) and all thermodynamical quantities are finally averaged over them.

## III. Results and discussion

Computational simulations have been developed for triangular lattices with $L = 96$ and periodic boundary conditions. With this size of the lattice we verified that finite size effects, which affect the isotherms in the case of repulsive interactions at much smaller sizes, are negligible. Care had to be taken in order to select the precise size which would allow the formation of the ordered phases.

We consider in the first place the behavior of the completely ordered system ($\rho = 0$ or $r = 1$ and any value of $\rho$). Fig. 1 shows the adsorption isotherm (a) and the differential heat of adsorption (b) for different values of $w/k_BT$ and the behavior of the order parameter (c) for a fixed value of $w/k_BT$. These results, which have been previously reported in ref. 17, are

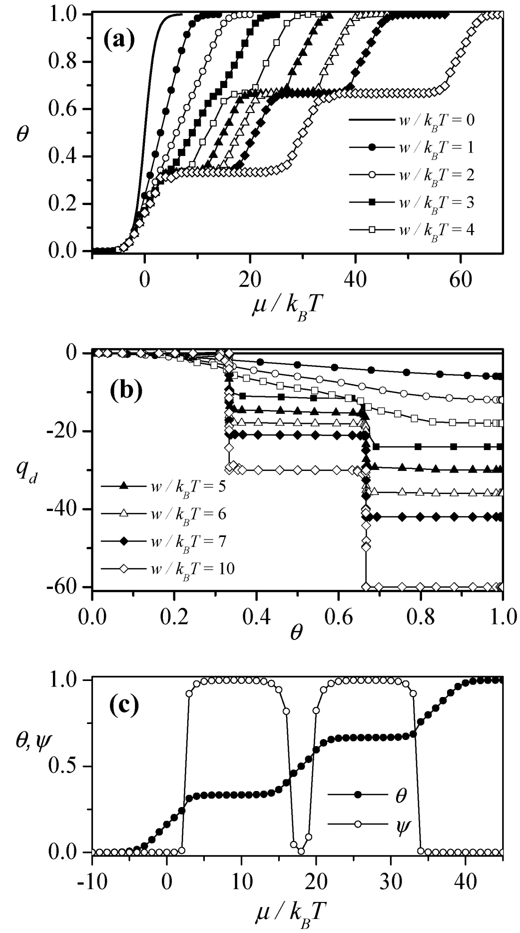

**Fig. 1** (a) Adsorption isotherm for $\rho = 0$ and different values of $w/k_BT$ as indicated. (b) Same as part (a) for differential heat of adsorption. (c) Adsorption isotherm (solid circles) and order parameter $\Psi$ (empty circles) for a regular triangular lattice ($\rho = 0$) at a fixed interaction strength ($w/k_BT = 6$). As discussed in the text, the results in Fig. 1 have been previously reported in ref. 17.

included here in order to help the reader understand the basic phenomenology.

In the limit $w/k_BT \to 0$, the coverage grows monotonically with chemical potential and the corresponding isotherm is of Langmuir type (solid line in the figure). For higher values of $w/k_BT$, such that $w/k_BT$ is above the critical value $w_c/k_BT = 2.985$,[25] three regimes appear in the isotherms. This behavior can be interpreted as follows: (i) for $0 < \theta < 1/3$, the adatoms do not interact with each other and the adsorption sites are filled until a $(\sqrt{3} \times \sqrt{3})$ ordered phase is formed on them; (ii) for $1/3 < \theta < 2/3$, the filling continues up to a $(\sqrt{3} \times \sqrt{3})^*$ structure appears on the lattice; and (iii) for $2/3 < \theta < 1$, the surface is totally covered.

The plateaus in the adsorption isotherms, which are clearly associated to different structural rearrangements of the adsorbate molecules, are accompanied by characteristic signals in the differential heat of adsorption. In fact, a plateau in the adsorption isotherm appears as a step in the differential heat of adsorption. Thus, the regimes described in Fig. 1(a) can be reinterpreted by analyzing the differential heat of adsorption [Fig. 1(b)]: from $\theta = 0$ to $\theta = 1/3$ the particles are adsorbed avoiding nearest-neighbor interactions, which gives $q_d = 0$; from $\theta = 1/3$ to $\theta = 2/3$, each incoming particle is allocated on the lattice with three occupied nearest-neighbor sites in the plane and $q_d = 3w$. Finally, from $\theta = 2/3$ to $\theta = 1$, to adsorb a new monomer it is necessary to occupy an empty site on the $(\sqrt{3} \times \sqrt{3})^*$ structure, this process involves an energy variation of $q_d = 6w$.

It is also important to test the stability of the order parameter in terms of the lattice dimensions. Fig. 1(c) shows simultaneously the variation of coverage and $\Psi$ as a function of $\mu/k_BT$ for a fixed value of $w/k_BT = 6$, where $\Psi \approx 1$ over a wide range of values of $\mu$ spanning the two coverage plateaus at $\theta = 1/3$ and $\theta = 2/3$. In fact, when the system is disordered, all sublattices are equivalents and the order parameter is minimum. However, when a configuration of the local phase appears at low temperature [as is the case in Fig. 1(c)], this is allocated on a sublattice. Let us suppose that this configuration lies on the sublattice $\alpha = 1$ (see eqn (4) and (5)). Then, the coverage $\theta_\alpha$ is maximum ($\theta_\alpha = 1$) and the coverage of the rest of the sublattices is zero or minimum. Consequently, $\Psi$ is also maximum.

As some of the bonds are randomly attenuated in the lattice, this becomes disordered with $\rho > 0$ and $r < 1$. Adsorption isotherm and differential heat of adsorption for $w/k_BT = 6$ and different values of $\rho$ and $r$ are shown in Fig. 2(a) and (b), respectively. It can be observed that for increasing values

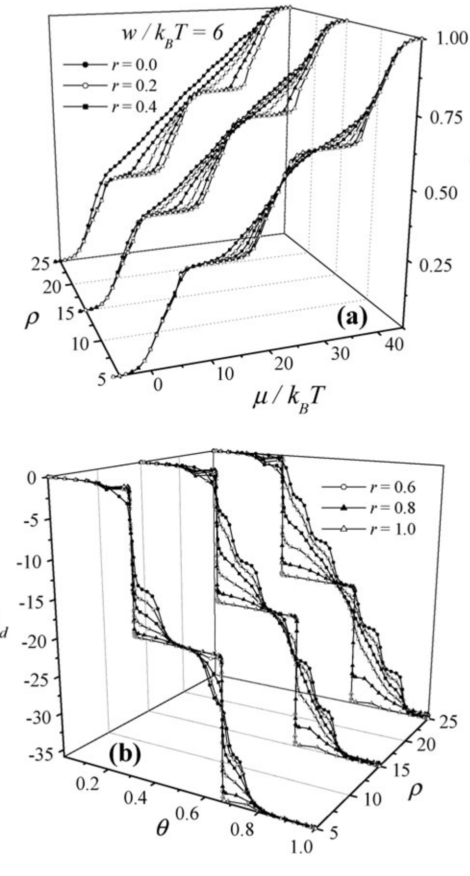

**Fig. 2** Adsorption isotherm (a) and differential heat of adsorption (b), for triangular lattices with $w/k_BT = 6$ and different degrees of disorder as indicated.

of $\rho$ and $r$, the plateaus in the adsorption isotherm and the corresponding steps in the differential heat of adsorption are gradually smeared out. An interesting phenomenon occurs for $r = 0$ (diluted bonds) and values of $\rho$ larger than $\rho \approx 0.5$. For this disorder degree, the differential heat of adsorption presents six steps (seven plateaus) at characteristic concentrations. This situation can be explained as follows: each incoming particle is adsorbed in such a way that it does not have any NN occupied site. This occurs until all possible sites with this characteristic are filled. Then, a first plateau in $q_d$ is formed where $q_d = 0$. Taking into account that the substrate is a bond-diluted lattice, the remaining empty sites can be divided in six groups according to the number of bonds that they have. Thus, upon increasing the reduced chemical potential each one of those groups will be sequentially filled. As a consequence, after the saturation of all sites of each group a plateau is formed in $q_d$. The value of this quantity in each plateau is $q_d = nw$, where $n$ is the connectivity of each kind of site. In addition, the particle-vacancy symmetry is lost. This symmetry breaking can be explained by taking into account the fact that, due to repulsive interactions, sites attached to attenuated bonds will be filled preferentially as the coverage increases.

The above results suggest the existence of a critical degree of disorder ($\rho_c$ and $r_c$), below which the order–disorder phase transition observed for the ordered lattice will survive. In what follows we explore in more details this possibility and work out a way of estimating these critical values and the extent to which the critical temperature is affected by the degree of disorder.

The effect of the disorder on the order parameter is studied in Fig. 3, where $\Psi$ is plotted *versus* $\mu/k_BT$ for $w/k_BT = 6$, $\rho = 0.25$ and different values of $r$ ranging between 0 and 1. It can be seen that all curves are contained between the two limit ones: the one corresponding to $r = 1$ (regular lattice), where the order parameter indicates the existence of the order–disorder phase transition at $\theta = 1/3$ and $\theta = 2/3$, and the one corresponding to $r = 0$ (bond-diluted lattice), where the disorder destroys the phase transition and the order parameter is practically zero over the whole range of chemical potential. The curves for intermediate values of $r$ vary continuously between the two limit cases.

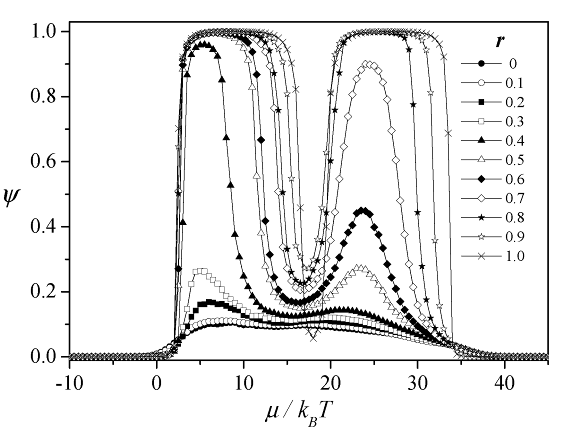

**Fig. 3** Order parameter $\Psi$ *versus* chemical potential for $w/k_BT = 6$, $\rho = 0.25$ and different values of $r$ as indicated.

On the basis of the behavior of the curves in Fig. 3, and in order to quantify the disorder degree in the adsorbate for different values of $\rho$ and $r$, a new order parameter will be defined by the following procedure:

- One of the two possible phases is selected. In this case, we restrict the analysis to the low-coverage phase.
- Given fixed values of $\rho$, $r$ and $w/k_BT$, and the corresponding $\Psi(\mu/k_BT)$ curve, the area $A_{1/3}$ is measured (see Fig. 4). $A_{1/3}$ represents the area under the $\Psi(\mu/k_BT)$ curve in the range of chemical potential where the low-coverage phase is formed ($\mu_l/k_BT - \mu_c/k_BT$). As it is shown in Fig. 4, ($\mu_l/k_BT$) corresponds to a point in the low-chemical-potential region where $\Psi = 0$, and $\mu_c/k_BT$ corresponds to the value of the chemical potential at which $\Psi$ has a local minimum in the region of intermediate chemical potential. Thus,

$$A_{1/3} = \int_{\mu_l/k_BT}^{\mu_c/k_BT} \Psi(\mu/k_BT)\mathrm{d}(\mu/k_BT). \tag{6}$$

- Finally, the new order parameter $\delta_{1/3}$ is calculated as

$$\delta_{1/3} = \frac{A_{1/3}}{A_{1/3}^{\rho=0}}, \tag{7}$$

where $A_{1/3}^{\rho=0}$ represents the value of $A_{1/3}$ for the regular lattice, and consequently, $\delta_{1/3}$ varies between 0 and 1.

The order parameter $\delta_{2/3}$, characterizing the high-coverage phase transition, is defined in a similar way. In this case, $A_{2/3}$ is calculated in the range ($\mu_c/k_BT - \mu_r/k_BT$), see Fig. 4. As an illustrative example, Fig. 5(a) [(b)] shows $\delta_{1/3}$ [$\delta_{2/3}$] as a function of $r$ for $w/k_BT = 8$, $\rho = 0.15$ and $\theta = 1/3$ [$\theta = 2/3$]. Clearly, the curves exhibit the typical behavior corresponding to an order parameter, which reinforces the idea that the phase transition survives up to a certain critical degree of disorder. In the following, $\delta_{1/3}$ and $\delta_{2/3}$ will be used to study the critical behavior of the present model.

Now, the variation of $\delta_{2/3}$ with $r$ for different values of $\rho$ and a fixed value of $w/k_BT = 3.5$ is represented in Fig. 6(a). For each curve, a critical value of $r$ ($r_c$) is obtained from the position of the inflexion point. Thus, the ordered phase is separated from the disordered state by a order–disorder phase transition occurring at a critical $r_c$.

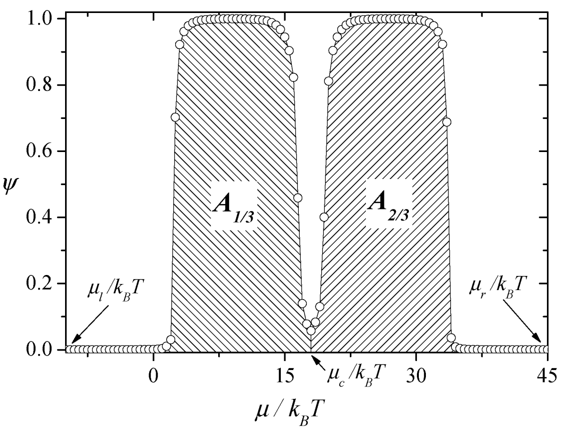

**Fig. 4** Typical curve of the order parameter $\Psi$ *versus* coverage showing the different quantities used to build the order parameter $\delta$ (see the corresponding text).

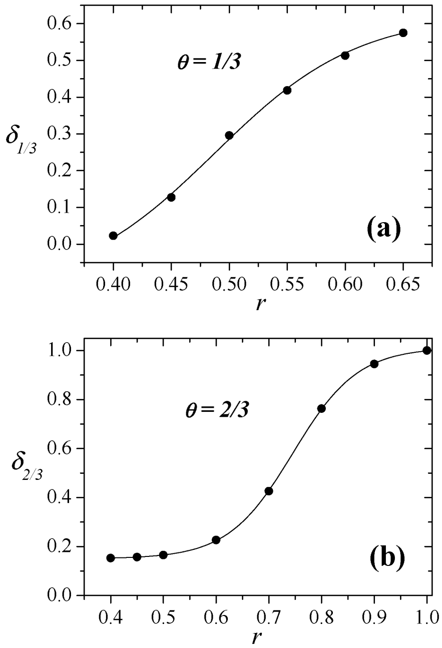

**Fig. 5** (a) Order parameter $\delta$ as a function of $r$ for $\theta = 1/3$, $w/k_BT = 8$ and $\rho = 0.15$. (b) As in part (a) for $\theta = 2/3$.

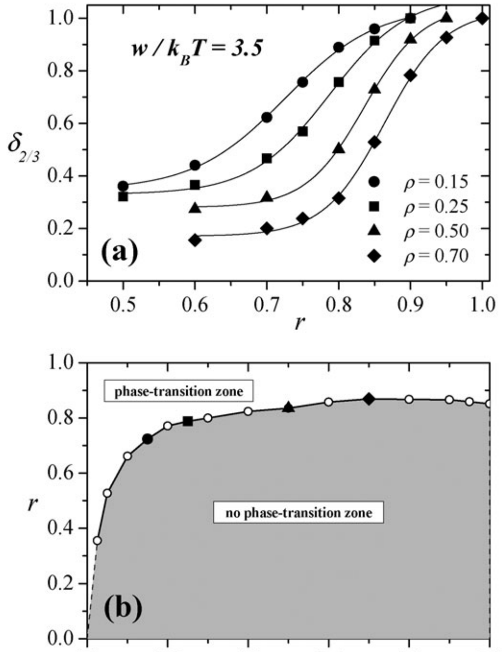

**Fig. 6** Analysis at the high coverage transition, $\theta = 2/3$: (a) variation of the order parameter $\delta$ with $r$ for $w/k_BT = 3.5$ and different values of $\rho$ as indicated; (b) phase diagram, in the ($\rho$–$r$) space, for a disordered triangular lattice at $\theta = 2/3$ and a fixed interaction strength ($w/k_BT = 3.5$). Solid symbols on the critical line have been obtained from the position of the inflexion point of the curves in part (a): circle, $\rho = 0.15$; square, $\rho = 0.25$; triangle, $\rho = 0.50$; and diamond, $\rho = 0.70$.

Repeating the procedure of Fig. 6(a) for different values of $\rho$ between 0 and 1, the phase diagram of Fig. 6(b) is obtained. Solid symbols on the critical line have been obtained from the position of the inflexion point of the curves in part (a): circle, $\rho = 0.15$; square, $\rho = 0.25$; triangle, $\rho = 0.50$; and diamond, $\rho = 0.70$.

The extreme points of the critical curve can be calculated in an analytical way. In fact, for $\rho = 0$ (regular lattice), the behavior of the system is well-known: if $w/k_BT \geq 2.985$,[25] the phase transition occurs for all values of $r$; and the phase transition does not take place for $w/k_BT < 2.985$. On the other hand, in the limit $\rho = 1$, the system corresponds to a regular lattice with homogeneous lateral interactions equal to $rw/k_BT$. In this case, the value of $r_c$ is obtained from the condition $r_cw/k_BT = 2.985$.[25]

To conclude with the analysis of the results presented in Fig. 6(b), we briefly analyze the behavior of the system for $\rho \approx 0$ and $r = 0$. As studied in ref. 17, the phase transition survives up to a critical value of $\rho$, which is of the order of $10^{-3}$. The dashed line in Fig. 6(a) indicates that this region of the phase diagram, where $\rho \approx 0$ and $r \approx 0$, has already been studied following the scheme of ref. 17.

The study of Fig. 6 was repeated for a wide range of values of $w/k_BT$. In this way, a detailed ($\rho$–$r$–$w/k_BT$) phase diagram was obtained for the low-coverage phase (Fig. 7) and the high-coverage phase (Fig. 8). As discussed in Fig. 6, the region below the critical curves (line-symbol curves in Fig. 7 and 8) corresponds to the no phase-transition region, and the region above the critical curves corresponds to the phase-transition region. Several conclusions can be extracted from Fig. 7 and 8.

(i) The particle-vacancy symmetry is lost. It is therefore clear that critical parameters are different at the two phase transitions located at $\theta = 1/3$ and at $\theta = 2/3$, the latter being more sensitive to the degree of disorder. The reason for this behavior can be traced down to the particularities of the geometry of each ordered phase. At $\theta = 1/3$ the ordered phase consists of a configuration where any central filled site is surrounded by an hexagon with six empty sites at the corners. If just one bond between a filled and an empty site is attenuated, no new configurations arise with the same or lower

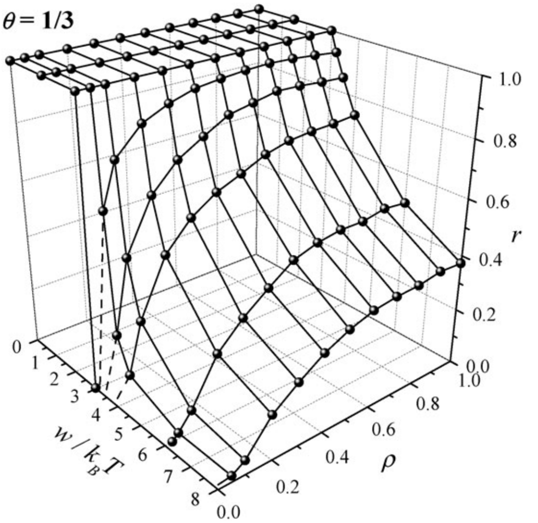

**Fig. 7** Phase diagram (in the $\rho$–$r$–$w/k_BT$ parameter space) corresponding to repulsive monomers adsorbed on disordered triangular lattices at 1/3 coverage. Line-plus-symbol curves correspond to critical lines that separate the phase-transition and no phase transition regions.

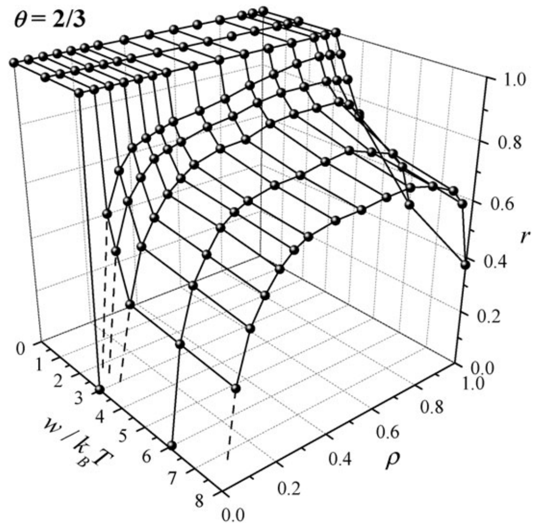

**Fig. 8** Same as Fig. 7 for $\theta = 2/3$.

energy. At $\theta = 2/3$, on the contrary, the ordered phase is characterized by the fact that any central empty site is surrounded by an hexagon with six filled sites at the corners. If just one bond between a filled and an empty site is attenuated (a radial bond in an hexagon) there are several new configurations with lower energy, namely those where the eliminated bond is transformed into one of the sides of an hexagon of filled sites. The system will try to evolve toward one of the new configurations passing through a huge number of intermediary partially disordered states.

(ii) According to the discussion of Fig. 6(b), the critical curves for $\rho = 0$ and $\rho = 1$ show a marked step in $w/k_BT = 2.985$, which corresponds to the critical interaction for the regular lattice.

(iii) As $w/k_BT$ is increased, the low- and high-coverage phases exhibit two well-differentiated behaviors. At $\theta = 1/3$, the overall effect of $w/k_BT$ is to decrease the critical $r$ *vs.* $\rho$ curves for all $\rho$. On the other hand, for the high-coverage phase, the ($\rho$–$r$) curves tend to a limit curve as $w/k_BT$ is increased. The limit curve was obtained for $w/k_BT = 30$, with an effort reaching almost the limits of our computational capabilities (data do not shown here for clarity).

The results in (iii) indicate that an analysis of the delicate balance between the lateral interaction energy and the degree of disorder ($\rho$ and $r$) allows to interpret the critical behavior of the system. Thus, for the low-coverage phase, the effects of the disorder can be "compensated" by an appropriate $w/k_BT$, such that the phase transition survives. On the contrary, there exists a wide region of $\rho$ and $r$ where the high-coverage phase disappears, independently of the value of $w/k_BT$. These findings reinforce the arguments in point (i), *i.e.* the high-coverage phase is more sensitive to the degree of disorder than the low-coverage phase.

## IV. Conclusions

In the present work, we have addressed the critical properties of repulsively interacting particles adsorbed on disordered triangular lattices. The results were obtained by using grand canonical Monte Carlo simulations.

Disorder was introduced by a simple model where each bond (which represents the adsorbate–adsorbate interaction between two particles adsorbed at the connected sites) can be either a regular bond, associated to a NN interaction $w$, or an attenuated bond, associated to a NN interaction $rw$ ($0 \leq r \leq 1$). Attenuated and regular bonds were randomly distributed with a concentration $\rho$ and $1 - \rho$ ($0 \leq \rho \leq 1$).

Thermodynamic quantities like adsorption isotherm and differential heat of adsorption were calculated and their behavior discussed. In addition, we have introduced an order parameter, $\delta$, which is particularly useful for describing adsorption on disordered systems at critical regime. This parameter is well behaved and computationally convenient. Taking advantage of its definition, a complete ($\rho$–$r$–$w/k_BT$) phase diagram of the studied system was obtained.

In the limit of $r = 1$ (regular lattice), two order–disorder phase transitions exist at $\theta = 1/3$ and at $\theta = 2/3$ when $w/k_BT$ is above the critical value $w_c/k_BT = 2.985$ and all thermodynamic quantities show a particle-vacancy symmetry around $\theta = 1/2$. As the degree of disorder increases, the critical behavior of the system is characterized by the following properties:

(1) The particle-vacancy symmetry is lost and, consequently, the critical parameters are different at the two phase transitions located at $\theta = 1/3$ and at $\theta = 2/3$. This symmetry breaking can be explained by taking into account the fact that, due to repulsive interactions, sites attached to attenuated bonds will be filled preferentially as the coverage increases.

(2) Even though the presence of defects affects the formation of ordered structures in the adlayer, the phase transition survives up to a certain critical degree of disorder $\rho_c$. In the limit of $r = 0$, which corresponds to the case reported in ref. 17, this critical value is of the order of $10^{-3}$ (a very small quantity of defects break down the order of the low-temperature phases). The results obtained here show that the value of $\rho_c$ increases significantly as $r$ is increased.

(3) As $w/k_BT$ is increased, the low- and high-coverage phases exhibit two well-differentiated behaviors. At $\theta = 1/3$, the overall effect of $w/k_BT$ is to decrease the critical $r$ *vs.* $\rho$ curves for all $\rho$ (or to diminish the area of the no phase-transition region). On the other hand, for the high-coverage phase, the ($\rho$-$r$) curves tend to a limit curve as $w/k_BT$ is increased. Thus, for the low-coverage phase, the effects of the disorder can be "compensated" by an appropriate $w/k_BT$, such that the phase transition survives. On the contrary, there exists a wide region of $\rho$ and $r$ where the high-coverage phase disappears, independently of the value of $w/k_BT$. These findings indicate that the high-coverage phase is more sensitive to the degree of disorder than the low-coverage phase.

Future efforts will be directed to (a) include attractive interactions between the adparticles and (b) develop an exhaustive study on critical exponents and universality.

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