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Scaling laws in adsorption on bivariate surfaces

F. Bulnes, A. J. Ramirez-Pastor, and G. Zgrablich*
Laboratorio de Ciencias de Superficies y Medios Porosos, Universidad Nacional de San Luis—CONICET, Chacabuco 917,
5700 San Luis, Argentina

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The adsorption of particles with nearest-neighbor attractive and repulsive interactions is studied through Monte Carlo simulation on bivariate surfaces characterized by patches of weak and strong adsorbing sites of size *l*. Patches are considered to have either a square or a strip geometry and they can be either arranged in a deterministic ordered structure or in a random way. Quantities are identified that scale obeying power laws as a function of the scale length *l*. The consequences of this finding are discussed for the determination of the energetic topography of the surface from adsorption measurements.

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I. INTRODUCTION

The role of the adsorptive surface characteristics in many processes of practical importance is a topic of increasing interest in surface science. Adsorption, surface diffusion, and reactions on catalysts are some of the phenomena that are strongly dependent upon surface structure. Most materials have heterogeneous surfaces which, when interacting with gas molecules, present a complex spatial dependence on the adsorptive energy. It is of substantial interest to attempt a complete characterization of such heterogeneity.

Through the last 50 years adsorption has been used for determining energetic properties of heterogeneous substrates, but this still remains an open problem in many aspects [1–4]. 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 [5]. More recently [6–9] it became clear that many gas-solid surface processes are strongly affected, not only by the adsorptive energy distribution, but also by the way these energies are spatially distributed (energetic topography). It is then a challenge in the field of gas-solid interactions to envisage methods for the determination of the energetic topography of heterogeneous substrates from adsorption experiments (characterization problem).

Unfortunately, the characterization problem for a general heterogeneous surface, represented, for example, by a multivariate distribution function with spatial correlations, has been shown to be a formidable problem far from being solved [10,11]. A more modest goal would be to attempt the characterization of simpler topographies, like those arising in bivariate surfaces, i.e., surfaces composed by two kinds of sites, say weak and strong sites with adsorptive energies ε_1 and ε_2, respectively, arranged in patches of size *l*. Recent developments in the theory of adsorption on heterogeneous surfaces, like the supersite approach [12], and experimental advances in the tailoring of nanostructured adsorbates [13,14], encourage this kind of study. Bivariate surfaces may also mimic, to a rough approximation, more general heterogeneous adsorbates. Just to give a few examples, we may mention the surfaces with energetic topography arising from a continuous distribution of adsorptive energy with spatial correlations, like those described by the dual site-bond model [8], or that arising from a solid where a small amount of randomly distributed impurity (strongly adsorptive) atoms are added [9]. In both cases the energetic topography could be roughly represented by a random spatial distribution of irregular patches (with a characteristic size) of weak and strong sites.

Adsorption on bivariate surfaces with square-patches topography has recently been studied for the case of particles with nearest-neighbor repulsive interaction energy [15]. It was found that both adsorption isotherms and isostheric heat of adsorption follow scaling laws involving the patch size *l* and that this characteristic length defining the topography could, in principle, be obtained from the analysis of experimental results. It is of interest to determine if such property is a general one or if it is due to the particularity arising either from the geometry of patches or from the repulsive lateral interactions between adsorbed particles.

Accordingly, the scope of the present work is to determine, via Monte Carlo simulation, the general properties of the adsorption of particles with repulsive and attractive nearest-neighbor interaction on model bivariate surfaces with square and strip patches geometry with a characteristic correlation length *l*, and find out to what extent the scaling laws are preserved and if the length scale could be determined from adsorption measurements. In Sec. II we present the adsorption model and simulation method. The behavior of relevant quantities, such as adsorption isotherms and isosteric heat of adsorption, is discussed in Sec. III. Section IV is dedicated to the determination of general scaling properties leading to power-law behavior and to the discussion of its implications in the determination of *l* from experimental measurements. General conclusions are given in Sec. V.

II. MODEL AND SIMULATION METHOD

We assume that the substrate is represented by a two-dimensional square lattice of $M=L\times L$ adsorption sites,

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*Corresponding author. Departamento de Física, Universidad Nacional de San Luis, Chacabuco 917, 5700 San Luis, Argentina. FAX: +54-2652-430224. Email address: giorgio@unsl.edu.ar

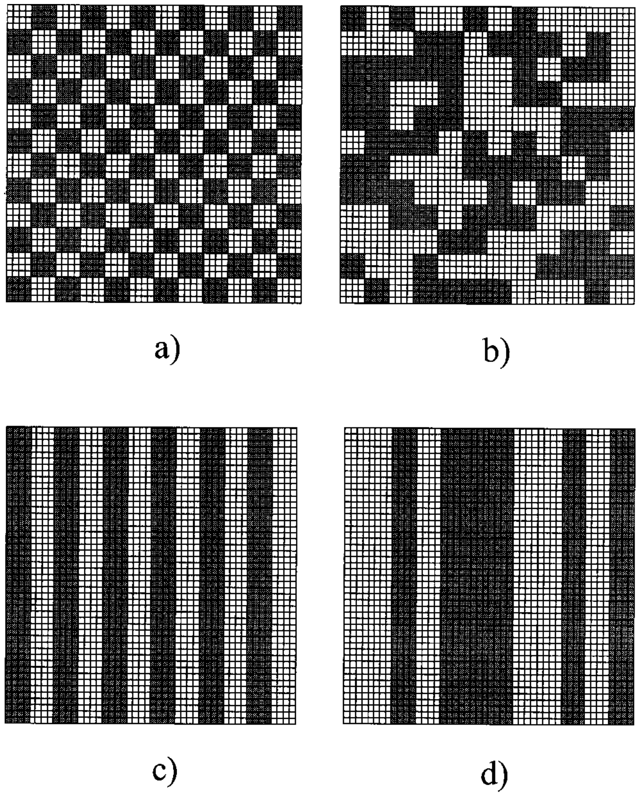

FIG. 1. Schematic representation of heterogeneous bivariate surfaces with chessboard (a), random square patches (b), ordered strips (c), and random strips (d) topography. The patch size in this figure is $l=4$.

with periodic boundary conditions. Each adsorption site can be either a "weak" site, with adsorptive energy ε_1, or a "strong" site, with adsorptive energy $\varepsilon_2(\varepsilon_1<\varepsilon_2)$. Weak and strong sites form patches of different geometry: (1) Square patches of size l ($l=1,2,3,\ldots$), which are spatially distributed either in a deterministic alternate way (chessboard topography), Fig. 1(a), or in a nonoverlapping random way (random topography), Fig. 1(b); (2) Strips of transversal size l ($l=1,2,3,\ldots$), which are spatially distributed either in an ordered alternate way, Fig. 1(c), or in a nonoverlapping random way (random topography), Fig. 1(d).

In order to easily identify a given topography, we introduce the notation l_C for a chessboard topography of size l and, similarly, l_R for random square patches, l_{OS} for ordered strips, and l_{RS} for random strips. Then, in Figs. 1(a) to 1(d), the topographies are 4_C, 4_R, 4_{OS}, and 4_{RS}, respectively. We also use the notation "bp" to refer to the extreme case of big patches topography ($l\rightarrow\infty$), i.e., a surface with one-half of weak sites and one-half of strong sites.

The substrate is exposed to an ideal gas phase at temperature T and chemical potential μ. Particles can be adsorbed on the substrate with the restriction of at most one adsorbed particle per site and we consider a nearest-neighbor (NN) interaction energy w among them (we use the convention $w>0$ for repulsive and $w<0$ for attractive interactions). Then the adsorbed phase is characterized by the Hamiltonian

$$H=-M[(\varepsilon_1\theta_1+\varepsilon_2\theta_2)-\mu\theta]+\frac{1}{2}w\sum_{(i,j)} n_i n_j, \qquad (1)$$

where $\theta=\theta_1+\theta_2$ is the total surface coverage (summing the coverages on weak and strong sites), n_i is the site occupation number ($=0$ if empty or $=1$ if occupied), and the sum runs over all pairs of NN sites (i,j). Without any loss of generality, we can consider that all energies are measured in units of k_BT, and that $\varepsilon_1=0$ and $\varepsilon_2=\Delta E$ in such a way that the adsorptive energy is characterized by the single adimensional parameter ΔE.

The adsorption process is simulated through a grand canonical ensemble Monte Carlo (GCEMC) method [16].

For a given value of the temperature T and chemical potential μ, an initial configuration with $N=M/2$ particles adsorbed at random positions is generated. Then an adsorption-desorption process is started, where a site is chosen at random and an attempt is made to change its occupancy state with probability given by the Metropolis rule

$$P=\min\left[1,\ \exp\left(-\frac{\Delta H}{k_BT}\right)\right], \qquad (2)$$

where $\Delta H=H_f-H_i$ 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. The approximation to thermodynamical equilibrium is monitored through the fluctuations in the number N of adsorbed particles; this is usually reached in 10^4 to 10^5 MCS. After that, mean values of thermodynamic quantities, such as the surface coverage θ and the internal energy U, are obtained by simple averages over m configurations:

$$\theta=\frac{\langle N\rangle}{M}, \quad U=\langle H\rangle-\mu\langle N\rangle, \qquad (3)$$

where the brackets denote averages over statistically uncorrelated configurations.

By changing the value of μ, the adsorption isotherm at a given temperature can be obtained. Furthermore, from the simulation results, the differential heat of adsorption q_d as a function of the coverage is calculated as [17]

$$q_d(\theta)=\left[\frac{\partial U}{\partial\theta}\right]_T. \qquad (4)$$

In our calculations we have used $L\approx100$, $M\approx10^4$, and $m=10^5$. With this size of the lattice ($L\approx100$, in such a way that it is a multiple of l) we verified that finite size effects, which affect the isotherms in the case of repulsive interactions at much smaller sizes, are negligible.

III. ADSORPTION RESULTS

We treat separately the cases of repulsive and attractive interactions.

A. Repulsive interactions

Given that all energies are being measured in units of k_BT, all results will be independent of the temperature and, furthermore, since the critical temperature for the appearance of a $c(2\times2)$ ordered phase in a zero-field Ising model is

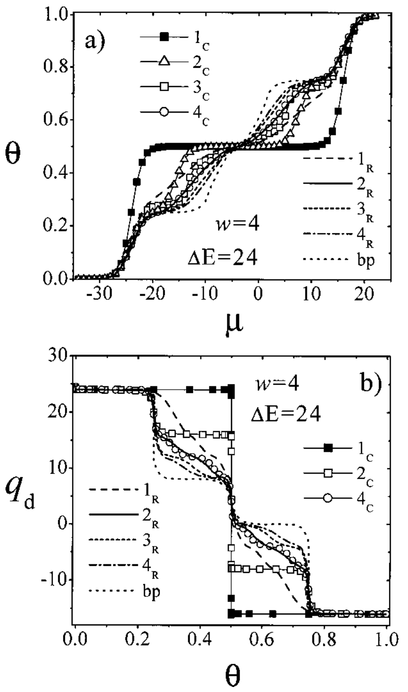

FIG. 2. Adsorption isotherm (a) and differential heat of adsorption (b) for different topographies and repulsive interactions in Regime I.

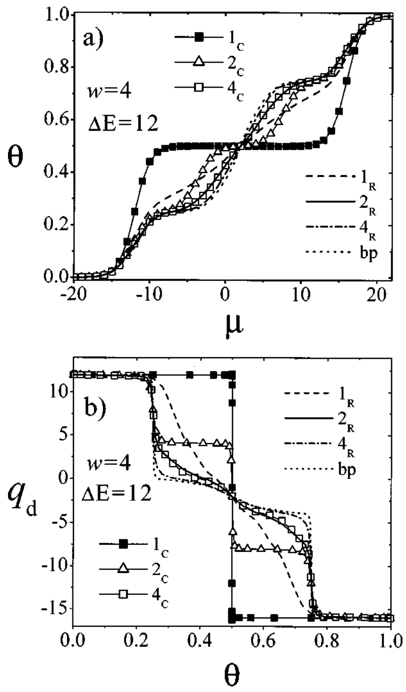

FIG. 3. Adsorption isotherm (a) and differential heat of adsorption (b) for different topographies and repulsive interactions in Regime II.

given by $k_BT_C = 0.567w$ [18], there will be a critical NN interaction $w_C = 1.763\,668$, above which the formation of the ordered phase is possible at $\theta = 0.5$.

Figure 2 shows the behavior of adsorption isotherms, [Fig. 2(a)], and $q_d(\theta)$, [Fig. 2(b)], for different square patches topographies for $w=4$ and $\Delta E = 24$. It can be seen that all curves are contained between two limit ones: the one corresponding to 1_C and the one corresponding to bp. For chessboard topographies, four different adsorption processes can be visualized, separated by shoulders in the adsorption isotherm and by steps in q_d: (i) strong site patches are filled first up to $\theta = 0.25$, where a $c(2\times2)$ structure is formed on them (in this region $q_d = 24$); (ii) since $4w < \Delta E$, the filling of strong site patches is completed up to $\theta = 0.5$ (in this region q_d decreases continuously from 24, zero occupied NN, to 8, four occupied NN); processes (iii) and (iv), corresponding to the regions $0.5 < \theta < 0.75$ and $0.75 < \theta < 1$, respectively, are equivalent to processes (i) and (ii) for weak site patches. Random topographies are seen to behave in a similar way with a particularly interesting feature: the behavior of a random topography of size l seems to approach that of a chessboard topography with an effective size $l_{\mathrm{eff}} > l$. As it can be easily understood, as long as the condition $w/\Delta E \leqslant 1/4$ is satisfied, the adsorption process is similar to the one described above, i.e., strong site patches are filled first and weak site patches are filled after. We call this feature "Regime I."

Figure 3 shows the behavior of adsorption isotherms, [Fig. 3(a)], and $q_d(\theta)$, [Fig. 3(b)], for different square patches topographies for $w=4$ and $\Delta E = 12$. In this case, where $w/\Delta E \leqslant 1/3$, the adsorption process follows a different regime, which we call "Regime II" [19]: (i) the strong site patches are filled until the $c(2\times2)$ ordered phase is formed on them, (ii) the weak site patches are filled until the $c(2\times2)$ ordered phase is formed on them, (iii) the filling of the strong site patches is completed, and (iv) the filling of the weak site patches is completed.

It should be noticed that Regimes I and II are disconnected. In between, i.e., $1/4 < w/\Delta E < 1/3$, the system behaves in a mixed transition regime changing continuously from one to another.

Strip topography presents a similar behavior as square patches topography, with the feature that ordered strips behave like chessboard square patches with a higher l_{eff} and random strips behave like random square patches also with a higher l_{eff}. Results are shown in Fig. 4, for ordered strips, and in Fig. 5 for random strips, corresponding to Regime I $(\Delta E = 12, w = 3)$. Figure 6 shows a comparison of adsorption isotherms between strips and square patches topographies for Regime I. The behavior for Regime II, not shown, follows the same pattern, with obvious modifications, as that of square patches.

B. Attractive interactions

In the case of attractive interactions only Regime I is possible, i.e., for all values of ΔE and w strong patches fill first and weak patches fill last.

Figures 7 and 8 show the typical behavior for square patches and for strips, respectively. In the last case only the ordered strips topography has been represented, since the density of curves is already high. The plateau in the isotherms and the corresponding abrupt drop in the differential heat of adsorption are indicating that the strong patches are being filled before adsorption starts on the weak patches.

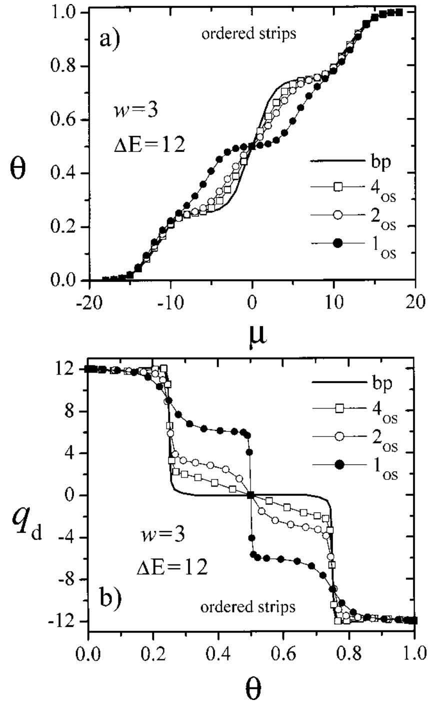

FIG. 4. Adsorption isotherm (a) and differential heat of adsorption (b) for ordered strips topography and repulsive interactions in Regime I.

Again we observe that all curves vary between the bp topography and the 1_C topography and that random topographies behave like the ordered ones with a larger effective size.

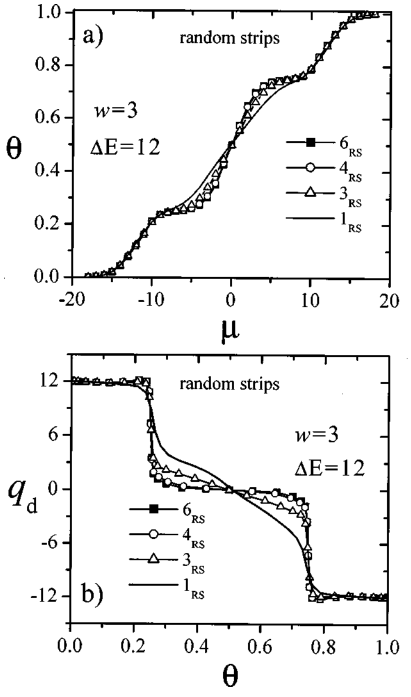

FIG. 5. Adsorption isotherm (a) and differential heat of adsorption (b) for random strips topography and repulsive interactions in Regime I.

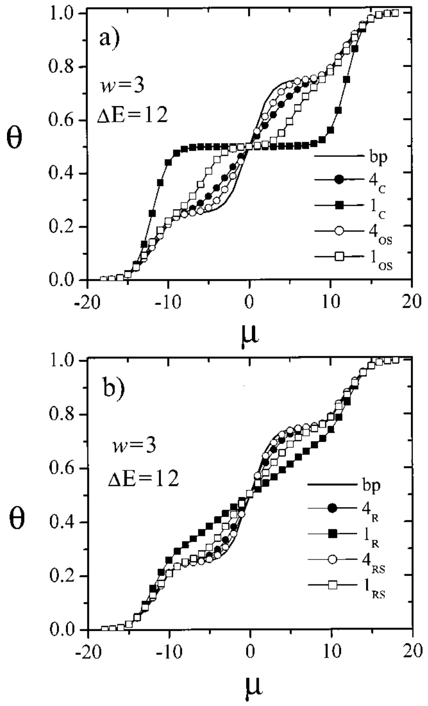

FIG. 6. Comparison between adsorption isotherms corresponding to square patches and strips geometry for repulsive interactions in Regime I: (a) ordered topography; (b) random topography.

IV. SCALING AND POWER-LAW BEHAVIOR

The fact that both adsorption isotherm and heat of adsorption curves for different topographies, characterized by a length scale l, vary between two extreme curves, suggests that we should search for some appropriate quantity to measure the deviation among these curves and study the behavior of such quantity as the length scale is varied.

The quantity we found most suitable is the area between a given curve and a reference curve. For adsorption isotherms, this quantity χ_a is defined as

$$\chi_a = \int_{-\infty}^{\infty} |\theta(\mu) - \theta^R(\mu)| d\mu, \tag{5}$$

where $\theta^R(\mu)$ is the reference adsorption isotherm. A similar quantity χ_h can be defined for adsorption heat curves. By taking as a reference curve the one corresponding to the bp topography, we obtain the plot of χ_a as a function of l for different topographies corresponding to Regime I as shown in Fig. 9. Here we can see that χ_a behaves as a power law in l with an exponent $\alpha \approx -2$. Exactly the same behavior is also found for χ_h.

It is interesting to note that the exponent α is the same for repulsive (corresponding to Regime I) and attractive interactions and for all topographies, i.e., chessboard, random square patches, ordered strips, and random strips, since logarithmic plots are parallel. Straightforward calculations (see Appendix) demonstrate that the curves for χ (either χ_a or χ_h)

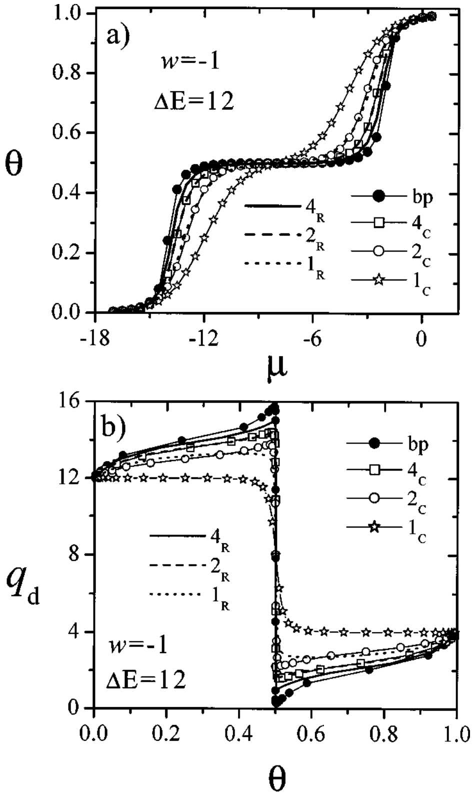

FIG. 7. Adsorption isotherm (a) and differential heat of adsorption (b) for square patches topographies and attractive interactions.

corresponding to the different topographies should collapse on the same curve as a function of an effective length scale (representing an effective patch size) l_{eff} given by

$$l_{\text{eff}} = sl, \tag{6}$$

where $s=1$ for chessboard topography, $s=2$ for random square patches and for ordered strips, and $s=4$ for random strips. The insets in Figs. 9(a) and 9(b) show that this is indeed what happens.

For repulsive interactions and for values of ΔE and w corresponding to Regime II, we find similar results, except that the exponent has now a different value, $\alpha \approx -3$.

As we have already mentioned, Regimes I and II are disconnected. What happens in between? By changing w and ΔE we have also found a power law for intermediate regimes, obtaining for exponent α the general behavior in the adimensional variable $w/\Delta E$ represented in Fig. 10. We find that this can be expressed as

$$\alpha = \alpha_1 = -1.952 \pm 0.053 \quad \text{for } w/\Delta E \leqslant 1/4,$$

$$\alpha = \alpha_2 + [12(1/3 - w/\Delta E)]^{\beta}(\alpha_1 - \alpha_2)$$

$$\text{for } 1/4 \leqslant w/\Delta E \leqslant 1/3, \tag{7}$$

$$\alpha = \alpha_2 = -3.049 \pm 0.065 \quad \text{for } w/\Delta E \geqslant 1/3,$$

with $\beta = 0.42 \pm 0.04$, for repulsive interactions, while

$$\alpha = \alpha_1 = -1.952 \pm 0.053 \tag{8}$$

for attractive interactions.

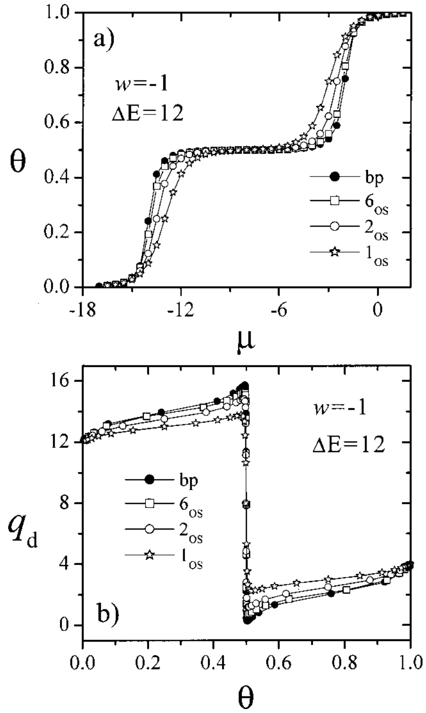

FIG. 8. Adsorption isotherm (a) and differential heat of adsorption (b) for strips topographies and attractive interactions.

Up to now it is clear that this behavior of exponent α is universal in the sense that it is unique for all values of ΔE, for all topographies considered here, for repulsive and attractive interactions and for both χ_a and χ_h. However, we have found that this universality goes far beyond. In fact, exactly the same behavior is found by taking as a reference curve for the calculation of χ any curve (either adsorption isotherm or heat of adsorption) corresponding to a system with the appropriate values of w and ΔE. Even more, a suitable reference curve can be any theoretical approximation reflecting the appropriate values of w and ΔE, like, for example, the mean field approximation for bp topography, whose adsorption isotherm is given by

$$\theta_i = \frac{\exp(\varepsilon_i - 4w\theta_i + \mu)}{1 + \exp(\varepsilon_i - 4w\theta_i + \mu)}, \quad i=(1,2), \quad \theta = \frac{1}{2}(\theta_1 + \theta_2). \tag{9}$$

The corresponding reference curve for q_d can be found by numerical differentiation through the general thermodynamical relation

$$q_d = \left[\frac{d\mu}{d\ln(T)}\right]_{\theta} - k_B T. \tag{10}$$

Then, as a result of the above findings, we can establish with great generality that the quantity χ, calculated either for the adsorption isotherm or for the differential heat of adsorp-

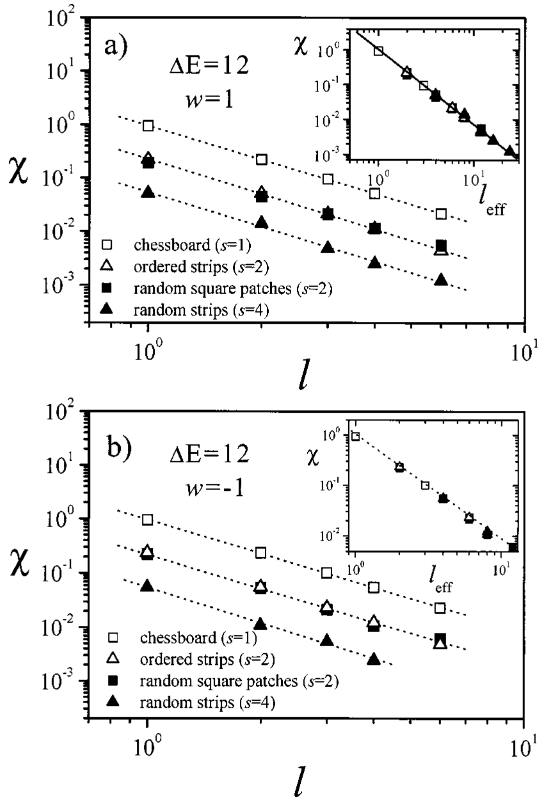

FIG. 9. Power-law behavior of the quantity χ_a showing the collapse of data for different topographies on a single curve when the effective length scale l_{eff} is used: (a) repulsive interactions in Regime I; (b) attractive interactions.

tion by using any suitable reference curve, behaves as a power law in the effective length scale given by Eq. (6), like

$$\ln(\chi) = \text{const} - \alpha \ln(l_{\text{eff}}), \tag{11}$$

where the exponent α has a universal behavior given by Eqs. (7) and (8). These results suggest a method to solve the problem of the characterization of the energetic topography of heterogeneous substrates, which can be approximated by bivariate surfaces, through adsorption measurements. For this it is necessary to obtain first an estimation of the adsorbate-adsorbate interaction energy, w. This energy can be obtained in the case of repulsive interactions by LEED or STM measurements at different temperatures to determine the critical temperature for the formation of the ordered $c(2\times2)$ structure. In the case of attractive interactions w can be estimated from adsorption measurements at very low pressure. With this, and since $q_d(0) = \varepsilon_2$ and $q_d(1) = \varepsilon_1 + 4w$, it is possible to determine ε_1, ε_2, and ΔE from calorimetric measurements of the differential heat of adsorption as a function of coverage. Then, given the value of $w/\Delta E$, the value of α can be obtained from Eq. (7) or (8). Finally, by choosing an appropriate theoretical approximation as a reference curve for $\theta(\mu)$ or $q_d(\theta)$, like, for example, Eq. (9), the value of χ_a or χ_h can be calculated allowing l_{eff} to be obtained from Eq. (11). Note that the measurement of adsorption isotherms is not necessary in the case of repulsive interactions, though it would be convenient to get an alternative value of l_{eff} to check the accuracy of the result.

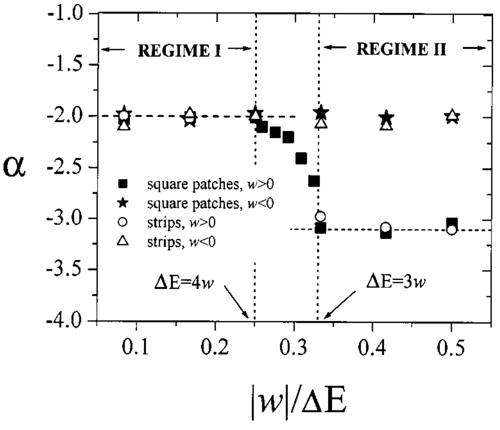

FIG. 10. Universal behavior of exponent α as a function of the adimensional variable $w/\Delta E$.

V. CONCLUSIONS

We have studied by Monte Carlo simulations the adsorption of particles, interacting through a NN interaction w, on heterogeneous bivariate surfaces characterized by different energetic topographies. The heterogeneity is determined by two parameters: the difference of adsorptive energy between strong and weak sites ΔE, and an effective correlation length l_{eff}, representing the length scale for homogeneous adsorptive patches.

Unique scaling properties and power-law behavior have been established for relevant adsorption quantities, such as the adsorption isotherm and the differential heat of adsorption. The exponent α as a function of $w/\Delta E$ is found to follow a universal behavior. Present results extend those obtained in Ref. [15], which were restricted to the case of repulsive interactions and square patches geometry.

These findings provide for the first time a method to characterize the energetic topography (i.e., obtain the parameters from experimental measurements) of a class of heterogeneous surfaces that can be approximately represented as bivariate surfaces.

ACKNOWLEDGMENT

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APPENDIX

We introduce the following general notation: let f_{ij} be the fraction of NN pairs of sites of type (i,j) (i or j takes the values 1, 2), n_k^{ij} be the number of NN pairs of sites of type (i,j) on patches (either square patches or strips) of type k, n_{ci}^{ii} be the number of NN pairs of type (i,i) corresponding to the contact between two patches of type i, n be the total number of NN pairs, N_i be the number of patches of type i, and N_{ci} be the mean number of contacting patches of type i.

1. Chessboard

For a square lattice of size L with a chessboard topography of patches of sites 1 and 2, each of size $2l$, the fraction of pairs of NN sites of type 11, f_{11}, is given by

$$f_{11}=\frac{n_1^{11}N_1}{n}. \tag{A1}$$

Now, in our model

$$n_1^{11}=2(2l-2)^2+2(2l-2)3+4, \quad N_1=\frac{1}{2}\left[\frac{L}{2l}\right]^2=\frac{L^2}{8l^2},$$

$$n=2L^2$$

so that we obtain

$$f_{11}=\frac{2l-1}{4l}. \tag{A2}$$

2. Random square patches

On the other hand, for a random topography of square patches of size l, we have

$$f_{11}=\frac{n_1^{11}N_1+n_{C1}^{11}N_{C1}}{n}. \tag{A3}$$

In this case

$$n_1^{11}2(l-2)^2+2(l-2)3+4, \quad N_1=\frac{1}{2}\left[\frac{L}{l}\right]^2, \quad N_{C1}=\frac{1}{2}\left[\frac{L}{l}\right]^2,$$

so that, replacing in Eq. (A3), we again obtain for f_{11} the same value as given in Eq. (A2). Since similar results are valid for f_{22} and f_{12}, we conclude that random square patches of size l behave like chessboard patches of size $2l$.

3. Strips

For an ordered strips topography, with strips of size l, we have

$$f_{11}=\frac{n_1^{11}N_1}{n}, \tag{A4}$$

with $n_1^{11}=3L+2(l-2)L$; $N_1=L/2l$; $n=2L^2$. Hence we obtain

$$f_{11}=\frac{2l-1}{4l}, \tag{A5}$$

which is identical to Eq. (A2). We then conclude that ordered strips of size l behave like chessboards of size $2l$ (i.e., ordered strips behave like random square patches of the same size).

The analysis for random strips can be carried out as an obvious extension of that for random square patches, with the result that random strips of size l behave like chessboards of size $4l$.

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