Determination of the energetic topography of bivariate heterogeneous surfaces from adsorption isotherms

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Abstract The reversible adsorption process occurring on patchwise heterogeneous bivariate surfaces is studied by Monte Carlo simulation and mean-field approximation. These surfaces are characterized by a collection of deep and shallow adsorbing patches with a typical length scale l. Patches can be either arranged in a deterministic chessboard structure or in a random way. Previous studies showed that the topography of a given surface can be obtained from the knowledge of the corresponding adsorption isotherm and a reference curve. In the present work, we discuss the advantages and disadvantages of using different reference curves. One of the main consequences of this analysis is to provide an improved method for the determination of the energetic topography of the surface from adsorption measurements.

Keywords Lattice-gas models · Adsorption thermodynamics · Heterogeneous surfaces · Monte Carlo simulations

1 Introduction

The adsorption of gases on solid surfaces is a topic of fundamental interest for various applications (Tóth 2002; Keller and Staudt 2005). Most materials possess complex heterogeneous surface where elementary surface processes such as adsorption, desorption, surface diffusion, and surface reactions are strongly affected by structural and/or energetic disorder (Ross and Olivier 1964; Rudzinski et al. 1997;

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Jaroniec and Madey 1988; Rudzinski and Everett 1992). It is well known that, in addition to the adsorption energy distribution function, the surface topography is also a very important factor in those processes. The patchwise heterogeneous surface, introduced by Ross and Olivier (1964), and the random heterogeneous surface are two examples of disordered surfaces with different topographies, which have been extensively used in the analysis of surface processes (Rudzinski et al. 1997). When correlation between the energies of the adsorption sites is present, the appropriate description of the heterogeneous surface is through the use of an intermediate adsorption site topography (Ross and Olivier 1964; Ripa and Zgrablich 1975; Riccardo et al. 1992, 1993; Ramirez-Pastor et al. 1995, 2000).

The adsorption of gases has been used to obtain information about the energetic characteristics of heterogeneous surfaces as well as the adsorption energy distribution (Steele 1974; Ross and Olivier 1964; Rudzinski et al. 1997; Jaroniec and Madey 1988; Rudzinski and Everett 1992; House 1983; Jaroniec and Braüer 1986; Sircar and Myers 1988; Mamleev and Bekturov 1996a, 1996b). In this sense, a method for characterization of bivariate heterogeneous surfaces from adsorption measurements has recently been proposed (Bulnes et al. 2001, 2002, 2007; Romá et al. 2003). The method allows to obtain the topography of a given surface from the knowledge of the corresponding adsorption isotherm and a reference curve. The fact that the adsorption isotherms for different topographies, each one characterized by a length scale l, vary between two extreme curves (the one corresponding to $l = 1$ and the one corresponding to $l \to \infty$; Bulnes et al. 2001), suggests the existence of some appropriate quantity to measure the deviation among these curves and the convenience to 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 (Bulnes et al. 2001). For adsorption isotherms, this quantity, χ, is defined as

$$\chi = \int_{-\infty}^{\infty} |\theta(\mu) - \theta^R(\mu)| d\mu, \tag{1}$$

where $\theta(\mu)$ is the adsorption isotherm (surface coverage, θ, as a function of chemical potential, μ) and $\theta^R(\mu)$ is a reference adsorption isotherm. It was found that the adsorption isotherms follow scaling laws involving the patch size l with a universal exponent α. These findings provide for a method to characterize the energetic topography (i.e., obtain the parameters from experimental measurements) of a class of heterogeneous surfaces, which can be approximately represented as surfaces with two kind of sites.

Following this scheme, adsorption on bivariate surfaces with square-patches and strip topographies was studied through Monte Carlo simulations for the case of particles with nearest-neighbor interaction energy, at a fixed temperature such that $k_B T = 1$ (k_B being the Boltzmann constant and T the temperature) (Bulnes et al. 2001, 2002). Later, the study was extended to include the effects of temperature on the adsorption process (Romá et al. 2003).

Despite these results, no physical explanation was found for this behavior. Recently it was shown that the scaling function χ is directly related to the free energy per site of the adsorbed layer at half coverage (Bulnes et al. 2007). Taking advantage of the fact that the configurational entropy at half coverage is null, it was shown how the function χ scales as a power law with the effective length characterizing the energetic topography of the surface and how the scaling exponent can be obtained. The analysis led to a physical interpretation of the scaling behavior.

As mentioned above, in order to obtain the function χ of an unknown topography, the adsorption isotherm $\theta^R(\mu)$ of a reference system must be known. Thus, the lack of knowledge of $\theta^R(\mu)$ is a major limitation for the application of the scaling laws to many adsorption models. In this context, it is of interest and of value to inquire how a given choice of the reference curve influences the scaling laws associated with the adsorption process. The objective of this article is to provide a thorough study in this direction.

The outline of the paper is as follows. In Sect. 2 we describe the lattice-gas model and the Monte Carlo (MC) simulation scheme. In Sect. 3, we present the theory to calculate the reference adsorption isotherm and compare the MC results with the theoretical calculations. The behavior of the function χ, obtained by an adequate choice of the reference curve, is discussed in Sect. 4. Finally, the general conclusions are given in Sect. 5.
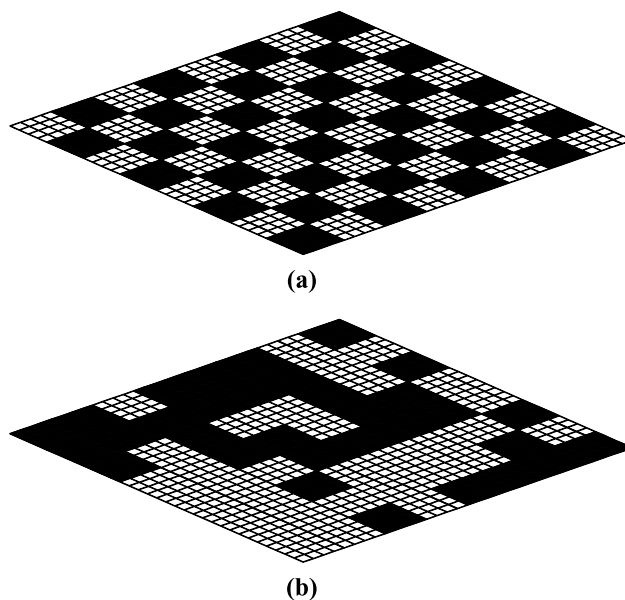

Fig. 1 Schematic representation of heterogeneous bivariate surfaces with chessboard (**a**) and random square patches (**b**) topography. The patch size in this figure is $l = 4$

2 Model and Monte Carlo simulation

We assume that the substrate is represented by a two-dimensional square lattice of $M = L \times L$ adsorption sites, with periodic boundary conditions. Each adsorption site can be either a "shallow" site, with adsorptive energy ε_S, or a "deep" site, with adsorptive energy ε_D. Weak and strong sites form 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).

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. Then, in Figs. 1(a) and 1(b), the topographies are 4_C, and 4_R, respectively. We also use the notation "bp" to refer to the extreme case of big patches topography ($l \to \infty$), 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

$$H = w \sum_{\{i,j\}} c_i c_j + \sum_{i=1}^{M} (\varepsilon_i - \mu) c_i \tag{2}$$

where c_i is the occupation variable, which can take the following values: $c_i = 0$, if the corresponding site is empty, and $c_i = 1$, if the site i is occupied; $\{i, j\}$ represents pairs of NN sites and ε_i $(= \varepsilon_S$ or $\varepsilon_D)$ is the adsorption energy of an adsorbed particle on a site i. Without any loss of generality, we can consider that all energies are measured in units of $k_B T$ and that $\varepsilon_S = 0$ and $\varepsilon_D = \varepsilon_S + \Delta\varepsilon$, in such a way that the adsorptive energy is characterized by the single adimensional parameter $\Delta\varepsilon$.

The adsorption process is simulated through a grand canonical ensemble Monte Carlo method (Nicholson and Parsonage 1982).

For a given value of the temperature and chemical potential, 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 (Metropolis et al. 1953)

$$P = \min\{1, \exp(-\Delta H/k_B T)\}, \qquad (3)$$

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 10^5 to 10^6 MCS. After that, the mean value of the surface coverage θ, is obtained by simple averages over m configurations:

$$\theta = \frac{1}{M} \sum_i^M \langle c_i \rangle \qquad (4)$$

where the brackets denote averages over m statistically uncorrelated configurations. By changing the value of μ, the adsorption isotherm at a given temperature can be obtained.

In our calculations we have used $L \approx 100$, $M \approx 10^4$, and $m = 10^5 - 10^6$. With this size of the lattice ($L \approx 100$, in such a way that it is a multiple of l) we verified that finite-size effects are negligible.

3 Analytical approximation and comparison between simulation and theoretical results

3.1 Detailed mean field approximation

We now study the adsorption process in the framework of a detailed mean field approximation (DMFA) (Ramirez-Pastor et al. 2000; Bulnes et al. 2001). In this theory, for a particle adsorbed on a given site, we consider the usual mean

field interaction energy with particles adsorbed on neighboring sites, however we distinguish among six different kinds of sites, $K = 1, \ldots, 6$:

$K = 1$ ($K = 2$): center of weak (strong) patches

$K = 3$ ($K = 4$): sides of weak (strong) patches   (5)

$K = 5$ ($K = 6$): corners of weak (strong) patches.

The frequencies of occurrence of K-type sites, $f(K)$, which depend on the patch size l, can be obtained as (Ramirez-Pastor et al. 2000; Bulnes et al. 2001)

$$\begin{aligned} f(1) &= f(2) = (l-2)^2/2l^2 \\ f(3) &= f(4) = 2(l-2)/l^2 \\ f(5) &= f(6) = 2/l^2. \end{aligned} \qquad (6)$$

The partial mean field coverage of K-type sites, θ_K, can be written as (Ramirez-Pastor et al. 2000; Bulnes et al. 2001)

$$\theta_1 = \frac{\exp[-(\varepsilon_S + 4w\theta_1 - \mu)/k_B T]}{1 + \exp[-(\varepsilon_S + 4w\theta_1 - \mu)/k_B T]} \qquad (7)$$

$$\theta_2 = \frac{\exp[-(\varepsilon_D + 4w\theta_2 - \mu)/k_B T]}{1 + \exp[-(\varepsilon_D + 4w\theta_2 - \mu)/k_B T]} \qquad (8)$$

$$\theta_3 = \frac{\exp[-(\varepsilon_S + 2w\theta_3 + w\theta_1 + w\theta_4 - \mu)/k_B T]}{1 + \exp[-(\varepsilon_S + 2w\theta_3 + w\theta_1 + w\theta_4 - \mu)/k_B T]} \qquad (9)$$

$$\theta_4 = \frac{\exp[-(\varepsilon_D + 2w\theta_4 + w\theta_3 + w\theta_2 - \mu)/k_B T]}{1 + \exp[-(\varepsilon_D + 2w\theta_4 + w\theta_3 + w\theta_2 - \mu)/k_B T]}$$

$$\qquad (10)$$

$$\theta_5 = \frac{\exp[-(\varepsilon_S + 2w\theta_3 + 2w\theta_4 - \mu)/k_B T]}{1 + \exp[-(\varepsilon_S + 2w\theta_3 + 2w\theta_4 - \mu)/k_B T]} \qquad (11)$$

$$\theta_6 = \frac{\exp[-(\varepsilon_D + 2w\theta_3 + 2w\theta_4 - \mu)/k_B T]}{1 + \exp[-(\varepsilon_D + 2w\theta_3 + 2w\theta_4 - \mu)/k_B T]}. \qquad (12)$$

The last system of equations can be easily solved through a standard computing procedure; in our case, we used Maple software. Finally, the adsorption isotherm is obtained as the weighted average of partial coverages:

$$\theta = \sum_K f(K)\theta_K. \qquad (13)$$

The procedure described in (5)–(13) is applicable to topographies with $l \geq 2$. In the particular case of a surface 1_C, the corresponding adsorption isotherm can be written as

$$\theta = \frac{1}{2}\left\{\frac{\exp[-(\varepsilon_D - \mu)/k_B T]}{1 + \exp[-(\varepsilon_D - \mu)/k_B T]}\right\} + \frac{1}{2}\left\{\frac{\exp[-(\varepsilon_S + 4w - \mu)/k_B T]}{1 + \exp[-(\varepsilon_S + 4w - \mu)/k_B T]}\right\}. \qquad (14)$$

The first (second) term of the right hand side of (14) takes into account the adsorption on the deep (shallow) sites. In
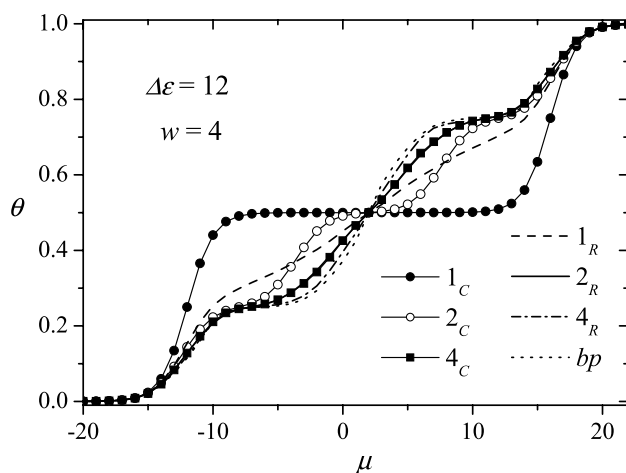
Fig. 2 Adsorption isotherms for $w = 4$, $\Delta\varepsilon = 12$ and different topographies as indicated

the case of the shallow sites, the energy involved in the adsorption process is $\varepsilon_S + 4w$ due to the fact that each S site is surrounded by 4 occupied sites.

3.2 Comparison between simulation and theoretical results

In order to understand the basic phenomenology, we analyze in the first place the effect of the topography on the adsorption process.

Figure 2 shows the behavior of the adsorption isotherms for $w = 4$, $\Delta\varepsilon = 12$ and different square patches topographies.[1] It can be seen that all curves are contained between the two limit ones: the one corresponding to 1_C and the one corresponding to bp. The fact that the adsorption isotherms for different topographies vary between two extreme curves, allowed us to propose the curve corresponding to bp as reference adsorption isotherm ($\theta^R(\mu)$ in (1); Bulnes et al. 2001). However, the 1_C adsorption isotherm could also be chosen as reference adsorption isotherm.

As discussed previously (Bulnes et al. 2001, 2002, 2007; Romá et al. 2003), the application of scaling laws to characterize the topography of heterogeneous surfaces from adsorption isotherms requires of the knowledge of the function θ vs μ in a reference state, $\theta^R(\mu)$. In practice, the calculation of $\theta^R(\mu)$ can be rigorously accomplished by analytical methods in only a very few cases. In the following we will discuss the advantages and disadvantages of using the bp and 1_C adsorption isotherms as reference curves.

An extensive comparison between simulated adsorption isotherms and isotherm equations obtained from DMFA is shown in Fig. 3 for the two limit topographies. The symbols joined by dotted lines represent the simulation data (cir-

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[1]Interested readers are referred to Bulnes et al. (2001) for a detailed description of each curve in Fig. 2.

cles, 1_C; squares, bp) and the solid lines correspond to theoretical isotherms. The behavior of the analytical approach can be explained as follows: in the case of attractive interactions [parts (a)–(c)], theoretical results agree very well with the simulation points for values of w up to approximately $w = -2$; however, the disagreement turns out to be significantly large for $w > 2$ (in absolute value). On the other hand, appreciable differences can be seen for repulsive lateral interactions [parts (d)–(f)]. In fact, bp theoretical equation provides a good approximation for very small values of w, but fails when the magnitude of the interaction energy is increased. In the case of 1_C topography, an excellent agreement is observed between simulation and theoretical results in all range of positive w's.

As is shown in Fig. 3, the 1_C curve is the most accurate approximation to this problem. However, its range of applicability for attractive interactions must be determined. For this purpose, numerical and theoretical data corresponding to a 1_C topography were compared for different values of $\Delta\varepsilon$ and w. The differences between numerical and theoretical curves were calculated with the help of the average absolute error, E_a, which is defined as

$$E_a = \frac{\sum_\mu |\theta_{theor} - \theta_{sim}|_\mu}{\text{number of points (or values of } \mu)} \tag{15}$$

where θ_{sim} (θ_{theor}) represents the coverage obtained by using MC simulation (analytical approach). Each pair of values (θ_{sim}, θ_{theor}) is obtained at fixed μ.

The dependence of E_a on $|\Delta\varepsilon/w|$ is shown in Fig. 4. As it can be observed, a good agreement is obtained for $|\Delta\varepsilon/w| > 6$. The results of the analysis of Figs. 3 and 4 are collected in the inset of Fig. 4. The shaded area corresponds to the region of applicability of the 1_C theoretical adsorption isotherm as reference curve.

4 Scaling laws to characterize the topography of bivariate surfaces

In this section, we study the behavior of the function χ (1) obtained by using the 1_C isotherm as reference curve.

We begin by analyzing the case of ordered patches with $\Delta\varepsilon = 12$ and different values of $w(= -1.75, -1.5, -1, -0.5, 0.5, 1, 1.5$ and $1.75)$. The results for $\chi(l)$ are shown in Fig. 5. Open and full symbols (joined by dotted lines) represent simulation data corresponding to attractive and repulsive lateral interactions, respectively. It can be seen that the curves for different w increase monotonically as the patch size is increased. In addition, the function $\chi(l)$ appears to be independent of the sign (either attractive or repulsive) of the lateral interaction.

It is therefore important to base the understanding of the observed behavior on an appropriate physical interpretation.
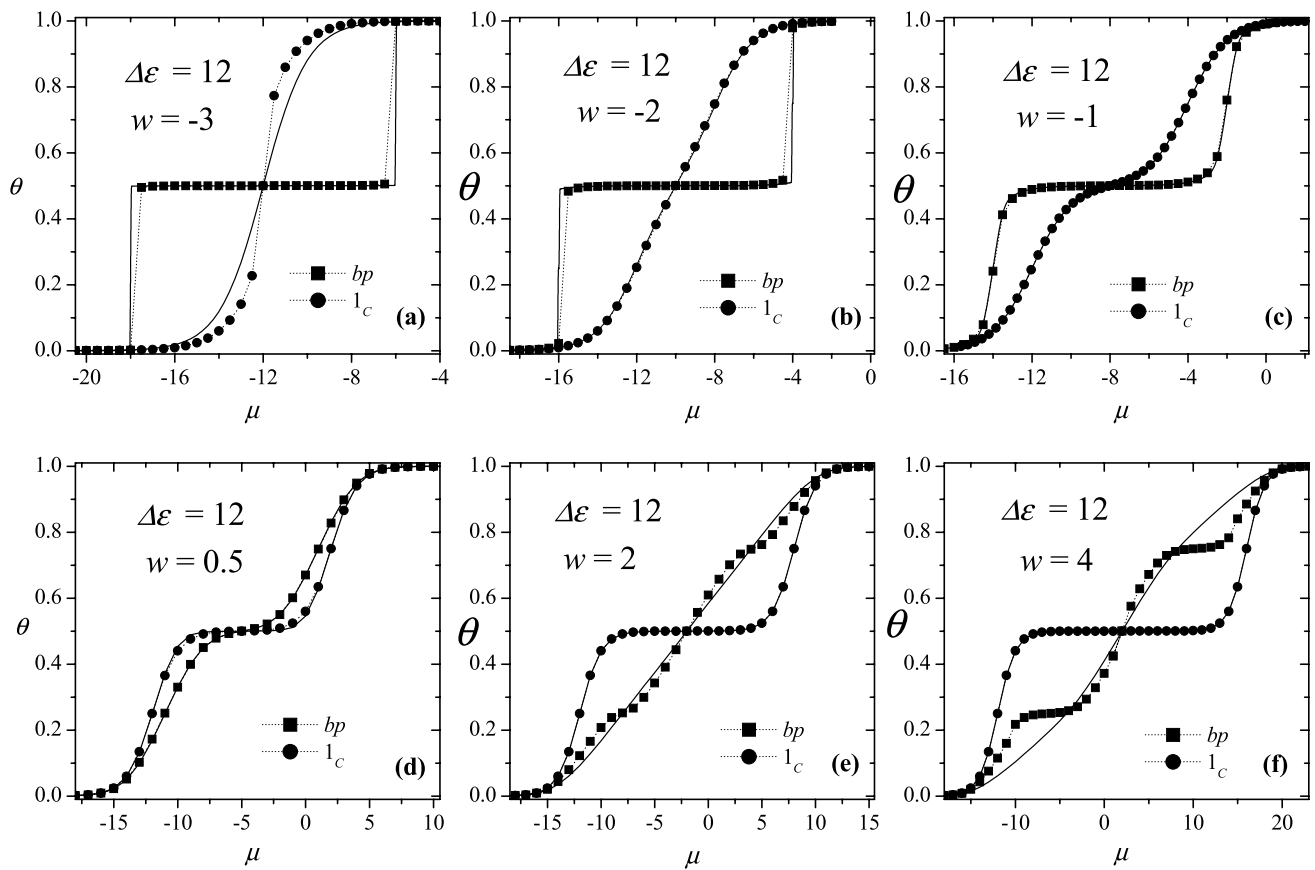
Fig. 3 Comparison between simulated adsorption isotherms (*symbols joined by dotted lines*) and isotherm equations obtained from DMFA (*solid lines*) for $\Delta\varepsilon = 12$ and different values of w as indicated. *Circles* and *squares* represent data corresponding to 1_C and bp topographies, respectively

With this purpose, we start from the basic thermodynamic relationship (Hill 1960)

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,M}, \tag{16}$$

where F is the Helmholtz free energy. Introducing the free energy per site, $f = F/M$, the last equation can be rewritten in terms of intensive variables in the form: $\mu = (\partial f/\partial \theta)_T$. Accordingly, the area to the left of each adsorption isotherm corresponding to a topography characterized by l in Fig. 2 up to a determined coverage θ is given by

$$A(\theta, l) = \int_0^\theta \mu\, d\theta = f(\theta, l) - f(0, l). \tag{17}$$

Therefore, this area represents the variation in free energy per site in filling a surface, with topography characterized by the patch size l, up to a coverage θ.

Following this line of reasoning, and making use of the symmetry properties of the adsorption isotherm, which are a consequence of the vacancy-particle symmetry, the function χ, representing the area between a given isotherm and the 1_C reference isotherm, turns out to be

$$\chi(l) = 2|A(1/2, 1_C) - A(1/2, l)|. \tag{18}$$

From (17) and (18) we obtain

$$\chi(l) = 2|f(1/2, 1_C) - f(1/2, l)|. \tag{19}$$

Therefore, the function χ defined in (1) is simply twice the difference in free energy per site between the reference isotherm (in this case that corresponding to 1_C) and the given isotherm, at half coverage. This result also explains why it depends on the topography parameter l: because the free energy at half coverage depends strongly on the structure of the adsorbate, which changes with l.

Calculation of the way in which this free energy changes with l leads to the physical significance of the function $\chi(l)$. Considering that $f = u - Ts$, where u and s are the internal energy and configurational entropy per site, respectively, we obtain
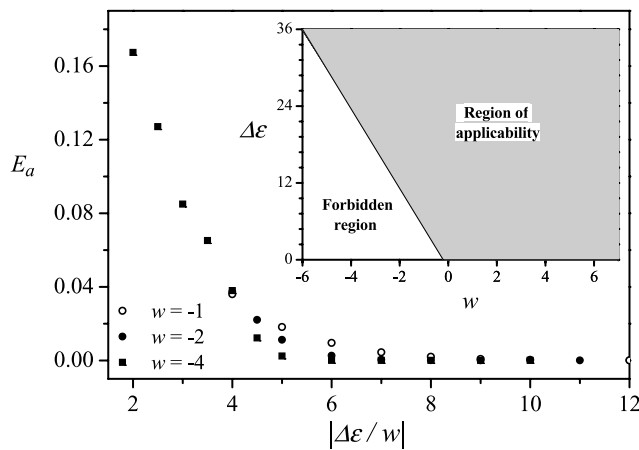
$$f(1/2, 1_C) = u(1/2, 1_C) \tag{20}$$

Fig. 4 Average absolute error, E_a, versus $|\Delta\varepsilon/w|$ for 1_C topography and different values of w as indicated. *Inset*: Diagram ($\Delta\varepsilon - w$) indicating the region of applicability of the 1_C theoretical adsorption isotherm as reference curve
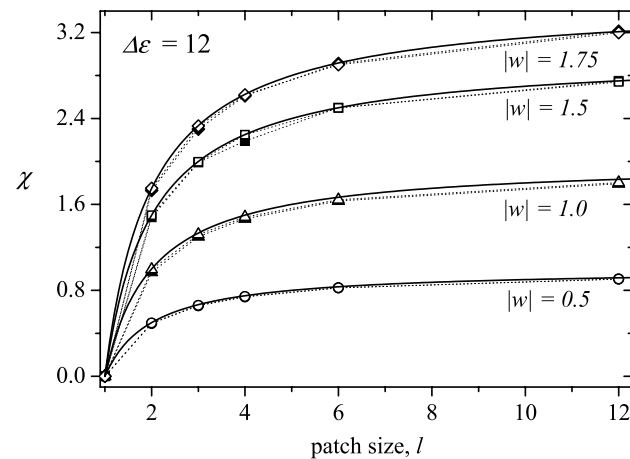

Fig. 6 Behavior of the quantity χ as a function of the patch size l for $\Delta\varepsilon = 12$, $w = 1$ and different topographies as indicated. The *inset* shows the collapse of the data on a single curve when the effective length scale l_{eff} is used. *Solid line* represents theoretical results from (26). Data corresponding to random and ordered topographies are denoted by RP and OP, respectively

Fig. 5 Behavior of the quantity χ as a function of the patch size l for chessboard surfaces with $\Delta\varepsilon = 12$ and different values of w as indicated. *Open* and *full symbols* (*joined by dotted lines*) represent simulation data corresponding to attractive and repulsive lateral interactions, respectively. *Solid lines* represent theoretical results from (26)

and

$$f(1/2, l) = u(1/2, l) \tag{21}$$

since $s(1/2, 1_C) = s(1/2, l) = 0$. For 1_C topography and $\theta = 0.5$, strong site patches are completely filled while weak site patches are empty. In addition, the geometric distribution of the patches does not allow the formation of NN pairs of occupied sites. Then,

$$f(1/2, 1_C) = u(1/2, 1_C) = \frac{\varepsilon_D}{2}. \tag{22}$$

With respect to $u(1/2, l)$, some assumptions have to be made: (1) in order to reproduce the results in Fig. 5, the $l \times l$ patches are spatially distributed in a deterministic alternate way (chessboard topography); and (2) the magnitude
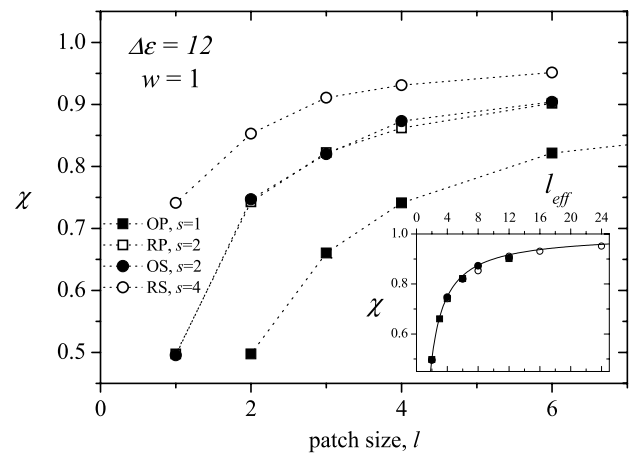
of lateral interaction w is small with respect to $\Delta\varepsilon$.[2] Consequently, at half coverage strong site patches are completely filled while weak site patches are empty. Under these considerations, we can write

$$f(1/2, l) = u(1/2, l) = \frac{\varepsilon_D}{2} + w f_{NN}(l), \tag{23}$$

where $f_{NN}(l)$ represents the fraction of pairs of NN occupied sites for a chessboard topography characterized by a patch size l. Thus,

$$f_{NN}(l) = \frac{N_{NN}(l)N_D}{M} \tag{24}$$

where $N_{NN}(l)$ is the number of pairs of NN occupied sites on one $l \times l$ patch $[2(l-2)^2 + 2(l-2)3 + 4]$; and N_D is the number of deep patches $[M/(2l^2)]$. By simple algebra,

$$f(1/2, l) = u(1/2, l) = \frac{\varepsilon_D}{2} + \frac{w(l-1)}{l}, \tag{25}$$

and

$$\chi(l) = 2\left|\frac{w(l-1)}{l}\right|. \tag{26}$$

The results from (26) are shown as solid lines in Fig. 5. The agreement between theory and simulation is excellent. The present analysis provides fundamental physical insight into the behavior of the function $\chi(l)$.

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[2]It is important to remark that the condition (2) is not pure mathematical construction. Most of the experiments in surface science are carried out in this regime of adsorption energies (Danner and Wenzel 1969; Miller et al. 1987; Huang 1972; Koubek et al. 1975).

We now analyze the behavior of $\chi(l)$ for random surfaces. Figure 6 shows a typical case corresponding to $\Delta\varepsilon = 12$ and $w = 1$. The results for random surfaces (circles) are presented in comparison with the corresponding ones for chessboard topographies (squares). It is interesting to note that both curves of $\chi(l)$ are parallel. This suggests the idea that a random topography characterized by a scale length l behaves like a chessboard topography with a larger scale length. To understand this effect, we repeat the calculations above for random topographies. In this case, (23) must be modified to include the contribution from the number of pairs of NN occupied sites corresponding to the contact between two deep patches N_{NN}^C,

$$N_{NN}^C = \frac{z f_D N_D}{2}, \tag{27}$$

where z is the lattice connectivity ($z = 4$ for square lattices), f_D is the fraction of deep patches (in this case $f_D = 0.5$) and the division by 2 is to avoid double counting. Then, for the case of random topographies,

$$f(1/2, l) = u(1/2, l) = \frac{\varepsilon_D}{2} + \frac{w(l-1)}{l} + \frac{w}{2l}$$
$$= \frac{\varepsilon_D}{2} + \frac{w(2l-1)}{2l}, \tag{28}$$

and

$$\chi(l) = 2 \left| \frac{w(2l-1)}{2l} \right|. \tag{29}$$

Equations (26) and (29) demonstrate that chessboard and random topography curves for χ should become the same curve as a function of an effective length scale (representing an effective patch size), l_{eff}, given by

$$l_{eff} = sl, \tag{30}$$

where $s = 1$ for chessboard topography and $s = 2$ for random topography. In the inset of Fig. 6, we can see how the simulation data for different topographies cast over a single curve when the effective length scale is used. The solid line represents theoretical results from (26).

From the theoretical arguments given above, it is possible to obtain an universal curve, which allows one to determine the behavior of the function $\chi(l_{eff})$ for any lateral interaction and topography. This universal curve becomes given by

$$\frac{\chi(l_{eff})}{|w|} = 2 \left(\frac{l_{eff} - 1}{l_{eff}} \right). \tag{31}$$

As an example of the validity of the last equation, Fig. 7 shows how all the curves used in the experiment collapse into an universal function according to the theoretical prediction. The figure not only includes results for random and
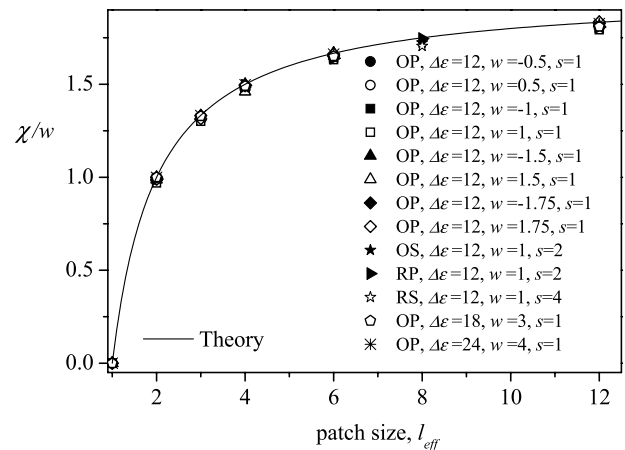

Fig. 7 Collapsing plot of the curves of $\chi(l_{eff})$ for different topographies and lateral interactions as indicated. *Solid line* corresponds to (31) and *symbols* represent results from Monte Carlo simulation. Data corresponding to random patches, ordered patches, random strips, and ordered strips, are denoted by RP, OP, RS, and OS, respectively

chessboard topographies but also data from surfaces characterized by the presence of strips of transversal size l, which are spatially distributed either in an ordered alternate way, or in a nonoverlapping random way. This gives an additional proof for the theoretical results presented here.

The results of the analysis in this section allow us to establish a criterion to determine the characteristics of the topography of heterogeneous substrates which can be approximated by bivariate surfaces from a simple analysis of the adsorption isotherms. Adsorption measurements that are strictly necessary are the variation of the coverage as a function of the chemical potential (adsorption isotherm), and the adsorbate-adsorbate interaction energy, w, which can be obtained by LEED or STM measurements. With this, the corresponding reference 1_C curve can be obtained from (14). Then, after integrating the experimental and theoretical isotherms according to (1), the corresponding value of χ can be calculated allowing l_{eff} to be obtained from (31).

5 Conclusions

The adsorption process of interacting particles on heterogeneous bivariate surfaces has been studied via grand canonical Monte Carlo simulations and a detailed mean field approximation. The adsorptive surface has been modeled by considering two kind of adsorption sites, deep and shallow wells, forming homotatic square patches. These patches can be either arranged in a deterministic chessboard structure or in a random way.

Previous studies showed that the topography of a given surface can be obtained from the knowledge of the corresponding adsorption isotherm and a reference curve. In the

present work, this procedure has been reviewed by using a different reference curve than that used in previous studies.

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. Further developments may require to investigate to what extent a general heterogeneous surface can be satisfactorily approximated by a bivariate patch surface of variable size l_{eff}.

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