Scaling properties in the average number of attempts until saturation in random sequential adsorption processes

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In the present paper we investigate the exact average number of attempts until saturation when a square lattice is ceaselessly bombarded with β-bell ($\beta \geqslant 1$) particles, i.e., linear particles that require β consecutive lattice sites to be adsorbed. When that average number is normalized with the corresponding single-particle average, a scale invariant behavior is revealed with a scaling exponent $\alpha = 0.017 \pm 0.001$, independent of β ($\beta > 1$). The scale behavior is suggested by the branching characteristics governing the sequential random adsorption of β-bell ($\beta > 1$) particles, which is indeed a consequence of configurational correlations.

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I. INTRODUCTION

Chemisorption on single-crystal surfaces, at low temperatures where surface diffusion is inhibited, provides a natural application of random sequential adsorption (RSA) processes. In the (100) face of single-crystal fcc substrates the adsorption sites form a square lattice. We are interested in considering RSA processes of molecules that can occupy more than one site in a lattice space. In such systems there is configurational correlation in the sense that if a compartment is occupied, then at least one of its neighbors is also occupied.

Much attention has been placed in the scientific literature to study the kinetic aspects of RSA processes as well as the jammed coverage values [1–10]. In the present paper we wish to focus the attention on another interesting question within RSA processes, that is, what is the average time to arrive at a jamming state when a *large* square lattice is ceaselessly bombarded by linear particles? As we shall consider linear particles of varying length β (=1,2,3,4,...,), β-bell particles, a unit of time based on the average number of impacts per lattice site is adopted. We then calculate the Monte Carlo steps to saturate a lattice of β-bell particles, $\langle S_\beta \rangle_{M\times N}$.

For *small* lattices and *arbitrary* values of β, we have developed a branch counting probability approach to calculate $\langle S_\beta \rangle_{M\times N}$ *exactly* [11,12]. Also, $\langle S_{\beta=1} \rangle_{M\times N}$ can be *exactly* determined for *arbitrary* size lattices, i.e., $M \times N$ values [13].

In the present paper we calculate, by Monte Carlo simulations, $\langle S_\beta \rangle_{M\times N}$ for both *arbitrary* β values and *arbitrary* large lattice sizes. We find a scale invariant behavior and determine the scaling exponent $\alpha = 0.017 \pm 0.001$, independent of β.

The paper is organized as follows. In Sec. II a brief description of how to find the *exact* $\langle S_\beta \rangle_{M\times N}$ value for *small* lattices is outlined. For comparison purposes in Sec. III we present the *exact* $\langle S_{\beta=1} \rangle_{M\times N}$ value for lattices of *arbitrary* size and no configurational correlation, i.e., $\beta = 1$.

In Sec. IV *numerical simulations* are presented for *large* lattice sizes and *with* configurational correlations, i.e., $\beta > 1$. In Sec. V the conclusions of the present paper are summarized.

II. EXACT SOLUTION FOR *SMALL* LATTICES AND *ARBITRARY* β VALUES

In a previous paper [11,12] we derived analytical expressions to describe the average number of attempts $\langle m_\beta \rangle$ until the jamming state when small lattices ($3\times 4, 3\times 5$) are ceaselessly bombarded by β-bell ($\beta \geqslant 2$) particles. The goal of the present paper is to investigate this property for very large lattices $M \times N$ by computer simulations.

To evaluate $\langle m_\beta \rangle$ on small lattices it was necessary to previously identify all the different microstates that can be distinguished with 1,2,3,..., adsorbed particles until the jammed state. The number of microstates increases very fast as the lattice size increases. For example, Fig. 1 shows those 18 microstates found for trimers ($\beta = 3$) on a 3×5 lattice. The asterisk indicates a jamming microstate. Figure 2 shows the complex branched structure generated by the interconnected microstates with the corresponding probabilities to pass from one to another or to remain in a given microstate. There are two ways to come into the branched structure, either through microstates A or B with probabilities 1/2 in each case. Once in microstate A we can go on to C, D, E, or F with probabilities 4/60, 8/60, 8/60, and 12/60, respectively, and there is a probability 28/60 to remain in A. An analogous procedure can be followed if we start from B. This "diffusion" probability process ends up when we arrive at the sink microstates (or jamming) identified by K^*, P^*, and R^* with probabilities $\frac{129}{704}$, $\frac{1073}{4928}$, and $\frac{369}{616}$. These probabilities were found by developing a branch counting probability approach for this random sequential process [12]. The method allows an easy evaluation of the probability of observing the different jammed microstates, once the branching structure formed by the interconnected microstates is determined, and without the complication of solving first the kinetic rate equation.

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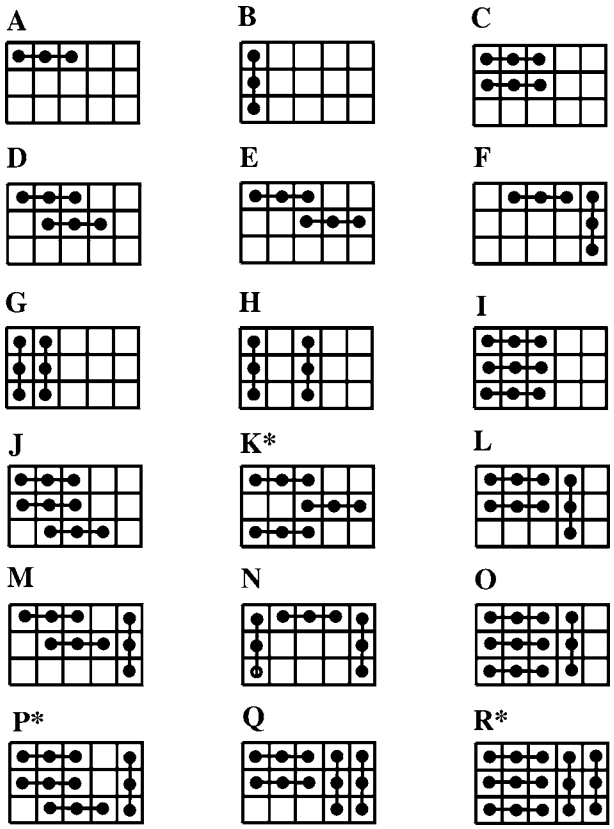

FIG. 1. The 18 microstates $(A,B,C,\ldots,I,J,\ldots,Q^*,R^*)$ found on a 3×5 lattice. The asterisk indicates a jamming microstate.

These probabilities, together with their corresponding jammed coverages $\frac{6}{10}$, $\frac{8}{10}$, and 1 for K^*, P^*, and R^*, respectively (see Fig. 1), enable us to find the average saturation coverage when a 3×5 lattice is ceaselessly bombarded by trimers. At the jamming limit we found a coverage value $\langle\theta\rangle_{\mathrm{JL}}$

$$\langle\theta\rangle_{\mathrm{JL}} = \frac{3}{5}\frac{129}{704} + \frac{4}{5}\frac{1073}{4928} + \frac{5}{5}\frac{369}{616} = \frac{21761}{24640}. \tag{1}$$

The average number of attempts from the i-microstate m_i until the corresponding jammed microstates K^*, P^*, or R^* is a summation of probabilities on a branched structure. Let us see how this summation is if we wish to evaluate m_A

$$m_A = 1 + \frac{28}{60}m_A + \frac{4}{60}m_C + \frac{8}{60}m_D + \frac{8}{60}m_E + \frac{12}{60}m_F. \tag{2}$$

In an analogous way m_C, m_D, m_E, m_F should be evaluated

$$m_C = 1 + \frac{38}{60}m_C + \frac{2}{60}m_I + \frac{4}{60}m_J + \frac{12}{60}m_L, \tag{3}$$

$$m_D = 1 + \frac{44}{60}m_D + \frac{4}{60}m_J + \frac{6}{60}m_M, \tag{4}$$

$$m_E = 1 + \frac{50}{60}m_E, \tag{5}$$

$$m_F = 1 + \frac{46}{60}m_F + \frac{4}{60}m_L + \frac{4}{60}m_M + \frac{6}{60}m_N. \tag{6}$$

The procedure should be applied now to evaluate m_I, m_J, m_L, m_M, and m_N. If this branching method is repeatedly applied we arrive at the result $m_A = \frac{54423}{2464} \approx 22.087\cdots$. In an analogous way, if we come into the branched structure through microstate B we find that $m_B = \frac{1756}{63} \approx 27.873\cdots$.

Finally, the average number of attempts until the jamming state $\langle m_{\beta=3}\rangle$ is reached on a 3×5 lattice is

$$\langle m_{\beta=3}\rangle = 1 + \frac{1}{2}[m_A + m_B] = \frac{1\,152\,271}{44\,352} \approx 25.980\cdots. \tag{7}$$

If the average number of adsorption attempts $\langle m_\beta\rangle$ is normalized by $(M\times N)/\beta$, we obtain the average number of Monte Carlo steps $\langle S_{\beta=1}\rangle_{M\times N}$ for lattice saturation. $\langle S_\beta\rangle_{M\times N}$ is then defined as

$$\langle S_\beta\rangle_{M\times N} = \beta\langle m_\beta\rangle/M\times N. \tag{8}$$

By defining a Monte Carlo step as $M\times N/\beta$ attempts to fill the lattice, we imply that the average occupation number per lattice site is equal to one.

III. EXACT SOLUTION FOR $\beta=1$ AND *ARBITRARY* LATTICE SIZES

To investigate the particular case of single particles (sp) that is, particles that require a single adsorption site ($\beta=1$) and that upon the collision with the lattice are irreversibly adsorbed, we consider a two-dimensional lattice with n adsorption sites [13]. Without loss of generality we can consider a square lattice $n=M\times N$. The results can be extended straighforwardly to lattices of an arbitrary symmetry (hexagonal, honeycomb, etc.) because with this kind of particle there is no configurational correlations.

Figure 3 shows the chain of configurations that results in a sequential filling process. Configuration 1 $[C(1)]$ represents the n possibilities to place the first particle on the lattice, all of which are equivalent. For the present purposes there is an equivalence between occupied and unoccupied lattice sites, a property that is absent when linear particles with $\beta>1$ are considered. There are $n-1$ possibilities to place the second one and to arrive at Configuration 2 $[C(2)]$ and *one* possibility to remain in $C(1)$. In general there will be $n-2,n-3,\ldots,n-(i-1),\ldots,1$ possibilities to place *the third*,…., *fourth*,… ith,…., and nth particles, respectively, and to arrive at $C(3),C(4),\ldots,C(i),\ldots,C(n)^*$. Consequently there will be $2,3,\ldots,i-1,\ldots,n-1$ possibilities to remain in $C(2),C(3),\ldots,C(i-1),\ldots,C(n-1)$. The asterisk identifies the final configuration, that is, when the surface is completely saturated.

In Fig. 3 the rings are linked by the probability $p(i\rightarrow i+1)$ to arrive at $C(i+1)$ from $C(i)$, see Eq. (9). Figure 3 also shows the probability $p(i\rightarrow i)$ to remain in the same configuration, see Eq. (10).

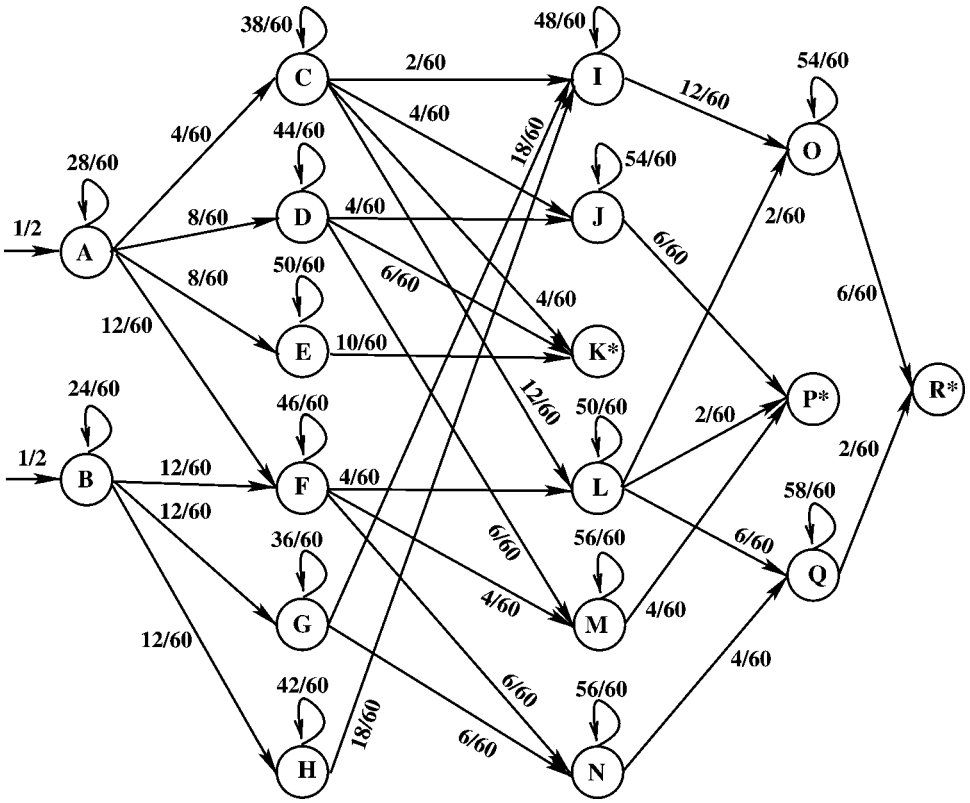

FIG. 2. The branched structure generated by the interconnected microstates with the corresponding probabilities to pass from one to another or to remain in a given microstate. From Ref. [12].

$$p(i \to i+1) = \frac{n-i}{n} \tag{9}$$

$$p(i \to i) = \frac{i}{n} \tag{10}$$

The average number of adsorption attempts, m_i, from the configuration $C(i)$ until the saturated configuration $C(n)^*$, is calculated as

$$m_{n-i} = \frac{n}{i} + m_{n-i+1} \tag{11}$$

with the boundary condition $m_n = 0$.

The average number of adsorption attempts from $C(1)$ until lattice saturation will be

$$m_1 = n \sum_{i=1}^{n-1} \frac{1}{i}. \tag{12}$$

At configuration $C(1)$ we arrive in just one step with probability one, therefore the average number of adsorption attempts $\langle m_{\beta=1} \rangle$ from $C(0)$ (the clean lattice) until saturation, $C(n)^*$, will be

$$\langle m_{\beta=1} \rangle = 1 + m_1 = n \sum_{i=1}^{n} \frac{1}{i}. \tag{13}$$

If the average number of adsorption attempts $\langle m_{\beta=1} \rangle$ from $C(0)$ to $C(n)^*$ is normalized by the number of adsorption lattice sites $n = M \times N$, we obtain the average number of Monte Carlo steps $\langle S_{\beta=1} \rangle_{M \times N} = \frac{\langle m_{\beta=1} \rangle}{M \times N}$ for lattice saturation

$$\langle S_{\beta=1} \rangle_{M \times N} = \sum_{i=1}^{M \times N} \frac{1}{i}. \tag{14}$$

If the number of adsorption sites is very large, then the summation can approach $\ln(M \times N)$. Therefore the average number of Monte Carlo steps to saturate a lattice of any symmetry, with single particles, is an extensive quantity given by the following equation

$$\langle S_{\beta=1} \rangle_{M \times N} \approx \ln(M \times N). \tag{15}$$

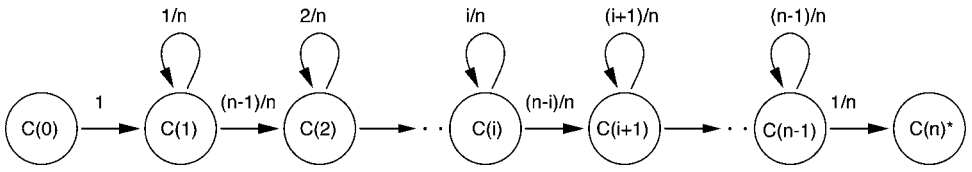

FIG. 3. The sequential adsorption process of single particles as a chain of configurations. $p(i \to i+1)$ links the rings and is the probability to arrive at $C(i+1)$ from $C(i)$. $p(i \to i)$ is the probability to remain in the same configuration. Ref. [13]

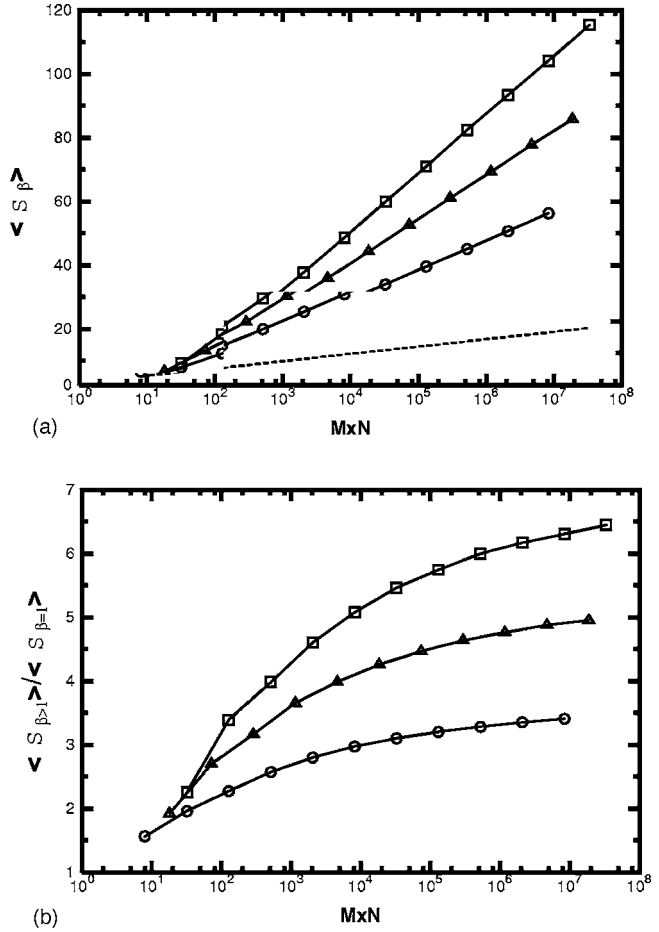

FIG. 4. (a) Average number of attempts, in Monte Carlo steps $\langle S_\beta \rangle_{M\times N}$, until the jamming state, against the $\log_{10}(M\times N)$. (b) Dependence of $\langle S_{\beta>1}\rangle_{M\times N}/\langle S_{\beta=1}\rangle_{M\times N}$ on $\log_{10}(M\times N)$, see Eq. (16). Circles: dimers, Triangles: trimers, Squares: tetramers. The dashed line is the exact solution for monomers, Eq. (14).

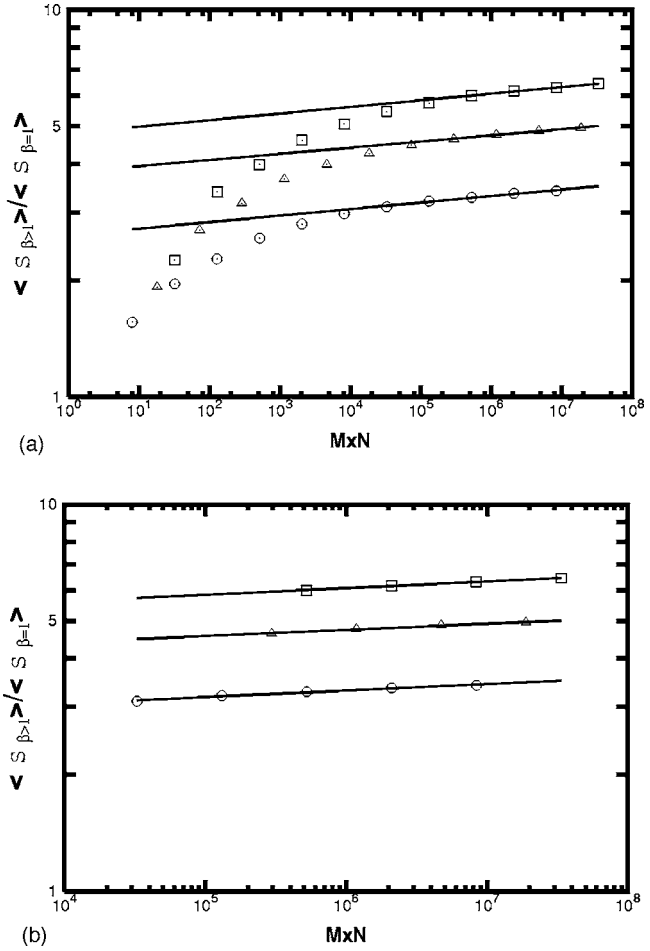

FIG. 5. (a) Dependence of $\log_{10}(\langle S_{\beta>1}\rangle_{M\times N}/\langle S_{\beta=1}\rangle_{M\times N})$ on $\log_{10}(M\times N)$, see Eq. (17). (b) A closer view of the linear behavior observed in Fig. 5(a). Circles: dimers, Triangles: trimers, Squares: tetramers.

IV. NUMERICAL SIMULATION FOR *ARBITRARY* β VALUES AND *ARBITRARY* LATTICE SIZES

We have simulated the random sequential filling process of a two-dimensional lattice space with periodic boundary conditions, with dimers, trimers and tetramers. Figure 4(a) shows the average number of attempts, in Monte Carlo steps $\langle S_\beta \rangle_{M\times N}$, until the jamming state is attained plotted against the $\log_{10}(M\times N)$.

For comparison purposes in the same figure we include the corresponding values for single particles derived from Eq. (14), where the linear behavior is a consequence of Eq. (15).

Figure 4(b) shows the dependence of

$$\frac{\langle S_{\beta>1}\rangle_{M\times N}}{\langle S_{\beta=1}\rangle_{M\times N}} vs\ \log_{10} M\times N. \tag{16}$$

Dimers, trimers, and tetramers seem to approach a common behavior for large lattices. On the other hand, from the analysis made on small lattices we realized that the procedure that enables us to find $\langle m_\beta \rangle, \beta>1$ keeps a close resemblance to processes of diffusion on a fractal structure towards the jamming microstates. We therefore seek a scale invariance dependence of the LHS of Eq. (16) on the lattice size $M\times N$ such as

$$\frac{\langle S_{\beta>1}\rangle_{M\times N}}{\langle S_{\beta=1}\rangle_{M\times N}} \approx [M\times N]^\alpha. \tag{17}$$

Figure 5(a) shows a $\log_{10}-\log_{10}$ plot of Eq. (17). A power-law behavior is observed at lattice sizes $M\times N \gtrapprox 10^4$, as well as a remarkable parallelism for the three kinds of particles. Figure 5(b) shows a closer view of the linear behavior when the lattice size is increased even 256 times. From these simulations, a scaling exponent $\alpha = 0.017\pm 0.001$ is determined, independent of β ($\beta>1$).

From the exact analysis made with β-bell particles (with $\beta>1$) on small lattices, we also observe that the number of ways to come into the branched structure and the number of jamming microstates increase as the lattice size increases (see Fig. 2). Computer simulations reveal that as the lattice size increases, the coverage distribution values of the jamming microstates become strongly peaked at the average jammed value $\langle \theta \rangle_{\mathrm{JL}}$.

V. CONCLUSIONS

In the present paper we investigated the average number of attempts $\langle S_\beta \rangle_{M\times N}$ until saturation (in Monte Carlo steps) when a square lattice $M \times N$ is ceaselessly bombarded with β-bell particles, $\beta \geqslant 1$. When that average value is normalized with the corresponding single particle average [LHS of Eq. (16)], a scale invariant behavior is revealed with a scaling exponent $\alpha=0.017$ independent of β ($\beta>1$). The branching characteristics governing the sequential random adsorption of β-bell ($\beta>1$) particles (which is a consequence of configurational correlations), see Fig. 2, suggest the existence of scaling properties in the RSA process.

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