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Effect of particle size distribution and dynamics on the performance of two-dimensional packing

M. Carvalho Vieira^a, M.A.F. Gomes^{b,*}, J.P. de Lima^c

^a Universidade Estadual do Piauí, 64002-150, Teresina, PI, Brazil

^b Departamento de Física, Universidade Federal de Pernambuco, 50670-901, Recife, PE, Brazil

^c Universidade Federal do Piauí, 64049-550, Teresina, PI, Brazil

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ABSTRACT

Extensive computer simulation is used to revisit and to generalize two classical problems: (i) the random car-parking dynamics of A. Rényi and (ii) the irreversible random sequential adsorption (RSA) of parallel squares of same size on a planar substrate of area L^2 . In this paper, differently from the classical RSA, the squares obey the size distribution $n(a) = n(1)a^{-\tau}$, where $a = 1, 2, 3, \dots$ is the area of the squares. Using this scaling distribution and three classes of packing dynamics we study the final packing fraction of particles, $\Theta(\tau, L)$, and in particular its thermodynamic limit $L \rightarrow \infty$. We show that the efficiency to attain a high/low packing density of particles on the substrate is strongly dependent on the value of the exponent τ and on the characteristics of the dynamics.

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1. Introduction

Packing problems and adsorption are subjects of great interest for the structure of physical systems and for surface science, respectively. Both types of study are as well of great importance in technology [1,2]. Some examples in these areas include the structural aspects in crystalline and disordered matter, the efficiency in heterogeneous catalysis, and the action of drugs on biological tissues, besides the importance of adsorption in vital fields as the control of pollution and environmental protection, and purification of water, sewages, and air [3].

Among the statistical physics algorithms trying to capture basic aspects present in the phenomenon of adsorption, there is the classical Random Sequential Adsorption (RSA) of elements, a packing dynamics inspired in the famous mathematical model of Rényi [4] for random car-parking. In Ref. [4] a 1D large parking lot of length L , initially empty, is occupied by cars of unit-width coming one after the other randomly in sequence, with equal probability somewhere in the space that is available. The dynamics is subject to non-overlap conditions, i.e. newly added cars can not touch cars previously parked. The process continues until there are no available spaces left of length greater than the unit. In these circumstances, the parking lot gets filled up with $N(L)$ cars, such that $N(L)/L = 0.747597 \dots$, as $L \rightarrow \infty$. The immediate multidimensional generalization of this problem is well-defined [5] and, in particular, the 2D version (adsorption of unit area elements on a plane squared domain of area L^2), the 2D irreversible RSA of elements, is obviously of relevance in surface physics and chemistry, as well as in technology and in the physical aspects of the packing of units on 2D surfaces. To assure that no available space is left to further adsorption, the classical RSA allows, in principle, infinite attempts to occupy sites. If the adsorbed elements are equal squares (circles), the final jamming fraction or maximum coverage, defined as $\Theta_j = \Theta_j(L) = [(\text{total area occupied by adsorbed elements at the jamming limit})/L^2]$, assumes the value $\Theta_j \rightarrow \Theta_\infty = 0.562009 \pm 0.000004$ [6] (0.547 ± 0.002 [7]) for $L \rightarrow \infty$. Feder and Giaever [8] attempted to measure experimentally the

* Corresponding author.

E-mail address: maf@ufpe.br (M.A.F. Gomes).

random-packing limit in 2D using ferritin proteins adsorbed onto both Lexan[®] polycarbonate and carbon surfaces. They found an average value for the jamming fraction approximately 13% larger than the results from their own computer-simulated value of 0.547, although their average experimental value $\Theta_{\text{exp}} = 0.625 \pm 0.100$ had a large uncertainty bar that could accommodate the final fraction coverage obtained in simulations. Afterwards Onoda and Liniger [9] carried out an experimental determination of this packing limit utilizing a spherical colloid that sticks irreversibly to a flat substrate. The experimental value obtained was 0.55 ± 0.01 , in better agreement with simulation results.

Here, in contrast with the classical RSA, we are interested in the study of different dynamics of irreversible packing of parallel (aligned) squares of area a with the squares obeying a two-parameter scaling distribution of the type $n(a) = n(1)a^{-\tau}$. This distribution characterized by a critical exponent τ reduces to the monodisperse case for $\tau \gg 1$. In the opposite limit $\tau \rightarrow 0$ we get a distribution describing the maximum diversity of sizes or the maximum polydispersity of the packed squares. Using the proposed scaling law, and three different packing dynamics of physical interest with only monolayer distributions of squares we find the final packing fraction of squares $\Theta = \Theta(\tau, L)$, in particular its limit $L \rightarrow \infty$. The last packing fraction is defined as $\Theta(\tau, L) = (\text{total area occupied by packed elements when the dynamics must stop})/L^2$, i.e. differently from $\Theta_j(L)$ of the previous paragraph, here depending on the dynamics and on the size L , the packing process can finish before the jamming limit to be reached. Our choice of power law distributions of squares is based on two aspects: firstly, there is an intrinsic theoretical interest in examine the effect of scaling functions in processes of packing, and in statistical physics modeling in general. This particular simple type of distribution function with only two parameters could be used to simulate more realistic distributions of packed particles. Secondly, and perhaps most importantly, we know that both power law functions and scaling distributions are frequently associated with optimization procedures in many areas as polymer physics, random media, interface physics, as well as in statistical physics and complex systems in general [10–14]. In this context it is important, in particular, to compare how close to the asymptotic jamming limit $\Theta_\infty = 0.562009 \pm 0.000004$ [6] observed within the classical RSA process for unit area squares, we can reach using such a class of scaling distributions. We paid particular attention to the evaluation of the performance or efficiency of the packing dynamics studied here. The efficiency in this paper is measured by the final packing fraction $\Theta = \Theta(\tau, L)$ defined above. This quantity obviously can assume values only in the interval [0, 1]. A large numerical value $\Theta(\tau, L)$ means a high packing performance. As a final remark, as the packing dynamics studied here are inspired in the RSA algorithm, in the text we are using the words packing and adsorption as synonymous; equivalently the words square, particle, and element are used with the same meaning.

This paper is organized as follows. In Section 2 we describe the packing models used in our computer simulation; in Section 3 a discussion of the results is presented, and in Section 4 we conclude with a brief description of the paper and a summary of our findings.

2. Description of the models

Basically, our simulation deals with a 2D squared support or substrate of area L^2 and a reservoir of squares of area a distributed according to the truncated power law

$$n(a) = n(1)a^{-\tau}, \quad (1)$$

with $a = 1, 2, 3, 4, \dots, a_{\text{max}}$, and under the following constraints: (i) there is a single square with the largest area a_{max} , that is $n(a_{\text{max}}) = 1$, or $n(1) = a_{\text{max}}^\tau$ or again $n(a) = (a/a_{\text{max}})^{-\tau}$. The value a_{max} defines, of course, the polydispersity index of the distribution of particle size for a fixed value of L . (ii) The function $n(a)$ is chosen so that the corresponding squares provide the best coverage for the total area of the substrate. The use of the last constraint allows us to properly implement the distribution given in Eq. (1), and it also furnishes an adequate normalization condition in order to compare directly the performance or yield of different dynamics of packing. To accomplish (ii) we optimize simultaneously a_{max} and L in such a way that the difference $\Delta = L^2 - \sum an(a)$ is minimized. In general, it is easily understood that Δ tends to decrease as τ and L increase, because the limit of large τ means a monodisperse distribution of squares with unit area. For the sake of completeness, it is interesting to observe that even in the opposite case of small τ (i.e. a long tail distribution with large diversity of size of squares) and small L , the largest relative deviation Δ/L^2 observed in our simulations is already small; as an example, $\Delta/L^2 = 0.013$, for $\tau = 0$, and $L = 100$. As additional information for the reader to develop insight on the degree of accuracy of our simulations, we obtain $\Delta/L^2 = 0.001009$, for $\tau = 0$, $L = 1,000$, and $\Delta/L^2 = 0.000435$, for $\tau = 0$, $L = 3,200$. Furthermore, we have imposed a maximum value of 0.001 (0.1%) for the relative standard deviation of the quotient Δ/L^2 . As a consequence, the total number N of equivalent experiments performed varies in order to satisfy this degree of accuracy, and in general this number is quite high ($N \gg 10$) as we will detail in due time. In addition, the minimum number of equivalent experiments cannot by definition be inferior to 10, even for the largest size simulations.

During the simulation, a selected element in the reservoir has its position in the 2D support of area L^2 randomly chosen; if in this position the selected element does not overlap one or more elements already adsorbed, the new adsorption choice will be irreversibly implemented. Otherwise, this element is irreversibly eliminated from the dynamics and it does not return to the reservoir. That is, any square element chosen from the reservoir has only a single chance to be packed/adsorbed on the support. This process is repeated until the reservoir is empty or the jammed state is reached (A jammed state of adsorbed particles on the support can coexist with a non-empty reservoir if the adsorption dynamics is limited by diffusion, as will

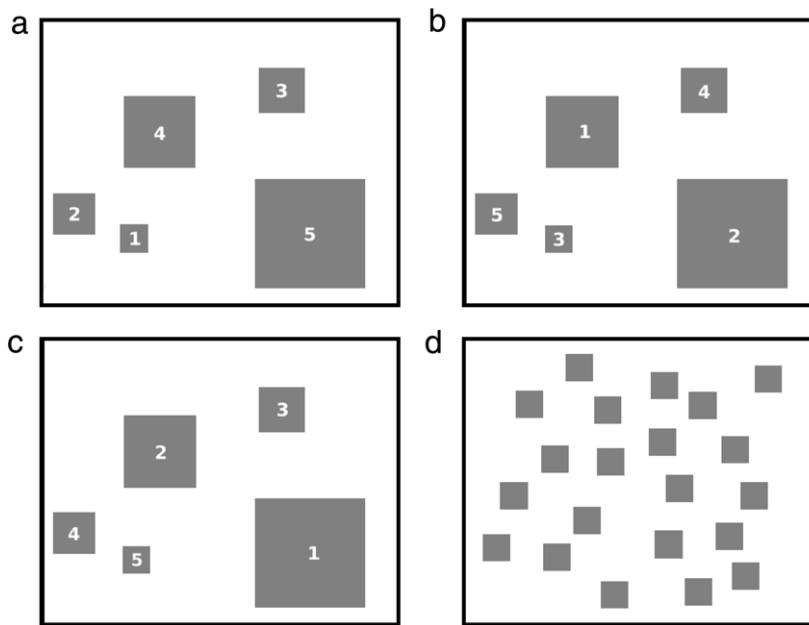


Fig. 1. The four types of dynamics studied in this paper for the sequential adsorption of squares discussed in Section 2: (a) represents the beginning of the adsorption process with the scaling distribution given in Eq. (1) considering the SSF-rule: we try to adsorb first the smallest squares and then the larger squares in sequence (SSF-rule). (b) The intermediary situation in which the squares are added at random (RSS-rule). (c) The first steps of the process according to the LSA-rule. In this case, the adsorption proceeds from the largest square to the small ones. The numbers inside the squares define the temporal order of the adsorption. (d) Classical RSA studied in several articles [6]. See text, Section 2 for detail.

be explained in Section 3.). After this stage, the final packing density $\Theta(\tau, L)$ as defined in Section 1 is calculated. Here we are concerned only with the packing of squares with edges aligned parallel to each other, as in classical RSA of squares.

Recently, Wackenhut and Herrmann [15] studied the compaction of vibrated polydisperse media within the parking lot model using a scaling distribution of elements like ours. However, those authors were interested in a different *reversible* version of the parking lot model in which particles are adsorbed with a rate k^+ and desorbed with a rate k^- , and their simulations were restricted to the one-dimensional case.

There are numerous ways to select a square in the reservoir and to carry out the sequential adsorption. As previously anticipated in Section 1, in this paper we study three (general) theoretical and quite different classes of physical dynamics. In the first dynamics, termed *small squares first*, SSF-rule, the sequential adsorption proceeds from the element with smallest area, $a = 1$, to the elements with progressively larger areas up to $a = a_{max}$ (Fig. 1(a)). The SSF-rule is inspired in a physical process that is rigorously limited by thermal diffusion; i.e. the basic aspect that is important in this case is that particles with area a always reach the support plane before particles of area a^* provided $a < a^*$, on the basis that the former have larger thermal velocity and smaller mass than the latter. It must be remembered that the diffusion we considered here is diffusion of the adsorbate particles limited to the approach to the surface, and that no diffusion on the surface is permitted. It is easily understood that in this important limit, the small particles that are adsorbed firstly block the possibility of packing/adsorption of the larger particles in the future and the final packing fraction Θ does not reach a high value. This type of process in thermal systems tends to be more relevant in the physical situations with not too low temperature.

Secondly, we tested a packing dynamics, named *random sequence of squares*, RSS-rule, which uses a sequence of adsorption events involving particles with area randomly chosen from a reservoir containing adsorbate squares according to the distribution given in Eq. (1). This type of packing dynamics (Fig. 1(b)) can be interpreted as one involving a competition between the previous process limited by diffusion and another process limited by the strength of the interaction between the packed particles and the adsorbing plane.

Finally, in the third dynamics, termed *large squares first*, LSF-rule, the sequence of adsorption proceeds from the element with the largest area, a_{max} , to the elements of decreasing area up to $a = 1$ (Fig. 1(c)). Physically, the LSF-rule refers clearly to a process that is not limited by thermal diffusion. Instead, the LSF-rule simulates a physical process in which large size particles come firstly on the surface because the interaction between adsorbate and support plane is stronger as the particle size increases. This rule is interesting from the practical point of view because it is known that gases and vapors as well as organic and biological molecules in general present an increase in the intensity of the physical adsorption with the molecular size [16–19]. If the temperature is not too high, the fast diffusion of the small molecules in direction of the adsorbing surface is attenuated and the LSF-rule can simulate the packing/adsorption of large molecules interacting more strongly with the support via a short range interaction. For the sake of completeness we show in Fig. 1(d) the classical RSA dynamics, with all potentially adsorbed elements with unit area [6].

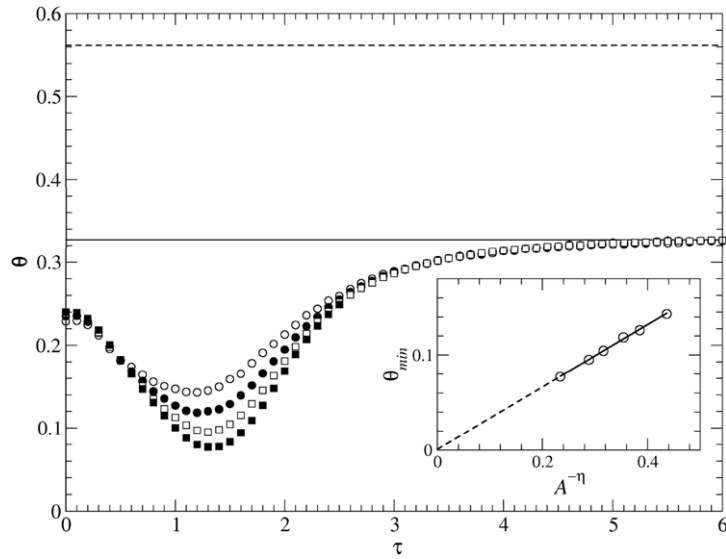


Fig. 2. Dependence of the final packing fraction $\Theta(\tau)$ defined in Section 1 as a function of the exponent τ appearing in Eq. (1) for SSF-rule, and for some values of the support area $A = L^2$ (10^4 (\circ), 10^5 (\bullet), 10^6 (\square), and 10^7 (\blacksquare)). Each value of $\Theta(\tau, L)$ in this figure represents in general an average in hundreds of equivalent experiments (see Section 3 for detail). The error bars in this figure do not exceed the size of the symbols used to express the data. From this figure we can observe a clear minimum, Θ_{min} , in $\Theta(\tau)$ for τ in the interval (1, 2), depending on the size L . For comparison, we show the asymptotic packing fraction $\Theta_\infty = 0.562009 \pm 0.000004$ (dashed line) obtained with the classical RSA, corresponding to a uniform monodisperse distribution of equal squares (equivalent to $\tau \gg 1$ in Eq. (1)). The horizontal continuous line, $\Theta_1 = 0.327 \pm 0.001$ denotes the packing fraction obtained with squares of unit area but with a *single* adsorption trial per square. The inset of the figure shows that $\Theta_{min} \sim A^{-\eta} \rightarrow 0$ as the area $A = L^2 \rightarrow \infty$. The value of the exponent η used to obtain the linearization of the data is $\eta = 0.090 \pm 0.002$.

Our simulations were executed in a cluster of CPUs with 3.00 GHz Intel[®] Xeon[™] processors, cache size 2048 KB and 2 GB RAM. In these machines simulations for lattices of size $L^2 = 1000^2$, for a complete variation in the exponent τ in the interval $0 \leq \tau \leq 6$, and with the fixed standard deviation criterion, as explained above, consumed 7 days of processing. More detailed information on the simulation and in particular on the sampling in our experiment is given in Section 3.

3. Results and discussion

Firstly we consider the dynamics with preference to adsorb the elements in increasing order of size, the SSF-rule (Fig. 1(a)). This corresponds to physical situations frequently encountered in thermal systems, namely situations in which the small adsorbate particles diffuse more rapidly in the medium reaching the support before the larger particles. The results for the final packing fraction $\Theta(\tau)$ in this case are quantified in Fig. 2 for supports of different areas, and for the exponent τ varying from $\tau = 0$ to $\tau = 6$. The final packing fraction in this case is always small when compared with Θ_∞ due to the blockage effect of the small adsorbate particles as explained in the previous section. Interestingly, the reader can observe in the figure that there is a minimum Θ_{min} in the packing fraction that appears to occur in the interval $1 < \tau < 2$. A detailed numerical analysis shown in the inset of Fig. 2 suggests that $\Theta(\tau)$ reaches the minimum value $\Theta_{min} = 0$ for $L \rightarrow \infty$. Qualitatively, the behavior of $\Theta(\tau)$ in Fig. 2 and in particular the existence of a minimum can be understood as follows: if τ is zero, we have a single square element for each integer area a and as the adsorption proceeds a finite fraction of the area of the support is occupied ($\Theta(\tau = 0) \approx 0.24$), however when τ increases the number of squares with small area increases as well and the blockage of adsorption of the large squares becomes more stringent and, as a consequence, the packing fraction decreases. But if τ continues to increase, the number of small squares increases too much compared to the larger area squares and the surface of the support can be occupied more efficiently because the cost of the loss of an adsorption event is low and the next adsorption trial can be successful. In particular, for τ in the interval (4, 6) the size distribution of squares approaches effectively a monodisperse distribution which optimizes the occupied fraction of the surface and we get $\Theta(\tau = 6) > \Theta(\tau = 0)$. The error bars in this and subsequent figures do not exceed the size of the symbols used to express the data. As commented in the previous section, the numbers of equivalent experiments needed to obtain relative fluctuations in the packing density within a maximum value of 0.1% depend on the size of the surface and on the value of the exponent τ considered. As an example and additional information to the reader, the data reported in Fig. 2 is based on averages on 435 equivalent experiments for $A = 10^4$, 152 experiments for $A = 10^5$, and 51 experiments for $A = 10^6$, if $0.0 < \tau < 0.5$. When τ increases, the averages in the number of equivalent experiments diminishes in proportion. The numerical analysis synthesized in the inset of the figure shows that $\Theta_{min} \sim A^{-\eta}$, $A = L^2$, $\eta = 0.090 \pm 0.002$, with $\Theta_{min} \rightarrow 0$ at the thermodynamic limit $L \rightarrow \infty$. In practical terms, this figure shows that the SSF-rule lead to an anomalously low density of adsorbate particles in the diffusion-limit regime for large area and $1 < \tau < 2$. In these cases, we have low

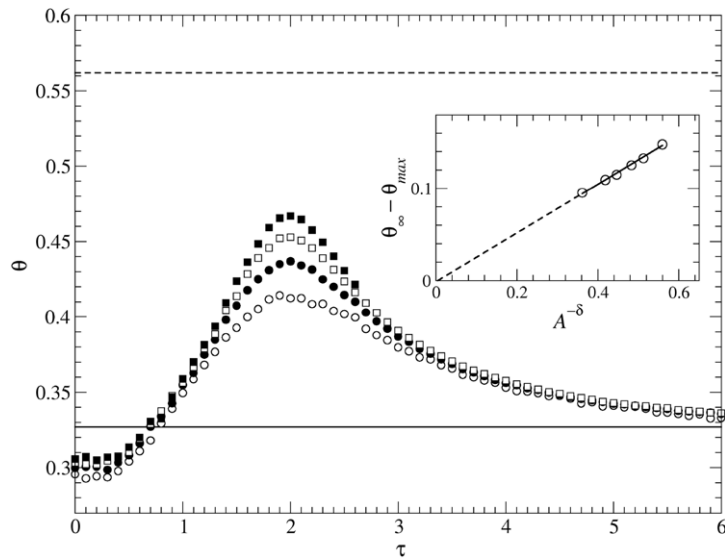


Fig. 3. The same as in Fig. 2 but for the RSS-rule. The support area A is 10^4 (\circ), 10^5 (\bullet), 10^6 (\square), and 10^7 (\blacksquare). For comparison, we show the asymptotic packing fraction $\Theta_\infty = 0.562009 \pm 0.000004$ (dashed line) and $\Theta_1 = 0.327 \pm 0.001$ (continuous line). Inset: the maximum $\Theta_{max}(\tau)$ converges to the jamming fraction $\Theta_\infty = 0.562009 \pm 0.000004$, as the lattice approaches the thermodynamic limit: $(\Theta_\infty - \Theta_{max}) \sim A^{-\delta} \rightarrow 0$ as the area $A = L^2 \rightarrow \infty$, $\tau = 2$, and $\delta = 0.063 \pm 0.002$. (\blacksquare). Each value of $\Theta(\tau, L)$ in this figure represents in general an average in hundreds of equivalent experiments (see Section 3 for detail). The error bars in this figure do not exceed the size of the symbols used to express the data.

performance packing (adsorption) processes. In conformity with this result, we conjecture that distributions of particle size $n(a) \sim a^{-\tau}$, with $1 < \tau < 2$ tend to give origin to strong depletion in the density of adsorbate particles in all situations where the diffusion limited regime has importance. If τ is progressively out of the interval $1 < \tau < 2$, the final packing fraction $\Theta(\tau)$ in Fig. 2 grows reaching a value close to 0.24 for $\tau = 0$, and in the opposite direction, $\tau = 6$, it converges to the limit of monodisperse adsorption of squares of unit area, for which $\Theta = \Theta_1 = 0.327 \pm 0.001$, as signaled by the continuous horizontal line in the figure. That is, in this paper it is shown that in addition to the asymptotic jamming limit Θ_∞ previously discussed, there is the second asymptotic limit Θ_1 . For completeness, the dashed line in the Fig. 2 indicates the asymptotic jamming packing fraction $\Theta_\infty = 0.562009 \pm 0.000004$ obtained in Ref. [6].

If use is made of the dynamics illustrated in Fig. 1(b), which considers a random choice of elements from the reservoir, the RSS-rule, we get the result shown in Fig. 3. In this case, on the contrary, the final packing fraction $\Theta(\tau)$ presents a maximum close to $\tau = 2$ as the size of the system approaches the thermodynamic limit. More precisely, the inset in Fig. 3 suggests that in this case $(\Theta_\infty - \Theta_{max}) \sim A^{-\delta}$, with $\delta = 0.063 \pm 0.002$, and then $\Theta_{max} \rightarrow \Theta_\infty$ when L or $A \rightarrow \infty$. In a first view, this is very surprising, because in classical RSA of squares we give in principle infinite opportunities for a square to be adsorbed, while in our simulation making use of the scaling distribution given in Eq. (1), it is allowed just a *single* opportunity of adsorption per square. Physically, the RSS-rule represents a situation in which the diffusion limited regime suffers a competition from a regime where adsorbate particles of increasing sizes tend to present increasing strengths of interaction with the support. This is due to the fact that RSS-rule is intermediary between the SSF-rule (which favors the adsorption of small particles as in thermal diffusion limited processes) and LSF-rule (which favors the adsorption of large particles by supposing that these interact more strongly with the surface than the small ones). From the practical point of view, Fig. 3 suggests that a distribution of particle size of the type $n(a) \sim a^{-2}$ lead to the largest possible packing density of particles on the substrate if the diffusion limit is not clearly dominant. The number of equivalent experiments needed to obtain relative fluctuations in the packing density within a maximum value of 0.1% depends on the size of the surface and on the value of the exponent τ considered. For the data reported in Fig. 3 we have used averages on 485 equivalent experiments for $A = 10^4$, 165 experiments for $A = 10^5$, and 57 experiments for $A = 10^6$, if $0.0 < \tau < 0.5$. When τ increases, the number of equivalent experiments needed to attain the required upper bound in the relative fluctuations diminishes in proportion.

As any grocer knows, the space within a container is better occupied by items of diverse shape and size if the largest volumes are accommodated first. This simple fact of everyday life is systematically investigated and quantified in our simulation. In Fig. 4, we present the plot of the final packing fraction $\Theta(\tau)$ as a function of the exponent τ , for RSA with the LSF-rule (Fig. 1(c)). As observed for the RSS-rule in Fig. 3, Fig. 4 presents a clear maximum in Θ for $\tau = 2$, when the lattice size approaches the thermodynamic limit. The figure illustrates the convergence of the final packing fraction $\Theta(\tau) \rightarrow \Theta_1$, as $\tau \rightarrow \infty$. In the inset, it is shown that the maximum packing fraction of $\Theta(\tau)$, Θ_{max} , converges to the jamming fraction Θ_∞ when the size of the lattice diverges: $\Theta_\infty - \Theta_{max} \sim A^{-\xi}$, with $\xi = 0.072 \pm 0.003$. This seems to be also a surprise as we observe for the RSS-rule. However, we believe this is only apparent surprise and in the next paragraph we present a simple explanation for the fact Θ_{max} (for RSS and LSF) seem to converge to Θ_∞ of RSA. The data reported in Fig. 4 are based

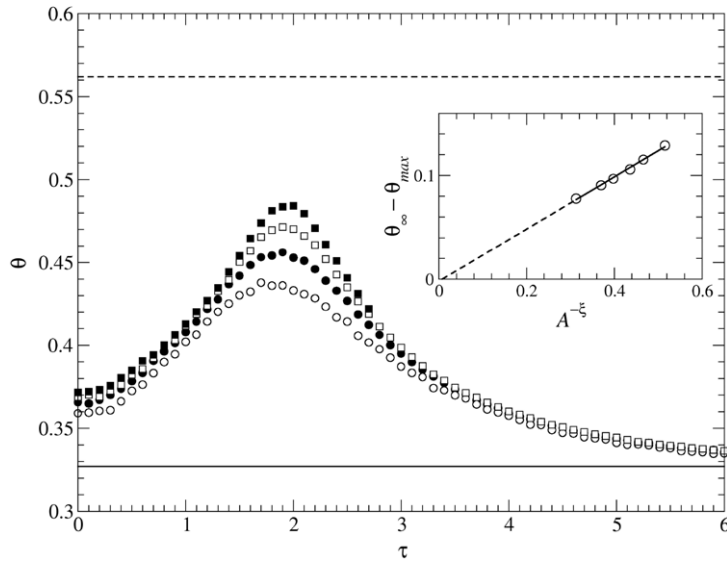


Fig. 4. Dependence of the final packing fraction $\vartheta(\tau)$ defined in Section 1 as a function of the exponent τ appearing in Eq. (1) for LSF-rule and for some values of the support area $A = L^2$ (\circ) 10^4 , (\bullet) 10^5 , (\square) 10^6 , and (\blacksquare) 10^7 . We observe a clear maximum, ϑ_{max} , in $\vartheta(\tau)$ located progressively close to $\tau = 2$, as the lattice approaches the thermodynamic limit. The inset of the figure shows that $(\vartheta_\infty - \vartheta_{max}) \sim A^{-\xi}$, with $\xi = 0.072 \pm 0.003$. The asymptotic packing fraction $\vartheta_\infty = 0.562009 \pm 0.000004$ (dashed line) and $\vartheta_1 = 0.327 \pm 0.001$ (continuous line) are shown. Each value of $\vartheta(\tau, L)$ in this figure represents in general an average in hundreds of equivalent experiments (see Section 3 for detail). The error bars in this figure do not exceed the size of the symbols used to express the data.

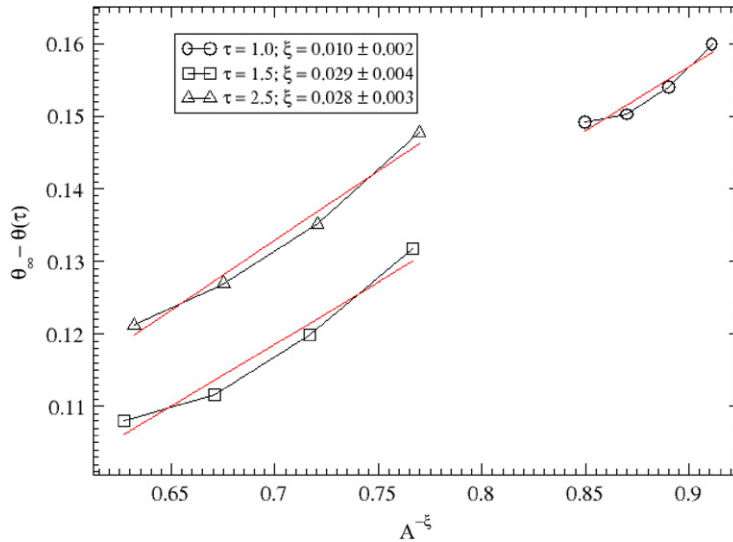


Fig. 5. Three plots similar to those presented in the inset of Fig. 4 ($\tau = 2$) but for $\tau = 1.0, 1.5,$ and 2.5 and the corresponding power law best fits. It can be observed that in these cases corresponding to LSF-rule the difference between the asymptotic packing fraction ϑ_∞ defined in Section 1 and the maximum packing fraction associated with the exponent τ in Eq. (1) does not decay perfectly to zero as a power law as occur for $\tau = 2$.

on averages on 383 equivalent experiments for $A = 10^4$, 126 experiments for $A = 10^5$, and 51 experiments for $A = 10^6$, if $0.0 < \tau < 0.5$. For larger values of τ , the number of equivalent experiments diminishes in proportion.

Why indeed should ϑ_{max} (for RSS and LSF) $\rightarrow \vartheta_\infty$, when $L \rightarrow \infty$? A possible answer, though, is that there is a sort of compensation that appears when we compare the three types of adsorption rules (RSA versus RSS or LSF): while in classical RSA there is the possibility to do an infinite number of adsorption trials using elements with small area ($a = 1$), for RSS or LSF rules the adsorption process is more optimized because elements with large and medium area representing a finite fraction of the area of the substrate are adsorbed early in the adsorption process (and so avoiding the blockage effect commented in the fourth paragraph of Section 2) albeit with a number of adsorbing attempts per particle limited to a single event.

In Fig. 5 we show plots for the LSF-rule that are similar to those exhibited in the inset of Figs. 3 and 4 ($\tau = 2$) but for $\tau = 1.0, 1.5,$ and 2.5 together with the power law best fits. The fit $\vartheta_\infty - \vartheta(\tau) \sim A^{-\xi}$ is indicated by continuous lines, and

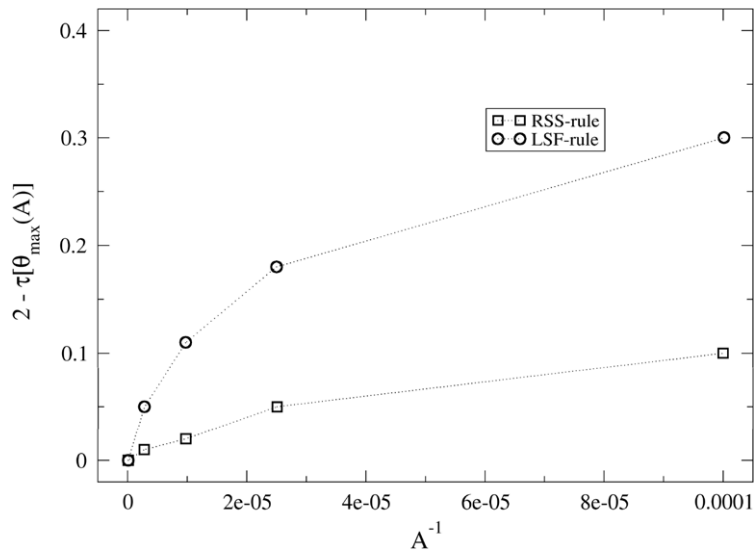


Fig. 6. Difference $2 - \tau [\theta_{\max}(A)]$ versus area A of the support for the two adsorption rules RSS (Fig. 3) and LSF (Fig. 4): for both rules the exponent τ goes precisely to 2.0 as the area A goes to the infinity.

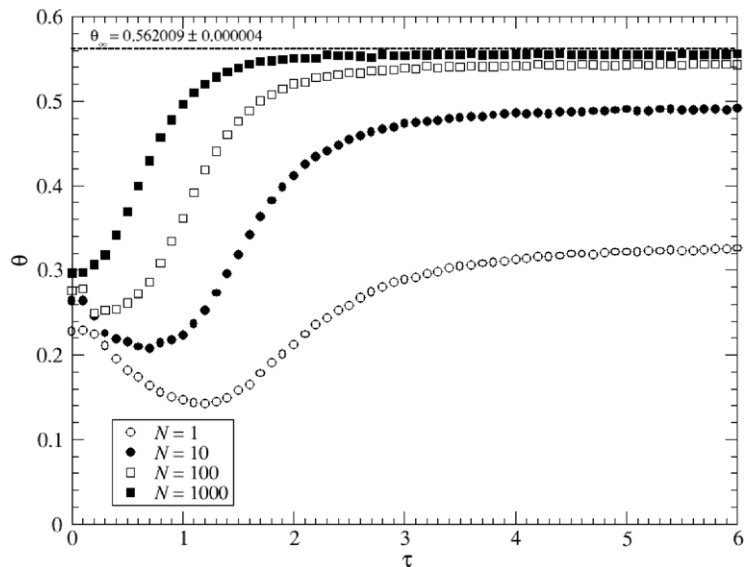


Fig. 7. Final packing fraction $\theta = \theta(\tau, N)$ as a function of the exponent τ appearing in Eq. (1) for some values of the number N of adsorption trials with the SSF-rule of adsorption. We observe that for $N = 1000$, $\theta(\tau)$ goes to a value close to θ_{∞} as expected. See Section 3 for detail.

the value of the exponent ξ is given in the inset. It can be observed that in these three cases the difference $\theta_{\infty} - \theta(\tau)$, does not decay perfectly to zero in the domain of large areas as a power law as occur for $\tau = 2$.

In order to better justify the previous statement that $\theta(\tau, L)$ presents a maximum progressively near $\tau = 2$ as the size of the system approaches the thermodynamic limit, we show in Fig. 6 the plot of the difference $2 - \tau [\theta_{\max}(A)]$ versus the support area A for the two adsorption rules considered in Fig. 3 and in Fig. 4. The reader can observe that the random case, RSS-rule, and the LSF-rule justify precisely the previous statement, with τ going to 2.0 as the area A goes to the infinity.

For completeness we show in Fig. 7 the dependence of the packing fraction $\theta = \theta(\tau, N)$ as a function of τ for some values of the number N of chances of adsorption per particle for adsorption with the SSF-rule on a support of area 100^2 . This particular class of dynamics is interesting because $\theta(\tau, N)$ is expect to converge to θ_{∞} when $\tau \gg 1$, and $N \rightarrow \infty$. We can see that for $\tau = 6$, which approaches quite well the monodisperse limit of adsorbing particles of square shape and unit area, $\theta(\tau, N = 1)$ converges to $\theta_1 = 0.327$. In this same plot we observe as expected that for $N = 1000$, $\theta(\tau, N)$ approaches asymptotically to $\theta_{\infty} = 0.562 \dots$ which is the value of θ for $N \rightarrow \infty$ in the monodisperse case.

4. Conclusions

Extensive computer simulation is used to study in detail three classes of models of irreversible packing of squares inspired in the classical random car-parking dynamics of Rényi [4] and Random Sequential Adsorption (RSA) of squares onto a flat uniform surface [6]. In our models the particles (area a) that can be adsorbed satisfy a scaling distribution $n(a) = n(1)a^{-\tau}$. This distribution reduces to the monodisperse limit of particles with fixed area for $\tau \gg 1$, a situation that is observed in RSA. The classical RSA of parallel squares of unit area is used to model adsorbate molecules able to be irreversibly adsorbed on the plane, provided the molecules do not overlap and provided there are infinite chances of adsorption to each of them. Under these circumstances, the maximum fraction of the plane covered is $\theta_\infty = 0.562009 \pm 0.000004$ [6]. We have found in the present work that using the previous scaling distribution (Eq. (1) of the text) with $\tau = 2, L \rightarrow \infty$, it is possible to reach the same maximum value θ_∞ if packing proceeds from the larger squares to the small squares, or even if packing occurs with squares adsorbed in a random sequence, under two very restrictive conditions: (i) the adsorbing squares come from a reservoir that contains just the sufficient number of squares to cover entirely the total area of the support, and (ii) each square has a *single* chance of adsorption on the support. Furthermore we have found that in the diffusion limit or SSF-rule, the final packing density presents a depletion of the surface coverage, with θ decaying to zero in the interval $1 < \tau < 2$ as the size of the support increases. Beyond its intrinsic theoretical interest as a packing model for a wide class of distributions of squares in two dimensions, the simulations described in this paper with emphasis on the packing of polydisperse units are amenable to be verified from real packing experiments, and they impose appropriate lower-bounds limits to packing density in new adsorption experiments [20–23]. In particular, it is suggested that a scaling distribution of squares of the type $n(a) \sim a^{-2}$ lead to significantly larger packing density (as compared with θ_∞) if several adsorption trials per square are allowed as in the RSA of unit squares.

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