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On the random sequential adsorption of d-dimensional cubes

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Abstract

The jamming coverage θ_d for the random sequential adsorption of aligned d-dimensional cubes in R^d is studied through a one-gap distribution function. Heuristic arguments generally used to describe the large time kinetics are found to imply that this distribution is rather independent of the space dimension. This is shown to give a quantitative explanation of the so-called Palasti approximation $\theta_d \approx \theta_1^d$.

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1. Introduction

The random filling of R^d by non-overlapping aligned d-dimensional cubes is one of the simplest random sequential adsorption (RSA) models [1]. Its one-dimensional version is the car-parking (CP) problem, solved a long time [2]. As for any RSA model in higher dimension, it remains unsolved and series expansions [3] or Monte Carlo (MC) simulations [4–6] have been devoted to its study.

A quantity of central interest is the fraction $\theta(t)$ of the total volume occupied by the adsorbed objects at time t, and in particular its asymptotic value, the jamming coverage $\theta_d = \theta(t \to \infty)$. The kinetics of the deposition process close to the jamming limit is also widely studied. In our case one knows [5, 7] that the asymptotic expansion of the coverage is $\theta(t \to \infty) \approx \theta_d - \rho_d[\ln(t)]^{d-1}/t$ where θ_d has been measured in two [4,5], three and four [6] dimensions, the constant ρ_d being known in two dimensions [4].

There is a curious fact about the values of θ_d, that one can call the Palasti's approximation, which is that the d-dimensional jamming coverage value is very close to the value of the one-dimensional coverage $\theta_1 = 0.747\,598$ raised at the dth power, $\theta_d \approx \theta_1^d$. In fact, the strict equality $\theta_d = \theta_1^d$, conjectured long ago by Palasti [8], is not valid as shown in 1991 by a precise MC simulation of the two-dimensional model [4]. It has been found that $\theta_2 = 0.562\,009(4)$, which is close but not equal to θ_1^2, since $\theta_1^2 = 0.5589$. This false conjecture remains, at least up to $d = 4$, an accurate and unexplained approximation.

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In this work we give an explanation of the Palasti approximation that originates from the particular behaviour of the one-gap distribution function. The first section is devoted to the study of this function in the one-dimensional case, where it represents the density $G(x)$ of gaps of length x between two adsorbed segments, and which is well known from the analytical solution of the CP model. Our aim here is to find an approximate expression as a consequence of the heuristic arguments of Pomeau and Swendsen [7,9] used to analyse the asymptotic kinetics. We are then able, without need of the exact solution, to give an accurate approximation of the constants θ_1 and ρ_1. The generalization of this method to any dimension is done in the third section, where we consider a one-gap distribution function $G_d(x)$ defined on parallel lines intersecting the adsorbed cubes. The asymptotic heuristic arguments of the second section are found to imply that $G_d(x) \approx G(x)$, from which the Palasti approximation and a constraint on the value of the constant ρ_d can be derived.

2. The car-parking model as an example

This solved model, where unit segments are randomly adsorbed on the line without overlap, is used here as a testing ground for the method we apply in higher dimensions. We consider the one-gap distribution function $G(x, t)$ which represents the density of voids of length x between two adsorbed segments [10]. Since the numbers of gaps and segments are equal, the following sum rules hold

$$\int_0^\infty G(x,t)\,\mathrm{d}x = \theta(t) \qquad \int_0^\infty (1+x)G(x,t)\,\mathrm{d}x = 1 \tag{1}$$

and $G(x, t)$ is computed from its evolution equation

$$\frac{\partial}{\partial t} G(x,t) = 2\int_{1+x}^\infty \mathrm{d}y\, G(y,t) - H(x-1)(x-1)\,G(x,t) \tag{2}$$

where $H(x)$ is the Heaviside step function. The solution of this equation, in the case of an empty line at the initial time $t = 0$, is

$$\begin{aligned} G(x,t) &= 2\int_0^t \mathrm{e}^{-xu} u g(u)\,\mathrm{d}u \qquad &\text{for} \quad x \leqslant 1 \\ G(x,t) &= t^2 g(t)\mathrm{e}^{-(x-1)t} \qquad &\text{for} \quad x \geqslant 1 \end{aligned} \tag{3}$$

where $g(t) = \exp(-2\int_0^t [1-\mathrm{e}^{-u}]\,\mathrm{d}u/u)$. From relations (1) and (3) one obtains the coverage $\theta(t) = \int_0^t g(u)\,\mathrm{d}u$ whose asymptotic expansion reads

$$\theta(t) \approx \theta_1 - \rho_1/t \qquad \theta_1 = 0.7476 \qquad \rho_1 = G(x=1, t=\infty) = \mathrm{e}^{-2\gamma} \approx 0.315. \tag{4}$$

One also finds a singularity at $x = 0$, $G(x \approx 0, t \to \infty) = -2\rho_1 \ln(x)$, which is characteristic of the RSA process [7,9].

It thus appears that $G(x, t)$ at infinite time has a limiting function $G(x)$, vanishing for $x > 1$, whose values at $x = 0$ and 1 are linked by the relation $G(x \approx 0) = -2G(1)\ln(x)$. It fulfils the sum rules given in equation (1) which become

$$\int_0^1 G(x)\,\mathrm{d}x = \theta_1 \qquad \int_0^1 (1+x)G(x)\,\mathrm{d}x = 1. \tag{5}$$

Our aim is now to derive the asymptotic expansion of equation (4), including the numerical values of θ_1 and ρ_1, without the exact solution given in equation (3). We apply the method of Pomeau and Swendsen [7,9]. At large time, the increase of the coverage is due to segments falling into voids of length x, where $1 \leqslant x \leqslant \Lambda$, Λ being a cut-off quantity expected around 2, and there are $(x-1)$ ways of filling this gap. Thus

$$\frac{\partial}{\partial t} G(x,t) \approx -(x-1)\, G(x,t) \qquad \text{for} \quad x \geqslant 1 \tag{6}$$

and

$$\frac{\mathrm{d}\theta}{\mathrm{d}t}(t) = \int_1^{\Lambda} (x-1)\, G(x,t)\, \mathrm{d}x. \tag{7}$$

One solves the asymptotic evolution equation (6) for $G(x,t)$,

$$G(x,t) \approx \rho \mathrm{e}^{-(x-1)t} \qquad \text{for} \quad x \geqslant 1 \tag{8}$$

ρ being an unknown constant, and inserting this estimate in equation (7) gives $\frac{\mathrm{d}\theta}{\mathrm{d}t}(t \to \infty) \approx \rho/t^2$, i.e. $\theta\,(t \to \infty) \approx \theta_1 - \rho/t$, θ_1 being considered here as an unknown constant. We then evaluate $G(x,t)$ for $x \leqslant 1$ at large time, which is the probability to find two deposited segments S_1 and S_2 separated by a distance x. This event happens when S_2, for example, falls into the gap between S_1 and S_3, S_3 being a segment already adsorbed at some distance y of S_1, with $1 + x \leqslant y \lessapprox \Lambda$. There are $(y-1)$ events of this kind but only one is selected, which corresponds to the assigned distance x between S_1 and S_2: its probability is $(y-1)^{-1}$, and we finally obtain

$$G(x,t) \approx 2 \int_{1+x}^{\Lambda} G(y,t)\, \mathrm{d}y/(y-1) \qquad \text{for} \quad x \leqslant 1 \tag{9}$$

where the factor 2 arises from the $S_1 - S_2$ symmetry in this argument. In the integral appearing in equation (9), $y \geqslant 1$ and the estimate previously derived in equation (8) for $G(y,t)$ can be used. One thus obtains $G(x,t) \approx 2\rho \int_{1+x}^{\Lambda} \mathrm{e}^{-(y-1)t}\, \mathrm{d}y/(y-1)$ which in the infinite time limit indicates a logarithmic singularity for $x = 0$, such that $G(x \to 0, t \to \infty) \approx -2\rho \ln(x)$, and since $G(1,\infty) = \rho$ from equation (8) this can be written $G(x \to 0, t \to \infty) \approx -2G(1,\infty) \ln(x)$.

In this heuristic approach, it thus appears that there is, for $t \to \infty$, a limiting one-gap distribution function $G(x)$, vanishing for $x > 1$, such that $G(x \to 0) = -2G(1) \ln(x)$. All these results agree with the exact ones, but the constants θ_1 and $G(1)$ are left unspecified.

On the other hand, the sum rules of relation (5) have not been used: they can be used to fix these constants if one can express $G(x)$ without introducing other parameters. We thus assume that $G(x)$ on the whole range $0 \leqslant x \leqslant 1$, can be parametrized according to the simple expression

$$G(x) = G(1)(x - 2\ln(x)) \tag{10}$$

which embodies the $x \approx 0$ singularity. As $\int_0^1 (x - 2\ln(x))\, \mathrm{d}x = 5/2$ and $\int_0^1 (1+x)(x - 2\ln(x))\, \mathrm{d}x = 10/3$ one obtains $G(1) = 3/10 = 0.3$ and $\theta_1 = 3/4 = 0.75$, which is an acceptable approximation of the exact values $G(1) = 0.315$ and $\theta_1 = 0.7476$. We have also checked that the parametrization (10), in spite of its crudeness, is a good fit of the exact function.

We show in the next section how a d-dimensional generalization of these arguments constrains the asymptotic parameters and can explain why the Palasti approximation is an accurate estimate of the jamming coverage.

3. Asymptotic estimates in any dimension

We consider firstly the two-dimensional case, easy to visualize. In this model, non-overlapping squares of unit area are adsorbing on a plane in such a way that their edges stay parallel with two orthogonal directions X and Y.

The late stages of the RSA process are dominated by the filling of voids which can adsorb one square but in contrast with the one-dimensional case, the unfilled regions percolate and have complicated shapes. However, one can select inside such voids the largest rectangles (x, y) fitting between adsorbed squares. The rectangles (x, y) are parallel to the X and Y directions and are of size x and y along these directions, with $1 \leqslant x, y \leqslant \Lambda$, the cut-off Λ being expected of size ≈ 2. As it has been shown in the work of [5], this subset of voids is essential to correctly reproduce the features of the RSA process in its late stages. The distribution $G(x, y; t)$ of these rectangular cells (x, y) is a generalization of the one-gap distribution function $G(x, t)$ of the one-dimensional case, as it allows us to extend equations (6) and (7) in the following way. As there are $(x - 1)(y - 1)$ ways of adsorbing a square in an (x, y) void, one has

$$\frac{\partial}{\partial t} G(x, y; t) = -(x - 1)(y - 1)G(x, y; t) \qquad \text{for} \quad x, y \geqslant 1 \tag{11}$$

the corresponding increase of the coverage being

$$\frac{\mathrm{d}}{\mathrm{d}t}\theta(t) = \int_1^\Lambda (x - 1) \int_1^\Lambda (y - 1)G(x, y; t)\,\mathrm{d}y\,\mathrm{d}x. \tag{12}$$

One thus obtains from equation (11) $G(x, y; t) = \rho_2 \mathrm{e}^{-(x-1)(y-1)t}$ where ρ_2 is some normalization constant. Inserting this expression in equation (12) gives the asymptotic behaviour of the coverage

$$\theta(t) \approx \theta_2 - \rho_2 \frac{\ln t}{t} \tag{13}$$

in terms of two unknown constants θ_2 and ρ_2 that we have to determine.

To make contact with the one-dimensional case previously studied, we consider in the adsorbing plane lines L_X and L_Y parallel with the directions X and Y. The intersections of these lines with the adsorbed squares are sequences of unit segments which partially cover the lines, and we denote by θ_L the average value of these coverages. To compare θ_L and θ_2, we consider a line L_X and an associated strip S_X, infinite in the X direction and of width $2H$ in the Y direction (the width is H above L_X and H below L_X). Close to the jamming limit, a regular distribution on L_X is made of adsorbed segments separated by some distance 2ϵ in such a way that $\theta_L = 1/(1 + 2\epsilon)$ and it also appears as the periodic succession of the following pattern: a void of size ϵ, an adsorbed segment and, again, a void of size ϵ. Thus if one chooses $H = 1/2 + \epsilon$, the strip S_X can be decomposed into adjacent squares of area $(1 + 2\epsilon)^2$, each cell containing an adsorbed square. The coverage of the cell is thus $1/(1 + 2\epsilon)^2$, which is also the coverage of the strip S_X and the coverage of the plane from the (X, Y) symmetry. We thus obtain $\theta_2 = 1/(1 + 2\epsilon)^2 = \theta_L^2$ for this regular case and we assume more generally that $\theta_L(t) = \sqrt{\theta(t)}$ at large time. We now study $\theta_L(t)$.

For this we define a distribution $G_2(x, t)$ according to

$$G_2(x, t) = \frac{1}{2\sqrt{\theta_2}} \int_1^\Lambda (y - 1)G(x, y; t)\,\mathrm{d}y \tag{14}$$

in such a way that we have, from equation (12),

$$\frac{1}{2\sqrt{\theta_2}} \frac{\mathrm{d}}{\mathrm{d}t}\theta(t) = \int_1^\Lambda (x - 1)G_2(x, t)\,\mathrm{d}x \tag{15}$$

and, as the left-hand side member of equation (15) is at leading order $\frac{\mathrm{d}}{\mathrm{d}t}\theta_L(t)$ according to our assumption $\theta_L(t) = \sqrt{\theta(t)}$, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\theta_L(t) = \int_1^\Lambda (x - 1)G_2(x, t)\,\mathrm{d}x \tag{16}$$

which indicates that $G_2(x, t)$ is the one-gap distribution function on the lines L_X.

We now study the asymptotic behaviour of $G_2(x,t)$ in the infinite time limit. We know from equation (11) that $G(x,y;t) = \rho_2 \mathrm{e}^{-(x-1)(y-1)t}$ for $x, y \geqslant 1$ which can be inserted in equation (14) and one obtains for $x \geqslant 1$

$$G_2(x,t) = \frac{\rho_2\big[1 - \big(1 + (x-1)(\Lambda-1)t\mathrm{e}^{-(x-1)(\Lambda-1)t}\big)\big]}{2\sqrt{\theta_2}(x-1)^2t^2}. \tag{17}$$

This equation shows that, in the infinite time regime, $G_2(x,t)$ has a limiting distribution $G_2(x)$ which vanishes for $x \geqslant 1$, as in the one-dimensional case. This behaviour is however not obvious from simple geometric considerations since in higher dimensions some gaps greater than one are allowed on the line L_X even in the jammed configurations. These gaps, which are taken into account in our analysis, are thus insignificant in the determination of $G_2(x)$. For $x = 1$ one finds from equation (17) that $G_2(x=1) = \rho_2\ (\Lambda-1)^2/4\sqrt{\theta_2}$ and more generally $G_2(x)$ is positive definite for $0 \leqslant x \leqslant 1$. The arguments of the previous section can be repeated and imply the presence of a logarithmic singularity at contact $G_2(x \approx 0) = -2G_2(1)\ln(x)$, and $G_2(x)$ fulfils the sum-rules of equation (5) where θ_1 is replaced by $\theta_L\ (t \to \infty) = \sqrt{\theta_2}$.

To complete the derivation we parametrize $G_2(x)$ as illustrated in equation (10) for $G(x)$, in such a way that the sum-rules imply $\sqrt{\theta_2} = 0.75$ which is the Palasti approximation $\theta_2 = \theta_1^2$ and $G_2(1) = 0.3$. Now from equation (14), $G_2(1) = \rho_2(\Lambda-1)^2/4\theta_1$ and we cannot predict ρ_2, for which the value 0.378 has been measured in the MC simulation of [4]. We simply observe that it implies, for the cut-off Λ, a value $\Lambda = 2.543$, which is a realistic one.

The generalization to any dimension d of this result is then straightforward. Assuming that the jamming coverage θ_L on a line L_X is $\theta_d^{\frac{1}{d}}$, we have to arrive at $\theta_L = \theta_1$. This appears possible if one can define on L_X a one-gap distribution function $G_d\,(x)$ which is a simple rescaling of its one-dimensional analogue, $G_d\,(x) = G_d\,(1)\,G(x)/G(1)$, since then the sum-rules imply $\theta_L = \theta_1$ and $G_d\,(1) = 0.3$ (and thus $G_d\,(x) = G(x)$).

To define $G_d\,(x)$ one considers first the density $G(x_i;t)$ of voids $(x_1,\ldots,x_d)$ where $1 \leqslant x_i \leqslant \Lambda$ for $1 \leqslant i \leqslant d$, asymptotically given by $G(x_i;t) = \rho_d \exp\left(-t\Pi_{i=1}^{i=d}(x_i-1)\right)$. The increase of the coverage at large time is

$$\frac{\mathrm{d}}{\mathrm{d}t}\theta\,(t) = \int_1^\Lambda \prod_{i=1}^{i=d}[\mathrm{d}x_i\,(x_i-1)]G(x_i;t) \tag{18}$$

which gives, as already shown in the work of [5], $\theta\,(t) \approx \theta_d - \rho_d(\ln(t))^{d-1}/t$. The one-gap distribution function on the line L_X is

$$G_d(x_1,t) = \int_1^\Lambda \prod_{i=2}^{i=d}[\mathrm{d}x_i(x_i-1)]G(x_i;t)/\mathrm{d}\theta_d^{1-1/d} \tag{19}$$

since then

$$\frac{\mathrm{d}}{\mathrm{d}t}\theta_L\,(t) = \frac{\mathrm{d}}{\mathrm{d}t}\theta^{1/d}(t) = \int_1^\Lambda (x-1)G_d(x,t)\,\mathrm{d}x. \tag{20}$$

Taking the infinite time limit of $G_d(x,t)$ we obtain $G_d\,(x)$ for which we can assume the parametrization $G_d\,(x) = G_d\,(1)\,G(x)/G(1)$ with $G_d\,(1) = \rho_d(\Lambda-1)^{2d-2}/\mathrm{d}2^{d-1}\theta_d^{1-1/d}$, as given by equation (19). This ensures the results $\theta_L = \theta_1$ and $G_d\,(1) = 0.3$. If the cut-off Λ is fixed at the two-dimensional value, we obtain $\rho_3 = 0.357$ and $\rho_4 = 0.3175$, but we do not have any data to compare.

4. Summary

We have applied to the CP model the arguments used to analyse the large time kinetics of the RSA process. This leads us to propose a parametrization of the one-gap distribution function determining $G(x)$ up to a scaling factor, which is then fixed by the normalization sum-rule. As a consequence the asymptotic coverage θ_1 is also fixed in good agreement with its exact value.

In higher dimensions we have considered a one-gap distribution function $G_d(x)$ defined on a line parallel with one of the deposition axes. The dominance and universality of the contact singularity leads us to assume that $G_d(x) \approx G_d(1)G(x)/G(1)$, which implies $G_d(x) \approx G(x)$ through the normalization condition. Thus the coverage θ_L on the line is the one-dimensional one θ_1. This gives the Palasti relation $\theta_d = \theta_1^d$ under the regularity assumption $\theta_L = \theta_d^{\frac{1}{d}}$.

The simplicity of these results is a consequence of the high symmetry of the present model. Nevertheless, it may happen that this kind of approach gives some quantitative phenomenological constraints on the asymptotics of other RSA models.

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