Random sequential adsorption of binary mixtures on a line

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A jamming coverage for the random sequential adsorption of binary mixtures of segments on the infinite line is derived. It always appears to be smaller than the coverage associated with the car parking problem. This has to be contrasted with dicrete models, where the coverage of the lattice by mixtures of segments of different sizes is more efficient than by single species.

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I. INTRODUCTION

In the random sequential adsorption model (RSA), objects are fixed at random on a substrate if they do not overlap the previously deposited objects. This process, usually initiated on an empty substrate, ends due to blocking and the coverage $\theta(t)$ reaches a maximal value θ_∞. This model, used in various contexts, is reviewed in Ref. [1]. In the recent past, subjects, such as pattern formation [2], percolation [3], adsorption of objects of complicated shape [4], or with desorption [5] have been investigated.

Some results have been also obtained for competitive adsorption [6] and in particular for RSA of mixtures of segments of different lengths deposited on lattices of various dimensionality [7]. The most striking feature is that mixtures cover the lattice more efficiently than either of the species separatly. The exact results available for one-dimensional lattices confirm this fact [8,9]. Our aim here is to investigate this property for the continuous model, and we find that it does not hold any more.

We consider binary mixtures of segments on the infinite line. The smallest segments have a length α, with $0 \leqslant \alpha \leqslant 1$, and are chosen with a probabilty λ, the longest ones being of unit length and chosen with a probability $\mu = \lambda - 1$. These lengths and probabilities are time independent. We thus recover the standard car parking (CP) model [10] for $\lambda = 0$, with an asymtotic coverage $\theta_1 = 0.7476$. We exactly derive the asymptotic coverage $\theta(\alpha,\lambda)$ as a function of the parameters α and λ and we numerically find that $\theta(\alpha,\lambda) \leqslant \theta_1$.

Our derivation uses the method of the empty intervals [1,11] and in Sec. II we give the rate equations of their associated probabilities. In Sec III these equations are solved in order to give the coverage and our numerical results and comments are given in Sec. IV.

II. RATE EQUATIONS FOR THE EMPTY INTERVALS PROBABILITY

One considers an uncovered interval of length x (which could be part of a longer empty interval). The probability to find such an interval at time t is denoted by $P(x,t)$, with $P(x,0) = 1$ since the line is empty initially. The coverage $\theta(t)$ is then given by

$$\theta(t) = 1 - P(0,t), \tag{1}$$

which is a general relation also valid in case of mixtures. To derive $P(0,t)$ one writes the rate equation of $P(x,t)$, which expresses the various ways of filling the empty interval in the RSA process. According to the size x of the interval compared to the size of the deposited segments, there are three cases.

a. Case $x \geqslant 1$. One finds

$$-\frac{\partial}{\partial t}P(x,t) = \{\lambda(x-\alpha) + \mu(x-1)\}P(x,t) + 2\lambda\int_0^\alpha P(x+y,t)\,dy + 2\mu\int_0^1 P(x+y,t)\,dy, \tag{2}$$

where the first term is for the segments falling inside the interval and the remaining integrals for the depositions having some overlap with it.

The other cases are similar.

b. Case $\alpha \leqslant x \leqslant 1$.

$$-\frac{\partial}{\partial t}P(x,t) = \lambda(x-\alpha)P(x,t) + \mu(1-x)P(1,t) + 2\lambda\int_0^\alpha P(x+y,t)\,dy + 2\mu\int_0^x P(1+y,t)\,dy. \tag{3}$$

c. Case $0 \leqslant x \leqslant \alpha$.

$$-\frac{\partial}{\partial t}P(x,t) = \lambda(\alpha-x)P(\alpha,t) + \mu(1-x)P(1,t) + 2\lambda\int_0^x P(\alpha+y,t)\,dy + 2\mu\int_0^x P(1+y,t)\,dy. \tag{4}$$

Equation (4) with $x = 0$ indicates that

$$-\partial P(0,t)/\partial t = \lambda\alpha P(\alpha,t) + \mu P(1,t) \tag{5}$$

and as $d\theta(t)/dt = -\partial P(0,t)/\partial t$ from Eq. (1) we write the coverage as a sum of two contributions associated with $P(\alpha,t)$ and $P(1,t)$. In the infinite time limit it reads

$$\theta(t\to\infty) = \theta(\alpha,\lambda) = \theta_1(\alpha,\lambda) + \theta_2(\alpha,\lambda) \tag{6}$$

with

$$\theta_1(\alpha,\lambda)=\mu\int_0^\infty P(1,t)dt, \quad \theta_2(\alpha,\lambda)=\alpha\lambda\int_0^\infty P(\alpha,t)dt. \tag{7}$$

We have to solve Eq. (2) to know $P(1,t)$ and Eq. (3) for $P(\alpha,t)$. This is detailed in the following section but we can make here some comments. The first case $x\geqslant 1$ is easy to solve as all the values of $P(z,t)$ involved in Eq. (2) correspond to $z\geqslant x\geqslant 1$, as for a single species: an exact solution that we denote by $P_1(z,t)$ is available for $z\geqslant 1$, which is needed to solve Eq. (3). Due to this contribution, we cannot solve analytically Eq. (3), which is, moreover, complicated by the term

$$I(x,t)=\int_0^\alpha P(x+y,t)dy=\int_x^{x+\alpha} P(z,t)dz. \tag{8}$$

The simplest case corresponds to $\alpha\geqslant 1/2$. When x varies in the range $[\alpha,1]$, the upper limit $x+\alpha$ of the integral defining $I(x,t)$ varies in the range $[2\alpha,1+\alpha]$ and is then always greater than 1. The term $I(x,t)$ thus splits into two components

$$I(x,t)=\int_x^1 P_2(z,t)dz+\int_1^{x+\alpha} P_1(z,t)dz, \tag{9}$$

where $P_2(z,t)$ denotes the determination of $P(z,t)$ on the range $1/2\leqslant\alpha\leqslant z\leqslant 1$. Collecting the contribution $F_1(x,t)$ of $P_1(z,t)$ in Eq. (3) one arrives at

$$-\partial P_2(x,t)/\partial t=\lambda(x-\alpha)P_2(x,t)+2\lambda\int_x^1 P_2(y,t)dy + F_1(x,t), \tag{10}$$

where $F_1(x,t)$ is given by

$$F_1(x,t)=\mu(1-x)P_1(1,t)+2\lambda\int_1^{x+\alpha} P_1(y,t)dy + 2\mu\int_0^x P_1(1+y,t)dy. \tag{11}$$

The next case corresponds to $1/3\leqslant\alpha\leqslant 1/2$ where we have to divide the interval $[\alpha,1]$ into $I_-=[\alpha,\beta]$ and $I_+=[\beta,1]$ with $\beta=1-\alpha$ and to consider the determinations $P_-(x,t)$ and $P_+(x,t)$ of $P(x,t)$ on I_- and I_+, respectively. The integral $I(x,t)$ reads on these intervals

$$I_-(x,t)=\int_x^\beta P_-(z,t)dz+\int_\beta^{x+\alpha} P_+(z,t)dz, \quad \alpha\leqslant x\leqslant\beta \tag{12}$$

$$I_+(x,t)=\int_x^\beta P_-(z,t)dz+\int_\beta^1 P_+(z,t)dz + \int_1^{x+\alpha} P_1(z,t)dz, \quad \beta\leqslant x\leqslant 1. \tag{13}$$

The rate equation on the range $\alpha\leqslant x\leqslant 1$ thus appears as a couple of two equations that generalize Eq. (10) to the two unknown probabilities $P_-(x,t)$ and $P_+(x,t)$. More generally, for $1/(N+1)\leqslant\alpha\leqslant 1/N$ we must consider a linear system of N equations. On the other hand, as we show in Sec. IV, the limit $\alpha=0$ is easily derived and the corresponding numerical results are in agreement with our findings for the simplest case $1/2\leqslant\alpha\leqslant 1$. We thus restrict in the following our analysis to this case.

III. SOLUTION OF THE RATE EQUATIONS

The case $x\geqslant 1$ appears as a very simple generalization of the CP model, and the probability is found to be

$$P(x,t)=\exp\{-(x-\alpha\lambda-\mu)t\}G(t), \tag{14}$$

where $G(t)=g^\mu(t)g^\lambda(\alpha t)$ and $g(t)$ is a function already appearing in the CP model, defined by

$$g(t)=\exp\left\{-2\int_0^t(1-e^{-u})du/u\right\}=\exp\{2E_i(-t)-2\gamma\}/t^2. \tag{15}$$

In the previous expression, γ is the Euler constant and $E_i(t)=\int_{-\infty}^t e^u du/u$. This gives $P(1,t)$ and through Eq. (7) the partial coverage $\theta_1(\alpha,\lambda)$ according to

$$P(1,t)=e^{-\lambda(1-\alpha)t}G(t),$$

$$\theta_1(\alpha,\lambda)=\mu\int_0^\infty e^{-\lambda(1-\alpha)t}g^\mu(t)g^\lambda(\alpha t)dt. \tag{16}$$

One checks that $\theta_1(\alpha,\lambda=0)=\theta_1$, the CP model coverage. More generally, one can observe that the asymptotic limit is reached as $e^{-\lambda(1-\alpha)t}/t^2$, that is to say more quickly than for continuous or lattice models.

Considering now the case $\alpha\leqslant x\leqslant 1$, with $\alpha\geqslant 1/2$, we first express $F_1(x,t)$ appearing in Eq. (11) by inserting the result of Eq. (14). One finds

$$F_1(x,t)=e^{-\lambda(1-\alpha)t}G(t)\{2\lambda(1-e^{-(x+\alpha-1)t})/t+\mu(1-x + 2[1-e^{-xt}]/t\} \tag{17}$$

and due to this term we cannot find the solution of Eq. (10) in closed form. Instead we use this equation to generate the t expansion of $P(x,t)$ [from now on we omit the subscript since it is clear that in Eq. (10) we search $P(x,t)=P_2(x,t)$], which reads

$$P(x,t)=1+\sum_{n\geqslant 1} P_n(x)t^n. \tag{18}$$

The corresponding expansion of $F_1(x,t)$ is

$$F_1(x,t)=\sum_{n\geqslant 0} Q_n(x)t^n, \tag{19}$$

where the $Q_n(x)$ are $(n+1)$th order known polynomials [for example, $Q_0(x)=\mu-2\lambda(1-\alpha)+x(\mu+2\lambda)$]. Inserting these expressions in Eq. (10) and equating the coefficients of t^m in the two members give the recursive relation

$$P_{m+1}(x)=-\left\{\lambda(x-\alpha)P_m(x)+Q_m(x)+2\lambda\int_x^1 P_m(y)dy\right\}\bigg/(m+1),\quad m\geqslant 0, \tag{20}$$

which gives the $P_n(x)$ as nth-order polynomials. For example $P_1(x)=-(x+\mu+\alpha\lambda)$. Large order formal expansions can easily be derived using MAPLE (up to $n=20$ which is sufficient). We thus obtain $P(\alpha,t)$ as a finite sum, but we also know its asymptotic behavior as t goes to infinity. In this regime one finds $P(x,t)\simeq C\exp[-\lambda(x-\alpha)t]/t^2$ as the result of Eq. (10) when the nonleading term $F_1(x,t)\simeq 0(\exp[-\lambda(1-\alpha)t])$ is neglected. The constant C is obtained by the continuity constraint at $x=1$ of this asymptotic expression with the exact one $P(1,t)=e^{-\lambda(1-\alpha)t}G(t)\approx\exp[-\lambda(1-\alpha)t-2\gamma-2\lambda\ln(\alpha)]/t^2$. This gives $C=\exp[-2\gamma-2\lambda\ln(\alpha)]$ and thus $P(\alpha,t)\simeq C/t^2$, which also means that asymptotically $P(\alpha,t)\simeq G(t)$.

We are thus left with a standard problem of summation and the most efficient way that we have found is to use the parametrization

$$P(\alpha,t)=G(t\Phi(t)) \tag{21}$$

where $G(t)=g^{\mu}(t)g^{\lambda}(\alpha t)$ and $\Phi(t)$ is a rational expression in t, such that $\Phi(t\to\infty)=1$, and whose parameters are defined in such a way that the coefficients of the t expansion of $G(t\Phi(t))$ are equal to the $P_n(\alpha)$ previously computed. Usually more than five parameters do not improve the numerical accuracy of this parametrization, also obtained with the help of MAPLE. We have checked that $t\Phi(t)$ is a monotonic increasing function of t, and we finally obtain

$$\theta_2(\alpha,\lambda)=\alpha\lambda\int_0^{\infty}G(t\Phi(t))dt. \tag{22}$$

The numerical results of the integrations defined in Eqs. (16) and (22) are given in the following section.

IV. NUMERICAL RESULTS AND CONCLUSION

We have already observed that $\theta_1(\alpha,\lambda=0)=\theta_1$, where $\theta_1=0.7476$ is the CP model coverage at jamming. On the other hand, when $\lambda=1$, $(\mu=0)$, Eq. (2) and Eq. (3) are the same, which implies that on the whole range $x\geqslant\alpha$ their solution is given by Eq. (14), i.e.,

$$\lambda=1,\quad P(x,t)=e^{-(x-\alpha)t}G(t)=e^{-(x-\alpha)t}g(\alpha t) \tag{23}$$

and thus $P(\alpha,t)=g(\alpha t)$ [we have checked that in this case $\Phi(t)=1$] and then

$$\theta_2(\alpha,\lambda=1)=\alpha\int_0^{t\to\infty}g(\alpha u)du=\int_0^{\alpha t\to\infty}g(u)du=\theta_1. \tag{24}$$

We thus have

$$\theta_1(\alpha,\lambda=0)=\theta_2(\alpha,\lambda=1), \tag{25}$$

which is the obvious property of scale invariance of the coverage when only one species is present. However, we observe more generally an approximate symmetry

$$\theta_1(\alpha,\lambda)\approx\theta_2(\alpha,1-\lambda) \tag{26}$$

on the whole range of λ, at least when $\alpha\geqslant 1/2$. These numerical results are given in Table I where for fixed values of α and λ, the first line is $\theta_1(\alpha,\lambda)$, the second line $\theta_2(\alpha,\lambda)$ and the third one their sum, i.e., the total coverage $\theta(\alpha,\lambda)$.

These results also show that in spite of the important variation of $\theta_1(\alpha,\lambda)$ and $\theta_2(\alpha,\lambda)$ with λ, their sum $\theta(\alpha,\lambda)$ is slowly varying and always smaller than θ_1.

This has to be contrasted with the situation known for discrete lattices [7,9]. In order to emphasize this point, we consider deposited segments of arbitrary lengths L_1 and L_2, with $L_1<L_2$. We denote by $\theta(L_i)$ the asymptotic coverage for RSA of the single species L_i, and by $\theta(L_1L_2,\lambda)$ the asymptotic coverage for RSA of the L_1-L_2 mixture, the probability λ corresponding to L_1 and $1-\lambda$ to L_2. In the

TABLE I. Numerical values of the asymptotic coverages. For fixed values of α and λ, the first line is $\theta_1(\alpha,\lambda)$, the second line $\theta_2(\alpha,\lambda)$, and the third one is their sum, i.e, the total coverage $\theta(\alpha,\lambda)$.

$\lambda\rightarrow$ $\downarrow\alpha$	0.1	0.3	0.5	0.7	0.9
	0.664	0.509	0.361	0.215	0.071
0.9	0.074	0.222	0.371	0.522	0.672
	0.738	0732	0.732	0.737	0.744
	0.660	0.504	0.357	0.213	0.071
0.8	0.072	0.219	0.368	0.519	0.671
	0.732	0.723	0.725	0.732	0.742
	0.656	0.502	0.356	0.214	0.071
0.7	0.070	0.214	0.363	0.515	0.670
	0.726	0.716	0.719	0.729	0.741
	0.655	0.502	0.378	0.216	0.072
0.6	0.066	0.206	0.354	0.509	0.668
	0.720	0.707	0.712	0.725	0.740
	0.654	0.504	0.362	0.219	0.074
0.5	0.061	0.194	0.341	0.500	0.666
	0.715	0.698	0.702	0.719	0.740

continuum case, scale invariance of the coverage implies $\theta(L_1)=\theta(L_2)=\theta_1$ and $\theta(L_1,L_2,\lambda)=\theta(L_1/L_2,1,\lambda)=\theta(\alpha,\lambda)$ with $\alpha=L_1/L_2$. We have obtained in addition that $\theta(L_1,L_2,\lambda)\leqslant\theta_1$ and that $\theta(L_1,L_2,\lambda=0)=\theta(L_1,L_2,\lambda=1)=\theta_1$. In the discrete case, the lengths L_1 and L_2 measured in lattice spacing units are integers and $\theta(L_1)>\theta(L_2)$. For example, $\theta(0)=1$ (the monomer deposition) and $\theta(\infty)=\theta_1$. In case of mixtures one finds [9] $\theta(L_1,L_2,\lambda)\geqslant\theta(L_1,L_2,\lambda=1)=\theta(L_1)>\theta(L_2)$ for any value of the probability λ, including the limit $\lambda=0$, which indicates that $\theta(L_1,L_2,\lambda=0)$ is strictly greater than $\theta(L_2)$.

Arbitrary mixtures thus cover the lattice more efficiently than either of species. It is exactly the opposite in the continuous model. For the lattice case, the increase of the coverage is due to the smallest particles that fill the gaps in a better way. For the continuous model, the smallest particles seem to work in an opposite fashion. This feature is well understood by observing the behavior of the coverage when $\alpha=0$, which corresponds to RSA of a mixture of pointlike particles and segments of fixed length (on a lattice one obtains full coverage). In this case the solution of the rate equations is very simple to obtain and is $P(\alpha,t)=e^{-\lambda t}g^{\mu}(t)$, which implies that $\theta_1(\alpha,\lambda)=\mu\int_0^\infty e^{-\lambda t}g^{\mu}(t)dt$ and $\theta_2(\alpha,\lambda)=0$, in agreement with the particular scaling limit considered in Ref. [8]. Pointlike particles do not contribute to the total coverage, but once adsorbed they forbid some depositions of the large size particles. They affect the deposition process is such that the total coverage decreases as the population of pointlike particles increases: one finds, for example, that $\theta(\alpha=0,\lambda)=\{0.67,0.55,0.42,0.27,0.1\}$ when $\lambda=\{0.1,0.3,0.5,0.7,0.9\}$, respectively.

In conclusion, one can say from our numerical results that this mechanism persists for any value of α, and that the total coverage in the continuum is always smaller than it is with only one species.

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