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Generalized random sequential adsorption in one dimension

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Abstract. The process of random sequential adsorption in one dimension is generalized so that the rate at which a particle is placed in an empty space is dependent on the size of the space being destroyed and on the sizes of the two spaces created on either side of the particle. We write down the equation for this process involving $p(z)$, the probability of choosing to deposit a particle of size z, and $F(x, y|z)$, the rate at which spaces of length x and y are created from a space of length $x+y+z$, given that a particle of size z is deposited. A scaling theory is given for this process and solutions are presented for two special cases. The results of a numerical simulation of a third case are presented.

1. Introduction

When particles are deposited irreversibly onto a surface there are two characteristic time scales: the time between depositions, t_d, and the time taken for the particles on the surface to reorganize, t_r. If $t_d \gg t_r$, the particles on the surface have time to move around between depositions and the distribution of particles on the surface is an equilibrium distribution. Conversely, if $t_d \ll t_r$ the particles are effectively fixed in position once deposited, there is a non-equilibrium distribution of particle positions and the kinetics are described by the process of random sequential adsorption (RSA). It is the latter situation with which this paper is concerned.

Random sequential adsorption is one of the simplest ways in which one can study deposition phenomena. In each time step a position for the deposition of a particle is chosen at random. If the chosen position is vacant, i.e. no particle deposited previously occupies or overlaps it, then the new particle is placed in the chosen position. If the particle cannot be placed then no deposit is made, the time step is over and a new position is chosen for the next possible deposit. This process is analysed by looking at the evolution with time of the fraction of the surface covered ('the coverage') and the distribution of the spaces between the particles. For a review of the literature on RSA models, see [1, 2].

RSA captures the behaviour of many experimental systems: the adhesion of proteins and colloidal particles to uniform surfaces [3, 4], the reaction of various polymer chain systems such as methyl vinyl ketone [5], the formation of irregular conducting channels in cellular material [6] and the adsorption of non-ionic surfactants [7] are just a few.

Perhaps the most interesting feature of RSA is the highly irreversible nature of the kinetics—once a particle has been placed it is fixed for all time and will influence all subsequent attempted placements. It is this non-equilibrium, irreversible behaviour which makes many of the techniques developed for equilibrium statistical mechanics redundant.

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If the particles being deposited are of finite size then, obviously, after a certain amount of time the surface will become full and no particle can be deposited in the spaces that remain. The surface is then said to be jammed or saturated. The packing of the particles in this limit is very different from that of equilibrium close packing.

The wide range of experimental systems to which these models can be applied is reflected by the large number of possible models; objects of dimension D can be deposited onto a surface of dimension d provided that $D \leqslant d$. The 'surface' can be a continuum or a lattice.

The one-dimensional continuum model, which has been solved analytically [8, 9], is called the random car-parking problem. The cars are of unit length and the road is infinitely long. When the road is full all the gaps between the cars are less than unit length so that no further cars can be deposited on the line.

The one-dimensional lattice model [5, 10, 11] can also be solved exactly. In this model k-mers are adsorbed onto a line until all the spaces of size k or more are occupied, i.e. all the spaces which remain are less than or equal to $k-1$ lattice sites long. This model has been applied successfully to various polymer chain systems [5]. The results are qualitatively very similar to those obtained for the one-dimensional continuum model. In the limit $k \to \infty$ the continuum model can be recovered from the discrete model after suitable rescaling of the variables [12].

The placing of an object on a line divides the system into two independent systems which can be treated separately. It is this property, which obviously does not exist in two or more dimensions, that has made analytical progress in one dimension possible. Attempts have been made to bridge the gap between one- and two-dimensional problems by introducing a set of hierarchical rate filling equations [13, 14] or by examining the problem on a Bethe lattice [15]. Unfortunately, these have not led to the solution of a two-dimensional problem and nearly all other studies have been numerical. On the lattice the coverage has been examined for different shapes [16, 17] and for squares of different sizes [18, 19]. In the continuum there are more possibilities: needle-like objects have been considered [20] for which there is no jamming limit, as it is always possible to place another needle. Finite-sized shapes, for which the coverage is well defined, have also been examined on a continuum [21, 22].

In this paper we generalize the normal RSA continuum process so that the rate at which a particle is placed in a vacant position is dependent on the size of the empty space being destroyed and on the sizes of the two empty spaces created on either side of the particle. In section 2 this model is introduced and in section 3 a scaling theory is given for the case of a mixture of particle sizes being deposited with a power-law rate of deposition. Section 4 contains the exact solution of two models in which the particle is always deposited in the centre of an empty space. The models differ in the rate at which this occurs. In section 5 the results of two numerical simulations are compared: one, the standard 'random car-parking problem', and the other a model in which the rate of deposition is quadratic with a maximum at the centre of the empty space. The final section contains some conclusions concerning this work and some ideas for future studies.

2. The model

The concentration $c(x, t)$ of spaces of size x at time t obeys the integro-differential equation

$$\frac{\partial c(x,t)}{\partial t} = -c(x,t)\int_0^x \mathrm{d}z\, p(z)\int_0^{x-z}\mathrm{d}y\, F(x-y-z,y|z)$$
$$+2\int_x^\infty \mathrm{d}y\, c(y,t)\int_0^{y-x}\mathrm{d}z\, p(z)F(x,y-x-z|z) \tag{1}$$

where $p(z)$ is the probability of attempting to deposit a particle of size z. $F(x,y|z)$ is the rate with which a space of $x+y+z$ is destroyed by the placement of a particle of size z creating two spaces x and y, given that it is a particle of size z that is to be deposited. The first term in equation (1) represents the destruction of spaces of size x and the second their creation from spaces of size y. If one chooses $F(x,y|z)=1$ then (1) reduces to the standard RSA equation [9]. If one takes zero-length particles, $(p(z)=\delta(z))$, then (1) becomes the standard binary fragmentation equation [23].

3. Scaling theory

A scaling theory for this process can be developed by considering the deposition of a mixture of different sized particles. This can be achieved by choosing $p(z)$ as

$$p(z)=\begin{cases}\gamma z^{\gamma-1} & z>1\\ 0 & z>1\end{cases} \tag{2}$$

where, to ensure that $p(z)$ is normalized, we take $\gamma>0$. We also need to define $F(x,y|z)$ as

$$F(x,y|z)=(x+y+z)^\beta \tag{3}$$

where β can take any value. Following the method of Krapivsky [9], who solved this problem for $F(x,y|z)=1$ (or $\beta=0$), we write equation (1), for $x<1$, as

$$\frac{\partial c(x,t)}{\partial t} = -c(x,t)\frac{x^{\gamma+\beta+1}}{\gamma+1}+2\int_x^\infty \mathrm{d}y\, c(y,t)y^\beta(y-x)^\gamma. \tag{4}$$

In the integral we have replaced 1 with $(y-x)^\gamma$ for $y-x>1$. This approximation is good in the scaling region we are about to identify.

We can obtain an equation for the αth moment $M_\alpha(t)$, defined by

$$M_\alpha(t)=\int_0^\infty x^\alpha c(x,t)\,\mathrm{d}x \tag{5}$$

by multiplying (4) by x^α, integrating with respect to x, and then rearranging. Notice that, whilst (4) is only valid for $x<1$, we integrate between 0 and ∞ to obtain $M_\alpha(t)$. This is possible because the contribution to the moments from the spaces with $x>1$ is negligible in the scaling region. These manipulations yield

$$\frac{\mathrm{d}M_\alpha(t)}{\mathrm{d}t}=\left[\frac{2\Gamma(\alpha+1)\Gamma(\gamma+1)}{\Gamma(\alpha+\gamma+2)}-\frac{1}{\gamma+1}\right]M_{\alpha+\beta+\gamma+1}(t). \tag{6}$$

The scaling hypothesis for the distribution of empty spaces can be written as

$$c(x, t) \approx S^{-\theta}(t)\Phi(x/S(t)) \tag{7}$$

where

$$S(t) \approx t^{-z} \qquad \text{when } t \gg 1. \tag{8}$$

The scaling regime is then described by $x \ll 1$, $t \gg 1$, but with $\xi = x/S(t)$ remaining finite. We now see that the approximations made in obtaining the moment equation (6) are valid in this region. The moments $M_\alpha(t)$ are connected to the scaling function via

$$M_\alpha(t) = S^{1+\alpha-\theta}(t) \int_0^\infty d\xi\, \xi^\alpha \Phi(\xi). \tag{9}$$

The exponent θ can now be determined; it is given by $\theta = 1 + \alpha^*$, where α^* is the moment of $c(x, t)$ which is time-independent. By looking at (6) we see that α^* is given by

$$\frac{1}{\gamma+1} = 2\frac{\Gamma(\alpha^*+1)\Gamma(\gamma+1)}{\Gamma(\alpha^*+\gamma+2)}. \tag{10}$$

This equation has been obtained previously [9], when it was noted that for $\gamma > 0$ there is only one solution for α^*, that furthermore $\alpha^*(\gamma) < 1$ and hence that $\theta < 2$. It is perhaps a little surprising that α^* does not depend on β. The second exponent can be obtained by inserting the scaling form (7) into the kinetic equation (4) and separating variables. After some simple manipulations this gives the exponent z as

$$z = \frac{1}{\beta+\gamma+1}. \tag{11}$$

We need to impose the condition $\beta + \gamma + 1 > 0$ in order to keep z positive. When this inequality is violated a singularity occurs in the scaling solution which is the analogue of the shattering transition in fragmentation models. Combining the results for the two exponents together gives the coverage for large times as

$$\theta(t) = 1 - At^{-(1-\alpha^*)/(\beta+\gamma+1)} \tag{12}$$

where α^* is given by (10) and A is a time-independent constant. All initial conditions give rise to this behaviour in the scaling limit with $F(x, y|z)$ given in (3).

4. Solutions

In this section we present two solutions for the deposition of particles of size 1 on a line. This means that we take $p(z) = \delta(z-1)$ and the kinetic equation (1) becomes

$$\frac{\partial c(x, t)}{\partial t} = -c(x, t)\theta(x-1) \int_0^{x-1} dy\, F(x-y-1, y) + 2\int_{x+1}^\infty dy\, c(y, t)F(x, y-x-1). \tag{13}$$

In this section we will drop the third argument in F—it is redundant for problems where the particle sizes are monodisperse. At this point it is useful to make the following remark about systems of this type; when two models have rates $F(x, y)$ which differ only by a multiplicative function of $x+y$, they have the same saturated state, but, in general, different kinetics. This means that all systems with $F(x, y)=g(x+y)$ have the same saturated state; similarly, all systems with $F(x, y)=f(x+y)\delta(x-y)$.

We will present exact analytical solutions for two different systems where the particle is always deposited in the middle of the vacant space, i.e. where $F(x, y)$ is given by

$$F(x, y)=f(x+y)\delta(x-y). \tag{14}$$

In particular, we solve the cases where $f(x)=1$ (model A) and $f(x)=x$ (model B). As we indicated in the previous paragraph, both these systems have the same saturated state; the difference between them arises from the kinetics of the process leading up to that state.

Model A

Taking the $F(x, y)$ in equation (14) with $f(x)=1$, and solving equation (13) via a generating function method, subject to the initial condition $c(x, 0)=\delta(x-L)/L$, where L is the length of the line at $t=0$, yields

$$c(x, t)=\begin{cases}\dfrac{1}{L}\dfrac{\delta(x-\omega_N)}{(N-1)!}\displaystyle\int_0^t d\tau\, e^{-\tau/2}\tau^{N-1} & 0<x<1 \\ \dfrac{e^{-t/2}}{L}\displaystyle\sum_{r=0}^{N-1}\frac{t^r}{r!}\delta(x-\omega_r) & 1<x<L\end{cases} \tag{15}$$

where N is determined via the relation

$$N=\operatorname{int}\left\{\frac{\log(L+1)}{\log 2}\right\} \tag{16}$$

and is simply the number of 'generations' of the deposition process. The constants $\{\omega_k, k=1, 2, \ldots, N\}$ are given by

$$\omega_k=\frac{L+1}{2^k}-1. \tag{17}$$

The coverage, defined by

$$\theta(t)=1-\int_0^\infty dx\, x\, c(x, t) \tag{18}$$

is given by

$$\theta(t)=\frac{1}{L}\left\{\frac{2^N}{(N-1)!}\int_0^{t/2} du\, e^{-u}u^{N-1}+e^{-t/2}\sum_{r=0}^{N-1}\frac{t^r}{r!}-1\right\} \tag{19}$$

which taking the limit $t\to\infty$ gives

$$\theta(\infty)=\frac{2^N-1}{L}. \tag{20}$$

Hence, using (16), the coverage in the saturated state oscillates between 0.5 and 1 as L increases, with discontinuities at $L=2^N-1$, where $n=0, 1, 2, \ldots$. We can expand $\theta(t)$ for small t to reveal that $\theta(t)\sim t/2L$.

Model B

This model is defined by (13) and (14) with $f(x)=x$. The resulting kinetic equation is more difficult to solve than that for model A. However we can again adopt a generating function method, giving a solution for $c(x, t)$ as

$$c(x, t)=\frac{2}{L}A_{N-1}\omega_N\delta(x-\omega_N)\sum_{s=1}^{N}c_s^{N-1}\frac{(1-e^{-\omega_s t})}{\omega_s} \qquad x<1$$

and

$$c(x, t)=\frac{1}{L}\{e^{-\omega_1 t}\delta(x-L)+\sum_{k=1}^{N-1}A_k\delta(x-\omega_k)\sum_{s=1}^{k+1}c_s^k e^{-\omega_s t}\} \qquad 1<x<L. \tag{21}$$

The coefficients $\{c_s^k\}$ are given by the recursion relations

$$c_s^k=-\frac{c_s^{k-1}}{2^{k+1-s}-1} \tag{22}$$

for $k=2, \ldots, N-1$ and $s=1, \ldots, k$ and

$$c_{k+1}^k=\sum_{s=1}^{k}\frac{c_s^{k-1}}{2^{k+1-s}-1} \tag{23}$$

with initial conditions

$$c_2^1=-c_1^1=1. \tag{24}$$

The coefficients $\{A_k\}$ are given by

$$A_k=\prod_{r=1}^{k}\frac{4\omega_r}{\omega_r+1}. \tag{25}$$

The expression for $c(x, t)$ gives the coverage at time t as

$$\theta(t)=\frac{1}{L}\left\{2A_{N-1}\omega_N\sum_{s=1}^{N}\frac{c_s^{N-1}(1-e^{-\omega_s t})}{\omega_s}+e^{-\omega_1 t}+\sum_{k=1}^{N-1}A_k\sum_{s=1}^{k+1}c_s^k e^{-\omega_s t}-1\right\} \tag{26}$$

which in turn gives the saturation coverage in equation (20). We can also look at the approach to the saturation coverage, where a simple analysis reveals

$$\theta(\infty)-\theta(t)\approx\exp\left(-\left[\frac{L+1}{2^N}-1\right]t\right). \tag{27}$$

This indicates that in the jamming limit the kinetics are controlled by the destruction of the smallest-sized empty spaces it is possible to destroy; those of size $(L+1)2^{-N}-1$. For small t the behaviour of $\theta(t)$ is different to that in model A, with $\theta(t)\sim(L-1)t/2L$. This means that for $L\gg1$, $\theta(t)\sim t/2$, independent of L.

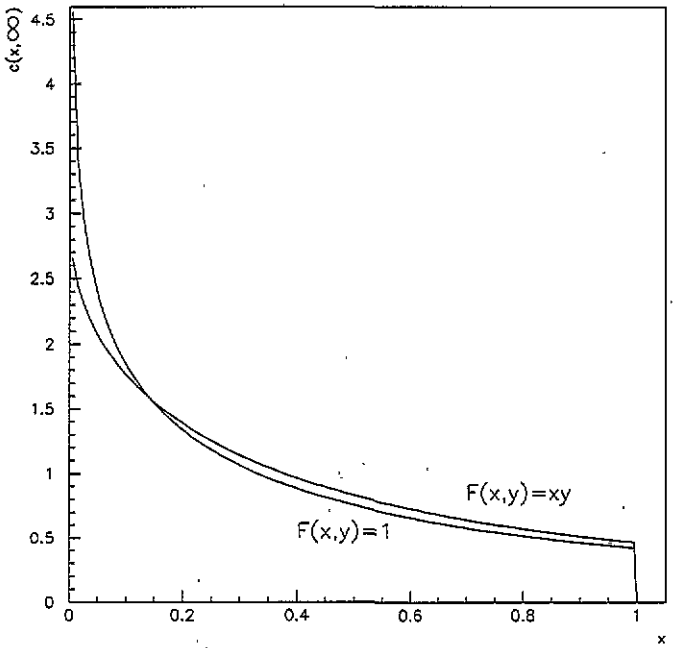

Figure 1. The distribution of empty spaces in the jamming limit for $p(z)=\delta(z-1)$ for (*a*) $F(x, y)=1$ and (*b*) $F(x, y)=xy$.

5. Numerical work

We have performed numerical simulations of two systems where the deposited particles are all of the same size ($p(z)=\delta(z-1)$). For both systems the distribution of gaps in the jamming limit is shown in figure 1. The $F=1$ model is the standard continuum RSA model and gives a saturation coverage of 0.747 .... The second system, $F(x, y)=xy$, is one which we attempted, unsuccessfully, to solve analytically. As figure 1 illustrates, it has a different distribution of gaps in the jamming limit to the standard model and has a saturation coverage of 0.732 ....

6. Conclusions

We have generalized the standard continuum RSA model in one dimension so that we can deal with problems in which the particles are placed onto a line at a general rate which depends on the size of the empty space available and the position the particle takes within it. This means that we can study problems in which a particle is more likely to be placed in the middle of an empty space than at the edges. This is the physically more relevant case; any amount of repulsion between particles produces this effect. Two problems in which the particles are always placed in the centre of the empty space have been solved exactly. We have also developed a scaling theory for the deposition of a mixture of particles with a particular deposition kernel. We found that whilst the exponent z depended on the rate of deposition, the exponent θ was independent of the rate. Finally, we used a numerical simulation to exhibit the difference between two systems in which particles of the same size were deposited, but with different deposition rates. We found, as would have been expected, that the saturation

coverage was smaller for the system that preferred to place particles in the centre of an empty space.

The ideas developed in this paper could be taken further by looking for analytical solutions for other rates $F(x, y|z)$, such as $(x+y+z)^{\nu}$, $(x+y)^{\nu}$ and $(xy)^{\nu}$. Models such as these are more closely related to real physical systems and as such are of more interest to experimentalists.

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