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Random sequential adsorption on a dashed line

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Abstract. We study analytically and numerically a model of random sequential adsorption (RSA) of segments on a line, subject to some constraints suggested by two types of physical situation: (i) deposition of dimers on a lattice where the sites have a spatial extension and (ii) deposition of extended particles which must overlap one (or several) adsorbing sites on the substrate. Both systems involve discrete and continuous degrees of freedom and, in one dimension, are equivalent to our model which depends on one length parameter. When this length parameter is varied, the model interpolates between a variety of known situations: monomers on a lattice, the 'car parking' problem and dimers on a lattice. An analysis of the long time behaviour of the coverage as a function of the length parameter exhibits a $1/t^2$ approach to the jamming limit at the transition point between the fast exponential kinetics, characteristic of the lattice model, and anomalous to the $1/t$ law of the continuous model.

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1. Introduction

The model of random sequential adsorption (RSA) describes deposition processes in which desorption is negligible and surface diffusion is very slow on the experimental time scale. Particles land successively and randomly on the surface; if an incoming particle overlaps a previously deposited one it is rejected as a result of the geometrical exclusion effect. This model applies to many physical situations such as adsorption of latex balls, proteins or chemisorption at a low temperature [1]. The substrate is either a lattice or a continuous surface, depending on the size of the particles relative to the microscopic scale. Many versions of the model have been studied so as to adapt it to various physical situations, but all share a common universal behaviour for the long time approach to the asymptotic coverage depending on the discrete or continuous nature of the substrate. As long as the minimum interval between two neighbouring particles on the substrate remains non-zero, which is the case on a lattice, one can show that the jamming limit is approached exponentially [1, 2]. Conversely, on a continuum substrate the kinetics follow a power-law decay with an exponent that depends on the number of degrees of freedom per particle [3–11]. For instance, in the one-dimensional case where the model is exactly soluble we have

$$\theta_k(t) = \theta_k(\infty) - A(k)\mathrm{e}^{-\phi t}$$

for the deposition of k-mers on a lattice with flux ϕ, whereas

$$\theta(t) = \theta(\infty) - A/t$$

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for the continuous 'car parking' problem [12].

In fact, at the mesoscopic scale many physical situations involve both continuous and discrete degrees of freedom. For example, with the recent advances in nano-technologies it is conceivable to realize a lattice of small gold droplets deposited on a silicon surface [13]. The adsorption on this substrate of elongated particles (polymers) with lengths that are of the order of the distance between two gold dots can be modelled by the adsorption of dimers [14]. However, since the size of the gold dots (typically some nanometres in radius) is not negligible with respect to the length of the particles, there will be a continuous range of positions for the dimer to be fixed on two neighbouring dots.

Alternatively, large particles like proteins or enzymes can be absorbed on a latticized substrate. Such a physical situation is described in [15] and modelled in the following way. Adsorbing sites are randomly or regularly disposed on a continuum substrate; extended particles, represented by disks, land on the surface but remain stuck only if they overlap one, or several, adsorbing sites. Here the deposition process is again driven by the discrete degree of freedom imposed by the location of the sites, and by a continuous degree of freedom associated with the position of the adsorbed particle with respect to the site.

In this paper, we investigate a one-dimensional RSA model which involves both discrete and continuous degrees of freedom. We show that the two physical situations mentioned above, when reduced to a one-dimensional substrate, are equivalent to our model. In section 2 we present the model and analyse its jamming limit using the result of a numerical simulation. Section 3 is devoted to an analysis of the long time behaviour of the coverage as derived from the master equations of the model. Our results and the conclusions are summarized in section 4. The appendices contain the technical details of the derivation of the master equations (appendix A) and of their solution (appendix B).

2. The model

2.1. Two equivalent one-dimensional models

Consider the first example depicted in the introduction. This can be considered as a generalization of the lattice dimer model in which the lattice sites have a non-zero extension which we set to unity. In the deposition process the dimer ends must stick on this *discrete* set of *continuous* intervals, the situation where a given interval contains both the end of one dimer and the origin of another now being allowed (see figure 1(a)). Moreover, the dimer length is no longer constrained to be equal to the lattice spacing, but is arbitrary within bounds compatible with these adsorbing rules, thereby introducing a new length scale. We denote the edge-to-edge distance between two neighbouring sites by a. The dependence of the model on this parameter occurs only in a trivial redefinition of the effective flux of incoming particles. Therefore, the model is independent of a provided that we impose the condition that a deposited particle overlaps an inter-site interval. The length ℓ of the dimer lies in the interval $[a, a+2]$. We set $\ell = a + r$, where $r \in [0, 2]$ will be the unique parameter of the model. This model corresponds to RSA of dimers on a *dashed line* and in the following we will refer to it as model (I).

Consider now the second example in the introduction where the adsorbing sites are regularly disposed and the radius of the particles is smaller than the inter-site distance. In one dimension the substrate is a regular lattice, the particle is a segment of length $r < 2$ lattice units and the adsorbing rule, aside from the RSA rules, is that the segment must cover a site (see figure 1(b)). This model corresponds to RSA of segments on a *dotted line* and in the following we will refer to it as model (II).

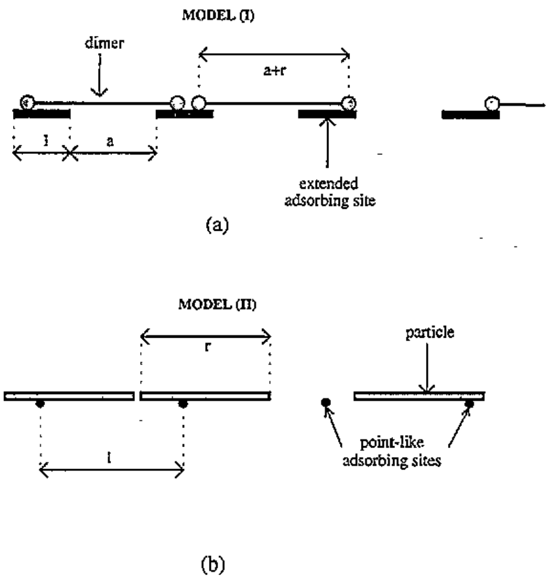

Figure 1. (*a*) Description and parametrization of model (I): deposition of dimers on extended adsorbing sites (*dimers on a dashed line*). (*b*) Description and parametrization of model (II): deposition of segments on localized adsorbing sites (*segments on a dotted line*).

For $r \leqslant 1$ the two models are exactly equivalent: let the inter-site interval in model (I) be identified with the adsorbing site of model (II) (see figure 1). Then, the rule of model (I) that a deposited particle must overlap an inter-site interval is equivalent to the adsorbing rule of model (II). For $r > 1$ the constraint imposed in model (I) on the position of the particle by the rule that both ends of the dimer must stick on adjacent sites appears in model (II) by requiring that a deposited particle cannot overlap two sites.

In what follows we will consider the one-dimensional model from this point of view and from now on everything will refer to model (II).

2.2. *The jamming limit*

The constraint that a deposited particle must overlap one and only one adsorbing site only modifies the incoming flux ϕ by a multiplicative factor of r for $r < 1$ and $2-r$ for $r > 1$. We define the occupancy rate θ as the fraction of occupied sites. The covering of the whole substrate is $r\theta$.

The jamming limit for this quantity, obtained from a numerical simulation, is presented in figure 2 as a function of r. Let us first analyse this curve qualitatively. Clearly, for $r \leqslant \frac{1}{2}$ the adsorption of a particle on the site i, regardless of its position on the site, cannot prevent the deposition on neighbouring sites. Therefore, each site will be occupied independently of its neighbours and the model is completely equivalent to the deposition of monomers on a lattice; we expect the asymptotic limit $\theta = 1$ to be reached exponentially fast.

Consider now for the site i the most unfavourable situation in the case $r < 1$, (figure 3(*a*)), where the site $i-1$ is occupied by the extreme left edge of a particle and the site $i+1$ by the extreme right edge of another particle. In this situation the interval for a deposition at site i is minimum and has extension $2(1-r)$. The deposition is allowed if $2(1-r) > r \Longleftrightarrow r < \frac{2}{3}$. Therefore, for $r < \frac{2}{3}$, we still expect a coverage of *all* the sites, which is effectively observed in figure 2 where $\theta(t=\infty) = 1$ up to $r = \frac{2}{3}$. Furthermore, since in this r-interval the smallest target has a non-zero extension, the kinetics must remain lattice-like and the jamming limit is again approached exponentially fast.

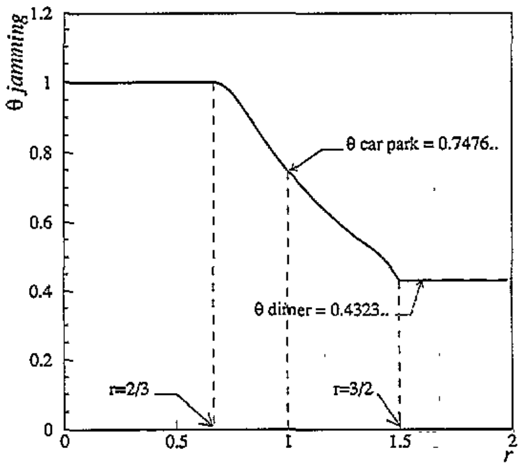

Figure 2. The jamming limit of the model as a function of the length r of the adsorbed segments. The values of r separating the different regimes are indicated.

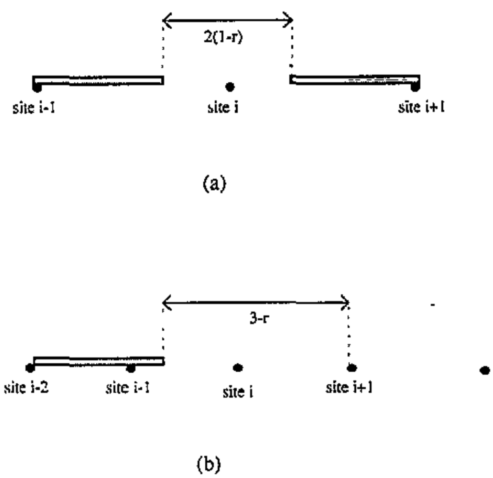

Figure 3. Two extreme situations for the deposition in model (II).

Conversely, consider now the most favourable situation in the case $r > 1$ (figure 3(*b*)) where the particle deposited on the site $i-1$ has its extreme left edge close to site $i-2$. The space remaining to adsorb a particle on site i has extension $3-r$. If this interval is less than r ($\Rightarrow r > \frac{3}{2}$), deposition is impossible and the particle at site $i-1$ *effectively occupies two sites*†. In this situation, for $r > \frac{3}{2}$, the model is completely equivalent to the lattice dimer model [16] and one expects $\theta(t=\infty) = (1-\mathrm{e}^{-2})/2 = 0.432\,33\ldots$ (see figure 2).

Between these two extreme cases, for $\frac{2}{3} \leqslant r \leqslant \frac{3}{2}$, the asymptotic occupancy rate $\theta(t=\infty)$ decreases continuously. Furthermore, since the target intervals for a particle deposition can be arbitrarily small, one expects a power-law dynamics characteristic of a *continuous* model. The case $r = 1$ is special: the particle length matches exactly the inter-site distance and the constraint for a landing particle to overlap one and only one adsorbing site is automatically satisfied; the discrete nature of the substrate no longer plays any role and we recover the 'car parking' problem [12] with jamming limit $\theta = 0.747\,597\ldots$.

† This result is more clearly seen in the framework of model (I).

3. The long time behaviour of the coverage

3.1. The master equations

We have derived the master equations for the time evolution of the probability of finding at time t a gap of given length. All the technical details are given in appendix A. The result is that the coverage $\theta(t)$ can be expressed in terms of a reduced probability $P(x,t)$:

$$\theta(t) = \int_0^t \mathrm{d}t'\, \mathrm{e}^{rt'} \int_0^r \mathrm{d}x\, P(x,t')P(r-x,t') \qquad \text{for } r \in [0,1] \tag{1}$$

$$= \int_0^t \mathrm{d}t'\, \mathrm{e}^{(2-r)t'} \int_{r-1}^1 \mathrm{d}x\, P(x,t')P(r-x,t') \qquad \text{for } r \in [1,2] \tag{2}$$

where $P(x,t)$ is the solution of the following integral equation:

case $r \leqslant 1$, $x \in [0,r]$

$$-\frac{\partial P(x,t)}{\partial t} = xP(x,t) + \int_x^r P(x',t)\,\mathrm{d}x' + u(x+r-1)\mathrm{e}^{-rt}\int_0^{x+r-1} P(x',t)\,\mathrm{d}x' \tag{3}$$

case $r \geqslant 1$, $x \in [r-1,1]$

$$-\frac{\partial P(x,t)}{\partial t} = (x-r+1)P(x,t) + \int_x^1 P(x',t)\,\mathrm{d}x' + \mathrm{e}^{-(2-r)t}\int_{r-1}^{b(x)} P(x',t)\,\mathrm{d}x' \tag{4}$$

subject to the initial condition $P(x,0) = 1$. In equation (3) $u(t)$ is the Heaviside step function and in the last integral of equation (4) $b(x) = \inf\{x+r-1, 1\}$.

These equations can be solved exactly in a few special cases corresponding to $r \leqslant \frac{1}{2}$, $r = 1$ and $r \geqslant \frac{3}{2}$, which are presented in the next section. For the generic case $\frac{1}{2} < r < \frac{3}{2}$ ($r \neq 1$), we have devised an iterative construction of the general solution which is developed in appendix B and which leads to the following result.

As a result of the last term in equations (3) and (4), $P(x,t)$ appears to be piecewise defined with respect to x in successive intervals of length $(1-r)$ within the range $(0,r)$ for $r \leqslant 1$, or of length $(r-1)$ within the range $(r-1, 2-r)$ for $r \geqslant 1$. The number of intervals thus depends on the value of r and is given by (see appendix A)

$$\begin{aligned} k &= \left[\frac{r}{1-r}\right] + 1 \qquad \text{for } \tfrac{1}{2} < r < 1 \\ k &= \left[\frac{2-r}{r-1}\right] + 1 \qquad \text{for } 1 < r < \tfrac{3}{2} \end{aligned} \tag{5}$$

where $[X]$ denotes the integer part of X.

The function $P_\ell(x,t)$ which coincides with $P(x,t)$ in the ℓth interval is expressed in terms of a unique x-independent function $q(t)$:

$$\begin{aligned} P_\ell(x,t) &= q(t) + \int_0^t K_\ell(x,t|t')q(t')\,\mathrm{d}t \qquad 2 \leqslant \ell \leqslant k \\ P_1(x,t) &\equiv q(t) \end{aligned} \tag{6}$$

where the kernels $K_\ell(x,t|t')$ are constructed recursively. The function $q(t)$ is itself a solution of a linear integral equation

$$q(t) = u_0(t)\left\{1 + \int_0^t \rho_k(t,t')q(t')\,\mathrm{d}t'\right\} \tag{7}$$

where $u_0(t)$ is defined by

$$u_0(t) = \mathrm{e}^{-rt} \qquad \tfrac{1}{2} < r < 1$$
$$u_0(t) = \exp\left[\mathrm{e}^{-(2-r)t} - (2-r)t - 1\right] \qquad 1 < r < \tfrac{3}{2}$$

and the kernels ρ_k are expressed in terms of K_ℓ.

Even in the simplest case, $k = 2$, we are unable to find analytic solutions of equation (7). However, from these expressions we can extract both approximate solutions and the exact asymptotic behaviour for the dynamics of the model which allow us to understand the various regimes which interpolate between the special cases depicted in section 3.2. This is the object of the following sections.

3.2. Special cases

There are three special cases where the rate equations (3) and (4) reduce to a simple form which is exactly solvable.

(i) $0 \leqslant r \leqslant \frac{1}{2}$. The number of intervals k is equal to one (see equation (5)). Equation (3) yields directly $P(x,t) \equiv \mathrm{e}^{-rt}$ and $\theta(t) = 1 - \mathrm{e}^{-rt}$ which is, as expected, the exact result for the deposition of monomers on a lattice up to a factor r in the flux corresponding to the target area for each deposition. The limit $r \to 0$ has to be taken carefully: first define through equation (1) a coverage $\hat{\theta}$ as a function of a rescaled time $T = rt$ and then let r tend to zero at fixed T.

(ii) $r = 1$. The two rate equations (3) and (4) become identical. By means of the *ansatz* $P(x,t) = \mathrm{e}^{-xt} q(t)$, we get

$$q(t) = \exp - \int_0^t \frac{1 - \mathrm{e}^{-t'}}{t'}\,\mathrm{d}t'.$$

Through equation (1) we recover the well known 'car parking' solution [1, 12].

(iii) $\frac{3}{2} \leqslant r \leqslant 2$. There is again only one interval. From the rate equation we get directly

$$P(x,t) \equiv u_0(t) = \exp\left[\mathrm{e}^{-(2-r)t} - (2-r)t - 1\right]$$

and

$$\theta(t) = (2-r)\int_0^t \mathrm{d}t'\,\mathrm{e}^{(2-r)t'} u_0^2(t') = \tfrac{1}{2}\left[1 - \exp[-2 + 2\mathrm{e}^{-(2-r)t}]\right]$$

which is exactly the lattice dimer solution up to a factor $\frac{1}{2}$ due to our definition of θ. The limit $r \to 2$ has to be considered, like the $r \to 0$ limit, as a scaling limit with respect to the rescaled time $T = (2-r)t$.

3.3. The case $\frac{1}{2} < r \leqslant \frac{2}{3}$

According to equation (5) this is the interval (for $r < 1$) corresponding to the lowest non-trivial value $k = 2$. There are only two reduced probabilities, $q(t)$ and $P_2(x,t)$. The function $\rho_2(t,t')$ of equation (7) is given by

$$\rho_2(t,t') = \frac{\mathrm{e}^{(2r-1)(t-t')} - 1}{t - t'} - (2r - 1)$$

and $K_2(x, t|t')$ of equation (6) by

$$K_2(x, t|t') = \mathrm{e}^{-rt'} \frac{\mathrm{e}^{-x(t-t')} - \mathrm{e}^{-(1-r)(t-t')}}{t - t'}$$

(see appendix B). After some elementary algebra based on the integral representation equation (6), one gets from equation (1) a very simple expression for θ:

$$\theta = 1 - q^2(t)\mathrm{e}^{rt}. \tag{8}$$

We obtain the exact asymptotic behaviour of the coverage in the following way. From the inequality $0 \leqslant q(t) \leqslant 1$ and equation (7) it follows that $q(t) < C\mathrm{e}^{-(1-r)t}/t$ which implies that the functions

$$C_n(x, t) = \int_0^t \mathrm{e}^{-(r-x)t'} q(t') t'^n \, \mathrm{d}t'$$

have a positive, finite, $t \to \infty$ limit for all $n \geqslant 0$ and for all $x \in [0, r]$. We denote these functions $C_n(x)$. Expanding the denominator of the kernel $\rho_2(t, t')$ in powers of t'/t, we get from equation (7) the asymptotic expansion of $q(t)$ at large t:

$$q(t) = \frac{\mathrm{e}^{-(1-r)t}}{t} \left[C_0(1-r) + \frac{C_1(1-r)}{t} + \mathrm{O}\left(\frac{1}{t^2}\right) \right]. \tag{9}$$

Inserting this result in equation (8) we obtain for the coverage the asymptotic value $\theta(t = \infty) = 1$, as expected, with the approach

$$\theta(t) = 1 - C_0^2(1-r) \frac{\mathrm{e}^{-(2-3r)t}}{t^2} + \cdots. \tag{10}$$

This equation shows that the kinetics remain exponentially driven over the open interval $\frac{1}{2} < r < \frac{2}{3}$ but become $1/t^2$ at the end point $r = \frac{2}{3}$.

3.4. *The case* $\frac{2}{3} < r < \frac{3}{4}$

We have studied this case explicitly, where three x-intervals ($k = 3$) are involved, since we expect it to be typical of what happens over the remaining range $r < 1$.

Following the method of the previous section, we can derive for the reduced probabilities P_2 and P_3 the following large time behaviour:

$$P_2(x, t) = C_0(x, t) \frac{\mathrm{e}^{-xt}}{t} \left[1 + \mathrm{O}\left(\frac{1}{t^2}\right) \right]$$

$$P_3(x, t) = P_2(x, t) + \mathrm{O}\left(\frac{\mathrm{e}^{-(2r-1)t}}{t^2} \right)$$

whereas the asymptotic behaviour of $q(t)$ is still given by equation (9) in spite of it being defined from a different kernel ρ_3.

The time derivative of θ may be expressed in terms of the reduced probabilities as follows:

$$\dot{\theta}(t) = \mathrm{e}^{rt} \left\{ \int_{1-r}^{2r-1} P_2(x, t) P_2(r-x, t) \, \mathrm{d}x + 2q(t) \int_{2r-1}^{2(1-r)} P_2(x, t) \, \mathrm{d}x \right.$$
$$\left. + 2q(t) \int_{2(1-r)}^{r} P_3(x, t) \, \mathrm{d}x \right\}.$$

Inserting the previous asymptotic expansion in this expression we get

$$\dot{\theta}(t) = \frac{A}{t^2} + \frac{2B}{t^3} \tag{11}$$

where A and B are constants depending only on r. In particular

$$A = \lim_{t\to\infty} \int_{1-r}^{2r-1} C_0(x,t) C_0(r-x,t)\,\mathrm{d}x.$$

We see that, except at $r = \frac{2}{3}$ where A vanishes, the leading behaviour of θ is of the form

$$\theta(t) = \theta(\infty) - \frac{A}{t}. \tag{12}$$

We have checked this behaviour numerically for $r = 0.70$ by a simulation on a lattice of size $L = 10^4$ sites and up to times $t = 100$ (in units of number of deposition attempts per site). A plot of $t(\theta(\infty) - \theta(t))$ against t clearly exhibits a constant behaviour for times greater than 60, yielding for the constant A of equation (12) a value $A = 0.11$. We expect the long time behaviour of equation (12) to hold over the whole range up to $r = 1$ where it is proved. By reproducing our numerical simulation for $r = 0.9$ we obtain a perfect agreement with equation (12) with $A = 0.34$.

For $r = \frac{2}{3}$ we recover the result of the previous section:

$$\theta(t) = \theta(\infty) - \frac{B}{t^2}$$

which confirms that this unusual behaviour occurs only at this special value of r.

3.5. *The case* $\frac{4}{3} \leqslant r < \frac{3}{2}$

As in the previous section, this corresponds to the first non-trivial interval where $k = 2$ in the case $r > 1$. The kernels K_2 and ρ_2 are defined by

$$K_2(x,t|t') = \mathrm{e}^{-t'}\mathrm{e}^{(r-1)t}\frac{\mathrm{e}^{-x(t-t')} - \mathrm{e}^{-(2-r)(t-t')}}{t-t'}$$

$$\rho_2(t,t') = \mathrm{e}^{-(2-r)t'} \int_0^{t-t'} \frac{\mathrm{e}^{-(3-2r)t''}[1+(3-2r)t''] - 1}{t''^2} \exp\left[1 - \mathrm{e}^{-(2-r)(t'+t'')}\right] \mathrm{d}t''.$$

The expression for θ in terms of the reduced probability $q(t)$ is obtained from equation (2):

$$\theta = 1 - q^2(t)\mathrm{e}^{2(2-r)t} - (2-r)\int_0^t \mathrm{e}^{(2-r)t'} q^2(t')\,\mathrm{d}t'. \tag{13}$$

One observes that ρ_2 is negative, which implies the bound $0 < q(t) \leqslant u_0(t)$ and, from the mean-value theorem, the estimate

$$\rho_2(t,t') = \mathrm{e}^{-(2-r)t'} G(t-t') \left\{ \frac{1 - \mathrm{e}^{-(3-2r)(t-t')}}{t-t'} - (3-2r) \right\}$$

where

$$1 \leqslant \exp(1 - \mathrm{e}^{-(2-r)t'}) \leqslant G(t-t') \leqslant \exp(1 - \mathrm{e}^{-(2-r)t}) < \mathrm{e} = 2.718\ldots.$$

Inserting this result in equation (7) leads to the asymptotic time expansion of $q(t)$:

$$q(t) = e^{-(2-r)t}\left\{A(r) + \frac{B(r)}{t} + \cdots\right\}$$

where the bracket reduces to a constant when r goes to $\frac{3}{2}$. From equation (13) this shows that the jamming limit $\theta(\infty)$ is reached as $1/t$.

4. Summary and conclusions

We have studied a one-dimensional model of RSA with discrete and continuous degrees of freedom. The model depends on one length parameter r; when this parameter varies over the range $0 < r < 2$ the model goes through the following regimes.

(i) $0 < r \leqslant 1/2$. Monomer on a lattice; $\theta(t) = 1 - e^{-rt}$.

(ii) $\frac{1}{2} \leqslant r < \frac{2}{3}$. Total coverage; non-trivial lattice dynamics: $\theta(t) = 1 - Ae^{-(2-3r)t}/t^2$ for large t.

(iii) $r = 2/3$. Total coverage; anomalous continuous dynamics: $\theta(t) = 1 - A/t^2$ for large t.

(iv) $2/3 < r < 3/4$. Non-trivial asymptotic coverage; normal continuous dynamics: $\theta(t) = \theta(\infty) - A/t$ for large t.

(v) $r = 1$. 'Car parking' problem: $\theta(t) = 0.7476\cdots - A/t$ for large t.

(vi) $\frac{4}{3} \leqslant r \leqslant \frac{3}{2}$. Same as for $\frac{2}{3} < r < \frac{3}{4}$.

(vii) $\frac{3}{2} \leqslant r < 2$. Lattice dimer model; $\theta(t) = \frac{1}{2}\left[1 - \exp[-2 + 2e^{-(2-r)t}]\right]$.

(viii) $\frac{3}{4} < r < \frac{4}{3}$. Although we have not investigated this interval analytically (except for $r = 1$), we expect the same regime as in the bordering intervals $\frac{2}{3} < r < \frac{3}{4}$ and $\frac{4}{3} \leqslant r \leqslant \frac{3}{2}$ to hold, that is, a non-trivial asymptotic coverage decreasing with r and $1/t$ normal continuous dynamics. We have checked this conjecture numerically.

The remarkable point is that the kinetics of the model exhibit three 'phases': for $0 \leqslant r < \frac{2}{3}$ where it is lattice-like, for $\frac{2}{3} < r < \frac{3}{2}$ where it is continuous and for $\frac{3}{2} \leqslant r \leqslant 2$ where it is lattice-like again. At the transition point $r = \frac{2}{3}$ it becomes 'anomalous' since the jamming limit is approached as $1/t^2$, in contrast with the general belief that the exponent n of the power-law decay is equal to the inverse of the number of degrees of freedom per particle.

The regime on both sides of the transition is characterized by the same typical cross-over time† $\tau = 1/|2-3r|$, defined from the slope of the exponential in equation (10) or from the ratio B/A in equation (11). This time is such that for $t \ll \tau$ the dynamics are dominated by a $1/t^2$ behaviour in the two 'phases'; only for $t \gg \tau$ does the characteristic long time behaviour, exponential for $r < \frac{2}{3}$, as $1/t$ for $r > \frac{2}{3}$, emerge. Since $\tau \to \infty$ when $r \to \frac{2}{3}$, this long time regime is squeezed at the transition point $r = \frac{2}{3}$, leaving only the $1/t^2$ behaviour.

To find an expression for $\theta(t)$ in a closed form is a very difficult technical problem, comparable to the determination of the correlation function in the standard 'car parking' model [17]. However, the properties of the kernel ρ_k allow us to obtain an iterative solution of equation (7) from which approximate expressions for the long time coverage can be obtained.

Finally, it may be interesting to investigate these types of models in a more realistic physical context, such as a two-dimensional substrate, a disordered distribution of adsorbing

† A similar cross-over effect has been observed in the RSA kinetics of very elongated particles in [11].

sites or the possibility of a particle overlapping several sites. It is, presumably, difficult to obtain an analytical insight into such models, but their properties can be numerically analysed using the one-dimensional results as a guide.

Acknowledgment

We thank G Tarjus for discussions and for pointing out to us that models (I) and (II) are equivalent.

Appendix A. The master equations

In this appendix we derive the master equations for the probability of finding at time t, an unoccupied interval (*gap*) of given length. Let $P_n(x, y, t)$ be the probability for finding a gap of length at least $x + y + n - 1$, where n is the number of adsorbing sites in the gap and $x(y)$ the distance between the left(right) edge of the gap and the last left(right) site in the gap (see figure A1). $P_1(0, 0, t)$ is the probability of finding a gap containing at least one site, its complement $1 - P_1(0, 0, t)$ defines the probability that a site is covered by a particle, which is equivalent to the occupancy rate:

$$\theta(t) = 1 - P_1(0, 0, t).$$

The rate equation for this quantity is

$$-\frac{\partial P_1(0,0,t)}{\partial t} = \int_0^r P_1(x, r-x, t)\,\mathrm{d}x \qquad \text{for } r \in [0,1] \tag{A1}$$

$$= \int_{r-1}^1 P_1(x, r-x, t)\,\mathrm{d}x \qquad \text{for } r \in [1,2]. \tag{A2}$$

(In equations (A1) and (A2) and in the subsequent rate equations we have set the effective flux of the particles to unity.) Therefore, to determine θ one needs to know $P_1(x, y, t)$ only for x and y less than r (case $r \leqslant 1$) or greater than $r - 1$ (case $r \geqslant 1$) and to set $x + y = r$. The general rate equations are obtained, as usual, by counting the different ways of destroying a gap using the following equations:

case $r \leqslant 1$, $x \in [0, r]$, $y \in [0, r]$, and $n \geqslant 2$

$$\begin{aligned}-\frac{\partial P_n(x,y,t)}{\partial t} &= [x + y + (n-2)r]P_n(x,y,t) + \int_x^r P_n(x', y, t)\,\mathrm{d}x' \\ &\quad + \int_y^r P_n(x, y', t)\,\mathrm{d}y' + u(x+r-1)\int_0^{x+r-1} P_{n+1}(x', y, t)\,\mathrm{d}x' \\ &\quad + u(y+r-1)\int_0^{y+r-1} P_{n+1}(x, y', t)\,\mathrm{d}y'.\end{aligned} \tag{A3}$$

case $r \geqslant 1$, $x \in [r-1, 1]$, $y \in [r-1, 1]$ and $n \geqslant 2$

$$\begin{aligned}-\frac{\partial P_n(x,y,t)}{\partial t} &= [(x - r + 1) + (y - r + 1) + (n-2)(2-r)]P_n(x,y,t) \\ &\quad + \int_x^1 P_n(x', y, t)\,\mathrm{d}x' + \int_y^1 P_n(x, y', t)\,\mathrm{d}y' + \int_{r-1}^{b(x)} P_{n+1}(x', y, t)\,\mathrm{d}x' \\ &\quad + \int_{r-1}^{b(y)} P_{n+1}(x, y', t)\,\mathrm{d}y'\end{aligned} \tag{A4}$$

where $u(t)$ is the Heaviside step function and, in the last equation, $b(x) = \inf\{x + r - 1, 1\}$. The probability $P_n(x, y, t)$ is subject to the initial condition

$$P_n(x, y, t = 0) = 1.$$

From these equations we see that for $n \geqslant 2$ the n dependence can be factorized out:

$$P_n(x, y, t) = \mathrm{e}^{-(n-2)rt} P_2(x, y, t) \qquad \text{for } r \in [0, 1] \tag{A5}$$

$$= \mathrm{e}^{-(n-2)(2-r)t} P_2(x, y, t) \qquad \text{for } r \in [1, 2]. \tag{A6}$$

The function $P_2(x, y, t)$ must be symmetric in its spatial arguments. Moreover, for $n \geqslant 2$ the left- and right-hand parts of the gap cannot be simultaneously affected by the deposition of one dimer, hence the x and y dependence are uncorrelated. We deduce from these considerations that

$$P_2(x, y, t) = P(x, t)P(y, t) \tag{A7}$$

reducing the problem to that of finding one unknown function $P(x, t)$ which we will call a *reduced probability*.

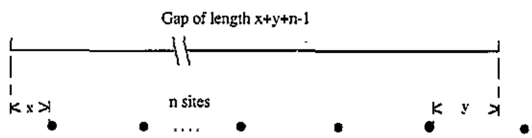

Figure A1. The parametrization of the gap.

The rate equation for the function $P_1(x, y, t)$ is different from equations (A3) and (A4) and depends on the value of $x + y$ with respect to r. However, the arguments leading to the factorization of the x and y dependences and of the n dependence remain valid for $x + y \geqslant r$ which is precisely the region of interest. This leads to

$$P_1(x, y, t) = \mathrm{e}^{rt} P(x, t)P(y, t) \qquad x + y \geqslant r.$$

From this factorization property and the rate equations (A1) and (A2), we can express the occupancy rate in terms of the function P, leading to equations (1) and (2):

$$\theta(t) = \int_0^t \mathrm{d}t' \, \mathrm{e}^{rt'} \int_0^r \mathrm{d}x \, P(x, t')P(r - x, t') \qquad \text{for } r \in [0, 1]$$

$$= \int_0^t \mathrm{d}t' \, \mathrm{e}^{(2-r)t'} \int_{r-1}^1 \mathrm{d}x \, P(x, t')P(r - x, t') \qquad \text{for } r \in [1, 2].$$

From equations (A3) and (A4) and the factorization properties of $P_n(x, y, t)$, equations (A5)–(A7), we deduce the rate equations for the function P, equations (3) and (4) of section 3.1, as follows.

Case $r \leqslant 1$, $x \in [0, r]$

$$-\frac{\partial P(x, t)}{\partial t} = xP(x, t) + \int_x^r P(x', t)\, \mathrm{d}x' + u(x + r - 1)\mathrm{e}^{-rt} \int_0^{x+r-1} P(x', t)\, \mathrm{d}x' \tag{A8}$$

case $r \geqslant 1$, $x \in [r - 1, 1]$

$$-\frac{\partial P(x, t)}{\partial t} = (x - r + 1)P(x, t) + \int_x^1 P(x', t)\, \mathrm{d}x' + \mathrm{e}^{-(2-r)t} \int_{r-1}^{b(x)} P(x', t)\, \mathrm{d}x'. \tag{A9}$$

Due to the last term in equations (A8) and (A9), $P(x, t)$ appears to be piecewise defined with respect to x, i.e. in successive intervals of length $(1 - r)$ within the range $(0, r)$ for

$r \leqslant 1$, or of length $(r-1)$ within the range $(r-1, 2-r)$ for $r \geqslant 1$. To be more explicit, let us define the set of intervals I_ℓ in the following way.

For $0 \leqslant r < 1$ define $k \geqslant 1$ such that $(k-1)/k < r \leqslant k/(k+1)$ then

$$I_\ell = [(\ell-1)(1-r), \ell(1-r)] \qquad 1 \leqslant \ell \leqslant k-1$$
$$I_k = [(k-1)(1-r), r]$$

which are such that

$$\bigcup_{\ell=1}^{k} I_\ell = [0, r].$$

For $1 < r \leqslant 2$ define $k \geqslant 1$ such that $(k+2)/(k+1) < r \leqslant (k+1)/k$ then

$$I_1 = [(2-r), 1]$$

for $k \geqslant 2$ only

$$I_2 = [(k-1)(r-1), (2-r)]$$

for $k \geqslant 3$ only

$$I_\ell = [(k-\ell+1)(r-1), (k-\ell+2)(r-1)] \qquad 3 \leqslant \ell \leqslant k$$

which are such that

$$\bigcup_{\ell=1}^{k} I_\ell = [r-1, 1].$$

The number k of such intervals is directly expressed in terms of r:

$$k = \left[\frac{r}{1-r}\right] + 1 \qquad \text{for } 0 \leqslant r < 1$$
$$k = \left[\frac{2-r}{r-1}\right] + 1 \qquad \text{for } 1 < r \leqslant 2$$

where $[X]$ means the integer part of X.

In the following appendix, for a given value of r, we will denote the restriction of $P(x,t)$ to the interval I_ℓ by $P_\ell(x,t)$, $\ell = 1, \ldots, k$.

Appendix B. Integral equations for the generic case $\frac{2}{3} < r < \frac{3}{2}$, $r \neq 1$

In this appendix we derive the representation of equations (6) and (7) from equations (A8) and (A9) and we give the expressions for the kernels K_ℓ and ρ_k and of the function u_0.

We first remark that the reduced probability $P_1(x,t)$ is in fact independent of x: $P_1(x,t) \equiv q(t)$. Consider the left-hand bordering site of the gap in the case $r \leqslant 1$. There is a vacant space of length *at least* $1-r$ from its right-hand edge independent of the occupation of its left-hand neighbour; this means that $P(x,t)$ is independent of x for $x \in [0, 1-r]$. The same property holds in the case $r \geqslant 1$ for $x \in [2-r, 1]$.

We start with the case $r < 1$. For $1-r \leqslant x \leqslant r$ we differentiate equation (A8) with respect to x to obtain

$$-\frac{\partial^2 P(x,t)}{\partial x \partial t} = x\frac{\partial P(x,t)}{\partial x} + \mathrm{e}^{-rt} P(x+r-1, t).$$

Then integrating with respect to t, using the initial condition $\partial P(x,0)/\partial x = 0$, we obtain

$$\frac{\partial P(x,t)}{\partial x} = -\int_0^t e^{-rt'-x(t-t')}\, P(x+r-1,t')\,dt'.$$

Finally, we integrate with respect to x, taking into account the boundary condition $P(x=1-r,t) = q(t)$, to obtain

$$P(x,t) = q(t) - e^{-(1-r)t}\int_0^t dt'\, e^{-(2r-1)t'}\int_0^{x+r-1} dx'\, e^{x'(t'-t)}P(x',t'). \tag{B10}$$

By using equation (B10) repeatedly as x increases, one obtains equation (6):

$$P_\ell(x,t) = q(t) + \int_0^t K_\ell(x,t|t')q(t')\,dt \qquad 2 \leqslant \ell \leqslant k.$$

when $x \in I_2$ then $x' \in I_1$ where $P(x',t') = q(t')$, equation (B10) gives equation (6) with $\ell = 2$ and the following expression for the kernel K_2:

$$K_2(x,t|t') = e^{-rt'}\frac{e^{-x(t-t')} - e^{-(1-r)(t-t')}}{t-t'} \qquad r < 1. \tag{B11}$$

When $x \in I_3$, by including the previous result in equation (B10) we obtain equation (6) for $\ell = 3$ with the explicit form of the kernel K_3, and so on.

Analogous manipulations can be performed on equation (A9) for the case $r > 1$ for $x \leqslant 2-r$, where the boundary condition is now $P(x=2-r,t) = q(t)$. The equation equivalent to equation (B10) is

$$P(x,t) = q(t) + e^{2(r-1)t}\int_0^t dt'\, e^{-rt'}\int_{x+r-1}^1 dx'\, e^{x'(t'-t)}P(x',t') \tag{B12}$$

which by repeated application as x decreases gives the representation of equation (6). For $x \in I_2$ one obtains the kernel K_2:

$$K_2(x,t|t') = e^{-t'+(r-1)t}\frac{e^{-x(t-t')} - e^{-(2-r)(t-t')}}{t-t'} \qquad r > 1. \tag{B13}$$

Assuming that for a given value of r all the K_ℓ are known, one can define a kernel $\sigma_k(t,t')$:

$$\sigma_k(t,t') = \sum_{\ell=2}^{k}\int_{I_\ell} dx\, K_\ell(x,t|t')$$

and derive an integral equation for $q(t)$. Considering equations (A8) and (A9) where x is fixed to the value $x = 1-r$ (case $r < 1$) or $x = 2-r$ (case $r > 1$) and using equation (6) for $P_\ell(x,t)$, one obtains respectively

$$-\frac{dq}{dt}(t) = rq(t) + \int_0^t q(t')\sigma_k(t,t')\,dt' \qquad r < 1$$
$$-\frac{dq}{dt}(t) = (2-r)[1+e^{-(2-r)t}]q(t) + e^{-(2-r)t}\int_0^t q(t')\sigma_k(t,t')\,dt' \qquad r > 1.$$

By integrating with respect to t with the initial condition $q(0) = 1$ we obtain equation (7):

$$q(t) = u_0(t)\left\{1 + \int_0^t \rho_k(t,t')q(t')\,dt'\right\}$$

where for $r < 1$

$$u_0(t) = \mathrm{e}^{-rt} \qquad \rho_k(t, t') = \int_t^{t'} \mathrm{e}^{rt''} \sigma_k(t'', t')\,\mathrm{d}t''$$

and for $r > 1$

$$u_0(t) = \exp\left[\mathrm{e}^{-(2-r)t} - (2-r)t - 1\right] \qquad \rho_k(t, t') = \int_t^{t'} \exp\left[1 - \mathrm{e}^{-(2-r)t''}\right] \sigma_k(t'', t')\,\mathrm{d}t''.$$

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