J. Phys. A: Math. Gen. 27 (1994) L657–L662. Printed in the UK

LETTER TO THE EDITOR

Traces of the arrival history in the jammed state of random sequential adsorption

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Received 11 June 1994

Abstract. In the final jammed state of the random sequential adsorption of dimers on a one-dimensional lattice, the average gap neighbouring a particle that originally adsorbed at time t is $e^{-t}e^{-e^{-t}}$. Thus, the average final gap adjacent to the first particle to adsorb is e^{-1}, while that for the last particle is infinitesimally small. This result shows that there remains a (statistically) measurable imprint of the sequence of arrival frozen into the RSA system.

In the random sequential adsorption (RSA) process, particles are adsorbed irreversibly, and one at a time at randomly chosen locations in the system. Eventually a jammed state is reached in which no space large enough for an additional particle remains. There has been a great deal of work on various aspects of this problem; see [1–23] and particularly the review of Evans [1].

Recently, Brosilow and the author [11] found that the pair correlation function in the final jammed state of parallel squares adsorbing on a plane is different for particles that adsorb at different times. The correlation functions about the first, an intermediate, and last squares to adsorb (averaged over many runs) implied that a fair amount of space remains around the early squares, while the final squares are jammed in tightly between their neighbours. These results, which followed from Monte Carlo simulations, showed that some memory of the order of arrival remains frozen into the system, highlighting the intrinsic irreversible nature of the RSA process.

To demonstrate this phenomenon analytically, I consider in this paper the problem of the RSA of dimers on a discrete one-dimensional lattice, a model that has been studied extensively since being introduced by Flory [12–23]. I derive an explicit expression for the average nearest-neighbour gap between a particle and its neighbour at jamming as a function of the time at which the particle in question originally adsorbed. Note that this quantity is not simply the time-dependent gap distribution (which is well known), but a measure of the gaps in the jammed state only, around particles that adsorbed at specific times or 'epochs' previously.

The one-dimensional dimer problem is illustrated in figure 1: a pair of neighbouring sites on a lattice are chosen at random, and if both are empty, they are filled with a dimer. Between adsorbed dimers, there can be a gap of length 0, 1, 2, ..., as shown in that figure. Also shown is the equivalent representation of this problem as adsorption of point particles

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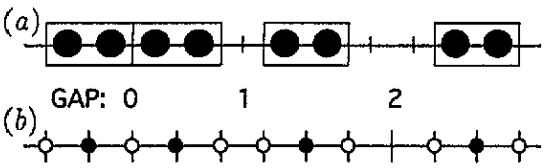

Figure 1. (*a*) The dimer adsorption process and (*b*) the equivalent problem of particles with nearest-neighbour exclusion, where the open circles represent the excluded sites. The size of the gaps between the dimers is shown.

with nearest-neighbour exclusion, which can also be interpreted as a kind of fragmentation process.

Let $c_n(t)$ be the concentration (number per lattice site) of interparticle gaps in the system of length $n = 0, 1, 2\ldots$ at time t. It satisfies the kinetic equation [19, 20]

$$\frac{dc_n}{dt} = -(n-1)c_n + 2\sum_{j=n+2}^{\infty} c_j \qquad n = 1,\ 2,\ 3,\ldots \tag{1a}$$

$$\frac{dc_0}{dt} = 2\sum_{j=2}^{\infty} c_j \tag{1b}$$

and conservation law

$$\sum_{n=0}^{\infty}(n+2)c_n = 1\,. \tag{2}$$

Note that (1) is a form of the fragmentation equation but with n shifted by 2 because n is the edge-to-edge, rather than centre-to-centre, distance. The solution to (1) for an initially empty infinite system is given by [17, 20]

$$\begin{aligned} c_n(t) &= e^{-(n-1)t}(1-e^{-t})^2 e^{2(e^{-t}-1)} \qquad n = 1, 2, 3\ldots \\ c_0(t) &= \tfrac{1}{2} + \left(e^{-t} - \tfrac{3}{2}\right)e^{2(e^{-t}-1)} \end{aligned} \tag{3}$$

implying that the total number of dimers (per site) adsorbed by time t is given by

$$N(t) \equiv \sum_{n=2}^{\infty} c_n(t) = \frac{1-e^{-2(1-e^{-t})}}{2} \tag{4}$$

as there is one dimer per gap.

When $t \to \infty$, the only gaps remaining in the system are those of length zero and one, with concentrations given by

$$c_0(\infty) = \frac{1-3e^{-2}}{2} \qquad c_1(\infty) = e^{-2} \qquad c_n(\infty) = 0 \qquad n > 1\,. \tag{5}$$

In this limit, (2) reduces to $2c_0(\infty) + 3c_1(\infty) = 1$, and $N(\infty)$ is given by [12]

$$N(\infty) = c_0(\infty) + c_1(\infty) = \frac{1-e^{-2}}{2} = 0.432\,332\,358\,38\ldots\,. \tag{6}$$

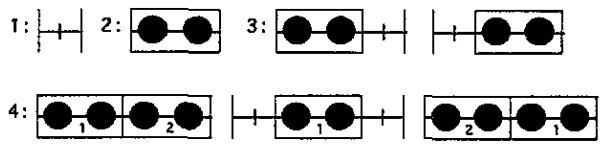

Figure 2. Calculation of the function g_n, which gives the average remaining gap at one end of the system of length n in the jammed state, showing $g_1 = 1$, $g_2 = 0$, $g_3 = \frac{1}{2}$, and $g_4 = \frac{1}{3}$. For $n = 4$, the numbers on the dimers represent the order of arrival.

The fraction of sites covered by dimers is twice the above value, and the fraction of sites that are vacant is

$$c_1(\infty) = e^{-2} = 0.135\,335\,283\,24\ldots. \tag{7}$$

Finally, the average gap between adjacent dimers at saturation is given by

$$\frac{0 \times c_0(\infty) + 1 \times c_1(\infty)}{c_0(\infty) + c_1(\infty)} = \frac{2}{e^2 - 1} = 0.313\,035\,285\,50\ldots. \tag{8}$$

To investigate the history dependence of these gaps, I first consider g_n, defined as the average remaining gap at either end of a bounded open interval of length n after that interval has been filled to saturation. By simple enumeration (see figure 2) one finds $g_0 = 0$, $g_1 = 1$, $g_2 = 0$, $g_3 = \frac{1}{2}$, $g_4 = \frac{1}{3}\ldots$. For $n > 1$, g_n satisfies the recursion relation

$$g_n = \frac{1}{n-1}\sum_{i=0}^{n-2} g_i \tag{9}$$

because the first particle to adsorb occupies any of the $n-1$ possible positions with equal probability and, in so doing, reduces the gap on one side from n to i. The solution to (9) is

$$g_n = \sum_{i=0}^{n-1} \frac{(-1)^i}{i!} \tag{10}$$

(for $n > 0$), as may be verified.

Next I calculate the average final gap around all particles that have adsorbed *up to* time t. At t, the gap distribution is given by $c_n(t)$. When gaps of length n ultimately become jammed, the average remaining gap at either end will be equal to g_n. Thus, the average final gap adjacent to particles that have adsorbed from time zero to time t is given by

$$\begin{aligned}\langle \text{gap(ads. time} \leqslant t)\rangle &= \frac{1}{N(t)}\sum_{n=1}^{\infty} c_n(t) g_n \\ &= \frac{1}{N(t)}(1-e^{-t})^2 e^{-2(1-e^{-t})} \sum_{n=1}^{\infty} e^{-(n-1)t} \sum_{i=0}^{n-1} \frac{(-1)^i}{i!} \\ &= \frac{1}{N(t)}(1-e^{-t})^2 e^{-2(1-e^{-t})} \sum_{i=0}^{\infty} \frac{(-1)^i}{i!} \sum_{n=i+1}^{\infty} e^{-(n-1)t} \\ &= \frac{(1-e^{-t})e^{e^{-t}-2}}{N(t)}\end{aligned} \tag{11}$$

where $N(t)$ is given by (4).

The average final gap about particles that adsorb exactly *at* time t can be found in two different ways. For the first way, consider particles that adsorb during a small time interval $(t, t+\mathrm{d}t)$. The number of new gaps (of length n) that are formed during this time interval is given by the last term of (1*a*) (the *gain* term), multiplied by $\mathrm{d}t$. When these gaps finally become jammed, the average remaining gaps at the ends can be found by multiplying that gain term by g_n, summing over all n, and dividing by the number of new gaps that appear during the time interval

$$\langle \text{gap(ads. time} = t)\rangle = \frac{\sum_{n=1}^{\infty} g_n \, 2\sum_{j=n+2}^{\infty} c_j(t)}{\sum_{n=1}^{\infty} 2\sum_{j=n+2}^{\infty} c_j(t)}. \tag{12}$$

This yields

$$\langle \text{gap(ads. time} = t)\rangle = \mathrm{e}^{-t}\mathrm{e}^{\mathrm{e}^{-t}} \tag{13}$$

by a calculation similar to that shown in (11).

The average final gap can also be derived by the following calculation:

$$\langle \text{gap(ads. time} = t)\rangle = \frac{(\mathrm{d}/\mathrm{d}t)[N(t)\,\langle \text{gap(ads. time} \leqslant t)\rangle]}{(\mathrm{d}/\mathrm{d}t)N(t)}. \tag{14}$$

Here, the numerator ($\times \mathrm{d}t$) gives the change in the final gap distribution due to particles that arrive in the interval $(t, t+\mathrm{d}t)$, while the denominator ($\times \mathrm{d}t$) gives the number of particles that arrive in that interval. Thus, this ratio gives the average gap for those particles that arrive in just that interval. Note that, while this approach gives the same final results as (12), the corresponding expressions in the numerators and denominators of (12) and (14) are quite different from each other.

The final gap probability distribution (13) has the limiting behaviour

$$\mathrm{e}^{-t}\mathrm{e}^{\mathrm{e}^{-t}} \sim \begin{cases} \mathrm{e}^{-1}(1 - \frac{1}{2}t^2 + \ldots) & \text{small } t \\ \mathrm{e}^{-t} - \mathrm{e}^{-2t} + \ldots & \text{large } t \end{cases} \tag{15}$$

so that particles that adsorb near the beginning end up with an average gap of $\mathrm{e}^{-1} \approx 0.367\,879\,441\,2\ldots$, while those that adsorb near the end of the process leave a gap that is infinitesimally small (for an infinite system). For a finite system, of course, the system will jam in a finite amount of time, and the gaps on the two sides of the final dimer will not necessarily be zero. However, as the system size goes to infinity, the time for jamming will become infinite, and the expected gaps around the last particle will go to zero.

The result (13) can also be written in terms of the fraction of occupied sites $\theta(t) = 2N(t) = 1 - \mathrm{e}^{-2(1-\mathrm{e}^{-t})}$ and $\theta(\infty) = 1 - \mathrm{e}^{-2}$:

$$\langle \text{gap(ads. coverage} = \theta)\rangle = \frac{1}{2}\sqrt{\frac{1-\theta(\infty)}{1-\theta}}\ln\left(\frac{1-\theta}{1-\theta(\infty)}\right). \tag{16}$$

A plot of this function is given in figure 3; the average gap around particles at first decreases slowly but then falls precipitously to zero for particles arriving near the end of the process. Note that the average value of (16) over the interval $0 \leqslant \theta \leqslant \theta(\infty)$ agrees with (8).

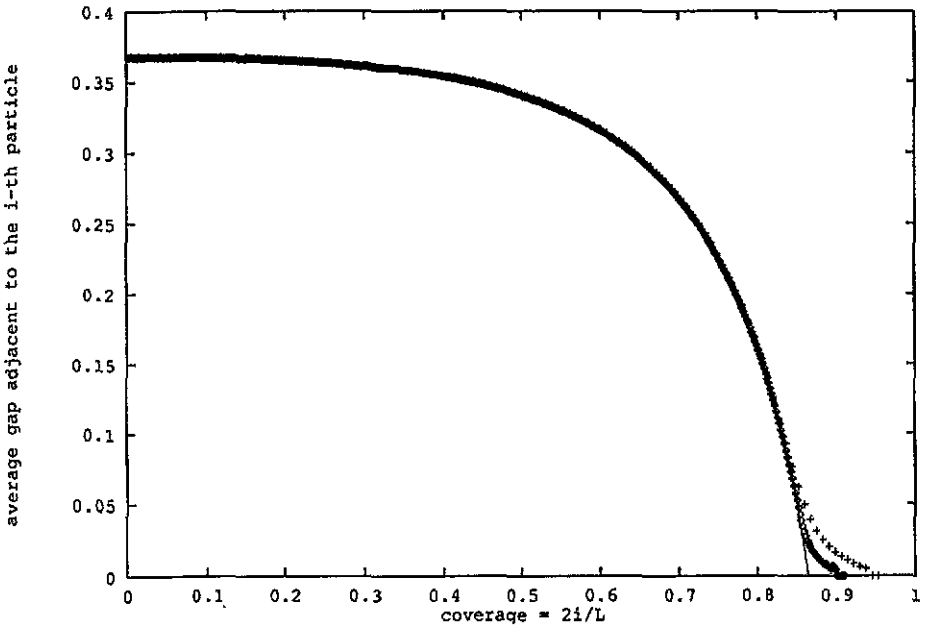

Figure 3. Results from theory (equation (16), full curve) and simulation for the average nearest-neighbour gap distance in the jammed state as a function of the coverage $= 2i/L$, where i is the sequential particle index, for $L = 256$ (+) and $L = 1024$ (◇).

To verify these results, I have also carried out some Monte Carlo simulations. Each dimer was labelled sequentially as it was adsorbed, and, when the jammed state was reached, the gap to the right of each particle was measured. These gaps were then averaged over all runs for a fixed particle index. A total of 5×10^7 independent runs on a lattice of size $L = 256$, and 5×10^6 runs with $L = 1024$ were carried out. Periodic boundary conditions were used. The resulting average gaps are shown in figure 3, plotted as a function of $\theta = 2i/L$, where i is the particle index $1, 2, 3, \ldots$. For the lattice of size 256, the average number of particles at jamming was found to be 110.6774, consistent with the theoretical value $128\theta(\infty) = 110.677\,083\,8\ldots$. For i smaller than this number, the measured average gaps agreed closely with the values predicted by (16). However, for larger i, which represents runs in which the number of partices to adsorb went beyond the expected (average) value, a tail in the gap distribution appeared. This tail represents a relatively small number of runs: for example, for $L = 256$, only 579 968 runs (about 1%) reached 116 particles, and only 3 runs reached 122 particles, the maximum that was found. (An iterative calculation shows that the maximum possible value, 128, would occur with probability $1.053\,39 \times 10^{-10}$.) For larger L, that tail shrinks, as the results for $L = 1024$ show; this is consistent with recent results on the decrease of the fluctuations in the coverage at jamming with increasing size of the system [21, 22]. I have not carried out a study of the finite-size scaling of this tail.

In the simulations, I also kept track of the time that each particle adsorbed, with time increasing by $1/L$ for each attempt, and averaged these times over all runs for fixed index i. A plot of (13) using this average time for t gave a curve indistinguishable to that representing (16), except for the last few points where large fluctuations occurred due to the small number of runs at those points.

Thus, in conclusion, I have derived an explicit formula for the jammed-state gap

distribution for dimers as a function of the time or epoch of adsorption. This result shows clearly that in RSA, all particles are not created equal: particles that arrive near the beginning have, on average, more space around them in the jammed state, while those that arrive near the end have little. The reason for this is that, as the system saturates, the larger remaining openings tend to be filled first, leaving the spaces where just one particle can fit for last. Even for a simple system like dimers, this process leaves a record in the jammed state that can be observed (statistically) in the gap spacing.

Undoubtedly, these results can be generalized to longer discrete particles and also to a continuum (in 1D). For these cases, one may study the entire distribution of gaps rather than just their average value (which is sufficient for dimers). Another interesting question is to find the jammed-state particle–particle correlation function (as opposed to just the nearest-neighbour gap distribution studied here) as a function of particle arrival time; this would allow a more direct comparison with the Monte Carlo work on squares of [11].

This material is based upon work supported by the US National Science Foundation under grant no DMR-9122341. An account of this work was presented at the CECAM workshop on RSA held in Orsay, France, June 1992.

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