J. Phys. A: Math. Gen. 23 (1990) 5103-5108. Printed in the UK

COMMENT

Kinetics and fractal properties of the random sequential adsorption of line segments

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Received 31 July 1990

Abstract. The random sequential adsorption (RSA) of infinitely-thin line segments is studied by computer simulation. It is shown that the exponent for the time dependence of the surface coverage increases beyond the value 0.33, recently reported by Sherwood, to a value of 0.38, at later times. It is also argued that the fractal dimension of the adsorbed lines is about 1.8, making use of a previous result on the RSA of rectangular objects.

The problem of random sequential adsorption, although an old one (e.g., Flory 1939, Renyi 1958, Mackenzie 1962, Widom 1966, Solomon 1967, Gonzales *et al* 1974) has recently been attracting renewed interest (e.g., Rosen *et al* 1986, Burgos and Bonadeo 1987, Meakin *et al* 1987, Schaaf and Talbot 1989, Baram and Kutasov 1989). In two dimensions, where most results can be found only by extensive computer simulation, earlier work generally concerned simple discs (e.g., Feder 1980), aligned squares (Tory and Pickard 1979, Brosilow *et al* 1990) and lattice models (Evans *et al* 1983, Nakamura 1986). The study of unsymmetrical objects has begun in earnest fairly recently. On lattices, various animals have been considered by Nord and Evans (1985) and Barker and Grimson (1988), while on a continuum surface, randomly-oriented ellipses have been investigated by Talbot *et al* (1989), and rectangles by Vigil and Ziff (1989, 1990). These last two systems are the subject of this comment.

In their work, Talbot *et al* argued that the saturation coverage, Θ_{SAT}, should follow the behaviour

$$\Theta_{SAT} - \Theta(t) \sim kt^{-p} \qquad \text{for } t \to \infty \tag{1}$$

where t is the time and k is a constant, with $p = \frac{1}{3}$. Here time is proportional to the number of trials T, and is made dimensionless by defining it by $t = TA_{obj}/A_{tot}$, where A_{obj} is the area of the object being adsorbed and A_{tot} is the total area of the surface. Talbot *et al*'s result is in contrast to the behaviour for discs, where (1) is followed, with $p = \frac{1}{2}$ ('Feder's law') (Feder 1980, Pomeau 1980, Swendsen 1981). Before the work of Talbot *et al*, Feder's law was believed to be rather universal, but now it appears that discs are a special case, as Talbot *et al* argue that $p = \frac{1}{3}$ should apply to any non-circular object that is adsorbed in random orientation, on a continuum two dimensional surface. Talbot *et al* carried out simulations with ellipses which showed fair agreement with their prediction. It was also shown to be followed fairly well for randomly-oriented rectangles by Vigil and Ziff (1989), as described in the note at the end of that paper and in more detail in a forthcoming publication (Vigil and Ziff 1990).

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0305-4470/90/215103+06$03.50

In a recent work, Sherwood (1990) provided further numerical evidence that $p = \frac{1}{3}$ for ellipses. Sherwood also noted that the saturation coverage Θ_{SAT} reaches a maximum at aspect ratio (or eccentricity) $b/a = 0.5$, a result that was also indicated in Talbot *et al*'s work. Here we wish to point out that this same behaviour was seen previously for rectangles by Vigil and Ziff (1989), where it was found that Θ_{SAT} also reaches a maximum at an aspect ratio of just about 0.5. In figure 1, we plot Sherwood's results for ellipses (taken off the figure), and the result for rectangles from Vigil and Ziff (1989), corrected for $p = \frac{1}{3}$ as mentioned in the note at the end of that paper. The two curves can be seen to show similar qualitative behaviour, with the saturation coverage for ellipses somewhat higher than that for rectangles at the same aspect ratio.

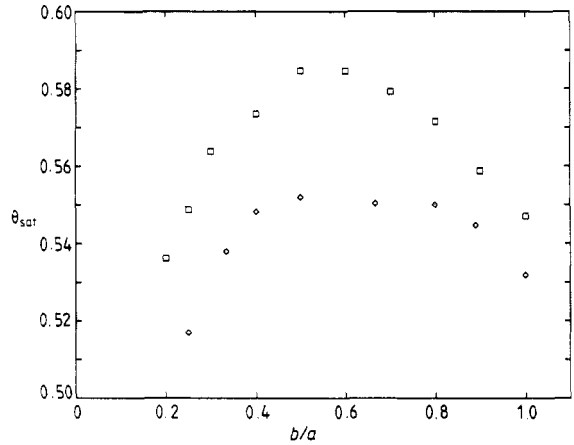

Figure 1. The saturation (=maximum, jamming) coverage Θ_{SAT} as a function of the eccentricity or aspect ratio b/a for ellipses (⊡) (Sherwood 1990) and rectangles (◇) (Vigil and Ziff 1989). Both seem to peak at about $b/a = 0.5$. The error bars for both works are of the order of ± 0.01.

While one can easily make 'plausibility' arguments for Θ_{SAT} going through a maximum, there is no rigorous proof for it, and certainly no proof that the maximum should occur at $b/a = 0.5$, for either rectangles or ellipses. To check numerically whether the maximum is at $b/a = 0.5$ within a small error would require a substantial amount of computer work, although the answer would be interesting. Furthermore, it may be noted that Sherwood's result $\Theta_{SAT}(0.5) = 0.585 \pm 0.010$ appears to be the highest value of Θ_{SAT} for any randomly-oriented object in a continuum (off-lattice) system. However, there is no proof that this is the case.

A natural extension of ellipses and rectangles is the limit of infinite aspect ratio, that is line segments. This system was also studied by both Sherwood (1990) and Vigil and Ziff (1990). While Sherwood finds that the long-time behaviour of the time dependence of the coverage of lines follows

$$n'(t') \sim (t')^z \tag{2}$$

with $z \approx 0.33$, Vigil and Ziff find that at later times, $z \approx 0.38$. Note that Sherwood gives a rather general argument (but with simplifying assumptions) that predicts $z = \frac{1}{3}$. Here we present the results of a more thorough investigation of RSA of lines to clarify this point.

In (2), $t' \equiv T(l/L)^2$ is the dimensionless time as used by Vigil and Ziff (1990), where l is the length of the lines ($=2a$) and L is the length of the side of the system. (Of course, $A_{obj} = 0$, so the scaling used previously cannot be used here.) Sherwood used the semi-major axis ($a = l/2$) as the characteristic length scale, and his time $\hat{t}$ is related to ours by $t' = 4\hat{t}$. Furthermore, n' in (2) is the number of adsorbed lines per unit area and is related to the total number of adsorbed lines N by $n' = N(l/L)^2$, and to Sherwood's density $\hat{n}$ by $n' = 4\hat{n}$.

We have carried out additional simulations for t' up to $2^{22} = 4\,194\,304$, compared to Sherwood's maximum of $t' = 6400$ (with $L/l = 10$). For $L/l = 16$, we carried out 40 runs for t' up to 2^{13}, four runs up to 2^{15}, one run up to 2^{18}, and finally three runs at $L/l = 8$ with time up to $t' = 2^{22}$ (the last corresponding to $T = 2^{28} = 2.7 \times 10^8$ trials each). These simulations were carried out on an Apollo 4000 workstation computer running over several weeks.

In figure 2 the results of this work are plotted. The results of Sherwood, when plotted on the same figure, are indistinguishable from ours. It can be seen that for times just beyond where Sherwood stopped his simulation, the slope increases again and reaches a value of about 0.38. The region where this final slope is attained is over about two orders of magnitude in time. It is possible that the slope continues to change as t' increases even further, and indeed there is no certainty that the coverage shows power-law behaviour (although this seems reasonable). Note that our line for times between 10 and 1000 has a slope of 0.32, slightly less than the value (0.331) found by Sherwood. The numerical values of $n'(t')$ are listed in table 1.

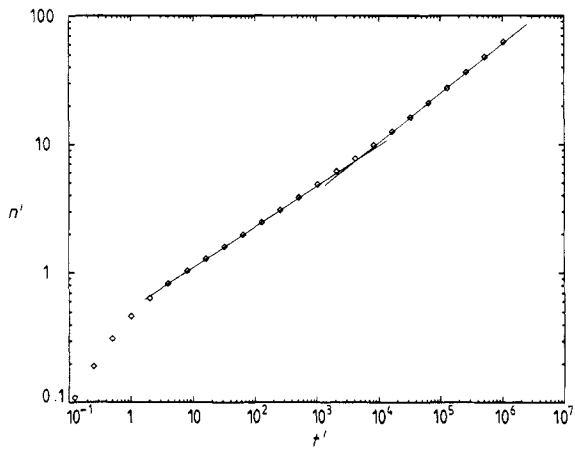

Figure 2. The number of lines adsorbed per unit area as a function of the dimensionless time t', which equals the number of attempts per unit area. This data agrees with those of Sherwood, who simulated up to $t' = 6400$. The line for $t' < 10^4$ has slope 0.32, while the line for $t' > 10^4$ has slope 0.38. At the latest time, there were 42 949 attempts in each unit area for a successful adsorption (where a unit area equals l^2).

We have not carried out an analysis of the errors, but find close agreement between different simulations. The increase in slope at high t' occurred for each of the four runs with $t'_{max} > 2^{15}$. However, there still remains the possibility that this increase in slope is some kind of artefact of the simulation procedure, such as round-off or discretization (finite-precision) error.

Table 1. Numerical values of the data plotted in figure 2.

$\log_2 t'$	n'	$\log_2 t'$	n'
−3	0.120	10	12.32
−2	0.232	11	15.44
−1	0.434	12	19.49
0	0.766	13	24.71
1	1.245	14	31.04
2	1.861	15	39.64
3	2.543	16	50.97
4	3.303	17	65.71
5	4.160	18	85.22
6	5.175	19	111.4
7	6.407	20	145.5
8	7.941	21	187.5
9	9.861	22	245.3

Note that an increase in slope in this plot does *not* indicate that the rate of adsorption (which equals $dn'(t')/dt' \sim (t')^{z-1}$) is increasing. Instead, it indicates that the *rate of decrease of the adsorption rate* lessens for long time. We have no explanation for this behaviour.

Finally, we discuss the question of the fractal dimension of this system. An example of an enlarged section of a simulation at the latest time in our simulation is shown in figure 3. We determine the fractal dimension by considering how the 'mass' of adsorbed lines changes as we change the length scale of the resolution. Here we define the length scale as the typical distance between lines, and we can get a measure of this quantity by looking at the RSA of rectangles. In Vigil and Ziff (1990) it is shown that for thin

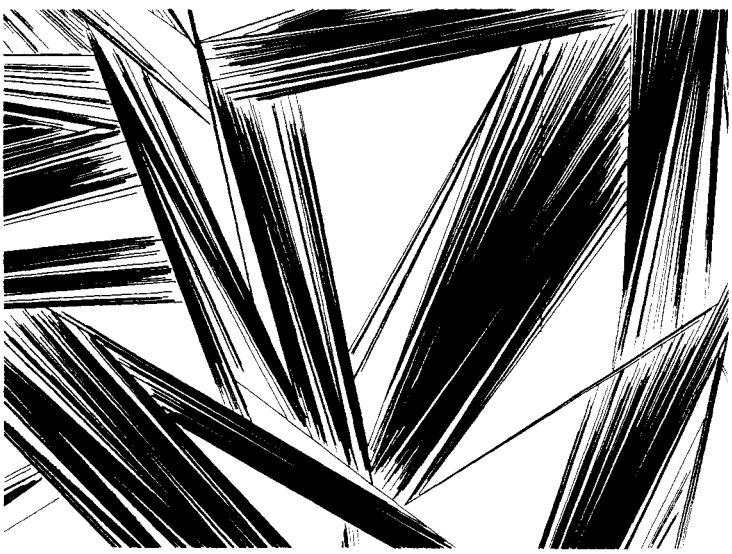

Figure 3. An example of a small region of dimensions $1.5l \times 2l$, from a simulation of size $L^2 = (8l)^2$ and at $t' = 2^{22} = 4.19 \times 10^6$ where the number density is $n' = 245.3$ lines per unit area. We argue that the fractal dimension of this system is about 1.8.

rectangles, the rate of adsorption follows that of lines very closely, until a certain time, after which the rate decreases rapidly. Very thin rectangles are essentially equivalent to lines until the typical distance between adsorbed rectangles becomes of the order of their width. To understand why this should be so, consider the rejection process for rectangles. Most of the time, an overlap occurs because the major centreline of the rectangle overlaps the centreline of another adsorbed rectangle—which is the same criterion as if they were lines. In the early stages, it is very rare that the overlap of rectangles occurs without the overlap of the centrelines because the probability that just a corner overlaps is relatively small. However, near saturation, when the spaces available are very small, the overlap of just the corners will also be very important. Then, of course, the kinetics of the two systems are different: while the RSA of lines goes on forever, that of rectangles eventually stops.

Therefore we interpret the width of the rectangles as a measure of the characteristic separation distance of the lines, when the rectangular system is at saturation and the number of lines and rectangles per unit area is the same. In Vigil and Ziff (1989) it is shown that the saturation coverage depends upon the aspect ratio $l/w = a/b (>1)$ by

$$\Theta_{SAT} \sim (l/w)^{-0.2} \qquad \text{for } (l/w) \to \infty \tag{3}$$

where $w = 2b$ is the width of the rectangle, which we set equal to the length scale ε. Here we consider that l is fixed, and that $\varepsilon = w$ decreases. Because Θ_{SAT} is proportional to the mass of the system, we find that the mass scales as $\varepsilon^{0.2}$. Using the relation that $M \sim \varepsilon^{2-D}$ (Mandelbrot 1983), we thus conclude that the fractal dimension D is equal to 1.8.

Acknowledgment

The authors thank the National Science Foundation (grant #DMR-8619731) for its support of this research.

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