Random sequential adsorption: line segments on the square lattice

1991 J. Phys. A: Math. Gen. 24 L671

(http://iopscience.iop.org/0305-4470/24/12/003)

J Phys A Math Gen 24 (1991) L671–L676 Printed in the UK

LETTER TO THE EDITOR

Random sequential adsorption: line segments on the square lattice

S S Manna and N M Švrakić

Hochstleistungsrechenzentrum der Forschungszentrum, Postfach 1913, D-5170 Julich 1, Federal Republic of Germany

Received 22 April 1991

Abstract. We study kinetics of the single-layer random sequential adsorption of line segments of fixed length on the square lattice by a Monte Carlo simulation. The area covered by the line segments grows with time and finally reaches a jamming limit when no more adsorption is possible. The jamming coverage depends on the segment length and its variation is studied At the late stage, approach of the coverage to the jamming limit is asymptotically exponential, with a rate found to be independent of the segment length. Based on our Monte Carlo data, an exact expression for the late-stage deposition kinetics is conjectured.

Random sequential adsorption (RSA), has been the subject of much recent experimental and theoretical investigation. Objects of finite size are randomly deposited (adsorbed) on an initially empty substrate so that no two objects overlap. The quantity of interest is the fraction of the total area $\theta(t)$ in time t, covered by the depositing particles. Due to the blocking of the area by the already randomly adsorbed particles, the limiting ('jamming') coverage, $\theta(\infty)$, is less than the close packing. The emergence of this jammed state is influenced by the infinite memory effects. Consequently, its formation cannot be described by mean-field theory, except for very early times, when $\theta(t)\propto t$.

Experimental studies [1–4] include, e.g., adhesion of colloidal particles [3] and proteins [2] on homogeneous substrates, with relaxation times much longer than the formation time of deposits.

Theoretical studies [5–17] of RSA include series expansions [8, 10], numerical Monte Carlo (MC) simulations [9, 14–16], and some analytical results [17], mostly for one-dimensional systems. In such studies, it was shown that the precise form of the long-time behaviour of $\theta(t)$ depends on the shape and orientational freedom of the adsorbing particles. Earlier studies have focused on continuum deposition models for which a power-law behaviour of the late-stage deposition [17]

$$\theta(t)=\theta(\infty)-\frac{\text{constant}\times(\ln t)^q}{t^p} \tag{1}$$

generally holds. In most cases the logarithmic factor is absent (i.e. $q=0$), while p is found to depend on spatial dimensionality d. In one dimension analytic results [13] yield $p=1$ and $q=0$. For higher dimensions, analytical arguments and numerical conjectures give $p=1/d$ and $q=0$ for deposition of spherical objects in d dimensions. Studies of deposition of *non-spherical* objects (ellipses and line segments) have shown

[15, 16] that in this case the power law behaviour (1) still holds, but that the value of p is modified. Specifically, for the adsorption of the ellipses on the plane it was found that $p=\frac{1}{3}$. Also, the jamming coverage, $\theta(\infty)$, for the ellipses depends on their aspect ratio.

The problem of RSA of lines on continuum is studied by Sherwood [15] and Ziff and Vigil [16]. Here lines are of zero thickness, and the only restriction is that no two lines can intersect. At very early times, deposited lines do not feel the presence of others and are adsorbed in arbitrary orientations. Later, these lines have to be deposited more and more parallel to the already adsorbed ones in order to avoid intersection. After a long time the resulting structure consists of regions with densely packed approximately parallel lines and some empty zones where no line can be placed in any orientation. The typical size of such domains is comparable to the length of the line segments deposited (see [15, 16] for beautiful pictures of such configurations). For objects of zero area one cannot reach the jamming limit. From numerical simulation and some general arguments Sherwood claimed that the number of line segments n adsorbed in time t grows as $n\sim t^z$ where $z\sim\frac{1}{3}$ [15]. Later, more extensive numerical simulation results suggested that z is actually around 0.38 [16]. Ziff and Vigil also claimed that the late stage configuration has a fractal dimension around 1.8 [16].

Studies of RSA on the lattices have been initiated quite recently. In these models, the adsorbing objects considered were squares [13] or oriented rectangles [14], or their appropriate higher-dimensional analogues. Here, the late stage jamming coverage is approached exponentially [13, 14], i.e.,

$$\theta_l(t)=\theta_l(\infty)-A_l\,e^{-t/\sigma_l}. \tag{2}$$

In the present work we study a single-layer random sequential adsorption of line segments on the square lattice by a Monte Carlo simulation. The lengths of the line segments are always integral multiples of the lattice unit, and the lines can be placed along the lattice axes only. The orientation of the adsorbing line is randomly chosen at each deposition attempt. The Monte Carlo procedure goes as follows: we take the square lattice of the size L and a line segment of length l, and randomly select a lattice site. We fix one end of the line at this site and try to place the segment in any of the four possible directions. If the chosen site is already occupied, the attempt is abandoned, and a new site is selected. If the site is unoccupied, we randomly pick one of the four possible orientations and search whether all successive l sites in that direction are unoccupied. If so, we occupy these l sites and deposit the segment. If the attempt fails we choose randomly another direction and so on until all four possibilities are exhausted. If the segment cannot be placed in any of the four directions, we denote this site as inaccessible. In the course of simulation we record the number of all inaccessible sites in the lattice. These include the occupied sites and the sites which are unoccupied but cannot be one end of the line segment. Further in the simulation we do not attempt deposition if an inaccessible site is selected. In difference with the RSA of lines in continuum, the jamming limit can be reached exactly in our case when the number of inaccessible sites becomes equal to the total number of sites in the lattice. Periodic boundary conditions were used in both directions. The time is counted by the number of attempts to select a lattice site and is scaled by the total number of lattice sites L^2.

A typical jamming configuration obtained in the simulation is shown in figure 1. In this figure, line segments of length $l=5$ are adsorbed on a 100×100 lattice. Several

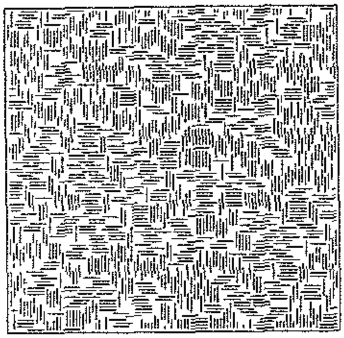

Figure 1. A typical jamming configuration for line segments of length $l = 5$ on a lattice of size $L = 100$ having a total of 1272 lines

interesting features are immediately apparent. First, there are 'voids' (connected clusters of inaccessible sites) of sizes ranging from a single site to the length of the lines deposited. Secondly, deposited lines tend to align parallel with one another and form domains. These domains vary in size, and some can be quite long and chain-like. This is in sharp contrast with random deposition of lines in continuum where long domains are never observed. The difference is due to the fact that in our case only two possible orientations along the lattices axes are allowed.

First we study how jamming coverage of line segment of certain length l depends on the lattice size L. We simulate 50 independent jamming configurations for lines of lengths 1, 2, 4, 8, 16 and 32 on two lattice sizes $L = 128$ and 256. We find that the difference of the average jamming coverages for the two lattices differs by a maximum of 0.3% for these line lengths. In latter simulations on bigger lattices we keep the line lengths $l \leq L/8$. This is done to avoid the finite-size effects, which become important when $l \propto L$. (These effects are generally weak, but must be carefully dealt with when l and L are comparable.)

The value of the jamming coverage depends on the length l of the segments deposited. We simulated the lattice size $L = 1024$ for lines of lengths 1, 2, 4, 8, 16, 32, 64 and 128. We used Sun4 workstations, one for each line segment, running for some days. Averaging over around 1300 independent jamming configurations for each line segment, we were able to reduce the error bars below 1 in the fourth distinct place. Since we do not know the precise form of variation of $\theta(\infty)$ on l, different functional forms were tried. In figure 2 the jamming coverage $\theta_l(\infty)$ is plotted against $1/\ln l$. It is linear for large values of l and approaches a definitive value, $\theta_\infty(\infty) = 0.583 \pm 0.010$. The slope of the line is 0.32 ± 0.02. Thus, for large l, the jamming density has a form

$$\theta_l(\infty) = \theta_\infty(\infty) + \frac{0.32}{\ln l} + \ldots \qquad (l \gg 1). \tag{3}$$

Turning back to time dependence, we expect that the late-stage coverage will have exponential behaviour, as in (2), where we have allowed for the l-dependence of the constants A_l and the rates σ_l. The plot of $\ln[\theta_l(\infty) - \theta_l(t)]$ against t, for longer times, should then give the straight line behaviour for the fixed segment lengths l. This plot is shown in figure 3, for $l = 1, 2, 4, 8, 16, 32, 64, 128$, with the topmost line corresponding to $l = 1$. Initially, the curves are not linear, but as the coverage builds up, the linear

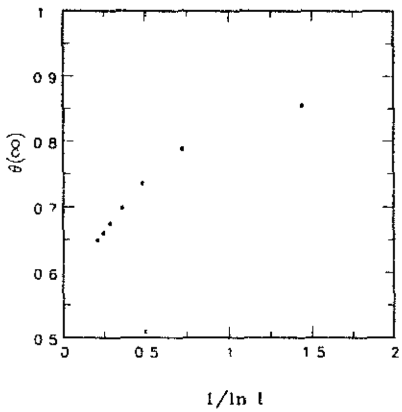

Figure 2. The average jamming coverage $\theta(\infty)$ for lines of length l plotted with respect to $1/\ln l$. Extrapolation to $l\to\infty$ gives $\theta_\infty(\infty) = 0.583 \pm 0.010$

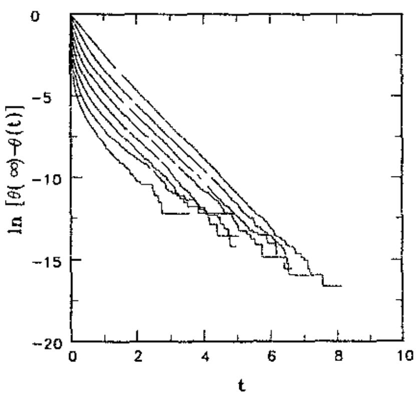

Figure 3. The approach of the average coverage $\theta_l(t)$ to the jamming coverage $\theta_l(\infty)$ is plotted using a semilog scale with time t for line lengths 1, 2, 4, 8, 16, 32, 64 and 128 from top to bottom

behaviour is clearly observed. The averages are made over 30 runs, on the lattices of the size 1024×1024. The noisy curves for $l = 64$ and 128 reflect that averaging over 30 configurations was not sufficient to obtain $\theta(t)$ for large values of t. Within the limits of accuracy, the late stage deposition lines (intermediate regime of graphs) are parallel, suggesting that σ_l is independent of l, i.e., the rate of approach to the jamming coverage is the same irrespective of the segment lengths. From the slopes of these lines we get $\sigma_l \equiv \sigma \simeq 0.53 \pm 0.05$.

The behaviour of A_l for different l-values is obtained from the intercepts in figure 3. Since we have taken the segment lengths to be $l = 2^m$, with $m = 0, 1, 2, \ldots, 7$, and since the lines in figure 3 are nearly equidistant, it is natural to assume that $A_l = c \cdot l^{-\omega}$, where ω is the exponent to be determined, while c is some constant. For the lengths we use, $A_l = c \cdot 2^{-m\omega}$. The plot of $\ln(A_l)$ against m is shown in figure 4 and gives nearly a straight line. From the least squares fit we obtain $\omega = 1.1 \pm 0.1$, and $c = 0.55 \pm 0.10$.

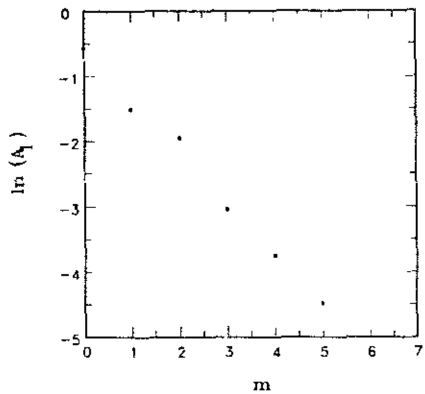

Figure 4. The logarithm of the amplitude $A_l = c \cdot l^{-\omega}$ for different line lengths $l = 2^m$ is plotted against m. A straight line fit of the data gives a slope $\omega = 1.1$ and the constant $c = 0.55$

It seems that the exact form for the approach to the late-stage jamming coverage

$$\theta_l(t) = \theta_l(\infty) - \frac{1}{2l}\exp(-2t) \tag{4}$$

may be conjectured.

In summary, we have performed a numerical Monte Carlo simulation of single-layer RSA of line segments on the square lattice. The jamming coverage $\theta_l(\infty)$ is calculated for various line lengths and extrapolated to obtain $\theta_\infty(\infty)$. The exponential approach (2) to the jamming limit is obtained, and the constants $\theta_l(\infty)$, A_l, and $\sigma = \sigma_l$, are calculated. Our data suggest that the exact form of (2) might be conjectured, as given by (4).

All computations were performed using around 10 hours of CPU time on an IBM 3090 and around 2 weeks of CPU time on Sun4 workstations.

We thank H J Herrmann, J Kertèsz, V Privman and M Henkel for discussions and the critical reading of the manuscript, and M Konstantinović for the explanation of the experimental aspects of RSA

References

[1] Feder J and Giaver I 1980 *J Colloid Int Sci* **78** 144
[2] Onoda G Y and Linigier E G 1986 *Phys Rev* A **33** 715
[3] Kallay N, Tomić M, Biškup B, Kunjašić I and Matijević E 1987 *Colloids Surf* **29** 185
[4] Konstantinović M and Patel R 1991 *Preprint*
[5] Flory P J 1939 *J. Am. Chem. Soc.* **61** 1518
[6] Widom B 1966 *J. Chem Phys* **44** 3888
[7] Pomeau Y 1980 *J. Phys. A: Math Gen* **13** L193
[8] Evans J and Nord R S 1985 *J Stat Phys.* **38** 681
[9] Nakamura M 1987 *Phys Rev* A **36** 2384
[10] Schaaf P, Talbot J, Rabeony H M and Reiss H 1988 *J Phys Chem* **92** 4826
[11] Vigil R D and Ziff R M 1989 *J Chem Phys* **91** 2599

[12] Schaaf P and Talbot J 1989 *Phys Rev Lett* **62** 175
[13] Bartelt M C and Privman V 1990 *J Chem. Phys* **93** 6820
[14] Nielaba P, Privman V and Wang J-S 1990 *J Phys A Math Gen* **23** L1187, 1991 *Phys Rev* B **43** 3366
[15] Sherwood J D 1990 *J. Phys A Math Gen* **23** 2827
[16] Ziff R M and Vigil R D 1990 *J Phys A Math Gen* **23** 5103
[17] Swendsen R 1981 *Phys Rev* A **24** 504