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Random sequential adsorption of lines and ellipses

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Abstract. Infinitely many lines of zero thickness may be adsorbed onto a plane without overlap, and it is shown that the number of lines adsorbed should scale as $\hat{t}^{1/3}$, where $\hat{t}$ is the number of adsorption trials per unit area of surface. This is confirmed by numerical simulation. The adsorption of ellipses with major and minor axes $2a$, $2b$ respectively, is also studied. The area coverage θ approaches its maximum value θ_{max} as $\hat{t}^{-\alpha}$ as $\hat{t}\to\infty$, where α is typically $\frac{1}{3}$. As b/a decreases from unity, θ_{max} first increases to a maximum value 0.58 ± 0.01 when $b=0.5$, and then decreases, a feature not noted in previous work.

1. Introduction

Random sequential adsorption has been studied as a model for the adsorption of a monolayer of proteins onto a surface (Feder 1980). This adsorption is irreversible on some substrates (e.g. glass), and since the proteins do not stick to one another, only a single monolayer of non-overlapping proteins is adsorbed. For a review, see MacRitchie (1978). As adsorption proceeds, so the remaining unoccupied surface decreases, inhibiting further adsorption. Eventually all spaces sufficiently large to accept a protein are filled, and no further adsorption can occur. This is sometimes known as the 'jamming limit'.

The problem may be set in an arbitrary n-dimensional space. In one dimension, lines of unit length are sequentially placed at random on a longer line (of length $L\gg1$), such that no overlap occurs. Eventually all the remaining unoccupied spaces are too short for further adsorption to be possible. This is known as the 'parking problem', and represents cars (of identical length) parking against the side of the road. Exact analytic results are available in this case (reviewed by Feder 1980).

Two-dimensional work has relied largely on computer simulations. The proteins are represented by identical circular discs, which are dropped one at a time, at random, onto the surface. Only those discs which do not overlap any previously adsorbed discs are themselves adsorbed. Discs which are not adsorbed are immediately removed, and the next trial commences. The maximum area coverage $\theta_{max}=0.547$, and Feder (1980) found that the area coverage θ approaches this value as

$$\theta_{max}-\theta\sim t^{-1/2} \tag{1}$$

where the time variable t counts the number of trials. The theoretical basis for this time dependence was established by Pomeau (1980) and Swendsen (1981).

In this paper we consider the two-dimensional adsorption of lines (or of ellipses), rather than circular discs. The motivation for this work came originally from simulations of the motion of lines on a plane. Such simulations require an initial configuration, which was obtained by random sequential adsorption (RSA). It is perhaps appropriate to warn the reader that it is far from clear that RSA is an appropriate algorithm for generating such configurations. The rate of adsorption decreases throughout the adsorption process. While we shall see that arbitrarily high number densities of lines may be obtained, it is clear that for shapes with a non-zero area the maximum coverage θ_{max} generated by RSA may be well below that of maximum close packing (which for discs is 0.91). The coverage could be increased by allowing motion of the particles after adsorption, so that small open spaces could combine into larger spaces. However, the final stages of adsorption would proceed exceedingly slowly, especially if the motion of previously adsorbed particles was uncorrelated with the attempts to adsorb new particles. (If the system was in thermal equilibrium, the rate of adsorption would be related to the chemical potential, as discussed by Widom (1965) and by Eppenga and Frenkel (1984).) Moreover, although the configuration obtained by RSA is disordered, this does not necessarily reduce the time required for a simulation to forget the choice of initial configuration below the time required if the initial configuration is based on a regular array. The radial distribution function $g(r)$ generated by RSA is *not* the same as the equilibrium distribution function of a hard-disc fluid (Widom 1966, Feder 1980). RSA leads to logarithmic divergence of $g(r)$ for particles close to contact: very rapid motion can occur at the start of a simulation if soft inter-particle repulsions are present.

In section 2 we present results for the kinetics of adsorption of lines of zero thickness, together with a simple model. In section 3 we extend this study to the adsorption of ellipses. Talbot *et al* (1989) have recently shown that the asymptote (1) for coverage at long times does *not* hold when the discs are replaced by ellipses with major and minor axes $2a$ and $2b$, respectively. This makes extrapolation of numerical simulations to the limit θ_{max} somewhat more problematic. We shall discuss simulations which approach very close to the jamming limit, and we shall show that as b/a decreases from unity, θ_{max} first increases to a maximum value 0.584 ± 0.01 when $b \simeq 0.5$, and then decreases.

2. Adsorption of lines of zero thickness

We consider first lines of length $2a$ and of zero thickness, dropped onto a plane. Figure 1 shows 228 such lines which have landed on a square of side $10a$ after 10^4 trials. The first few lines can fall at random. Later lines are forced to lie approximately parallel to these first lines, in order to prevent overlap. We see in figure 1 that there are domains, of typical size $2a$, in which the lines are approximately parallel.

Since the lines have zero thickness, the jamming limit is never reached. The rate at which lines are adsorbed may be studied by considering a single ordered domain consisting of lines parallel to the x-axis at a typical spacing $h \propto n^{-1}$, where n is the number density of the lines. The domain is bounded by adjacent domains, and thus lies within $-a-h<x<a+h$. We now attempt to add another line, with centre (x_0, y_0) and orientation θ_0, within a single gap of width h. The probability that y_0 and θ_0 permit this is proportional to h^2, whilst the probability that $-h<x_0<h$ introduces an additional factor h. There are h^{-1} gaps within the domain, and hence $\mathrm{d}n/\mathrm{d}t$, the rate of adsorption per unit area, is proportional to h^2 i.e. to n^{-2}. Integration leads to

$$n \propto t^{-1/3}.$$

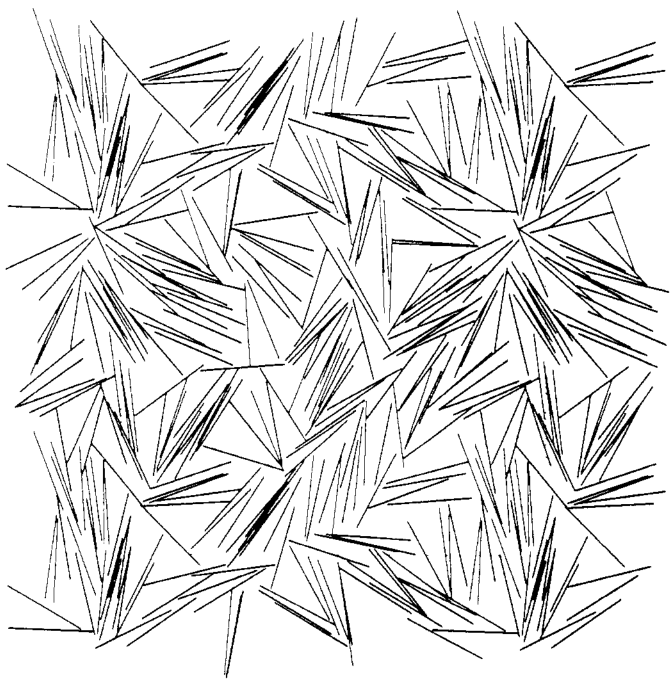

Figure 1. 228 lines of length $2a$ adsorbed on a square of side $10a$ after 10^4 trials.

Ten independent numerical simulations were performed to test this. In each, 640 000 lines were dropped onto a square of side $L = 20a$. We non-dimensionalise area by a^2, and adopt a scaled time variable $\hat{t}$, related to the number of attempts to adsorb, N, by $\hat{t} = Na^2/L^2$. Figure 2 shows results for the non-dimensional number-density $\hat{n}$ as a function of $\hat{t}$, averaged over the 10 trials. A least-squares fit of results for $\hat{n} > 3$ to the form $\hat{n} = A\hat{t}^{\alpha}$ gives $\alpha = 0.331$ and $A = 0.493$. Forcing $\alpha = 1/3$ gives $A = 0.486$.

If the centre of the ith rod is at $\boldsymbol{r}_i$, with orientation θ_i, then we expect that $|\theta_i - \theta_j| \ll$ if $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j| \ll a$. Figure 3 shows $\langle \cos^2(\theta_i - \theta_j) \rangle$ as a function of $\hat{r} = r_{ij}/a$. It decreases from 1 (parallel lines) when $\hat{r} \ll 1$ to 0.5 (random orientations) when $\hat{r} \gg 1$, and we see

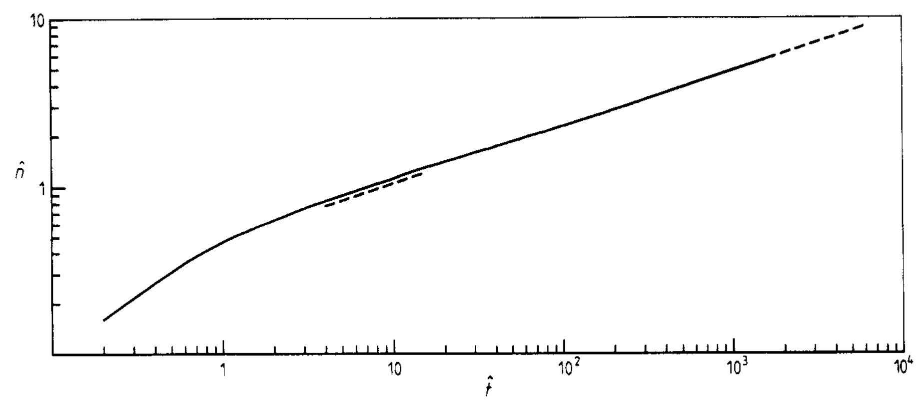

Figure 2. The non-dimensional number-density $\hat{n}$ as a function of $\hat{t}$, the number of attempts to adsorb per unit area.

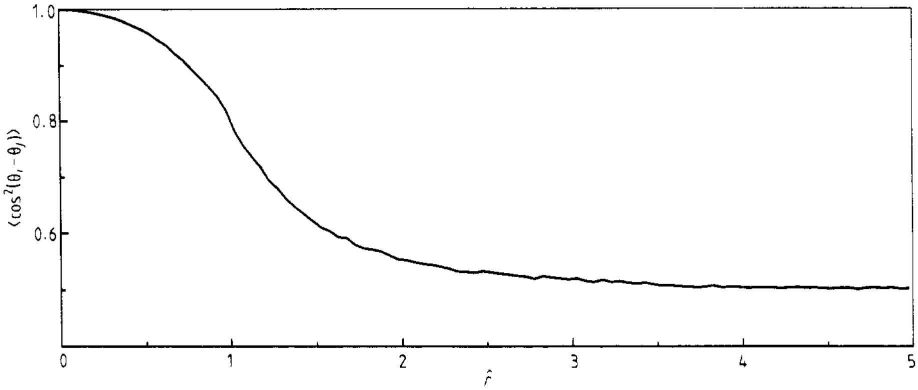

Figure 3. $\langle\cos^2(\theta_i-\theta_j)\rangle$ as a function of the separation $\hat{r}=r_{ij}/a$, for lines at $\hat{t}=1600$.

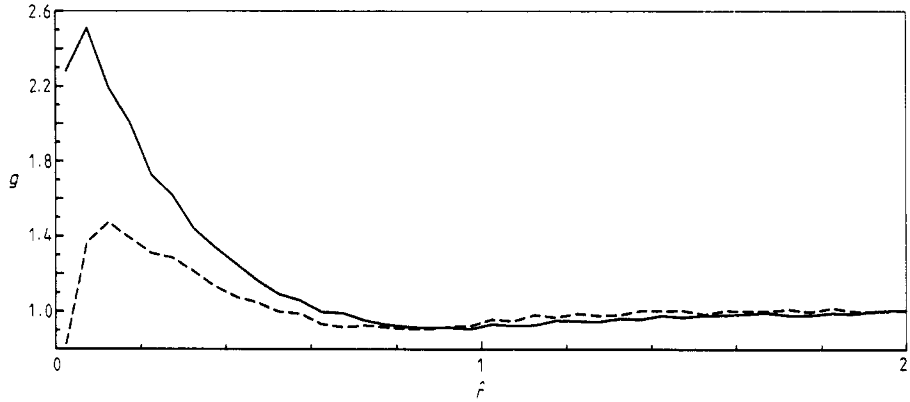

Figure 4. The radial pair distribution function $g(r)$ for lines. Full curve: $\hat{t}=1600$; broken curve: $\hat{t}=200$.

that the ordered domains are approximately of size $2a$. Figure 4 shows the two-dimensional radial pair distribution function $g(r)$, defined such that when the number density of lines is n_0, the expected number of lines to be found within a circle of radius r from the centre of a given line is $n_0\int_0^r g(r)2\pi r\,\mathrm{d}r$. The logarithmic divergence usually found at small separations at the jamming limit (Pomeau 1980, Swendsen 1981) cannot be attained, since the jamming limit is never reached.

3. Adsorption of ellipses

In section 2 we saw that an infinite number of lines may be adsorbed onto a surface without overlap. Each line has zero surface area, so that at any finite time the coverage $\theta=0$. The particles in any *real* system are likely to have a finite area, and we therefore consider the adsorption of ellipses (major axis $2a$, minor axis $2b$). It is clear that there will now be a maximum packing number density $n_{\max}$, which will be large when $b/a\ll 1$, and which will decrease as $b/a\to 1$. However, it is far from clear how the area coverage $\theta_{\max}=\pi abn_{\max}$ will vary as a function of b/a.

Swendsen (1981) gave a simple argument to explain the kinetics of adsorption of discs, and the root time behaviour (1) has been successfully used by Hinrichsen *et al* (1986) and others to extrapolate numerical simulations to the limit of an infinite number of trials. However, Swendsen's arguments break down when the adsorbed particles are no longer circular. This case has been recently discussed by Talbot *et al* (1989), and there is no need to repeat the arguments they present. A straightforward extension of the analysis leads to a prediction that the area coverage θ increases to its limiting value θ_{max} as

$$\theta \sim \theta_{max} - Bt^{-1/3} \qquad t \to \infty.$$

This hypothesis was tested by numerical simulations on ellipses of aspect ratio $1 > b/a > 0.2$. The ellipses were dropped onto a square, usually of side $20\sqrt{2}a$, and ten independent trials were performed. Periodic boundary conditions were applied at the edges of the square. Random numbers were generated by the FORTRAN function *rand* available on a Sun, and the algorithm of Viellard-Baron (1972) was used to check for overlap. When b/a was small, the number density of ellipses eventually became large, and for $b/a \leq 0.4$ the target area was reduced to a square of side $20a$. For $b/a \leq 0.3$ the number of independent trials was reduced to 5, each with 4×10^7 attempts to adsorb.

Figure 5 shows the area coverage θ, after averaging over the independent trials, plotted against $\hat{t}^{-1/3}$. We see a good straight line over a large portion of the curve. The results of a least-squares fit to a function of the form $\theta = A + Bt^{-\alpha}$ depend on the range of values of t over which the fit is made. At small times the asymptotic behaviour has not yet been attained, while at large times the area coverage increases in a series of widely separated discrete jumps, because of the finite size of the simulation. There is evidence that α approaches values smaller than 0.3 as $b/a \to 0$, but the results are not sufficiently strong to confirm the observations of Talbot *et al* of a definite departure of α from the predicted value of $\frac{1}{3}$. Because of these uncertainties, the simulations were performed on rather small systems. Final coverages were close to maximum, so that errors introduced by extrapolation to an infinite number of trials were reduced:

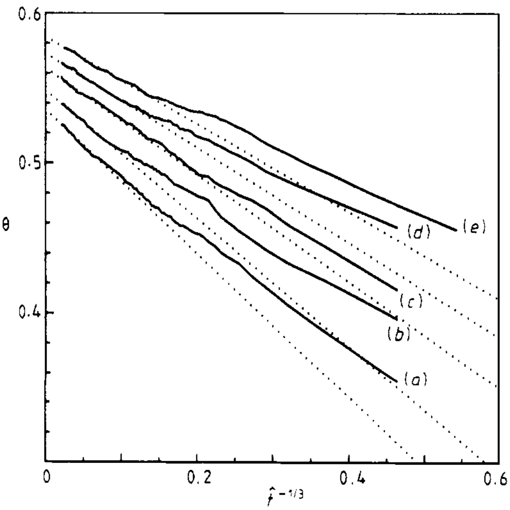

Figure 5. The area coverage θ as a function of the scaled time variable $\hat{t}^{-1/3}$. Aspect ratios b/a (*a*) 0.2, (*b*) 0.25, (*c*) 0.3, (*d*) 0.4, (*e*) 0.5. The broken lines show the least-squares straight line fit for $10^3 < \hat{t} < 10^5$.

this, of course, had the disadvantage of increasing the errors due to the finite size and periodic boundaries.

Figure 6 shows the limiting area coverage θ_{max} as a function of the aspect ratio b/a. The error bars indicate the standard deviation of the 10 independent trials. Experiments were performed to test that varying the size of the square did not affect the results, which still lay within the error bars. The extrapolation to the jamming limit was performed by means of a least-squares fit with the exponent α set equal to $\frac{1}{3}$. However, the simulations finished sufficiently close to the jamming limit that extrapolation as $t^{-1/4}$ or $t^{-1/2}$ led to area coverages which lay within the error bars of figure 6. For discs, the value $\theta_{max} = 0.547 \pm 0.014$ agrees with published values (see Hinrichsen *et al* 1986), but the bounds on the error are much poorer than have been established previously. At an aspect ratio $b/a = 0.2$, the value $\theta_{max} = 0.542 \pm 0.003$ obtained by Talbot *et al* lies within the error bars. The statistical error decreases slightly at higher aspect ratios, since the total number of adsorbed ellipses increases in this limit. The most striking feature of figure 6 is the maximum which occurs at an aspect ratio of about 0.5. This is a novel result. Although Talbot *et al* do not in general report results for θ_{max} (Θ_∞ in their notation), it is not unlikely (from their table 1) that they obtained a similar maximum.

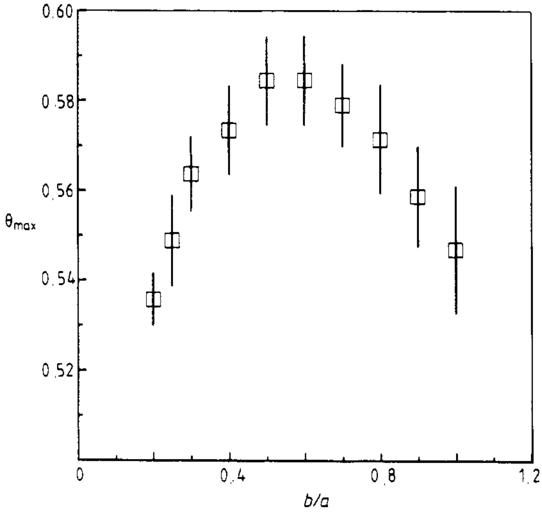

Figure 6. The maximum area coverage θ_{max}, as a function of the aspect ratio b/a. The error bars indicate the standard deviation of the independent trials.

We have chosen to work with $b/a \leqslant 1$, but it is clear that $\theta_{max}(b/a) = \theta_{max}(a/b)$. This might suggest that θ_{max} should be stationary at $b/a = 1$. However, we see in figure 6 that the slope $d\theta_{max}/d(b/a) \simeq -0.15$ as b/a approaches 1 from below.

It is not obvious why θ_{max} should attain a maximum when $b/a \simeq 0.5$. For the reasons explained in section 1, there is no relation between this system and one which is at thermal equilibrium, such as that discussed by Wadati and Isihara (1972).

In figure 6 we see that θ_{max} decreases as $b/a \to 0$ i.e. in the limit as the ellipses approach the lines of zero thickness discussed in section 2. Clearly θ_{max} is bounded below by zero, but at present it is not known whether $\theta_{max} \to 0$ as $b/a \to 0$.

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