Random sequential adsorption with restructuring in two dimensions

1992 J. Phys. A: Math. Gen. 25 L189

(http://iopscience.iop.org/0305-4470/25/4/007)

J. Phys. A: Math. Gen. 25 (1992) L189–L194. Printed in the UK

LETTER TO THE EDITOR

Random sequential adsorption with restructuring in two dimensions

Rémi Jullien† and Paul Meakin‡

† Bâtiment 510, Physique des Solides, Université Paris-Sud, Centre d'Orsay, 91405 Orsay, France

‡ Central Research and Development Department, The du Pont Company, Wilmington, DE 19880-0356, USA

Received 25 November 1991

Abstract. A modified version of the random sequential adsorption model for the deposition of spherical particles onto a plane is presented. Successive particles are added via randomly positioned vertical trajectories and, if they do not stick to the plane at first contact, follow the path of steepest descent on the previously deposited particles before being adsorbed. All particles reaching a stable position in contact with three previously adsorbed particles are removed. The limiting coverage is found to be $0.610\,56 \pm 0.000\,05$ (larger than that of the standard RSA model) and is shown to be reached exponentially with the number of trials. The size distribution of connected clusters of spheres is analysed and is found to exhibit an exponential decay for large cluster sizes.

In the random sequential absorption model (RSA) in two dimensions, disks are sequentially deposited at random positions on a plane; if the last deposited disk overlaps with any of those already present it is removed, otherwise it is permanently fixed. Starting from an empty plane the process continues up to the 'jamming limit' at which it is impossible to deposit further disks. It has been shown [1–3] that the coverage c (fraction of the surface occupied by disks) reaches its jamming limiting value $c_j \simeq 0.547$ as a power law with time (time being defined to be proportional to the number of trials):

$$c_j - c \sim t^{-1/2}. \tag{1}$$

This model has been used to explain several experiments like the adsorption of proteins [4] and latexes [5] on solid surfaces.

However, when applied to experiments, the most important constraint of the model appears to be the strict rejection when a next deposited particle overlaps previously accepted particles. In real processes it seems quite likely that if a deposited particle first contacts a previously deposited particle instead of the bare substrate it can reach the substrate by moving on the previously deposited particles. In this letter we present a modified version of the RSA model in which such motion is allowed in a simple way. In our model spheres are deposited along randomly positioned vertical trajectories and if they do not first contact (and stick to) the horizontal plane, they follow the path of steepest descent on the previously deposited particles before being adsorbed. All spheres reaching a stable position in contact with three previously deposited spheres without contacting the plane are removed. By use of numerical simulations we find that the jamming coverage is substantially increased and is reached more quickly (exponentially) than in the standard RSA model. Moreover, the jamming configuration consists of an assembly of connected clusters of spheres whose size distribution decays

0305-4470/92/040189+06$04.50

exponentially with increasing cluster size. After completing this work, we learned of similar studies of restructuring by diffusion [6, 7]. Our process corresponds to conditions under which gravity effects are more important than diffusion.

Our simulations were carried out using an underlying lattice with a size of $L \times L$ lattice units in the $z=0$ horizontal plane. The particles are spheres of radius $r=0.71$, a value slightly larger than $1/\sqrt{2}$ in order that the centre of at most one deposited sphere can lie within any particular site of the underlying lattice. Each element in the underlying lattice which is occupied by the horizontal projection of the centre of a deposited sphere is labelled with a number that points to the position of that sphere in a list of coordinates. This facilitates the process of searching for contacts between the new sphere and the previously deposited ones. At each attempt to deposit a new sphere, the two coordinates x and y of its centre are chosen at random, uniformly, between 0 and L. Then this new sphere is released from above the deposit (i.e. with a z coordinate larger than $3r$) along a vertical trajectory and a search is performed to find the sphere of the deposit that it will first contact. If no contact is found, the new sphere is deposited with its centre at x, y, r. If a contact is found, the new sphere starts to roll on the contacted particle in a vertical plane and a search is performed to find the sphere of the deposit that it will first contact during this rotational motion. If the new sphere reaches the plane before finding any other contact, it is immobilized on the plane at this new position (i.e. on the plane and in contact with one previously deposited sphere). If a contact with another sphere is found, the new sphere continues its motion by rolling down around an axis joining the centres of the two contacting particles and another search for a contact is performed. If the new sphere reaches the plane without finding a third contacting sphere, it is immobilized at its new position (i.e. on the plane and in contact with two previously deposited spheres). If a third contacting sphere is found, the stability against gravity in the position with three contacts is determined. If the projection on the plane of the new sphere's centre lies outside the triangle made with the projections of the centres of the three contacting spheres, a further rotational motion is performed around two spheres and so on. During all this motion periodic boundary conditions are used on the edges of the square. It is only when a stable position is found (i.e. when the projection of the new sphere lies inside the triangle) that the sphere is discarded and another attempt is made. At each attempt (successful or not) the time t is increased by:

$$\delta t = \frac{\pi r^2}{L^2}.$$

The coverage $c(t)$ is calculated from the number of (successfully) deposited spheres, $N(t)$, at time t:

$$c(t) = N(t)\frac{\pi r^2}{L^2}.$$

During the deposition process, we have identified the clusters of connected deposited particles and determined their size distribution by calculating $f(n)$ which is the fraction of clusters of contacting particles containing n spheres. In a sense, the observed cluster growth can be viewed as a cluster–cluster aggregation process [8], since sometimes a newly deposited particle can contact particles in two disconnected clusters and thus create a new (larger) cluster by connecting two (smaller) clusters.

To determine the time evolution of $c(t)$ and estimate the jamming limit c_j, $c(t)$ has been averaged, for each t, over $N_s=500$ independent simulations with $L=256$

and an upper time $t \sim 8$ corresponding to a total number of attempts of about 270 000. In figure 1, we show how $c(t)$ depends on t at early times (for $t < 4$) and we compare with the corresponding results for the standard RSA model. The qualitative behaviour is completely different in the two models. While in the standard RSA model $c(t)$ converge quite slowly (as a power law, equation (1)) to the jamming limit $c_j \simeq 0.547$, in our case the convergence is much more rapid and turns out to have an exponential form. Based on previous analytical studies explaining the power-law behaviour of the regular RSA model [2-4], it can be easily understood why, in our case, the asymptotic behaviour is changed into an exponential. This comes from the fact that the area of the targets that the centres of the added disks must reach to be successfully deposited does not tend to zero at the jamming threshold.

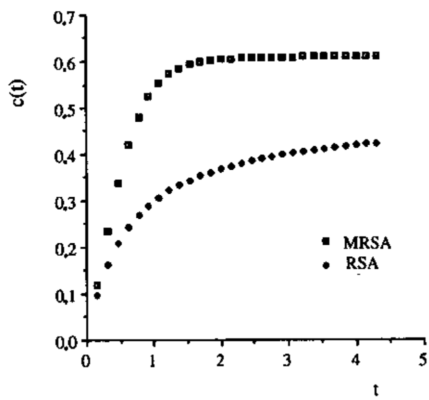

Figure 1. Plot of the coverage fraction $c(t)$ as a function of time t for our MRSA model compared with the standard RSA model.

In our model, $c(t)$ is found to converge so quickly to its limit that it is necessary to average over a relatively large number of simulations to get a continuous curve up to the largest time and to obtain reliable results on the asymptotic behaviour. The analysis of the asymptotic behaviour is given in figure 2(a, b). In figure 2(a), we have plotted $\ln(c_j - c(t))$ as a function of t for different trial values for c_j. From this analysis, it might be concluded that c_j can be estimated with a very high precision (within 10^{-6} error). However the same analysis with comparable results, obtained using a different seed for the random generator, can give an estimated c_j value which differs by 5×10^{-5}. By comparing ten different series of simulations (with $N_s = 500$ each), we give the following final estimate for the jamming coverage:

$$c_j = 0.610\,56 \pm 0.000\,05.$$

Comparisons with simulations of lower size (with $L = 128$) show that this estimate for the jamming coverage is quite independent of the box size.

In figure 2(b), we compare the preceding plot, corresponding to the 'best' value for c_j ($c_j = 0.610\,591$) for this particular simulation, with a plot of $\ln(t^{\alpha}(c_j - c))$ versus t with $\alpha = 3, 4, 5$. This suggests that $c(t)$ might approach c_j exponentially with a power-law prefactor:

$$c - c_j \sim t^{-\alpha}\, e^{-t/t_0}.$$

From this analysis we roughly estimate $\alpha \sim 4$ and $t_0 \sim 2.5$.

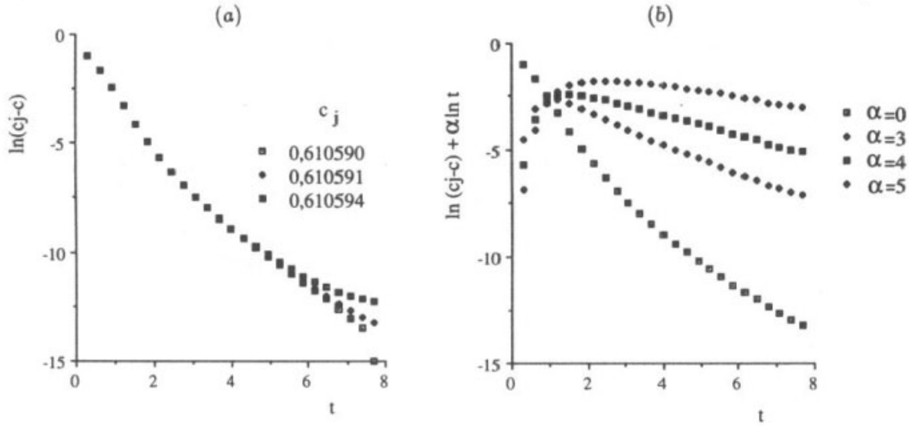

Figure 2. (*a*) Plot of $\ln(c_j - c)$ as a function of time t for different values of c_j. (*b*) Plot of $\ln t^{\alpha}(c_j - c)$ as a function of time t for $c_j = 0.610\,591$ and different values of α. In these plots $c(t)$ has been averaged over 500 independent runs made with $L = 256$ up to time $t \sim 8$.

In figure 3, we provide a picture of a simulation made with $L = 128$ showing the clusters of connected particles near to the jamming limit. The largest cluster does not extend from one side of the box to the other and simulations done with boxes of different sizes show that its averaged size is almost independent of the box size. This means that the present mechanism is completely different from percolation. This is also reflected in the quantitative results for the cluster size distribution $f(n)$, shown in figure 4(a, b). In these figures $f(n)$ has been averaged over 500 simulations with $L = 128$ and with a sufficiently high t ($\sim$8) to estimate that the jamming limit has been practically reached. To reduce the statistical uncertainties due to the existence of only

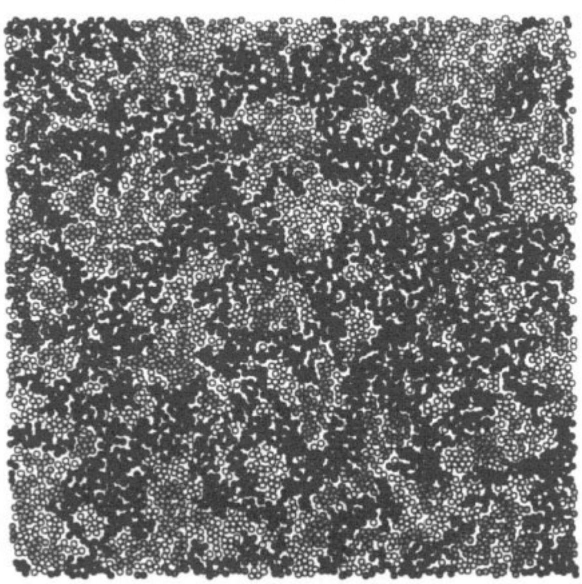

Figure 3. A typical example of coverage obtained with $L = 128$, almost at jamming ($t \sim 8$) where clusters of connected particles are shown with different grey tones depending on their number of particles.

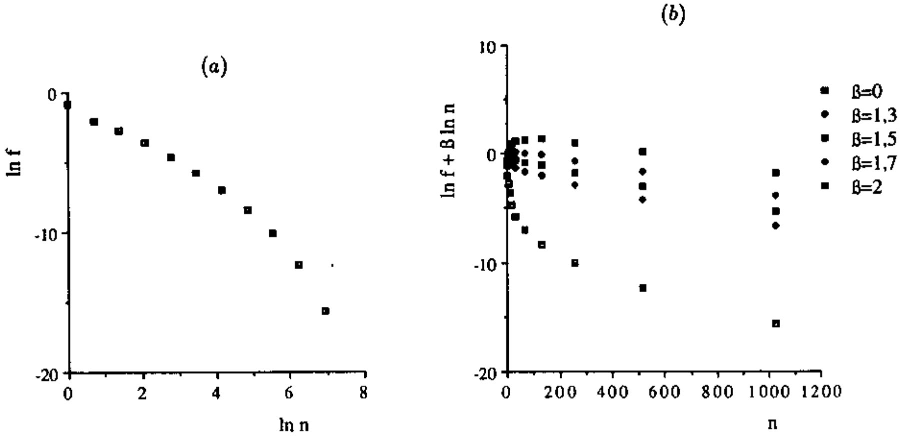

Figure 4. (a) Plot of $\ln f(n)$, where $f(n)$ is the proportion of clusters with n particles, as a function of $\ln n$. (b) Plot of the same quantity as a function of n. On the same figure is shown the plot of $\ln n^{\beta} f(n)$ as a function of n for different values of β. In these plots $f(n)$ has been cumulated between 2^i (with i integer) values of n and averaged over 500 independent runs for $L = 128$ almost at jamming ($t \sim 8$).

few clusters of large sizes, the histogram has been cumulated from values of n varying by a factor 2. Figure 4(a) shows $\ln f$ as a function of $\ln n$. This figure suggests that the large-n behaviour of the size distribution is certainly not a power law. In figure 4(b) we have plotted instead $\ln f$ as a function of n. On this plot there is a more convincing tendency to a linear behaviour for large n. We have also tried to estimate a power law prefactor by plotting $\ln(n^{\beta} f)$ with $\beta = 1.3$, 1.5, 1.7, 2. This suggests the following behaviour of $f(n)$ for large n:

$$f(n) \sim n^{-\beta}\, \mathrm{e}^{-n/n_0}$$

with $\beta \sim 1.6$ and $n_0 \sim 200$. The size-distribution is thus completely different than that associated with percolation. Finally we have tried to estimate the fractal dimension of these clusters by analysing their radius of gyration as a function of their size but we did not get any linear behaviour up to the largest size we could reach. This negative result is not surprising since, in contrast to the percolation situation, our clusters are of limited size so that a fractal analysis is highly questionable.

In conclusion, we have studied a quite natural extension of the random sequential absorption model which includes some simple restructuring. The jamming limit is substantially increased compared to the standard RSA model and the convergence to the jamming limit is much more rapid. This model leads to the formation of connected clusters of spheres whose size distribution exhibits an exponential decay at large sizes. We intend to extend this study to the case of a mixture of spheres of different sizes since it has been shown that different kinds of asymptotic behaviours can be found in the case of the standard RSA model [10]. Note that our model can be entirely defined in two dimensions, where the rules consists of a series of disk shifts in the plane. In this way it can simply be extended to three dimensions where it can provide a model to build disordered packings of spheres with a larger packing fraction than that of the 3D RSA model ($c_j \sim 0.38$) [11].

One of us (RJ) would like to acknowledge D Bideau for useful discussions.

References

[1] Feder J 1980 *J. Theor. Biol.* **87** 237
[2] Pomeau Y 1980 *J. Phys. A: Math. Gen.* **13** L193
[3] Swendsen R H 1981 *Phys. Rev.* A **24** 504
[4] Feder J and Giaever I 1980 *J. Colloid Interf. Sci.* **78** 144
[5] Onoda G Y and Liniger E G 1986 *Phys. Rev.* A **33** 715
[6] Elaissari A, Haouam A, Huguenard C and Pefferkorn E 1991 *J. Colloid Interf. Sci.* in press
[7] Schaaf P Private communication
[8] Meakin P 1983 *Phys. Rev. Lett.* **51** 1119
Kolb M, Botet R and Jullien R 1983 *Phys. Rev. Lett.* **51** 1123
[9] Hinrichsen E L, Feder J and Jossang T 1986 *J. Stat. Phys.* **44** 793
[10] Talbot J and Schaaf P 1989 *Phys. Rev.* A **40** 422
Meakin P and Jullien R submitted for publication
[11] Cooper D W 1987 *J. Colloid Interf. Sci.* **119** 442
Talbot J, Schaaf P and Tarjus G 1991 *Mol. Phys.* **72** 1397