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1986 J. Phys. A: Math. Gen. 19 1727

(http://iopscience.iop.org/0305-4470/19/9/043)

J. Phys. A: Math. Gen. 19 (1986) 1727-1734. Printed in Great Britain

# Aggregation at a surface: crossover behaviour in a biased diffusion model

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Received 20 June 1985, in final form 20 August 1985

**Abstract.** We introduce a biased diffusion model of aggregation at a surface, which reduces to a ballistic model in one limit. We characterise the structure of the aggregates by a variety of properties and find that it is a strong function of the parameter governing the diffusion process. For thin films there is a crossover between a regime where there are several highly ramified pseudo-one-dimensional clusters and another regime where there is a single cluster which spans the lattice in both directions.

## 1. Introduction

Many naturally occurring processes, such as crystal growth and the formation of colloidal particles, involve the phenomenon of aggregation. One can imagine a number of different types of growth process ranging from diffusion-limited aggregation (Witten and Sander 1981) to ballistic processes where the particles are constrained to move along straight lines (Vold 1963, Sutherland 1966, 1967, Bensimon *et al* 1984a, b, Liang and Kadanoff 1986, Ramanlal and Sander 1985). The structure of the aggregate strongly depends on the dynamics of the growth process.

A variety of models has been constructed to study the importance of various features of the growth process, and a great deal of attention has been directed to characterising the growing cluster by its fractal dimension (Forrest and Witten 1979, Meakin 1983a, b, Meakin and Stanley 1983, Meakin and Deutch 1984, Muthukumar 1983). The effect of anisotropic diffusion on aggregation at a single seed has been considered by Meakin (1983c, 1984).

Much of the recent literature has focused on the growth of an aggregate from a single seed particle but some work has been carried out on aggregation at a surface (Vicsek 1984, Meakin 1983d, Racz and Vicsek 1984, Voss 1984, Jullien *et al* 1984). Of course there is an enormous literature on crystal growth at a surface (Weeks and Gilmer 1979, Leamy *et al* 1980) but recent papers have been concerned with the fractal nature of the object and with a comparison between growth at a surface and growth from a single seed.

In this paper we introduce a new biased diffusion model for crystal growth at a surface. It possesses features of both the diffusion-limited aggregation (DLA) model and the ballistic model. (As is usual in models of this type effects of surface tension

0305-4470/86/091727+08$02.50  

are ignored.) In the DLA model, clusters are generated by the adhesion of diffusing particles to the surface of a growing aggregate. In the ballistic model there is no diffusion and particles move rectilinearly towards the surface of the growing cluster to which they adhere. In our biased diffusion model particles move on a lattice, towards the surface with probability $p$ and parallel to the surface with probability $(1-p)$. Clearly, for $p=1$ this diffusion process reduces to a ballistic model while for small $p$ the lateral diffusion dominates. In any aggregation process in an external (e.g. gravitational) field, the diffusion process is biased and our model, while idealised, incorporates this feature. We study a variety of properties which characterise the fractal nature of the aggregates. For thin films, we observe a qualitative difference in the structure of the aggregate for small and large $p$ and the main results of this paper are concerned with the characterisation of this crossover phenomenon.

## 2. Model for the aggregation process

We consider a subset of the square lattice with $1 \leqslant x \leqslant N$, $1 \leqslant y \leqslant M$ and periodic boundary conditions on $x$, in order to simulate an infinite half plane. Particles are introduced one at a time at a randomly chosen $x$ coordinate on the upper boundary, $y=M$, and perform a biased random walk with zero probability for an upward step, probability $p$ for a downward step and equal probabilities, $\frac{1}{2}(1-p)$, in the positive and negative $x$ directions. A particle continues to move until it either reaches the lower boundary, $y=1$, at which point it sticks, or until it reaches a point adjacent to a site already occupied by a particle. Of course, $p$ must be positive since otherwise the particle does not move towards the line of absorbing sites.

The process is continued until a site on the line $y=M$ is occupied, so that a connected set of occupied sites (which we call a cluster) spans the lattice in the $y$ direction. This is reminiscent of a percolation problem at the percolation threshold and suggests an analysis of the results using concepts from that field (Stauffer 1979).

During the aggregation process we distinguish between the different clusters and focus attention on the cluster with a site in $y=M$, which we call the spanning cluster. In particular we examine the fractal dimension of this cluster, the span in the $x$ direction and its variance, the fraction of occupied sites in the spanning cluster and its variance, as well as the mean valence of a site in the spanning cluster. These quantities allow us to characterise, in various ways, the degree of ramification of the spanning cluster.

## 3. Results

We have carried out calculations for a range of $p$ values, on square arrays of size up to $200 \times 200$ and on various rectangular arrays. All of the numerical results represent averages over between 100 and 200 realisations of the growth process. Initially we focus attention on the results for square arrays. The first quantity which we examine is the mean valence of sites in the spanning cluster, $v(p)$. This quantity, shown in figure 1, exhibits a shallow minimum at about $p=0.3$ followed by a nearly linear increase; $v(p)$ is relatively independent of lattice size. At all $p$ the valence is quite small, corresponding to a ramified structure with few cycles. The corresponding values of the mean valence of sites in the incipiently percolating cluster for bond and site

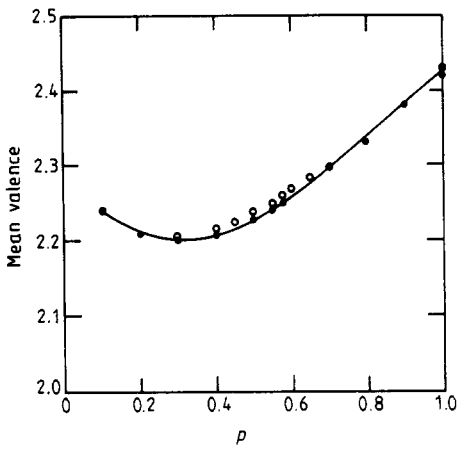



**Figure 1.** The $p$ dependence of the mean valence of a site in the spanning cluster: ○, 200 × 200; ●, 100 × 100.

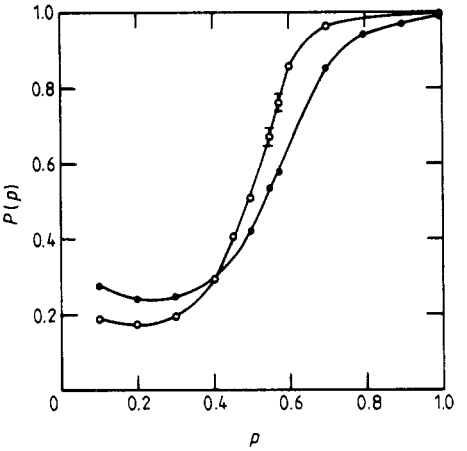



**Figure 2.** Probability that an occupied site lies in the spanning cluster, as a function of $p$: ○, 200 × 200, ●, 100 × 100. Error bars are shown in some typical cases.

percolation on the square lattice (Whittington *et al* 1981) are about 2.25 and 2.50, respectively. In the aggregation model the bonds are induced by the occupation of the sites and so the value of $v$ for this model should be compared with that for site percolation. The clusters in the aggregation model are somewhat more ramified than in Bernoullian site percolation, even for large values of $p$.

The $p$ dependence of the fraction of occupied sites in the spanning cluster has a sigmoidal shape (figure 2), which sharpens as the lattice size increases. For small $p$ the spanning cluster accounts for only a small proportion of the occupied sites, but at large $p$ almost all the occupied sites are in this cluster. These results suggest a crossover between the above kinds of behaviour. At intermediate values of $p$ one would therefore expect large fluctuations and this is borne out in the behaviour of the variance of the corresponding distribution.

To investigate this crossover behaviour further we have calculated the mean span in the $x$ direction of the spanning cluster, and its variance, and the results are shown in figure 3. For small $p$ the clusters have a small span and are highly anisotropic; the span increases until for large $p$ the cluster extends over the whole cell and so, because of the periodic boundary conditions, over the entire lattice.

Some of the results discussed above are evident in pictures of typical clusters shown in figure 4. At $p = 0.1$ (figure 4($a$)) there are several highly ramified, almost-spanning clusters, each of which have emanated from a single site in $y = 1$. As $p$ increases the coalescence of clusters becomes important in the growth process, which leads to an increase in the average span, as is evident in figure 4($b$). In the crossover region (around $p = 0.5$) there are fluctuations between clusters which resemble those at small $p$ (figure 4($c$)) and those which span the lattice in the $x$ direction (figure 4($d$)).

To investigate the importance of boundary effects we have examined some rectangular arrays. When the lateral dimension of the array is increased with the height fixed ('wide' arrays) we find that, at small $p$, there are several almost-spanning clusters each having about the same width as the spanning cluster in the corresponding square array with the same height, see figure 5($a$). At larger values of $p$ we find, at fixed $p$,

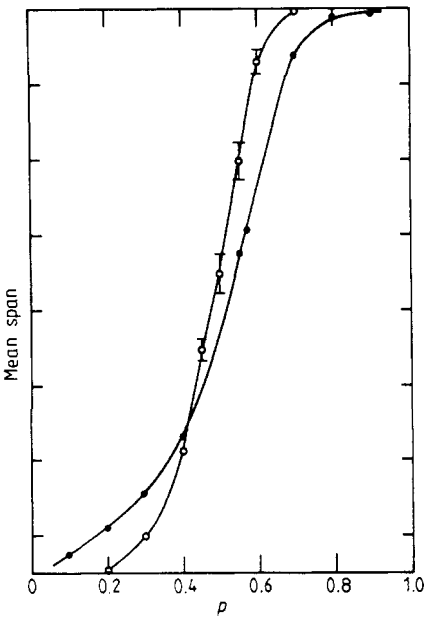



**Figure 3.** Mean span as a function of $p$: ○, $200 \times 200$; ●, $100 \times 100$, arbitrary units.

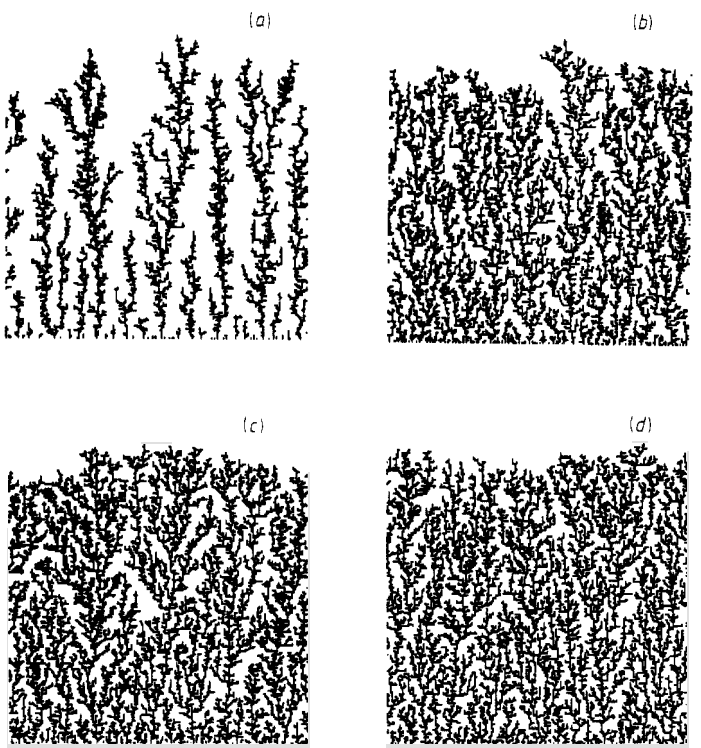
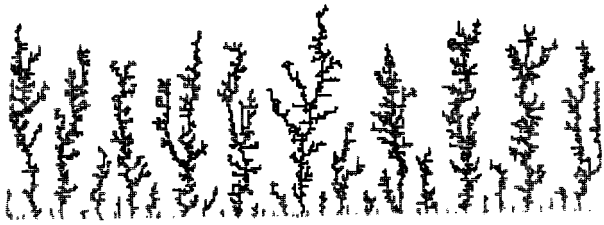



**Figure 4.** Configurations at (*a*) $p = 0.1$, (*b*) $p = 0.4$, (*c*) and (*d*) $p = 0.5$ for a $200 \times 200$ lattice. In these figures the sites of the spanning cluster are represented by full squares while the sites belonging to all other clusters are represented by open squares.

(*a*)



(*b*)

**Figure 5.** Configurations for $400 \times 100$ rectangular arrays for (*a*) $p = 0.1$ and (*b*) $p = 0.7$.

that the fluctuations in the $x$ span of the clusters increases as the width of the array increases, and at fixed array width ($N$) these fluctuations increase as $p$ decreases towards the crossover region. One example of a cluster at $p = 0.7$ is shown in figure 5(*b*).

If the mean span in the $x$ direction (figure 3) is taken as a characteristic length $L$ of the cluster, the calculations suggest that this length would diverge beyond the crossover region for a lattice infinite in the $x$ direction. This conclusion is supported by calculations on wide arrays ($400 \times 100$) at $p = 1.0$, which yield clusters that have an $x$ span equal to the array width $N$. Another length scale in this problem is the lattice spacing $l$. However, all our results indicate that the crossover phenomenon is insensitive to the value of $l$. The qualitative nature of the crossover remains as one changes the system from $100 \times 100$ to $400 \times 400$, which can be viewed either as decreasing the lattice spacing, or as increasing the system size, by a factor of four.

It is clear from figures 4 and 5 that the structure of the spanning cluster changes as $p$ varies. We can characterise this change in terms of the fractal dimension of the cluster. Two useful quantities which reflect the fractal nature of such objects are the capacity and information dimension, defined as follows (Farmer 1982, Farmer *et al* 1983). Consider partitioning the array into square boxes of length $\varepsilon$. Let $N(\varepsilon)$ be the number of boxes of length $\varepsilon$ occupied by sites of the spanning cluster. The capacity ($D_C$) is given by

$$D_C = \lim_{\varepsilon \to 0} \frac{\log N(\varepsilon)}{\log(1/\varepsilon)}.$$

The capacity should be distinguished from the Hausdorff dimension, which is defined in terms of a covering of the set by boxes with variable edge length. While these two dimensions are equal in many instances, in general they are not (Farmer *et al* 1983).

If $p_i$ is the probability that a randomly chosen site in the spanning cluster occupies box $i$, of length $\varepsilon$, then the information dimension ($D_I$) is defined as

$$D_I = \lim_{\varepsilon \to 0} \frac{\sum_{i=1}^{N(\varepsilon)} p_i \log(1/p_i)}{\log(1/\varepsilon)}.$$

When the probabilities $p_i$ are equal then $D_C = D_I$. In general these probabilities will not be equal and in this sense one may say that the difference between the values of these two dimensions reflects inhomogeneities in the fractal object. These dimensions satisfy the inequality $D_C \geqslant D_I$. We estimate these quantities for each realisation, and average over 100 to 200 realisations, at each value of $p$; thus we may also estimate the fluctuations in the dimension. The results for the capacity of the spanning cluster for $200 \times 200$ arrays are shown in figure 6. The sigmoidal shape reflects the crossover from

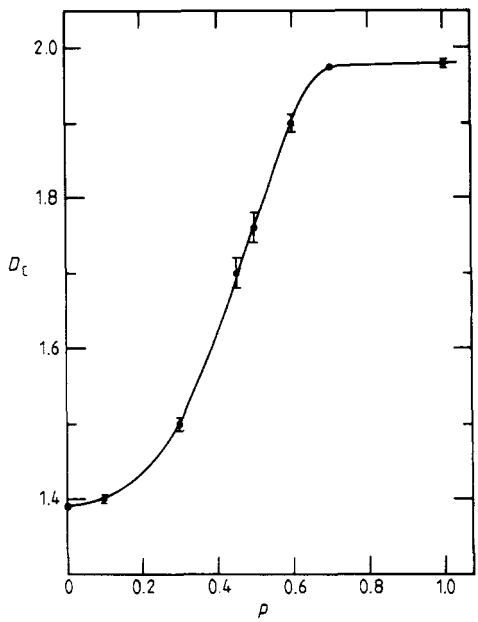



**Figure 6.** The $p$ dependence for the capacity of the spanning cluster for $200 \times 200$ arrays.

a low-dimensional spanning cluster at small $p$ to an object with dimension close to two at high $p$. (Since our model reduces to the ballistic model for $p = 1$, a dimension of two is consistent with the results of Bensimon *et al* (1984a, b).) The results for the information dimension are very similar, with values characteristically lower by only one to two per cent (consistent with the above inequality), indicating that the clusters are quite homogeneous.

The dimension is insensitive to the size of the square array. For instance, at $p = 0.1$, the capacity is $1.39 \pm 0.01$ for $100 \times 100$, $1.401 \pm 0.006$ for $200 \times 200$ and $1.42 \pm 0.02$ for $400 \times 400$. For wide arrays the dimension is very close to that found for square arrays. For instance, at $p = 0.1$ the capacity is $1.39 \pm 0.02$ for a $400 \times 100$ array. At $p = 0.7$ the capacity is 1.98 for a $400 \times 100$ array and 1.97 for a $200 \times 200$ array. This provides further evidence that the qualitative difference in the structure of the cluster at small and large $p$ is insensitive to variations of the array size and shape.

## 4. Discussion

The parameter $p$ introduced above reflects the importance of diffusion in the aggregation process. The growth process is rather different at small and large $p$: at small $p$ the particle typically makes many moves in the $x$ direction between downward moves in the $y$ direction; this means that clusters tend to grow by addition of particles at or near the top of the cluster and leads to several isolated clusters of similar size. This process leads to a gradual spreading, and pinching out of small clusters. At large $p$ the particles do not explore the $x$ direction between successive moves in the $y$ direction, and this favours the formation of a large more compact cluster by aggregation of smaller clusters.

We wish to contrast our results with those of Jullien *et al* (1984) who considered directed diffusion at a surface. They concentrated on arrays whose height is much greater than their lateral dimension. They found that the fractal dimension was close to two for all values of their anisotropy parameter. The compact nature of their clusters arises from the shape of the array. On the other hand, our work has focused on the other extreme of thin films.

One of the main results of this paper is the existence in thin films of a sudden crossover between the two regimes. The large fluctuations in the span and in the fractal dimensions of the cluster suggest a close analogy with critical phenomena. This crossover reflects the difference in the mechanism of growth in the two regimes.

It is clear that the nature of the diffusion process strongly affects the morphology of the thin film.

## Acknowledgment

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support.

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