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Pattern formation and a clustering transition in power-law sequential adsorption

Ofer Biham,[1] Ofer Malcai,[1] Daniel A. Lidar (Hamburger),[2] and David Avnir[3]
[1]*Racah Institute of Physics, The Hebrew University, Jerusalem 91904, Israel*
[2]*Department of Chemistry, University of California, Berkeley, California 94720*
[3]*Institute of Chemistry, The Hebrew University, Jerusalem 91904, Israel*

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We present a model that describes adsorption and clustering of particles on a surface. A *clustering* transition is found that separates between a phase of weakly correlated particle distributions and a phase of strongly correlated distributions in which the particles form localized fractal clusters. The order parameter of the transition is identified and the fractal nature of both phases is examined. The model is relevant to a large class of clustering phenomena such as aggregation and growth on surfaces, population distribution in cities, and plant and bacterial colonies, as well as gravitational clustering. [S1063-651X(99)50404-2]

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Many of the growth and pattern formation phenomena in nature occur via adsorption and clustering of particles on surfaces [1,2]. The richness of these phenomena may be attributed to the great variety of structures and symmetries of the adsorbed particles and substrates. Nonequilibrium growth models often give rise to fractal structures, which are statistically self-similar over a range of length scales [3]. In a large class of surface adsorption systems, the dominant dynamical process is the *diffusion* of the adsorbed particles, which hop randomly on the surface until they nucleate into immobile clusters [2]. The formation of *fractal clusters*, which are typical in these systems, can be described by the diffusion-limited aggregation (DLA) process [4]. In DLA a cluster of particles grows due to a slow flux of particles that diffuse as random walkers until they attach to the cluster. The model describes a great variety of aggregation processes such as island growth in molecular-beam epitaxy [2], electrodeposition, viscous fingering, dielectric breakdown, and various biological systems [5]. In many other physical systems, once an adsorbed particle sticks to the surface it becomes immobile. These systems can be described by random-sequential-adsorption (RSA) processes [6]. Within the RSA processes, one should distinguish between systems in which particles cannot overlap and systems in which they can adsorb on top of each other. Systems in which particles cannot overlap tend to reach a jamming limit, in which the sticking probability of a new particle vanishes [7]. Models that allow multilayer growth describe a large class of physical systems, including deposition of colloids, liquid crystals [8], polymers, and fiber particles [9,10]. Recently, the case of power-law distribution of particle sizes was studied both for uncorrelated adsorption [11] and for nonoverlapping particles [12]. In the case of uncorrelated adsorption, it was found that the boundary of the particle clusters is fractal [11]. For nonoverlapping particles, it was found that the area that remains exposed is fractal [12].

Models that describe growth dynamics have been employed in recent years in a vast range of scientific fields as diverse as city organization and growth [13,14], city and highway traffic [15], and growth of bacterial colonies [16]. A common feature is the tendency of the basic objects to form clusters of high density (typically of fractal shape), surrounded by low density areas or voids. Other examples of clustering appear in the distribution of mass in the universe [17], in dissipative gases and granular flow [18], as well as in step bunching on crystal surfaces during growth [19] and due to electromigration [20]. The phenomenon of cluster formation is therefore generic in a broad class of systems in spite of the fact that the pattern-forming dynamical processes may vary substantially from system to system. This richness of clustering phenomena is not yet fully backed up by appropriate models.

In this paper, we present the power-law sequential-adsorption (PLSA) model, which describes a variety of surface adsorption and clustering processes. This model leads to a rich variety of structures, many of which are fractal, which mimic the experimental morphologies found in the examples cited above. In particular, it exhibits a unique *clustering* transition that separates between a weakly correlated phase in which the adsorbed particles are distributed homogeneously on the surface and a strongly correlated phase in which they form clusters.

In the PLSA model, circular particles of diameter d are randomly deposited on a two-dimensional (2D) surface one at a time. The deposition process starts from an initial state where there is one seed particle on the surface. The sticking probability $0 \leqslant p \leqslant 1$ of a newly deposited particle is determined by the distance r from its center to the center of the nearest particle already on the surface. This probability is given by

$$p(r)=\begin{cases}1 & r\leqslant d\\ (d/r)^{\alpha} & r>d,\end{cases} \tag{1}$$

where the exponent $\alpha \geqslant 0$ is a parameter of the model. The model thus exhibits a positive feedback clustering, like many of the clustering phenomena listed above. The random deposition process is repeated until the desired number of particles M stick to the surface. Since the sticking probability is given by a power-law function, which is of a long range nature, this process should have been studied, in principle, in the infinite system limit. Numerical simulations, however, are done on a finite system of area $L \times L$, where $L/d \gg 1$. The coverage is given by $\eta = A/L^2$, where A is the total area covered by the particles. Also, let $\eta_0 = \pi(d/2)^2 M/L^2$.

The limit of *uncorrelated adsorption*, in which the sticking probability is uniformly $p=1$ is obtained for $\alpha=0$. This limit was studied recently using fractal analysis, and the box-counting and Minkowski functions were calculated analytically [21]. It was found that for a range of low coverages, apparent fractal behavior is observed between physically relevant cutoffs. The lower cutoff r_0 is given by the particle diameter $r_0=d$ while the upper cutoff r_1 is given by the average gap between adjacent particles, namely, $r_1=\rho^{-1/2}-d$, where $\rho=M/L^2$ is the particle density.

The limit of *strongly correlated adsorption* is obtained for $\alpha\rightarrow\infty$. In this case only a single, connected cluster is generated on the surface. The perimeter of this cluster grows slowly when new particles are deposited on its edge, while it becomes more dense inside [9,10].

We will now examine the morphological properties of the configurations of adsorbed particles for the full range of $0<\alpha<\infty$ using fractal analysis. For this analysis we use the box-counting (BC) procedure in which one covers the plane with nonoverlapping boxes of linear size r. The box-counting function $N(r)$ is obtained by counting the number of boxes that have a nonempty intersection with the (fractal) set. A fractal dimension D_{BC}, is declared to prevail at a certain range of length scales if a relation of the type $N_{BC}(r)\sim r^{-D_{BC}}$ holds or, equivalently, if the slope of the log-log plot

$$D_{BC} = -\mathrm{slope}\{\log r, \log[N_{BC}(r)]\} \quad (2)$$

is found to be constant over that range.

Two configurations of particles, randomly deposited and adsorbed according to Eq. (1) onto the unit square ($L=1$), are shown in Fig. 1 for $\eta_0=0.01$. For $\alpha=1.5$ the particle distribution exhibits local density fluctuations but on larger scales it is rather homogeneous and extends over the entire system [Fig. 1(a)]. For $\alpha=2.5$ we observe a strongly clustered structure [Fig. 1(b)]. This structure resembles the set of turning points of a Lévy flight random walker [22]. In fact, a Lévy flight corresponds to the special case in which the sticking probability of the next deposited particle depends only on the position of the latest particle adsorbed on the surface. Unlike Lévy flights, which typically describe dynamic behavior, our model describes clustering in spatial structures. It is also related to other models of spatial structures such as the continuous percolation model, which is approached when the interaction is suppressed, at $\alpha\rightarrow 0$. Another related model, which describes the growth of a percolation cluster and exhibits power-law correlations between growth sites is presented in Ref. [23].

The box-counting functions for the configurations generated by the PLSA model are shown in Fig. 2. It is observed that for $\alpha<2$ the box-counting function resembles the shape obtained for the uncorrelated case [21]. This indicates that the basic features of the model studied in Ref. [21] are maintained not only for short range correlations but for an entire class of long range correlations. The box-counting function for $\alpha>2$ exhibits a nearly linear behavior for the entire range from the particle size to the cluster size.

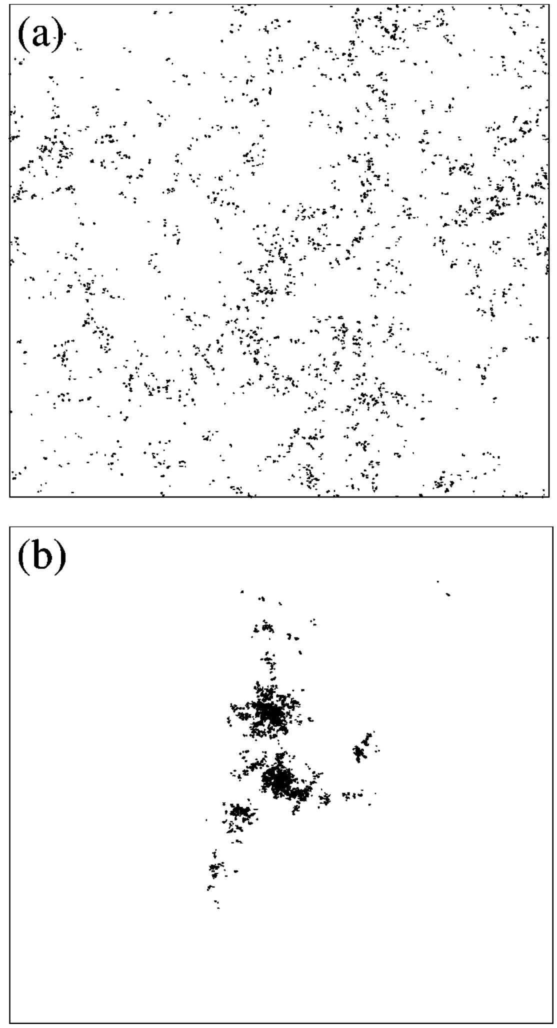

FIG. 1. Particles adsorbed on the surface of a unit square ($L=1$) according to the PLSA model for $\eta_0=0.01$. (a) For $\alpha=1.5$ we observe density fluctuations at small scales; however, at larger scales the distribution is rather homogeneous and extends over the entire system. (b) For $\alpha=2.5$ we observe a strongly clustered structure and vacant area elsewhere. The number of particles in both (a) and (b) is 3184 and their diameter is $d=0.002$.

To obtain the fractal dimensions of the sets from the box-counting functions, one should identify the relevant range of length scales over which the linear fit should be done. For the weakly correlated distributions the relevant range of length scales spans the range from $r_0=d$ to $r_1=\rho^{-1/2}-d$ [21]. For the strongly correlated distributions where clusters are formed, the relevant range is limited from above by the linear size of the entire cluster. The quality of the linear fit is measured by the coefficient of determination $\mathcal{R}^2$ [21]. In both cases, given a desired value of $\mathcal{R}^2$ one can further narrow the range within the cutoffs described above to find the broadest range (r_0, r_1) within which the linear regression maintains the given value of $\mathcal{R}^2$ [24].

The fractal dimension D as a function of α is shown in Fig. 3 for $\eta_0=0.1$, 0.01, and 0.001. Two domains are identified: a plateau of low dimension for the weakly correlated case and a plateau of high dimension for the strongly correlated case.

Consider a seed particle located at the origin of an infinite

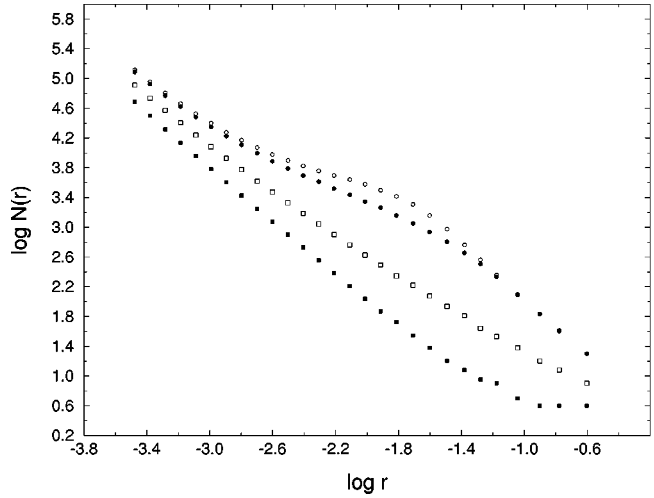

FIG. 2. The box-counting function for four configurations with $\eta_0=0.01$, and $\alpha=0$ (empty circles), 1.5 (full circles), 2.5 (empty squares), and 3.5 (full squares). It is observed that for $\alpha<2$ the shape of this function resembles that of the uncorrelated case. For $\alpha>2$, where strongly clustered distributions arise, there is a broad scaling range. The units are dimensionless and the logarithms are in base 10.

plane. Particles are randomly deposited one at a time according to the PLSA model until one particle sticks to the surface. Consider the probability that the distance r between the first particle that sticks and the seed particle at the origin will be larger than some value r_f, where $r_f>d$. This probability is given by

$$P(r>r_f)=\frac{\int_{r_f}^{\infty}2\pi r(d/r)^{\alpha}dr}{\int_0^d 2\pi r dr+\int_d^{\infty}2\pi r(d/r)^{\alpha}dr}. \tag{3}$$

One readily verifies that for $\alpha<2$ the probability $P(r>r_f)=1$ for any finite r_f. For $\alpha>2$, on the other hand, this probability is given by

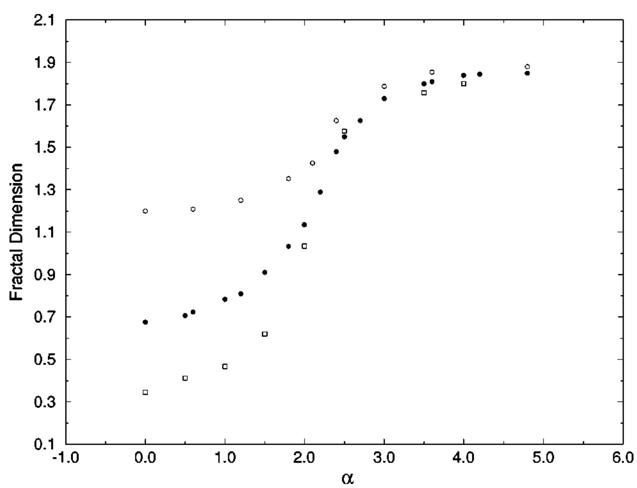

FIG. 3. The fractal dimension of the configurations produced by the PLSA model as a function of α (in dimensionless units) for $\eta_0=0.1$ (empty circles), 0.01 (full circles), and 0.001 (empty squares). A plateau of low dimension is found for the weakly correlated limit and a plateau of high dimension for the strongly correlated limit.

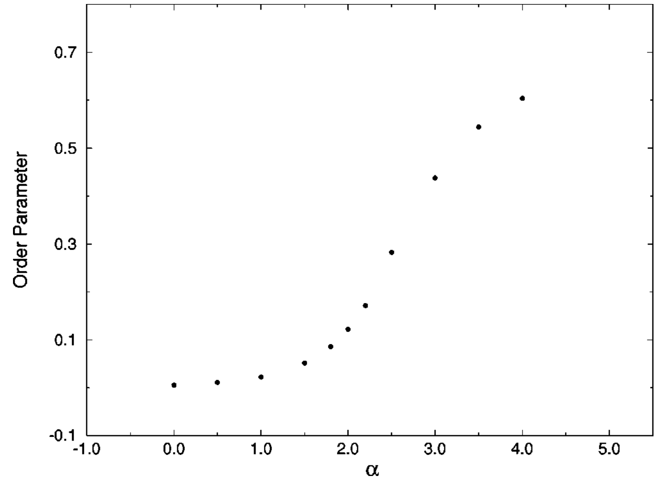

FIG. 4. The order parameter of the clustering transition, $V=(\eta_0-\eta)/\eta_0$, is shown as a function of α for $\eta_0=0.01$. It represents the fraction of the total area of the adsorbed particles lost due to overlap. For $\eta_0\ll 1$, this order parameter vanishes for $\alpha<2$ and increases above $\alpha=2$.

$$P(r>r_f)=\frac{2}{\alpha}\left(\frac{d}{r_f}\right)^{\alpha-2}. \tag{4}$$

Therefore, in the infinite system limit of the weakly correlated phase ($\alpha<\alpha_c$), the probability that the next particle will stick within any finite distance from an existing cluster is zero [25]. In the strongly correlated phase ($\alpha>\alpha_c$), the probability that the next particle will stick within a finite distance r_f from the cluster can be made arbitrarily close to one, by an adjustment of r_f according to Eq. (4) [26]. In general, the value of α_c for which the clustering transition takes place is equal to the space dimension.

The order parameter of the clustering transition is $V=(\eta_0-\eta)/\eta_0$, namely, the fraction of the total area of the adsorbed particles lost due to overlap. Consider a finite number M of particles of diameter $d=1$ adsorbed on the surface in the infinite system limit ($L\to\infty$). For $\alpha<2$, in this low coverage limit overlaps are negligible and $V=0$. For $\alpha>2$, clusters become more dense and overlaps more dominant as α increases. Our numerical studies are done on a finite system of size $L=1$ for a range of coverages. The order parameter V as a function of α, for $\eta_0=0.01$, is shown in Fig. 4.

To examine the critical behavior in the infinite system limit, we performed analytical calculations in one dimension (1D). In 1D the configuration is fully specified by the ordered list of $M-1$ gaps between the M particles. For the 1D case, we have obtained the critical exponent β for the order parameter $V\sim(\alpha-\alpha_c)^{\beta}$ in the $L\to\infty$ limit by constructing the probability distribution P_i, $i=0,\ldots,M$ that the next particle that sticks will stick within the gap g_i (where g_0 and g_M are the two semi-infinite gaps on both sides). The overlap was then calculated as a weighted average over all gaps. The result we obtain is that the exponent $\beta=1$. We also found that the fractal dimension exhibits critical behavior of the form $D\sim(\alpha-\alpha_c)^{\gamma}$, where $\alpha_c=1$ with the exponent $\gamma=1$. For the weakly correlated phase at $\alpha<1$ the fractal dimension in the $L\to\infty$ is $D=0$ while for $\alpha>2$ the dimension is $D=2$.

In summary, we present a model for random sequential adsorption characterized by a power-law distribution of sticking probabilities. This model exhibits a continuous phase transition between weakly correlated adsorption, in which the particle distribution is homogeneous on large scales and extends over the entire system, and strongly correlated adsorption, in which a highly clustered structure is generated. We thus identified a broad class of distributions that maintain the basic properties of the weakly correlated random structures studied in Ref. [21] and found the borderline between this class and the class of strongly correlated structures that exhibit clustering phenomena. The model should be useful in the study of a great variety of clustering problems.

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[24] For the linear regression of the box-counting function in Fig. 2 we chose $\mathcal{R}^2 = 0.996$ and obtained that for $\alpha = 0$, $\log r_0 = -2.7$ and $\log r_1 = -1.8$. For $\alpha = 2.5$, the same value of $\mathcal{R}^2$ is obtained for a broader range between $\log r_0 = -3.5$ and $\log r_1 = -0.8$. Note that in the latter case $\log r_0$ is somewhat smaller than $\log d$, since the gaps between particles in the cluster can be smaller than d.

[25] Note that the fiber deposition model of Ref. [10] with sticking coefficient $P(r) = 1$ for $r \leqslant d$ and $P(r) = p$ for $r > d$ shares this property for any $0 < p \leqslant 1$.

[26] Note that the class of models that give rise to strong clustering is broad and includes all models in which $p(r)$ decays faster than a power law. For example, a model with $P(r) = 1$ for $r \leqslant d$ and $P(r) = e^{-k(r-d)}$ for $r > d$ also gives rise to strong clustering for any $k > 0$.