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Influence of surface heterogeneities on the formation of diffusion-limited aggregates

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Abstract

In the present paper, we study the influence of surface energetic heterogeneities on the main features of fractal aggregates generated through a diffusional mechanism. The diffusion-limited aggregation (DLA) model was introduced by Witten and Sander (Phys. Rev. Lett. 47 (1981) 1400) and has stimulated growing interest in the study of a variety of nucleation and growth processes since then. In the DLA model, growth begins with a seed particle in the center of a two-dimensional lattice. Then, individual particles are launched uniformly from a launching circle, sufficiently big, and they perform activated random walk until they stick to the growing cluster. The DLA clusters formed in this way are fractal objects with a well determined fractal dimension $d_f = 1.72 \pm 0.02$. In order to include surface heterogeneities, we have used a square lattice with two kinds of sites which are assembled in such a way that the resulting structures have patchwise topography. Lattices formed by collections of orderly localized patches of different sizes are generated. DLA clusters are clearly affected in their morphology due to the presence of the surface heterogeneities which is analyzed and explained in terms of the different energetic topographies. © 2001 Published by Elsevier Science B.V.

Keywords: Surface structure, morphology, roughness, and topography; Diffusion and migration; Computer simulations; Monte Carlo simulations

1. Introduction

In the last years, we have witnessed increasing activity in the study of formation of fractal structures [1–11]. In particular, considerable attention has been paid to the diffusion-limited aggregation (DLA) model [1,12,13]. This interest is based in the essential role that this phenomenon play in many

experimental situations, such as electrodeposition, fluid–fluid displacement (viscous fingering), dielectric breakdown, chemical dissolution, just to name a few. As a consequence, an increasing interest has been also devoted to enhance our understanding of the theoretical basis of growing processes. The detailed understanding of such processes is essential for technological improvements but appears to be also very important from the fundamental aspects of basic science.

It is quite obvious that even single crystal surfaces are not perfect and contain structural and electronic heterogeneities. In general, the real adsorbent solid surfaces are heterogeneous because

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of a large number of contributing factors that can be sorted into two different classes: geometrical heterogeneity (cracks, pits, vacancies, etc.) and chemical heterogeneity (impurities, substitutional atoms, etc.). These heterogeneities may produce a complex spatial dependence of the solid–gas interaction potential, which can be denoted as adsorption energy topography [14–17].

The description of thermodynamic phenomena taking place on a substrate which presents the inherent complexity of energetic heterogeneities, is a challenging topic in the modern surface science. As a consequence, most of the contributions dealing with DLA consider the fractal aggregate growing over an homogeneous surface. In contrast, considerable less attention has been paid to the study of the influence of heterogeneous substrates on the formation of DLA clusters [18]. The aim of the present paper is to study the influence of surface heterogeneities on the formation of DLA. For that purpose, aggregates are formed on, perhaps, one of the simplest disordered surfaces, the patchwise heterogeneous surface (PHS).

In the PHS model, which has been proposed by Ross and Olivier [19], it is assumed that the surface is formed by a collection of homogeneous patches. Every adsorption site within a given patch has the same adsorption energy. However, different patches have different adsorption energies. For simplicity, we consider only two kinds of square patches with different energies, i.e. deep and shallow patches, which are arranged in a chessboard-like ordered structure. In order to characterize the DLA process by means of Monte Carlo modeling, we have studied the effect of the patch size and the energy difference between patches on both the exponents and the topology of DLA.

The understanding of the effects of such strong correlated heterogeneities on several surface processes is an interesting subject because: (a) it represents a limiting case of a more general description of surface heterogeneity [20,21]; (b) the results obtained for this limit can help us to establish criteria to characterize the surface topography according to a well defined correlation length [22] and (c) it can help to describe experimental findings [23]. Therefore, the present work is an extension of previous studies in which different surface

processes (such as adsorption [24], percolation [25], collective surface diffusion [22,26] and multi-site-occupancy adsorption [27]) taking place on such chessboard-like ordered surfaces were investigated.

The paper is organized as follows. In Section 2, we introduce basic definitions and technical details involved in our study. In fact, in Section 2.1 a description of the heterogeneous surface where the aggregate will be grown is given. Sections 2.2 and 2.3 are devoted to present the Monte Carlo scheme used for simulating the DLA model and for evaluating topological properties of a fractal structure, respectively. We summarize our results in Section 3. Finally, the conclusions are drawn in Section 4.

2. Basic definitions and simulational details

2.1. The heterogeneous substrate

It is well known that, in addition to an adsorption energy distribution, the energetic topography must be also considered in order to obtain a proper characterization of surface heterogeneity [14]. Amongst the simplest models describing surface energy topographies are the PHS model and the independent sites model. In the first one, proposed by Ross and Olivier [19], the surface is thought as a collection of homogeneous patches, in such a way that every site within a given patch has the same adsorption energy but different patches have different adsorption energies. In the independent sites model, after Hill [28], each adsorption site has a randomly distributed energy which is completely independent of the energy of any other site. In spite of simplicity, these models have allowed practical interpretations of experimental data for adsorption on a great variety of real surfaces.

A more general description for heterogeneous surfaces was introduced through a generalized gaussian model [20], which is based on the simple fact that energies of different sites may be correlated. This fact is then formulated through a correlation function defined in terms of a typical correlation length for a given surface. In the

generalized gaussian framework, the former models appear naturally as two limiting topographic cases. Highly correlated surfaces (very large correlation length) correspond to the Ross and Olivier's homotatic patches picture, while uncorrelated or random heterogeneous surfaces (null correlation length) correspond to the Hill's independent sites description. A great variety of intermediate topographies can be obtained by finite correlation lengths appearing as the most realistic cases [21,29,30]. These ideas have motivated the development of an alternative description for heterogeneous surfaces, namely, the dual site-bond model, in which the energy distributions for the two basic elements of an energetic surface, i.e. sites (total energy minima) and bonds (energy saddle points between nearest neighbor sites) are both taken into account. Remarkable results emerging from the dual site-bond model are that adsorption and surface diffusion depend on the bond energy distribution which induces correlations constrain on the site energy structure [31]. It has also been shown that intermediate topographies in the dual site-bond description can be readily qualified by means of finite correlation lengths between sites (or bonds) [32].

The simplest pattern of intermediate topography is a finite patch of energetically identical sites. Accordingly, the energetic correlation length is intrinsically given by the patch's size. Let us consider a square lattice with only two kinds of adsorption traps, namely shallow and deep traps, having adsorption energies ε_S and ε_D , respectively. On the basis of this so-called bivariate trap model, simple energetic topographies are created by placing square patches of $l \times l$ deep or shallow traps onto the adsorption lattice, which is represented by a two-dimensional array of $L \times L$ sites with periodic boundary conditions, see Fig. 1(a). Within a given patch all sites have the same adsorption energy. The chessboard-like topography can be easily generated on the computer and it mimics an experimental situation reported in literature (for a recent paper on this topic see, for instance, Ref. [23]). A typical profile of the energetic surface potential along one of the symmetry axes is shown in Fig. 1(b). Here, we have assumed, without losing generality, that the saddle point energy, ε_{sp} , remains constant throughout the whole lattice.

For simplicity, we also assume that (a) the number of deep traps is equal to the number of shallow traps; (b) an overlapping between two

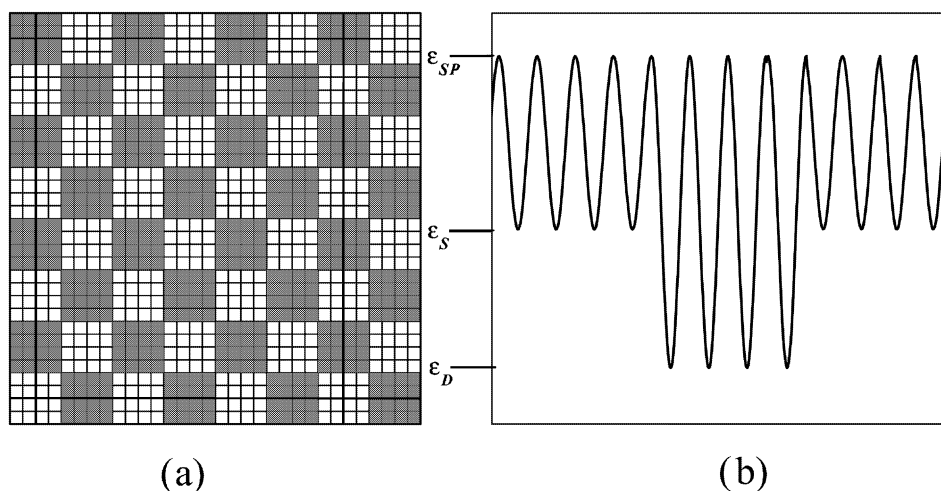


Fig. 1. (a) The chessboard-like heterogeneous surface formed by only two kinds of square patches. The lattice size used here is $L = 32$ and the patch size corresponds to $l = 4$. (b) A typical profile of the energetic surface potential along one of the symmetry axes for the surface shown in (a). Deep and shallow patches have adsorption energies ε_S (white sites) and ε_D (black sites), respectively. The saddle point energy, ε_{sp} , is kept constant throughout the whole lattice. Both types of traps are present with the same concentration.

different patches is not allowed and (c) multiple occupation of adsorption sites is excluded in the present work.

2.2. Computational simulations of diffusion-limited aggregation

The DLA algorithm is rather simple and has been discussed in detail in the literature [1,33–37]. Growth begins with a seed particle in the center of the two-dimensional lattice described above. Individual particles then execute an unbiased random walk in the lattice and either reach a site adjacent to the existing cluster and stop or reach a distance far enough from the seed that the probability of a return to the cluster is assumed to be negligible and is discarded.

Two parameters enter into the algorithm, the radius R_i at which new particles begin their random walk and the distance R_o at which they are discarded. The former become irrelevant as long as R_i is enough large in order to prevent the influence of the energetic topography on the initial conditions of launching. R_i is several times greater than both (a) the patches sizes and (b) the maximum extent of the cluster. The ratio between R_o and R_i is usually a fixed number and in our simulations we have varied this quantity between 2 and 10.

Each particle launched from the circle of radius R_i performs jumps to nearest neighbor empty sites using the following procedure. As in Ref. [38] the activation energy E for such jumps is taken as the energy difference between the final and the initial site energies,

$$E = \epsilon_j - \epsilon_i. \quad (1)$$

The associated jump probability W_{ij} is given by

$$W_{ij} = \frac{1}{\kappa} \exp\left(-\frac{E}{k_B T}\right) \quad (2)$$

with κ as normalization factor. κ essentially determines the time in which an adatom is allowed to attempt a jump. A suitable choice of κ is indispensable in order to optimize the computational time of the Monte Carlo algorithm. An obvious choice would be

$$\kappa = \kappa_{\max} = \exp\left(-\frac{E_{\min}}{k_B T}\right). \quad (3)$$

Here E_{\min} represents the activation energy for the most favorable physically realizable jump [39,40]. This choice avoids jump events with $W_{ij} > 1$.

The construction of DLA clusters is quite time consuming and, therefore, many different procedures to speed up the process have been presented [41]. In our simulations, we have extensively used the following

- (a) the z associated jump probability, W_{ij} are evaluated. Here, z is the coordination number of the lattice (in our case $z = 4$);
- (b) a random number ξ is chosen ($0 < \xi < 1$),
- (c) the particle jumps to the site $j = k$ if

$$\sum_{j=1}^k \frac{W_{ij}}{W} < \xi < \sum_{j=k+1}^4 \frac{W_{ij}}{W} \quad (4)$$

being $W \equiv \sum_j W_{ij}$. Of course, the election of W_{ij} depends of the model of jumps considered.

The quantities reported in the present contribution have been calculated for up to 5×10^4 -particles aggregated. In order to obtain accurate values of the desired quantities averaging up to 25 different aggregates generated in the same conditions have been used.

2.3. Evaluation of the characteristic exponents for the diffusion-limited aggregation model

In the remaining part of this section we shall focus on the definitions of the parameters which have been used in the present paper in order to characterize the main features of the aggregates obtained by using the above discussed Monte Carlo scheme.

Let us suppose the motion of a particle (“an ant”) which performs a Pólya random walk (unbiased, nearest neighbor random walk) on the occupied sites of a DLA cluster (“the labyrinth”). The root mean square displacement R of the random walk is related to time t through the relation [42]

$$R \sim t^{\nu}, \quad (5)$$

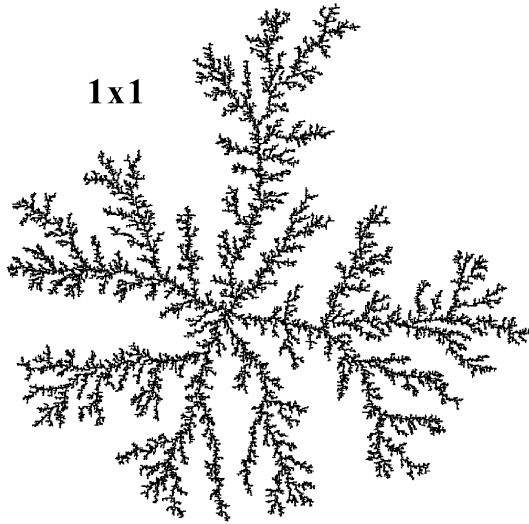
where ν is a constant that depends only on the dimensionality d of the system. A fractal dimension d_w is defined for the random walk by $d_w = 1/\nu$. In a regular square lattice $d_w = 2$. However, on fractal structures R grows slower with time and d_w is usually larger than 2.

Another intrinsic property of a fractal aggregate is the well-known spectral dimension d_s . This quantity can be calculated from Ref. [43,44]

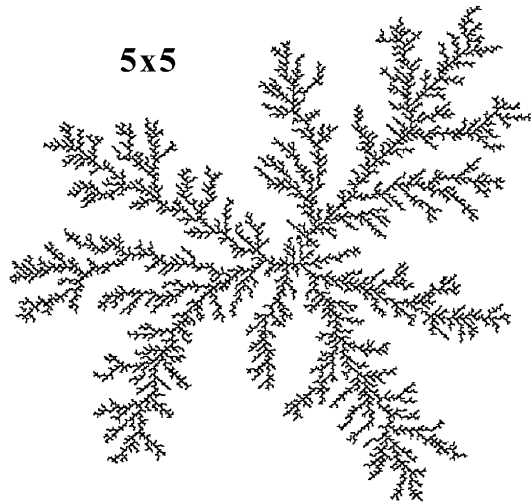
$$S_0(t) \sim t^{d_s/2}, \quad (6)$$

where $S_0(t)$ is the mean number of distinct sites visited by the random walks.

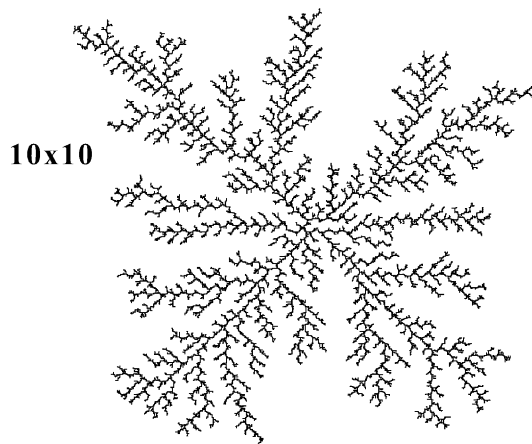
(a)



(b)



(c)



(d)

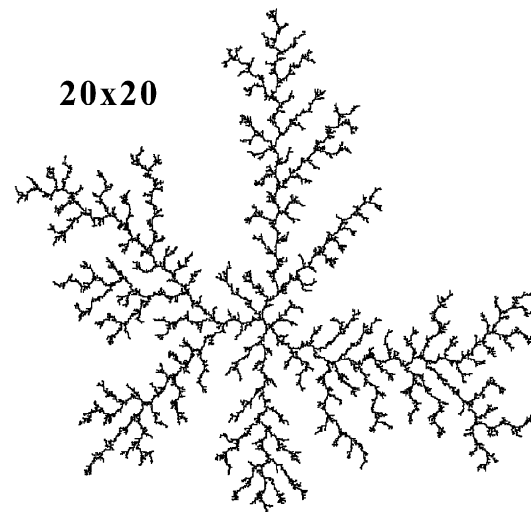


Fig. 2. Snapshot of a DLA structure grown on a chessboard-like heterogeneous surface with (a) $l = 1$; (b) $l = 5$; (c) $l = 10$ and (d) $l = 20$.

Typically 10^4 different random walkers have been used for averaging the above mentioned quantities.

The fractal structures are grown up to a maximum size in steps of 50 particles and the positions of the stuck particles are recorded. At the end of such a step, the center of mass of the aggregate r_{cm}

$$r_{cm}(N) = \left\langle \frac{1}{N} \sum_{i=1}^N r_i \right\rangle \quad (7)$$

is determined and its radius of gyration $\zeta(N)$ is calculated as

$$\zeta^2(N) = \left\langle \frac{1}{N} \sum_{i=1}^N [r_i - r_{cm}(N)]^2 \right\rangle, \quad (8)$$

where the angular brackets denote an average over the ensemble of different aggregates. It has been shown that the “mass” N of a fractal structure is related to its radius of gyration, ζ , through

$$N \sim \zeta^{d_f}, \quad (9)$$

where d_f is the fractal dimension of the system.

3. Results and discussion

In this section, we show how the surface heterogeneity affects the main features of DLA clusters. The substrate on which the aggregate is grown has been modeled by using the bivariate trap model with a chessboard-like topography. The surface heterogeneities have been introduced by means of two different parameters: (a) the patches size l (which has been ranged between $l = 1$ and $l = 20$) and (b) the adsorption energy difference between a deep and a shallow patch (expressed throughout the paper in units of $k_B T$), $\Delta\varepsilon \equiv (|\varepsilon_D - \varepsilon_S|)/k_B T$.

Fig. 2 shows the DLA clusters obtained for four different values of l ((a) $l = 1$; (b) $l = 5$; (c) $l = 10$ and (d) $l = 20$). From a simple inspection of the figure, it can be concluded that the aggregates present different structure upon increasing the patches size. In fact, the cluster become more diluted as the patches size, l , is increased. In order to characterize these qualitatively observed differ-

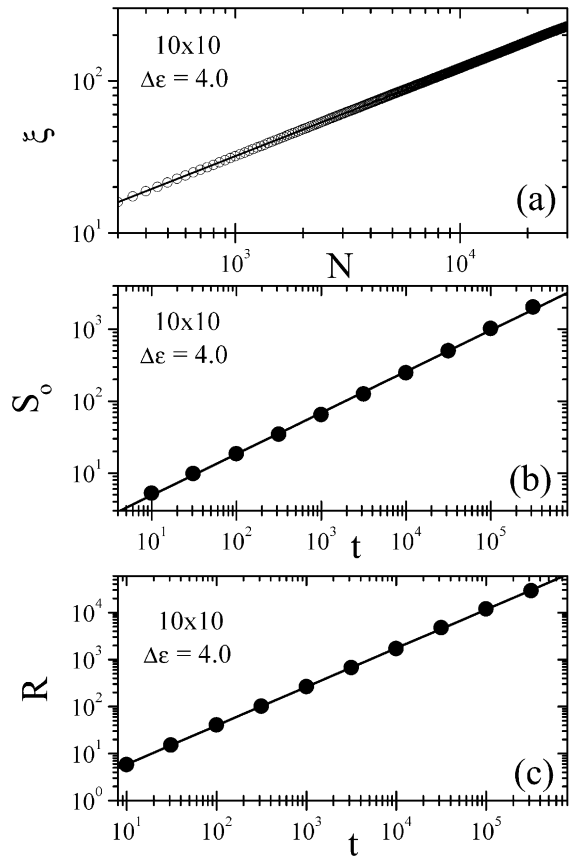


Fig. 3. (a) The “mass” (number of particles) of the fractal aggregate as a function of the gyration radius; (b) the mean number of distinct visited sites for fractal and (c) the root mean square displacement of a random walker on an aggregate as function of time, t . Note the log–log scale in all the figures. From the slopes of these curves the exponents d_f , d_s and d_w can be respectively obtained. The solid lines represent the homogeneous case.

ences, we shall show how the exponents d_f , d_s and d_w are influenced by changing both l and $\Delta\varepsilon$.

Fig. 3 illustrates the procedure used to determine the exponents d_f , d_s and d_w according to their definitions given in Section 2.3. We present here curves for $l = 10$ and $\Delta\varepsilon = 4$ in comparison with the homogeneous case i.e. $\Delta\varepsilon = 0$ (solid lines in Fig. 3). A similar analysis have been done for the complete range of the studied parameters. According to Eq. (9); d_f is determined from the slope of the “mass” of the fractal aggregate as a function of the gyration radius (note the log–log scale in

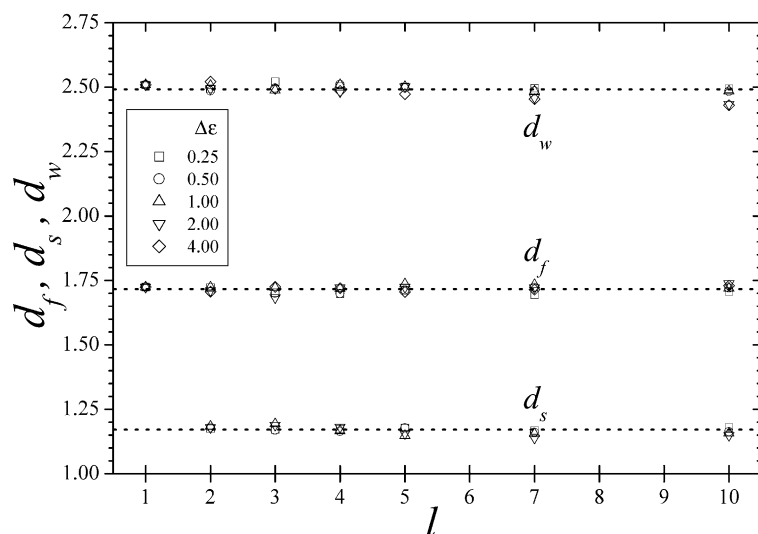


Fig. 4. Exponents d_f , d_s and d_w for all values of the parameters l and $\Delta\varepsilon$ used in the present work as indicated. The dotted line is only a guide to the eye.

Fig. 3(a)). The mean number of distinct visited sites, S_o , for (The root mean square displacement, R , of) a random walker on the fractal is plotted as a function of time in Fig. 3(b) (Fig. 3(c)). From the slopes of these curves, the exponents d_s and d_w can be respectively obtained.

A compilation of the exponents d_f , d_s and d_w for all values of the parameters l and $\Delta\varepsilon$ used in the present work is presented in Fig. 4. Even considering the error in the measurements, it is not conceivable to establish a concrete dependence between this parameters and the energetic topography. By the contrary, it can be concluded that the exponents are not affected by the presence of a strongly correlated surface in agreement with Ref. [45]. In particular, it is interesting to note that the number of particles belonging to a DLA cluster grown on this simple patchwise surface is not only a function of a given radius A but also of the patches size l and the energy difference between a deep and a shallow patch, $\Delta\varepsilon$:

$$N = C(l, \Delta\varepsilon)A^{d_f}. \quad (10)$$

As it was already shown d_f is independent of the energetic surface topography. However, $C(l, \Delta\varepsilon)$ is a non-universal function of the controlling parameters of the surface heterogeneity. In other

words, this equation establish that, for a given area, the patch size l (the energetic correlation length) and $\Delta\varepsilon$ govern the number of particles of the aggregate. In the same line of thinking, this equation suggests that experimental measurements of the mass of the cluster contains information about the energetic surface heterogeneity. In Fig. 5(a) and (b) is shown that $C(l, \Delta\varepsilon)$ is a monotonic decreasing function of both l and $\Delta\varepsilon$. This behavior clearly explains the tendency of DLA clusters to be more sparse upon increasing the patch size l as is shown in Fig. 2.

In order to establish some geometrical difference between the clusters grown on substrates characterized by different correlation length, we have investigated the behavior of the mean number of nearest neighbors per occupied site, A_{nn} as a function of both l and $\Delta\varepsilon$, see Fig. 6(b) and (c), respectively. A_{nn} can be evaluated as an average for all particles belonging to a cluster until a given radius A . In Fig. 6(a), A_{nn} is plotted as a function of the radius A . After strong fluctuations for small values of A , A_{nn} becomes constant. Thus, this quantity has been evaluated when becomes independent of the radius (being A enough large to consider an appropriate statistics) in order to neglect effects due to borders. There is a striking

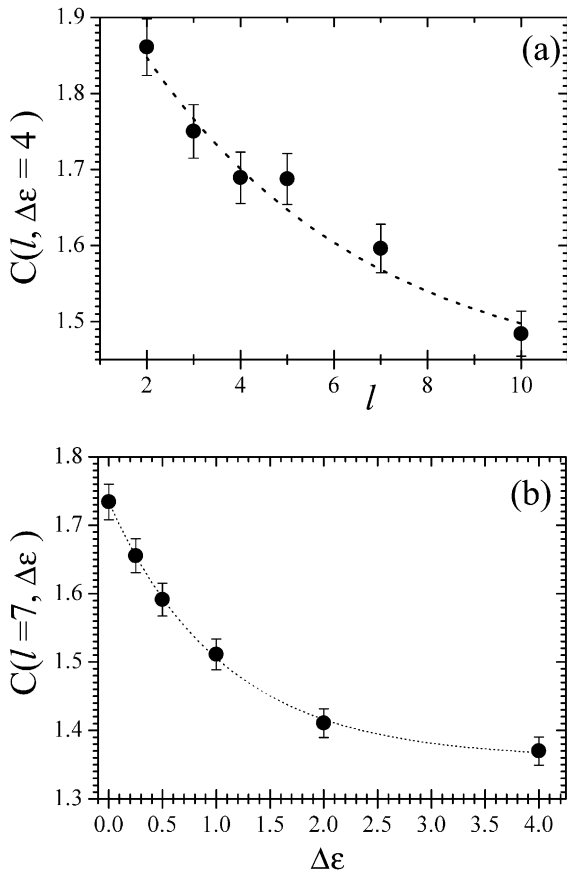


Fig. 5. $C(l, \Delta\epsilon)$ defined in Eq. (10) as a function of (a) the patch size l for a fixed value of $\Delta\epsilon = 4$; and (b) the energy difference $\Delta\epsilon$ for a fixed value of $l = 7$.

dependence of A_{nn} as a function of the lattice size l , see Fig. 6(b). The curves for different values of $\Delta\epsilon$ show a clear minimum around $l \approx 3$ while an asymptotic tendency towards the homogeneous value can be seen upon increasing the patches size l ($l \rightarrow \infty$). In order to explain such behavior, it is interesting to know how the particles are distributed over the deep and shallow patches. Thus, we define the site specific surface coverage, θ_D and θ_S , as the fraction of occupied deep and shallow trap sites, respectively. The dependence of θ_D and θ_S as a function of the patches size, l , shows that the partial coverage θ_D (θ_S) increases (decreases) monotonically as $l \rightarrow \infty$, see Fig. 7(a). For small patches size ($l \leq 2$) the number of occupied sites on

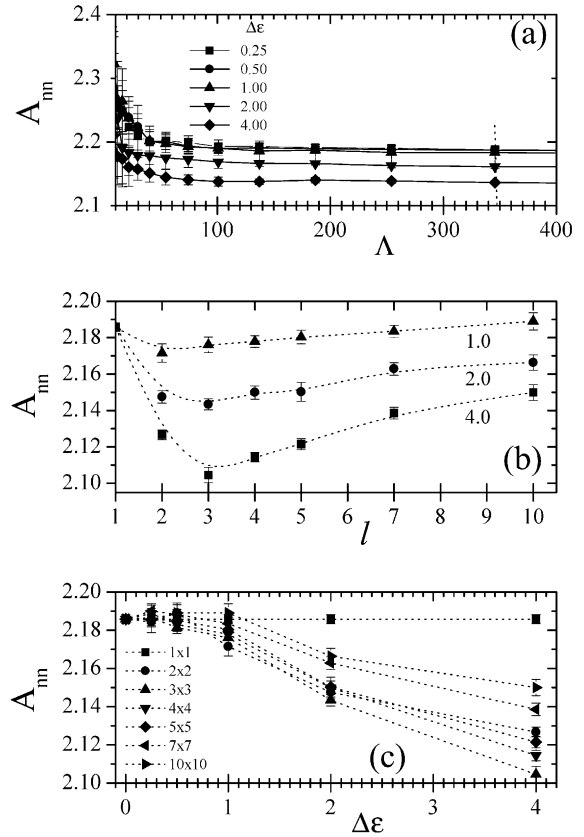


Fig. 6. (a) A_{nn} evaluated as an average for all particles belonging to the cluster up to a given radius A . The vertical dotted line indicates the value of A used for the evaluation of A_{nn} . Different values of the energy difference between deep and shallow traps, $\Delta\epsilon$, are used for the case when the patch size $l = 7$ is kept fixed (b) A_{nn} as a function of the lattice size l for $\Delta\epsilon = 1, 2$ and 4 as indicated; and (c) A_{nn} versus $\Delta\epsilon$ for several values of the patch size l as indicated. The dotted line is only a guide to the eye.

deep and shallow traps is quite similar and, as a consequence, A_{nn} behaves as in the homogeneous case. For large values of l , the aggregate can be described as a collection of fractal structures (formed on deep patches) linked by few particles located on shallow patches. These particles have a less value of A_{nn} and govern the process. The proportion of these particles reduce as $l \rightarrow \infty$ and A_{nn} goes downwards to the value in the homogeneous limit. Such a behavior is enhanced (diminished) whether the value of $\Delta\epsilon$ is increased (decreased), see Figs. 6(c) and 7(b).

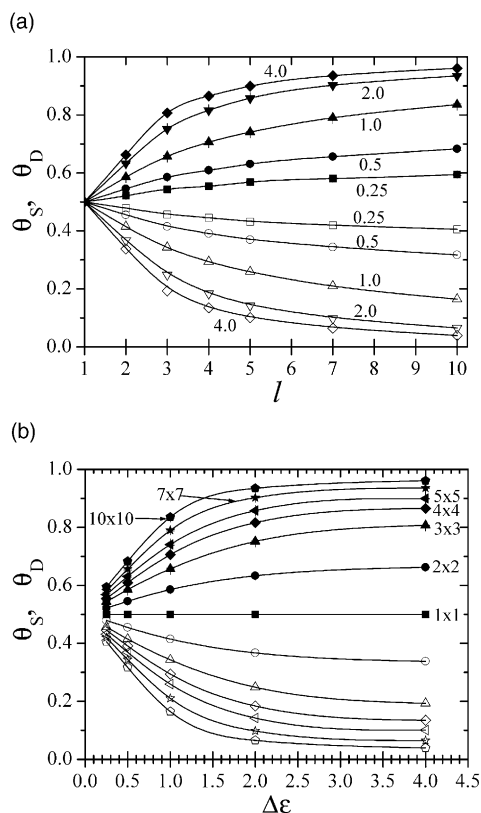


Fig. 7. (a) Site specific coverages, θ_D (filled symbols) and θ_S (empty symbols) versus l for several values of $\Delta\epsilon$ as indicated. (b) θ_S (filled symbols) and θ_D (empty symbols) as a function of $\Delta\epsilon$. The curves are labeled according to the lattice size l used.

4. Conclusions

In the present work we have used the bivariate trap model in order to study how the surface topography affects the formation of aggregates. In the framework of this model, it is assumed that the surface is formed by a collection of homogeneous patches. Every adsorption site within a given patch has the same adsorption energy. However, different patches have different adsorption energies. We have considered only two kinds of square patches with different energies, i.e. deep and shallow patches, which are arranged in a chessboard-like ordered structure. In particular, we focus our studies on the effect of (a) the patches size, (b) their arrangement and (c) the energy difference between

shallow and deep patches, $\Delta\epsilon$, on the structure of DLA clusters.

The Monte Carlo method has been utilized to (a) simulate the growing process, (b) evaluate the characteristic parameters and structural features of the DLA and (c) compare with the same phenomenon taking place on an homogeneous surface. The work presented here has clearly shown that the growing process termed DLA is affected by the energetic topography of the bivariate trap surfaces. The effect is stronger in lattices composed by small patches of traps, where the importance of borders become more evident. However, as it is expected, in the limit $l \rightarrow \infty$ the system becomes independent on the energetic topography.

We have also evaluated the exponents which characterize the DLA structure, such as the fractal dimension, d_f , the fractal dimension of a random walk on the aggregated, d_s , and the spectral dimension, d_w , by using their own definitions explained above for different patches size, l , and different energetic surface topographies. It can be concluded that the exponents are not affected by the presence of a strongly correlated surface. However (from Fig. 2), it seems to be clear that the aggregates are structurally different. This observation is in agreement with the behavior observed for both the mean number of nearest neighbors per occupied site and the number of sites of the cluster for a fixed value of the radius A . The former goes through a minimum when is plotted as a function of the patch size while recovers the value of the homogeneous case as $l \rightarrow \infty$. The analysis of $N(A, l, \Delta\epsilon)$, Eq. (10), reveals the importance of both the energetic correlation length and $\Delta\epsilon$ as the controlling parameters to describe the influence of the energetic surface topography on different processes taking place on such strong correlated surfaces [22,24–27].

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