Locally Frozen Defects in Random Sequential Adsorption with Diffusional Relaxation

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ABSTRACT

Random sequential adsorption with diffusional relaxation, of two by two square objects on the two-dimensional square lattice is studied by Monte Carlo computer simulation. Asymptotically for large lattice sizes, diffusional relaxation allows the deposition process to reach full coverage. The coverage approaches the full occupation value, 1, as a power-law with convergence exponent near $\frac{1}{2}$. For a periodic lattice of finite (even) size $L$, the final state is a frozen random rectangular grid of domain walls connecting single-site defects. The domain sizes saturate at $\sim L^{0.8}$. Prior to saturation, i.e., asymptotically for infinite lattice, the domain growth is power-law with growth exponent near, or possibly somewhat smaller than, $\frac{1}{2}$.

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1. Introduction

Random sequential adsorption (RSA) models have been studied extensively due to their relevance to surface deposition [1-2]. The depositing particles are represented by hard-core extended objects; they are not allowed to overlap. In monolayer deposition of colloidal particles and macromolecules [3-6] one can further assume that the adhesion process is irreversible. However, recent experiments on protein adhesion at surfaces [7-8] indicate that in biomolecular systems effects of surface relaxation, due to diffusional rearrangement of particles, are observable on time scales of the deposition process. The resulting large-time coverage is denser than in irreversible RSA and in fact it is experimentally comparable to the fully packed (i.e., locally semi-crystalline) particle arrangement.

Irreversible RSA has been studied extensively by many authors [1-2]. The most interesting aspect of such processes is the power-law large-time convergence to the jamming coverage in continuum off-lattice deposition. This slow time-dependence, as opposed to exponential convergence in lattice deposition, is due to gaps arbitrary close in size (and shape) to that of the depositing particles and therefore reached with low probability. Asymptotic arguments describe this rare-event dominated process [9-10]. Crossover from lattice to continuum can be also elucidated analytically [11].

Studies of RSA with added diffusional relaxation by analytical means encounter several difficulties associated with collective effects in hard-core particle systems at high densities (such as, for instance, phase separation), and with the possibility, in certain lattice models, of locally “gridlocked” vacant sites.

Both complications are not present in 1d: there are no equilibrium phase transitions (in models without deposition), traces of which might manifest themselves as collective
effects in $d > 1$ RSA with diffusion [12], and furthermore diffusional relaxation leads to simple hopping-diffusion interpretation of the motion of vacant sites in $1d$ which recombine to form larger open voids accessible to deposition attempts. Thus, both extensive numerical studies and their analytical interpretation were possible in $1d$ [13-15].

For $d > 1$ models, a low-density-expansion approximation scheme was applied [16] to off-lattice deposition of circles on a plane, accompanied by diffusional relaxation. However, no analytical studies were reported of the high-density behavior and the associated collective effects.

Extensive numerical simulations were reported [12], of the RSA process with diffusional relaxation, for the lattice hard-square model [17], i.e., the square-lattice hard-core model with nearest-neighbor exclusion. This model is well studied for its equilibrium phase transition [17] which is second-order with disordered phase at low densities and two coexisting ordered phases, corresponding to two different sublattice particle arrangements, at high densities. Another simplifying feature of the hard-square model is that the only possible gridlocked (locally frozen) vacancies are parts of domain walls [12]. As a result the coverage reaches the full crystalline limit at large times, by a process of diffusional domain wall motion leading to cluster growth reminiscent of spinodal decomposition in quenched binary alloys and fluids at low temperatures [18-20].

In this work we report extensive computer simulation results for RSA with diffusion on the two-dimensional square lattice with objects occupying two by two squares of four sites. One can view the deposition of such $2 \times 2$ objects as equivalent to a hard-core model with nearest-neighbor and next-nearest-neighbor exclusions. The distinctive feature of this model is the existence of locally frozen single-site defects. RSA with diffusion on a periodic lattice then leads to frozen states with domains of four different phases. The corresponding equilibrium ground states are highly degenerate [17,21-22].
The model is detailed in Section 2. The frozen states in the large-time limit are described in Section 3. Time-dependence of the single-site defect density, of the coverage, and of the ordered domain size, are discussed in Sections 4, 5, 6, respectively. These sections also contain discussion of the results.

2. Definition of the Model

We consider a square lattice of size $L \times L$, where $L$ is even. Initially all sites are empty. Each trial Monte Carlo step starts with choosing at random a lattice site $(i,j)$. With probability $p$ we try deposition of a two by two square to cover sites $(i,j)$, $(i+1,j)$, $(i,j+1)$, $(i+1,j+1)$. Deposition attempt is successful if these four sites are all empty. The sites are then marked as occupied. In the actual computer program the site $(i,j)$ is further listed as the lower-left corner of a block, for later use.

We perform a diffusion attempt with probability $1 - p$. Diffusional move is attempted only if the chosen site $(i,j)$ is already one of the lower-left corner sites. We try to diffuse (move) the square in one of the four directions (up, down, left, right) chosen at random, by one lattice spacing. Diffusion is successful if the move is not blocked by other squares. The time $t$ is measured in terms of Monte Carlo steps per site: one time unit is defined as $L^2$ deposition or diffusion attempts (successful or not).

In comparing data for different $p$ values, it is further convenient to rescale time by $p$, see [12-14] for details. However, we report specific results only for $p = 0.1$ here. Furthermore, all lattice sizes used were powers of 2. This restriction to one $p$ value, and generally the scope of the results presented, were due to numerical difficulties involved
in simulating RSA with diffusion in $2d$. For instance, results reported here took over 2 months of CPU time on an HP Apollo Model 720 workstation. However, we checked some of the observations reported in the later sections also for $p = 0.8$. The formation of the frozen states on periodic even-sized lattices (Section 3) was also checked for sizes other than powers of 2, and for several $p$ values other than 0.1.

The corresponding equilibrium model has been studied in [17, 21-22]. The equilibrium phase transition from the low-density disordered state to the high-density ordered state with four phases, is still not fully classified. The distinctive feature of the equilibrium case is large entropy of the ordered arrangements of $2 \times 2$ square objects [17, 21-22].

3. Frozen States at Large Times

Let us consider first the case of the periodic (even-sized) two-dimensional square lattice. Due to diffusional relaxation the coverage $\theta$ reaches almost the fully crystalline value 1 for large times, $t \to \infty$. However, the final configuration on a finite-size lattice typically has frozen defects which are single-site and serve as points of origin of domain walls separating four different sublattice arrangements (“phases”). One such configuration is illustrated in Figure 1. The defects are locally “gridlocked,” and any state that contains all the empty area in such single-site isolated defects no longer evolves dynamically.

The defect lines are either horizontal or vertical so that the resulting structure is essentially a random rectangular grid. There are no other types of defects here
that can survive in the large-time limit, unlike other studies of the formation of two-dimensional frozen polycrystalline structures (by other growth mechanisms) available in the literature [23-24].

This freezing-in rectangular grid was also observed for a related equilibrium model [21] by slow cooling from a disordered configuration to zero temperature. The frozen network seems to depend profoundly on the boundary conditions; the rectangular grid is characteristic of periodic boundary conditions. Indeed, when a fixed boundary is used, where the particles are not allowed to occupy the sites outside the $L \times L$ square ($L$-even), the final configuration is always a regular pattern of $L \times L$ sites. In this case, it is obvious that whenever there are unoccupied defect sites, there must be also some unoccupied sites at the boundary. Through diffusion and deposition, the defect sites in the interior as well as the empty sites at the boundary are fully eliminated.

The geometrical nature of the frozen grid pattern is illustrated by the following consideration. On a periodic two-dimensional lattice with even dimensions, the “frozen” network will have the geometry of the rectangular grid (Figure 1), i.e., a distribution of rectangular fully ordered domain shapes. Since each horizontal domain wall implies a shift of 1 lattice site, on an even periodic lattice the number of horizontal domain walls in each cross-section must be even. Similarly the number of vertical domain walls must be even. Thus the total number of domains, equal the number of single-site defects, is a product of two even numbers and must therefore be a multiple of 4. On the fixed-boundary lattice defined earlier, one simply cannot fit a rectangular array of domain walls with all vertices of coordination number 4. Thus, frozen states are not allowed due to purely geometrical constraints.

Let $\rho(t)$ denote the density of the single-site defects. Numerically, we counted the number of unoccupied single sites fully surrounded by occupied sites, and divided by the total number of lattice sites, $L^2$. The large-time limiting values are plotted in Figure 2.
vs. the linear system size $L$. For system sizes $L > 128$ it is difficult to reach the final limiting state. The data shown were obtained for the largest simulation times and they may be just upper bounds on the actual asymptotic values.

The data indicate that the density decreases at least as fast as $1/L$. This also yields the deviation of the coverage at large time from the monocrystalline value 1. Thus, $1 - \theta(\infty) \sim 1/L$, on a periodic lattice. The number of domains in the rectangular grid is equal to the number of vertices. If the domain size distribution were sharply peaked at some central value then the domain areas would saturate at $\sim L$. However, numerical evidence presented in Section 6 suggests that the domain linear size squared rather grows $\sim L^{1.6}$. This seems to suggest that the domain size, and possibly shape (i.e., rectangle size ratio), distributions are nontrivial and must be further investigated. Accurate domain statistics would require simulation of much larger lattices then those reported here.

4. Time-Dependence of the Single-Site Defect Density

The single-site density $\rho(t)$ is plotted in Figure 3, on logarithmic scale, for several system sizes, $L$. It is interesting to note that $\rho(t)$ has a peak around $t = 10$. For times $t < 10$ the single-site density increases with time, and then decreases for large $t$. This is presumably due to the difference between dominant dynamical mechanisms for short and long times. In fact, results of this and later sections suggest that the dynamics has three distinct regimes.

**Regime I.** For short times, the configuration is mainly build up by deposition. All types
of structures, including the single-site defects, are produced.

**Regime II.** At later times cluster coarsening occurs leading to ordering and formation of the frozen-grid defect structure. The defect structure in turn evolves from complicated to grid-like.

**Regime III.** The latest stage of the dynamics consists of straightening up of defect lines and final freezing of the rectangular grid. This regime will be further commented on in the later sections.

Finite-size effects show up already in Regime II: \( \rho(t) \) saturates at \( \sim 1/L \). The curves in Figure 3 then break off the main “envelope” which presumably corresponds to domain coarsening before the finite-size effects set in. This infinite-\( L \) envelope in Regime II, i.e., for times \( t > 50 \) in Figure 3, fits quite accurately the power law

\[
\rho(t) \sim t^{-0.573 \pm 0.004}.
\]

The precision of the power-law fit here is much higher than all other such fits reported in the present work. This presumably reflects absence of competing mechanisms in the Regime II.

However, the exponent value for the growth of the linear domain size assuming one domain per one single-site defect, half the value in (1), 0.2865 ± 0.002, is smaller than the accepted value, 0.5, for the non-conserved dynamics in 2d [18-20]. Thus the simple domain-per-defect picture does not hold suggesting that Regime II corresponds not just to cluster coarsening but also to rearrangement of the empty area which consists not only of isolated single-site defects but includes more complicated, evolving structures. Thus, the power law in (1) cannot be simply explained by theories of cluster coarsening. The latter process will be further addressed in Section 6.
5. Time-Dependence of the Coverage

The empty area fraction, $1 - \theta$, is shown in Figure 4. Generally for large times we expect the empty area to be represented by terms with different time dependence: single-site, dimer vacancies, trimers, etc.,

$$\theta(t) = 1 - \rho(t) - 2\rho_{\text{dimer}}(t) - \ldots$$

(2)

Specifically, the eventual saturation of the different-$L$ curves suggested in Figure 4, is due to the fact that $\rho(t)$ remains small but finite (of order $1/L$) for large times.

Consideration of the actual dynamical time steps achieved by writing a “movie” program to reproduce the consecutive configurations on the X-windows screen, has lead us to believe that the longest-surviving multiple-site empty area fragments are dimers. In the time Regime III, the grid structure has already been formed. However, the domain walls have kinks which are formed by dimer (two-site) empty-area defects. These can diffuse along the domain walls and “interact” with single-site defects while turning $90^\circ$ at each such encounter. The kinks can also sometimes “annihilate” pairwise due to deposition when they come in contact in the appropriate configurations.

A mapping to a reaction-diffusion system is suggested. However, here it will be more complicated than in $1d$ [13-15] where the “diffusers” were all identical and annihilated (with some probability) on pairwise encounters. If we speculate that the random grid is effectively one-dimensional and the reaction-diffusion system of dimer defects is otherwise similar to the $1d$ case, then we have the prediction

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\[ \rho_{\text{dimer}}(t) \sim 1/\sqrt{t}, \quad (3) \]

for large times, in the Regime III.

Upon onset of saturation, the curves in Figure 4 become size-dependent. If we select the portions of the curves which follow the \( L \)-independent “envelope,” then we can fit the effective power-law,

\[ 1 - \theta(t) \sim t^{-\alpha}. \quad (4) \]

However, least-square fits give exponent \( \alpha \) values decreasing from 0.61 to 0.53, as \( t \) increases. This deviation from the prediction (3) may be in part due to the use of 1 instead of the correct, \( L \)-dependent limiting value \( \theta(\infty) = 1 - \rho(\infty) \), and in part due to higher-order terms in (2). Indeed, for lattice sizes and times reached in our simulation the effective power-law fit here can be seen to largely cover Regime II rather than Regime III.

6. Domain Size Measures

We considered two definitions for the linear domain size. The first is obtained via the average “magnetization” vector, \( \mathbf{M} \), where each \( 2 \times 2 \) object is labeled by a unit vector, directed up, down, left, right depending on which sublattice the object is in. The domain size is defined by
\[ \ell_m = \frac{4}{L} \left\langle M^2 \right\rangle^{1/2}. \]  
\[ (5) \]

Here \( \mathbf{M} \) is defined as the vector sum of the unit vectors of each of the deposited objects. The average \( \langle \ldots \rangle \) is with respect to different Monte Carlo runs. Note that for a uniform single domain without defects, the domain size is \( L \).

The second definition is via the average square cluster size,

\[ \ell_c = \frac{4}{L} \left\langle \sum_i c_i^2 \right\rangle^{1/2}, \]
\[ (6) \]

where the clusters are defined as sets of squares on the same sublattice and continuously connected with each other; \( c_i \) is the number of squares in the cluster \( i \).

Figure 5 shows the domain sizes, \( \ell_c \), vs. time, for various values of \( L \). The results for \( \ell_m \) (not shown) is similar but less accurate. By comparison between different sizes, we concluded that the data for \( L = 512 \) and \( t < 2000 \) should not show finite-size effect. Power-law least-squares fit

\[ \ell_{m,c} \propto t^\beta \]
\[ (7) \]

to the infinite-size result gives the exponent \( \beta \) varying from 0.50 (for small \( t \)) to 0.36 (for large \( t \)) in different time intervals. It is therefore unlikely that the standard non-conserved-dynamics cluster growth exponent, \( \frac{1}{2} \) [12,18-20], can be accurately confirmed for this model without further much more extensive simulations.

The domain size saturates for finite \( L \). The dependence of the saturation value on the size \( L \) is plotted in Figure 6, on logarithmic scale. These data are quite well fit by the power law,

\[ -11 - \]
\[ \ell_{c,m}(t \to \infty) \sim L^{0.80 \pm 0.02}. \] (8)

Finally, let us stress that the results of this section were for periodic boundary conditions. Preliminary data indicate that the behavior of the cluster sizes, at least as far as their magnitudes go, is quite different for fixed boundary conditions.

In summary we reported empirical observations and numerical exponent fits for the problem of lattice RSA with diffusional relaxation which is distinctive in that isolated defects are frozen in, leading to domain formation and strong dependence on boundary conditions. Unfortunately, both analytical understanding of such dynamical systems is very limited, and numerical results should be considered as preliminary. Future effort must be focussed on exploring other models but also on obtaining further high-quality numerical Monte Carlo results for the $2 \times 2$ model on the square lattice considered in this work.

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FIGURE CAPTIONS

Fig. 1. A “frozen” configuration with four defect sites, on the $32 \times 32$ lattice. The $2 \times 2$ deposited objects are shown as square outlines while the defects are shown as four “holes” half the linear size of the outlined objects. The periodic lattice was cut in such a way as to keep the $2 \times 2$ objects whole.

Fig. 2. Density of the isolated single-site defects at large times, plotted vs. the linear system size $L$, on logarithmic scale. The sizes and times, $(L, t)$, were $(8, 100), (16, 400), (32, 800), (64, 10^3), (128, 10^4), (256, 10^4), (512, 10^5)$. The data were averaged over several hundreds to few thousands of independent Monte Carlo runs.

Fig. 3. The single-site density plotted on logarithmic scale as a function of time. The numbers indicate the system size $L$. The data were averaged over several hundreds to few thousands of independent Monte Carlo runs.

Fig. 4. Empty area fraction, $1 - \theta$, plotted vs. time, $t$, on logarithmic scale. The system sizes were $L = 2^n$, with $n$ from 3 to 9, from left to right, respectively.

Fig. 5. Effective domain size $\ell_c$ plotted vs. time $t$ on logarithmic scale, for system sizes $L$ indicated in the figure. (The noise in the larger-$L$ data and the break in the $L = 64$ data are, respectively, due to low statistics and due to combining data from different-statistics runs.)
Fig. 6. Domain size at saturation vs. the system size $L$ on logarithmic scale. The solid circles are data for $\ell_c$, and open triangles are data for $\ell_m$. The straight line has slope 0.8.