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Random sequential adsorption with diffusional relaxation in two dimensions

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Abstract. – The time dependence of the RSAD filling process on the 2D square lattice is investigated for two exclusion models. It is shown that the long-time filling is via a one-dimension–like process, and consequently the asymptotic behavior of the density is $O(t^{-1/2})$ as in the 1D case. In both models considered the limiting density is that of closest packing, in the thermodynamic limit. However, in the next-nearest-neighbours exclusion model the limiting configuration is a polycrystalline one.

Recent experimental studies [1, 2] suggest that the formation of monolayers on surfaces is dominated by the combined effect of random deposition of particles on the surface followed by in-plane diffusion of the deposited particles. The irreversible random deposition process of extended immobile particles, known as random sequential adsorption (RSA), is dominated asymptotically by the formation of holes too small to be filled by a new particle. Thus a RSA process results in a jammed state with a characteristic jamming limit density ρ_r, depending on the nature of the adsorption process (continuum, lattice) and on the details of the interparticle repulsion [3]. Diffusion may correct non-effective depositions, allowing the adsorption of additional particles and increasing the coverage density beyond the jamming density. The structure of the final state is not always known. It may be a crystalline state with density $\rho(\infty)$ that equals the density of closest packing $\rho_{\rm cp}$, or it may be a polycrystalline state or an amorphous state with densities lower than the closest-packing density.

The dynamics of one-dimensional RSA models modulated by diffusional relaxation (RSAD) have been investigated extensively recently [4-9]. It has been shown [4, 7] that at the long-time limit the filling process may be mapped onto the standard model of annihilating random walks, for which a rigorous result is known [10]. This argument suggests that the coverage density $\rho(t)$ converges via a $t^{-1/2}$ power law behavior to its closest-packing limit density. Expressions for the density as a function of time have been derived for the monomer model in the fast-deposition limit [7], for both short-time and long-time regimes. In particular the density in the long time regime is given by

$$\rho(t) = 1/2 - 1/(8\sqrt{\pi\varepsilon t}) + a_2/(\varepsilon t)^{3/2} + O((\varepsilon t)^{-5/2})\,, \tag{1}$$

where $a_2 = (2e^4 - 4e^2 + 1)/512\sqrt{\pi} = 0.08886\ldots$.

Since the 1D filling process is mapped to the model of annihilating random walks, one would expect the analogous 2D process to behave asymptotically like $1/t$. However, as discussed by Wang *et al.* [11, 12], new interesting effects have to be considered in $D > 1$. At each stage of the one-dimensional RSAD process every vacancy may be filled due to diffusion of one of its neighbours. In higher spatial dimensionalities configurations with immobile vacancies may be constructed during the RSAD process. Thus, for $D > 1$, it is not clear if the resulting reduction in the diffusion mobility can lead to an asymptotic coverage density less than the closest-packing density, and/or slowing-down of the convergence to the asymptotic coverage.

Previous works [11, 12] studied the combined effect of deposition and diffusion on the two-dimensional square lattice for two models of interparticle hard-core repulsion: nearest-neighbours exclusion (nn), and nearest-neighbours and next-nearest-neighbours exclusion (nnn). It has been shown that the limiting density is that of closest packing, and that in the long time regime the configuration consists of ordered regions separated by domain walls. the numerical results for the coverage density were found to fit asymptotic $t^{-1/2}$ power law.

In this latter, we revisit these models. It is assumed that the time scales of the two dynamic processes are completely separated, and the deposition rate is infinitely high relative to the diffusion process. This condition is obeyed in many experimental cases of interest [1, 2].

Our RSAD model is defined as follows. We start with an empty two-dimensional square lattice containing $N = L^2$ sites, with periodic boundary conditions. Particles are deposited randomly on the lattice according to the RSA and exclusion rules. Each deposited particle fills a lattice site and excludes further deposition on its four nearest-neighbours-sites (nn model), or it excludes further deposition in its eight neighbours (nnn model). Since the deposition is infinitely fast the jammed states are formed in zero time. The jamming densities of the two models are known to very high accuracy [13]: $\rho_r(\text{nn}) = 0.364133(1)$, $\rho_r(\text{nnn}) = 0.186985(2)$ (the figures in parentheses indicate the uncertainty of the last digit). Then in each time step each particle moves, if possible, with probability $\varepsilon/4$ from its site to one of its four neighbouring sites. Migration of a particle is possible only if it does not violate the exclusion rules among particles. After every movement of a particle, if a space available for additional particles is formed it is immediately filled by new particles. In the nn case such a fruitful motion may result in the deposition of one, or two, or three new particles, while in the nnn case a fruitful motion may result in the deposition of one, or two, new particles. Obviously, the density is a monotonically increasing function of time.

In order to simplify the analysis, we first treat the nn case. At any stage of the process, the lattice is filled by ordered regions, in which the particles are densely packed on the same sub-lattice. Neighbouring regions are separated by two lines of empty sites, and their particles belong to different sub-lattices. Only particles that are located on the perimeter of a region, *i.e.* along the border line between two regions, may diffuse to a neighbouring site. A movement of a particle results in a transfer of the particle from a region whose particles are located, say, on sub-lattice A, to its neighbouring region whose particles are located on sub-lattice B. In the case of a fruitful diffusion the newly deposited particles are added to sub-lattice B.

At the early stage of the process the density gain $(\rho(t) - \rho_r)$ is given by an expansion in powers of εt, and the expansion coefficients are spatial correlation functions at the jamming limit. In contrast to the 1D case where these correlation functions are analytically known [7,8], the 2D correlation functions are obtained approximately by numerical computations:

$$\rho(t) - \rho_r = 0.03415(5)\varepsilon t + O((\varepsilon t)^2)\,. \tag{2}$$

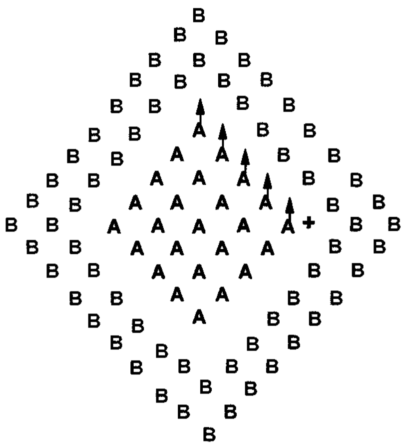

Fig. 1

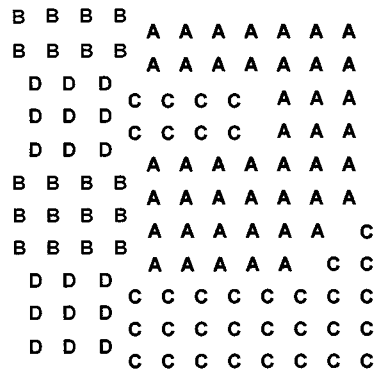

Fig. 2

Fig. 1. – A typical long-time configuration of the nn model. Only A-type particles can move. The ordered motion along the arrows results in an addition of one more particle at the site designated by +.

Fig. 2. – A typical long-time configuration of the nnn model. The four region junctions on the left-hand side are stable. The boundaries between the A region and the C region on the right-hand side are unstable.

The accuracy of the higher-order coefficients is comparable to the accuracy of MC computations, therefore it is not worthwhile to compute them.

At the late stage of the process local bulges have already been destroyed, and a typical configuration consists of a square-shaped region on, say, sub-lattice A surrounded by a larger region on sub-lattice B (see fig. 1). Diffusion of B-type particles towards the inner A region is impossible. Furthermore, only the four particles at the corners of the inner square may diffuse towards the outer region. A space for a single new particle is formed only if all the particles of an edge row of the inner square move in an ordered way towards the outer region. Thus the long-time filling, or equivalently the destruction of the inner region, is performed through a line by line migration, and it is essentially a one-dimensional process. As a result the density is expected to reach the density of closest packing via a $t^{-1/2}$ power law, as in the 1D case.

The analysis of numerical results for $\rho(t)$ obtained by averaging 300 MC simulations of the RSAD process on a periodic square lattice with length of $L = 1500$ sites confirms the above argument, and suggests that the long-time behavior of the density is given by

$$\Delta\rho(t) = 1/2 - \rho(t) = 0.2660(2)/\sqrt{\varepsilon t} - 0.310(5)/\varepsilon t\,. \tag{3}$$

The correction term to the asymptotic behavior in the 1D case is of the order of $(\varepsilon t)^{-3/2}$ (eq. (1)). The two-dimensional character of the problem reflects itself only in the correction term in eq. (3) that is of order $(\varepsilon t)^{-1}$.

The pair correlation function $g_{kk}(t)$ (the probability that at time t the site (k,k) is occupied provided the site (0, 0) is occupied) approaches unity at the long-time regime like

$$g_{kk}(t) = 1 - 2k\Delta\rho(t)\,, \tag{4}$$

provided $k < \sqrt{\varepsilon t}$. It means that the typical linear size l of an ordered region on the main sub-lattice grows with time like $l \approx \sqrt{\varepsilon t}$.

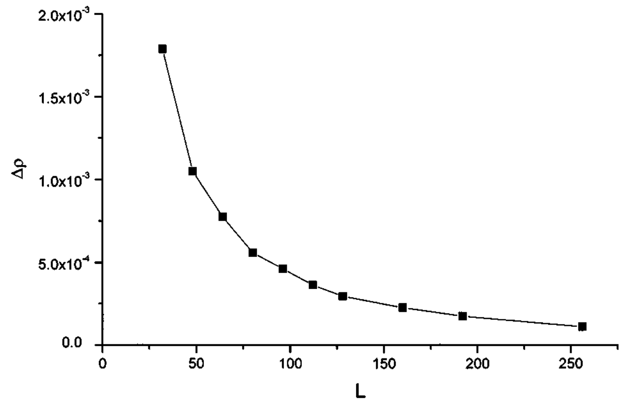

Fig. 3. – The average residual density as a function of the lattice length L.

In the early stage of the RSAD process in the nnn model fruitful motions correct small irregularities, and start to form ordered regions. The filling rate at the begining of the process is given by

$$\rho(t) - \rho_r = 0.01725(2)\varepsilon t + O((\varepsilon t)^2)\,. \tag{5}$$

The filling rate is very similar to the filling rate of the nn model (eq. (2)); recall that $\rho_r(\text{nn}) \approx 2\rho_r(\text{nnn})$.

At later stages of the process ordered regions are formed on the sub-lattices. At a junction of four regions diffusion is totally blocked, and a locally stable border is formed (see fig. 2). A necessary condition for a total blockage of diffusion on the entire lattice is that all the border lines between crystalline regions intersect in such junctions. Otherwise a longer region will swallow a shorter neighbour. The number of junctions is four times the number of vacancies. The above condition implies that the lattice consists of rectangular strips, and the width of any region in a strip is fixed. It is very unlikely that such a condition is obeyed in a macroscopic lattice unless the regions themselves are macroscopic. In order to check this point, we computed the deviation of the average final density from the density of closest packing $\Delta\rho(\infty) = \rho_{\text{cp}} - \rho(\infty)$ as a function of lattice size. The lattices are relatively small, therefore the RSAD process in all cases terminates either at closest packing, or in a blocked configuration, whose density is $\rho(\infty) < \rho_{\text{cp}}$. In fig. 3 the final density deviation $\Delta\rho(\infty)$ is plotted *vs.* L, the length of the lattice. Each value of the final density deviation is the average of 200 MC runs. A numerical fit suggests that $\Delta\rho(\infty)$ approaches zero asymptotically via an $N^{-2/3}$ power law behavior. As a result at the thermodynamic limit the density converges to the density of closest packing. The final state is a polycrystalline state consisting of $O(N^{1/3})$ crystalline regions, with a typical length of a region of order $L^{2/3}$.

At the long-time regime a space available for the deposition of a new particle is formed as a result of an ordered motion of a row of particles in a given direction. Therefore we expect the asymptotic approach of the density to its limiting value to be a one-dimensional–like process of order $t^{-1/2}$. The analysis of numerical results for $\rho(t)$ obtained by averaging 200 MC simulations of the RSAD process of the nnn model on a periodic square lattice of length $L = 500$ sites confirms that the limiting density is the density of closest packing, but it suggests that the asymptotic dynamics is of order $y = \ln(\varepsilon t)/\sqrt{\varepsilon t}$,

$$\Delta\rho(t) = 1/4 - \rho(t) = 0.0131(2)y + 0.028(5)y^2\,. \tag{6}$$

The logarithmic correction, that slightly impedes the filling process, reflects probably the existence of four region junctions, that form stable border lines between neighbouring regions.

In summary, we have studied the time dependence of the RSAD filling process on the 2D square lattice. It was shown that for both models the long-time filling is via a one-dimension–like process, and this manifests itself in the asymptotic behavior of the density which is $O(t^{-1/2})$ as in the 1D case, resulting from the properties of the 1D random walk. In both models the limiting density is that of closest packing, in the thermodynamic limit. However, in the nnn case the limiting configuration is a polycrystalline one, and this fact manifests itself in the logarithmic correction to the long-time coverage (eq. (6)).

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