Diffusional Relaxation in Random Sequential Deposition

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Abstract

The effect of diffusional relaxation on the random sequential deposition process is studied in the limit of fast deposition. Expression for the coverage as a function of time are analytically derived for both the short-time and long-time regimes. These results are tested and compared with numerical simulations.

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Diffusional relaxation in irreversible deposition processes of extended particles have been investigated recently [1–6]. In the deposition process of immobile particles, terms random sequential adsorption (RSA) the asymptotic behavior is dominated by the formation of 'holes' too small for a new particle to fill in, resulting in the jamming of the available area. Diffusion allows non-effective depositions to be corrected in latter stages of the process. Thus, the coverage reaches its maximal value - the closest packing value - for long times. The asymptotic filling process is dominated by diffusive, power-law, approach to the steady state, as opposed to the exponential convergence to the jamming limit in the immobile case of lattice models.

Mainly, two kinds of relaxation mechanisms were studied. Firstly, particle detachment has been studied, both experimentally and analytically. Exact results were obtained for special values of the parameters (detachment rate equal to deposition rate) [3]. In many experimental situations, another relaxation process, diffusion of the deposited particles, is more significant. It has been shown numerically that the effect of this diffusional relaxation process in 1D is a $1/\sqrt{t}$ asymptotic approach to the closest packing value. This result was supported by analytical arguments as well [4]. A somewhat different model was also considered, in which the absorbed dimers are allowed to dissociate into two independent monomers. Each monomer can diffuse to its nearest neighbor sites. For this version of the model, for special values of the parameters (deposition rate twice the diffusion probability) exact solution is available [6].

In this letter we study the combined effect of deposition and diffusion in 1D, in the regime in which separation of time scales is possible - the deposition rate is high, and may be considered infinite with respect to the diffusion process. This regime is highly relevant for experimental interest. We find two series expansions, relevant for short and long times, which describe the whole dynamics of the filling process.

Our model is defined as follows. We take an initially empty linear 1D lattice containing $N$ sites, with periodic boundary conditions to minimize finite-size effects. First, particles are deposited randomly on the lattice up to the jamming limit. Each deposited particle fills
one lattice site, and excludes further deposition in his nearest neighbors sites (This is also equivalent to the deposition of dimers with no neighbor exclusion). Since the deposition is considered fast, this process takes zero time. Then, in each step one particle is selected, and with probability $\epsilon/2$ moves to the right or left, if possible. Each $N$ steps are considered a time step, and thus the probability for a particle to move is $\epsilon$ per time unit. Practically, when simulating the model numerically, we can select at each time step only $\epsilon N$ particles and move them with probability $1/2$ to the right or to the left. After every movement, if a space for another particle was formed it is immediately deposited. We then look at the density as a function of time.

In order to simplify the following analysis, we first set up our terminology. At any stage of the process, the lattice is filled by ordered regions, in which the particles are densely packed such that there is only one empty site between adjacent particles. In the border between these regions, there are two successive empty sites separating the areas. Each region is termed “$k$-mer” were $k$ is the number of particles in the area. The initial concentration of the $k$-mers can be easily calculated to be

$$c_k^0 = \frac{2e^{-4}}{1-e^{-2}} \left( \frac{1-3e^{-2}}{1-e^{-2}} \right)^{k-1}$$

(1)

The only particles that move in any time are those which are at the edges of the $k$-mers. As a result of these motions the $k$-mers change their lengths. When a monomer moves, successive three empty sites are obtained, a new particle is deposited, and the $k$-mer and $k'$-mer at two sides of the monomer become one big $(k+k'+2)$-mer.

Therefore, any change in the coverage results from monomer movement. Consequently, short times behavior is dominated firstly only by the monomer concentration. In latter times, monomers formed by the destruction of dimers contribute to the coverage as well, and thus the dimers, trimers, ... concentrations also play a role. In the short time regime, the dynamics of the $k$-mers concentration $c_k$ is dominated by the transitions of a $k$-mer to a $(k \pm 1)$-mer. The other process of a unification of a $k$-mer, a monomer and a $k'$-mer to a long $(k+k'+2)$-mer can be neglected to first orders in time, since it generates only 4-mers
or longer chains, and these do not contribute to the density up to fifth order. We thus have the following rate equations

\begin{align}
\dot{c}_1 &= \epsilon(-2c_1 + c_2) \\
\dot{c}_k &= \epsilon(c_{k-1} - 2c_k + c_{k+1}), \quad k > 1 \tag{2}
\end{align}

with the initial conditions \([1]\). Successive approximations can be obtained by truncating the equation system after \(n\) equations, fixing \(c_{n+1}\) at its initial value. The result for \(c_1\) is then exact for \(n\) orders, and the coverage, which is given by

\[ \Delta \rho(t) = \epsilon \int_0^t c_1(t)dt \] \tag{3}

is exact for \(n + 1\) orders. We thus get the first 4 approximations

\[ \Delta^{(4)} \rho(t) = c_1^0(\epsilon t) + (-2c_1^0 + c_2^0) \frac{(\epsilon t)^2}{2} + (5c_1^0 - 4c_2^0 + c_3^0) \frac{(\epsilon t)^3}{6} + (-14c_1^0 + 14c_2^0 - 6c_3^0 + c_4^0) \frac{(\epsilon t)^4}{24} + O(t^5) \] \tag{4}

Figure 1 presents a comparison of the first 4 approximations with the results obtained from a numerical simulation using a \(N = 256K\) lattice. Clearly, the fourth order expansion approximate the real curve up to \(\epsilon t = 1\).

In order to study the long time behavior, we change our point of view. We term each two adjacent empty sites between successive \(k\)-mers a “hole”. Diffusion of particles at the edges of the monomers is equivalent to the diffusion of these holes \([4]\). At the course of the hole diffusion, when two such holes are on adjacent sites, a space for a new particle is formed, and after its deposition the two holes annihilate. We thus see that our model is equivalent to the model of \(N\) random walkers on a lattice which annihilate each other when joined. This model is well known and was used especially to describe the dynamics of chemical reactions of the type \(A + A \rightarrow \text{inert} \) \([7–9]\). In what follows we apply the analytical treatment developed for the reaction-diffusion problem to our model, and obtain an asymptotic series for the density. The two series, the asymptotic one and the previous short times expansion, describe the entire time regime very well, as can be shown by numerical results.
We wish to map our model to a standard model of annihilating random walks for which a rigorous result is known. We note that there are some differences between this standard model and the diffusing holes: (a) when a particle at the edge of a \( k \)-mer moves, the hole changes its position by two lattice sites. Thus, the diffusion constant is four times larger. (b) The distance between adjacent holes is always an odd number of sites. In particular, in the initial configuration the distances are odd. (c) The annihilation process occurs whenever the distance between the holes is one site and not when they are on the same site as in the standard model. Accordingly, in the initial state the minimal distance between successive \( k \)-mers is three sites. However, one expects these two differences to have no effect for long times for which the behavior is dominated by holes far from each other. This is confirmed by our numerical results.

Thus we consider a model of random walks (RWs), originally distributed randomly on the lattice, with density

\[
\tilde{\rho} \equiv \tilde{\rho}(0) = 2(1 - \rho_r) = e^{-2}, \tag{5}
\]

where \( \rho_r \) is the jamming limit density. The RWs moves with probability \( \epsilon \) two sites to right or left. When two such RWs join, they are annihilated. This model was solved exactly \cite{8,9}, and we here follow the derivation given by Spouge \cite{8}. Define \( \beta_k(n) \) to be the probability of the \( k \)th RW to be at a distance \( n \) from the origin

\[
\beta_k(n) = \tilde{\rho}^k(1 - \tilde{\rho})^{n-k} \left( \frac{n-1}{k-1} \right). \tag{6}
\]

\( \beta_-(n) \) is then defined by

\[
\beta_-(n) := \delta_{n,0} + 2 \sum_{k=1}^{\infty} (-)^k \beta_k(n) = \delta_{n,0} - 2\tilde{\rho}(1 - 2\tilde{\rho})^{n-1}. \tag{7}
\]

One also defines \( a(t; n) \) which is the probability that two RW whose original distance was \( n \) have meet until time \( t \). In our model

\[
a(t; n) = \tilde{I}_n(4Dt) + 2 \sum_{k=n+1}^{\infty} \tilde{I}_k(4Dt) \tag{8}
\]
where $\tilde{I}_n(x) := e^{-x}I_n(x)$, $I_n(x)$ is the modified Bessel function of integer order, and $D$ is the diffusion constant of the particles.

Given the above definitions, Spouge’s main result is

$$\tilde{\rho}(t) = \tilde{\rho} \sum_n a(t;n)\beta_n$$  \hspace{1cm} (9)

Substituting the above expressions for our model we get

$$\tilde{\rho}(t)/\tilde{\rho} = 1 - 2\tilde{\rho} \sum_{n=0}^{\infty} (1 - 2\tilde{\rho})^n [\tilde{I}_{n+1}(4Dt) + 2 \sum_{k=n+2}^{\infty} \tilde{I}_k(4Dt)]$$

$$= 1 - 2\tilde{\rho} \sum_{k=1}^{\infty} \tilde{I}_k(4Dt)[q^{k-1} + 2q^{k-2} + \ldots + 2q^0]$$

$$= 1 - \sum_{k=1}^{\infty} (2 - q^{k-1} - q^k)\tilde{I}_k(4Dt)$$

$$= \tilde{I}_0(4Dt) + (1 + q) \sum_{k=1}^{\infty} q^{k-1}\tilde{I}_k(4Dt)$$  \hspace{1cm} (10)

where $q = 1 - 2\tilde{\rho}$. A similar expression was given by Balding et al \[3\]. The particle density is given in terms of the hole density through the relation $\rho = (1 - \tilde{\rho})/2$, and thus one obtains for the difference between the density and the maximal, closest packing, density

$$\rho_{cp} - \rho(t) = \tilde{\rho}(t)/2 = \frac{e^{-2}}{2} [\tilde{I}_0(4Dt) + (1 + q) \sum_{k=1}^{\infty} q^{k-1}\tilde{I}_k(4Dt)]$$  \hspace{1cm} (11)

The diffusion constant is determined easily through the relation $< r^2 > = 2Dt$ resulting in $D = 2\epsilon$. Now, the asymptotic behavior follows from the known asymptotics of the Bessel functions \[10\].

$$\tilde{I}_k(z) = \frac{1}{\sqrt{2\pi z}} [1 - \frac{\mu - 1}{8z} + \frac{(\mu - 1)(\mu - 9)}{2!(8z)^2} - \ldots], \quad \mu = 4k^2$$  \hspace{1cm} (12)

To the first order, all the $\tilde{I}$s are identical ($k$ independent) and one has

$$\rho_{cp} - \rho(t) \sim \frac{\tilde{\rho}}{2\sqrt{16\pi\epsilon t}} [1 + \frac{1 + q}{1 - q}] = \frac{1}{8\sqrt{\pi\epsilon t}} = \frac{0.0705 \ldots}{\sqrt{\epsilon t}}.$$  \hspace{1cm} (13)

In a similar way, next orders can be extracted. For example, the next correction is

$$\rho_{cp} - \rho(t) = \frac{1}{8\sqrt{\pi\epsilon t}} - \frac{a_2}{(\epsilon t)^{3/2}} + O((\epsilon t)^{-5/2}).$$  \hspace{1cm} (14)
where

\[ a_2 = \frac{2e^4 - 4e^2 + 1}{512\sqrt{\pi}} = 0.08886... \]  \hspace{1cm} (15)

Figure 2 presents a comparison of the asymptotic leading order (13) and the series (10) with numerical results obtained from a lattice of \( N = 1.2M \) sites. One sees that the whole series fits the results even for small values of \( \epsilon t \) down to \( \epsilon t = 0.1 \).

In summary, it has been shown that the 1D deposition-diffusion process leads to full coverage. The short time dynamics is determined by the temporal monomer concentration. A fourth order expansion is given, valid up to \( \epsilon t = 1 \). The long time kinetics is dominated by the attachment of two relatively long \( k \)-mers which forms one long \( k' \)-mer. This process is equivalent to the dynamics of a reaction-diffusion process, or to the probability of a RW to return to the origin. Thus, the asymptotic approach of the density to its saturated value in 1D is \( O(1/\sqrt{t}) \). We derive an asymptotic series, based on this equivalency, valid for the intermediate and long time regimes (\( \epsilon t > 0.1 \)).
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FIGURES

FIG. 1. Numerical results for the coverage for short times, plotted vs. $\epsilon t$, compared to the first four short-times approximations.

FIG. 2. Numerical results for the coverage for long times, plotted vs. $\epsilon t$, compared to the asymptotic leading order, and the Bessel functions’ sum.
Density vs Time; Short time filling

Fig. 1
Density vs. Time; Long time Filling

Fig. 2