

LETTER TO THE EDITOR

Diffusional relaxation in random sequential depositionEli Eisenberg^{†‡} and Asher Baram[‡][†] Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel[‡] Soreq NRC, Yavne 81800, Israel

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Abstract. The effect of diffusional relaxation on the random sequential deposition process is studied in the limit of fast deposition. Expressions 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.

Diffusional relaxation in irreversible deposition processes of extended particles have been investigated recently [1–7]. In the deposition process of immobile particles, called random sequential adsorption (RSA), the asymptotic behaviour 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 the 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.

Two kinds of relaxation mechanisms were predominantly studied. First, particle detachment was studied, both experimentally and analytically. Exact results were obtained for special values of the parameters (detachment rate equal to deposition rate) [6]. In many experimental situations, another relaxation process, diffusion of the deposited particles, is more significant [3, 4]. It has been shown numerically that the effect of this diffusional relaxation process in one dimension is a $1/\sqrt{t}$ asymptotic approach to the closest-packing value. This result was supported by analytical arguments as well [5]. 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-neighbour sites. For this version of the model, for special values of the parameters (deposition rate twice the diffusion probability) an exact solution is available [7].

In this letter we study the combined effect of deposition and diffusion in one dimension, in the regime in which the 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 one-dimensional (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 its nearest-neighbour sites.

(This is also equivalent to the deposition of dimers with no neighbour exclusion.) Since the deposition is considered fast, this process takes zero time. Then in each time step each particle moves with probability $\epsilon/2$ to the right or left, if possible. Thus the probability for a particle to move is ϵ per time unit. Practically, when simulating the model numerically, we can select at each time step only ϵN particles and move them with probability $1/2$ to the right or to the left. After every movement, if a space for an additional 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. Neighbouring regions are separated by two successive empty sites. Each region is termed ' k -mer' where k is the number of particles in it. The probability of finding, at the initial state (jamming limit), two empty sites to the right (left) of a filled site is $p_2 = e^{-2}/\rho_r$, where ρ_r is the jamming limit density [8] (obviously, the probability of finding only one such site is $p_1 = 1 - p_2$). The probability of finding a ' k -mer' at a certain position is thus given by $c_k^0 = \rho_r p_2^k p_1^{k-1}$. Therefore the initial concentration of the ' k -mers' is

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

The only particles that may 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. The only process enabling the deposition of a new particle is a movement of a monomer. When a monomer moves, three successive 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, the short-time behaviour is dominated first only by the monomer concentration. At later 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 concentration of k -mers c_k is dominated by the transitions of a k -mer to a $(k \pm 1)$ -mer. The other process of unification of a k -mer, a monomer and a k' -mer into a long $(k + k' + 2)$ -mer can be neglected to first order 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

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

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

$$\Delta\rho(t) = \epsilon \int_0^t c_1(t) dt \quad (3)$$

is exact for $(n + 1)$ orders. Up to the fourth order in (ϵt) the density is given by

$$\begin{aligned} \Delta^{(4)}\rho(t) &= c_1^0(\epsilon t) + (-2c_1^0 + c_2^0) \frac{(\epsilon t)^2}{2} + (5c_1^0 - 4c_2^0 + c_3^0) \frac{(\epsilon t)^3}{6} \\ &\quad + (-14c_1^0 + 14c_2^0 - 6c_3^0 + c_4^0) \frac{(\epsilon t)^4}{24} + O(t^5). \end{aligned} \quad (4)$$

Figure 1 presents a comparison of the first four partial sums with the results obtained from a numerical simulation using a $N = 256K$ lattice. Clearly, the fourth-order expansion approximates the real curve up to $\epsilon t = 1$.

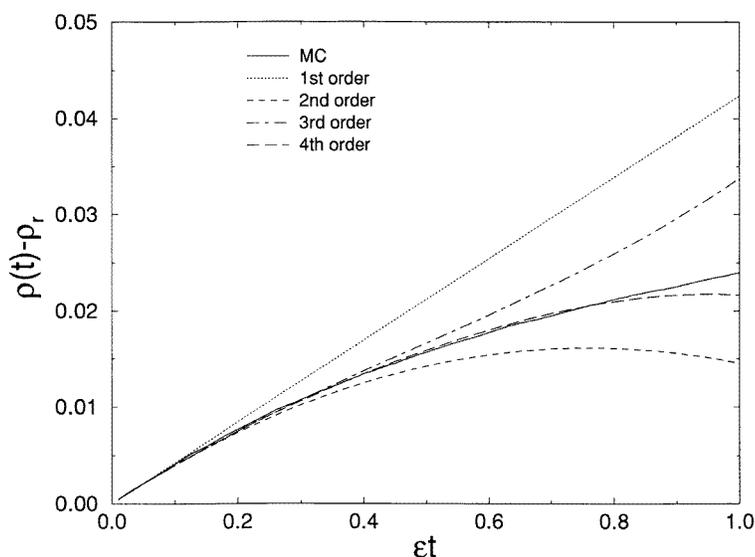


Figure 1. Numerical results for the coverage for short times, plotted against ϵt , compared to the first four short-time approximations.

In order to study the long-time behaviour, we change our point of view. We call each two adjacent empty sites between successive k -mers a ‘hole’. The diffusion of particles at the edges of the monomers is equivalent to the diffusion of these holes [5]. 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 $A + A \rightarrow \text{inert}$ [9–11]. 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-time 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 behaviour 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

$$\tilde{\rho} \equiv \tilde{\rho}(0) = 2(1 - \rho_r) = e^{-2}. \quad (5)$$

The RWs moves with probability ϵ two sites to the right or left. When two such RWs join, they are annihilated. This model was solved exactly [10,11] and we here follow the derivation given by Spouge [10]. Define $\beta_k(n)$ to be the probability of the k th RW to be at a distance n from the origin

$$\beta_k(n) = \tilde{\rho}^k (1 - \tilde{\rho})^{n-k} \binom{n-1}{k-1}. \quad (6)$$

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

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

One also defines $a(t; n)$ which is the probability that two RW, whose original distance was n , do not meet until time t . In our model

$$a(t; n) = \tilde{I}_n(4Dt) + 2 \sum_{k=n+1}^{\infty} \tilde{I}_k(4Dt) \quad (8)$$

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

$$\tilde{\rho}(t) = \tilde{\rho} \sum_n a(t; n) \beta_-(n). \quad (9)$$

Substituting the above expressions for our model we get

$$\begin{aligned} \tilde{\rho}(t)/\tilde{\rho} &= 1 - 2\tilde{\rho} \sum_{n=0}^{\infty} (1 - 2\tilde{\rho})^n \left[\tilde{I}_{n+1}(4Dt) + 2 \sum_{k=n+2}^{\infty} \tilde{I}_k(4Dt) \right] \\ &= 1 - 2\tilde{\rho} \sum_{k=1}^{\infty} \tilde{I}_k(4Dt) [q^{k-1} + 2q^{k-2} + \dots + 2q^0] \\ &= 1 - \sum_{k=1}^{\infty} (2 - q^{k-1} - q^k) \tilde{I}_k(4Dt) \\ &= \tilde{I}_0(4Dt) + (1 + q) \sum_{k=1}^{\infty} q^{k-1} \tilde{I}_k(4Dt) \end{aligned} \quad (10)$$

where $q = 1 - 2\tilde{\rho}$. A similar expression was given by Balding *et al* [11]. 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

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

The diffusion constant is determined easily through the relation $\langle r^2 \rangle = 2Dt$ resulting in $D = 2\epsilon$. Now, the asymptotic behaviour follows from the known asymptotics of the Bessel functions [12]

$$\tilde{I}_k(z) = \frac{1}{\sqrt{2\pi z}} \left[1 - \frac{\mu - 1}{8z} + \frac{(\mu - 1)(\mu - 9)}{2!(8z)^2} - \dots \right] \quad \mu = 4k^2. \quad (12)$$

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

$$\rho_{\text{cp}} - \rho(t) \sim \frac{\tilde{\rho}}{2\sqrt{16\pi\epsilon t}} \left[1 + \frac{1+q}{1-q} \right] = \frac{1}{8\sqrt{\pi\epsilon t}} = \frac{0.0705\dots}{\sqrt{\epsilon t}}. \quad (13)$$

The following orders can be extracted in a similar way. For example, the next correction is

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

where

$$a_2 = \frac{2e^4 - 4e^2 + 1}{512\sqrt{\pi}} = 0.08886\dots \quad (15)$$

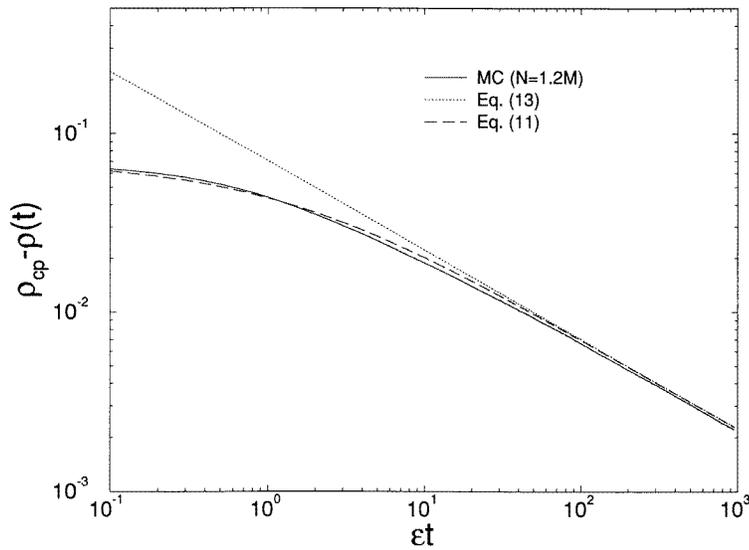


Figure 2. Numerical results for the coverage for long times, plotted against ϵt , compared to the asymptotic leading order and the Bessel functions' sum.

Figure 2 presents a comparison of the asymptotic leading order (13) and the series (11) with numerical results obtained from a lattice of $N = 1.2M$ sites. It is worth noting again that the mapping to the reaction–diffusion model is valid only for the long-time regime, for which the behaviour is dominated by holes far from each other. However, one sees that the whole series fits the results even for small values of ϵt 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 one dimension 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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