On Irreversible Deposition on Disordered Substrates

E. Ben-Naim and P. L. Krapivsky
Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215

The kinetics of random sequential adsorption of k-mers on a one-dimensional lattice, occupied initially by point impurities with a random distribution, is solved exactly. The solution of the process on a continuum substrate is also derived from the discrete case.

A number of processes in physics, chemistry and biology may be modelled by random sequential adsorption (RSA) on a lattice [1]. In this model, particles arrive randomly and adsorb irreversibly unless they are in the exclusion zone of previously adsorbed particles. In an arbitrary dimension, RSA processes reach a jamming configuration, where further adsorption events are impossible. The final coverage as well as the temporal approach to the jammed state are of interest. Exact analytical results have been obtained mainly in one dimension, where the problem is also known as the parking problem [1-3], and for the Bethe lattice [4,5]. In these studies, the substrate is usually assumed to be initially empty. In a very recent paper [6], the kinetics of RSA of k-mers on the one-dimensional lattice, occupied initially by point impurities with a Poissonian distribution, has been investigated numerically (mostly for dimers). In this comment we aim to to point out that for the dimer case the model has been solved exactly for the dual process $A + A \to 0$ with immobile reactants [7,8]. Moreover, we point out discrepancies between the exact solution and the simulation results. We also present an exact analytical solution for the k-mer case with arbitrary k and exploit this solution to obtain the solution to the same process on a line.

In the RSA process, k-mers land uniformly on a lattice with a constant rate, to be taken as unity without loss of generality. An adsorption event is successful if all k sites are empty. Let $P_m(t)$ denote the probability that m consecutive lattice sites are empty. The rate equations for these probabilities are

$$\frac{dP_m(t)}{dt} = -(m-k+1)P_m(t) - 2\sum_{j=1}^{k-1} P_{j+m}(t) \qquad (1)$$

for $m \geq k$. The first term in the right-hand side describes adsorption events inside the original m-site sequence. The next terms describe desorption events involving sites outside the original sequence.

Since the initial density of point impurities is ρ_0 and the distribution of impurities is random, $P_m(0) = (1-\rho_0)^m$. Solving Eq. (1) subject to these initial conditions yield

$$P_m(t) = (1-\rho_0)^m \exp\Big[-(m-k+1)t - 2\sum_{j=1}^{k-1} \frac{1-e^{-jt'}}{j}(1-\rho_0)^j\Big] \qquad (2)$$

For an initially empty lattice, $\rho_0 = 0$, the solution of Eq. (2) agrees with the well-known exact solution [3].

Similarly, one can write rate equations and solve them exactly for the probabilities $P_m(t)$ with $m < k$. The most interesting quantity, $P_1(t)$, satisfies the equation

$$\frac{dP_1(t)}{dt} = -kP_k(t), \qquad (3)$$

which involves only $P_k(t)$. Integrating Eq. (3) we find the coverage $\rho(t)$, $\rho(t) = 1 - P_1(t)$,

$$\rho(t) = \rho_0 + k(1-\rho_0)^k \int_0^t dt' \exp\Big[-t' - 2\sum_{j=1}^{k-1} \frac{1-e^{-jt'}}{j}(1-\rho_0)^j\Big] \qquad (4)$$

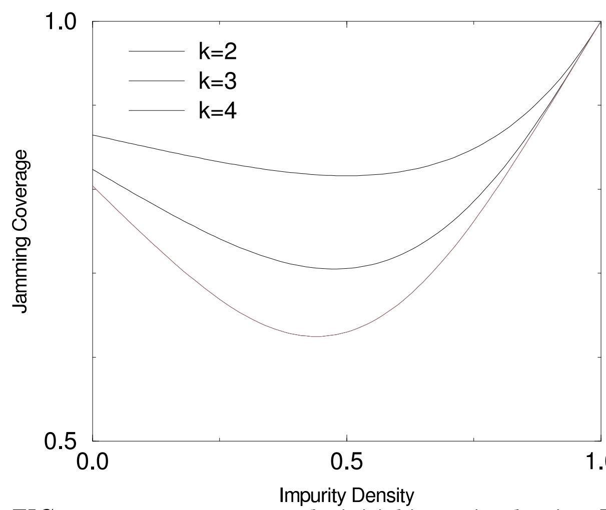

FIG. 1. ng coverage versus the initial impurity density. The exact solution of equation (4) is plotted for the cases of $k = 2$, $k = 3$ and $k = 4$.

The jamming coverage, $\rho_{\rm jam} \equiv \lim_{t\to\infty} \rho(t)$, for the case of dimer deposition, $k = 2$, is obtained from Eq. (4),

$$\rho_{\rm jam} = 1 - (1-\rho_0)\exp[-2(1-\rho_0)]. \qquad (5)$$

Thus, we reproduced the result first derived in the context of two-particle annihilation reaction with immobile reactants [7,8]. From Eq. (5) one sees that the jamming concentration has a minimum $\rho_{\rm jam}^{\rm min} = 1 - e^{-1}/2 = 0.8160\ldots$ at $\rho_0 = 1/2$. This behaviour is reminiscent of the general k-mer deposition problem where the jamming coverage is a nonmonotonic function of the impurity density (see Figure 1). Clearly, in the limit of a full initial state $\rho_0 \lesssim 1$, $\rho_{\rm jam} \cong \rho_0$. The simulational result of Milošević and Švrakić exhibits a minimum at $\rho_0 \cong 0.13$. Moreover, the minimal jamming density is found to be $\rho_{\rm jam}^{\rm min} \cong 0.8564$. Both values differ significantly from the exact values.

The exact k-mer solution can be used to obtain the continuum limit. In this limit, objects of unit length are deposited on a one-dimensional line, initially occupied by point defects. The initial density of the defects is set to λ. To attain this limit we rescale the density $k\rho_0 \to \lambda$ and the time $kt \to t$. Thus, we take the limit $k \to \infty$ of Eq. (4), with the rescaled density and the rescaled time remaining finite, and obtain the following continuum coverage function

$$\rho(t) = \int_0^t dt' \exp\Big[-\lambda - 2\int_\lambda^{\lambda+t'} du \frac{1-e^{-u}}{u}\Big]. \qquad (6)$$

In the limit $\lambda \to \infty$ this coverage approaches zero exponentially, $\rho_{\rm jam} \cong \lambda \exp(-\lambda)$. Conversely, when $\lambda \to 0$ the jamming coverage approaches the well known Rényi number $\rho_{\rm jam} = 0.7475\ldots$. Unlike the lattice case, the coverage monotonically decreases to zero, as the density of impurities increases.

Using the exact solution for the density, we study the approach to the jamming limit. In the lattice case we find from Eq. (4) an exponential approach $\rho_{\rm jam} - \rho(t) \sim \exp(-t)$. This decay was confirmed by the simulation performed by Milošević and Švrakić. Interestingly, in the continuum case the approach is slower, and from Eq. (6) one finds algebraic decay $\rho_{\rm jam} - \rho(t) \sim t^{-1}$.

We thank Vladimir Privman and Sidney Redner for useful discussions. We also greatfully acknowledge grant #DAAH04-93-G-0021, NSF grant #DMR-9219845, and the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[1] for a comprehensive review see J. W. Evans, *Rev. Mod. Phys.* **65**, 1281 (1993).
[2] A. Rényi, *Publ. Math. Inst. Hung. Acad. Sci.* **3**, 109 (1958).
[3] J. J. Gonzalez, P. C. Hemmer, and J. S. Hoye, *Chem. Phys.* **3**, 228 (1974).
[4] J. W. Evans, *J. Math. Phys.* **25**, 2527 (1984).
[5] Y. Fan and J. K. Percus, *Phys. Rev. A* **44**, 5099 (1991).
[6] D. Milošević and N. M. Švrakić, *J. Phys. A* **26**, L1061 (1993).
[7] V. M. Kenkre and H. M. van Horn, *Phys. Rev. A* **23**, 3200 (1981).
[8] S. M. Majumdar and V. Privman, *J. Phys. A* **26**, L743 (1993).