Random sequential filling of a finite line

M. C. Bartelt
Department of Physics, Clarkson University, Potsdam, New York 13699-5820
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We present a detailed analysis of the finite-size and boundary effects for one-dimensional irreversible monolayer adsorption of dimers on a lattice, within the rate-equation approach. Asymptotic expressions for short- and long-time coverages are derived for periodic and free boundary conditions.

Random, irreversible, consecutive placement of nonoverlapping objects onto uniform surfaces results in nonequilibrium, less than close-packed deposits whose kinetic behavior and final distribution of gaps are known exactly in one-dimensional, infinite systems.[1-8] Protein adsorption on solid surfaces[9,10] and particle adhesion in colloids[11] are examples of experimental realizations of such processes, the latter reported to exhibit multilayer phenomena, theoretical models of which have just begun to appear in the literature.[11-13] Similar problems arise in one dimension in the chemistry of polymer-group reactions.[2,5] Analytical solvability of one-dimensional models has often offered much insight into the mechanism and control of these deposition processes as well as providing a reference to explore new techniques in higher dimensions, where most new results are numerical.[13-21]

Corrections due to the size of the system and the choice of boundary conditions are generally important in implementing efficient algorithms in high dimensions as well as testing the agreement of their conjectures with results from series analysis and hierarchical truncation procedures. Some discussion of finite-size effects in one dimension can be found in Ref. 4 and a solution for the coverage of an open lattice chain by dimers is derived in Ref. 5. However, no explicit discussion of the boundary effects and leading size corrections is available, even in one dimension. In two dimensions, computer simulations have always reported rather small size effects, for systems with typical length larger than ten lattice spacings,[13] decreasing with the ratio of the size of the adsorbed objects over the size of the substrate.[17] The purpose of this Brief Report is to present a thorough assessment of these effects in one dimension and, at the same time, develop a systematic formulation of the rate-equation approach for finite systems. Detailed exact expressions are only derived for the deposition of dimers. The coverage (fraction of the N lattice spacings long line covered with objects) expands in powers of the time variable, for short times, with leading deviations from the infinite-line behavior as small as $1/N$ in the linear term, for free boundary conditions, and $2^N/N!$ in the Nth power, for periodic boundary conditions. For long times, the coverage approaches its saturation (jamming) value exponentially. The jamming value and the first coefficient of the expansion in exponentials of time differ from the corresponding infinite-line parameters by terms of order $2^N/N!$, for both boundary conditions.

On one-dimensional lattices with sites either filled or empty, we call a sequence of m adjacent empty sites an m-gap. For adsorption of k-mers ($k \geq 1$) on an infinite line, one can define probabilities $P(m,t;k)$ to find, at time t, gaps of m lattice spacings ($m \geq 1$), possibly part of larger voids.[5,7] The infinite hierarchy of rate equations one obtains for $P(m,t;k)$ contains only terms that account for the destruction of those gaps and therefore reduction of $P(m,t;k)$, usually starting with $P(m,0;k)=1$. The coverage $\theta_\infty(t;k)$ is then obtained directly from $P(1,t;k)=1-\theta_\infty(t;k)$. The adsorption of a k-mer results in decreasing $P(m,t;k)$ provided it fills at least one site of an m-gap without overlapping previously deposited k-mers. The resulting rate equations for $P(m,t;k)$ are

$$-\frac{dP(m,t;k)}{dt}=\begin{cases}(k-m+1)P(k,t;k)+2\sum_{j=1}^{m-1}P(k+j,t;k), & m\leq k\\ (m-k+1)P(m,t;k)+2\sum_{j=1}^{k-1}P(m+j,t;k), & m\geq k\ .\end{cases} \tag{1}$$

The time has been reduced by the frequency of attempts to deposit an object. The solutions of (1), starting with an empty line $[P(m,0;k)=1]$, have the form

$$P(m,t;k)=\begin{cases}1-\int_0^t\left[(k-m+1)+2\sum_{j=1}^{m-1}e^{-ju}\right]e^{-u}F(u;k)du, & m\leq k\\ e^{-(m-k+1)t}F(t;k), & m\geq k\ ,\end{cases} \tag{2}$$

where $F(t;k)$ is independent of m and given by

$$F(t;k)=\exp\left[-2\sum_{j=1}^{k-1}\frac{1-e^{-jt}}{j}\right], \tag{3}$$

with $F(0;k)=F(t;1)=1$. The k dependence of $\theta_\infty(t;k)$ and $\theta_\infty(\infty;k)$ is of interest in itself,[13] both for finite k and in the continuum limit $k\to\infty$.

On a line of length $N<\infty$, these probabilities lose meaning. For $1\le m\le N$, we define the total number of gaps of exactly size m as $Q(m,t;k)$, for *free* boundary conditions (FBC's), and $\tilde{Q}(m,t;k)$, for *periodic* boundary conditions (PBC's), as well as the total number of m-gaps (possibly part of larger gaps) as $T(m,t;k)$ and $\tilde{T}(m,t;k)$ for FBC's and PBC's, respectively. They vanish if $m>N$. The two quantities, for each type of boundary conditions, are simply related:

$$T(m,t;k)=\sum_{l=m}^{N}(l-m+1)Q(l,t;k) \tag{4}$$

and

$$\tilde{T}(m,t;k)=\sum_{l=m}^{N-1}(l-m+1)\tilde{Q}(l,t;k)+[N-(N-1)\delta_{m,N}]\tilde{Q}(N,t;k)\;, \tag{5}$$

or

$$Q(m,t;k)=T(m,t;k)-2T(m+1,t;k)+T(m+2,t;k) \tag{6}$$

and

$$\tilde{Q}(m,t;k)=\tilde{T}(m,t;k)-[2+(N-2)\delta_{m,N-1}]\tilde{T}(m+1,t;k)+[1+(N-1)\delta_{m,N-2}]\tilde{T}(m+2,t;k)\;, \tag{7}$$

corresponding, of course, to

$$T(m,t;k)-T(m+1,t;k)=\sum_{l=m}^{N}Q(l,t;k) \tag{8}$$

and

$$\tilde{T}(m,t;k)-\tilde{T}(m+1,t;k)=\sum_{l=m}^{N-1}\tilde{Q}(l,t;k)+(m\delta_{m,N-1}+\delta_{m,N})\tilde{Q}(N,t;k)\;. \tag{9}$$

The factor $l-m+1$ is just the total number of distinct empty sequences of size m that can fit in a void of size l. We start at $t=0$ with an empty line. Therefore, $Q(m,0;k)=\tilde{Q}(m,0;k)=\delta_{m,N}$ and $T(m,0;k)=N-m+1$; $\tilde{T}(m,0;k)=N-(N-1)\delta_{m,N}$. The coverage is simply

$$\theta_N(t;k)=1-\frac{\sum_{l=1}^{N}lQ(l,t;k)}{N}=1-\frac{T(1,t;k)}{N}\;, \tag{10}$$

with a similar definition for $\tilde{\theta}_N(t;k)$. The jamming coverages are obtained in the limit when $t\to\infty$. The size of the adsorbed particles enters only while writing the rate equations for Q and $\tilde{Q}$ (and thereby for T and $\tilde{T}$). Note that these are discrete functions of time and obtaining a continuous rate equation already involves an averaging over a large ensemble of identical deposits. For $k\le 2$, the only case that we study below, the rate-equation solutions are obtained easily in closed form and are suitable for asymptotic analysis. We have not been able to write the solutions for general k in a simple form. However, the leading size and boundary corrections should not depend strongly on the choice of k, as long as $k\ll N$.

The total number of gaps of exactly size m decreases if a k-mer lands inside the gap (for $m\ge k$) but can increase if the k-mer lands on a sufficiently larger void whose remaining empty sites form a sequence of size m. In general, this can happen on either size of the larger gap, whenever its size is not equal to $2m+k$ in which case the k-mer has to land in the middle of the gap to create *two* m-gaps. For periodic boundary conditions one has to consider separately the cases $N-m<k$ because configurations in which the k-mer does not overlap the m-gap are forbidden by the finite length N of the (closed) line. For $k=1$ and 2, we have

$$\frac{dQ(m,t;k)}{dt}=-(m-k+1)Q(m,t;k)+2\sum_{l=m+k}^{N}Q(l,t;k) \tag{11}$$

and

$$\frac{d\tilde{Q}(m,t;k)}{dt}=-(m-k+1)\tilde{Q}(m,t;k)+2\sum_{l=m+k}^{N-1}\tilde{Q}(l,t;k)+N[\delta_{m,N-k}-(k-1)\delta_{m,N}]\tilde{Q}(N,t;k)\;. \tag{12}$$

Combining Eqs. (11) and (12) with the time derivative of (4) and (5), respectively, yields

$$\frac{dT(m,t;k)}{dt}=-(m-k+1)T(m,t;k)-2\sum_{j=1}^{k-1}T(m+j,t;k) \tag{13}$$

and

$$\frac{d\tilde{T}(m,t;k)}{dt}=-(m-k+1)\tilde{T}(m,t;k)-2(1+m\delta_{m,N-1})\sum_{j=1}^{k-1}\tilde{T}(m+j,t;k)-(k-1)\delta_{m,N}\tilde{T}(N,t;k)\;. \tag{14}$$

The solutions for $k=1$,

$$T(m,t;1)=(N-m+1)e^{-mt} \tag{15}$$

and

$$\tilde{T}(m,t;1)=[N-(N-1)\delta_{m,N}]e^{-mt}, \quad (16)$$

reduce to $T(1,t;1)=\tilde{T}(1,t;1)=Ne^{-t}$. Therefore, $\theta_N(t;1)=\tilde{\theta}_N(t;1)=\theta_\infty(t;1)$.

For $k=2$, successive integration, starting from $T(N,t;2)$ and $\tilde{T}(N-1,t;2)$, gives

$$T(m,t;2)=e^{-(m-1)t}\sum_{n=0}^{N-m}(-2)^n(N-m-n+1)\times I_n(t), \quad (17)$$

the same as Eq. (2.7) in Ref. 5, and

$$\tilde{T}(m,t;2)=\begin{cases} Ne^{-(m-1)t}\left[\sum_{n=0}^{N-m-2}(-2)^nI_n(t)+(-2)^{N-m}\sum_{n=3}^{N-m}\frac{(-1)^nI_{N-m-n+1}(t)}{n!}\right. \\ \left.\qquad -\frac{2^{N-m}(1-e^{-(N-m+1)t})}{(N-m+1)!}\right], & m\le N-2 \\ [N-(N-1)\delta_{m,N}]e^{-Nt}, & m=N-1,N \end{cases} \quad (18)$$

with

$$I_n(t)=\int_0^t e^{-x_1}dx_1\int_0^{x_1}e^{-x_2}dx_2\cdots\int_0^{x_{n-1}}e^{-x_n}dx_n =\frac{(1-e^{-t})^n}{n!}.$$

Thus, for the coverages we obtain

$$\theta_N(t;2)=\theta_\infty(t;2)+\frac{1}{N}\sum_{n=0}^{N-1}(-2)^n nI_n(t) + \sum_{n=N}^{\infty}(-2)^nI_n(t) \quad (19)$$

and

$$\tilde{\theta}_N(t;2)=\theta_\infty(t;2)+(-2)^{N-1}\frac{(1-e^{-t})^N}{N!} + \sum_{n=N}^{\infty}(-2)^nI_n(t), \quad (20)$$

thereby recovering $\theta_\infty(t;2)=1-e^{-2(1-e^{-t})}$, when $N\to\infty$. Figure 1 shows the coverages for $N=5$ and $N=\infty$. The size effects are unnoticeable in a coverage plot for $N\gtrsim 10$.

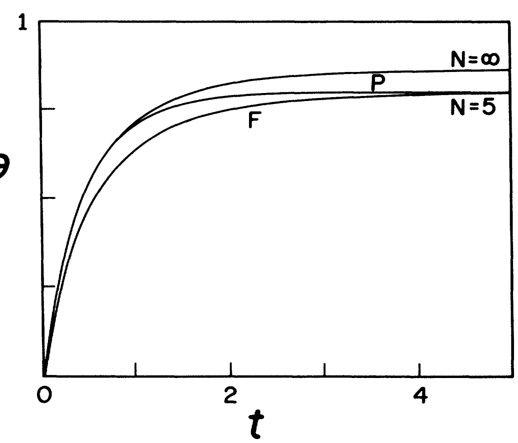

FIG. 1. The coverage of dimers on an infinite line ($N=\infty$) and for $N=5$ with periodic (P) and free (F) boundary conditions. The time variable was reduced by the frequency of depositions.

For $k<\infty$, the coverage expands for $t\to 0$ and $t\to\infty$, in the variables t and e^{-t}, respectively, with coefficients that we define for $\theta_N(t;k)$ [and similarly for $\tilde{\theta}_N(t;k)$] as follows. For *short times,*

$$\theta_N(t;k)=\sum_{n=0}^{\infty}A_{N,k}^{(n)}t^n \quad (21)$$

(with $A_{N,k}^{(0)}=0$ if one starts with an empty lattice) and, for *long times,* as

$$\theta_N(t;k)=\sum_{n=0}^{\infty}B_{N,k}^{(n)}e^{-nt} \quad (22)$$

[with $B_{N,k}^{(0)}=\theta_N(\infty;k)$]. Clearly, $A_{N,1}^{(n)}=\tilde{A}_{N,1}^{(n)}=A_{\infty,1}^{(n)}$ and $B_{N,1}^{(n)}=\tilde{B}_{N,1}^{(n)}=B_{\infty,1}^{(n)}$, for all n. From (19) and (20) and just until the first coefficients that differ from their $N=\infty$ counterparts,

$$A_{N,2}^{(1)}=A_{\infty,2}^{(1)}-\frac{2}{N},$$
$$\tilde{A}_{N,2}^{(1)}=A_{\infty,2}^{(1)};\ldots,\quad \tilde{A}_{N,2}^{(N-1)}=A_{\infty,2}^{(N-1)}, \quad (23)$$
$$\tilde{A}_{N,2}^{(N)}=A_{\infty,2}^{(N)}-\frac{(-2)^{N-1}}{N!},$$

and

$$B_{N,2}^{(0)}=B_{\infty,2}^{(0)}-\frac{(-2)^N}{N!} -e^{-2}\left[\frac{N+2}{N!}\Gamma(N,-2)-1\right],$$

$$\tilde{B}_{N,2}^{(0)}=B_{\infty,2}^{(0)}+\frac{(-2)^{N-1}}{N!} -e^{-2}\left[\frac{1}{(N-1)!}\Gamma(N,-2)-1\right], \quad (24)$$

$$B_{N,2}^{(1)}=B_{\infty,2}^{(1)}+\frac{(-2)^{N+1}}{N!}-2e^{-2}\left[\frac{N+1}{N!}\Gamma(N,-2)-1\right],$$

$$\tilde{B}_{N,2}^{(1)}=B_{\infty,2}^{(1)}+\frac{(-2)^{N-1}}{(N-1)!}-2e^{-2}\left[\frac{1}{(N-1)!}\Gamma(N,-2)-1\right],$$

where

$$\Gamma(N-2)/N!-1\approx-(e^{-N}/\sqrt{N}),\quad \text{for } N\gg 1 .$$

The overall size effects are milder for periodic boundary conditions throughout the process. At long times, the space available for new depositions is reduced to small gaps, very likely away from the boundaries, and the end corrections are essentially dominated by the size effects.

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