THE END-ON MECHANISM FOR LATTICE FILLING: COMPARISON WITH THE CONVENTIONAL MECHANISM AND APPLICATION TO THE CAR-PARKING PROBLEM

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Abstract

We present the exact solution for the sequential, random, irreversible filling of one-dimensional lattices by linear n-mers using the end-on filling mechanism. The results are extrapolated to the $n \to \infty$ limit (a variation on the car-parking problem) to yield a saturation coverage (packing density) of 0.7350. The end-on filling mechanism involves two steps for a single filling event. First, the landing site for one endpoint of the filling species is chosen and then the second endpoint is subsequently chosen (from *unfilled* sites an appropriate distance from the first endpoint). We compare this mechanism to the conventional, one-step filling mechanism, where both endpoints of the filling species are chosen simultaneously. We present results detailing how the lattice saturation coverage varies for the two mechanisms. In addition, we extend our analysis to consider filling in the presence of a time-dependent, random distribution of inactive sites.

1. Introduction

A problem that has received considerable attention is the car-parking problem, where intervals of unit length are randomly and sequentially placed on an infinite line such that the intervals do not overlap. The solution to this problem was first obtained by Rényi [1]. Here, we consider a variation on the problem, where we vary the mechanism used to place the intervals.

In the standard car-parking problem, the intervals are placed by simultaneously choosing both endpoints or, equivalently, choosing the left (right) endpoint which specifies the location of the right (left) endpoint (conventional mechanism). If this new interval overlaps a previously-placed interval, the new interval is removed.

In the variation considered here (end-on mechanism), we first choose one endpoint of the interval, then sequentially place the second endpoint (an appropriate distance away) on a randomly-chosen side of the first endpoint. *If the new interval overlaps a previously-placed interval, the second endpoint is removed and placed on* *the opposite side of the first endpoint (which remains fixed).* If this also results in overlap with a previously-placed interval, the new interval is removed.

The first phase of end-on filling is identical to conventional filling (both mechanisms randomly choose a pair of endpoints). However, the testing (if necessary) on the second side of the initial site distinguishes the end-on filling mechanism from the conventional filling mechanism.

The distinction between these two mechanisms has not always been recognized and the end-on mechanism has only been considered in a few previous treatments for simple discrete lattice filling by dimers [2–7]. The case of simultaneous end-on filling by monomers and dimers has also been considered [2,3].

The car-parking problem is equivalent to the $n \to \infty$ limit of one-dimensional (1D) n-mer filling of a discrete lattice. An n-mer is a filling species which occupies a string of n adjacent lattice sites; it places no other restrictions on the filling species. By studying n-mer fillings over a wide range of values of n, we expect to be able to extrapolate to obtain information about the $n \to \infty$ limit.

The discrete lattice problems are of interest themselves, since numerous physical processes have been modelled as sequential, irreversible (immobile), n-mer filling of a lattice (for a brief review, see Nord and Evans [4] and references therein). One-dimensional examples include reactions at specific sites on a polymer chain (see also [5]); and two-dimensional (2D) examples include adsorption onto surfaces and reactions between groups on adjacent surface sites. The results we obtain here should aid in the determination of the actual mechanism by which a particular physical process occurs.

Here, we confine our attention to random-filling processes, where the rates at which filling events occur are independent of the local environment of the site(s) being filled. In general, since there is no equilibrating mechanism present, the final, stationary state contains unfillable, empty sites (see fig. 1). A primary quantity of interest is the saturation coverage Θ^{sat}, which equals the final fraction of sites which are filled.

To illustrate the difference between the mechanisms, consider the landing of a single dimer ($n = 2$) upon a string of four adjacent empty sites (see fig. 2) [5]. Using conventional filling, there are three possible filling events (filling the left pair, middle pair, or right pair), resulting in three distinct final states (each occurring with a probability of 1/3). Using end-on filling, the same three states are still possible; however, the probability of each occurring is different (3/8, 1/4, 3/8, respectively). There is an enhanced probability of filling a pair of sites near the end relative to the pair in the middle.

Here, we compare the results obtained when infinite 1D (linear) lattices are filled by linear n-mers using the two different mechanisms. For the end-on mechanism, we extrapolate to obtain results for the car-parking (infinite n) limit. We also briefly comment on the extension to 2D (square) lattices. Additionally, we consider filling processes where the lattice contains a time-independent random distribution of inactive sites (which cannot be filled).

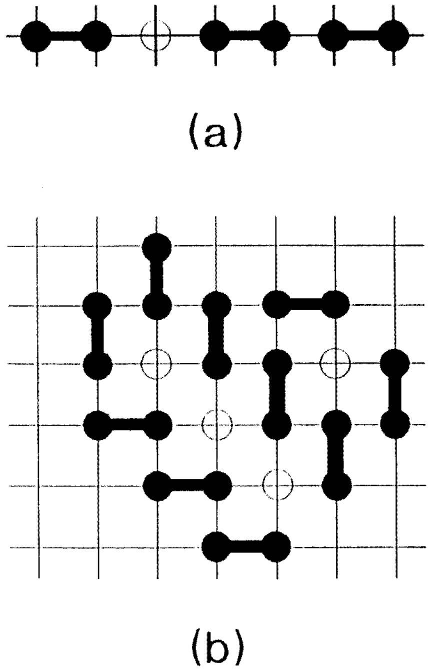

Fig. 1. Irreversible filling of a (a) linear, (b) square lattice by dimers. A site labelled with an "*o*" can never fill.

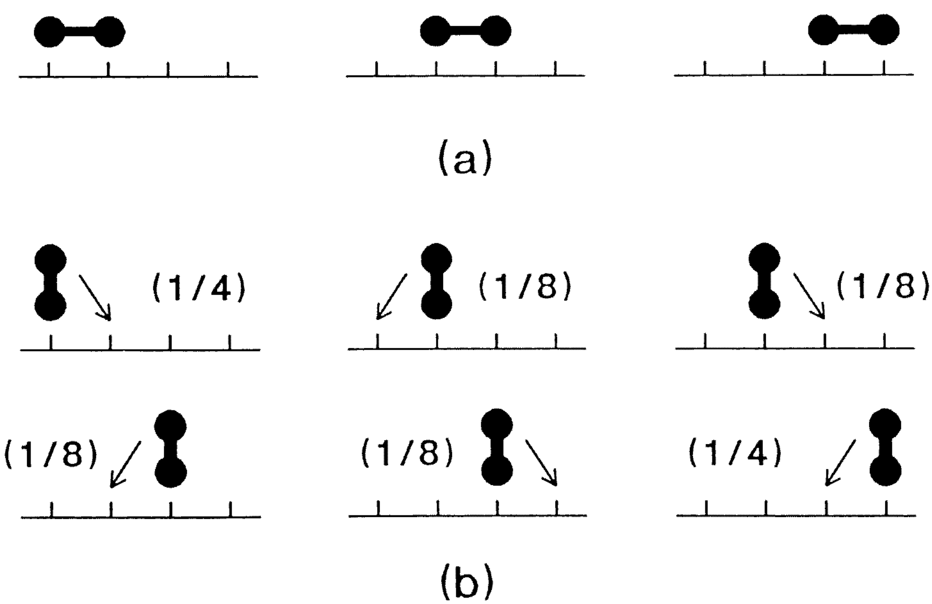

Fig. 2. Possible dimer filling events on a string of four empty sites using the (a) conventional, (b) end-on filling mechanism. The probability of each event is 1/3 in (a) and as labelled in (b).

2. Method

The 1D conventional filling results have previously been determined by a variety of techniques. For arbitrary length n, the most extensive published set of results are those of Gonzalez et al. [8] and many of these have been recalculated by Wolf et al. [9] with higher precision. For the 1D end-on filling mechanism, only results for dimer filling, mostly approximate, have previously been published [2,3,5–7]. Page [6] was the first to consider the end-on mechanism, and he found $\Theta^{sat} = 0.87668$ for end-on dimer filling (which is consistent with the more recent results). Here, we present the exact solution for 1D end-on n-mer filling for arbitrary length n.

The end-on filling results are obtained from the numerical integration of rate equations for the probabilities of various configurations of empty sites. These equations result when the appropriate master equation is recast in hierarchical form and the resulting (infinite) hierarchy is truncated. The truncation leads to exact results in 1D [10].

Let Po_i denote the probability that a randomly-chosen string of i sites contains all empty sites and let Pa denote the probability that a randomly-chosen site is filled. Thus, Po_1, Po_2, ... denote the probabilities that a randomly-chosen single site, pair of adjacent sites, ..., are all empty, respectively, and $Pao_i a$ is the probability that a randomly-chosen string of $i+2$ sites contains i empty sites surrounded by a pair of filled sites. The Po_i can be considered as functions of time t or lattice coverage Θ. The hierarchy of rate equations for 1D, end-on, n-mer filling can be written down as follows:

$$\mathrm{d}/\mathrm{d}t(Po_1) = -k\Bigg[Po_1 - \sum_{i=0}^{n-2}\sum_{j=0}^{n-2} Pao_{i+1+j}\,a + (2n-2)\Bigg(\tfrac{1}{2}Po_{2n-1} + \sum_{l=n-1}^{2n-3} Po_{l+1}\,a\Bigg)\Bigg], \tag{1}$$

$$\mathrm{d}/\mathrm{d}t(Po_n) = -k\Bigg[2Po_n + \sum_{l=0}^{n-3}\Bigg(Po_n - \sum_{i=0}^{l}\sum_{j=0}^{n-3-l} Pao_{i+1+j}\,a\Bigg) + 2\sum_{l=0}^{n-2}\Bigg(\tfrac{1}{2}Po_{2n+l} + \sum_{i=1+l}^{n-1+l} Po_{n+i}\,a\Bigg)\Bigg], \tag{2}$$

$$\mathrm{d}/\mathrm{d}t(Po_{n+m}) = -k\Bigg[2(m+1)Po_{n+m} + \sum_{l=0}^{n-3-m}\Bigg(Po_{n+m} - \sum_{i=0}^{l}\sum_{j=0}^{n-3-l-m} Pao_{i+n+m+j}\,a\Bigg) + 2\sum_{l=0}^{n-2}\Bigg(\tfrac{1}{2}Po_{2n+m+l} + \sum_{i=1+l}^{n-1+l} Po_{n+m+i}\,a\Bigg)\Bigg] \qquad m \le n-2, \tag{3}$$

where k is the rate constant for the filling process. Since we are only concerned with random-filling processes, the rate constant is the same for all of the terms. In eq. (2), the sum over $l = 0$ to $n-3$ is set equal to zero if $n = 2$ and in eq. (3), the sum over $l = 0$ to $n-3-m$ is set equal to zero if $m = n-2$.

We consider only the filling of uniform, infinite, initially-empty lattices, which ensures both translational invariance (all sites are equivalent) and that $Po_i = 1$ at $t = 0$ for all i.

We will consider the physical interpretation of these equations term by term. In eq. (1), the first term results from the destruction of the empty site by the first end of an n-mer landing on it. The rate that this occurs depends upon the probability a single site is empty (where the first end of the n-mer can land) and adjacent to a set of empty sites of sufficient length for the second end of the n-mer to land. Hence, the probabilities of all lattice configurations containing filled sites, placed such that the second end cannot land, are subtracted from the probability that a single site is empty.

The second term in eq. (1) results from an n-mer landing with its first end sufficiently close to, but not on, the site of interest, such that the site of interest may be filled when the second end of the n-mer lands. Since there are two sides to the site, there is a factor of 2 in front of this term (one for each side). If the second end of the n-mer may land in either direction, the probability that it fills the site of interest is only 1/2. However, a filled site may exist such that the second end of the n-mer may only land covering the site of interest (thus, for those configurations, the probability that the site of interest is filled is unity).

As an example, consider trimer filling ($n = 3$). For clarity, we underline the site of interest. We note, however, that since all sites on the lattice are equivalent, the underline has no mathematical significance.

$$\begin{aligned} \mathrm{d}/\mathrm{d}t(P\underline{o}) = -k[&P\underline{o} - Pa\underline{o}a - Pao\underline{o}a - Pa\underline{o}oa - Pao\underline{o}oa \\ &+ 2(1/2\, Po\underline{o}ooo + Po\underline{o}oa + Po\underline{o}ooa) \\ &+ 2(1/2\, P\underline{o}oooo + P\underline{o}ooa + P\underline{o}oooa)], \end{aligned} \tag{4}$$

where $Paooa = Pao_2a$, $Paooo = Pao_3$, $Pooooo = Po_5, \ldots$. In eq. (4), the middle term corresponds to cases where the first end of the n-mer lands on the site adjacent (arbitrarily, on the right) to the site of interest, and the last term corresponds to cases where the first end lands on the next-nearest neighbor to the site of interest.

The first term in eq. (2), as well as in eq. (3), corresponds to the ways an n-mer can land such that it only fills sites contained in the configuration of interest.

The second term in eq. (2), or eq. (3), corresponds to all ways that an n-mer can destroy the configuration of interest by having its first end land on some site within the configuration, but its second end lands on some site external to the configuration. Thus, this term is analogous to the first term of eq. (1) and the interpretation is similar.

The third term in eq. (2), or eq. (3), corresponds to the first end of the n-mer landing external to the configuration of interest and the second end landing somewhere within the configuration, and is completely analogous to the second term of eq. (1).

These equations can be recast in terms of configurations involving only empty sites through conservation of probability. Since any site must either be empty, "o", or filled, "a", we know $Po + Pa = 1$. Similarly, $Po = Poo + Poa$, since the site to the right of the empty site must either be filled or empty. Hence, $Poa = Po - Poo$. By continuing in this fashion, eqs. (1)–(3) can be written as follows:

$$\mathrm{d}/\mathrm{d}t(Po_1) = -k[2nPo_n - nPo_{2n-1}], \tag{5}$$

$$\mathrm{d}/\mathrm{d}t(Po_n) = -k\left[2Po_n + \sum_{l=1}^{n-1}(4Po_{n+l} - Po_{2n+l-1}) - nPo_{2n-1}\right], \tag{6}$$

$$\begin{aligned}\mathrm{d}/\mathrm{d}t(Po_{n+m}) = -k\Bigg[&(2m+2)Po_{n+m} - (n-m-2)Po_{2n-1}\\ &+ \sum_{l=1}^{n-m-2}(4Po_{n+m+l} - Po_{2n+m+l-1})\\ &+ \sum_{l=0}^{m}(2Po_{2n+l-1} - Po_{3n+l-2})\Bigg] \qquad m \le n-2,\end{aligned} \tag{7}$$

where the sum over $i = 1$ to $n - m - 2$ in eq. (7) is set equal to zero if $m = n - 2$. For $m > n - 2$, it is possible to show that

$$Po_{n+m} = Po_{2n-2}\exp[-k(m-n+2)t] \qquad m > n-2, \tag{8}$$

through the use of a shielding property for strings of empty sites (see appendix).

Given this closed set of coupled equations, it is now possible to numerically integrate to obtain the various probabilities as functions of time (or coverage).

The above equations can be modified to consider the case where the lattice contains a time-independent, random distribution of inactive sites. Since filling events only occur at active sites, we need to consider the hierarchy of equations for the probabilities that strings contain sites which are all *both* empty *and* active [11]. Therefore, each term in the equations is multiplied by a factor related to the probability that all of the sites in the string are active. For a randomly-chosen string of length i, since the distribution of inactive sites is random, the probability that all of the sites in the string are active is β^i, where β is the probability that any given site is active. The results are described below.

3. Results

3.1. SIMPLE FILLING

In table 1, we present the results for the saturation coverage for 1D n-mer filling. As the length n increases, we observe that Θ^{sat} decreases since larger groups of sites can remain empty (up to $n-1$ sites). A plot of the saturation coverage

Table 1

Comparison of saturation coverages for 1D conventional and end-on filling mechanisms

Length of filling species	Saturation coverage Conventional[a]	End-on
2	0.86466	0.87668
3	0.82365	0.82762
4	0.80389	0.80351
5	0.79227	0.78930
6	0.78463	0.78000
7	0.77921	0.77335
8	0.7751	0.76843
9	0.7720	0.76463
10	0.7695	0.76160
100	0.7497	0.73758
∞	0.7476	0.73512[b]

[a]The results for lengths 2–7 are taken from Wolf et al. [9] and the results for longer lengths are taken from Gonzalez et al. [8].
[b]Result from Monte Carlo simulation [12] (±0.00100).

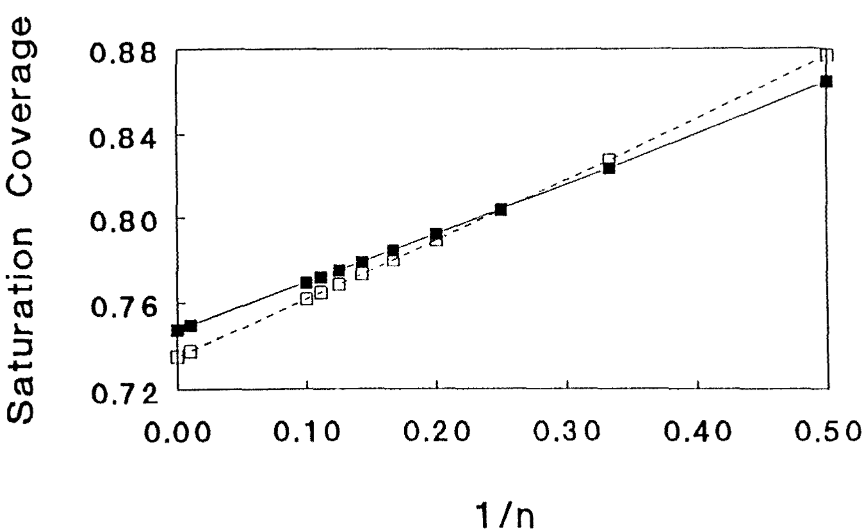

Fig. 3. A plot of saturation coverage versus $1/n$ for (– –■– –) conventional, (– –□– –) end-on filling.

versus $1/n$ is presented in fig. 3 for each mechanism [13]. We observe that the plot is almost linear for both mechanisms (a slight curvature exists in both cases). Since the curvature is slight, we used a linear extrapolation of the end-on results to obtain the end-on car-parking saturation coverage. In order to improve the extrapolation, we ran an additional data point for $n = 200$ ($\Theta^{sat} = 0.73628$). We then used the line defined by the points for $n = 100$ and $n = 200$, which gave a value of 0.73498 for the end-on car-parking saturation coverage. (Note that the number of coupled differential equations increase as n increases, which leads to difficulty in numerically integrating for large n.) Due to the slight upward curvature, this is the *minimum* possible value and it seems reasonable to assume a value of 0.7350 for Θ^{sat}. This value is consistent with the Monte Carlo result given in table 1.

From fig. 3, we also observe that, for end-on filling relative to conventional filling, Θ^{sat} is initially larger (for small n) but decreases faster. This can be explained by considering the ratio R of the number of filling events that occur *immediately adjacent to a filled site* to the number of possible filling events.

Let us begin by considering dimer filling ($n = 2$) for simplicity. An unfillable, empty site is created when a dimer fills a pair of sites which is separated by one site from a previously-filled site. If the dimer, by landing, creates an enclosed string of m empty sites, where m is odd, at least one of those m sites will eventually become unfillable (since sites are filled in pairs). Furthermore, even if m is even, it is likely that some of the sites will become unfillable. Even for a string of four sites there is substantial probability that a dimer will land in the middle isolating the two end sites (see fig. 2). The only way a dimer can fill sites which does not create additional enclosed strings of m empty sites is to fill sites at the end (other than the obvious trivial cases). We therefore postulate that the filling mechanism which has the greater probability of filling the end sites, of an empty string, will have the higher saturation coverage (less isolated, unfillable sites). To illustrate, we begin by considering dimer filling of a string of $m > 3$ sites by the two mechanisms (for $m \leq 3$, the mechanisms are trivially equivalent).

For conventional filling there are $m - 1$ possible filling events, corresponding to the locations where the left (right) end of the dimer may be placed (see fig. 4(a)). Two of these events correspond to filling at an end. Hence, $R_c = 2/(m - 1)$ for conventional dimer filling.

For end-on dimer filling there are m possible filling events, corresponding to the locations where the first end of the dimer may be placed (see fig. 4(b)). Two of these events correspond to the first end of the dimer landing on the site at the end of the string. Additionally, if the first end of the dimer lands at a site adjacent to the end site, there is a probability of 1/2 that the second end will fill the end site (since it is equally likely to fill either adjacent empty site). Since there are two sites which are located adjacent to end sites, this adds an additional $2(1/2) = 1$ possible filling event at the end. Therefore, $R_e = 3/m$ for end-on filling.

For $m > 3$, $R_e > R_c$ since $3/m > 2/(m - 1)$. Consequently, there is an enhanced probability of filling at the end for the end-on mechanism. Therefore, we expect the

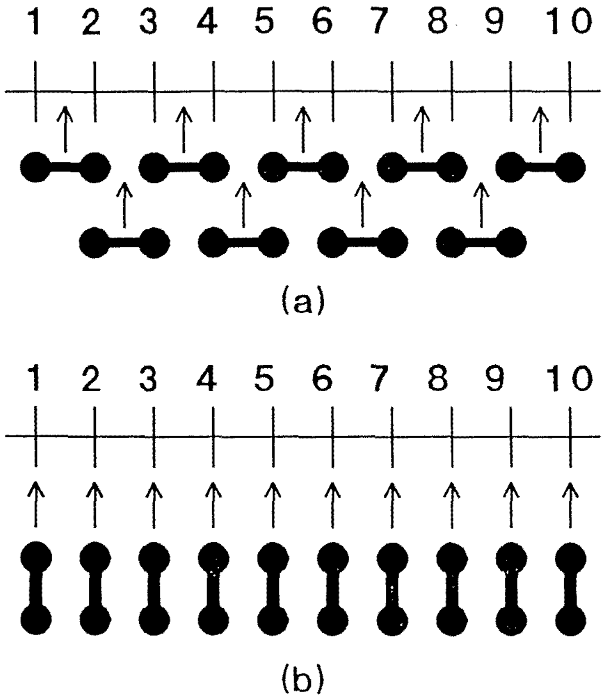

Fig. 4. Possible dimer filling events on a string of ten empty sites using the (a) conventional, (b) end-on filling mechanism.

saturation coverage to be greater for end-on filling, which agrees with the results given in table 1.

If we extend this argument to $n = 3$, trimer filling, we find $R_c = 2/(m-2)$ and $R_e = 3/m$, for $m > 4$ (nontrivial cases). If $m = 5$, then one trimer will land, regardless of the mechanism. If $m = 6$, then $R_e = R_c$. If $m > 6$, then $R_e > R_c$, as for dimers. Therefore, we again expect to find a greater saturation coverage for end-on filling (in agreement with the results in table 1).

For $n = 4$, tetramer filling, $R_c = 2/(m-3)$ and $R_e = 3/m$, for $m > 6$. If only one tetramer can fill a string, the mechanisms are effectively equivalent. In order to have two tetramers fill a string, $m \geq 8$. For $m = 8$, $R_e < R_c$, for $m = 9$, $R_e = R_c$, and for $m > 9$, $R_e > R_c$. Hence, for a string of exactly eight empty sites, conventional filling is more likely to fill the string with two tetramers. However, for longer strings, end-on filling is more likely to fill at the end of the string (which should decrease the number of small isolated strings of empty sites and hence increase the number of tetramers that can be placed). The net result is that the saturation coverages, for the two mechanisms, are almost equal (see table 1).

For arbitrary n, we observe that $R_c = 2/(m-n+1)$ and $R_e = 3/m$ ($m \geq 2n-1$). Therefore, as n increases further, $R_c > R_e$ for strings of length $2n$ (and slightly longer). Since these lengths cannot be subdivided into shorter strings where further filling can occur, they seem to have the greatest impact upon the saturation coverage. Therefore, conventional filling becomes the mechanism with the larger saturation coverage for longer filling species.

We anticipate that the behavior will be similar in higher dimensions. Preliminary Monte Carlo simulation results for 2D dimers and trimers indicate a higher saturation coverage for end-on filling, as expected (see table 2). Results for longer filling species in 2D are not yet available.

Table 2

Comparison of saturation coverages for 2D conventional and end-on filling mechanisms

Length of filling species	Saturation coverage[a)] Conventional	End-on
2	0.90687	0.91882
3	0.84659	0.85411

[a)]Results from Monte Carlo simulation [12] (±0.00015).

3.2. FILLING WITH INACTIVE SITES

It may be that the lattice contains a time-independent distribution of (immobile) sites which are inactive with regard to the filling event being studied. We assume that the inactive sites are randomly distributed, which simplifies the solution [11]. Define α as the fraction of sites which are inactive and β as the fraction of sites which are active ($\beta = 1 - \alpha$).

By introducing inactive sites, it is possible to increase the fraction of *active, empty sites* at saturation P_0^{ACT}. This then leads to an increase in the fraction of active, empty sites *which are adjacent to filled sites* at saturation P_0^{ER}. For a reaction which proceeds by the Eley–Rideal mechanism, P_0^{ER} is an important quantity since it gives the number of sites where reaction can occur. For example, being able to vary this quantity could be useful in determining the composition of a surface for optimum catalytic activity. Monte Carlo simulations using the end-on mechanism have been found to be consistent with experiment for, at least, one such system [14].

In 1D, exact solutions can be obtained. For conventional filling we find:

$$P_0^{\mathrm{ER}} = \beta \mathrm{e}^{-2\beta} - \beta\alpha^2, \tag{9}$$

where the first term is the familiar result (see Evans and Nord [11] and references therein) for the fraction of active sites which are empty P_0^{ACT}, and the second term $\beta\alpha^2$ subtracts off the fraction of active, empty sites which are surrounded by inactive sites.

For 1D end-on dimer filling, we find:

$$P_0^{ER} = (2\pi)^{1/2}\exp[(2-\beta)^2/2]\{\mathrm{erf}(\sqrt{2}) - \mathrm{erf}[(2-\beta)/\sqrt{2}]\} - \beta - \beta\alpha^2, \tag{10}$$

where erf is the error function. Again, the last term $\beta\alpha^2$ subtracts off the fraction of active, empty sites which are surrounded by inactive sites.

P_0^{ER} and P_0^{ACT} are plotted as a function of α for 1D dimer filling in fig. 5. From fig. 5, we find that P_0^{ER} reaches a maximum value of 0.1402 (0.1280) when $\alpha \approx 0.925$ (0.922) for conventional (end-on) filling.

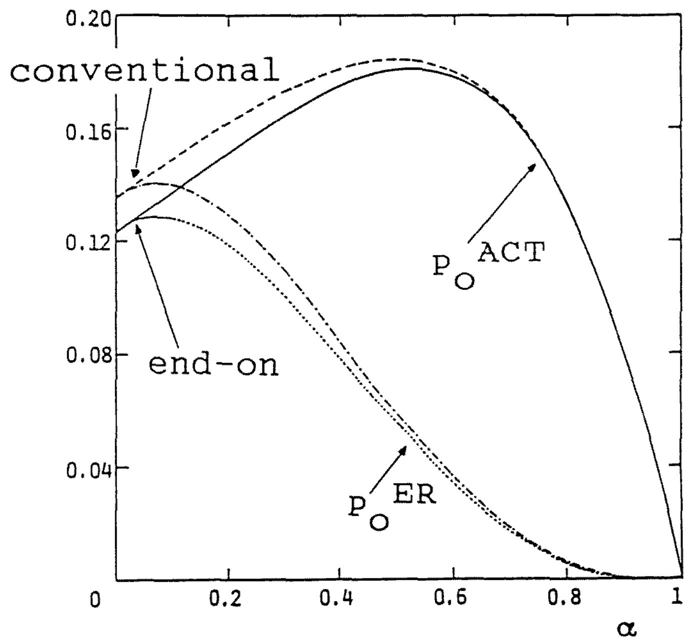

Fig. 5. α dependence of P_0^{ACT} and P_0^{ER} for random dimer filling of a 1D linear lattice for both conventional and end-on mechanisms.

Approximate 2D square lattice results were obtained by truncating the infinite hierarchy of rate equations using techniques described by Nord and Evans [4] (specifically, we employed a third-order severe truncation). The accuracy of the 2D approximate truncation results has been confirmed by Monte Carlo simulations [3,12]. The results for P_0^{ER} and P_0^{ACT} are presented in fig. 6. We see in fig. 6, as we did in fig. 5, that the peak values are smaller and occur at higher values of α for end-on filling; however, the differences are not large.

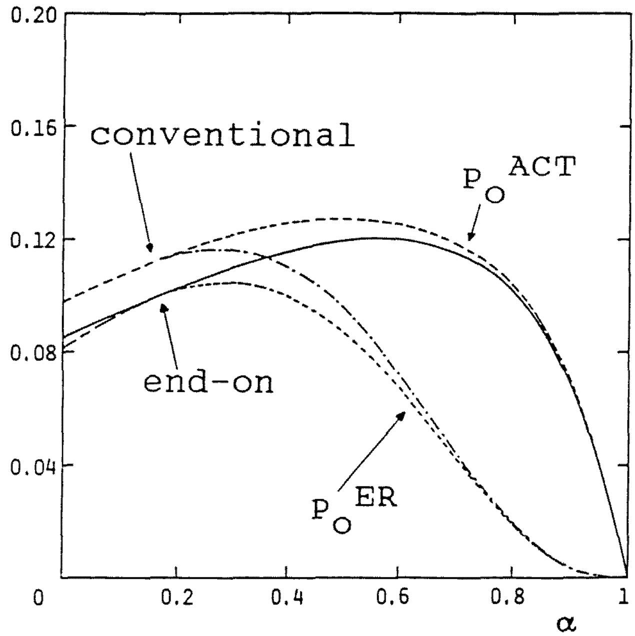

Fig. 6. α dependence of P_0^{ACT} and P_0^{ER} for random dimer filling of a 2D square lattice for both conventional and end-on mechanisms.

4. Conclusions

A plot of Θ^{sat} versus $1/n$ is almost linear, allowing approximate results to be obtained for arbitrary values of n. For the end-on car-parking problem, the extrapolated value of $\Theta^{sat} = 0.7350$, which is consistent with the Monte Carlo simulation result.

While the conventional and end-on mechanisms produce similar results, the results are noticeably different. Our preliminary 2D studies indicate that the variation in results, due to the mechanism, appears to be similar for 1D and 2D processes.

The end-on mechanism yields a higher saturation coverage for 1D dimer, trimer, and tetramer filling, but as the filling species becomes longer, the conventional mechanism has the higher saturation coverage. This can be explained by considering the ratio of the possible filling events at an end site relative to the number of possible filling events.

The presence of inactive sites has a similar effect on the two mechanisms. For dimer filling, the end-on mechanism's superior ability to fill sites at the end of a string makes it necessary to go to a slightly higher fraction of inactive sites in order to isolate a large number of active, empty sites at saturation.

Finally, the effect due to the mechanism varies depending upon the length of the filling species, the presence of inactive sites, and competitive filling [3]. Thus, it would seem reasonable that the effects would be cumulative. Therefore, if a problem was considered which involved all of these considerations, it would be very important to use the correct mechanism for the process being considered. An example of such a problem is the simultaneous chemisorption of one-point and two-point CO on binary alloys consisting of both active and inert component metals, as considered by Hayden and Klemperer [14].

Appendix

For $m \geq n-2$, eq. (7) simplifies to

$$d/dt(Po_{n+m}) = -k\left[(n+m)Po_{n+m} + 2\sum_{l=0}^{n-2}(2Po_{n+m+l+1} - Po_{2n+m+l})\right], \quad (A1)$$

since the second term in eq. (7) is no longer applicable. Define the conditional probability $Qo\phi_n \equiv Po_{n+1}/Po_n$ that a site is empty given that it is adjacent to a string of n empty sites.

We can now make use of the following shielding property [10]: *Consider a wall of sites specified empty which divides the lattice into two disconnected regions, and which is sufficiently thick that a filling event occurring on the lattice is not simultaneously affected by the state of sites on both sides of the wall; then such a wall completely shields sites on one side from the influence of those on the other.* For end-on n-mer filling, a filling event is influenced by $n-1$ sites on each side of the site where there first end lands; hence, $2n-1$ sites are involved. Therefore, for a filling event to not be influenced by sites on both sides of the wall, the wall must be of thickness $2n-2$. Therefore, a string of empty sites of length $2n-2$ is sufficient to block the influence of sites on one side on sites on the other side. Consequently, $Qo\phi_{2n-2} = Qo\phi_{2n-1} = Qo\phi_{2n} = \ldots$. Proof of the shielding property is via self-consistency.

Next, we derive the rate equation for the time-dependence of $Qo\phi_{2n-2} = Po_{2n-1}/Po_{2n-2}$:

$$d/dt(Qo\phi_{2n-2}) = \frac{Po_{2n-2}(d/dt(Po_{2n-1})) - Po_{2n-1}(d/dt(Po_{2n-2}))}{Po_{2n-2}^2} \quad (A2)$$

$$= Qo\phi_{2n-2}\left\{\frac{d/dt(Po_{2n-1})}{Po_{2n-1}} - \frac{d/dt(Po_{2n-2})}{Po_{2n-2}}\right\}. \quad (A3)$$

By use of (A1), we find:

$$d/dt(Po_{2n-2}) = -k\left[(2n-2)Po_{2n-2} + 2\sum_{l=0}^{n-2}(2Po_{2n+l-1} - Po_{3n+l-2})\right], \quad (A4)$$

$$\mathrm{d}/\mathrm{d}t\,(Po_{2n-1}) = -k\left[(2n-1)Po_{2n-1} + 2\sum_{l=0}^{n-2}(2Po_{2n+l} - Po_{3n+l-1})\right]. \tag{A5}$$

Hence,

$$\frac{\mathrm{d}/\mathrm{d}t\,(Po_{2n-2})}{Po_{2n-2}} = -k\left[(2n-2) + 2\sum_{l=0}^{n-2}\left(\frac{2Po_{2n+l-1}}{Po_{2n-2}} - \frac{Po_{3n+l-2}}{Po_{2n-2}}\right)\right] \tag{A6}$$

$$= -k\left[(2n-2) + 2\sum_{l=0}^{n-2}(2Qo_{l+1}\phi_{2n-2} - Qo_{n+l}\phi_{2n-2})\right], \tag{A7}$$

$$\frac{\mathrm{d}/\mathrm{d}t\,(Po_{2n-1})}{Po_{2n-1}} = -k\left[(2n-1) + 2\sum_{l=0}^{n-2}\left(\frac{2Po_{2n+l}}{Po_{2n-1}} - \frac{Po_{3n+l-1}}{Po_{2n-1}}\right)\right] \tag{A8}$$

$$= -k\left[(2n-1) + 2\sum_{l=0}^{n-2}(2Qo_{l+1}\phi_{2n-1} - Qo_{n+l}\phi_{2n-1})\right], \tag{A9}$$

which, by virtue of the above shielding property,

$$= -k\left[(2n-1) + 2\sum_{l=0}^{n-2}(2Qo_{l+1}\phi_{2n-2} - Qo_{n+l}\phi_{2n-2})\right]. \tag{A10}$$

Therefore, inserting (A7) and (A10) into (A3), we find:

$$\mathrm{d}/\mathrm{d}t\,(Qo\phi_{2n-2}) = Qo\phi_{2n-2}(-k). \tag{A11}$$

By use of the initial condition $Qo\phi_{2n-2} = 1$ at $t = 0$, we may integrate (A11) to find:

$$Qo\phi_{2n-2} = \exp(-kt). \tag{A12}$$

Therefore,

$$Po_{2n-1} = (Po_{2n-2})(Qo\phi_{2n-2}) = Po_{2n-2}\exp(-kt). \tag{A13}$$

The probabilities that longer strings of sites are all empty can be found trivially from this result by noting that:

$$Po_{2n+r} = Po_{2n+r-1}\left(\frac{Po_{2n+r}}{Po_{2n+r-1}}\right) = Po_{2n+r-1}(Qo\phi_{2n+r-1}), \tag{A14}$$

which, by invoking the shielding property,

$$= Po_{2n+r-1}(Qo\phi_{2n-2}) = Po_{2n+r-1}\exp(-kt), \tag{A15}$$

and continuing in a similar manner

$$\begin{aligned} &= Po_{2n+r-2}\exp(-2kt) = Po_{2n+r-3}\exp(-3kt) \\ &= \ldots = Po_{2n-2}\exp[-(r+2)kt]. \end{aligned} \tag{A16}$$

This can be rewritten as:

$$Po_{n+m} = Po_{2n-2}\exp[-(m-n+2)kt] \qquad m \geq n-2, \tag{A17}$$

by choosing $m = r + n$.

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