Exact solution of a class of cooperative sequential adsorption problems

1998 J. Phys. A: Math. Gen. 31 185

(http://iopscience.iop.org/0305-4470/31/1/019)

J. Phys. A: Math. Gen. **31** (1998) 185–194. Printed in the UK PII: S0305-4470(98)84853-1

Exact solution of a class of cooperative sequential adsorption problems

D J Stacchiola, T P Eggarter and G Zgrablich

Departamento de Física and Centro Latinoamericano de Estudios Ilya Prigogine, Universidad Nacional de San Luis, Chacabuco 917, 5700 San Luis, Argentina

Received 2 June 1997, in final form 21 October 1997

Abstract. We solve the cooperative sequential adsorption problem on a linear chain consisting of periodically repeating sequences of sites with different adsorption rates, patches, for example $ABCCABCCAB\ldots$. The problem is reduced to a system of s first-order differential equations, where s is the patch size. A simple iterative method to solve the equations numerically is presented. A few examples are calculated in detail.

1. Introduction

The growing interest, over the past two decades, in irreversible processes has resulted in the emergence of new branches of statistical mechanics. Particulary active among them is the study of cooperative sequential adsorption (CSA) phenomena. There one considers a flux of particles falling at random on a lattice of sites or a continuum of points (the substrate) and each particle has a given probability of sticking irreversibly to vacant sites. Cooperativity arises when the sticking probability depends on the occupation state of neighbouring sites. For example, a well-known CSA process is the adsorption of monomers with nearest-neighbour (NN) exclusion (i.e. a particle can be adsorbed on a vacant site only if its NN sites are empty). CSA models have been applied to a variety of problems, ranging from chemical reactions on polymer chains and surface growth phenomena to biological, ecological and sociological systems. A very complete review of the field up until 1993 is given in the classical paper by Evans [1]. For more recent works, see [2–5].

Most work on CSA is concerned with homogeneous lattices or continua, so that the solutions exhibit the full symmetry of the lattice. Even the random chains studied in [3], on average, have this symmetry. However, the study of CSA on heterogeneous substrates, i.e. those represented by a lattice of sites with different adsorption rates, is of great importance in many real processes, such as gases chemisorption and physisorption on metal surfaces [6, 7], on non-uniform polymers [8] and, in general, on any kind of real solid surfaces [9, 10]. In this work we address the problem of CSA, more precisely adsorption of monomers with NN exclusion, on a wide class of heterogeneous one-dimensional chains with truly inequivalent sites, characterized by finite, periodically repeating, sequences of sites with different adsorption rates (patches). The solution of this problem will include, as particular cases, all previously known solutions for homogeneous and heterogeneous one-dimensional chains. In section 2 we define the heterogeneous model and set up its basic equations, which will permit a unified treatment of homogeneous and random chains, and of patches of any size. In section 3, we apply the results to the known homogeneous and random

0305-4470/98/010185+10$19.50

cases. We also analyse the case of random sites with a Markovian correlation. Finally, in section 4, we turn to our specific goal: periodically repeating patches. We specialize the equations to this situation and present a simple method for their exact numerical solutions. Our conclusions are given in section 5.

2. Definition of the model

The system we wish to study is built from the following elements and rules.

(i) An infinite linear chain of sites s_n, n integer.

(ii) A random 'rain' of particles falling on the sites. The probability that a particle wets site n in any time interval $\mathrm{d}t$ is $\alpha_n \mathrm{d}t$, independently of all other sites and the previous history of site n. We call α_n the interaction strength of site n with the rain.

(iii) Sites may be empty or occupied. At $t = 0$ all sites are empty. Occupation is irreversible. Site n becomes occupied if it is wet while both NNs are empty.

An empty site is indicated by an o and an occupied site is indicated by an x. We furthermore introduce a distinction among o sites: a site that was never wet by a particle will be called a d (dry), providing a nice intermediate step to decouple uncorrelated aspects of the problem (the particle rain) from those correlated (occupations).

In what follows we shall use the general notation $P(ABC\ldots)$ for the joint probability of the simultaneous occurrence of events $A, B, C, \ldots$, and $P(ABC\ldots/KL\ldots)$ for the conditional probability of the occurrence of events $A, B, C\ldots$ given that events $K, L, \ldots$ have occurred.

From rule (ii) it follows that wetting of a site obeys a Poisson distribution. The probability that site n is a d at time t is: $P(d_n) = \exp(-\alpha_n t)$. Let R be an event involving only sites to the right of n and L to the left of n. We may write for the joint probability of Ld_nR

$$P(Ld_nR) = P(d_n)P(LR/d_n) = \exp(-\alpha_n t)P(LR/d_n). \tag{1}$$

According to rules (i)–(iii) the dynamics of the semi-infinite chain $n+1, n+2, \ldots$ is determined by the rain on these sites, and the state of site n as a neighbour of $n+1$. Thus, given d_n the conditional probability of R (L) can be computed from the rain on the right (left) half. Since there are no statistical correlations for the rain

$$P(LR/d_n) = P(L/d_n)P(R/d_n). \tag{2}$$

From these two equations it follows that

$$P(R/Ld_n) \equiv \frac{P(Ld_nR)}{P(Ld_n)} = \frac{P(d_n)P(R/d_n)P(L/d_n)}{P(d_n)P(L/d_n)} = P(R/d_n). \tag{3}$$

Thus, a d_n shields the left from the right semi-infinite subchain. Borrowing Evans nomenclature, we may say that the chain has the d-Markov property.

Let us now consider the joint probability $P(d_{n-1}o_n)$. For its time evolution, notice that a $d_{n-1}o_n$ configuration that survived until time t can be destroyed in the next $\mathrm{d}t$ in two ways: either site $n-1$ gets wet, or, requiring in addition o_{n+1}, site n becomes occupied

$$\begin{aligned}\frac{\mathrm{d}P(d_{n-1}o_n)}{\mathrm{d}t} &= -P(d_{n-1}o_n)[\alpha_{n-1} + \alpha_n P(o_{n+1}/d_{n-1}o_n)] \\ &= -\alpha_{n-1}P(d_{n-1}o_n) - \alpha_n P(d_{n-1}o_n o_{n+1}).\end{aligned} \tag{4}$$

However, $d_{n-1}o_no_{n+1}$ occurs if and only if $d_{n-1}d_no_{n+1}$ occurs: site n is surrounded by two empties and can only be empty if it was never wet. Using this and the d-Markov property

$$P(d_{n-1}o_no_{n+1}) = P(d_{n-1})P(d_n/d_{n-1})P(o_{n+1}/d_{n-1}d_n) = \exp(-\alpha_{n-1}t)P(d_no_{n+1}) \tag{5}$$

so (4) takes the form

$$\frac{\mathrm{d}P(d_{n-1}o_n)}{\mathrm{d}t} = -\alpha_{n-1}P(d_{n-1}o_n) - \alpha_n \exp(-\alpha_{n-1}t)P(d_n o_{n+1}) \tag{6}$$

providing a recursion relation for $P(d_{n-1}o_n)$ from one site to the next. An even simpler relation is obtained for the conditional probabilities

$$Q_n^- \equiv P(o_n/d_{n-1}) = \frac{P(o_n d_{n-1})}{P(d_{n-1})} = \exp(\alpha_{n-1}t)P(o_n d_{n-1}). \tag{7}$$

Substituting (7) in (6) we obtain for the Q's the recursion relation

$$\frac{\mathrm{d}Q_n^-}{\mathrm{d}t} = -\alpha_n \exp(-\alpha_n t)Q_{n+1}^-. \tag{8}$$

Each Q^- depends only on the α's of the right subchain starting at n, site n included. A similar treatment can be given with left and right interchanged to obtain Q^+.

Now, we have to show how the coverage θ_n=$P(x_n)$ of each site can be calculated. We have $P(x_n) + P(o_n) = 1$, so $\mathrm{d}P(x_n)/\mathrm{d}t = -\mathrm{d}P(o_n)/\mathrm{d}t$. We obtain

$$\frac{\mathrm{d}P(o_n)}{\mathrm{d}t} = -\alpha_n P(o_{n-1}o_n o_{n+1}) \tag{9}$$

where $o_{n-1}o_n o_{n+1}$ occurs if $o_{n-1}d_n o_{n+1}$ occurs, and using the *d-Markov* property

$$\frac{\mathrm{d}\theta_n}{\mathrm{d}t} = \alpha_n P(d_n)P(o_{n+1}/d_n)P(o_{n-1}/d_n) = \alpha_n \exp(-\alpha_n t)Q_{n+1}^- Q_{n-1}^+ \tag{10}$$

which allows us to compute the average occupation of each site once the Q's are known.

Equations (8) and (10) provide the solution to a large class of CSA problems.

3. Particular cases

3.1. Homogeneous chain

Let us now see how the equations apply to the homogeneous chain. This is the problem that started the whole field, solved as far back as 1939 by Flory [11] using a clever combinatorial method. It assumes the same α for all sites. By symmetry the Q's must be independent of n and of left–right direction, so equation (8) takes the form

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\alpha \exp(-\alpha t)Q = \frac{\mathrm{d}[\exp(-\alpha t)]}{\mathrm{d}t}Q \tag{11}$$

which, with the initial condition $Q(0) = 1$ is immediately integrated to give

$$Q = \exp[\exp(-\alpha t) - 1]. \tag{12}$$

Substitution into (10) gives

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \alpha \exp(-\alpha t)Q^2 = \alpha \exp(-\alpha t)\exp\{2[\exp(-\alpha t) - 1]\}. \tag{13}$$

The change of variable $u = \exp(-\alpha t)$ allows us to perform the remaining integration explicitly

$$\theta(t) = \tfrac{1}{2}[1 - \exp\{2[\exp(-\alpha t) - 1]\}]. \tag{14}$$

The jamming coverage is $\theta_j = \theta(\infty) = \frac{1}{2}(1 - \mathrm{e}^{-2}) = 0.432\,332$.

3.2. Random chain, independent sites

As the next step towards more heterogeneous systems, we assume the α_n to be independent random variables. By averaging equation (8) over the α's of all sites

$$\frac{\mathrm{d}\langle Q_n^- \rangle}{\mathrm{d}t} = \langle -\alpha_n \exp(-\alpha_n t)\rangle \langle Q_{n+1}^- \rangle \tag{15}$$

where the factorization of averages on the right-hand side follows from the fact that Q_{n+1}^- depends on sites $n+1, n+2, \ldots$ while the other term depends on site n. Also, on average the right and left directions are equivalent, so we can drop the $-+$ superscripts, and furthermore all sites are equivalent which allows us to drop the subscripts n, $n+1$. The average Q satisfies

$$\frac{\mathrm{d}\langle Q \rangle}{\mathrm{d}t} = \langle -\alpha \exp(-\alpha t)\rangle \langle Q \rangle \tag{16}$$

which has an analytical solution. Defining $F(t) \equiv \langle \exp(-\alpha t)\rangle$, so that $\langle -\alpha \exp(-\alpha t)\rangle = -\mathrm{d}F/\mathrm{d}t$, the solution is $\langle Q \rangle = \exp[F(t) - F(0)]$. For the coverage a similar treatment of equation (10) gives

$$\frac{\mathrm{d}\langle \theta \rangle}{\mathrm{d}t} = -\frac{\mathrm{d}F}{\mathrm{d}t} \exp\{2[F(t) - F(0)]\} \tag{17}$$

from which $\theta(t) = \frac{1}{2}\{1 - \exp\{2[F(t) - F(0)]\}\}$. The coverage has the same functional form as for a homogeneous chain, simply with the substitution of every $\exp(-\alpha t)$ by its average. We get the same θ_j as for the homogeneous chain, in fact this result was obtained by Fonk and Hillhorst [15], but of course the dynamics will be different, strong sites filling first. We can perform a more detailed analysis computing separately the coverage of sites with different α's. Suppose for instance a binary chain, where α_n can be either α_A or α_B (with probabilities p_A and p_B). Instead of averaging over site n in (10), we can write explicit equations for the cases $\alpha_n = \alpha_A$ and $\alpha_n = \alpha_B$

$$\frac{\mathrm{d}\langle \theta_A \rangle}{\mathrm{d}t} = \alpha_A \exp(-\alpha_A t)\langle Q \rangle^2 \qquad \frac{\mathrm{d}\langle \theta_B \rangle}{\mathrm{d}t} = \alpha_B \exp(-\alpha_B t)\langle Q \rangle^2 \tag{18}$$

and obtain the time evolution of the coverage of A and B sites separately. It is easily verified that the average θ of equation (18) is simply $\langle \theta \rangle = p_A\theta_A + p_B\theta_B$.

In figure 1 we present results for a binary mixture of 'strong' A sites ($\alpha_A = 1$) and 'weak' B sites ($\alpha_B = a$) for concentrations $p_A = 1, \frac{2}{3}, \frac{1}{2}$ and $\frac{1}{3}$. The plot is the 'sticking coefficient' graph. The inset of figure 1, presenting the same data with a log scale on the vertical axis, conveys more information. The $p_A = 0.5$ curve suddenly changes its slope at $\theta \cong 0.32$, suggesting a change in regime at this coverage. In fact, there is first a fast filling of A sites, followed by a much slower filling of B sites. Integration of the θ_A equation (18) confirms that θ_A starts growing rapidly and saturates at about 0.64 for t around 5. Since half of the sites are A's, this corresponds to a θ of 0.32. Then, on a much slower timescale, B sites start filling up as described by the second portion of the curve.

3.3. Random chain, Markov correlation between sites

We now assume that α's at different sites are statistically correlated and were deposited randomly according to a Markov process. Suppose a binary chain with A and B sites. We describe it by two parameters: c_A, the concentration of A sites (or $c_B = 1 - c_A$), and a correlation factor ρ. Given two consecutive sites, the probabilities of occupation are

$$p_{AA} = c_A(c_A + \rho c_B) \qquad p_{AB} = p_{BA} = c_A c_B(1 - \rho) \qquad p_{BB} = c_B(c_B + \rho c_A). \tag{19}$$

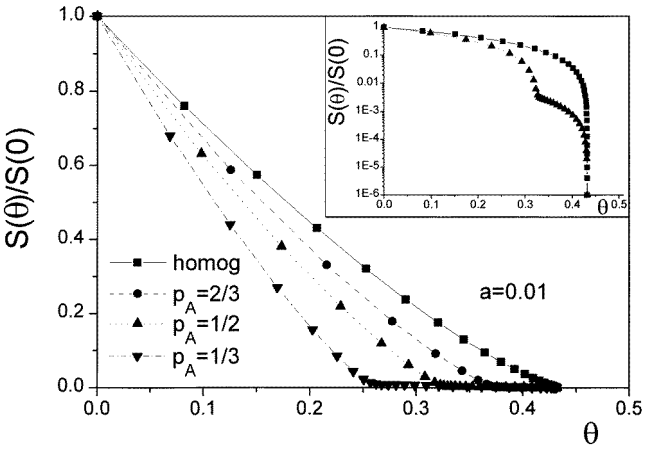

Figure 1. The sticking coefficient is defined as $S(\theta) = \mathrm{d}\theta/\mathrm{d}t$. Figure 1 shows the normalized sticking coefficient $S(\theta)/S(0)$ as a function of coverage for four different concentrations of strong sites and a strength ratio $a = 0.01$. Notice that all curves give the same final jamming coverage. The inset shows a subset of the data but now with a log scale for the sticking coefficient. The kink in the $p_A = 0.5$ curve for $\theta \cong 0.32$ indicates a switch from one regime (fast filling of strong sites) to another (slow filling of weak sites).

The conditional probabilities for a site when a neighbour is known are accordingly

$$\begin{aligned} p_{A/A} &= c_A + \rho c_B \qquad & p_{A/B} &= c_A(1-\rho) \\ p_{B/A} &= c_B(1-\rho) \qquad & p_{B/B} &= c_B + \rho c_A. \end{aligned} \tag{20}$$

If $\rho = 0$ these equations describe independent sites. For $\rho > 0$ the probability of AA and BB pairs is enhanced while that of AB and BA is diminished. Thus, $\rho > 0$ describes a tendency to form A and B islands. $\rho < 0$, in contrast, favours the mixture of A's and B's. We see that ρ measures the tendency towards segregation of the two types of sites.

For configurations involving more than two sites we make the usual Markov assumption that they are completely determined by NN correlations. Let us apply our equations to this situation. Taking a conditional average of (8) when site n is an A

$$\frac{\mathrm{d}\langle Q_n^- \rangle_{n=A}}{\mathrm{d}t} = -\alpha_A \exp(-\alpha_A t)\langle Q_{n+1}^- \rangle_{n=A} \tag{21}$$

where the average on the right-hand side can be expressed in terms of pair probabilities

$$\langle Q_{n+1}^- \rangle_{n=A} = p_{A/A}\langle Q_{n+1}^- \rangle_{n+1=A} + p_{B/A}\langle Q_{n+1}^- \rangle_{n+1=B}. \tag{22}$$

Using the short-hand notation $Q_A = \langle Q_n^- \rangle_{n=A}$, and the average equivalence of all sites

$$\begin{aligned} \frac{\mathrm{d}Q_A}{\mathrm{d}t} &= -\alpha_A \exp(-\alpha_A t)[p_{A/A}Q_A + p_{B/A}Q_B] \\ \frac{\mathrm{d}Q_B}{\mathrm{d}t} &= -\alpha_B \exp(-\alpha_B t)[p_{A/B}Q_A + p_{B/B}Q_B]. \end{aligned} \tag{23}$$

This set of equations must be solved numerically. But in CSA problems end effects decay very quickly, faster than exponential [11], and this suggests the use of an iterative method.

• Start with $Q_A = Q_B = 1$. This is equivalent to starting on the right end of a finite chain, say site N on a chain of N sites.

• Use the above Q on the right-hand side and integrate (23) to obtain new functions Q_A, Q_B. This iterative step is equivalent to moving one site inwards on a finite chain, from N to $N-1$.

• Repeat step (ii): re-insert Q_A, Q_B on the right-hand side of (23) and compute new Q's for sites $N-2, N-3, \ldots$. Stop when convergence to the desired accuracy has been reached.

The iterations involve just one type of funcions: $c\exp(-bt)$. Any linear combinations of exponentials on the right-hand side of (23) gives again exponentials as output. The iterative procedure must only keep track of an array of coefficients c and their respective exponents b.

Once the Q's are found, we can take a conditional average of (10) when site n is an A (and a similar equation for B), to obtain

$$\frac{\mathrm{d}\theta_A}{\mathrm{d}t} = \alpha_A \exp(-\alpha_A t)[p_{A/A}Q_A + p_{B/A}Q_B]^2. \tag{24}$$

As an example, we have solved the problem for a 50–50% mixture of strong A and weak B ($a = 0.1$) sites, first with a tendency of A and B to mix ($\rho = -0.9$) and then with a tendency to form islands ($\rho = 0.9$). The conditional probability of finding a neighbour of the same species is by (21) 0.05 in the first case and 0.95 in the second case.

We found that 20 iterations for the solution of (23) gave convergence up to the eighth decimal place in the Q's for all t values. Figures 2(a) and (b) show as 'total' the coverage $\langle\theta\rangle = p_A\theta_A + p_B\theta_B$ for the mixing and segregating correlations respectively.

4. Periodically repeating patches

Now we reach our final aim, CSA on a chain formed by periodic repetition of a patch pattern. Let us mention that for patch size 2, that is, an $ABABAB\ldots$ chain, there is an exact solution due to Oliveira and Tome [5]. By a true *tour de force* they map the problem into a modified Bessel equation whose order is related to the α's. It is hard to see how their procedure could be generalized to larger patch sizes.

For ease of notation we will explain our approach for a specific five-site pattern $AABCB$ repeated again and again. It will, however, be clear that the procedure is completely general, applying to any patch size and pattern. With five inequivalent sites there will be five different Q^- functions, which we label Q_1^- through Q_5^-. They satisfy (8), which here gives

$$\begin{aligned}
\frac{\mathrm{d}Q_1^-}{\mathrm{d}t} &= -\alpha_A \exp(-\alpha_A t)Q_2^- \qquad & \frac{\mathrm{d}Q_2^-}{\mathrm{d}t} &= -\alpha_A \exp(-\alpha_A t)Q_3^- \\
\frac{\mathrm{d}Q_3^-}{\mathrm{d}t} &= -\alpha_B \exp(-\alpha_B t)Q_4^- \qquad & \frac{\mathrm{d}Q_4^-}{\mathrm{d}t} &= -\alpha_C \exp(-\alpha_C t)Q_5^- \\
\frac{\mathrm{d}Q_5^-}{\mathrm{d}t} &= -\alpha_B \exp(-\alpha_B t)Q_1^-.
\end{aligned} \tag{25}$$

This can be solved numerically by the same iterative procedure as in section 3.3: start with $Q_1^- = 1$ and use it on the right-hand side of the last equation to compute Q_5^-, insert this in the right-hand side of the previous equation and compute Q_4^-, etc. After using all five equations we have again a (now improved) Q_1^- with which the procedure is repeated. Continue until convergence to the desired accuracy is reached.

A similar set of equations must in principle be solved for the Q_n^+. However, if the chain has centres of left–right symmetry (in our case site C, or between the two A's) no new

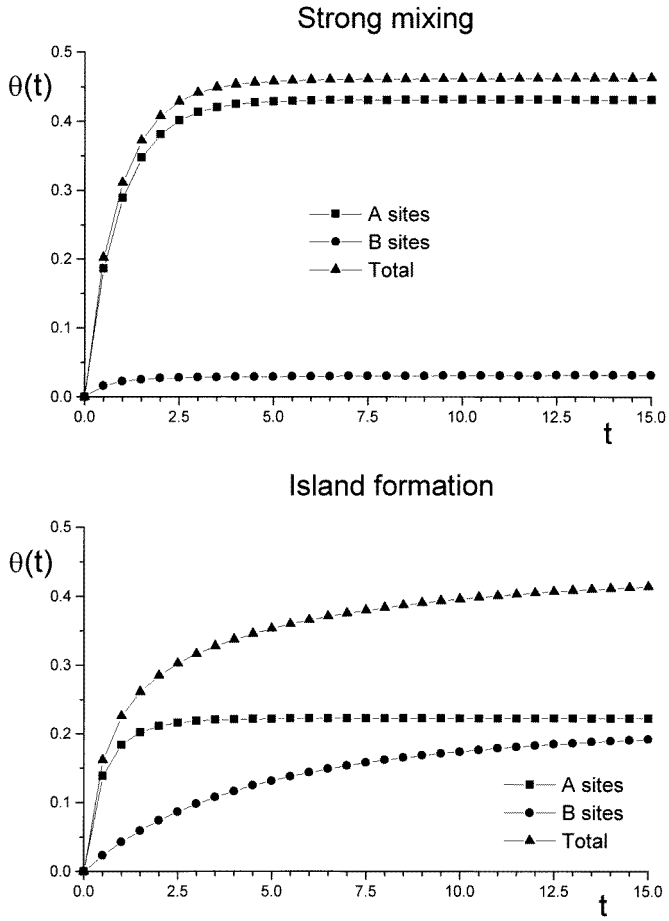

Figure 2. The coverage $\theta(t)$ versus the dimensionless time t of a random chain with a 50–50% mixture of strong A and weak B sites. The strength ratio is $a = 0.1$ and we have Markov correlation between sites. In (a) it is shown the mixing ($\rho = -0.9$) case and in (b) the segregating ($\rho = 0.9$) one.

calculations are necessary. From symmetry considerations $Q_1^+ = Q_2^-$, etc. Having found the Q's, equation (10) gives the occupation of the various types of sites

$$\frac{\mathrm{d}\theta_1}{\mathrm{d}t} = \alpha_A \exp(-\alpha_A t) Q_2^- Q_5^+ \tag{26}$$

for the left member of an AA pair, and similarly for the other types of sites. The total coverage is obviously the average of these expressions over a patch. Having explained the method, let us now turn our attention towards specific examples.

Zgrablich and Ciacera [12] have explored, by Monte Carlo simulations, the behaviour of what they call psn patches in one dimension. These consist of n 'strong' sites followed by n 'weak' sites (a= parameter to be varied) followed by another n strong sites, etc. Figures 3(a) and (b) compare the results of these previous simulations with our new theory.

As a last and somewhat fancier example, we considered $ABCDCB$ patches with a triangular profile for the interaction strengths: $\alpha_A = 1, \alpha_B = 0.75, \alpha_C = 0.5, \alpha_D = 0.25$. Figure 4 shows the time evolutions of θ_n for each type of site. Results are generally what

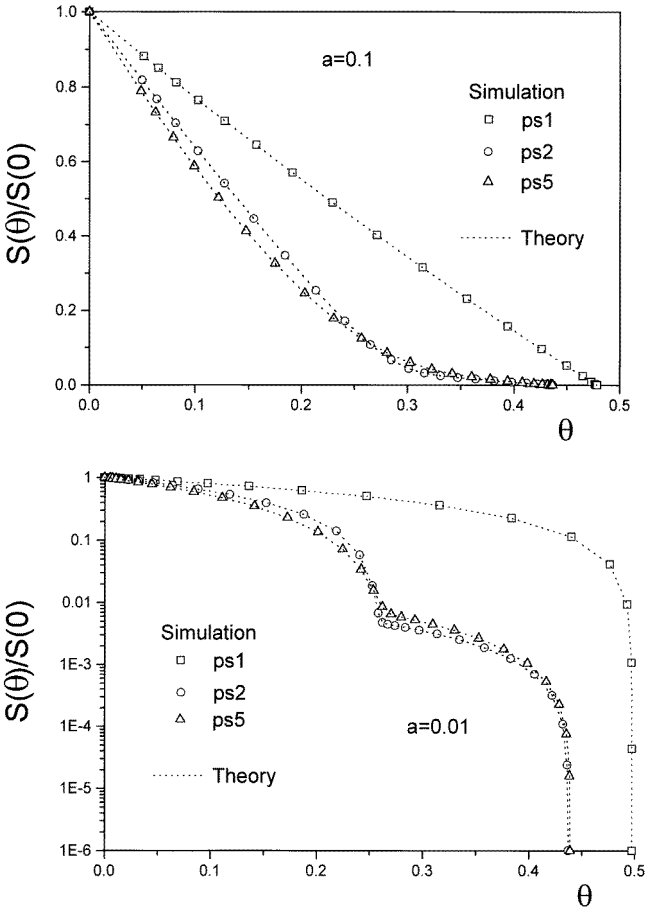

Figure 3. Comparison between results of previous Monte Carlo simulations and our theory about the sticking coefficient $S(\theta)$ for chains with periodically repeating patches. (*a*) The case of a strength ratio $a = 0.1$. At a lower strength ratio, $a = 0.01$ in (*b*) we can see a clear regime change.

one would expect. At small t, sites start filling at rates proportional to their interaction strengths. A sites are the first to fill, which decreases the probability of their B neighbours. This in turn gives the C's a good chance to fill.

5. Conclusions

In conclusion, we have shown that the Q's of equation (8) are the natural variables for the study of inhomogeneous chains, and we have given their physical interpretation as conditional probabilities. Equations (8) and (10) provided a unified treatment of homogeneous, random and inhomogeneous chains. A simple and fast iterative numerical method was proposed, and successfully applied to a variety of cases. In particular, we have seen that for a random chain with Markov correlation between sites, the highest possible coverage compatible with NN exclusion is 50% when every second site is occupied. This limit can be approached with a low enough strength ratio $a = \alpha_B/\alpha_A$ and sufficiently long

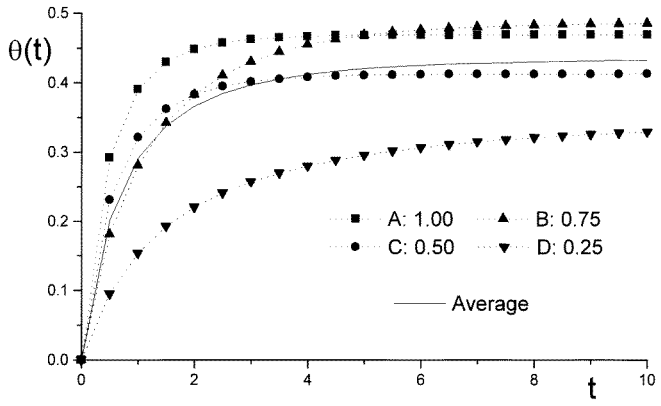

Figure 4. The coverage $\theta(t)$ versus the dimensionless time t for the different type of sites of a chain with triangular profile patches. The interaction strenghts are: $\alpha_A = 1, \alpha_B = 0.75, \alpha_C = 0.5$ and $\alpha_D = 0.25$.

$AB\ldots$ subchains, in which the A's will end up completely filled and the B's completely empty. Figure 2(a) reflects this tendency: coverage is higher than in the uncorrelated case. With segregation correlations (figure 2(b)), in contrast, the total coverage is more evenly split among A and B sites. The first saturate faster but the B's catch up on a longer timescale. There is no enhancement in total coverage as compared with the uncorrelated case. From the study of periodically repeating patches we expect that for very large n, psn should behave like two independent homogeneous chains of strong and weak sites filling at different rates with an evolution not too different from that of $ps2$. Figure 3 shows the sticking coefficient for different psn, in agreement with this expectation.

The extension of the analysis to heterogeneous lattices of dimensions higher than 1 is very difficult. Even in the case of homogeneous lattices only approximate solutions can be obtained via appropriate truncation rules for the hierarchical rate equations due to the variety of empty configurations to be considered [1]. For heterogeneous lattices, only the cases of random and Markov distributions of inactive sites has been given an approximate analytic treatment [13]. Monte Carlo simulation seems to be the most appropriate technique for the description of the kinetics and correlations for general heterogeneous substrates [14]. Our study of the one-dimensional heterogeneous chains may be illuminating in the interpretation of simulation results in higher dimensions, as we intend to discuss in a forthcoming publication.

Acknowledgments

This work was partially supported by CONICET. The European Economic Community, project ITDC-240, is greatly acknowledged for the provision of valuable equipment.

References

[1] Evans J W 1993 *Rev. Mod. Phys.* **65** 1281
[2] Jae Woo Lee 1996 *J. Phys. A: Math. Gen.* **29** 33
[3] Ben-Naim E and Krapivsky P L 1994 *J. Phys. A: Math. Gen.* **27** 3575
[4] Rodgers G J and Singh P 1995 *J. Phys. A: Math. Gen.* **28** 767
[5] Oliveira M J and Tome T 1994 *Phys. Rev.* E **50** 4523

[6] Somorjai G A 1981 *Chemistry in Two Dimensions* (New York: Cornell University Press)
[7] Hudson J B 1992 *Surface Science: An Introduction* (Boston, MA: Butterworths-Heinemann)
[8] Gonzáles J and Hemmer P C 1976 *Polym. Lett. Ed.* **14** 645
Gonzáles J and Hemmer P C 1977 *J. Chem. Phys.* **67** 2496
Gonzáles J and Hemmer P C 1977 *J. Chem. Phys.* **67** 2509
[9] Rudzinski W and Everett D H 1992 *Adsorption of Gases on Heterogeneous Surfaces* (New York: Academic)
[10] Rudzinski W, Steele W A and Zgrablich G (ed) 1997 *Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces* (New York: Elsevier)
[11] Flory P J 1939 *J. Am. Chem. Soc.* **61** 1518
[12] Zgrablich G and Ciacera M 1996 *Surfaces, Vacuum and Their Applications* ed I Hernández–Calderón and R Asomoza (New York: AIP) p 593
[13] Evans J W and Nord R S 1985 *J. Stat. Phys.* **38** 681
[14] Kozak E, Lajtar L, Patrykiejew A and Sokolowski S 1993 *Physica* **198A** 345
[15] Fonk Y and Hillhorst H J 1987 *J. Stat. Phys.* **49** 1235