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Deposition on disordered substrates with precursor layer diffusion

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Abstract. Recently we introduced a one-dimensional accelerated random sequential adsorption process as a model for chemisorption with precursor layer diffusion. In this paper we consider this deposition process on disordered or impure substrates. The problem is solved exactly on both the lattice and continuum and for various impurity distributions. The results are compared with those from the standard random sequential adsorption model.

1. Introduction

The adsorption of molecules from a gas phase onto a solid surface is one of the most common phenomena in the physical sciences. It has been extensively studied theoretically by a variety of techniques ranging from molecular dynamics simulations to analytical results for simplified models. All the studies endeavour to identify the underlying kinetic processes that control the phenomenon, and their physical origin.

The simplest model one can consider is that of *random sequential adsorption* (RSA) [1–4], which accounts for the hard core repulsion that prevents molecules from overlapping in the substrate. At each time step one randomly picks a position to deposit a molecule, if enough space is empty the molecule is deposited irreversibly, otherwise it returns to the gas phase. This process has been exactly solved in one dimension [1–4]. In higher dimensions it has been studied numerically (see for instance [5–8]), and analytically by using approximation techniques that truncate the rate equations [9], or by studying the process on a Bethe lattice [10]. Some additional insight into model behaviour in two dimensions can be gained by studying quasi-one-dimensional models [11, 12]. In all dimensions the system evolves into a saturated jammed state in which it is no longer possible to deposit any further molecules. The infinite time limit in which this occurs is sometimes called the ‘jamming limit’. For a comprehensive review of the kinetics of RSA see [13].

Recently, a variant of RSA has been introduced called *accelerated random sequential adsorption* (ARSA) [14, 15]. This process, motivated by the seminal work of Kisliuk [16], and by various experimental [17, 18] and numerical [19] studies, is designed to model the

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chemisorption of gas molecules onto a metal surface when there is diffusion in a precursor layer (physisorbed state). Other applications of this model in physics and biology were discussed in [14, 15]. ARSA is different from RSA in that when a molecule cannot be deposited because its target position is occupied, it diffuses on top of the previously deposited molecules until it finds an empty space on the substrate large enough to accept it.

The ARSA process models systems in which the timescale of diffusion is small compared with the timescale of deposition attempts (i.e. adsorption-limited systems). This includes systems in which the flux of gas particles onto the surface is low, except when the surface is almost full. There is a lengthier discussion of this point in [14].

The ARSA process has been studied numerically in [14] and its gap size distribution obtained exactly in one dimension in [15]. In this model the rate of successful surface depositions is independent of time, so the surface coverage $\theta(t)$ grows linearly with time t . Hence, it takes a finite amount of time (proportional to the system size) for the substrate to saturate. As was suggested in [20], we call the process ARSA to highlight the contrast with RSA, where the probability of a molecule being deposited goes to zero in the long time limit, therefore taking an infinite amount of time to reach the saturated state.

Both RSA and ARSA can be studied on a lattice [1–3] or on a continuum [4]. In the one-dimensional continuum RSA [4] and ARSA [15] problems particles of size 1 are randomly deposited on a line and an exact solution can be found for the evolution with time of the distribution of empty spaces between them. In both problems it is possible to move between the one-dimensional lattice, on which k -mers are deposited, and the corresponding continuum system by taking the limit $k \rightarrow \infty$ [21].

Motivated by the fact that real substrates are often disordered or impure, in this paper we enlarge the range of exactly solved ARSA systems to include an initial distribution of impurities.

The problem of RSA with random initial impurities was considered earlier [22–24]. In [22, 23] the impurities were modelled by monomers that were randomly distributed and the molecules were represented by k -mers. The coverage of the jammed state and the kinetics of the approach to saturation were determined as a function of the initial concentration of impurities and k [22]. In [24] this study was extended to impurities of arbitrary size k_0 placed on the substrate by RSA.

This paper is organized as follows. In section 2 we consider the ARSA of k -mers on disordered lattices with randomly distributed impurities. In section 3 we study the RSA and ARSA of k -mers on general disordered substrates and then in section 4 we consider the continuum problem. Finally, in section 5 we summarize our main conclusions.

2. ARSA on disordered substrates

We consider the ARSA of k -mers onto a lattice with an initial concentration ρ of monomer impurities. For simplicity, we assume that the physisorbed state of a k -mer is the same whether it is on top of impurities or molecules. In [15] the density of gaps of length r between occupied regions, $c_r(t)$, was shown to obey the differential equation

$$\frac{dc_r(t)}{dt} = -[r - (k - 1)]c_r(t) + 2 \sum_{s=0}^{\infty} c_{r+s+k}(t) + q(t)(c_{r+k}(t) - c_r(t)) \quad (1)$$

for $r \geq k$ and

$$\frac{dc_r(t)}{dt} = 2 \sum_{s=0}^{\infty} c_{r+s+k}(t) + q(t)c_{r+k}(t) \quad (2)$$

for $r < k$, where time t stands for the number of deposition attempts divided by the system size, and the rate of deposition attempts has been set to 1. By ‘density’ we mean the number of occurrences divided by the system size. The quantity

$$q(t) = \frac{1 - \sum_{r=k}^{\infty} [r - (k - 1)]c_r(t)}{\sum_{r=k}^{\infty} c_r(t)} \tag{3}$$

and is equal to the average length of the chains of site (not necessarily all occupied) in which it is not possible to deposit a k -mer. This is the average number of positions where a particle can physisorb before diffusing towards one of the edges of the chain where chemisorption takes place. The denominator and numerator represent, respectively, the number density of chains and the number density of positions in which chemisorption is not allowed.

The first term on the right-hand side in (1) represents the destruction of a gap of size r by direct deposition. The second term corresponds to the creation of a gap of size r by direct deposition in a larger gap. The last term represents the creation and destruction of gaps of size r by the diffusion of molecules on top of previously adsorbed molecules. Obviously, for $r < k$ some of these terms are not present. The equations describing the RSA process are obtained by dropping the terms in $q(t)$ on the right-hand side of (1) and (2).

These equations are derived under the *working hypothesis* that the size of an island is uncorrelated with the size r of the neighbouring gap if $r \geq k$. This hypothesis is borne out by numerical simulations of the system. Physically, it originates from the fact that the probability of deposition at the edge of an island is not affected by the size r of the neighbouring gap if $r \geq k$, together with the fact that deposition is irreversible, i.e. there is no gap creation.

The coverage is given in terms of $c_r(t)$ by

$$\theta(t) = 1 - \sum_{r=1}^{\infty} r c_r(t). \tag{4}$$

The differential equations for $c_r(t)$ can be solved [15,25] by making the assumption that gaps of size $r \geq k$ obey a Poissonian distribution,

$$c_r(t) = A(t) \exp\{-(r - k)B(t)\}. \tag{5}$$

This is based on the assumption of independence between the gaps and the evolving structure. If the initial monomer impurities are randomly distributed and have density ρ , ($1 \geq \rho > 0$), then we have as the initial condition

$$c_r(0) = (1 - \rho)^r \rho^2 \tag{6}$$

consistent with $\theta(0) = \rho$. Substituting (5) into (1) gives

$$\frac{dA(t)}{dt} = A(t) \left[q(t)(e^{-kB(t)} - 1) + \frac{2e^{-kB(t)}}{1 - e^{-B(t)}} - 1 \right] \tag{7}$$

and

$$B(t) = t - \ln(1 - \rho). \tag{8}$$

Substituting (5) into (3) gives

$$q(t) = \frac{1 - e^{-B(t)}}{A(t)} - \frac{1}{1 - e^{-B(t)}}. \tag{9}$$

Eliminating $q(t)$ between (7) and (9), substituting for $B(t)$ and solving the resultant differential equation for $A(t)$ gives

$$c_r(t) = [1 - (1 - \rho)e^{-t}]^2 (G(t) - 1) [(1 - \rho)e^{-t}]^{r-k} \tag{10}$$

for $r \geq k$, with

$$G(t) = \frac{(1 - \rho)^k + 1 - \int_0^t F(u) du}{F(t)} \quad (11)$$

and

$$F(t) = \exp \left\{ -t + \int_0^t \frac{1 - (1 - \rho)^k e^{-ku}}{1 - (1 - \rho)e^{-u}} du \right\} = \exp \left\{ \sum_{r=1}^{k-1} (1 - \rho)^r \frac{1 - e^{-rt}}{r} \right\}. \quad (12)$$

Then, substituting the solution (10) into (2) and solving the resultant equation we obtain

$$c_r(t) = (1 - \rho)^k \int_0^t [1 - (1 - \rho)e^{-u}] G(u) e^{-ru} du \quad (13)$$

for $r < k$. As the rate of successful depositions is 1, the coverage at time $t \leq t_c$, where t_c is the time when the lattice reaches the jammed state, is given by

$$\theta(t) = \rho + kt. \quad (14)$$

The saturation time t_c is defined by $c_r(t_c) = 0$ for all $r \geq k$, or $G(t_c) = 1$. Hence from (11), t_c obeys the equation

$$F(t_c) + \int_0^{t_c} F(u) du = (1 - \rho)^k + 1 \quad (15)$$

and the saturation coverage is

$$\theta(t_c) = \rho + kt_c. \quad (16)$$

These results are consistent with the standard ARSA model [15] when $\rho = 0$. As $\rho \rightarrow 0$

$$\theta_\rho(t_c) \approx \theta_0(t_c) - \left[\frac{k^2}{F(t_c) + F'(t_c)} - 1 \right]_{\rho=0} \rho + O(\rho^2)$$

where the square bracket on the right-hand side is evaluated at $\rho = 0$. Conversely, in the high impurity density limit, $\rho \rightarrow 1$, then $\theta(t_c) \approx 1 - (1 - \rho) + k(1 - \rho)^k + O((1 - \rho)^{k+1})$ for $k > 1$. Both of these asymptotics have a linear leading-order dependence on ρ .

Equation (15) can be solved numerically to give the saturation coverage as a function of k and ρ . This can be compared with the value of the saturation coverage obtained for the RSA process [20].

Figure 1 shows the graphs of the saturation coverage against ρ for dimer and trimer deposition using either RSA or ARSA. As expected, the saturation coverage is greater for ARSA than for RSA for all values of $\rho < 1$ because of the greater efficiency with which ARSA fills the lattice. This close-packing effect decreases as the fraction of the substrate available for deposition, $1 - \rho$, gets smaller. In both RSA and ARSA $\theta(t_c) \sim \rho$ as $\rho \rightarrow 1$. The asymptotic approach in time to the saturated state is the same as that for the systems without impurities; exponential for RSA and linear for ARSA. From figure 1 one can see that the position ρ_{\min} of the minimum coverage is shifted. In RSA $\rho_{\min} = 0.5$ whereas in ARSA, $\rho_{\min} \approx 0.57$, the solution for ρ of

$$F(t_c) + \frac{dF(t_c)}{dt_c} = 4(1 - \rho) \quad (17)$$

obtained from (15) and (16) when $k = 2$.

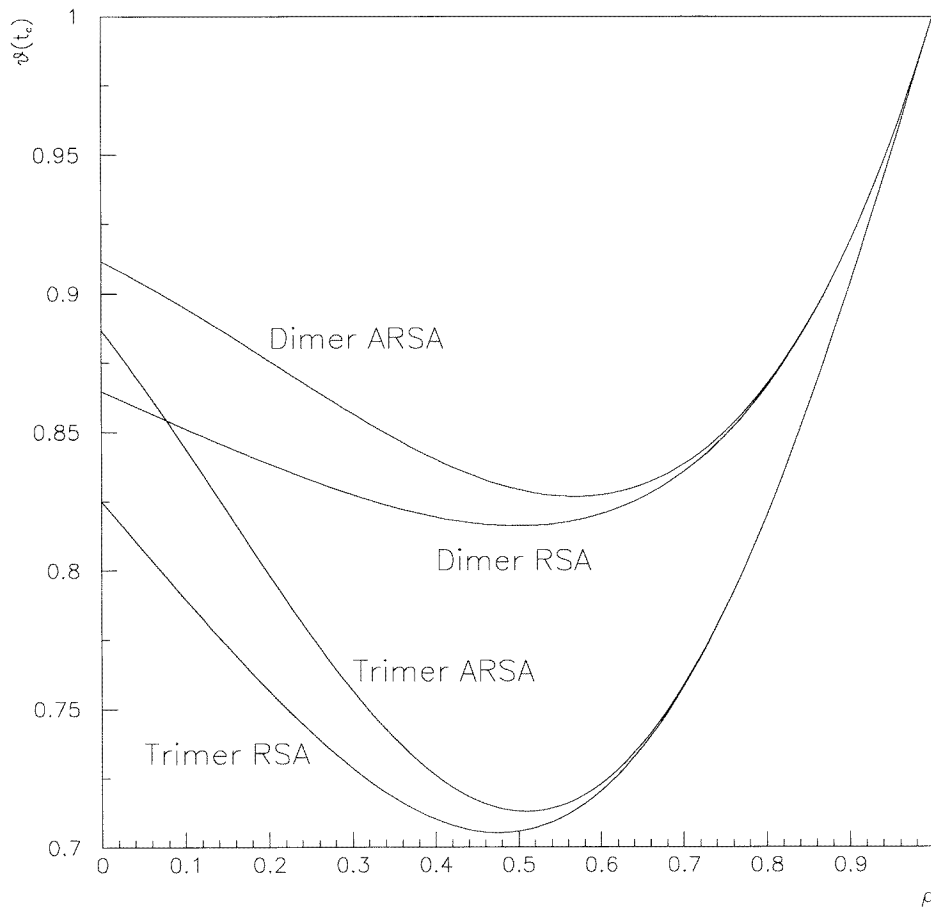


Figure 1. The saturation coverage against initial impurity concentration ρ for the RSA and ARSA dimer and trimer depositions.

3. ARSA and RSA with generalized impurities

In the previous section we considered the deposition of k -mers by ARSA onto lattices in which monomer impurities had been placed randomly. We can think of these impurities as having been placed by RSA up to a density ρ .

However, depending on their molecular properties, the impurities or heterogeneities might have been produced either by deposition processes such as RSA or ARSA, or by other processes on the substrate. In this section we extend the previous model to a more general situation in which impurities are k_0 -mers and have been produced by an unspecified process. In addition, we consider the deposition of k -mers on the impure substrate either by ARSA or RSA.

In order to be able to solve the model in a similar manner to that of section 2, we assume that the impurities occupy a fraction ρ of the substrate and have a gap distribution with Poissonian form. In other words, the gap distribution of the system at $t = 0$ is

$$c_r(0) = f(\rho) \exp\{-rg(\rho)\} \equiv f(\rho)X_0^r \quad (18)$$

for $r \geq k_0$ and by definition $X_0 = \exp(-g(\rho))$. In section 2 we had $k_0 = 1$, $g(\rho) = \rho$ and

$f(\rho) = (1 - X_0)^2(1 - \rho)/X_0$. The function $f(\rho)$ is related to $g(\rho)$ through the normalization constraint

$$\sum_{r=1}^{\infty} r c_r(0) = \frac{f(\rho)X_0^k}{(1 - X_0)^2} [X_0 + k_0(1 - X_0)] + \sum_{r=1}^{k_0-1} r c_r(0) = 1 - \rho. \quad (19)$$

In the limit when $\rho \rightarrow 0$, we require that $c_r(0) = 0$ for all r and that

$$\lim_{t \rightarrow 0} \sum_{r=1}^{\infty} r c_r(t) = 1 \quad (20)$$

which implies that $f(0) = 0$, $g(0) = 0$ (i.e. $X_0 = 1$) and

$$\lim_{\rho \rightarrow 0} \frac{f(\rho)}{(1 - X_0)^2} = 1. \quad (21)$$

For ARSA and RSA impurities, the gap number densities $c_s(0)$ for $s < k_0$ can be expressed in terms of the gap number densities $c_r(0)$ for $r \geq k_0$. However, the $c_s(0)$ do not have the Poissonian form (18). Consequently we restrict our considerations to $k_0 \leq k$ so that ansatz (5) holds for all $r \geq k$. For impurities produced by a generic process for which $f(\rho)$ is not known, when $k_0 > 1$ then $c_s(0)$ has to be specified.

Note that while the gap distribution is all we need to know about the impurities, it does not determine the distribution of impurity islands, whose only constraint is that its first moment must equal ρ . Therefore, the generality of this approach lies in the arbitrariness of $g(\rho)$ and of the distribution of impurity islands.

The derivation of the solution to the rate equations (1) (where $q = 0$ for RSA) is analogous to that of section 2 and gives the following results. Let us define

$$X = X_0 \exp\{-t\} = \exp\{-t - g(\rho)\} \quad (22)$$

and

$$F(t) = \exp\left\{\sum_{r=1}^{k-1} \frac{X_0^r - X^r}{r}\right\} \quad (23)$$

which extends (12) to general impurities.

For ARSA deposition of k -mers on the impure substrate, we obtain

$$c_r(t) = (1 - X)^2 [G_{\text{ARSA}}(t, \rho) - 1] X^{r-k} \quad (24)$$

when $r \geq k$, with

$$G_{\text{ARSA}}(t, \rho) = \frac{1}{F(t)} \left[\frac{f(\rho)X_0^k}{(1 - X_0)^2} + 1 - \int_0^t F(u) du \right]. \quad (25)$$

The saturation coverage is $\theta_c = \theta(t_c) = \rho + kt_c$, with t_c the solution of

$$F(t_c) + \int_0^{t_c} F(u) du = \frac{f(\rho)X_0^k}{(1 - X_0)^2} + 1. \quad (26)$$

For RSA deposition of k -mers we find

$$c_r(t) = (1 - X)^2 G_{\text{RSA}}(t, \rho) X^{r-k} \quad (27)$$

when $r \geq k$, with

$$G_{\text{RSA}}(t, \rho) = \frac{f(\rho)X_0^k}{(1 - X_0)^2} \frac{X}{F(t)^2} \quad (28)$$

and

$$\theta_c = \theta(\infty) = \rho + k \int_0^\infty G(u) du. \quad (29)$$

Regarding the impurity distribution we specify two cases. When it has been produced by ARSA,

$$g(\rho) = \frac{\rho}{k_0} \quad \text{and} \quad f(\rho) = \frac{(1 - X_0)^2 [G_{\text{ARSA}}(0, 0) - 1]}{X_0^{k_0}} \quad (30)$$

and when it has been produced by RSA,

$$g(\rho) = t_0(\rho, k_0) \quad \text{and} \quad f(\rho) = \frac{(1 - X_0)^2 G_{\text{RSA}}(0, 0)}{X_0^{k_0}} \quad (31)$$

where $t_0(\rho, k_0)$ is the time the RSA process would have taken, which is the solution of

$$\theta(t_0) = \int_0^{t_0} G_{\text{RSA}}(u) du = \rho.$$

Explicit expressions for $f(\rho)$ and t_0 in terms of ρ can be extracted from (30) for ARSA impurities and from (31) for RSA impurities with either monomers ($k_0 = 1$) or dimers ($k_0 = 2$). Results (27)–(29) and (31) for RSA deposition with RSA impurities reduce to previous results with $k_0 = 1$ [22] and with arbitrary $k_0 \leq k$ [24].

Next we illustrate the general solutions (24), (27), (30) and (31) in four particular cases in which dimers ($k = 2$) are deposited by RSA or ARSA onto a substrate where monomer impurities ($k_0 = 1$) have been placed by RSA or ARSA. We label these systems RR, RA, AR and AA (see table 1). System RR was considered in [22, 23] and system RA is that from the previous section with $k = 2$. Table 2 gives $f(\rho)$, $g(\rho)$ and X_0 for $k_0 = 1$. Solutions (24) and (27) depend on the impurity distribution through X and the factor $f(\rho)X_0^k/(1 - X_0)^2$. For $k_0 = 1$, we find either from table 2 or from (19) that this factor reads

$$\frac{f(\rho)X_0^k}{(1 - X_0)^2} = (1 - \rho)X_0^{k-1}$$

which equals $(1 - \rho) \exp[-(k - 1)\rho]$ for ARSA and $(1 - \rho)^k$ for RSA impurities. Figure 2 shows the saturation coverage θ_c as calculated from (24) and (27). A number of features can be discerned from the figure.

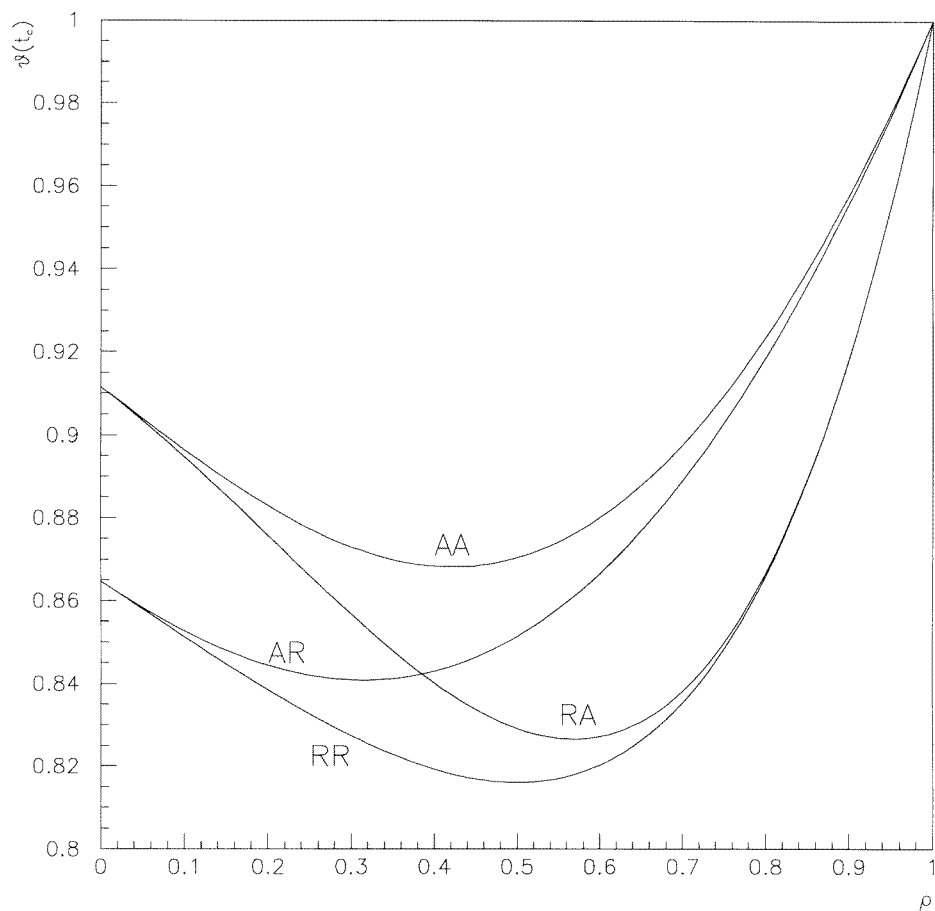
First, by comparing the saturation coverage of two systems, we see that: (a) for a given process of dimer deposition, θ_c is greater for ARSA impurities than for RSA impurities (AR versus RR, AA versus RA); (b) for a given a distribution of monomer impurities, θ_c is greater for ARSA deposition than for RSA deposition (AA versus AR, RA versus RR). This can be attributed to the more closely packed nature of ARSA distributions of both impurities and molecules, and the resulting reduction in the number of gaps of size $r < k$.

Table 1. Labelling of the four systems considered in section 3.

		Monomer impurities	
		RSA	ARSA
Dimer deposition	RSA	RR	AR
	ARSA	RA	AA

Table 2. $g(\rho)$, $f(\rho)$ and X_0 for monomer impurities deposited by ARSA and RSA.

	ARSA	RSA
$g(\rho)$	ρ	$-\log(1 - \rho)$
$f(\rho)$	$(1 - \exp(-\rho))^2(1 - \rho)$	ρ^2
X_0	$\exp\{-\rho\}$	$1 - \rho$

**Figure 2.** The saturation coverage against initial impurity concentration ρ for the four systems defined in table 1.

In addition, the area between curves AA–RA is greater than the area between curves AA–AR; similarly, it is greater between AR–RR than between RA–RR. This suggests that the distribution of monomer impurities can affect the clustering properties of deposited molecules more strongly than the mechanism of dimer deposition.

Second, as in section 2, there is an impurity concentration ρ_{\min} at which the saturation coverage has a minimum $\theta_{c,\min}$. The values of these quantities are summarized in table 3. The minimum can be understood as the point at which a balance occurs between two opposite effects of the impurities: blocking the deposition of molecules and occupying the substrate. The relative values of the minima agree with the above observations about

Table 3. Minimum saturation coverage and impurity concentration at which it occurs for the systems in table 1.

	$\theta_{c,\min}$	ρ_{\min}
RR	0.81606...	0.5
RA	0.82661...	0.5695...
AR	0.84085...	0.3149...
AA	0.86817...	0.4213...

θ_c . The location of the minima shows the following pattern: (a) for a given deposition process, ρ_{\min} is smaller for ARSA impurities than for RSA impurities, while (b) for a given impurity distribution, ρ_{\min} is greater for ARSA deposition than for RSA deposition. The interpretation of this behaviour is less simple. It seems to relate to the shape of the two curves: the minimum for which $\theta_{c,\min}$ is greater is shifted towards the side where the two curves are more similar. In fact, in (a) (ρ_{\min} smaller for greater $\theta_{c,\min}$) the two curves merge as $\rho \rightarrow 0$, while in (b) (ρ_{\min} greater for greater $\theta_{c,\min}$) they merge as $\rho \rightarrow 1$.

4. Continuum system

In [21] it was observed that one can study the continuum RSA system by taking the limit $k \rightarrow \infty$ of the k -mer deposition problem on a lattice after a suitable rescaling of the variables. This also applies in the case of impurity problems [22], where in this limit the impurities become points and the objects to be deposited become lines of unit length.

In [22] it was shown that for continuum RSA with impurities the saturation coverage is

$$\theta(\infty) = e^{-\lambda} \int_0^{\infty} ds \exp \left\{ -2 \int_0^s \frac{1 - e^{-v-\lambda}}{v + \lambda} dv \right\} \quad (32)$$

where λ is the number of impurities per unit length. Similarly, we can use the results of section 2 for k -mer ARSA on a lattice with monomer impurities, to obtain results for the continuum ARSA of unit length objects onto a line on which point impurities have been placed at random with number density λ . Alternatively, we could formulate and solve the rate equations for the continuum system as in [15].

By taking the limit $k \rightarrow \infty$ of (12), (14) and (15) while keeping $k\rho = \lambda$ and $kt = \tau$ fixed, we obtain the saturation coverage $\theta(\tau_c) = \tau_c$ (as in pure continuum ARSA [15]), which obeys the equation

$$\int_0^{\theta(\tau_c)} \frac{1 - e^{-v-\lambda}}{v + \lambda} dv = \log(1 + e^{-\lambda}). \quad (33)$$

As illustrated in figure 3, the saturation coverages in equations (32) and (33) decrease monotonically with λ . In particular, they decay to zero like $\lambda \exp(-\lambda)$ as $\lambda \rightarrow \infty$. This difference relative to lattice models, where θ_c has a minimum, is because impurities in lattices have finite size: although they block particle deposition they also contribute to the surface coverage. At $\lambda = 0$, θ_c takes the pure continuum RSA [4] and ARSA [15] values. As usual, the saturation coverage for ARSA is always greater than that for the RSA system.

5. Conclusions

The deposition of molecules onto substrates with precursor layer diffusion was considered in the case in which impurities, defects or other molecular species have previously been

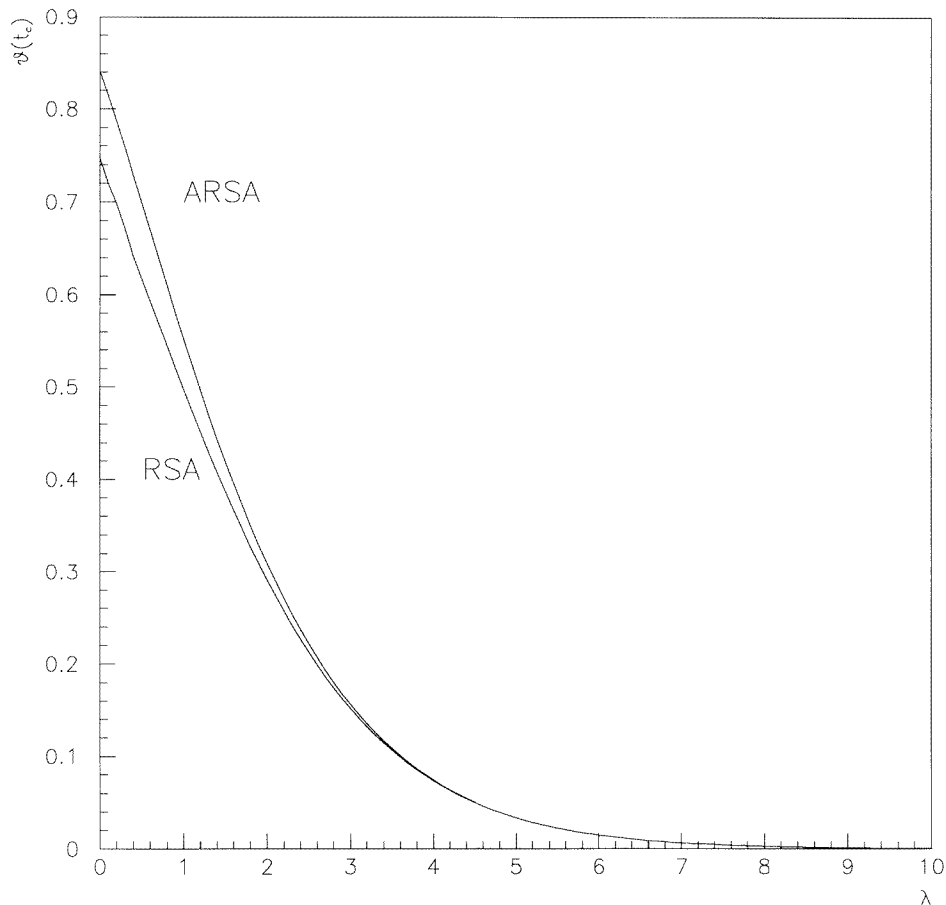


Figure 3. The saturation coverage in continuum ARSA and RSA against initial impurity density λ .

placed on the substrate.

We obtained exact results for the time evolution and saturation limit of ARSA (as well as RSA) deposition of k -mers onto a one-dimensional lattice with a generic distribution of impurities of size k_0 , including distributions produced by ARSA and RSA processes.

The results for RSA deposition with RSA impurities agree with earlier results. We restricted the study to the case in which the size of the impurities is not greater than the size of the molecules being deposited onto the surface ($k_0 \leq k$). We expect the blocking effect of the impurities to be greater in this case.

Our results show that the presence of impurity particles or other heterogeneities on the substrate can reduce the saturation coverage considerably, as compared with the pure system, by creating gaps smaller than k . Reductions as large as 10% (dimers) and 20% (trimers) were found in some cases (figure 2). For given k and k_0 , the saturation coverage has a minimum at non-trivial values of the impurity density, a non-monotonic behaviour already observed for RSA deposition on impure substrates. Some numerical values for the minima are given in table 3 for various systems.

Some features typical of ARSA deposition on pure substrates were also found in ARSA

on disordered substrates. Namely, a larger value of the saturation coverage as compared with RSA, and a linear approach (with time) to the saturated state as compared with an exponential one in RSA.

We also derived results for the continuum system in which particles of fixed size are deposited on a substrate with a given density number of point defects. In this case the saturation coverage decreases monotonically with the number of defects as a consequence of the defects having zero size. We expect, however, that most practical situations would be more adequately described by a lattice rather than by a continuum model.

Two interesting extensions to this work, would be: (1) to allow the molecule–impurity and molecule–molecule interactions to be different, and in particular to allow the precursor states on top of sites occupied by molecules and impurities to be different; (2) to study the problem numerically in two dimensions, and in particular to verify which behavioural features are shared with the one-dimensional system and which are not.

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