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## Random sequential adsorption of ‘hot’ dimers on one dimension

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**Abstract.** We study the kinetics of the single-layer random sequential adsorption of ‘hot’ dimers on one dimension by a Monte Carlo simulation. ‘Hot’ dimers are molecules which after adsorption dissociate and each of the remaining ‘hot’ monomers fly apart up to a maximum distance  $R$  from the original adsorption site. The surface coverage, by the adsorbed particles, grows with time and finally reaches a jamming limit when no more adsorption is possible. The jamming coverage ( $\theta_j$ ) depends on  $R$  according to  $\theta_j = 1 - \text{constant } R^{-x}$  ( $R \rightarrow \infty$ ,  $x \cong 0.9$ ). The sticking coefficient and the mean free path of the ‘hot’ species is also studied. Adsorption of dimers having a certain probability to undergo a flight after dissociation is also analysed.

### 1. Introduction

The irreversible monolayer particle deposition termed random sequential adsorption (RSA), or the car parking problem, has received considerable experimental and theoretical attention see, for example, [1–12] and references quoted therein). Also, very recently an extensive review article has been published [13]. This kind of process occurs in a great variety of physical, chemical, biological and ecological systems [1–13 and references therein]. Due to the blocking effect by already-deposited particles the space available for deposition becomes reduced and consequently the total space covered is less than that for close packing. So, a relevant quantity is the maximum fraction of the available space covered by the depositing particles in the  $t \rightarrow \infty$  limit, namely the jamming coverage  $\theta_j$ . RSA processes have been studied by means of various methods, for example, Monte Carlo simulations, series expansions, analytical techniques, etc. [1–13]. In particular, the RSA of dimers is known as the random dimer filling problem (RDFP) which has been extensively studied since the early work of Flory [1] (see also [4, 7, 13] and references therein). The jamming coverage for the RDFP in one dimension (1D) is known exactly [1, 13]:

$$\theta_j = 1 - e^{-2} \cong 0.864\ 66 \dots \quad (1)$$

On the other hand, very recently Ertl *et al.* [14] have nicely demonstrated, by means of scanning tunnelling microscopy (STM) observations, that oxygen molecules striking an Al(1 1 1) surface not only dissociate upon adsorption but also dissipate part

of their excess energy in degrees of freedom parallel to the surface. Therefore, after chemisorption of these 'hot' species, the resulting oxygen atoms (monomers) fly apart, on the average, up to a distance of at least 80 Å from the original impingement site, before being accommodated on their respective adsorption sites. After this ballistic flight oxygen atoms remain practically immobile at 300 K as judged by STM images [14]. Furthermore, it is estimated that each oxygen atom would exhibit an initial velocity of about  $6.5 \times 10^3 \text{ m s}^{-1}$ , travelling a distance of 40 Å within about 1 ps [14].

Considering this interesting new finding, this manuscript is devoted to the study of the RDPF of 'hot' dimers, which in principle may be different from the standard RDPF. The present study is based upon numerical Monte Carlo simulations in 1D rings.

## 2. Description of the model of 'hot' dimer adsorption

The adsorption process is simulated on 1D lattices of length  $L = 10^5$  assuming periodic boundary conditions, i.e. 1D rings. The adsorption algorithm is the following: (1) a site (say site 1) is selected at random, if site 1 is occupied the trial ends, i.e. dimer adsorption cannot take place. Otherwise, if site 1 is empty a nearest neighbour (nn) site (say site 2) is also selected at random. If site 2 is occupied the trial ends because again there is no place for dimer adsorption. Otherwise, if site 2 is also empty a dimer is adsorbed on the surface occupying two nn sites; (ii) after dimer deposition we decide at random, with probability  $p$ , if the already-adsorbed dimer may split into two flying monomers (i.e. a 'hot' dimer) or if the resulting monomers remain dissociatively adsorbed on the original sites (i.e. a standard dimer). Note that for  $p = 0$  we recover the standard RDPF while for  $p = 1$  we have a pure 'hot' dimer RDPF. After deposition of standard dimers the trial ends. Otherwise, for 'hot' dimers, both resulting 'hot' monomers are allowed to undergo a ballistic flight up to a maximum distance  $R$  from the original adsorption site. If during the flight one monomer hits another adparticle or ensemble which is already at rest, the flying monomer is frozen at the collision point.

The Monte Carlo time unit ( $t$ ) is defined such that each site of the sample would be visited once, on average, i.e.  $t = 1$  involves  $L$  trials. Averages are taken over  $10^3$  different samples. During the adsorption process the following quantities are measured: (i) the surface coverage  $\theta$  as a function of  $t$  and the jamming coverage  $\theta_j$  for  $t \rightarrow \infty$ ; (ii) the sticking coefficient  $S$ , defined as the ratio between the number of successful adsorption attempts and the total number of attempts; and (iii) the average mean free path (MFP) of the 'hot' monomers, i.e. the average distance travelled by a monomer from the adsorption site up to the site where it becomes motionlessly adsorbed.

## 3. Results and discussion

### 3.1. The kinetics of adsorption ( $p = 1$ )

Figure 1 shows plots of  $\theta$  versus the Monte Carlo time obtained for different values of  $R$  ( $1 \leq R \leq 1000$ ). For early times and low coverages ( $\theta < 0.4$ ) there is no appreciable difference in the adsorption kinetics when  $R$  is varied. Nevertheless, for  $\theta > 0.4$  a distinct behaviour is observed for different choices of the parameter  $R$ : for a fixed time, the greater is  $R$  the higher is  $\theta$ . Note that this effect is more marked for  $R \leq 50$ .

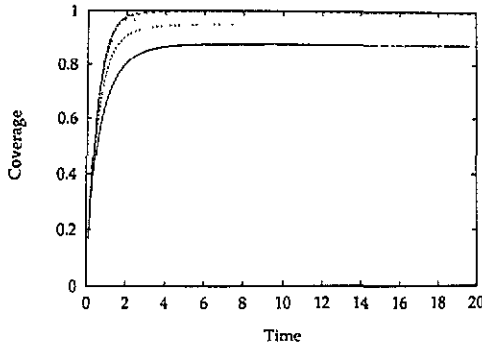


Figure 1. Plot of the coverage versus the Monte Carlo time for different choices of  $R$ , from bottom to top  $R=1, 10, 50, 100, 250$  and  $1000$ , respectively.

A qualitative understanding of this behaviour is straightforward: let us assume that between two adsorbed particles one has  $N$  empty sites. On the one hand it is easy to see that for  $N \leq 3$  the number of different configurations of adsorbed dimers is independent of  $R$ . But on the other hand, for  $N \geq 4$  the number of such configurations increases with  $R$  and consequently the greater  $R$  the higher  $\theta_j$ .

In spite of the fact that runs shown in figure 1 are performed up to  $t=20$ , one observes that  $\theta$  is almost saturated, i.e. close to the jamming value. From figure 1 it also follows that  $\theta_j \rightarrow 1$  for  $R \rightarrow \infty$ , so in order to further investigate this behaviour we have performed simulations up to the long time regime using a suitable routine which only visits the empty sites with one or more nn empty sites. Figure 2 shows a log-log plot of  $\{\theta_j(R = \infty) - \theta_j\}$  versus  $R$ , assuming  $\theta_j(R = \infty) = 1$ . This assumption is quite reasonable since in the  $R \rightarrow \infty$  limit monomers fly apart an infinite distance, completely covering the ring. The straight line obtained (figure 2) suggests that the following behaviour should hold:

$$\theta_j = 1 - \text{constant } R^{-x} \quad (R \rightarrow \infty) \tag{2}$$

and from the slope we obtain the exponent  $x \cong 0.9$ . This result is in contrast to simulations performed in 2D where  $\theta_j(R = \infty) \cong 0.943$  [15].

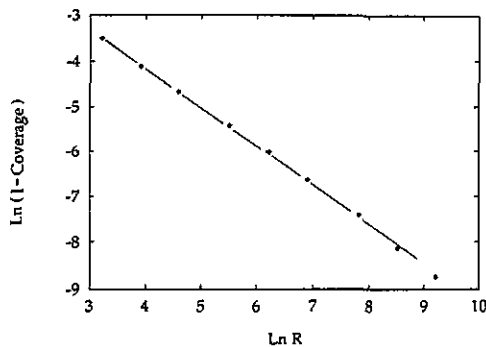


Figure 2. Ln-Ln plot of  $(1 - \theta_j)$  versus  $R$ . More details in the text.

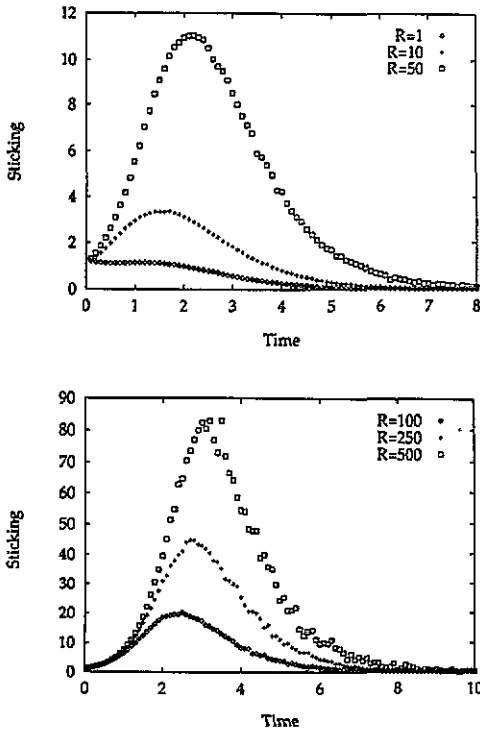


Figure 3. (a) and (b). Plots of the normalized sticking coefficient of 'hot' dimers versus the Monte Carlo time for different choices of  $R$  as indicated in the figures.

### 3.2. The sticking coefficient ( $p=1$ )

As mentioned in section 2, the sticking coefficient  $S$  is defined as the ratio between successful and total adsorption attempts. In order to study the dependence of  $S$  on time it is convenient to normalize the data with respect to the sticking coefficient ( $S_R$ ) which one may expect if the adsorbed particles were distributed on the surface at random. Since dimer adsorption requires two nn sites on has

$$S_R = (1 - \theta)^2. \quad (3)$$

Figures 3(a) and 3(b) show plots of  $S/S_R$  versus  $t$  for different choices of  $R$ . From these figures it follows that, except for  $R=1$ , the ballistic flight deposition of dimers causes an enhancement of  $S$ , with respect to  $S_R$ , at early times. Such enhancement is of about 85 for  $R=500$  and  $t \approx 3$ . Furthermore,  $S/S_R$  exhibits a maximum which becomes shifted toward later times for larger values of  $R$ . On the other hand for large  $t$ ,  $S/S_R$  drops considerably, approaching negligible values due to the increase of  $\theta$  (see figures 3(a) and (b)).

On the other hand, figure 4 shows the dependence of  $S$  on the coverage for different choices of  $R$  ( $1 \leq R \leq 100$ ). For large  $R$ -values, say  $R \geq 50$ , one observes that the sticking coefficient tends to decrease linearly with  $\theta$ , as is shown in figure 4 for  $R=100$ . From the results shown in figures 3 and 4, one concludes that for all choices of  $R$  the adsorbed particles are no longer distributed at random on the surface but, on the contrary, they are highly correlated.

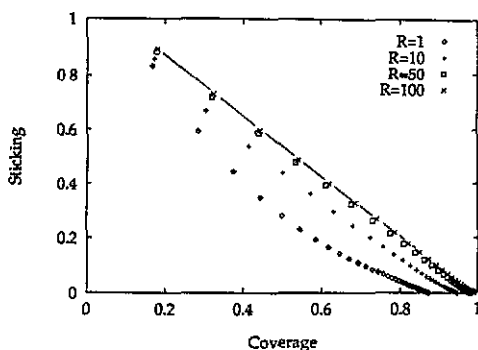


Figure 4. Plot of the sticking coefficient versus coverage for different choices of  $R$  as indicated in the figure. The straight line for  $R = 100$  has been drawn to guide the eyes.

### 3.3. The mean free path of the flying monomers ( $p = 1$ )

In order to gain insight to the actual distance travelled by the 'hot' monomers it is convenient to compute their averaged mean free path ( $MFP$ ). Figure 5 shows plots of  $MFP/R$  versus the coverage for different choices of  $R$ . For  $R = 1$ ,  $MFP/R$  decreases smoothly and almost linearly with increasing  $\theta$  ( $\theta \leq 0.6$ ). Nevertheless, for greater  $R$  values  $MFP/R$  drops considerably. For example, for  $R = 50$  one has that at lower coverage ( $\theta \approx 0.20$ ) the average distance travelled by the monomers is about  $0.5R$ . This value further decreases for greater  $R$ -values. Therefore we conclude that even at very low coverage the adparticles can effectively stop the flight of a considerable amount of hot monomers decreasing their  $MFP$ . This effect is more important for larger  $R$ -values. Since a flying monomer hitting a particle at rest becomes immobilized, one has to expect that the onset of adsorbate clustering would occur at low coverages as evidenced by the drop in  $MFP/R$ .

Furthermore, this result indicates that the dissociation-flying mechanism enhances the probability of encounters with other adparticles. In the present case this behaviour leads to the formation of adsorbed clusters, but in the case of catalyzed reactive coadsorption of different species (say  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$ ) this behaviour will certainly enhance the rate of production. This statement has been confirmed by Monte Carlo simulations [16].

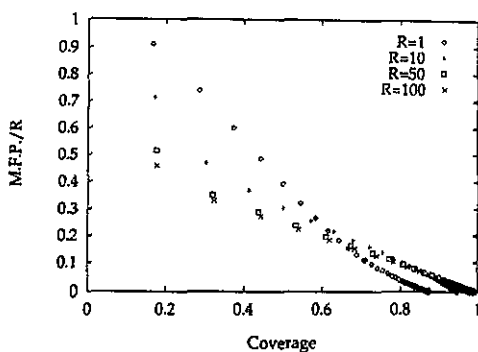


Figure 5. Plot of the  $MFP$  normalized with respect to  $R$  versus the surface coverage. Different choices of  $R$  are indicated in the figure.

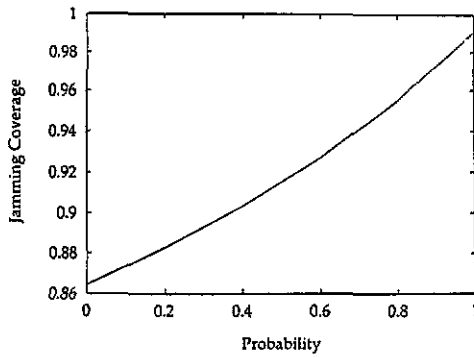


Figure 6. Plot of  $\theta_j$  versus  $p$  for  $R=100$ . More details in the text.

### 3.4. Dependence of the jamming coverage on $p$

As has already been mentioned in section 2 we have also studied the case  $p \neq 1$ , that is when the dissociatively adsorbed dimer can split into two flying monomers with a certain probability  $p$ . For example, figure 6 shows the dependence of  $\theta_j$  on  $p$  assuming  $R=100$ . For  $p=0$  we recovered the famous Flory's result given by equation (1). On the other hand for  $p>0$  one has that  $\theta_j$  increases smoothly reaching its maximum value for  $p=1$ .

Additional results obtained assuming  $p<1$ , not shown here, indicate that all the studied properties also depend smoothly on this parameter.

## 4. Conclusions

We have studied the adsorption kinetics of 'hot' dimers which after adsorption dissociate and fly apart up to a distance  $R$ . The jamming coverage depends on  $R$  and differs from the standard random dimer filling value. In the  $R \rightarrow \infty$  limit we obtain  $\theta_j^\infty \cong 1$ . The sticking coefficient also depends on  $R$  and a remarkable enhancement of  $S/S_R$  is found shortly after the beginning of the adsorption process. The average distance effectively travelled by the hot monomers strongly depends on  $\theta$  and becomes markedly reduced even at low coverages.

Hot monomers as simulated in this work exhibit an enhanced probability of encounters with other surface species, as evidenced from the study of the behaviour of the mean free path. This effect is relevant to the dynamics of some catalytic process, such as for example the oxidation of carbon monoxide. This problem is currently being addressed with promising preliminary results [16].

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