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In this work we study, by means of the Monte Carlo technique, the adsorption kinetics of "hot" dimers, i.e., molecules which after adsorption dissociate and each of the remaining monomers fly apart up to a maximum distance R from the original adsorption site. We have evaluated the jamming coverage (θ_j) which depends on R and differs from the standard random dimer filling problem. Also the dependence of both the sticking coefficient and the average distance traveled by the monomers on θ is studied and discussed. "Hot" monomers exhibit an enhanced probability for encounters with other adparticles. This behavior may be relevant in the dynamic of some catalytic processes.

I. INTRODUCTION

Very recently Ertl *et al.*,[1] based upon scanning tunneling microscopy observations, have demonstrated that oxygen molecules chemisorb dissociatively on the Al(111) surface and that at least part of their excess energy shows up in degrees of freedom parallel to the surface given rise to translational motion during which this energy is dissipated. Evidences are given in order to show that this "hot" species fly apart, on the average, by at least 80 Å before being immobilly adsorbed. Furthermore, it is estimated that each oxygen would exhibit an initial velocity of ~6.5 $\times 10^3$ m/s, traveling the distance of 40 Å within ~1 ps.[1] Based upon this interesting new finding, it is expected that the kinetics of "hot" dimer adsorption would be different than that of the largely studied irreversible monolayer particle deposition termed random sequential adsorption (RSA), or more specifically than that of the random dimer filling problem (RDFP) (see for example, Refs. 2–11). For a recent review on RSA see Ref. 12. In the RDFP, dimers are adsorbed at random on the surface neglecting the ballistic flight occurring just after deposition as reported by Ertl *et al.*[1] Due to the blocking effect by the already deposited dimers which limits the area available for the deposition of additional particles, the saturation coverage of the surface, i.e., the jamming coverage θ_j, is less than close packing. Therefore the aim of the present work is to study, by means of Monte Carlo simulations, relevant aspects of the adsorption kinetics of "hot" dimers, and to discuss differences that may appear when comparing results with the standard RDFP. Let us note that, on the one hand, the transient mobility caused by the inability to instantaneously dissipate the energy gained by a particle after formation of the surface bond has been considered in some models, such as for example the grazing incidence atomistic beam deposition of silicon,[13] the formation of metastable ordered structures upon oxygen adsorption on Pd(100)[14] (see also Ref. 12 and references therein). On

the other hand, surface hopping of "hot" adatoms resulting from dimer dissociation has also been considered in models for the chemisorption of nitrogen on the {100} face of tungsten.[15,16] Nevertheless, the adsorption kinetic of "hot" dimers, from the RDFP point of view, as described in the present work, has not been addressed yet.

II. MODELING THE ADSORPTION OF "HOT" DIMERS

The adsorption process is simulated on the square lattice of size $L \times L$ assuming periodic boundary conditions. Simulations always start with empty lattices. The adsorption algorithm is the following: (i) a surface site (site 1) is selected at random. If site 1 is occupied the trial ends, i.e., dimer adsorption cannot take place. But if site 1 is empty, then a nearest neighbor (nn) site, say site 2, is also selected at random. If site 2 is occupied the trial ends because again there is not place for dimer adsorption. But if site 2 is empty a dimer is adsorbed on the surface. (ii) After deposition both monomers resulting from the dissociation of the "hot" dimer undergo a ballistic flight up to a maximum distance R, being R the only parameter of the model. The flight is assumed to be parallel to the axis of the "hot" dimer upon adsorption. If during the flight one monomer hits another adparticle or ensemble which is already at rest, the flying monomer is frozen in at the collision point. This assumption is supported by the fact that one should expect a high efficiency for energy transfer and, as consequence, a high probability that these particles stick together.[1] Also, the formation of oxygen islands suggests the operation of net attractive forces between O atoms adsorbed on nn sites.[1]

The Monte Carlo time unit (t) is defined such as each site of the lattice would be visited once, in the average, i.e., t involves $L \times L$ trials. Simulations are performed on lattices of size $L = 400$ and averages are taken over 10^3 different samples. During the adsorption process the following quantities are measured: (i) the surface coverage θ; (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

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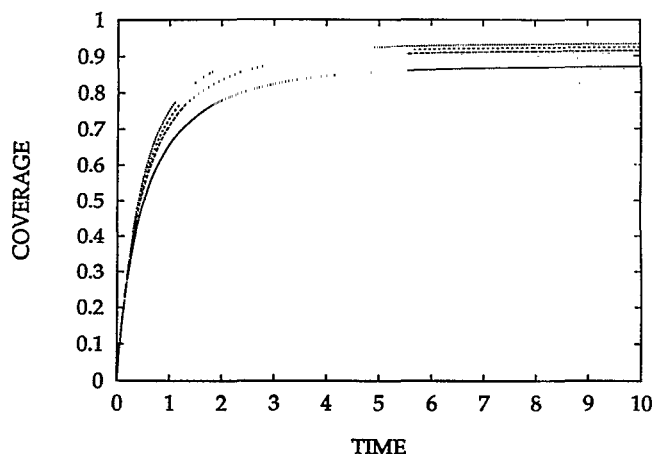[b] Permanent address: Intequi-Universidad Nacional de San Luis. Chacabuco y Pedernera. (5700) S. Luis, Argentina.

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

traveled by a monomer from the adsorption site up to the site where it becomes immobilly adsorbed.

As it has already mentioned, the "hot" dimer dissociation mechanism has also been assumed to describe the adsorption of nitrogen on $W(100)$.[15,16] Therefore, it is convenient to briefly discuss the different treatments employed. On the one hand, our work emphasized kinetics aspects of the "hot" dimer adsorption. On the other hand, authors of Refs. 15 and 16 have considered a quite different situation, namely the adsorption–desorption steady state regime. Furthermore, dimers are assumed to first adsorb in a physisorbed state (precursor). Physisorbed molecules may then dissociatively chemisorb, and the resulting "hot" adatoms are able to hop on the surface in order to relax their excess energy. In contrast to our model, this hopping is not ballistic and the parameter R does not appear explicitly. Lastly, the employed methodology is also different because a mean field approach with averaged quantities is used in Refs. 15 and 16. Due to these differences a detailed comparison between our results and findings of Refs. 15 and 16 is not possible.

III. RESULTS AND DISCUSSION

A. The kinetics of adsorption

Figure 1 shows plots of θ vs the Monte Carlo time obtained for different values of $R(1 \leqslant R \leqslant 100)$. For early times ($t < 0.3$) and low coverages ($\theta < 0.3$) there is not appreciable difference in the adsorption kinetics when R is varied. Nevertheless, for $t > 0.3$ ($\theta > 0.3$) a distinct behavior is observed for different choices of the parameter R: for a fixed time the greater R the higher θ. In spite of the fact that runs shown in Fig. 1 are performed up to $t = 10$ one observes that θ is almost saturated, and surprisingly, the jamming value for $R = 1$ ($R = 100$) appears to be lower (higher) than that of the standard RDFP that is $\theta_j^R \cong 0.907$.[7,10,12] In order to further investigate this behavior 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. The obtained results are
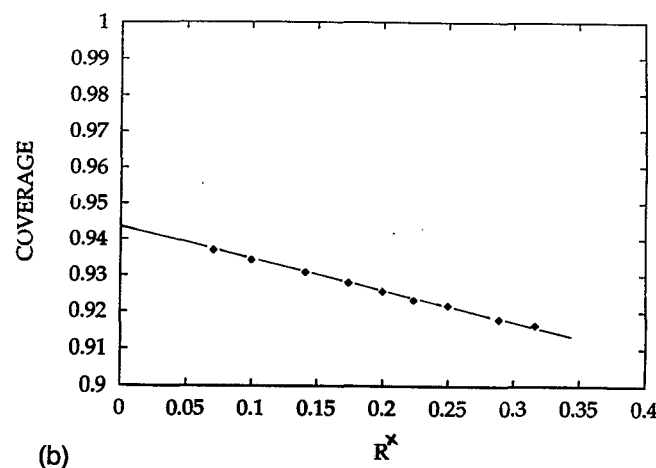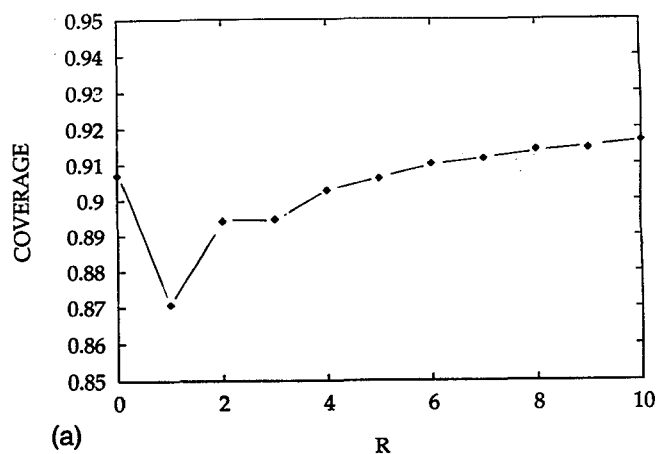

FIG. 2. (a) Plot of the jamming coverage vs R. The lines have been drawn to guide the eyes. (b) Plot of the jamming coverage vs R^x, with $x = -1/2$ and $10 \leqslant R \leqslant 200$. The intersection gives $\theta_j(R = \infty) \cong 0.943$.

shown in Fig. 2(a), where the jamming coverage in the $t \to \infty$ limit (θ_j) is plotted vs R. For $R = 0$ we obtain $\theta_j = 0.9069$, i.e., in excellent agreement with the best estimate of the standard RDFP value given by $\theta_j^R \cong 0.906\ 87$.[7,10,12] From Fig. 2(a) it follows that for $1 \leqslant R \leqslant 5$ the saturation coverage lies below θ_j^R. Therefore, one concludes that "hot" monomers flying short distances are responsible for a certain mechanism which enhances the site blocking probability for dimer adsorption. According to Fig. 1, this mechanism starts to become relevant at rather low coverages, i.e., for $\theta \approx 0.4$, that is when the curve corresponding to $R = 1$ bend downwards with respect to that of $R = 10$. Regrettably, we are not able to speculate on the operating mechanism.

On the other hand for $R \geqslant 6$ one has that $\theta_j > \theta_j^R$. In order to obtain the maximum jamming value in the $R \to \infty$ limit θ_j^∞ we have made plots of θ_j vs R^{-x} for different values of x. The best fit of the data are obtained assuming $x = 1/2$, so Fig. 2(b) shows a plot of θ_j vs $R^{-1/2}$ with data for $10 \leqslant R \leqslant 200$. The straight line behavior observed in Fig. 2(b) allows us to estimate $\theta_j^\infty \cong 0.943$. Therefore, even in
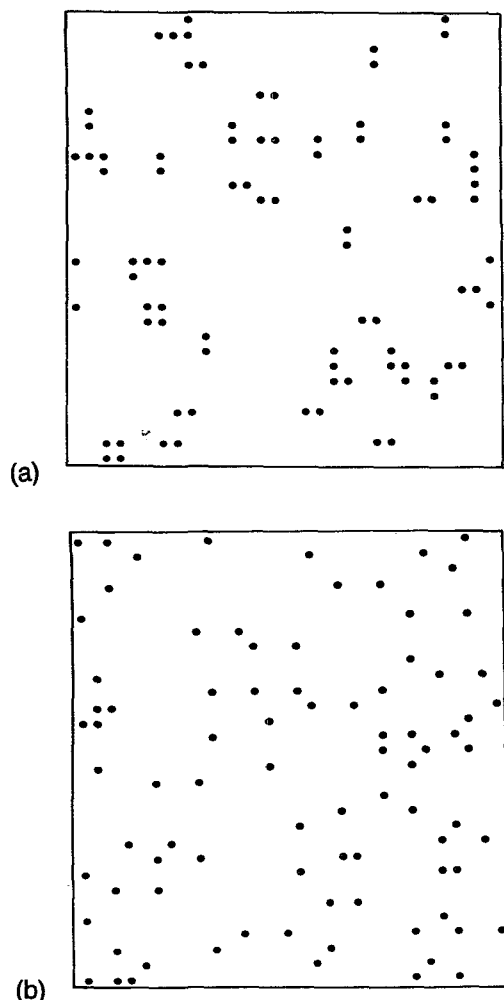
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(a)

(b)

FIG. 3. Snapshots configurations of the adparticles on the surface for a coverage $\theta=0.10$. (a) $R=0$; (b) $R=1$.

FIG. 4. Size distribution of islands for different coverages. ♦ experimental data taken from Refs. 1 and 14; + Monte Carlo results obtained assuming $R=20$ and averaging over 10^3 different samples. (a) $\theta=0.01$; (b) $\theta=0.04$; (c) $\theta=0.06$; and (d) $\theta=0.21$.

obtained experimentally correspond to a single surface configuration while the simulation results are averages over 10^3 different configurations. For this reason experimental points in Fig. 4(d) are "noisily" scattered around the smooth theoretical result.

B. The sticking coefficient

As mentioned in Sec. II, the sticking coefficient S is defined as the ratio between successful and total adsorption attempts. Figure 5(a) shows plots of S vs θ obtained using different values of R. Here one has that for a given coverage S increases when increasing R.

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 would be distributed on the surface at random. Since dimer adsorption requires two nn sites one has

$$S_R=(1-\theta)^2. \tag{1}$$

Figure 5(b) shows plots of S/S_R vs t for different choices of R. From this figure it follows that the ballistic flight deposition of dimers causes an enhancement of S, with respect to S_R, at early times. Such enhancement is of about a factor 2 for $R=100$ and $t=1$. Furthermore, S/S_R becomes maximum close $t\cong1$ almost independently of R. On the other hand for large t, S/S_R drops considerably approaching negligible values due to the increase of θ [see Fig. 5(a)]. From these results 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.

the $R=\infty$ and $t\rightarrow\infty$ limits, $\sim5\%$ of the surface corresponds to single empty sites which block the adsorption of dimers. Obviously, this statement is based on the assumption that data points for $R\gg200$ would not crossover into a different regime than that shown in Fig. 2(b). This result is also in contrast to Monte Carlo simulation results performed in one-dimensional rings where one has $\theta_j=1$ for $R=\infty$.[17]

In order to qualitatively appreciate the difference between surface configurations of adparticles formed using distinct values of the parameter R, it is useful to analyze the snapshots of Fig. 3. Figure 3(a) corresponds to $R=0$ ($\theta=0.10$) and in this case most islands are dimers while few tetramers can also be observed. For the same coverage, Fig. 3(b) has been obtained assuming $R=1$ and in this case one finds that monomers largely prevail while only few dimers are formed. A more quantitative understanding of this topic can be achieved by recording the cluster size distribution. In fact, Fig. 4 shows the abundance of various islands sizes at different coverages. Experimental results corresponding to the system $O_2/Al(111)$, taken from Refs. 1 and 18, are compared with Monte Carlo data and both results are in excellent agreement. Note that frequencies
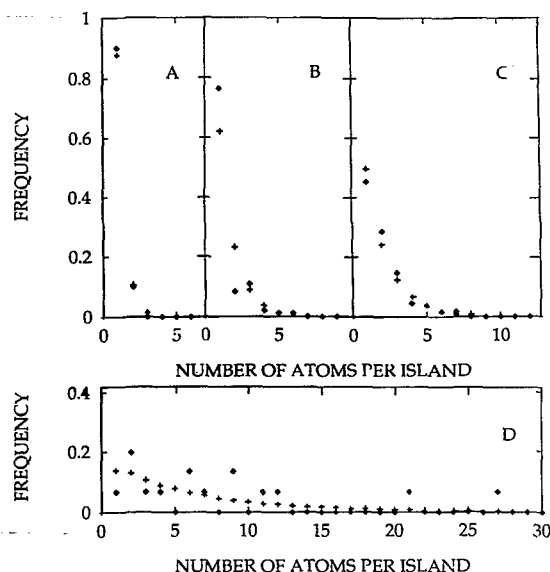
FIG. 6. Plot of the MFP normalized with respect to R vs the surface coverage. Different choices of R are indicated in the figure.
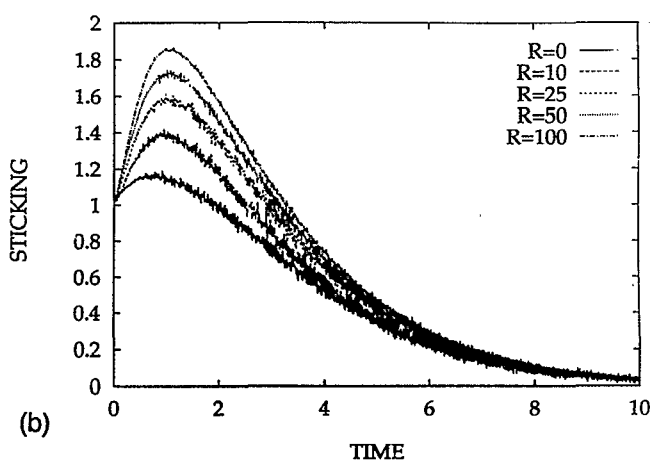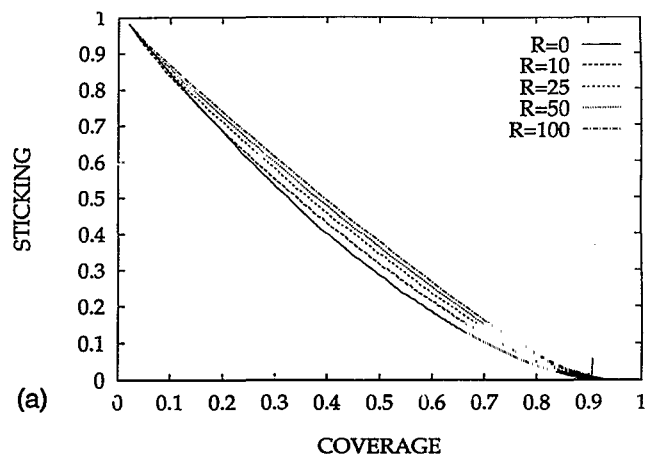

FIG. 5. (a) Plot of the sticking coefficient of "hot" dimers vs the coverage for different choices of R as indicated in the figure. (b) Plot of the sticking coefficient normalized with respect to S_R [Eq. (1)] vs time for different choices of R as indicated in the figure.

C. The mean free path of the flying monomers

In order to get insight on the actual distance traveled by the "hot" monomers it is convenient to compute their averaged MFP. Figure 6 shows plots of MFP/R vs the coverage for different choices of R. While for $R=1$, MFP/R decreases smoothly and almost linearly when increasing θ. For greater R values MFP/R drops considerably. For example, taking $R=10$ one has at lower coverage ($\theta \cong 0.20$) the average distance traveled by the monomers of about $0.4R$. This value decreases dramatically when taking $R=100$ since it accounts for only $0.12R$. Therefore we conclude that even at very low coverages, say $\theta \approx 0.05$ the adparticles can effectively stop the flight of a rather considerable amount of hot monomers decreasing their MFP in $\sim 20\%$ or more. Since a flying monomer hitting a particle at rest becomes immobilized, one has to expect that the onset of adsorbate clustering would occur at rather low coverages as evidenced by the drops of MFP/R. These statements are confirmed by both experimental and theoretical results shown in Fig. 4.
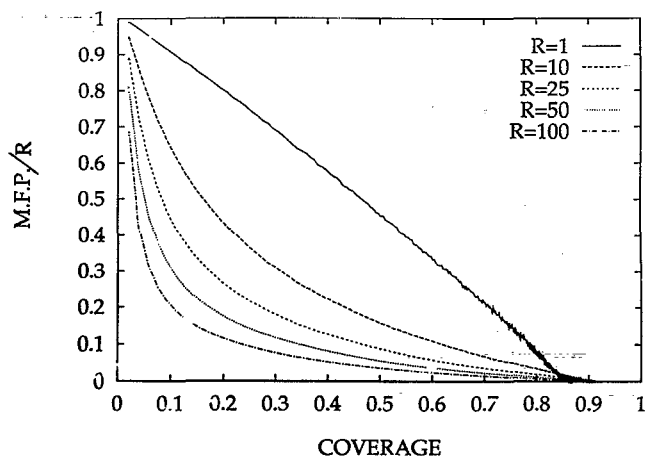
Furthermore, this result pointed out that the dissociation-flying mechanism enhances the probability of encounters with other adparticles. In the present case this behavior leads to the formation of adsorbed clusters, but in the case of a catalyzed reactive coadsorption of different species (say $CO + 1/2O_2 \rightarrow CO_2$) this behavior will certainly enhance the rate of production. This statement has been confirmed by Monte Carlo simulations.[19]

IV. 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 $\theta_j^R \cong 0.943$. The cluster size distribution of the adparticles predicted by the model is in good quantitative agreement with experimental results of the system $O_2/Al(111)$. 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 traveled by the hot monomers strongly depends on θ 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 behavior of the mean free path. This effect is relevant in the dynamics of some catalytic process, such as for example the oxidation of carbon monoxide. This problem is currently addressed with promising preliminary results.[19]

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