RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 48, NUMBER 5 NOVEMBER 1993

Exact solution of "hot dimer" adsorption in one-dimensional lattices

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(Received 8 June 1993)

An analytical solution for the kinetics of the "hot-dimer" adsorption in a one-dimensional lattice is reported. Hot dimers are molecules that dissociate after deposition, and each of the remaining monomers fly apart up to a maximum distance R from the original adsorption sites. The kinetics of this process is strongly dependent on the flying distance R. We find a particular behavior of the jamming coverage as a function of R. Monte Carlo simulation results are in agreement with such a calculation.

PACS number(s): 68.10.Jy, 82.65.−i, 02.50.−r

Based upon scanning tunneling microscopy observations, Brune *et al.* [1] have demonstrated that oxygen molecules chemisorb dissociatively on the Al(111) surface and that at least part of their excess energy is taken up in degrees of freedom parallel to the surface, giving rise to translational motion during which this energy is dissipated. Evidence is given in order to show that this species (monomers) flies apart a certain distance before becoming frozen and adsorbed. This process, in which prior to adhesion the arriving diatomic molecules break up into single-atom fragments that are flying a certain fixed distance, is the so-called "hot-dimer" adsorption (HDA). The analysis of the kinetics of such a process is an interesting problem in itself, and Monte Carlo simulation studies [2,3] have been introduced in order to analyze this problem, in the framework of the one-dimensional (1D) and two-dimensional (2D) random sequential adsorption. Recently a simplified one-dimensional model of the "HDA" has been solved by Privman [4].

Due to the vivid interest in this new kind of random sequential adsorption problem, it is instructive to obtain the one-dimensional analytical solution of the HDA kinetics in the general case. In this work, we present an analytical solution for this process in 1D lattices.

The adsorption of hot dimers is determined by two well-defined steps: (a) the dimers adsorb in at least two empty sites and (b) after each successful deposition attempt, the dimers break up into two monomers that fly up to a certain fixed distance R (in the following this flight distance is used in units of lattice constant). If during the flight one monomer hits another adparticle or cluster of particles which is already at rest, the flying monomer is frozen in at the collision point. The last point is very important in the kinetics process because, at early times, the initial configurations are strongly correlated and determine the temporal evolution of the system.

We consider one-dimensional lattices with N adsorptive sites; we disregard any end effect ($N\rightarrow\infty$). Each successful deposition attempt is followed by "instantaneous" fragmentation and the monomers fly apart up to a flying distance R, and empty gaps of at most exactly $2R$ sites are created in this process. Of course, the creation of such gaps means the destruction of bigger empty gaps and perhaps the creation of other gaps, so then we can use the standard random sequential adsorption [5–11] methodology. It is convenient to define the probabilities $P_m(t)$ to find, at time t, gaps of exactly m empty sites. The infinity hierarchy of rate equations that we obtain for $P_m(t)$ contains terms that account for the creation and the destruction of those gaps.

In order to solve this equation we used, as initial conditions [4,8],

$$P_m(0)=\Theta_0^2 a^m\ , \tag{1}$$

where $m=1,2,3,\ldots$, $a=1-\Theta_0$, and Θ_0 is the initial density of monomers that, of course, is a random configuration. The deposition attempts are random, with the rate w per site, and will be conveniently adsorbed in the definition of the dimensionless time variable $\tau=wt$. The dimers are adsorbed only if there are at least two empty sites; other attempts are rejected, as in the Monte Carlo experiment. The coverage fraction is

$$\Theta(\tau)=1-\sum_{m=1}^{\infty} mP_m(\tau)\ . \tag{2}$$

Since the fragments of the dissociation are instantaneously transported up to a maximum distance R, the time evolution of the gap probabilities $P_j(\tau)$ satisfies the following rate equations.

For $R>1$,

$$\frac{dP_1}{d\tau}=2P_3+\sum_{l=R+3}^{\infty} P_l\ . \tag{3}$$

For $R > j > 1$,

$$\frac{dP_j}{d\tau} = -(j-1)P_j + (j+1)P_{j+2} + 2\sum_{l=R+2+j}^{\infty} P_l \ . \tag{4}$$

For $j = R$,

$$\frac{dP_j}{d\tau} = -(j-1)P_j + (j+1)P_{j+2} + 2\sum_{l=R+3}^{2R+1} P_l + 4\sum_{l=2R+2}^{\infty} P_l \ . \tag{5}$$

For $2R > j > R$,

$$\frac{dP_j}{d\tau} = -(j-1)P_j + (2R+1-j)P_{j+2} + 2\sum_{l=j+3}^{R+1+j} P_l + 4\sum_{l=R+2+j}^{\infty} P_l \ . \tag{6}$$

For $j = 2R$,

$$\frac{dP_j}{d\tau} = -(j-1)P_j + \sum_{l=1}^{R} lP_{2R+1+l} + \sum_{l=3R+2}^{\infty} (l-2R+1)P_l \ . \tag{7}$$

For $j > 2R$,

$$\frac{dP_j}{d\tau} = -(j-1)P_j + 2\sum_{l=R+2+j}^{\infty} P_l \ . \tag{8}$$

This set of coupled linear equations can be solved in closed form. First we solve Eq. (8) by standard methods, and the result for $j > 2R$ is

$$P_j(\tau) = a^j X(\tau)^{j-1} G_R(a,\tau) \ , \tag{9}$$

where $X(\tau) = \exp(-\tau)$ and

$$G_R(a,\tau) = [1-aX(\tau)]^2 \exp\left[-2\sum_{l=1}^{R+1} \frac{a^l[1-X(\tau)^l]}{l}\right] . \tag{10}$$

Using Eq. (10), and with the initial conditions (1), it is possible to solve [12] Eqs. (3)–(7). Here we only present the expression for the coverage $\Theta_R(\tau)$ that we obtain using Eq. (2) as

$$\Theta_R(\tau) = 1 - \left[\sum_{m=1}^{2R} mP_m(\tau) + \frac{(2R+1)a^{2R+1}X^{2R} - 2Ra^{2R+2}X^{2R+1}}{(1-aX)^2} G_R(a,\tau)\right] . \tag{11}$$

Note that for the derivation of this result the evaluation of $P_m(\tau)$ with $1 \le m \le 2R$ is necessary; such functions are obtained by quadrature.

The main aspect of Eq. (11) is the R dependence of the coverage $\Theta_R(\tau)$. In our model the kinetics of the process is determined by the early deposition; as a consequence [12], the initial configurations are far from a random configuration of monomers. For this reason we neglect the initial random configurations taking the limit $\Theta_0 \to 0$ in the calculations of $\Theta_R(\tau)$ and $P_m(\tau)$ for all m.

Figure 1 shows the result for the coverage $\Theta_R(\tau)$ for $R = 1,2,3,4$. The analytical and the corresponding Monte Carlo simulation results agree for the complete time regime.

In Table I we show the jamming coverage $\Theta_R(\infty)$ obtained for our model and Monte Carlo calculations. Simulations are performed on 1D lattices of size $L = 10^5$, and averages are taken over 10^3 different samples. Details of this simulation have been given in Ref. [2]. The jamming coverage for $R \to \infty$ and for $\Theta_0 \to 0$ is $\Theta_\infty(\infty) = 1$, as we have shown [2] and as corroborated by Privman [4]. However, an interesting feature of this model is the oscillation of the jamming coverage depending on the flying distance R (see Fig. 1). It is observed that this effect is quite strong in one dimension, becoming negligible for $R \ge 10$. In two dimensions it is observed [3] only for $R \le 3$. The explanation of this effect takes into account the temporal evolution of the $P_m(\tau)$. Mainly, for odd values of R, we have always a bigger probability of a singlet (empty gap of size unity) than for even values.

TABLE I. Jamming coverage vs flying distance R.

$\Theta_R(\infty)$ \ R	1	2	3	4
Analytical	0.873 46	0.932 74	0.879 23	0.923 73
Monte Carlo	0.873 44	0.932 77	0.879 40	0.923 80

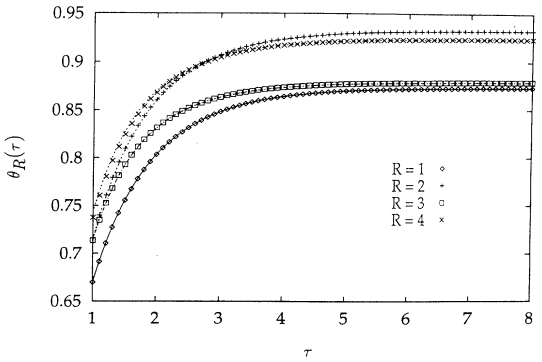

FIG. 1. Average coverage $\Theta_R(\tau)$ vs τ for $R = 1,2,3,4$, showing the analytical result (lines) and Monte Carlo simulation (points).

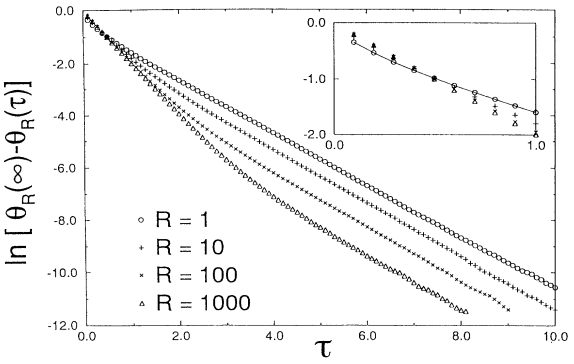

FIG. 2. Monte Carlo simulations for the approach of the average coverage $\Theta_R(\tau)$ to the jamming coverage $\Theta_R(\infty)$ for different values of R; in detail in the inset we show the short-time regime and the analytical calculation (line) for the case $R=1$.

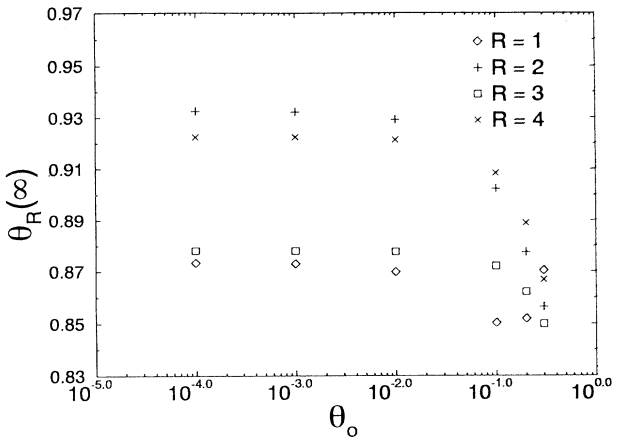

FIG. 3. Dependence of the jamming coverage $\Theta_R(\infty)$ on the initial concentration of monomers Θ_0.

Details of this analysis are given in Ref. [12].

In Fig. 2 we show the approach of the coverage $\Theta_R(\tau)$ to the jamming coverage $\Theta_R(\infty)$, for different values of R, obtained by Monte Carlo simulations (in the inset one can see the short-time behavior and the corresponding analytical calculation). Here it is possible to observe that for $R<10$, the short-time regime is different; however, the kinetics of the process (in all cases) is determined by two mechanisms, at short time the large gaps are destroyed for the flying of the monomers and consequently small gaps are created. This process has a characteristic time τ_I ($\tau_I=2$) (see Fig. 2). Of course, at very large times the kinetics depend on whether or not deposition of the dimers occurs in a very small empty gap ($m=2,3$), and the characteristic relaxation time τ_{II} corresponds mostly to the classic problem [7]. In between we can see a crossover region from the short- to the large-time regime. Such crossover starts when the probability $P_2(\tau)$ has a maximum; this maximum is shifted when R is increased, and ends when the gaps with $m>2$ are consumed by the process.

Finally, we show the effect of the initial configuration on the jamming coverage, see Fig. 3. As we can see, $\Theta_R(\infty)$ is sensitive to the initial configuration. This effect is mainly due to the strong correlation introduced by the early deposition, but is almost irrelevant for $\Theta_0<0.01$.

In summary, in this Rapid Communication we present the kinetic equations of the one-dimensional hot-dimer adsorption model and the analytical solution for the coverage $\Theta_R(\tau)$. Our model takes into account the complete evolution of the gaps, and as a consequence, the temporal behavior of this process is described by the solution of the rate equations. We show that the oscillations in the jamming coverage depend on the odd or even value of R. Two regimes of time are observed, as their origin is discussed. The analytical solution of our model is in good agreement with Monte Carlo results. We also show the effect of the initial condition on the jamming coverage.

This work was partial supported by the CONICET, Argentina. The authors thank Professor K. Binder, Institute of Physics, Johannes Gutenberg University of Mainz, for hospitality and for reading the manuscript. V.P. also thanks Dr. P. Nielaba for helpful discussions nd Professor V. Privman for sending the manuscript.

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