Collective Properties of Adsorption-Desorption Processes

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A reversible adsorption-desorption parking process in one dimension is studied. An exact solution for the equilibrium properties is obtained. The coverage near saturation depends logarithmically on the ratio between the adsorption rate, k_+, and the desorption rate, k_-, $\rho_{eq} \cong 1 - 1/\log(k_+/k_-)$, when $k_+/k_- \gg 1$. A time dependent version of the reversible problem with immediate adsorption ($k_+ = \infty$) is also considered. Both heuristic arguments and numerical simulations reveal a logarithmically slow approach to the completely covered state, $1 - \rho(t) \sim 1/\log(t)$.

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I. INTRODUCTION

The adsorption of large particles such as colloids, proteins, latex spheres, *etc.* on solid substrates is typically an irreversible process [1,2]. Indeed, in a number of situations, the energetic barriers for desorption are much higher than the corresponding barriers for adsorption. Moreover, particles cannot adsorb on top of previously adsorbed ones. This leads to the nonoverlapping irreversible random sequential adsorption (RSA) models which have been studied intensively. It was found that in arbitrary dimension, RSA processes reach a jamming configuration, where further adsorption events are not possible. The final coverage as well as the temporal approach to the jammed state are of interest [2-8]. Exact analytical results have been obtained mainly in one dimension, where the problem is also known as the "parking" problem [2,7-8].

It is clear that the usual RSA model provides an oversimplified description of actual adsorption processes. A more realistic treatment should incorporate various effects such as the transport properties of the particles, the interaction between particles, and possible desorption from the substrate to the bulk [9-13]. Very recently, RSA models where particles diffuse in the bulk and adsorb on the substrate were considered. Interestingly, introduction of bulk transport did not change the coverage and the structure of the jammed configuration. However, it was found that the approach to the jamming limit depends on the transport properties of the particles [9-10].

In this article, we study the influence of desorption on the one-dimensional parking problem. Such a generalization is appropriate for many physical, chemical and biological systems [1-17]. Allowing desorption makes the process manifestly reversible and the system ultimately reaches an equilibrium state. In the experimentally relevant desorption-controlled limit, the system approaches the saturated state in a non-trivial manner.

The rest of this paper is organized as follows. In Section II, we introduce the model, write the governing rate equations for the density of empty intervals, and then find the exact steady state solution to these equations. The primary result of this section is the weak logarithmic dependence of the equilibrium coverage on the ratio of the adsorption rate to the desorption rate, in the desorption-controlled regime. In Section III, we describe the temporal behavior of the system near saturation in the desorption-controlled limit. To study the evolution in this limit, we focus on a model with an infinite rate of adsorption and a finite rate of desorption. A heuristic argument as well as numerical simulations show that the coverage slowly approaches saturation, $1 - \rho(t) \sim 1/\log(t)$. Finally in Section IV, we discuss our findings and further outlook.

II. THE REVERSIBLE PARKING PROBLEM

In the irreversible parking problem, identical particles park on a line with an adsorption rate k_+. Particles attempt to park with an equal rate everywhere and a parking attempt fails if the space is partially occupied by a previously adsorbed particle. We are interested in the more general situation where particles are also allowed to desorb with a desorption rate k_-. Particles desorb regardless of their local environment. This system ultimately reaches an equilibrium state independent of the initial conditions. The primary aim of this study is to describe this final state and the asymptotic approach towards it. To this end we will apply the empty interval distribution method [14]. This technique is often applied to RSA problems, since simple and closed equations emerge. We generalize these equations to describe the reversible case and solve the static equations.

Denote the density of empty intervals of size exactly equal to x at time t by $P(x,t)$. Each empty interval borders a particle to its left and to its right. Since in the adsorption-desorption process one interval corresponds to one particle and since the total density of particles and intervals is equal to unity one has

$$1 = \int_0^\infty dx\,(x+1)P(x,t). \tag{1}$$

Without loss of generality the size of particles is taken as the unit of length. Moreover, from the same one-to-one mapping between particles and intervals, the density of particles can be obtained from the distribution function of empty intervals as

$$\rho(t) = \int_0^\infty dx P(x,t). \qquad (2)$$

To write the evolution equations one has to account for all possible processes leading to a change of $P(x,t)$. For $x < 1$, an interval disappears when either one of its neighboring particles desorbs. On the other hand, an interval of size x is created when a particle parks at one of two specific locations on an interval of size y with $y > x+1$. These two processes give rise to the following integro-differential equation for $P(x,t)$

$$\frac{\partial P(x,t)}{\partial t} = -2k_- P(x,t) + 2k_+ \int_{x+1}^\infty dy P(y,t), \qquad (3a)$$

Due to adsorption, intervals with length larger than a particle size are destroyed with a rate $k_+(x-1)$. In addition, two neighboring intervals can create a larger interval when the intervening particle desorbs. However, the mere knowledge of the interval distribution function is not sufficient for writing the rate equations. We introduce the interval-interval distribution function $P(y,z,t)$, defined as the density of pairs of neighboring intervals of length y and z, which are separated by a single particle. We further assume that this interval-interval distribution function is proportional to the product of single interval densities. This assumption, also known as the independence principle, has proved to be exact in a number of RSA problems [18,19]. In equilibrium at least, one expects such a relation to be exact and it is a natural starting point for investigating the time dependent problem. With this assumption, one finds for the rate equation for $x > 1$

$$\frac{\partial P(x,t)}{\partial t} = -2k_- P(x,t) + 2k_+ \int_{x+1}^\infty dy P(y,t) \qquad (3b)$$

$$+\frac{k_-}{\rho(t)} \int_0^{x-1} dy P(y,t) P(x-1-y,t) - k_+(x-1)P(x,t)$$

The convolution term involves the probability of finding a y interval, $P(y,t)$, and the normalized probability for its neighbor to be of size $x-1-y$, *i. e.*, $P(x-1-y)/\int_0^\infty dx P(x,t)$.

To verify that these equations satisfy the normalization condition of Eq. (1), one can check by direct integration of Eq. (3) that $\frac{\partial}{\partial t}\int_0^\infty dx\,(x+1)P(x,t) = 0$. Another useful check of self-consistency of the rate equations is provided by integration of the rate equations over all lengths. This gives the equation describing the change of the density,

$$\frac{d\rho(t)}{dt} = -k_-\rho(t) + k_+ \int_1^\infty dx\,(x-1)P(x,t), \qquad (4)$$

which can also be derived directly from the definition of the gap distribution. Equation (4) is a generalization of the Langmuir mean-field equation, $d\rho/dt = -k_-\rho + k_+(1-\rho)$, which is recovered by setting the integral on the right-hand side equal to $1-\rho(t)$.

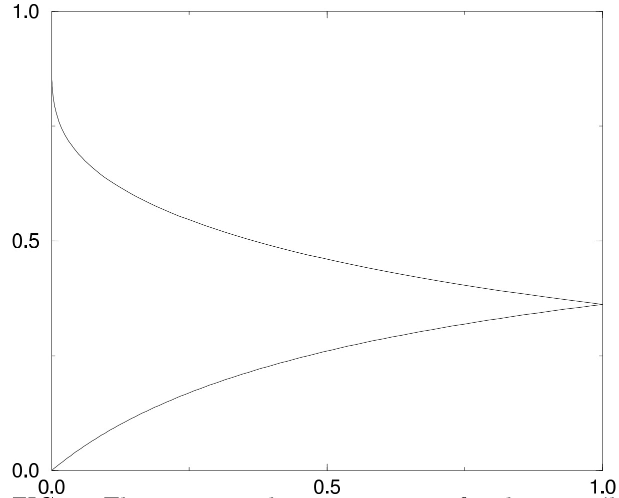

FIG. 1. The exact steady state coverage for the reversible parking problem. $\rho_{eq}(k_+/k_-)$ is plotted vs. k_-/k_+ for $k_+ > k_-$ (solid line) and vs. k_+/k_- for $k_- > k_+$ (dotted line).

The steady-state interval distribution has to satisfy the static version of Eq. (3), that is, both sides of the equation vanish. Interestingly, the simplest attempt, trying the Poissonian distribution $P_{eq}(x) = \beta e^{-\alpha x}$, is successful. We emphasize that despite the two different equations for $x < 1$ and $x > 1$, the solution is smooth at $x = 1$. From the normalization condition of Eq. (1) the prefactor is determined to be $\beta = \alpha^2/(1+\alpha)$, while from Eq. (2) the value of α is found via a transcendental equation involving k_+/k_-. One can now write the exact steady-state solution as

$$P_{eq}(x) = \frac{\alpha^2}{1+\alpha} e^{-\alpha x} \quad \text{with} \quad \alpha e^\alpha = k_+/k_-. \qquad (5)$$

To obtain the density of particles in the steady-state we use the correspondence between particles and intervals expressed in Eq. (2). Hence, it is easily found that $\rho_{eq} = \alpha/(1+\alpha)$. In the desorption-controlled regime, $k_+/k_- \gg 1$, one finds $\alpha \simeq \log(k_+/k_-)$, and consequently,

$$\rho_{eq} \cong 1 - \frac{1}{\log(k_+/k_-)} \quad k_+/k_- \gg 1. \qquad (6)$$

Notice that in the limiting case $k_+/k_- \to \infty$ the line is completely filled with particles at the steady state, in contrast to the case of no desorption where asymptotic coverage is $\rho_{\rm jam} \cong 0.7475$ [7,8]. However, as the adsorption rate increases while the desorption rate is kept fixed, the coverage increases very weakly, since the corresponding correction is logarithmic. Moreover, the gap distribution is regular at the origin, contrary to the logarithmic divergence occurring in the irreversible case. Thus, the presence of desorption, even if slight, significantly changes the long-time behavior. Note also that in the adsorption-limited case, the coverage displays an obvious linear dependence on the rate ratio, $\rho_{eq} \cong \alpha \cong k_+/k_-$.

To test the theoretical predictions we performed Monte-Carlo simulations of the reversible parking process. We have found that the equilibrium properties are essentially identical to the analytical results shown in Fig. (1). We also confirmed the Poissonian nature of the density of empty intervals. Furthermore, the relaxation to the the steady state have been investigated. As expected, the approach to the steady state coverage is exponential $\rho_{eq} - \rho(t) \propto e^{-t/\tau}$, where the relaxation time τ appears to be proportional to k_+/k_- with possible logarithmic corrections. Note that the corresponding approach to the jammed state in the irreversible case has a power-law dependence on time $\rho_{\rm jam} - \rho(t) \propto t^{-1}$. The distribution function $P(x,t)$ exhibits a transient discontinuous derivative at $x = 1$ due to the discontinuous structure of Eq. (3) . That feature does not permit us to construct an analytic solution for the time dependent problem.

We now outline the solution for the lattice version [15,16] of the reversible parking problem. In this model, objects occupy r lattice sites and will be referred to as r-mers. Analogous to the continuous case, r-mers land uniformly on a lattice with a rate k_+ and adsorb if all sites are empty. We define $P(m,t)$ as the density of empty intervals of exact length m. The equivalent to Eqs. (1-3) simply follows and we merely quote the final results. The density of empty intervals is again Poissonian

$$P_{eq}(m) = \frac{(1-\lambda)^2}{\lambda + r(1-\lambda)}\,\lambda^m \quad \text{with} \quad \frac{\lambda^r}{1-\lambda} = \frac{k_-}{k_+}. \tag{7}$$

Using the equivalent of Eq. (2) $\rho_{eq} = r\sum_0^\infty P_{eq}(m)$, we can find the steady state coverage $\rho_{eq} = r(1-\lambda)/\big(\lambda + r(1-\lambda)\big)$. In the desorption-controlled case, $k_+/k_- \gg 1$ we find that $\rho_{eq} = 1 - (k_-/k_+)^{1/r}/r$. As the size of the r-mer increases, the exponent of the power-law r^{-1} decreases and ultimately the aforementioned logarithmic nature is reached. Indeed, the solution to the continuous case given by Eqs. (5-6) can be found from Eq. (7) by taking the proper limits $x \to m/r$ and $k_+ \to k_+/r$.

III. DYNAMICS IN THE DESORPTION-CONTROLLED LIMIT

The second part of our study focuses on the dynamical properties of the system in the desorption-controlled limit. To attain this regime, immediate adsorption ($k_+ = \infty$) is imposed while the desorption rate is kept finite. Redefining the time $t \to k_- t$, corresponds to taking the desorption rate equal to unity. The evolution may be divided into two stages. First, the system instantaneously reaches a jammed state and then desorption comes into play. Since both the final coverage and the asymptotic behavior do not depend on the initial conditions produced at the end of first stage, one can use any initially jammed configuration satisfying the normalization constraint of Eq. (1). In the simulations, we have chosen a distribution where all gaps between particles are equal to x_0 with $x_0 < 1$,

$$P(x, t = 0) = \frac{\delta(x - x_0)}{1 + x_0}. \tag{8}$$

Once a desorption event has occurred, either one or two adsorption events are possible depending on the length of the two intervals bordering the particle. We have adopted a natural scheme where the first particle lands on a randomly picked segment in the open interval and then, if feasible, the second particle lands randomly on the remaining interval. Thus, after each desorption and subsequent adsorption event(s) the number of particles is either left unchanged or increased by one. Numerical simulations indicate that this process approaches complete coverage in the long-time limit.

A simple heuristic argument explains the behavior of the system near saturation. Let us imagine that a segment of length $L = N + 2$ is occupied by N particles. Consider a typical situation where the gaps between the particles are comparable ($\sim 1/N$). A successful density-increasing adsorption event may take place only as a result of a number of ordered cooperative desorption-adsorption events. First, the leftmost particle has to desorb and then adsorb near the left end of the segment. Second, the next leftmost particle has to desorb and then adsorb near the right side of the previous particle *etc.*. Finally, a gap larger than the unit length is cleared at the right edge of the segment, and an additional particle successfully adsorbs. The probability for the first event is R/N since the leftmost particle is desorbed first among N particles; the probability for the second event is $R/(N-1)$ *etc.*. The factor $R < 1$ accounts for the probability that the corresponding adsorption event happens in the proper location. The total probability for the cooperative event can be written as $p \sim R^N/N!$. We can now evaluate the time dependence of $N(t)$. The time required for a unit change in N is inversely proportional to p and one has

$$\frac{dN}{dt} \propto \frac{\Delta N}{\Delta t} \propto p \propto \left(\frac{eR}{N}\right)^N. \tag{9}$$

In the last step the Stirling's formula $N! \sim (N/e)^N$ was used. Solving Eq. (9) yields the following asymptotic relation for $N(t)$, $N \sim \log(t)/\log\big(\log(t)\big)$. Since the uncovered fraction obeys $1 - \rho(t) \propto 1/N$, an unexpectedly slow long-time behavior of the density emerges,

$$1 - \rho(t) \propto \frac{\log\big(\log(t)\big)}{\log(t)}. \tag{10}$$

We describe now a simpler heuristic argument that also predicts inverse logarithmic behavior but without double logarithmic correction. We observe that when the system approaches to the completely covered state the time interval between successive density-increasing adsorption events increases. Hence, the system has time to "equilibrate" and one can approximate the gap distribution by the Poissonian equilibrium distribution $P(x,t) = \alpha^2 e^{-\alpha x/(1+a)}$. To solve for the density we write Eq. (4) with a vanishing desorption term

$$\frac{d\rho(t)}{dt} = \int_1^\infty dx\,(x-1)P(x,t) = \frac{1}{1+\alpha}e^{-\alpha}. \tag{11}$$

On the other hand, one has $\rho(t) = \alpha/(1+\alpha)$ from Eq. (2) and consequently, the time derivative of the density can be expressed as $d\rho(t)/dt = (d\alpha/dt)/(1+\alpha)^2$. By equating the two expressions obtained for $d\rho(t)/dt$ we have

$$\frac{d\alpha}{dt} = (1+\alpha)e^{-\alpha}. \tag{12}$$

Solving this differential equation we arrive at the asymptotic behavior of the density, that is, $\alpha \propto \log(t)$ and

$$1-\rho(t) \propto \frac{1}{\log(t)}. \tag{13}$$

Both estimates predict that the desorption-limited process gives rise to a very slow inverse logarithmic approach to the completely covered state. Thus we conclude that in the desorption-controlled limit the dynamics of the system exhibits "glassy" relaxation.

Numerical simulations of the desorption-limited process were performed using the following simple procedure. A list of intervals $\{l_i < 1\}$ is kept, while the locations of the particles are ignored. A simulation step consists of choosing randomly a pair of neighboring intervals, $\{l_i, l_{i+1}\}$. Then the total length $l_i + l_{i+1}$ is redivided randomly to two new intervals, $\tilde{l}_i$ and $\tilde{l}_{i+1}$. If one of these new intervals is larger than unity, an additional particle adsorbs. Given $\tilde{l}_i > 1$, two new intervals are created randomly with their total length equal to $\tilde{l}_i - 1$. Time is updated after each event by the inverse of the total number of intervals in the system. To verify the predicted logarithmic approach to the saturated state, we write $f(t) = \big(1-\rho(t)\big)\log(t)$. The simulation results for $f(t)$ and $f(t)/\log\big(\log(t)\big)$ are shown in Fig. 2(a). Both functions are slowly varying in time. Since the former is an increasing function and the latter a decreasing one, we conclude that the estimates (10) and (13) provide the upper and lower bounds for the uncovered fraction, respectively. It seems that the upper bound provides a slightly better approximation for $f(t)$.

Similar to the general reversible case, the gap distribution is an important characteristic of the process. Rather cumbersome rate equations describe the time evolution of $P(x,t)$ in this case. We do not write these rate equations since we have not been able to obtain meaningful new results by analytical means. Instead, in Fig. 2(b) we present Monte-Carlo simulational results for the gap distribution function. In the long-time limit, the gap distribution function appears to be again Poissonian, at least over a significant range of the gap size. We believe that this supports the argument leading to the lower bound (13). However, the tail of the distribution, crucial for the adsorption of new particles, cannot be determined from these data.

The success of the Poissonian approximation suggests that the process is mean-field in nature. To check this feature, a mean-field variant of the above Monte-Carlo simulation was also considered. In this model, the two randomly chosen intervals are not required to be neighbors. In fact, the pair is chosen randomly from all available pairs. Simulations have shown little quantitative change and practically no qualitative change in the data similar to those presented on Fig. 2. We performed other numerical experiments including, *e. g.*, computation of the pair correlation function. Again, simulational results revealed an excellent agreement between the one-dimensional and the mean-field versions.

IV. DISCUSSION

We have considered near saturation properties of two one-dimensional adsorption-desorption processes. In the reversible case, we have obtained an exact solution that exhibits a slowly varying dependence of the coverage versus the rate ratio k_+/k_-, when $k_+ \gg k_-$. In the case of immediate adsorption, when the system approaches to the completely covered state, we have shown that $1-\rho(t) \sim 1/\log(t)$. We have performed numerical simulations both for the 1D model and for the mean-field version of the model. Comparison of numerical results have revealed a remarkably good agreement between both models. Despite the apparent difference in the definition of the reversible model and the desorption-controlled model the underlying physical mechanism for increase in coverage is similar. In a configuration where the coverage is large, $\rho \lesssim 1$, a growing number of cooperative desorption-adsorption events are necessary for an additional adsorption to occur. Moreover, the slow nature of the process allows for perfect mixing of different gaps and hence leads to a Poissonian distribution of gaps.

The situation found in this adsorption-desorption process is reminiscent of that encountered in a number of one-dimensional systems where phase transitions occur at zero temperature. Indeed, noting that in the parking problem the rate ratio k_+/k_- plays the role of temperature we conclude that all basic features of the reversible model such as disordered steady state and exponential approach towards equilibrium correspond to typical behaviors above the point of phase transition. In the desorption-controlled case, the system reaches the perfectly ordered final state while the approach towards it shows a critical slowing down. Furthermore, this analogy suggests that in the two-dimensional case a phase transition in the adsorption-desorption system may take place at a finite k_+/k_-. The desorption-controlled limit in two dimensions seems very interesting since the system can reach numerous metastable states which include, *e. g.*, two ordered perfect crystal structures, triangular and square, and a number of polycrystalline structures with a network of defects. Metastable states should be responsible for remanance effects, slow relaxation, and sensitivity to initial conditions. Elucidating properties of these metastable states and their basins of attraction, “glassy” phase transitions, *etc.*, is left for future studies.

After completing this article we became aware of similar results, derived by independent means, for the dynamics in the desorption-controlled limit [20]. We thank J. Talbot for letting us know of his work and for a useful correspondance. We are also thankful to D. ben-Avraham for pointing out some relevant references and especially to S. Redner for numerous discussions and for reading the manuscript. We gratefully acknowledge ARO grant #DAAH04-93-G-0021, NSF grant #DMR-9219845, and to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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FIGURE CAPTION

Fig. 2 Monte-Carlo simulation results for the infinite adsorption case. The simulation was performed on a ring of length 100,000. (a) The temporal approach to the fully occupied state. Shown are $f(t)$, $f(t) = \big(1-\rho(t)\big)\log(t)$ vs. t (circles) and $f(t)/\log\big(\log(t)\big)$ vs. (t) (squares). (b) The gap distribution at the 65536 time step.