

# **Four Lectures on Non-Equilibrium Statistical Physics**

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## Chapter 2

# ADSORPTION

This chapter is concerned with the kinetics of adsorption in which gas molecules impinge upon and then adsorb on a surface, or substrate. What is the rate at which adsorbed molecules fill the substrate? If the incident molecules are monomers that permanently attach to single adsorption sites on the surface and if there are no interactions between adsorbed monomers, then the fraction  $\rho$  of occupied sites increases at a rate proportional to the density of vacancies,

$$\frac{d\rho}{dt} = (1 - \rho),$$

where we set the an intrinsic adsorption rate to 1 without loss of generality. The solution to this rate equation is  $\rho(t) = 1 - e^{-t}$ , so that vacancies disappear exponentially in time. However, if each arriving molecule covers multiple substrate sites, then an unfilled region that is smaller than the molecule size can never be filled. The system reaches a *jammed* state in which the substrate cannot accommodate additional adsorption, even though it is not completely filled. What is the filling fraction of this jammed state? What is the rate at which this final fraction is reached? These are basic questions of adsorption kinetics.

### 2.1 Random Sequential Adsorption in One Dimension

#### Dimer adsorption

A simple example that exhibits non-trivial collective behavior is the irreversible and *random sequential adsorption* of dimers — molecules that occupy two adjacent sites of an infinite one-dimensional lattice (Fig. 2.1). We model the steady influx of molecules by adsorption attempts occurring one at a time at random locations on the substrate. An adsorption attempt is successful only if a dimer is incident onto two adjacent empty sites. If a dimer lands on either two occupied sites or on one occupied and one empty site, the attempt fails. That is, multilayer adsorption is forbidden, so that each site is either empty or contains 1 particle, but no more. The dimer coverage grows with time and eventually only isolated vacancies remain. When this occurs, the substrate is jammed and no further adsorption is possible.

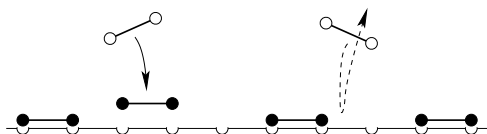


Figure 2.1: Irreversible dimer deposition. The dimer on the left successfully adsorbs onto two adjacent vacant sites, while the dimer on the right does not adsorb.

For dimer adsorption, a jammed state consists of strings with an even number of occupied sites ( $\bullet$ ) that are separated by isolated vacant sites ( $\circ$ ), as illustrated by:



Figure 2.2: A jammed configuration in random sequential adsorption of dimers.

In principle, the fraction of occupied sites in the jammed state,  $\rho_{\text{jam}} \equiv \rho(t = \infty)$ , can have any value between  $2/3$  and  $1$ , with the two extreme limits achieved by the respective configurations:

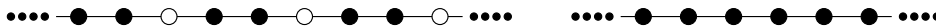


Figure 2.3: Minimum-density and maximum-density jammed dimer configurations.

A beautiful result, first derived by Flory, is that the value of  $\rho_{\text{jam}}$  in random sequential dimer adsorption is

$$\rho_{\text{jam}} \equiv \rho(t = \infty) = 1 - e^{-2} = 0.864664 \dots \tag{2.1}$$

Flory’s original derivation was based on enumerating all possible jammed configurations directly. Here we adopt a kinetic viewpoint and determine the time evolution of the coverage. The final coverage will then emerge as a natural consequence.

To determine the evolution of the substrate coverage, we need, in principle, the probabilities  $P(= \{n_j\}, t)$  for the occupation state of each lattice site. Here  $n_j = 1$  if the  $j^{\text{th}}$  site is occupied, and  $n_j = 0$  if this site is empty. However these probabilities contain more information than necessary. What we really need are the *empty interval probabilities*, namely, the probability that a string of  $m$  consecutive sites are empty:

$$E_m \equiv \text{prob}(\underbrace{\times \circ \dots \circ \times}_m) \equiv \mathcal{P}[\underbrace{\circ \dots \circ}_m]$$

Here the symbol  $\times$  signifies that the state of the sites on the periphery of the  $m$ -interval are unspecified; they could be either occupied or empty. Consequently,  $E_m$  is also the probability to find an empty interval of length  $m$  or greater. In particular,  $E_1$  is the density of empty sites and  $\rho(t) = 1 - E_1$  is the density of occupied sites. Thus from the empty interval probabilities, we can obtain the particle density. This is one reason why the empty interval probabilities are so useful.



Figure 2.4: Changes in the empty interval probability  $E_m$  for  $m = 4$ , with an adsorption event in the interior (left) and at the edge of the interval (right).

For irreversible dimer adsorption, the master equations that describe the evolution of the empty interval probabilities  $E_m$  are:

$$\frac{dE_m}{dt} = -(m - 1)E_m - 2E_{m+1} \quad m \geq 1. \tag{2.2}$$

The first term on the right side accounts for the loss of an  $m$ -interval due to the adsorption of dimers inside the interval. The factor  $m - 1$  counts the  $m - 1$  distinct locations at which the dimer can adsorb such that it lies entirely within the interval (Fig. 2.4). The second term accounts for the two adsorption events in which one end of the incident dimer is outside the  $m$ -interval. For these latter events, the empty interval must contain at least  $m + 1$  empty sites to accommodate this absorption of a dimer on the periphery of the  $m$ -interval; hence the factor  $E_{m+1}$ . Notice that (2.2) contains only loss terms. This feature is a consequence of using the empty interval probabilities  $E_m$  as the basic dynamical variables. Pictorially, we are looking at the substrate through eyes that see only  $m$  consecutive sites at a time and  $E_m$  is merely the fraction of

these intervals that are empty. In this representation, there is no way to create an empty interval of length  $\geq m$  by the adsorption of a dimer onto a still-larger empty interval.

It might seem more natural to write master equations for the *void densities*

$$V_m \equiv \mathcal{P}[\underbrace{\bullet \circ \cdots \circ \bullet}_m],$$

defined as the probability to find  $m$  consecutive empty sites that are bounded on either side by an occupied site. The master equations for the evolution of the void densities  $V_m$  for irreversible dimer adsorption are:

$$\frac{dV_m}{dt} = -(m-1)V_m + 2 \sum_{j=2}^{\infty} V_{m+j}. \quad (2.3)$$

The first term again accounts for the adsorption of a dimer in the interior of a void. The sum accounts for the *creation* of a void of  $m$  sites by adsorbing a dimer into a void that contains  $\geq m+2$  unoccupied sites. There is a close correspondence between these master equations and those for fragmentation. There are no hard and fast rules for which set of quantities —  $E_m$  or  $V_m$  — are more useful for determining the dynamics of these type of kinetic problems. For irreversible adsorption, the master equations for  $E_m$  are typically easier to solve and we focus on these quantities in what follows:

We now solve (2.2) for the initial condition of an initially empty system,  $E_m(0) = 1$ . Because the integrating factor for each master equation is  $e^{-(m-1)t}$ , it suggests seeking a solution of the form

$$E_m(t) = e^{-(m-1)t} \Phi(t), \quad (2.4)$$

where  $\Phi$  coincides with  $E_1(t)$ , and with  $\Phi(0) = 1$  to match the initial condition. In terms of the  $E_m(t)$ , the density of occupied sites  $\rho(t)$  is given by  $E_1(t) = 1 - \rho(t)$ . This connection allows one to determine how the surface coverage evolves. Using the ansatz of Eq. (2.4), the infinite set of master equations (2.2) miraculously reduces to the *single* equation  $\frac{d\Phi}{dt} = -2e^{-t} \Phi$ , whose solution immediately yields the empty interval probabilities

$$E_m(t) = e^{-(m-1)t-2(1-e^{-t})}. \quad (2.5)$$

Empty gaps of length greater than 1 decay exponentially with time and only gaps of length 1 remain in the final jammed state. From (2.5), the asymptotic density of such gaps is  $E_1(\infty) = e^{-2}$ , so that the jamming coverage is

$$\rho_{\text{jam}} \equiv \rho(t = \infty) = 1 - e^{-2} = 0.864664, \dots \quad (2.6)$$

as first derived by Flory from a direct enumeration of all possible final state configurations.

We have reproduced the classic Flory result with little labor, and we also have more — the coverage throughout the entire evolution:

$$\rho(t) = 1 - E_1(t) = 1 - e^{-2(1-e^{-t})}. \quad (2.7)$$

The coverage therefore approaches the jamming coverage exponentially in time,  $\rho(\infty) - \rho(t) \simeq 2e^{-(t+2)}$ , a feature that typifies lattice models of irreversible adsorption.

## Irreversible car parking

The limit of  $k$ -mer adsorption with  $k \rightarrow \infty$  defines the *car parking* problem. In this limit, the position of an adsorbed  $k$ -mer becomes continuous and one can think of unit-length “cars” that irreversibly park anywhere along a one-dimensional curb (no marked parking spots) and then are abandoned. The only constraint is that cars cannot overlap; however a car *can* fit into a parking spot that is infinitesimally larger than the car itself. For this parking problem, Rényi obtained a jamming coverage of 0.747597...; this result is the  $k \rightarrow \infty$  limit of the jamming coverage for  $k$ -mers.

We again solve this parking problem by the master equation approach. The length of a car is immaterial if we seek the fraction of the line that is covered, and for convenience we set the car length to be 1. The

appropriate dynamical variable is now  $E(x, t)$ , the probability that a randomly-chosen interval of length  $x$  is empty. As in the discrete case, this region may be part of an even longer empty interval. When the rate at which cars park equals 1, the master equation for  $E(x, t)$  is

$$\frac{\partial E(x, t)}{\partial t} = \begin{cases} -(x-1)E(x, t) - 2 \int_x^{x+1} E(y, t) dy & x > 1 \\ -(1-x)E(1, t) - 2 \int_1^{x+1} E(y, t) dy & x < 1. \end{cases} \quad (2.8)$$

For  $x > 1$ , the first term on the right in Eq. (2.8) accounts for adsorption events that lie completely within the interval, while the second term accounts for adsorption events that partially overlap the interval. A similar correspondence also applies for the second line of (2.8).

As an pedagogical digression, we write the master equations for the void density  $V(x, t)$

$$\frac{\partial V(x, t)}{\partial t} = \begin{cases} -(x-1)V(x, t) + 2 \int_{x+1}^{\infty} V(y, t) dy & x > 1 \\ +2 \int_{x+1}^{\infty} V(y, t) dy & x < 1, \end{cases} \quad (2.9)$$

to appreciate the correspondence with the master equation for the empty interval probabilities. For  $x > 1$  the first term accounts for adsorption in the interior of an interval of length  $x$  and it has the same form as in Eq. (2.8). The second term accounts for the creation of an  $x$  void by the ‘‘fragmentation’’ of an  $(x+1)$ -void by adsorption inside this larger void. There are exactly 2 locations for this adsorption event to give rise to an  $x$ -void. For  $x < 1$ , there is no loss term because adsorption cannot occur inside such a short void, but there still a gain term due to the fragmentation of a void of length  $x+1$  or greater.

To solve this master equation for  $E(x, t)$ , consider first the regime  $x > 1$ . As in the discrete case, we seek a solution of the form  $E(x, t) = e^{-(x-1)t} E(1, t)$ . Substituting this expression into the first of Eqs. (2.8), the  $x$ -dependent terms cancel, and integrating the resulting equation for  $E(1, t)$  gives

$$E(1, t) = \exp \left[ -2 \int_0^t \frac{1 - e^{-u}}{u} du \right], \quad (2.10)$$

which immediately gives  $E(x, t)$  for  $x > 1$ . From the second of Eqs. (2.8), we have  $\frac{\partial E(0, t)}{\partial t} = -E(1, t)$ , from which the coverage  $\rho(t) = 1 - E(0, t)$  is

$$\rho(t) = \int_0^t \exp \left[ -2 \int_0^v \frac{1 - e^{-u}}{u} du \right] dv. \quad (2.11)$$

For  $t \rightarrow \infty$ , numerical evaluation of this integral gives the jamming coverage  $\rho(\infty) = 0.747597\dots$

A qualitative new feature of continuum car parking is that the approach to jamming is slower than for adsorption of discrete molecules. Let’s examine how the deviation from the asymptotic coverage,  $\rho(\infty) - \rho(t)$ , vanishes as  $t \rightarrow \infty$ :

$$\begin{aligned} \rho(\infty) - \rho(t) &= \int_t^{\infty} \exp \left[ -2 \int_0^v \frac{du}{u} (1 - e^{-u}) \right] dv \\ &\sim \int_t^{\infty} \exp \left[ -2 \int_1^v \frac{du}{u} \right] dv \\ &\sim \int_t^{\infty} \frac{dv}{v^2} = \frac{1}{t}. \end{aligned} \quad (2.12)$$

The simplification in the second line results by replacing the smooth cutoff function  $1 - e^{-u}$  by a step cutoff that equals 0 for  $u < 1$  and equals 1 for  $u > 1$ . Then the integral in the exponent is elementary and the

asymptotic behavior follows straightforwardly. More precisely, the asymptotic behavior of the integral in Eq. (2.10) is

$$\int_0^t du \frac{1 - e^{-u}}{u} = \ln t + \gamma + t^{-1}e^{-t} + \dots,$$

where  $\gamma = 0.577215\dots$  is Euler's constant. Thus

$$\rho(\infty) - \rho(t) \rightarrow t^{-1} e^{-2\gamma} \quad t \rightarrow \infty;$$

the approach to jamming is slower on continuous substrates than on discrete substrates.

## 2.2 Adsorption in Higher Dimensions

Most applications of irreversible adsorption involve two-dimensional substrates. It is natural to begin with the adsorption of elementary objects such as disks, squares, rectangles, and sticks as a prelude to real systems, such as proteins and latex particles. To get a feeling for numbers, the jamming coverages for random sequential adsorption of various elementary objects in two dimensions are listed in Table 2.1. An exact analysis of adsorption is generally not possible in higher dimensions, and one has to resort to approximations and numerical simulations. Nevertheless, the evolution of the coverage in arbitrary dimensions has the same qualitative features as in one dimension. Namely, relaxation to the jamming density is exponential in time on discrete substrates and algebraic on continuous ones. Moreover, fluctuations in the number of adsorbed particles are extensive, *i.e.*, proportional to the area, while different jammed configurations are realized with different likelihoods and the dynamics is non ergodic.

object	substrate	$\rho_{\text{jam}}$
unoriented dimers	square lattice	0.9068
$2 \times 2$ squares	square lattice	0.74788
(aligned) squares	continuum	0.562009
disks	continuum	0.5472

Table 2.1: Jamming coverages for various objects in two dimensions.

### Discrete substrates

Adsorption is exactly soluble for one special high-dimensional substrate — the Bethe lattice, in which each site is connected to exactly  $z$  other sites in a tree structure (Fig. 2.5). For dimer adsorption on the Bethe lattice, the fundamental quantities are not the empty intervals of length  $\geq m$ , but rather empty connected *clusters* of  $\geq m$  sites that we again write as  $E_m$ . Because these clusters have a tree structure, it is straightforward to count the “boundary” configurations that enter into the master equations for  $E_m$ .

The probability  $E_m$  that all sites in an  $m$ -cluster remain vacant during dimer adsorption satisfies the master equation [compare with Eq. (2.2)]

$$\frac{dE_m}{dt} = -(m-1)E_m - [(z-2)m+2]E_{m+1}, \quad (2.13)$$

for  $m \geq 1$ , with the initial conditions  $E_m(0) = 1$ . The first term on the right accounts for deposition events in which the dimer lands somewhere within the cluster. The number of available locations for such “interior” adsorption events is just the number of bonds in the cluster. Since any cluster has a tree topology, its number of bonds is  $m-1$ . The second term accounts for adsorption events in which the dimer lands with one site in the cluster and one site outside. The number of ways that such an event can occur equals the number of cluster perimeter sites — sites that adjoin the cluster, but are not part of the cluster itself (Fig. 2.5). An important feature is that the number of perimeter sites to an  $m$ -cluster is always  $zm - 2(z-1)$ , *independent* of the topology of the cluster. This fact can be understood inductively: for a cluster of 2 sites, the number of perimeter sites is  $2(z-1)$ . When a site is added to the cluster, one perimeter site is lost, but  $(z-1)$  perimeter sites are gained. Continuing this counting for a cluster of  $m$  sites, the number of perimeter sites is  $zm - 2(z-1)$ .

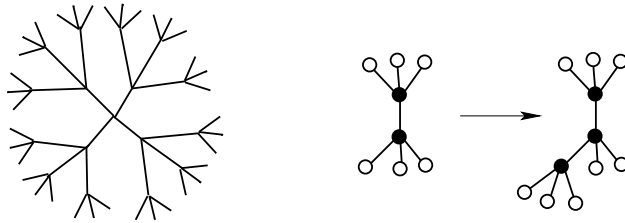


Figure 2.5: (Left) First three generations of a Bethe lattice with coordination number  $z = 4$ . (Right) Counting perimeter sites (circles) starting with a connected cluster of  $m = 2$  and 3 sites (dots).

### A second look at exponential solutions (continued from page 5, Sec. 1.1)

Consider a master equation of the generic form

$$\frac{dE_m}{dt} = \lambda(m + \alpha)E_m + \mu(m + \beta)E_{m+1}, \quad (2.14)$$

that encompasses Eq. (2.13). Again, the exponential ansatz provides an easy route to the solution. Let's assume that  $E_m$  has the form

$$E_m = \Phi(t)[\varphi(t)]^m. \quad (2.15)$$

Substituting into Eq. (2.14) and then dividing by  $E_m$  gives

$$\frac{\dot{\Phi}}{\Phi} + m\frac{\dot{\varphi}}{\varphi} = \lambda(m + \alpha) + \mu(m + \beta)\varphi.$$

This result shows the utility of the ansatz (2.15), as the above equation divides naturally into terms linear in  $m$  and terms independent of  $m$ .

From the terms linear in  $m$ , we have

$$\frac{\dot{\varphi}}{\varphi} = \lambda + \mu\varphi, \quad (2.16)$$

from which we obtain  $\varphi(t)$ . The  $m$ -independent terms give

$$\frac{\dot{\Phi}}{\Phi} = \lambda\alpha + \mu\beta\varphi, \quad (2.17)$$

which then gives  $\Phi(t)$ , after which the original problem is solved.

The essential point is that the factor  $\varphi^m$  in the original ansatz separates the initial set of equations (2.15) into two equations: one linear in  $m$  and one independent of  $m$ .

To solve the master equation (2.13), we again apply the exponential ansatz  $E_m(t) = [\varphi(t)]^{m-1} \Phi(t)$  with  $\varphi(0) = \Phi(0) = 1$  to match the initial condition (see the box on the next page). With this ansatz, the hierarchy of rate equations reduces to the pair of coupled differential equations

$$\frac{d\varphi}{dt} = -\varphi - (z-2)\varphi^2 \quad \frac{d\Phi}{dt} = -z\varphi\Phi,$$

whose solutions are  $\varphi = e^{-t}[(z-1) - (z-2)e^{-t}]^{-1}$  and  $\Phi(t) = [(z-1) - (z-2)e^{-t}]^{-z/(z-2)}$ . Consequently, the empty cluster probabilities are

$$E_m(t) = e^{-(m-1)t} [(z-1) - (z-2)e^{-t}]^{-m-2/(z-2)}. \quad (2.18)$$

The approach to the jamming coverage is exponential in time, with the jamming coverage equal to

$$\rho_{\text{jam}} = 1 - (z-1)^{-z/(z-2)}. \quad (2.19)$$

In the limit  $z \downarrow 2$ , the one-dimensional result,  $\rho_{\text{jam}} = 1 - e^{-2}$ , is recovered, while for large  $z$ , the uncovered fraction is inversely proportional to the coordination number,  $1 - \rho_{\text{jam}} \sim z^{-1}$ . Amusingly, the Bethe lattice



provides a good approximation for  $\rho_{\text{jam}}$  for a regular lattice with the same coordination number. For example, when  $z = 4$ , dimer adsorption on the Bethe lattice gives  $\rho_{\text{jam}} = 8/9$ , while for the square lattice,  $\rho_{\text{jam}} \approx 0.9068$ .

For discrete substrates in arbitrary spatial dimension, we can give only a heuristic argument that the relaxation to the jamming coverage decays exponentially in time

$$\rho_{\text{jam}} - \rho(t) \sim e^{-\lambda t}. \quad (2.20)$$

As a concrete example, consider dimer adsorption on the square lattice. At long times, the available spaces that can accommodate additional dimers are few and far between. These “target” regions are small continuous clusters of unoccupied sites: dimers, trimers (both linear and bent),  $2 \times 2$  squares, *etc.* To determine the rate at which these “lattice animals” get filled, we need the probabilities that these various configurations are empty. A basic fact is that the probability to find a vacant cluster on the substrate rapidly decreases with its size at long times. Thus only the smallest empty lattice animals persist and their asymptotic decay is dominated by the adsorption of dimers *inside* the animal. Thus for dimer adsorption on the square lattice, the probabilities of the lowest-order configurations (dimers, trimers, and  $2 \times 2$  squares) evolve according to

$$\frac{d}{dt} P[\circ\circ] \sim -P[\circ\circ], \quad \frac{d}{dt} P[\circ\circ\circ] \sim -2P[\circ\circ\circ], \quad \frac{d}{dt} P\left[\begin{smallmatrix} \circ\circ \\ \circ\circ \end{smallmatrix}\right] \sim -4P\left[\begin{smallmatrix} \circ\circ \\ \circ\circ \end{smallmatrix}\right].$$

Here, we use the shorthand  $P[\cdot]$  to denote the likelihood of a configuration, and the numerical prefactor counts the number of ways that a dimer can adsorb within the cluster. The time dependence of these configurations therefore evolve as

$$P[\circ\circ] \sim e^{-t}, \quad P[\circ\circ\circ] \sim e^{-2t}, \quad P\left[\begin{smallmatrix} \circ\circ \\ \circ\circ \end{smallmatrix}\right] \sim e^{-4t}. \quad (2.21)$$

Generally, the probability that a given lattice animal is empty decays exponentially in time,  $P(t) \sim e^{-\lambda t}$ , where  $\lambda$  counts the number of ways that a dimer can adsorb within a particular lattice animal. In particular, the coverage is determined by the rate equation  $d\rho/dt \sim -2P[\circ\circ]$ , so that

$$\rho_{\text{jam}} - \rho(t) \sim e^{-t}. \quad (2.22)$$

A similar exponential relaxation arises for the adsorption of arbitrarily-shaped objects on discrete substrates in any dimension.

## Continuous substrates

On continuous substrates, gaps between adjacent adsorbed objects can be arbitrarily small, and this feature leads to a slower algebraic relaxation of the density to the jamming density, in which  $\rho_{\text{jam}} - \rho(t) \sim t^{-\sigma}$ . For car parking in one dimension, we already demonstrated that  $\sigma = 1$  at the end of Sec. 2.1. Let’s derive the corresponding decay for the adsorption of disks in two dimensions. As the substrate approaches jamming, there will be only a few tiny and independent “target zones” within which the center of another disk can adsorb. To characterize these target zones, notice that around each disk there is an “exclusion zone” whose radius is twice that of the disk. An incident disk whose center lies within the exclusion zone of any already adsorbed disk cannot adsorb. The target zones are therefore the complement of the exclusion zones on the substrate (Fig. 2.6). In a jammed configuration, no target zones remain even though the adsorbed particles do not completely cover the substrate.

Let  $c(\ell, t)$  be the density of target zones of linear size  $\ell$ . Because the area of such a target zone is quadratic in  $\ell$ , the density of targets of linear size  $\ell$  obeys  $dc/dt \sim -\ell^2 c$ , leading to the exponential decay

$$c(\ell, t) \sim e^{-\ell^2 t}. \quad (2.23)$$

Since each disk has the same area, the deviation of the substrate coverage from its jamming value is just proportional to the area fraction of the target zones:

$$\rho_{\text{jam}} - \rho(t) \sim \int_0^\infty c(\ell, t) d\ell \sim \int_0^\infty e^{-\ell^2 t} d\ell \sim t^{-1/2}. \quad (2.24)$$

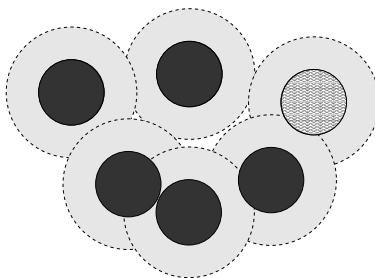


Figure 2.6: Two target areas (white), the exclusion zones (shaded), and the adsorbed disks (dark) near jamming. In the long-time limit only arc-triangular target areas, such as the tiny one on the left, remain.

Because target zones can be arbitrarily small, a power-law decay arises after rescaling the integral. Although the probability to find a target zone of a given size vanishes exponentially with time, the average over the sizes of all target zones leads to a power-law tail. This heuristic approach can be straightforwardly extended to arbitrary spatial dimension  $d$ . Now the area of a target zone of linear dimension  $\ell$  scales as  $\ell^d$ , and the corresponding, the density of target zones of linear dimension  $\ell$  scales as  $c(\ell, t) \sim e^{-\ell^d t}$ . The analog of Eq. (2.24) then gives  $\rho_{\text{jam}} - \rho(t) \sim t^{-1/d}$  in  $d$  dimensions.

## 2.3 Extensions and Applications

Thus far, we've focused on irreversible adsorption — once a particle adsorbs, it is immobile. Furthermore, we tacitly assumed that the only interaction is geometrical exclusion in which the adsorption probability depends only on the existence of sufficient empty space to accommodate an incoming particle, and not on the distance to previously-adsorbed particles. Both of these assumptions are idealizations of reality, however, and we now study physically-motivated extensions in which these assumptions are relaxed.

### Reversible car parking

In reality, an adsorbed molecule has a finite binding energy to the substrate. If a fixed density of molecules is maintained in a gas phase above the substrate, then *reversible* adsorption-desorption occurs: molecules adsorb with a rate  $k_+$  and desorb with a rate  $k_-$  that depends on the ratio of the binding energy to the temperature. It is fun to think of the monomers as cars that are trying to park at non-specific positions along a one-dimensional curb (Fig. 2.7) because we all know it is hard to find a good parking spot. If the rate at which cars leave (desorb) is small, the probability to find a parking spot also becomes small. The surprising aspect of parking is that the car density approaches the limit of complete packing as the desorption rate goes to zero, whereas the coverage is significantly less than complete for no desorption.

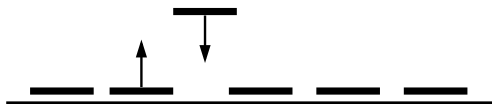


Figure 2.7: Adsorption-desorption of cars. Desorption attempts are always allowed, while the adsorption attempt shown fails because of insufficient parking space.

A physical motivation for studying reversible adsorption is its connection to granular compaction. Suppose that identical glass beads are placed randomly into a jar one at a time. The density of filled space in this bead packing — approximately 0.58 — is known as the *random packing density*. If this bead-filled jar is then vibrated vertically at a suitable intensity and frequency, the density will slowly increase and eventually reach the *random close-packing density* of approximately 0.68. The vibrations lead to occasional collective re-arrangements that allows a bead to “park” within an empty interstitial space that previously too small to

accommodate the bead. As the density increases, re-arrangements involve progressively larger regions and become rarer. The time scale over which this compaction occurs can be as long as months! This random close packing-density is still smaller than the maximal density of  $\pi/\sqrt{18} \approx 0.7405$  for a face-centered cubic lattice packing of spheres.

As we now discuss, this slow compaction can be captured in terms of reversible car parking. As a preliminary, consider the trivial example of monomers that adsorb onto and desorb from single sites on the substrate. The density of adsorbed particles  $\rho$  satisfies the Langmuir equation

$$\frac{d\rho}{dt} = -k_- \rho + k_+(1 - \rho), \quad (2.25)$$

*i.e.*, adsorption proportional to the vacancy density and desorption proportional to the adsorbate density. The time dependence of the density is

$$\rho(t) = \rho_\infty + (\rho_0 - \rho_\infty) e^{-t/\tau}, \quad (2.26)$$

with relaxation time  $\tau = (k_+ + k_-)^{-1}$  and final coverage  $\rho_\infty = k_+/(k_+ + k_-)$ . Notice that when  $h \equiv k_+/k_- \rightarrow \infty$ , the asymptotic coverage is  $\rho_\infty \approx 1 - h^{-1}$  is reached in a time  $\tau \simeq h^{-1}$ .

For the master equation for reversible car parking, it is more convenient to work with the density of voids of length  $x$  at time  $t$ ,  $V(x, t)$ , rather than the density of empty intervals  $E(x, t)$ . These master equations are (compare with Eq. (2.9)):

$$\frac{\partial V(x, t)}{\partial t} = \begin{cases} -k_+(x-1)V(x, t) + 2k_+ \int_{x+1}^{\infty} V(y, t) dy \\ -2k_- V(x, t) + \frac{k_-}{\int_0^{\infty} V(x, t) dx} \int_0^{x-1} V(y, t) V(x-y-1, t) dy & x > 1; \\ +2k_+ \int_{x+1}^{\infty} V(y, t) dy - 2k_- V(x, t) & x < 1. \end{cases} \quad (2.27)$$

The adsorption terms are just as previously written in Eq. (2.9) for irreversible adsorption. The term  $-2k_- V(x, t)$  accounts for the loss of an  $x$ -void because of the desorption of a car at either end of the void. The last term for  $x > 1$  accounts for the creation of an  $x$ -void when a unit-length car leaves a parking spot that has an empty space of length  $y$  at one end of the car and a space  $x - y - 1$  at the other end. The correct way to express the probability for this composite event is through a 3-body correlation function. However, this description is not closed, as the void evolution is coupled to a 3-body function, and then the evolution of the 3-body correlation function involves higher-body correlations, *ad infinitum*. To break this hierarchy in the simplest manner, we invoke the mean-field assumption that the 3-body correlation function for a car to be flanked by voids of length  $y$  and  $x - y - 1$  is the product of single-void densities. The factor  $\int_0^{\infty} V(x, t) dx$  in the denominator properly normalizes the probability that the neighbor of a  $y$ -void has length  $x - y - 1$ .

It is not feasible to solve the master equations (2.27) directly, but we can glean the most interesting results by physical reasoning and judicious approximations. First, since there is a one-to-one correspondence between voids and adsorbed particles, the density of voids of any size equals the car density; consequently  $\int_0^{\infty} V(x, t) dx = \rho$ . Also, any point on the line is either occupied by a car or is part of a void; thus  $1 = \int_0^{\infty} (x+1) V(x, t) dx$ . Because each adsorption and desorption event changes the overall density by the same amount, the rate equation for the total density is

$$\frac{\partial \rho}{\partial t} = -k_- \rho + k_+ \int_1^{\infty} (x-1) V(x, t) dx. \quad (2.28)$$

The interpretation of this generalization of the Langmuir equation (2.25) is straightforward: with rate  $k_- \rho$ , a parked car desorbs, thereby decreasing the density, while the second term accounts for the increase in density by the parking of a car in a space of length  $x > 1$ ; this same equation can also be obtained by integrating the master equations (2.27) over all lengths.

Let's now determine the steady-state coverage. For  $x < 1$ , the steady-state master equation (2.27) relates the void density to its spatial integral suggests the exponential solution  $V(x) = Ae^{-\alpha x}$ . Using this ansatz in the master equation for  $x < 1$  gives

$$h \equiv \frac{k_+}{k_-} = \alpha e^\alpha. \quad (2.29)$$

The normalization condition  $\int (x+1) V(x) dx = 1$  then gives the amplitude  $A = \alpha^2/(\alpha+1)$ . Thus the parked car density is

$$\rho = \int V(x) dx = \frac{\alpha}{\alpha+1}, \quad (2.30)$$

and eliminating  $\alpha$  in favor of  $\rho$ , the probability to find a parking space of length  $x$  is

$$V(x) = \frac{\rho^2}{1-\rho} e^{-\rho x/(1-\rho)}. \quad (2.31)$$

From Eqs. (2.29) and (2.30), the steady-state density has the following limiting behaviors:

$$\rho(h) \approx \begin{cases} h & h \rightarrow 0; \\ 1 - [\ln h]^{-1} & h \rightarrow \infty. \end{cases} \quad (2.32)$$

When desorption dominates over adsorption, plenty of parking spaces are available and the density of parked cars is simply proportional to the adsorption rate. Conversely, for a large adsorption rate exclusion dominates because parking places are typically too small to accommodate another car. Even though most parking attempts fail, the limiting behavior is  $\rho \rightarrow 1$  as  $h \rightarrow \infty$  (albeit quite slowly), because a small desorption rate eventually allows wasted space to be filled. However, analogous to the previous example of cooperative monomer adsorption, the behavior in the limit  $h \rightarrow \infty$  is different than that when  $h = \infty$  at the outset. For the latter case, there is no mechanism to utilize too-small parking spaces and the jamming density is  $\rho_{\text{jam}} = 0.747597\dots$

Finally, let's study how the time dependence of the density of parked cars for large  $h$  (or  $k_- \rightarrow 0$ ). This is the *desorption-controlled* limit in which any vacated parking space is immediately refilled and only the voids are altered. Thus desorption is effectively canceled out. Because of their rapid re-arrangement, voids are nearly in the steady state. Thus we use the steady-state void density (2.31) in the rate equation (2.28) to obtain the following effective equation for the evolution of the parked car density

$$\frac{d\rho}{dt} \approx k_+(1-\rho) e^{-\rho/(1-\rho)}. \quad (2.33)$$

To solve this equation, we write  $g = 1/(1-\rho)$  to give by  $dg/d(k_+t) \approx e^{-g}$  to lowest order, whose solution gives the logarithmic decay law

$$\rho(t) \sim 1 - (\ln k_+t)^{-1}. \quad (2.34)$$

Comparing with Eq. (2.28), the factor  $e^{-\rho/(1-\rho)}$  can be viewed as an effective sticking probability. We can understand its meaning by the following heuristic argument. For a nearly-full system, we may write the density as  $\rho = 1/(1+\langle x \rangle)$  where  $\langle x \rangle \ll 1$  represents the small average distance between neighboring parked cars. On a time scale of the order of  $1/k_-$  a car leaves a parking space and is typically immediately refilled. However, on a much larger time scale, the departure of parked car can lead to 2 spots opening up. Such a happy event occurs by a collective re-arrangement of  $N = \langle x \rangle^{-1} = \frac{\rho}{1-\rho}$  parked cars: the first moves forward by  $\langle x \rangle$ , the second by  $2\langle x \rangle$ , the third by  $3\langle x \rangle$ , *etc.*, until a space of length one is generated. The probability of this cooperative rearrangement decays exponentially in the number of cars, so that the effective sticking probability  $S \sim e^{-N} \sim e^{-\rho/(1-\rho)}$ . The essential point is that the collective nature of the rearrangements are responsible for the slow relaxation of the density.

## Assisted Polymer Translocation

A particularly appealing application of adsorption kinetics is to assisted translocation of a polymer through a small pore in a membrane. By diffusion alone, any biologically-relevant polymer would pass through a

pore too slowly to be relevant for cellular processes. One way to speed up translocation is to rectify diffusive fluctuations so that backwards motion is inhibited. As we now discuss, chaperone-assisted translocation provides a simple example of this rectification mechanism.

Consider a straight polymer chain of length  $L$  that passes through a pore in a membrane. By thermal fluctuations the polymer diffuses isotropically along its length with diffusion coefficient  $D$ . The medium on the right side of the membrane contains a fixed density of special molecules — “chaperones” — that adsorb irreversibly onto unoccupied adsorption sites of the polymer with rate  $\lambda$ . A chaperone is sufficiently large that it cannot pass through the pore. As a result, the chaperones rectify the polymer diffusion so that it passes through the pore at a non-zero speed  $V$ . The goal is to calculate this translocation speed as function of  $D$  and  $\lambda$ .

We can understand the dependence of  $V$  on the control parameters  $\lambda$  heuristically. Let  $\tau$  be the typical time between adsorption events within the leftmost chaperone-free segment of the polymer (Fig. 2.8). The polymer diffuses a distance  $\ell \sim \sqrt{D\tau}$  during this time. On the other hand, the time between adsorption events in this leftmost segment is  $\tau \sim 1/(\lambda\ell)$ . Combining these two relations, we have  $\tau \sim (D\lambda^2)^{-1/3}$  and  $\ell \sim (D/\lambda)^{1/3}$ . On dimensional grounds, the translocation speed should therefore scale as

$$V \sim \frac{\ell}{\tau} \sim D^{2/3} \lambda^{1/3} . \quad (2.35)$$

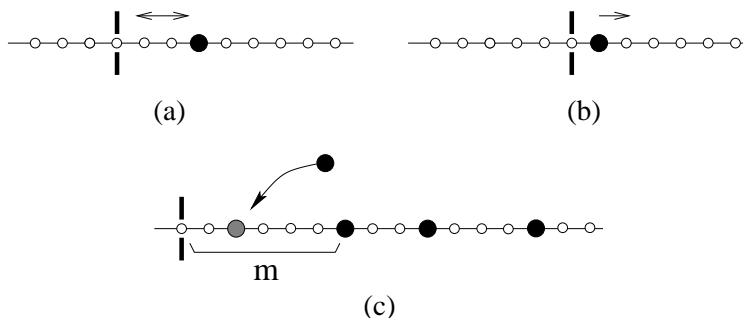


Figure 2.8: Illustration of chaperone-assisted translocation. (a) The polymer can hop in either direction. (b) The polymer can hop only to the right because an adsorbed chaperone (large dot) is next to the pore (gap in the barrier) and too large to enter. (c) Adsorption of a new chaperone (shaded) within the leftmost chaperone-free segment.

We can calculate  $V$  precisely in terms of the dynamics of the leftmost chaperone-free segment  $[1, m]$  of the polymer. The length  $m$  of this segment can: (i) change by  $\pm 1$  due to polymer hopping (with a reflecting constraint at  $m = 1$ ), or (ii)  $m$  can equiprobably change to any value in  $[1, m - 1]$  due to adsorption (Fig. 2.8). Consequently, the polymer advances only when a chaperone is at the site next to the pore and diffuses isotropically otherwise. The speed is therefore equal to the probability  $Q_1(\lambda, t)$  that the closest chaperone is adjacent to the pore at time  $t$ . However, to compute  $Q_1(\lambda, t)$ , we need the infinite set of probabilities

$$Q_j(\lambda, t) = \text{Prob}\{|\underbrace{\circ \dots \circ}_{j-1} \bullet\}$$

that the leftmost chaperone is a distance  $j$  from the pore; the symbol  $|$  denotes the pore,  $\circ$  an empty site, and  $\bullet$  an occupied site. These probabilities evolve according to

$$\begin{aligned} \frac{dQ_1}{dt} &= Q_2 - Q_1 + \lambda \sum_{k>1} Q_k \\ \frac{dQ_j}{dt} &= Q_{j-1} + Q_{j+1} - 2Q_j + \lambda \sum_{k>j} Q_k - \lambda(j-1)Q_j \quad j > 1. \end{aligned} \quad (2.36)$$

Here the hopping rate has been set to 1, corresponding to a diffusion coefficient  $D = \frac{1}{2}$ . In the first line, the factor  $Q_2$  accounts for the gain in  $Q_1$  due to the polymer hopping to the left with the leftmost chaperone at  $m = 2$ , while the factor  $-Q_1$  accounts for the loss of  $Q_1$  when the polymer hops to the right with the leftmost chaperone at  $m = 1$ . The last term accounts for the gain in  $Q_1$  due to chaperone adsorption at the site next to the pore. In the second line, the first three terms account for changes in  $Q_j$  due to hopping, while the next two terms account for changes due to adsorption. The last term accounts for the  $j - 1$  ways that adsorption can occur within an interval of length  $j$ , thereby decreasing  $Q_j$ .

In the long-time limit, a steady state is reached and the left-hand sides of (2.36) vanish. To simplify the equation for  $Q_j$  with  $j > 1$ , we sum it over all  $j$ . After simple steps, these two equations reduce to the single equation

$$Q_{m-1} - Q_m - \lambda(m-1) \sum_{j \geq m} Q_j = 0, \quad (2.37)$$

for all  $m$ . In keeping with our introductory discussion of section 2.1, we instead work with the empty interval probabilities

$$E_m = \text{Prob}\{\underbrace{|\circ \dots \circ|}_m\},$$

that are related to the segment probabilities  $Q_m$  by  $E_m = \sum_{j > m} Q_j$ . In term of the  $E_m$ , Eq. (2.37) become

$$E_{m-1} + E_{m+1} - (2 + m\lambda)E_m = 0. \quad (2.38)$$

We should solve this equation subject to the normalization requirement  $E_0 = \sum_{j \geq 1} Q_j = 1$  and then extract the speed from  $V = Q_1 = 1 - E_1$ .

Equation (2.38) is the discrete analog of an Airy equation and it admits a compact solution in terms of Bessel functions. We start with the well-known identity for the Bessel functions:

$$J_{\nu-1}(z) + J_{\nu+1}(z) - \frac{2\nu}{z} J_{\nu}(z) = 0.$$

Comparing with Eq. (2.38), we must have

$$\frac{2\nu}{z} J_{\nu}(x) = (2 + m\lambda)E_m(\lambda) = 2 \frac{m + 2/\lambda}{2/\lambda} E_m(\lambda).$$

Thus we identify  $\nu = m + 2/\lambda$  and  $z = 2/\lambda$ . While there is ostensibly one condition to fix  $\nu$  and  $z$ , the choice is unique because the difference between two successive indices must be an integer. Finally, requiring  $E_0 = 1$  gives the solution:

$$E_m = \frac{J_{m+2/\lambda}(2/\lambda)}{J_{2/\lambda}(2/\lambda)}, \quad (2.39)$$

from which the translocation speed is

$$V = 1 - E_1 = 1 - \frac{J_{1+2/\lambda}(2/\lambda)}{J_{2/\lambda}(2/\lambda)}. \quad (2.40)$$

The limiting behaviors of this translocation speed are instructive. In the small- $\lambda$  limit, we use the asymptotic formula that relates the Bessel function to the Airy function:

$$J_a(a+x) = \left(\frac{2}{a}\right)^{1/3} \text{Ai}(0) - \left(\frac{2}{a}\right)^{2/3} \text{Ai}'(0)x + \dots \quad a \rightarrow \infty, \quad (2.41)$$

where  $\text{Ai}(0) = [3^{2/3}\Gamma(2/3)]^{-1}$  and  $\text{Ai}'(0) = -[3^{1/3}\Gamma(1/3)]^{-1}$ , to give

$$V \simeq -\frac{\text{Ai}'(0)}{\text{Ai}(0)} \lambda^{1/3} = \frac{3^{1/3}\Gamma(2/3)}{\Gamma(1/3)} \lambda^{1/3}. \quad (2.42)$$

Conversely, for large  $\lambda$ ,  $V \rightarrow 1$ .