Chapter 5

ADSORPTION

In this chapter, we investigate the kinetics of adsorption in which molecules from a gas impinge upon a substrate and ultimately get adsorbed. By substrate, we usually mean an infinite flat surface in which it is energetically favorable for a site on the surface to bind an incident molecule. A basic question is: what is the rate at which the substrate get filled by the adsorbed molecules? If the incident molecules are monomers that permanently attach to single adsorption sites on the substrate and if there are no interactions between neighboring adsorbed monomers, then the fraction ρ of occupied sites evolves by the rate equation

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

That is, the rate of increase of occupied sites is simply proportional to the density of vacancies. Here r is the intrinsic adsorption rate that we will take to be 1 in this chapter. The solution to this rate equation is $\rho(t) = 1 - e^{-t}$; thus vacancies disappear exponentially in time and the substrate eventually becomes completely filled.

However, if each arriving molecule covers $k > 1$ sites on the substrate, then an unfilled region of less than k vacant sites can never be filled. Now the basic questions are: what is the filling fraction of the final *jammed* substrate and what is the rate at which this final fraction is achieved? Here a jammed state is one in which the substrate cannot accommodate any additional adsorption, even though it is not completely filled. The final substrate coverage is a quantity that occupied much attention and effort in the past. As we discuss in this chapter, questions about jamming can be answered completely for a one-dimensional substrate. The route to obtaining the jamming coverage is a bit indirect, however. Instead of seeking the jamming coverage directly, we will apply a kinetic approach and investigate the full time dependence of the coverage of the substrate. The techniques for determining this time dependence are quite beautiful and have a close relation with those used to treat fragmentation. A surprising feature of the kinetic approach is that the ultimate coverage of the substrate emerges as a byproduct.

When the dimension of the substrate is two or higher, the full solution for the evolution of the coverage is currently beyond the reach of current techniques. Here we will present qualitative, but general results about the approach to the final jammed state. We conclude this chapter with a discussion of adsorption processes with secondary relaxation mechanisms, such as desorption or the diffusion of adsorbed molecules on the substrate. When these processes are slow compared to the rate at which incoming particles hit the surface (as is often the case physically), the substrate gradually becomes even more filled as the relaxation processes create vacancies that can accommodate additional adsorption.

5.1 Random Sequential Adsorption in One Dimension

Kinetics of small-molecule 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 a one-dimensional lattice. Unless otherwise indicated, the size of the lattice is taken as infinite. While almost all physical adsorption processes occur on two-dimensional substrates, the one-dimensional system is an instructive laboratory upon which we can develop the tools to understand how a substrate gets filled. Starting with an initially empty substrate, adsorption attempts are made one at a time. An adsorption event is successful only if a dimer is incident two adjacent empty sites. (Fig. 5.1). If a dimer attempts to land onto either two occupied sites or onto one occupied and one empty site, the attempt is rejected. The coverage of dimers in this random sequential adsorption grows with time and eventually only isolated empty sites remain. At this point, the substrate is jammed and no further adsorption is possible.

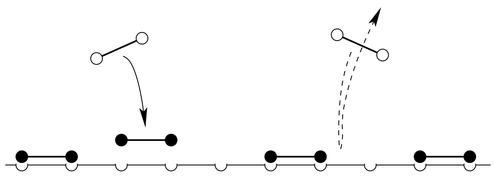

Figure 5.1: Illustration of irreversible dimer deposition. The dimer on the left will successfully adsorb onto two adjacent vacant sites on the substrate, while the dimer on the right does not adsorb.

For dimer deposition, a jammed state consists of strings of an even number of occupied sites (•) that are separated by isolated vacant sites (◦), such as:

Figure 5.2: A typical jammed configuration in random sequential adsorption of dimers.

Since multilayer adsorption is not allowed, each site is either empty or contains 1 particle, but no more. In principle, the fraction of occupied sites in the jammed state, $\rho_{\rm jam} = \rho(t = \infty)$, can have any value between 2/3 and 1, with the two extreme limits achieved by the respective configurations

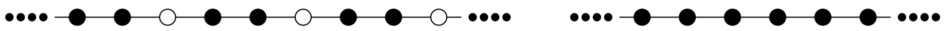

Figure 5.3: Minimum-density and maximum-density jammed dimer configurations.

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

$$\rho_{\rm jam} \equiv \rho(t = \infty) = 1 - e^{-2} = 0.864\,664\ldots \tag{5.1}$$

While Flory's original derivation was based on enumerating all possible final state configurations, here we adopt the kinetic viewpoint and determine the time evolution of the coverage. The final coverage will then emerge as a direct consequence. To fully characterize the configuration of the substrate, we need, in principle, the probabilities $P(\mathbf{n}, t)$ for the occupation state of each lattice site. Here $\mathbf{n} = \{n_j\}$, with $n_j = 1$ if the $j^{\rm th}$ site is occupied and $n_j = 0$ if this site is empty. It is possible to write master equations that govern these probabilities, but these equations are difficult, if not impossible to handle. Moreover, the probabilities $P(\mathbf{n}, t)$ contain "too much" information. If we merely seek the coverage of the lattice, this quantity can be obtained from the empty interval indicator function

$$e_m = (1 - n_j)(1 - n_{j+1}) \cdots (1 - n_{j+m-1}).$$

This indicator function equals 1 if m consecutive sites between j and $j + m - 1$ are all empty, and equals 0 otherwise. This indicator construction is a convenient way to characterize the surface coverage. As we shall see, the master equations for $E_m \equiv \langle e_m \rangle$, the probability that m arbitrary *consecutive* lattice sites are empty, are readily soluble. It bears emphasizing E_m specifies that an interval of length m is empty, but no constraint is imposed on the sites outside this interval; they could be either occupied or empty. More precisely, E_m is the probability of finding 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 if we can determine the empty interval probabilities, we can then obtain the particle density. This is one reason why the empty interval probabilities are so useful.

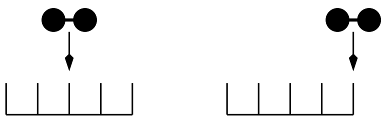

Figure 5.4: Changes in the empty interval probability E_n for $n = 4$. Shown are an adsorption event in the interior of the interval (left) and at the edge of the interval (right).

For the irreversible adsorption of dimers, the empty interval probabilities $E_m(t)$ satisfy the master equations

$$\frac{dE_m}{dt} = -(m-1)E_m - 2E_{m+1} \qquad m \geq 1. \tag{5.2}$$

The first term on the right side accounts for the loss of an m-interval due to the adsorption of dimers inside the interval. There are $m - 1$ distinct locations at which the dimer can adsorb such that it is entirely within the interval (Fig. 5.4). The second term accounts for the two adsorption events that eliminate an m-interval in which one end of the incident dimer is outside this interval. For these latter events, the empty interval must contain at least $m + 1$ empty sites, hence the factor E_{m+1}.

It needs to be emphasized that the master equation (5.2) contains only loss terms and no gain terms. This feature is a consequence of using the probability of finding an empty interval of length m or larger, E_m, as the basic dynamical variable. Pictorially, we are looking at the lattice through eyes that see only m consecutive sites at a time; E_m then merely counts 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 larger interval—if an empty interval of length $\geq m$ exists after the adsorption event, then it existed before the adsorption event. Thus there is no possibility of creating an empty interval of length $\geq m$ by dimer adsorption.

At this stage it is also worth mentioning that one could also write master equations for evolution of the system in terms of the *void density* V_m, defined as the probability of finding m consecutive empty sites that are bounded on either site by an occupied site, $\cdots\bullet\underbrace{\circ\circ\cdots\circ}_{m}\bullet\cdots$. There are no hard and fast rules for which set of quantities—E_m or V_m—are more useful. For adsorption problems the master equations for E_m and V_m are superficially similar, but typically the equations for E_m are somewhat easier to solve.

Returning to the adsorption problem, we now solve the master equations for the initial condition of an initially empty system is $E_m(0) = 1$, $\forall m$. First notice that an integrating factor for these equations is $e^{-(m-1)t}$. This fact suggests that we seek a solution of the form

$$E_m(t) = e^{-(m-1)t}\,\Phi(t), \tag{5.3}$$

with $\Phi(0) = 1$ to match the initial condition. With this ansatz, the infinite set of differential equations (5.2) miraculously reduces to the *single* equation $\frac{d\Phi}{dt} = -2e^{-t}\Phi$, whose solution immediately yields the empty interval probabilities

$$E_m(t) = e^{-(m-1)t-2\left(1-e^{-t}\right)}. \tag{5.4}$$

Empty gaps of length greater than 1 decay exponentially with time and only gaps of length 1 remain in the final jammed state.

We now have that the density of vacancies in the jammed state is $E_1(\infty) = e^{-2}$ and the jamming coverage is $\rho_{\rm jam} = \rho(\infty) = 1 - e^{-2}$, thus reproducing the classic Flory result with almost no labor. But we have much more—the coverage throughout the entire evolution:

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

The asymptotic approach to the jamming coverage is exponential in time, $\rho(\infty)-\rho(t)\to 2\,e^{-2}e^{-t}$; this exponential approach typifies lattice models of irreversible adsorption. The remarkable feature of the master equation approach is that it gives *all* the empty interval densities from the solution to just one equation.

What happens if the incident molecules occupy k consecutive sites (k-mers) on the substrate? A nice illustration of the power of the master equation is that the coverage for this more general adsorption can be obtained by the same empty interval method. For k-mer adsorption, the master equations for the empty interval probabilities E_m are

$$\frac{dE_m}{dt}=\begin{cases}-(m-k+1)E_m(t)-2\displaystyle\sum_{j=1}^{k-1}E_{m+j}(t) & m\geq k;\\[2ex] -(k-m+1)E_k(t)-2\displaystyle\sum_{j=1}^{m-1}E_{k+j}(t) & m<k.\end{cases}\tag{5.5}$$

The explanation for the terms in this equation mirrors that given for dimer adsorption (cf. Eq. (5.2)). In the first line, the first term on the right accounts for $m-k+1$ distinct ways that k-mer adsorption can occur in the interior of an m-site empty interval. The second term then accounts for $2(k-1)$ ways in which adsorption can occur with the k-mer partially outside and partially inside the original m-interval. For $m<k$, the first term accounts for the $k-m+1$ ways that the k-mer can cover the m-interval as well as $k-m$ sites outside the interval. The second term accounts for the ways in which the k-mer partially covers the interval.

For $m\geq k$, the structure of the master equations again suggests making the ansatz $E_m(t)=e^{-(m-k+1)t}\Phi(t)$; this reduces the master equations for $m\geq k$ to $\dot\Phi=-2\Phi\sum_{j=1}^{k-1}e^{-jt}$. Integrating this equation gives:

$$E_m(t)=\exp\Big[-(m-k+1)t-2\sum_{j=1}^{k-1}\frac{1-e^{-jt}}{j}\Big]\qquad m\geq k.\tag{5.6}$$

To obtain the time dependence of the coverage, $\rho=1-E_1$ we use the fact that $E_1(t)$ satisfies the master equation $dE_1/dt=-k\,E_k(t)$ and substitute in the solution of Eq. (5.6) for $m=k$. Thus the coverage $\rho=1-E_1$, may be expressed as the integral:

$$\rho(t)=k\int_0^t du\;\exp\Big[-u-2\sum_{j=1}^{k-1}\frac{1-e^{-ju}}{j}\Big].\tag{5.7}$$

Evaluating this integral numerically gives a jamming coverage that decreases monotonically with k (table 5.1 and Fig. 5.5). The jammed state becomes less full as k increases because empty regions as large as $k-1$ can arise.

k	$\rho_{\rm jam}$
1	1
2	0.864665
3	0.823653
4	0.803893
5	0.792276
∞	0.747597

Table 5.1: Jamming coverage for random sequential adsorption of k-mers in one dimension.

Irreversible car parking

The limit of k-mer adsorption with $k\to\infty$ corresponds to the *car parking* problem. In this limit, the position of an adsorbed k-mer becomes continuous and it is simpler to think of unit-length "cars" that irreversibly park anywhere along a one-dimensional curb (no marked parking spots) and then are abandoned forever. The

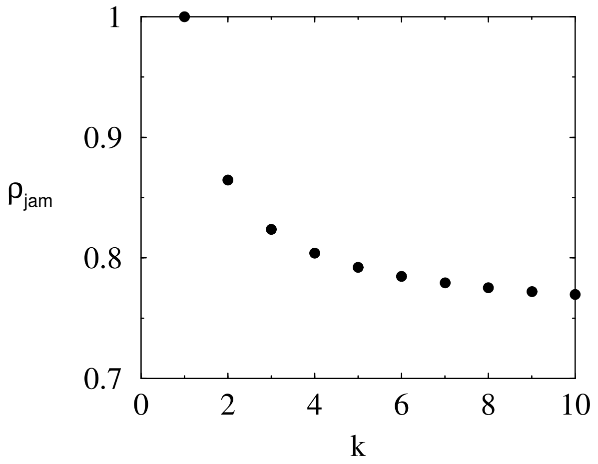

Figure 5.5: Jamming coverage for random sequential adsorption of k-mers in one dimension.

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, the jamming coverage—sometimes known as the *Rényi constant*—is $0.747597\ldots$. This coverage represents the $k \to \infty$ limit of the k-mer jamming coverage.

Let's solve this parking problem by the analog of the kinetic approach that we used to solve the random sequential adsorption of k-mers. The length of a car is immaterial if we seek the fraction of the line that is covered, and for convenience we choose a car length to equal 1. Instead of $E_m(t)$, we study with $E(x,t)$, 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. We could have studied empty intervals whose length is exactly specified, but this formulation leads to a more complicated master equation. When the rate at which cars park equals 1, the master equation for $E(x,t)$ is

$$\frac{\partial E(x,t)}{\partial t} = \begin{cases} -(x-1)E(x,t) - 2\displaystyle\int_x^{x+1} dy\, E(y,t) & x > 1 \\ \\ -(1-x)E(1,t) - 2\displaystyle\int_1^{x+1} dy\, E(y,t) & x < 1. \end{cases} \tag{5.8}$$

The meaning of the terms in the master equation is the same as the corresponding terms in the master equation (5.5) for random sequential adsorption of k-mers. In the first line of Eq. (5.57), the first term on the right accounts for adsorption events that lie completely within an interval of length $x > 1$, while the second term accounts for adsorption events that partially overlap the interval of length x. For the second line of (5.57), the first term accounts for adsorption events that completely cover the interval, while the second term accounts for partially covering events.

To solve the master equation, let's start with the first line. As in the discrete case, we seek a solution of the form

$$E(x,t) = e^{-(x-1)t}\, E(1,t) \tag{5.9}$$

Substituting (5.9) into the first of Eqs. (5.57), all the x-dependent term cancel, and integrating the resulting equation for $E(1,t)$ gives

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

Together with Eq. (5.9), we obtain the solution for $E(x,t)$ for $x > 1$. The second of Eqs. (5.57) may now be solved by substituting the solution for $E(x,t)$ into the integral. In particular, the equation for $E(0,t)$ is simply $\frac{\partial E(0,t)}{\partial t} = -E(1,t)$, from which the coverage $\rho(t) = 1 - E(0,t)$ is given by

$$\rho(t) = \int_0^t dv\, \exp\left[-2\int_0^v du\, \frac{1-e^{-u}}{u}\right]. \tag{5.10}$$

From the numerical evaluation of this integral, the jamming coverage in the car parking problem is $\rho(\infty) = 0.747598\ldots$.

A qualitative new feature of the continuum car parking problem is that the approach to the jamming coverage is much slower than for the adsorption of discrete molecules. To demonstrate this fact, let's examine $\rho(\infty) - \rho(t)$ for large t. In this limit, we may write

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

The crucial step occurs in the second line. As discussed in Section A.1, we replace the function $1 - e^{-u}$, which gradually crosses over from 0 to 1 as u passes through 1, by a step cutoff that equals 0 for $u < 1$ and equals 1 for $u > 1$. With this device, the integral in the exponent is elementary and the asymptotic behavior follows straightforwardly.

Combinatorics of dimer adsorption

As a complement to the kinetic description, we determine the jamming coverage by a combinatoric method. We present this approach so that the reader can appreciate the advantages and drawbacks of the kinetic and combinatoric viewpoints. In the combinatoric approach, we write a recursion for the jamming density on a finite interval of length L in terms of jamming densities on shorter intervals. In a sense to be discussed below, the calculation still has an evolutionary underpinning, but with the role of time now played by the interval length L.

For simplicity, we investigate dimer adsorption only. Let A_L by the number of sites that are occupied in the final jammed state averaged over all such states. If the first dimer lands on the sites $(i, i+1)$, then the remaining intervals of lengths $i-1$ and $L-i-1$ get filled independently. Therefore for $L \geq 2$, we can write the following recurrence for the coverage

$$A_L = \frac{1}{L-1}\sum_{i=1}^{L-1}(A_{i-1} + 2 + A_{L-i-1}). \tag{5.11}$$

That is, the number of occupied sites in the jammed state equals 2 for the initial dimer plus the sum of the number of sites occupied in the two remaining subintervals. A crucial element of this recursion is that it is based on adding dimers to the system one at a time. This evolution corresponds precisely to the adsorption process. Thus the final state of the system will be the same as the jamming density that was obtained previously by the master equation approach.

Obviously $A_0 = A_1 = 0$, and for $L \geq 2$ the two sums are identical, so that we can re-write (5.11) as

$$A_L = 2 + \frac{2}{L-1}\sum_{j=0}^{L-2} A_j. \tag{5.12}$$

To solve for A_L we introduce the generating function

$$A(x) = \sum_{L=2}^{\infty} A_L x^{L-2},$$

and then multiply (5.12) by $(L-1)\,x^{L-2}$ and sum over all L. For the left-hand side of (5.12), we have $\sum_2^\infty (L-1)\,x^{L-2}\,A_L = \frac{d(xA)}{dx}$. For the second term on the right-hand side, we interchange the order of summations (in close analogy with method to evaluate double integrals in Sec. 4.2) to give

$$\begin{aligned} 2\sum_{L=2}^{\infty} x^{L-2}\sum_{j=0}^{L-2} A_j &= 2\sum_{j=0}^{\infty} A_j \sum_{L=j+2}^{\infty} x^{L-2} \\ &= 2\sum_{j=0}^{\infty} A_j \frac{x^j}{1-x} \\ &= \frac{2x^2}{1-x}\,A(x). \end{aligned}$$

Using the above result, the recurrence can now be recast as the differential equation

$$\frac{d}{dx}(xA) = \frac{2}{(1-x)^2} + \frac{2x^2}{1-x}\,A\,.$$

This equation is subject to the initial condition $A(x=0) = A_2 = 2$. This equation can be solved by elementary techniques and the result is

$$A(x) = \frac{1-e^{-2x}}{x(1-x)^2}\,. \tag{5.13}$$

The small-x behavior of the generating function is $A(x) = 2 + 2x + \frac{10}{3}x^2 + 4x^3 + \frac{74}{15}x^4 + \cdots$ from which we can read off the average number of occupied sites in the jammed state for small systems: $A_2 = 2$, $A_3 = 2$, $A_4 = \frac{10}{3}$, *etc.*

It's worthwhile to understand what these numbers truly mean. For example, $A_4 = \frac{10}{3}$. This value for the the average number of occupied sites on a 4-site chain arises as follows: With probability $\frac{1}{3}$ the first dimer lands on the middle two sites and no further adsorption is possible. With probability $\frac{2}{3}$, the first dimer occupies one of the chain endpoints and the neighboring site. There are then still two more vacant adjacent sites that can accommodate one more dimer. Thus the average number of occupied sites is $\frac{1}{3}\times 2+\frac{2}{3}\times 4 = \frac{10}{3}$. In contrast, in the equilibrium microcanonical ensemble, each jammed configuration occurs with the same probability so that the average number of occupied sites equals 3. We will return to the difference between the equilibrium and non-equilibrium ensembles in the next section.

As $L\to\infty$, we can obtain the expansion coefficients in the generating function by examining the behavior of $A(x)$ as $x\to 1$ from below. Now if $A_L \to L\rho$ as $L\to\infty$, with ρ a constant, then in this limit $A(x)$ would have the form

$$\begin{aligned} A(x) = \sum_2^{\infty} \rho L\, x^{L-2} &= \frac{\rho}{x}\,\frac{d}{dx}\sum_{L=2}^{\infty} x^L \\ &= \frac{\rho}{x(1-x)^2}(2x-x^2). \end{aligned} \tag{5.14}$$

Comparing Eqs. (5.13) and (5.14) as $x\to 1$, we simply read off the value $\rho = 1-e^{-2}$, thus recovering the Flory result (5.1).

Phase space and broken ergodicity

A basic tenet of equilibrium statistical physics is the notion of *equal a priori probability*; that is, each microstate of an equilibrium system is realized with the same probability. This feature is termed *ergodicity* and it is the principle by which we make the equivalence between the formal ensemble average of statistical mechanics and the time average in a real equilibrium system. Here we show that jammed configurations do not fit into this picture. Namely, jammed configurations do not uniformly sample the state space of all possible configurations. This phenomenon is also known as *broken ergodicity*.

To begin this discussion, let us count the total number of jammed states in a finite system for irreversible dimer adsorption. Let F_L be the total number of jammed configurations on a finite chain of L sites. To determine F_L, we divide jammed configurations into two categories: (i) those with the first site of the chain occupied and (ii) those with the first site empty. Configurations in these two categories obviously look like:

$$\bullet\bullet\underbrace{\times\cdots\times}_{L-2} \quad \text{and} \quad \circ\bullet\bullet\underbrace{\times\cdots\times}_{L-3},$$

respectively. Thus the first category consists of F_{L-2} configurations and the second category consists of F_{L-3} configurations. Thus we have the recurrence

$$F_L = F_{L-2} + F_{L-3} \quad \text{for} \quad L > 2.$$

Writing this recurrence in terms of the generating function and making use of the boundary conditions $F_0 = F_1 = F_2 = 1$, we find that the generating function is

$$N(x) = \sum_{L=0}^{\infty} F_L x^L = \frac{1+x+x^2}{1-x^2-x^3}\ .$$

In principle, we can determine F_L by finding the $L^{\rm th}$ term in the generating function. However, if we only want the asymptotic behavior, it is sufficient to merely assume that $F_L \propto \zeta^L$ and substitute this assumption into the recursion relation for F_L to give $F_L = A\zeta^L + A_+\zeta_+^L + A_-\zeta_-^L$. Here ζ and $\zeta_\pm$ are the roots of the polynomial $z^3 - z - 1 = 0$ that explicitly are:

$$\zeta = a + b = 1.32472\ldots, \qquad \zeta_\pm = a\, e^{\pm i\pi/3} + b\, e^{\pm 2i\pi/3}$$
$$\text{with} \quad a = \frac{1}{3}\left[\frac{27+3\sqrt{69}}{2}\right]^{1/3}, \qquad b = \left[\frac{2}{27+3\sqrt{69}}\right]^{1/3}$$

Since $|\zeta_\pm| < 1$, the asymptotic behavior of the number of jammed configurations is given by

$$F_L \sim A\zeta^L, \tag{5.15}$$

where $A = (\zeta + \zeta^2 + \zeta^3)/(3 + 2\zeta) = 0.956614\ldots$ is obtained by matching the exact solution with the first few terms in the recursion relation. Thus the number of jammed configurations grows exponentially with the system size. This exponential growth arises in many complex equilibrium and non-equilibrium systems, such as spin glasses, fully frustrated Ising systems, and all sorts of packing problems. Associated with this macroscopic number of states is an extensive packing entropy, $S = \ln F_L \sim L \ln \zeta$.

Next, we determine the number of configurations with a specified coverage by a combinatoric approach. Let $F_{N,L}$ be the number of jammed configurations that contain N dimers in a system of size L. The number of dimers must be in the range $\lfloor (L+1)/3 \rfloor \le N \le \lfloor L/2 \rfloor$. Here the notation $\lfloor x \rfloor$ denotes the integer part of x. In a jammed configuration, a dimer must be followed either by another dimer or by a single vacant site. Thus a jammed configuration may be symbolically written as $\cdots DDODDOD\cdots$. That is, between each pair of dimers there may be either one vacancy or nothing. Every string of dimers and vacant sites corresponds to a distinct jammed state and vice versa. Since a vacancy can appear between pair of dimers and also between a dimer and the end of the chain, there are $N+1$ possible locations for the $L-2N$ vacant sites. Therefore total number of distinct arrangements with N dimers is given by the binomial coefficient

$$F_{L,N} = \binom{N+1}{L-2N}, \tag{5.16}$$

and the total number of configurations with any number of dimers is $F_L = \sum_N F_{L,N}$.

In the thermodynamic limit, we fix the coverage $\rho = 2N/L$ and then evaluate $\ln F_{L,\rho}$ by keeping only the leading terms in the Stirling formula $\ln x! \sim x\ln x - x$. In this approximation, the total number of configurations grows exponentially with the system size,

$$F_{L,\rho} \sim \exp[Lf(\rho)], \tag{5.17}$$

with

$$f(\rho) = \frac{\rho}{2}\ln\frac{\rho}{2} - (1-\rho)\ln(1-\rho) - \left(\frac{3\rho}{2}-1\right)\ln\left(\frac{3\rho}{2}-1\right). \tag{5.18}$$

Because $F_{L,\rho}$ grows exponentially with L, this function is asymptotically dominated by its most probable value that is obtained by maximizing the function f. Thus setting $f'=0$ gives the cubic equation

$$4\rho_{\rm eq}2(1-\rho_{\rm eq})^2 = (3\rho_{\rm eq}-2)^3, \tag{5.19}$$

whose root $\rho_{\rm eq} = 0.822991$ gives the asymptotic equilibrium density. The number of configurations quickly becomes small away from the equilibrium density, as seen from the expansion $f(\rho) \approx f(\rho_{\rm eq}) + \frac{1}{2}f''(\rho_{\rm eq})(\rho-\rho_{\rm eq})^2$, with $f''(\rho_{\rm eq}) = (2\rho_{\rm eq})^{-1} + (1-\rho_{\rm eq})^{-1} + (9/4)(3\rho_{\rm eq}/2-1)^{-1}$. Thus the density dependence of the number of jammed configurations approaches the Gaussian

$$F_{L,N} \simeq \frac{F_L}{\sqrt{2\pi\Delta^2}}\exp\left(-\frac{(\rho-\rho_{\rm eq})^2}{2\Delta^2}\right), \tag{5.20}$$

with variance $\Delta = (Lf''(\rho_{\rm eq}))^{-1/2} \approx 0.261378L^{-1/2}$. The prefactor in (5.20) is set to give the correct total number of configurations.

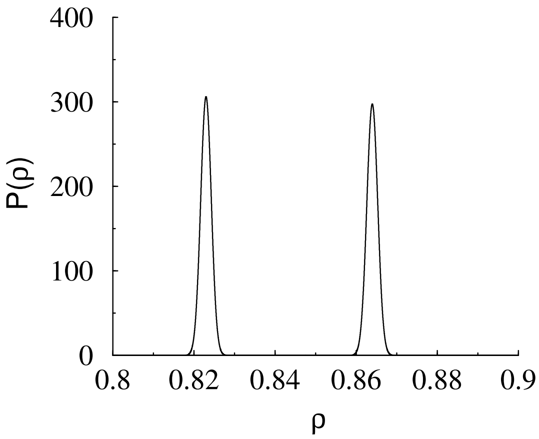

Figure 5.6: The equilibrium distribution (left) versus the jamming distribution (right) for a system of size $L = 10^4$.

We therefore conclude that the normalized distribution of configurations with density ρ, $P_{\rm eq}(\rho) \equiv F_{L,N}/F_L$, approaches the delta function

$$P_{\rm eq}(\rho) \to \delta(\rho - \rho_{\rm eq}), \tag{5.21}$$

as $L\to\infty$ (Fig. 5.6). This distribution has the same form as the distribution of jammed states, except that the peaks of these two distributions are at different coverages, $\rho_{\rm jam} \neq \rho_{\rm eq}$! If every jammed configuration had the same likelihood to occur, the jamming coverage should equal $\rho_{\rm eq} \approx 0.822991$ instead of $\rho_{\rm jam} \approx 0.864665$. Why are the jamming and the equilibrium distributions different? Equilibrium systems uniformly sample their phase space so that all microscopic configurations with the same energy are equiprobable. In contrast, for non-equilibrium systems, as manifested by irreversible adsorption, the dynamics dictates how the phase space is explored, and there is no reason that all microscopic configurations are sampled uniformly. Non-equilibrium systems need not minimize a free energy, nor explore all microscopic configurations equiprobably. While these two principles of free energy minimization and ergodicity underlie equilibrium statistical physics, they do not necessarily hold in non-equilibrium situations.

Correlations and fluctuations

The relation $\rho = 1 - E_1$ is the simplest example of expressing a fundamental physical quantity (the coverage) in terms of the empty interval probabilities E_m. In fact, the empty interval probabilities contain much more information about the occupancy of the substrate, such as spatial correlation functions between occupied sites and related measures of fluctuations in surface coverage. To develop this description, let's denote the probability of an arbitrary configuration by $\mathcal{P}[\cdots]$. Thus, for example, $E_2 = \mathcal{P}[\circ\circ]$ and notice again that the state of the sites external to the string is not specified. With this notation, $\rho = \mathcal{P}[\bullet] = 1 - E_1$ is the consequence of the conservation relation $\mathcal{P}[\circ] + \mathcal{P}[\bullet] = 1$. Other conservation relations, such as $\mathcal{P}[\circ\circ] + \mathcal{P}[\circ\bullet] = \mathcal{P}[\circ]$ or $\mathcal{P}[\circ\circ] + \mathcal{P}[\circ\bullet] + \mathcal{P}[\bullet\circ] + \mathcal{P}[\bullet\bullet] = 1$ allow us to express the probability of any configuration of occupied sites in terms of probabilities of empty configurations. For simple situations, these probabilities can be expressed in terms of the empty interval probabilities E_m. For example, using the conservation statement

$$\mathcal{P}[\underbrace{\circ\cdots\circ}_{m}\bullet] + \mathcal{P}[\underbrace{\circ\cdots\circ}_{m}\circ] = \mathcal{P}[\underbrace{\circ\cdots\circ}_{m+1}],$$

then the probability for a configuration with at least m empty sites followed by a filled site is

$$\mathcal{P}[\underbrace{\circ\cdots\circ}_{m}\bullet] = E_m - E_{m+1}, \tag{5.22}$$

while the probability to find a void of length exactly equal to m is

$$V_m = \mathcal{P}[\bullet\underbrace{\circ\cdots\circ}_{m}\bullet] = E_m - 2E_{m+1} + E_{m+2}. \tag{5.23}$$

A fundamental characterization of correlations between occupied sites on the substrate is given by the *pair correlation function* C_j that is defined as

$$C_j = \langle n_0\, n_j\rangle - \langle n_0\rangle\langle n_j\rangle. \tag{5.24}$$

Here n_j is the occupation density at site j and, the term $\langle n_0\, n_j\rangle$ may be graphically represented as

$$\langle n_0\, n_j\rangle = \mathcal{P}[\bullet\underbrace{\times\cdots\times}_{j-1}\bullet].$$

To compute correlation functions such as C_j, we need to determine more general disconnected empty configurations that look like: $\circ\cdots\circ\times\cdots\times\circ\cdots\circ$, that is, a central cluster of sites whose state is unspecified that is surrounded by empty sites. (here $\times$ denotes a site of an unspecified state). Let us denote

$$E_{i,j,k} = \mathcal{P}\big[\underbrace{\circ\cdots\circ}_{i}\underbrace{\times\cdots\times}_{j-1}\underbrace{\circ\cdots\circ}_{k}\big],$$

as the probability for two empty clusters of at least i and at least k sites that surround $j-1$ sites whose states are unspecified. Thus $E_{i,1,k} = E_{i+k}$, where the latter quantity is the previously-defined empty interval probability. For the case of dimer adsorption, notice also that $E_{i,2,k} = \mathcal{P}[\circ\cdots\circ\times\circ\cdots\circ] = E_{i+1+k}$, since a *single* site that is sandwiched between clusters of empty sites must also be empty.

The probabilities $E_{i,j,k}$ satisfy a hierarchy of master equations similar to (5.2). For $i,k\geq 1$ and $j\geq 2$,

$$\begin{aligned}\frac{d}{dt}E_{i,j,k} = &-(i-1)E_{i,j,k} - E_{i+1,j,k} - E_{i+1,j-1,k}\\ &-(k-1)E_{i,j,k} - E_{i,j,k+1} - E_{i,j-1,k+1}.\end{aligned} \tag{5.25}$$

The consecutive terms in the top line account for adsorption of a dimer within the empty i-string, overlapping the left end of this empty string, and overlapping the right end of this string; the terms in the bottom line are similarly associated with the empty k-string. To solve this master equation, we make use of the fact that the following generalization of the ansatz (5.3)

$$E_{i,j,k}(t) = e^{-(i+k-2)t}\,\Psi_j(t) \quad \text{for} \quad i,k\geq 1, \tag{5.26}$$

where

$$\Psi_j(t) \equiv E_{1,j,1} = \mathcal{P}[\circ\underbrace{\times\cdots\times}_{j-1}\circ],$$

simplifies the above master equations to:

$$\frac{d\Psi_j}{dt} = -2e^{-t}[\Psi_j + \Psi_{j-1}], \tag{5.27}$$

for $j \geq 2$, while for $j = 1$, $\Psi_1 = E_2$. Equations (5.27) are recursive and solvable by introducing the generating function

$$\Psi(x,t) = \sum_{j=2}^{\infty} x^j \, \Psi_j(t)$$

to recast (5.27) into

$$\frac{\partial \Psi(x,t)}{\partial t} = -2e^{-t}\left[(1+x)\Psi(x,t) + x^2\, E_2(t)\right]. \tag{5.28}$$

the initial condition is $\Psi_j(t=0) = 1$, or $\Psi(x,0) = x^2(1-x)^{-1}$. Solving the linear inhomogeneous differential equation (5.28) subject to this initial condition and expanding the solution in a Taylor series in x we obtain (for $j \geq 2$):

$$\Psi_j = (E_1)^2 - E_1\left[\frac{(\ln E_1)^j}{2\cdot j!} + \sum_{k\geq j+1} \frac{(\ln E_1)^k}{k!}\right].$$

Let's now exploit these results to compute the pair correlation C_j defined in Eq. (5.24). Using the conservation relations

$$\begin{aligned}
&\mathcal{P}[\bullet\times\cdots\times\bullet] + \mathcal{P}[\bullet\times\cdots\times\circ] + \mathcal{P}[\circ\times\cdots\times\bullet] + \mathcal{P}[\circ\times\cdots\times\circ] = 1,\\
&\mathcal{P}[\circ\times\cdots\times\bullet] + \mathcal{P}[\circ\times\cdots\times\circ] = \mathcal{P}[\circ] = E_1,
\end{aligned}$$

we have $\langle n_0 n_j\rangle = 1 + \Psi_j - 2E_1$. Since $\langle n\rangle = 1 - E_1$, we finally obtain $C_j = \Psi_j - (E_1)^2$. Explicitly, the correlation functions are:

$$C_1 = E_2 - (E_1)^2, \qquad C_j = -E_1\left[\frac{(\ln E_1)^j}{2\cdot j!} + \sum_{k\geq j+1}\frac{(\ln E_1)^k}{k!}\right] \quad j > 1. \tag{5.29}$$

In the jammed state $E_1(\infty) = e^{-2}$ and the limiting value of the pair correlation is

$$C_j \to -e^{-2}\frac{(-2)^{j-1}}{j!} \quad \text{as} \quad j\to\infty.$$

This super-exponential decay of correlations is unusual, as many equilibrium systems with short-range interactions, such as a system of hard disks, have correlations that decay exponentially at large distances.

While the above exact results for empty intervals E_m, voids V_m, the correlation function C_j, and the cluster probabilities $E_{i,j,k}$ provide detailed information about the structure of the substrate, they do not constitute a complete picture. What is still missing is information about strings of sites that are all occupied. For example, consider the probabilities for filled strings and islands,

$$F_m = \mathcal{P}[\underbrace{\bullet\cdots\bullet}_{m}], \qquad I_m = \mathcal{P}[\circ\underbrace{\bullet\cdots\bullet}_{m}\circ].$$

As with empty strings, (see (5.23)), the island probability is the discrete second derivative of the filled string probability,

$$I_m = F_m - 2F_{m+1} + F_{m+2}, \tag{5.30}$$

and therefore it is sufficient to focus on F_m. At present, the computation of F_m for all m is an open problem and we now outline the essential difficulty in solving this problem.

For $m \leq 3$, we may use conservation relations to relate F_m to the empty interval probabilities E_m:

$$F_1 = 1 - E_1,$$
$$F_2 = 1 - 2E_1 + E_2,$$
$$F_3 = 1 - 3E_1 + 2E_2.$$

The general form of the last identity is

$$F_3 = 1 - 3\mathcal{P}[\circ] + 2\mathcal{P}[\circ\circ] + \mathcal{P}[\circ \times \circ] - \mathcal{P}[\circ \circ \circ],$$

but, for adsorption of dimers, $\mathcal{P}[\circ \times \circ] = \mathcal{P}[\circ \circ \circ]$ so that the 3-body terms in this identity cancel. For $3 < m < 7$, we can express F_m in terms of E_j and the probability for two disconnected empty intervals $E_{i,j,k}$. Thus for F_5, for example, we find

$$F_5 = 1 - 5E_1 + 4E_2 - 2E_4 + E_5 + 2(1 - e^{-t})\Psi_3 + \Psi_4.$$

For $m \geq 7$, configurations with three disconnected empty parts contribute to F_m. This pattern proceeds as m increases; generally for $m \geq 3p - 2$, configurations with p disconnected empty parts contribute to F_m. We can extend the procedure utilized in computing the probabilities $E_{i,j,k}$ of configurations with two disconnected empty parts to the case of the simplest configurations with more empty parts. Overall, the entire approach gets very messy and seems unsuitable for determination of F_m with m above 20. A better approach would be to write *closed* equations for F_m. However such equations are unknown and perhaps they do not exist.

5.2 Adsorption in Higher Dimensions

Most applications of irreversible adsorption involve two-dimensional substrates. It is natural to begin be treating the irreversible adsorption of elementary objects such as sticks, squares, rectangles, disks, and ellipsoids. Such studies are a natural prelude to real systems, such as the adsorption of proteins and latex particles onto surfaces. An exact analysis of adsorption is generally not possible in higher dimensions, and so we will resort to heuristics, numerical simulations, and perturbative analysis. To get a feeling for numbers, the jamming coverage for random sequential adsorption of various elementary objects in two dimensions are listed in Table 5.2. The jamming coverage varies widely, much more so than in one dimension, and the coverage strongly depends on the shape of the object.

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

Table 5.2: The jamming coverage for various objects in two dimensions.

While no longer applicable, the one-dimensional theory still serves as a useful guide for the results. In fact, the qualitative behavior of one dimension is, for the most part, generic in arbitrary dimensions. Thus, for example, the relaxation is exponential on discrete substrates and algebraic on continuous ones. Moreover, fluctuations in the number of adsorbed particles are extensive, *i.e.*, proportional to the volume. Finally, different jammed configurations are realized with different likelihoods, i.e., the dynamics is non-ergodic.

Discrete substrates

Adsorption is exactly soluble for one special high-dimensional substrate—the Bethe lattice. This tree structure, in which each site is connected to exactly z other sites (Fig. 5.7), is often used to represent the mean-field limit. Let's consider the adsorption of dimers onto the Bethe lattice. Now the fundamental quantities are not empty intervals of length $\geq m$, but rather connected *clusters* of $\geq m$ sites that we again write as E_m.

The probability E_m that all sites in such a cluster remain vacant during adsorption of dimers satisfies the master equation

$$\frac{dE_m}{dt} = -(m-1)E_m - [(z-2)m+2]E_{m+1}. \tag{5.31}$$

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 itself. 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, the number of bonds is just $m-1$. 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 perimeter sites of the cluster. These are sites that are nearest neighbor to the cluster, but not part of the cluster itself. For a cluster of 2 sites, the number of perimeter sites is clearly $2(z-1)$. When a site is added to the cluster, 1 perimeter site is lost, but there is a gain of $(z-1)$ for the sites at the perimeter of the newly-added site. Continuing this counting for a cluster of m sites, the number of perimeter sites is $zm - 2(z-1)$.

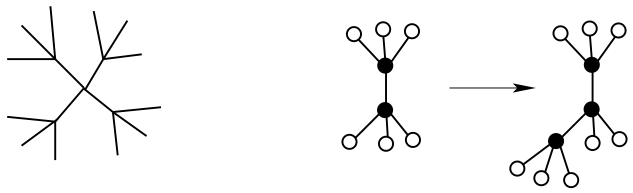

Figure 5.7: (Left) First two generations of a Bethe lattice with coordination number $z = 4$. (Right) Illustration of the counting perimeter sites (circles) starting with a connected cluster of $m = 2$ and 3 sites (dots).

To solve the master equation (5.31), 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 two coupled differential equations

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

The solutions to these two equations 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

$$E_m(t) = e^{-(m-1)t}\left[(z-1)-(z-2)\,e^{-t}\right]^{-m-2/(z-2)}\,. \tag{5.32}$$

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

$$\rho_{\rm jam} = 1-(z-1)^{-z/(z-2)}. \tag{5.33}$$

In the limit $z \downarrow 2$, we recover the one-dimensional result, while for large z, the uncovered fraction is inversely proportional to the coordination number, $1-\rho_{\rm jam} \sim z^{-1}$. The Bethe lattice provides a good approximation for $\rho_{\rm jam}$ for a regular lattice with the same coordination number. For example, when $z = 4$, dimer adsorption of the Bethe lattice gives a jamming coverage $\rho_{\rm jam} = 8/9$, while for the corresponding square lattice, $\rho_{\rm jam} \approx 0.9068$.

A second look at almost exponential solutions

Suppose we have a master equation with the generic form

$$\frac{dE_m}{dt} = \lambda(m+\alpha)E_m + \mu(m+\beta)E_{m+1}. \tag{5.34}$$

The structure of this equation encompasses the form of the master equation given in Eq. (5.31). Again, the almost exponential ansatz provides an easy route to the solution. Let's assume a solution that has the form

$$E_m = \Phi(t)[\varphi(t)]^m. \tag{5.35}$$

Substituting into Eq. (5.34) and then dividing by E_m itself, these steps give

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

In this form, we see the utility of making the ansatz in the form of (5.35), as the above equation divides naturally into terms linear in n and terms independent of n.

From the terms linear in n, we have

$$\frac{\dot{\varphi}}{\varphi} = \lambda + \mu\varphi, \tag{5.36}$$

from which, in principle, we obtain $\varphi(t)$. The n-independent terms give

$$\frac{\dot{\Phi}}{\Phi} = \lambda\alpha + \mu\beta\varphi. \tag{5.37}$$

Now we solve of Eq. (5.36) for $\varphi(t)$ and then we can, in principle, solve for $\Phi(t)$, from which the original problem is solved.

Once again, the almost exponential solution reduces an infinite set of equation to just two equations that are usually easy to solve. Here the crucial point is the factor φ^m in the original ansatz that ultimately separates of the initial set of equations (5.35) into a piece linear in m and an m-independent piece.

For general discrete substrates, we now give a simple and heuristic approach shows that the relaxation to the jamming coverage decays exponentially in time

$$\rho_{\rm jam} - \rho(t) \sim e^{-\lambda t}\,. \tag{5.38}$$

Consider, as a concrete example, the adsorption of dimers onto the square lattice. At long times, the available spaces that can accommodate additional dimers are few and far between. These "target" regions are small clusters of unoccupied sites: dimers, trimers (both linear and bent), 2×2 squares, *etc.* To determine the rate at which these "lattice animals" get filled, we need the probabilities that these various configurations are empty. A crucial point is that the probability to find a vacant cluster on the substrate is a rapidly decreasing function of its size at long times. Thus only the smallest possible 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 simplest configurations (dimers, trimers, and 2×2 squares) evolve according to

$$\frac{d}{dt}P[\circ\circ] \simeq -P[\circ\circ], \qquad \frac{d}{dt}P[\circ\circ\circ] \simeq -2\,P[\circ\circ\circ], \qquad \frac{d}{dt}P\begin{bmatrix}\circ\circ\\ \circ\circ\end{bmatrix} \simeq -4\,P\begin{bmatrix}\circ\circ\\ \circ\circ\end{bmatrix}.$$

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

$$P[\circ\circ] \sim e^{-t}\,, \qquad P[\circ\circ\circ] \sim e^{-2t}\,, \qquad P\begin{bmatrix}\circ\circ\\ \circ\circ\end{bmatrix} \sim e^{-4t}. \tag{5.39}$$

Generally, the probability that a given lattice animal is empty decays exponentially in time, $P(t) \sim \exp(-\lambda t)$, where λ 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 $d\rho/dt \simeq -2P[\circ\circ]$, so that

$$\rho_{\rm jam} - \rho(t) \sim e^{-t}. \tag{5.40}$$

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

Continuous substrates

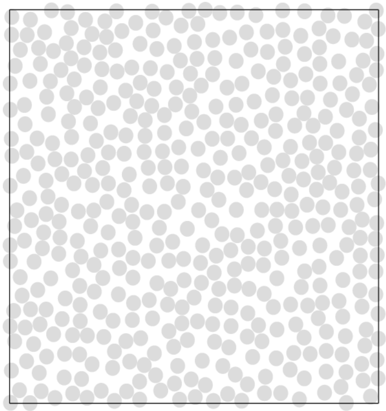

Figure 5.8: Random sequential adsorption of disks in two dimension. Shown is a jammed state.

On continuous substrates, the intervening gaps between adsorbed objects can be arbitrarily small. As we shall show, this feature ultimately leads to a slower algebraic relaxation of the density to the jamming density, $\rho_{\rm jam} - \rho(t) \sim t^{-\sigma}$, with σ dependent on the spatial dimension d. For the car parking problem in one dimension, we already demonstrated that $\sigma = 1$. Let's derive the corresponding algebraic decay for the adsorption of disks in two dimensions (Fig. 5.8). As the substrate approaches jamming, there will be only a small number of tiny and independent "target zones" within which the center of another disk can adsorb. To characterize these target zones, first 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. Thus the target zones of the substrate are the complement of the exclusion zones (Fig. 5.9). In a jammed configuration, no target zones remain even though the adsorbed particles do not cover the substrate completely.

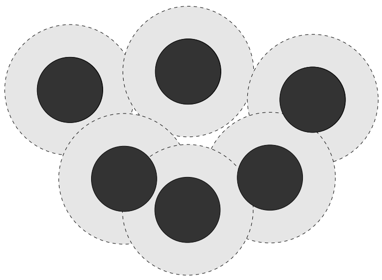

Figure 5.9: The target areas (blank), the exclusion zones (shaded), and the adsorbed disks (dark) near jamming. In the long-time limit only arc-triangular target areas, such as the tiny one on the left, remain.

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

$$c(\ell, t) \sim e^{-\ell^2 t}. \tag{5.41}$$

Each time a disk is adsorbed, the coverage of the surface changes by a fixed amount, namely the area of the disk. Thus using $c(\ell,t)\sim e^{-\ell^2 t}$, the coverage of the substrate asymptotically varies as

$$\rho_{\rm jam}-\rho(t)\sim \text{const.}\times\int c(\ell,t)\,d\ell\sim \text{const.}\times t^{-1/2}. \tag{5.42}$$

The power-law relaxation to the jamming density arises because target zones can be arbitrarily small. Although a target zone of a given size vanishes exponentially with time, the average over all sizes of target zones leads to a power-law tail.

In addition to the minimalist and intuitive nature of this derivation, this heuristic approach can be straightforwardly extended to arbitrary spatial dimension d. Now the area of a target zone of linear dimension ℓ scales as ℓ^d. Consequently, the density of target zones of linear dimension ℓ scales as $c(\ell,t)\sim e^{-\ell^d t}$. Then performing the analog of the integral in Eq. (5.42), we obtain $\rho_{\rm jam}-\rho(t)\sim$ const. $\times\, t^{-1/d}$ in d dimensions.

We may further extend this argument to determine the approach to the jamming density for elongated particles, for example, prolate ellipsoids with a large aspect ratio. Here the notion of a target zone is no longer a precise concept for unoriented ellipsoids. An incoming ellipsoid can adsorb closer to an already adsorbed ellipsoid if the two particles have the same orientation and are side-by-side, while their separation will be larger if they adsorb end-to-end or if their orientations are different. As target zones get filled, there is a strong tendency for a newly-adsorbed ellipsoid to be oriented with its neighbors. This restriction plays an important role in the adsorption of non-symmetrical objects at long times.

Let the range of allowed orientations for an ellipsoid that is incident on a target zone of linear dimension ℓ be θ. The density of target zones of linear size ℓ will asymptotically be governed by the rate equation $dc/dt\propto-\theta\ell^2\,c$. Since the orientational range vanishes in the long-time limit, we make the simplest self-consistent assumption that $\theta\cong a_1\ell+a_2\ell^2+\cdots$. Then using $\theta\propto\ell$ for small ℓm the concentration of target areas of linear dimension ℓ is governed by $dc/dt\propto-\ell^3\,c$. As a result,

$$c(\ell,t)\sim e^{-\ell^3 t}\,. \tag{5.43}$$

Substituting this form for $c(\ell,t)$ into Eq. (5.42), we find that the relaxation to the jamming coverage is given by $\rho_{\rm jam}-\rho(t)\sim$ const. $\times\, t^{-\sigma}$, with $\sigma=1/3$. Thus the orientational constraint hinders the approach to the jammed state. For general spatial dimension, the corresponding result is $\sigma=1/(d+1)$. In summary, the exponent governing the algebraic relaxation is

$$\sigma=\begin{cases}1/d & \text{spheres,}\\ 1/(d+1) & \text{prolate ellipsoids.}\end{cases} \tag{5.44}$$

For squares with fixed orientation, the relaxation follows yet another distinct law. The target areas asymptotically are rectangular and the density $n(x,y,t)$ of target rectangles of size $x\times y$ decays according to $dc/dt=-xy\,c$. Consequently, $c\sim e^{-xy\,t}$, from which we obtain

$$\begin{aligned}\rho_{\rm jam}-\rho(t)=\int_0^1\int_0^1 dx\,dy\;n(x,y,t)&\sim\int_0^1 dx\,\frac{1-e^{-xt}}{xt}\\ &=t^{-1}\int_0^t du\,\frac{1-e^{-u}}{u}\\ &\simeq t^{-1}\ln t.\end{aligned} \tag{5.45}$$

Similarly, the random sequential adsorption of aligned hypercubes in d dimensions exhibits an algebraic decay, modified by a dimension-dependent logarithmic correction,

$$\rho_{\rm jam}-\rho(t)\sim(\ln t)^{d-1}\,t^{-1}. \tag{5.46}$$

Needles

An intriguing special case is the deposition of zero-area, non-overlapping, identical needles—the limit of ellipsoids with a diverging aspect ratio. Here the coverage of the substrate vanishes, even though the number of adsorbed particles diverges with time.

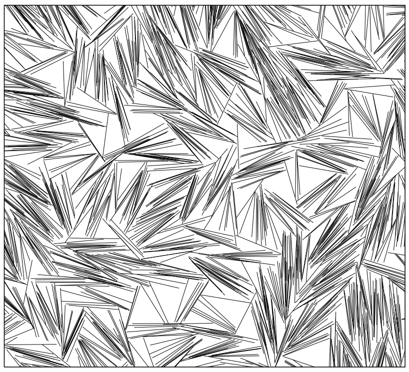

Figure 5.10: Random sequential adsorption of needles in two dimension.

Let's determine the adsorption kinetics for randomly-oriented needles that are incident on a two-dimensional substrate at a constant, unit rate. Early deposition attempts are mostly successful because the substrate is nearly empty. As a result, the number of adsorbed needles starts growing linearly with time and these initial needles have little orientational or positional order. After this transient, previously adsorbed needles impose a strong constraint on both the position and the orientation of subsequent successful adsorption events. In the long time limit, domains form in which neighboring needles are nearly aligned *and* their centers lie nearly on a line (Fig. 5.10). The orientation of each domain is fixed by the first few adsorption attempts, so that there is orientational order at small scales but not at large scales. Once this state is reached, most adsorption attempts fail and the number of adsorbed needles grows sub-linearly with time.

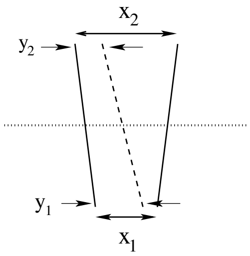

Figure 5.11: Random sequential adsorption of needles in one dimension as the fragmentation of trapezoids.

The formation of nearly aligned domains considerably simplifies the analysis of the late stages of adsorption. For a new needle to adsorb between two nearby needles, it must be closely aligned with them, both orientationally and positionally. The target area is essentially a unit-height trapezoid, and base widths x_1 and $x_2 \approx x_1$. A new needle may adsorb with its top end in the range $0 < y_1 < x_1$ and its bottom in the range $0 < y_2 < x_2$ (Fig. 5.11). Such a deposition event fragments the trapezoid into two smaller trapezoids of base widths y_1, y_2 and $x_1 - y_1, x_2 - y_2$. This defines a geometric fragmentation process similar to that analyzed in Sec. 4.4 and we can use the techniques of that discussion to treat the needle problem.

The density $c(x_1, x_2)$ of trapezoids with widths $\{x_1, x_2\}$ obeys the master equation

$$\frac{\partial}{\partial t}c(x_1, x_2) = -x_1 x_2\, c(x_1, x_2) + 2\int_{x_1}^{\infty}\int_{x_2}^{\infty} dy_1\, dy_2\, c(y_1, y_2). \tag{5.47}$$

The loss term is proportional to the total number of ways for the two ends of the needle to be placed along the bases of the trapezoid. The gain term accounts for the 2 ways in which the break-up of a larger trapezoid creates a trapezoid with base widths x_1, x_2.

The Mellin transform $M(s_1, s_2) = \int\int dx_1\, dx_2\, x_1^{s_1-1} x_2^{s_2-1} c(x_1, x_2)$ thus evolves according to

$$\frac{\partial}{\partial t} M(s_1, s_2) = \left(\frac{2}{s_1 s_2} - 1\right) M(s_1 + 1, s_2 + 1). \tag{5.48}$$

As in geometrical fragmentation, there is a family of hidden conservation laws in which all moments with $s_1^* s_2^* = 2$ are conserved. Assuming that the Mellin transform asymptotically varies algebraically with time as $M(s_1, s_2) \sim t^{-\alpha(s_1,s_2)}$, and substituting into Eq. (5.48), we find the condition $\alpha(s_1+1, s_2+1) = \alpha(s_1, s_2)+1$, as well as $\alpha(s_1^*, s_2^*) = 0$ along the parabola $s_1^* s_2^* = 2$. Just as in the discussion of Sec. 4.4, the exponent α for given point in the s_1-s_2 plane equals the projection onto the x-axis of a diagonal line that connects (s_1, s_2) with this parabola (Fig. 4.6). This gives the condition $\alpha(s_1^* + k, s_2^* + k) = k$, from which the exponent is the smaller root of the quadratic equation $(\alpha - s_1)(\alpha - s_2) = 2$, that is,

$$\alpha(s_1, s_2) = \frac{s_1 + s_2 - \sqrt{(s_1 - s_2)^2 + 8}}{2}. \tag{5.49}$$

In particular, the number density of needles $n(t) = M(1, 1)$ varies with time as

$$n(t) \sim t^{\nu} \qquad \text{with} \quad \nu = \sqrt{2} - 1. \tag{5.50}$$

This irrational value of the exponent was a great surprise when it was first derived, but is actually quite natural in view of our previous discussion of multiscaling in geometric fragmentation.

We may quantity the increasing alignment of adjacent needles inside domains by $\langle \mathbf{n}_i \cdot \mathbf{n}_{i+1} \rangle = \langle \cos\theta \rangle$, with $\mathbf{n}_i$ a unit vector parallel to ith needle and θ the angle between the two needles. This angle is related to the base lengths of the trapezoid defined by two needles, via $\theta = |x_1 - x_2|$ for $x_1, x_2 \ll 1$. Thus the orientational correlation function $\langle \cos\theta \rangle$ is related to the moments through $1 - \langle \cos\theta \rangle \sim \langle (x_1 - x_2)^2 \rangle = 2(\langle x^2 \rangle - \langle x_1 x_2 \rangle)$, with $\langle x_1^2 \rangle = \langle x_1^2 \rangle \equiv \langle x^2 \rangle$. $x \equiv x_1$. Using $\langle x^2 \rangle = M(3, 1)/M(1, 1) \sim t^{-(\alpha(3,1)-\alpha(1,1))}$, the orientational correlation function is

$$1 - \langle \cos\theta \rangle \sim t^{-\mu} \qquad \text{with} \qquad \mu = 1 + \sqrt{2} - \sqrt{3} = 0.682162\ldots. \tag{5.51}$$

Thus neighboring needles asymptotically become perfectly aligned and the relaxation to this aligned state decays algebraic with time.

The mapping between needle adsorption and geometrical fragmentation is based on a critical look at how adsorbed needles are organized in the long-time limit. This connection is certainly not obvious *a priori* and it involves dubious approximations and some leaps of faith. What we gain from this heuristic approach is a natural way to obtain the multiscaling and non-rational exponents that describe the long-time behavior of needle adsorption. There is a good lesson here in how the right geometrical perspective can transform a seemingly difficult problem—that of needle adsorption—to the much easier problem of the fragmentation of nearly aligned trapezoids.

5.3 Extensions

Thus far, our discussion has been focused on irreversible adsorption—once a particle adsorbs it remains immobile forever. Furthermore, we have tacitly assumed that an adsorbed particle does not have any lateral interactions on the substrate. That is, the adsorption probability of an incoming particle depends only on whether there exists sufficient empty space to accommodate the particle, and not on the distance to previously-adsorbed particles. Both of these assumptions are idealizations of reality, however. In this last section, we investigate several physically-motivated extensions of adsorption in which these assumptions are relaxed.

Cooperative Monomer Adsorption

What is the role of interactions between adsorbed molecules? Thus far, we have assumed that an incident particle necessarily adsorbs if there is sufficient space on the substrate to accommodate the particle. However, lateral interactions between previously-adsorbed molecules and the incident particle and affect the adsorption rate. The simplest example of such a lateral interaction is the irreversible adsorption of monomers in one dimension in which adsorption is forbidden at sites next to already occupied sites. Here we study an analytically tractable variant of this scenario in which adsorption on an empty site occurs with rate 1 if both neighbors are empty, with rate r if exactly one neighbor is occupied, and rate 0 if both neighbors are occupied.

The approach to jamming in this system can again be treated in terms of the empty interval probabilities $E_m(t)$. These probabilities now obey the master equations (compare with Eqs. (5.2))

$$\begin{aligned}
\frac{dE_1}{dt} &= -2rE_2 - (1-2r)E_3 & m=1\\
\frac{dE_m}{dt} &= -(m-2+2r)E_m - 2(1-r)E_{m+1} & m\geq 2.
\end{aligned} \tag{5.52}$$

The first equation accounts for all the ways that am empty interval of length 1 can disappear. Such an interval disappears with with probability $\mathcal{P}[\circ\circ\circ] + r\mathcal{P}[\bullet\circ\circ] + r\mathcal{P}[\circ\circ\bullet]$. The first term account for the loss of an empty site that is surrounded by empty sites, while the remaining terms account for the loss of an empty site in which one of its neighbors is already occupied. We then use the relations $\mathcal{P}[\circ\circ\circ] = E_3$ and $\mathcal{P}[\bullet\circ\circ] = E_2 - E_3$ (see Eq. (5.22)) to give the first equation. The second equation accounts for the ways in which an m-site empty interval can disappear. In such an empty interval, the particle can adsorb at $m-2$ sites in which both neighbors are empty. With probability $2r\mathcal{P}[\bullet\underbrace{\circ\circ\cdots\circ}_{m}]$ the monomer adsorbs next to an occupied site, and with probability $2\mathcal{P}[\underbrace{\circ\circ\cdots\circ\circ}_{m+1}]$, the monomer adsorbs one site in from the edge and an empty interval of length m is eliminated. Using Eq. (5.22), we then obtain the second of Eqs. (5.52).

For $m\geq 2$, we again seek an exponential solution of the form $E_m(t) = e^{-(m-2+2r)t}\Phi(t)$, similar to Eq. (5.3). Substituting this ansatz into (5.52) gives

$$\frac{d\Phi}{dt} = \left[-2(1-r)\,e^{-t}\right]\Phi,$$

whose solution, subject to the initial condition $\Phi(0)=1$, is

$$\Phi(t) = \exp\left[-2(1-r)\left(1-e^{-t}\right)\right].$$

Finally, by substituting $E_2(t) = e^{-2rt}\,\Phi(t)$ and $E_3(t) = e^{-(1+2r)t}\,\Phi(t)$ into the first of (5.52) and integrating we obtain

$$E_1(t) = 1 - \int_0^t du\,\Phi(u)\left[2re^{-2ru} + (1-2r)\,e^{-(1+2r)u}\right].$$

Hence the coverage of the surface is

$$\rho(t) = \int_0^t du\,\left[2r + (1-2r)\,e^{-u}\right]\,e^{-2ru-2(1-r)(1-e^{-u})}.$$

When $r=0$, $\rho_{\rm jam}(0) = (1-e^{-2})/2$, which is one-half the jamming coverage in dimer adsorption. This result has an intuitive explanation that is illustrated graphically in Fig. 5.12. For any jammed state for cooperative monomer adsorption in the $r=0$ limit, there is a direct correspondence to a jammed state for dimer adsorption. To construct this equivalence, we define a "dual" lattice in which each site is halfway between the sites on the original lattice. Then each adsorbed monomer in the monomer problem is mapped onto an adsorbed dimer in the corresponding dimer system. Because of this one-to-one mapping between the two problems and also because each dimer occupies only a single site, the jammed density is simply one-half that in the dimer problem, namely, $(1-e^{-2})/2$.

On the other hand, $\rho_{\rm jam}(0^+) = (1+e^{-2})/2$. Why is there a discontinuity in the jamming coverage? Physically, this discontinuity arises because of the infinitely wide separation of time scales in the types of adsorption events that occur for infinitesimal r. In a time of the order of one, adsorption events for the

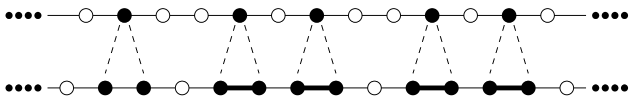

Figure 5.12: Top line: a jammed configuration for cooperative monomer adsorption when $r = 0$, where monomer adsorption requires that both neighbors are unoccupied. Bottom line: corresponding dimer configuration 0n the dual lattice.

$r = 0$ process occur until no further such events are possible and the system reaches the $r = 0$ jammed state. Then on a much longer time scale (of the order of r^{-1}), one site within each a pair of empty sites will get filled. That is, configurations of the form $\bullet\circ\circ\bullet$ evolve to $\bullet\bullet\circ\bullet$ or $\bullet\circ\bullet\bullet$. To determine $\rho_{\rm jam}(0^+)$, consider first the jammed state for cooperative monomer adsorption. Let ρ_1 be the density of monomers that are followed by a single vacancy and ρ_2 the density of monomers that are followed by two consecutive vacancies. By construction, $\rho_1+\rho_2 = \rho_{\rm jam}(0) = (1-e^{-2})/2$, and also $2\rho_1 + 3\rho_2 = 1$. Solving for ρ_2 gives $\rho_2 = e^{-2}$. After the final fill-in of one site in all consecutive pairs of vacancies, the final jamming density is $\rho_{\rm jam}(0^+) = (1-e^{-2})/2 + \rho_2 = (1+e^{-2})/2$.

Mathematically, the source of the discontinuity is the first term in Eq. (5.53). In the limit $r \to 0$, the leading contribution of this term is

$$\int_0^\infty du\, 2r\, e^{-2ru-2(1-e^{-u})}$$

When $r \to 0$, the main contribution to the integral is the region where u is large. In this regime, the factor e^{-u} in the exponent can be neglected and we are left with

$$\int_0^\infty du\, 2r\, e^{-2ru-2} = e^{-2}.$$

Thus for $r = 0^+$, the jamming density is $(1-e^{-2})/2 + e^{-2} = (1+e^{-2})/2$ as above.

Adsorbate Mobility

In irreversible adsorption, adsorbed molecules remain fixed forever where they first land on the substrate. In reality, however, particles can find more stable positions, diffuse, desorb, *etc.* These post-adsorption events are often slow compared to the adsorption rate, and we shall focus on this limit below. It is then useful to set the rate of post-adsorption processes to one; adsorption then proceeds with and infinite rate. That is, whenever a configuration on the surface permits an adsorption event, it occurs instantaneously. This separation of the time scales for the two types of processes helps simplify the analysis of such systems.

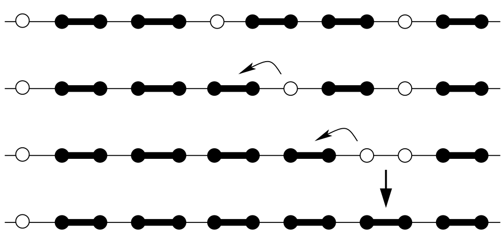

Figure 5.13: Example of the hopping of adsorbed dimers on a one-dimensional lattice. Each successive row shows the system after a single event. When two holes become adjacent, they are immediately occupied by a dimer.

Let us first study the problem in which adsorbed molecules and move by random walk motion to neighboring empty sites. A simple such example is the following: dimers adsorb onto a one-dimensional lattice at an infinite rate and then undergo a simple random walk on this lattice if there is an empty space adjacent to the dimer to accommodate the dimer (overlapping of dimers is forbidden). Since the deposition rate is infinite, the lattice immediately reaches a jammed state in which all empty sites are isolated. For this discussion, we call such sites "holes". Once this quasi-jammed state is reached, the dimers adjacent to holes can hop as illustrated in Fig. 5.13. This hopping of a dimer to the left results in the effective hopping of the hole by 2 steps to the right. Thus the nearest-neighbor hopping of a dimer corresponds to the hopping of a holes by 2 sites.

Because the holes have a non-zero density, two adjacent holes may arise. When this configuration occurs, it is instantaneously and irreversibly filled by a dimer. The number of holes gradually decreases and eventually every site of the lattice will be occupied. This evolution is equivalent to the holes undergoing diffusion-controlled binary annihilation,

$$H + H \to \emptyset,$$

whose dynamics is well-known. Here the term "diffusion-controlled" denotes that diffusion controls the rate of the reaction—annihilation occurs instantaneously whenever possible. Thus we infer that the density of holes decreases according to

$$1 - \rho(t) \sim \begin{cases} t^{-1/2} & d = 1; \\ t^{-1}\ln t & d = 2; \\ t^{-1} & d > 2. \end{cases} \tag{5.53}$$

In writing the result for spatial dimension $d > 1$, we have made the assumption that the motion of holes is asymptotically diffusive when the lattice is nearly completely occupied by dimers that are randomly oriented in space.

We can similarly analyze lattice deposition of trimers. In this case, holes hop by 3 lattice sites and when three holes are adjacent they undergo diffusion-controlled ternary annihilation,

$$H + H + H \to \emptyset,$$

whose dynamics is also known:

$$1 - \rho(t) \sim \begin{cases} t^{-1/2}\sqrt{\ln t} & d = 1; \\ t^{-1/2} & d > 1. \end{cases} \tag{5.54}$$

Here again, we have glossed over the issues of the shape of the trimer (straight or bent) and their orientation. It seems very plausible that these details do not matter in the long-time limit when very few holes remain.

For lattice deposition of M-mers that diffuse, the long-time relaxation is controlled by the M-body annihilation process

$$\underbrace{H + \cdots + H}_{M \text{ holes}} \to \emptyset,$$

which gives

$$1 - \rho(t) \sim t^{-1/(M-1)} \quad \text{when} \quad M \geq 4. \tag{5.55}$$

This should be valid for all $d \geq 1$, although the applicability of this simple argument to higher dimensions is a bit questionable, as holes should not merely be nearby but additionally they need to be properly aligned to accommodate additional adsorption. Nevertheless, in one dimension the results (5.53)–(5.55) are obviously correct.

Adsorption-Desorption and Car Parking

For any real adsorption process, an adsorbed molecule has a finite binding energy to the substrate. Thus an adsorbed molecule will desorb at a rate that depends on the ratio of the binding energy to the temperature. If a fixed density of molecules is maintained in the gas phase above the substrate, it is natural to describe this dynamics as a reversible adsorption-desorption process: molecules adsorb onto the surface with rate k_+ and they desorb with rate k_-. While adsorption is subject to the availability of space, desorption events occur independently for each adsorbed molecule. The competition between these two processes of adsorption and desorption leads to a steady state. The nature of this steady state is surprisingly rich; although the surface is incompletely covered for irreversible adsorption, the coverage becomes complete for infinitesimal desorption. This singularity is just one of the intriguing features of reversible adsorption.

To frame the problem, let's first consider the trivial example of monomers that interact only with single sites on the substrate. Here the density of adsorbed particles per site ρ satisfies the Langmuir equation

$$\frac{d\rho}{dt} = -k_-\rho + k_+(1-\rho). \tag{5.56}$$

The loss term is proportional to the number density and to the intrinsic desorption rate k_-; similarly, the gain term is proportional to the density of empty sites and to the intrinsic adsorption rate k_+. The linearity of this rate equation reflects the tacit assumption that neighboring adsorbed molecules do not interact. The steady state density is $\rho = k/(1+k)$, where $f = k_+/k_-$ is the ratio of the two rates. The approach to the steady state state is exponential in time, $\rho(t) = \rho_\infty + (\rho_0 - \rho)\, e^{-t/\tau}$, with relaxation rate equal to the sum of the rates, $\tau^{-1} = k_+ + k_-$. Thus for $h \to \infty$, the asymptotic coverage of $\rho =\approx 1 - h^{-1}$ is quickly reached, as the relaxation time τ is roughly h^{-1}.

The *reversible car parking problem* (Fig. 5.14) is a much richer adsorption-desorption process in which the steady state is approached extremely slowly and the nature of the steady state itself is non trivial. Here we view cars as unit-length segments that can adsorb anywhere inside of a void (parking space) of length greater than 1. It is fun to think of the segments as cars that are trying to park along a one-dimensional curb; here we ignore the fact that a car needs a little extra room to actually steer into a parking space. As we are all familiar from everyday experience, it is hard to find a good parking spot. If the rate at which cars leave—the desorption rate—is slow, the probability to find a parking spot large enough to accommodate your car becomes very small. When the position of individual parking spots is unregulated, such as in "resident-only" parking areas, cars will typically be very tightly packed. As we shall show, the steady-state density of cars increases to the limit of perfect packing as the desorption rate goes to zero.

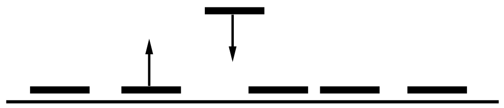

Figure 5.14: Adsorption-desorption of cars. Desorption attempts are always allowed, while the adsorption attempt shown fails because of insufficient parking space.

Part of the motivation for studying the reversible car parking problem is its connection to granular compaction. Suppose that you place glass beads of the same radius into a jar one at a time. The density of filled space in this random packing of beads—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 relax to the *random close-packing density* density of approximately 0.68. In experiments, the time scale over which this compaction occurs can be as long as months! This random close packing-density is still considerably smaller than the maximal packing fraction of $\pi/\sqrt{18} \approx 0.7405$ for spheres that are arranged at the vertices of a face-centered cubic lattice.

The compaction of beads is roughly analogous to a adsorption-desorption process. After the beads have initially been placed, there are lots of small interstitial empty spaces that are generally not large enough to accommodate a bead. Because of the vibration, there will be occasional local re-arrangements that allow a bead to drop down to a position of lower potential energy. As the density increases, these re-arrangements become progressively rarer. This slow relaxation is a phenomenon that seems to be captured mathematically in terms of adsorption-desorption.

To investigate the reversible car parking problem, 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 $E(x.t)$. As usual, the strategy is to write and then attempt to solve the master equations for the void densities. These master equations are:

$$\frac{\partial V(x,t)}{\partial t} = \begin{cases} 2k_+ \int_{x+1}^{\infty} dy\, V(y,t) - 2k_- V(x,t) & x<1; \\ 2k_+ \int_{x+1}^{\infty} dy\, V(y,t) - 2k_- V(x,t) - k_+(x-1)V(x,t) & \\ \quad + \frac{k_-}{\int_0^\infty dx V(x,t)} \int_0^{x-1} dy\, V(y,t)V(x-y-1,t) & x>1. \end{cases} \tag{5.57}$$

Each of the terms in these equations has a simple explanation. For both $x < 1$ and $x > 1$, the first term on the right accounts for the creation of a void of length x when a car parks in a void of length $x + 1$ or greater; the factor 2 accounts for the two places that the car can park to create an x-void. The second term accounts for the loss of an x-void because of the desorption of a car at either end of the void. For $x > 1$, the third term accounts for the loss of an x-void when a car parks inside it.

The last term is more subtle; it accounts for the creation of an x-void when a car leaves a parking spot that has and empty space of length y at one end of the car and a space $x - y - 1$ at the opposite end. Thus a void of length x is created by merging a voids of length y and $x - y - 1$, together with the vacated parking spot of length 1. The proper way to express this composite event is through a 3-body correlation function. However, this description is not closed as the void density is coupled to a 3-body function, we would then have to write an evolution for the 3-body correlation in terms of higher-body correlations, *etc., ad infinitum.* To break this hierarchy of equations at the simplest level, we invoke the mean-field approximation 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 $\int dxV(x,t)$ in the denominator properly normalizes the probability that the neighbor of a y-void has length $x - y - 1$.

Since there is a one-to-one correspondence between voids and adsorbed particles, the density of voids of any size equals the particle density; thus $\rho = \int dxV(x,t)$. Also, the mean fraction space occupied by voids and by cars equals 1; thus $1 = \int dx(x + 1)V(x,t)$. Because each adsorption and desorption event changes the overall density by the same amount, the rate equation for the total density is simply

$$\frac{\partial \rho}{\partial t} = -k_-\rho + k_+ \int_1^\infty dx\,(x-1)V(x,t), \tag{5.58}$$

which is the natural generalization of the Langmuir equation (5.56). The interpretation of this equation is straightforward: with rate $k_-\rho$ a desorption event occurs from among the parked cars, while the second term accounts for the increase in the density when a car parks in a space of size $x > 1$. As a useful check of the correctness of this equation, it can also be obtained by integrating the master equations over all lengths.

While the fully solution of the master equation (5.57) is difficult, most of the interesting behavior can be gleaned quite easily by solving this equation in the steady state. Setting $\frac{\partial P}{\partial t} = 0$, the first equation relates the void density to its spatial integral; this fact suggests an exponential solution

$$V(x) = Ae^{-\alpha x}.$$

Substituting this ansatz into the first for the master equations immediately leads to the condition

$$k = \frac{k_+}{k_-} = \alpha\, e^{\alpha}. \tag{5.59}$$

Next, applying the normalization condition $\int dx\,(1+x)\,V(x) = 1$ gives $A = \alpha^2/(\alpha + 1)$. Thus the overall density of parked cars is simply

$$\rho = \int dx\, V(x) = \frac{\alpha}{\alpha+1}, \tag{5.60}$$

and now eliminating α in favor of ρ, the probability distribution for parking spaces of length x is

$$V(x) = \frac{\rho^2}{1-\rho}\, e^{-\rho x/(1-\rho)}. \tag{5.61}$$

The limiting behaviors of the steady-state density as a function of the scaled adsorption rate are:

$$\rho(h) \approx \begin{cases} k & k \to 0; \\ 1 - [\ln k]^{-1} & k \to \infty. \end{cases} \tag{5.62}$$

For slow adsorption, excluded-volume effects are negligible and the equilibrium density simply equals the adsorption rate, $\rho \approx k$. However, when the adsorption rate is large, excluded-volume effects are dominant. For example, to attain a steady-state density of $\rho = 0.99$, an astronomical rate ratio of $k \approx e^{100}$ is needed for cars, in contrast with a mere $k = 100$ to attain a monomer density of 0.99. As mentioned at the beginning of this section, a particularly intriguing feature is the fact that the behavior of $\rho(k \to \infty) \to 1$ is distinct from the jamming density $\rho_{\rm jam} = \rho(k = \infty) = 0.747\ldots$. The crucial point is that any infinitesimal desorption ($k \to \infty$ but still finite) eventually allows all wasted space to get filled. However, if the problem is defined with $k = \infty$ at the outset, there is no mechanism to utilize too-small parking spaces.

Let's now study how the steady-state parking density is reached. For this purpose, it is extremely useful to apply the *quasi-static* approximation. We will see that this quasi-static approximation provides an extremely easy route to solving a wide variety of slow varying time-dependent phenomena. As a general rule, the basis of this approximation is the physical observation that for $k \to \infty$, the system evolves extremely slowly. Consequently, there is sufficient time for the voids to organize themselves into a state that is infinitesimally close to equilibrium. Thus we use the steady-state exponential void density given by (5.61) in the master equation (5.58). With this assumption, the density evolves as

$$\frac{d\rho}{dt} = -k_-\rho + k_+(1-\rho)\, e^{\rho/(1-\rho}. \tag{5.63}$$

The linear desorption term is the same as in the case of the adsorption of monomers. However, the form of the adsorption term is modified by an effective sticking probability $S(\rho) \equiv e^{\rho/(1-\rho)}$, that gives the probability that an adsorption event is successful. This sticking probability is extremely small when $\rho \to 1$, a feature that reflects the difficulty of finding a parking space when the density of parked cars is close to one.

We can obtain this effective sticking probability by the following heuristic argument. Consider a one-dimensional parking lot that is nearly filled to density $\rho = 1/(1 + \langle x\rangle)$. Here the quantity $langlex\rangle \ll 1$ represents the average value of a s(mall) bumper-to-bumper distance between neighboring parked cars. Thus a driver who tries to park his car by happening upon a sufficiently large parking spot is almost always out of luck. Instead a driver has to enlist the help of $N = \langle x\rangle^{-1} = \frac{\rho}{1-\rho}$ owners of consecutive parked cars to move each of their cars forward a little; the first 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. Since the probability for such a cooperative rearrangement events decays exponentially in the number of cars, we thereby obtain the effective sticking probability $S = \exp(-N) \sim \exp(\frac{\rho}{1-\rho})$.

The relaxation toward the steady state can be extremely slow, a fact that may be nicely demonstrated in the extreme desorption-controlled limit where $k_- \to 0$. This limit is equivalent to having a large population of cars that are cruising the streets looking for parking spots. As soon as a parking spot becomes available it is immediately taken by a new car that happens to be nearby when the spot becomes free. Since desorption events occur rarely, the time dependence of the density may be obtained by the approximation of neglecting the loss term in (5.63). Then to solve the rate equation $d\rho/d(k_+t) = (1-\rho)\exp[-\rho/(1-\rho)]$, we write $g = 1/(1-\rho)$ and approximate the equation by $dg/d(k_+t) \propto e^{-g}$ to yield the asymptotic behavior $g \sim \ln(k_+t)$. Thus

$$1 - \rho(t) \cong (\ln k_+t)^{-1}. \tag{5.64}$$

This extremely slow logarithmic relaxation of the density should be contrasted with the exponential decay of the density to its steady-state value for reversible monomer adsorption.

Post-Adsorption Relaxation

Another rich class of adsorption problems arises when we relax the condition that adsorption occurs only when the incoming molecule lands completely within an empty area. A very simple problem of this class is illustrated in Fig. 5.15. Here monomers are incident on a one-dimensional lattice. If the monomer lands on an empty site it adsorbs there. However, if the monomer lands on an already occupied site it moves laterally to the right until it encounters a hole and the monomer then adsorbs. One motivation for this class of problems comes from computer science where the filling of an array at the first available vacancy is the basis of the hash table construction. It is simplest to illustrate the basic idea from an example familiar all many daily gymnasium users. When you go to a locker room in which all locker use is transient, which locker should you choose so that you won't forget your locker at the end of your workout? The hash table approach is to start with a fixed number, say locker #123. If empty, take it. If occupied, move to #124 and take it, if it is free. If not, move to #125, *etc.* As long as the locker room is not too full, this approach provides a quick algorithm to find and remember a locker reliably. As described, this algorithm is also exactly the same as the monomer deposition process with lateral travel shown in Fig. 5.15.

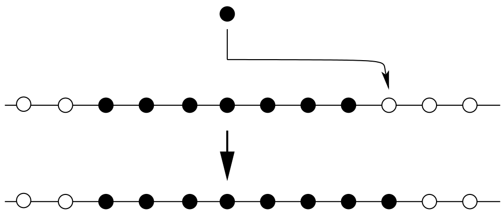

Figure 5.15: A monomer than is incident on an occupied site moves to the right and adsorbs when it first encounters a hole.

Let's assume that the deposition rate is slow, so when the next particle arrives the previous particle has already found a vacant position and has adsorbed. For convenience we set the deposition step equal to one, while the subsequent searching for an empty hole occurs infinitely quickly. Each deposition attempt is successful, so that the coverage grows as $\rho(t) = t$ and the system is completely filled at $t = 1$. We again solve this problem in terms of the empty interval probabilities $E_m(t)$. For our problem the empty interval probabilities satisfy the master equation

$$\frac{dE_m}{dt} = -mE_m - (E_m - E_{m+1})\,\langle m\rangle, \tag{5.65}$$

where $\langle m\rangle$ is the average size of occupied islands. The first term in this equation accounts for the direct deposition of a monomer into an empty m-site sequence. The next term accounts for the situation where the left boundary site is occupied. Here the empty m-interval gets filled when a monomer is transported along a row of occupied sites until the empty interval is encountered. Here $E_m - E_{m+1}$ is the probability to for an empty m-interval with the left boundary site occupied.

A subtle but important feature of the master equation (5.66) is that the last term involves an approximation of a mean field nature; namely, there is no correlation between the sizes of the island of occupied sites and the adjacent empty interval. This lack of correlation allows us to write the joint probability for an empty interval of length m and the mean size of the adjacent island as a product of one-body quantities. This type of decoupling in the master equation appears ubiquitously for cooperative phenomena in one dimension. In many cases, the decoupling is exact, while in many other situations it provides an excellent approximation.

The master equation (5.66) still looks formidable because it does not seem closed—the mean value $\langle m\rangle$ is not expressed in terms of the E_m. However, there is a simple relation between $\langle m\rangle$ and E_m. By definition, the average island size is given by

$$\langle m\rangle = \frac{\sum mI_m}{\sum I_m}.$$

By definition, the sum in the numerator is just the density occupied sites, which simply equals t. The sum in the denominator is total island density I. Now the probability to find an island is the same as $\mathcal{P}(\circ\bullet)$, and the latter quantity is simple $E_1 - E_2$.

To solve the resulting master equation, we again attempt the exponential ansatz $E_m = e^{-mt}\,\Phi(t)$. Substituting this into (5.66), and using the above connection between $\langle m\rangle$ and $E_1 - E_2$ and t, we reduce the infinite set of differential equations (5.66) into $\dot\Phi = -t\,e^t$. It is striking that the empty interval method leads to a fortuitous set of cancellations that makes the problem amenable to solution. Integrating the equation for Φ, we obtain $\Phi = (1-t)\,e^t$, leading to the empty interval probabilities

$$E_m(t) = (1-t)\,e^{-(m-1)t}.$$

From this expression, the density of islands $I = E_1 - E_2$ and the density of voids $\mathcal{P}[\bullet\circ\cdots\circ\bullet] = E_m - 2E_{m+1} + E_{m+2}$ are given by:

$$\begin{aligned} I(t) &= (1-t)\,(1-e^{-t}) \\ V_m(t) &= (1-t)\,(1-e^{-t})^2\,e^{-(m-1)t}\,. \end{aligned}$$

A remarkable property of this problem is that in addition to obtaining the empty interval and empty void probabilities, we can also determine their filled analogs F_m and I_m, namely the filled interval and the island probabilities, respectively. These are defined by

$$F_m = \mathcal{P}[\underbrace{\bullet\cdots\bullet}_{m}], \qquad I_m = \mathcal{P}[\circ\underbrace{\bullet\cdots\bullet}_{m}\circ].$$

Let's compute the island densities. These densities evolve according to the master equations

$$\begin{aligned} \frac{dI_1}{dt} &= -\left(3+\frac{tV_1}{I^2}\right)I_1 + \sum_{n=2}^{\infty}(n-2)V_n \\ \frac{dI_m}{dt} &= -\left(m+2+\frac{tV_1}{I^2}\right)I_m + \left(1-\frac{V_1}{I}\right)(m+1)I_{m-1} \\ &\qquad\qquad + \frac{V_1}{I^2}\sum_{n=1}^{m-2}(n+1)I_nI_{m-n-1} \qquad m\geq 2. \end{aligned} \tag{5.66}$$

(using the sum rules $\sum nV_n = 1-t$ and $\sum V_n = V$, the last term simplifies to $1-t-2V+V_1$). All terms in above equations are self-explanatory; the linear in densities terms are obviously exact while the nonlinear terms tacitly assume the lack of correlations between sizes of adjacent islands and voids. This subtle feature is also required in writing the second term on the right-hand side of Eq. (5.66).

Equations (5.67) are recursive and can be solved accordingly. For instance, we get $I_1 = (1-t)t\,e^{-2t}$ and $I_2 = \frac{3}{2}(1-t)t^2e^{-3t}$ leading to the conjectural behavior $I_m = a_m(1-t)t^me^{-(m+1)t}$. This ansatz indeed solves the problem if for $m \geq 2$ the amplitudes satisfy

$$ma_m = (m+1)a_{m-1} + \sum_{n=1}^{m-2}(n+1)a_na_{m-n-1}\,. \tag{5.67}$$

It is convenient to set $a_0 = 1$; then (5.68) holds for $m = 1$ since it gives $a_1 = a_0 = 1$. With the help of the generating $a(x) = \sum_{m\geq 0} a_mx^m$, we recast the recurrence (5.68) into the differential equation

$$\frac{da}{dx} = a^2 + xa\,\frac{da}{dx}\,. \tag{5.68}$$

Note that the scale transformation $x \to \lambda x$, $a \to \lambda^{-1}a$ leaves Eq. (5.69) unchanged thereby suggesting to use the scale invariant variable $y(x) = xa(x)$. The resulting equation $(1-y)y' = x^{-1}y$ is separable, and it is immediately solved to yield $x = y\,e^{-y}$. We sure can expand x in y but we must do the opposite and find $y = \sum a_mx^{m+1}$. This is accomplished as follows:

$$\begin{aligned} a_m &= \frac{1}{2\pi i}\oint dx\,\frac{y(x)}{x^{m+2}} \\ &= \frac{1}{2\pi i}\oint dy\,\frac{y\,x'(y)}{[x(y)]^{m+2}} \\ &= \frac{1}{2\pi i}\oint dy\,\frac{(1-y)e^{(m+1)y}}{y^{m+1}} \\ &= \frac{(m+1)^{m-1}}{m!}\,. \end{aligned}$$

This completes the derivation of the density of islands:

$$I_m(t) = \frac{(m+1)^{m-1}}{m!}\,(1-t)\,t^m\,e^{-(m+1)t}\,.$$

The density of the empty strings is then found by integrating Eq. (5.30) twice subject to the given boundary values F_1 and F_2. We get

$$F_m = (m-1)F_2 - (m-1)F_1 + \sum_{k=1}^{m-2}(m-1-k)I_k,$$

with the first two values given by

$$\begin{aligned} F_1 &= 1 - E_1 = t, \\ F_2 &= 1 - 2E_1 + E_2 = 1 - 2(1-t) + (1-t)e^{-t}\,. \end{aligned}$$

5.4 Notes

The first equation (5.1) in this chapter was actually the first exact result in the field; it was derived in a pioneering work by Paul Flory (1939) in the context of the cyclization reaction on the polymer chain (his approach is essentially described in section **??**). The jamming coverage for the car parking model was found by Alfred Rényi (1958) 1. In 60s, several people (particularly Cohen, Keller, Reiss, Widom) recognized the advantages of the evolution approach. Earlier exact results are reviewed and systematized in 43. More recent reviews 46; 47; 7; 6 are written by researches who were (and some still are) very active in the field in 80s and 90s. These reviews contain many useful things not covered in this chapter (e.g. multilayer adsorption — we discussed only monolayer case) and huge bibliography. Experimental techniques are reviewed by Ramsden 8.

The subject of sections 5.1–5.1 is classical although some of the results are quite recent and could not been found in reviews (e.g., models in which particles landing on the top of islands quickly diffuse to vacant sites 57). In sections 5.2 and 5.3 we gave a glimpse of adsorption problems for which there is currently no framework that allows to do analytical computations yet we already understand some interesting features, e.g. asymptotics. For adsorption on higher-dimensional substrates, the reader can like original papers that are short and lucid; see e.g. Refs. 44; 10 for discussion of (**??**)–(**??**). The deposition of needles is due to Tarjus and Viot 36. The connection with diffusion-controlled annihilation was recognized by Privman and co-workers (see 12), the parking lot model 53 is actively investigated due to success in explaining several features of granular materials.

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Flory and Rényi, again independently and apparently without even knowing each other existence, discovered percolation transition in random graphs. We shall discuss this phenomenon later in this book.

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Problems

1. Supposed that dimers are deposited onto the one-dimensional lattice of size L. Compute the average jamming coverage.

2. Compute the total number $J_{L,N}$ of the jammed configurations in the system of size L with exactly N absorbed dimers. Find the density at which $J_{L,N}$ reaches maximum and determine the magnitude of fluctuations.

3. Compute the total density of voids and the density of islands for a one-dimensional lattice with irreversible k-mer adsorption.

4. Compute the magnitude of fluctuations in the number of adsorbed dimers in a region of L sites.

5. Compute the "structure factor" $S(q) = \sum e^{iqm} C_m$ at the jamming limit for the adsorption of dimers.

6. Suppose that dimers are deposited onto the one-dimensional an initially partly filled lattice. Consider the case when each site of the lattice is initially occupied with probability ρ_0 and there were no spatial correlations. Compute the jamming coverage.

7. Determine the asymptotic approach to the jamming coverage for the car parking problem in one dimension.

8. Solve the parking model in the presence of defects that are sizeless and distributed with density λ without correlations.

Chapter 6

SPIN DYNAMICS

Kinetic spin systems are to nonequilibrium statistical physics what the Ising model is to equilibrium statistical physics: a rich and basic laboratory to elucidate fundamental concepts and to develop many important applications. It is usually the case, the one starts a discussion of the spin dynamics with the kinetic Ising model because it is often viewed as the simplest example of such a system. However, there is an even simpler kinetic spin system that is not so widely appreciated in the physics literature—the voter model—that will be the starting point for our discussion. The main reason for our initial focus on the voter model is that it is exactly soluble in all spatial dimensions, and this solution reveals the essential role played by the spatial dimension in determining the long-time behavior of the system.

6.1 Voter Model

The voter model was first introduced in the applied probability theory literature and it remains one of the most extensively studied interacting particle systems. In this model, voters "live" on the sites of a specified graph. Conventionally, this graph is assumed to be a regular lattice in d dimensions, but it is also possible to consider any type of graph—such as Erdos-Renyi random graphs or graphs with a broad distribution of degrees. Each voter can assume one of two states; for the purposes of this discussion, we think of these states are political leanings, say, Democrat and Republican.

The dynamics of the voter model is simplicity itself. Each voter can be viewed as possessing zero self confidence and looks to a neighbor to decide what to do. Concretely, the voter model dynamics consists of:

1. Pick a random voter.
2. The selected voter adopts the state of randomly-selected neighbor.
3. Repeat steps 1 & 2 *ad infinitum* or until consensus is achieved.

Symbolically, the state of a voter at $\mathbf{x}$, which may take one of two values $s(\mathbf{x}) = \pm 1$, evolves as follows:

$$s(\mathbf{x}) \to s(\mathbf{x} + \mathbf{e}_i). \tag{6.1}$$

Here, $\mathbf{e}_i$ is one of the Z nearest-neighbors of site $\mathbf{x}$, with $i = 1, \ldots, z$, and z is the coordination number of the graph. The update step occurs with a uniform ratethat set equal to $1/2$ for convenience. Of course, the opinion of a voter actually changes only when the neighbor of an initially selected site has an opposite opinion.

Why is the voter model exactly soluble?

The multiple-point correlation functions $S(\mathbf{x}, \ldots, \mathbf{y}) = \langle s(\mathbf{x}) \cdots s(\mathbf{y}) \rangle$ obey closed equations and they can be obtained exactly. We detail the derivation of the evolution equation for the single point average (the average opinion) $S(\mathbf{x}) \equiv \langle s(\mathbf{x}) \rangle$. Following the dynamical rule (6.1), the change in the voter's opinion during a small time interval Δt is

$$s(\mathbf{x}, t + \Delta t) = \begin{cases} s(\mathbf{x}, t) & \text{with probability } 1 - z\,\Delta t/2, \\ s(\mathbf{x} + \mathbf{e}_i, t) \qquad i = 1, \ldots, z & \text{with probability } \Delta t/2. \end{cases} \tag{6.2}$$