Chapter 6

ADSORPTION

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

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

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

6.1 Random Sequential Adsorption in One Dimension

Dimer adsorption

A simple example that exhibits non-trivial collective behavior is the irreversible and *random sequential adsorption* of dimers — molecules that occupy two adjacent sites of an infinite one-dimensional lattice (Fig. 6.1). We model the steady influx of molecules by adsorption attempts occurring one at a time at random locations on the substrate. An adsorption attempt is successful only if a dimer is incident onto two adjacent empty sites. If a dimer lands onto either two occupied sites or onto one occupied and one empty site, the attempt fails. That is, multilayer adsorption is forbidden, so that each site is either empty or contains 1 particle, but no more. The dimer coverage grows with time and eventually only isolated empty sites remain. When this occurs, the substrate is jammed and no further adsorption is possible.
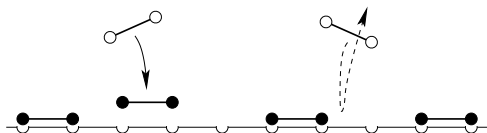

Figure 6.1: Irreversible dimer deposition. The dimer on the left successfully adsorbs onto two adjacent vacant substrate sites, while the dimer on the right does not adsorb.

For dimer adsorption, a jammed state consists of strings with an even number of occupied sites (●) that are separated by isolated vacant sites (○), as illustrated below:

Figure 6.2: A jammed configuration in the random sequential adsorption of dimers.

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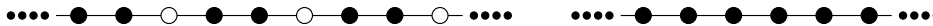

Figure 6.3: Minimum-density and maximum-density jammed dimer configurations.

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

$$\rho_{\text{jam}} \equiv \rho(t = \infty) = 1 - e^{-2} = 0.864\,664 \ldots \tag{6.1}$$

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

To determine the evolution of the substrate coverage, 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 jth site is occupied, and $n_j = 0$ if this site is empty. However these probabilities contain more information than necessary. What we really need are the *empty interval probabilities*, namely, the probability that a string of m consecutive sites are empty. We first define

$$E_m \equiv \text{prob}(\times \underbrace{\circ \cdots \circ}_{m} \times) \equiv \mathcal{P}[\underbrace{\circ \cdots \circ}_{m}]$$

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

Figure 6.4: Changes in the empty interval probability E_m for $m = 4$. Shown are an adsorption event in the interior of the interval (left) and at the edge of the interval (right).

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

$$\frac{dE_m}{dt} = -(m - 1)E_m - 2E_{m+1} \qquad m \geq 1. \tag{6.2}$$

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 lies entirely within the interval (Fig. 6.4). The second term accounts for the two adsorption events in which one end of the incident dimer is outside the m-interval. For these latter events, the empty interval must contain at least $m + 1$ empty sites, hence the factor E_{m+1}. Notice that (6.2) contains only loss terms. This feature is a consequence of using the empty interval probabilities E_m as the basic dynamical variables. Pictorially, we are looking at the substrate through eyes that see only m consecutive sites at a time and E_m is merely the

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

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

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

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

$$\frac{dV_m}{dt} = -(m-1)V_m + 2\sum_{j=2}^{\infty} V_{m+j}. \tag{6.3}$$

The first term again accounts for the adsorption of a dimer in the interior of a void. The sum accounts for the *creation* of a void of m sites by the adsorbing a dimer into a void that contains $\geq m+2$ unoccupied sites. Notice the close correspondence between this master equation and those for fragmentation [*e.g.*, Eq. (5.3)]. There are no hard and fast rules for which set of quantities — E_m or V_m — are more useful for determining the dynamics of these type of kinetic problems. For adsorption, the master equations for E_m are typically easier to solve and we focus on these quantities in what follows:

Returning to the E_m, we now solve (6.2) for the initial condition of an initially empty system, $E_m(0) = 1$. Because an integrating factor for the master equations is $e^{-(m-1)t}$, this fact suggests seeking a solution of the form

$$E_m(t) = e^{-(m-1)t}\,\Phi(t), \tag{6.4}$$

where Φ coincides with $E_1(t)$, and with $\Phi(0) = 1$ to match the initial condition. Notice also that $E_1(t) = 1 - \rho(t)$, where $\rho(t)$ is the density of occupied sites. This connection allows us to determine how the surface coverage evolves. Using (6.4), the infinite set of master equations (6.2) miraculously reduces to the *single* equation $\frac{d\Phi}{dt} = -2e^{-t}\Phi$, whose solution immediately yields the empty interval probabilities

$$E_m(t) = e^{-(m-1)t - 2\left(1 - e^{-t}\right)}. \tag{6.5}$$

Empty gaps of length greater than 1 decay exponentially with time and only gaps of length 1 remain in the final jammed state. From (6.5), the density of such gaps is $E_1(\infty) = e^{-2}$, so that the jamming coverage is

$$\rho_{\text{jam}} \equiv \rho(t = \infty) = 1 - e^{-2} = 0.864\,664\,,\dots \tag{6.6}$$

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

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

$$\rho(t) = 1 - E_1(t) = 1 - e^{-2\left(1 - e^{-t}\right)}. \tag{6.7}$$

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

Adsorption of longer molecules

What happens if the incident molecules are k-mers that occupy k consecutive substrate sites? A nice illustration of the power of the master equation is that the coverage for this more general adsorption process can be obtained by a straightforward extension of the theory for dimers. The master equations for the empty interval probabilities E_m in k-mer adsorption are now:

$$\frac{dE_m}{dt} = \begin{cases} -(m-k+1)E_m(t) - 2\sum_{j=1}^{k-1} E_{m+j}(t) & m \geq k; \\ \\ -(k-m+1)E_k(t) - 2\sum_{j=1}^{m-1} E_{k+j}(t) & m < k. \end{cases} \tag{6.8}$$

The terms in this equation mirror those in the master equation (6.2) for dimer adsorption. In the first line, the first term accounts for the $m - k + 1$ distinct ways that a k-mer can adsorb in the interior of an m-site empty interval. The second term accounts for $2(k - 1)$ ways that the k-mer can adsorb, 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. The equation for $m < k$ can be obtained quite simply by merely interchanging the roles of k and m in the equation for $m \geq k$.

For $m \geq k$, the structure of the equations again suggests the ansatz $E_m(t) = e^{-(m-k+1)t}\Phi(t)$ which reduces Eqs. (6.8) for $m \geq k$ to $\dot{\Phi} = -2\Phi \sum_{j=1}^{k-1} e^{-jt}$. Thus we obtain

$$E_m(t) = \exp\left[-(m - k + 1)t - 2\sum_{j=1}^{k-1} \frac{1 - e^{-jt}}{j} \right] \qquad m \geq k. \tag{6.9}$$

To find the time dependence of the coverage, $\rho = 1 - E_1$ we use the fact that $E_1(t)$ satisfies the master equation $\dot{E}_1 = -k\, E_k(t)$, with E_k determined from Eq. (6.9) with $m = k$. The coverage $\rho = 1 - E_1$, may then be expressed as

$$\rho(t) = k \int_0^t \exp\left[-u - 2\sum_{j=1}^{k-1} \frac{1 - e^{-ju}}{j} \right] du. \tag{6.10}$$

Numerical evaluation of this integral gives a jamming coverage that decreases monotonically with k (table 6.1 and Fig. 6.5). The jammed state becomes less full as k increases because empty regions as large as $k - 1$ can arise. **seems incomplete**

k	ρ_{jam}
1	1
2	0.864665
3	0.823653
4	0.803893
5	0.792276
∞	0.747597

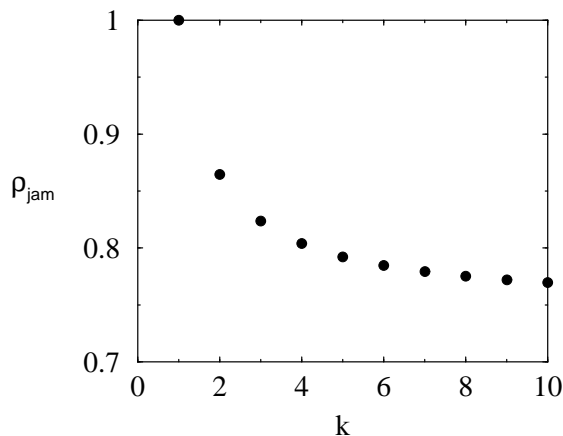Table 6.1: Jamming coverage for random sequential adsorption of k-mers in one dimension.

Figure 6.5: Jamming coverage for random sequential adsorption of k-mers in one dimension.

Irreversible car parking

The limit of k-mer adsorption with $k \to \infty$ defines 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. The only constraint is that cars cannot overlap; however a car *can* fit into a parking spot that is infinitesimally larger than the car itself. For this parking problem, the jamming coverage was found by Rényi to be $0.747597\ldots$, and is simply the $k \to \infty$ limit of the k-mer jamming coverage.

We may again solve this parking problem by the master equation approach. The length of a car is immaterial if we seek the fraction of the line that is covered, and for convenience we define the car length to be 1. The appropriate dynamical variable is $E(x,t)$, the probability that a randomly-chosen interval of length x is empty. As in the discrete case, this region may be part of an even longer empty interval. When the rate at which cars park equals 1, the master equation for $E(x,t)$ is [compare with Eq. (6.8)]

$$\frac{\partial E(x,t)}{\partial t} = \begin{cases} -(x-1)E(x,t) - 2\int_x^{x+1} E(y,t)\,dy & x > 1 \\[4mm] -(1-x)E(1,t) - 2\int_1^{x+1} E(y,t)\,dy & x < 1. \end{cases} \tag{6.11}$$

The terms in this master equation have direct counterparts with the terms in (6.8) for k-mer adsorption. For $x > 1$, the first term on the right of Eq. (6.11) accounts for adsorption events that lie completely within the interval, while the second term accounts for adsorption events that partially overlap this interval. A similar correspondence also applies for the second line of (6.11).

To solve this master equation, consider first the regime $x > 1$. As in the discrete case, we seek a solution of the form

$$E(x,t) = e^{-(x-1)t}\,E(1,t). \tag{6.12}$$

Substituting this expression into the first of Eqs. (6.11), the x-dependent terms cancel, and integrating the resulting equation for $E(1,t)$ gives

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

with which Eq. (6.12) gives $E(x,t)$ for $x > 1$. From the second of Eqs. (6.11), $\frac{\partial E(0,t)}{\partial t} = -E(1,t)$, from which the coverage $\rho(t) = 1 - E(0,t)$ is

$$\rho(t) = \int_0^t \exp\left[-2\int_0^v du\,\frac{1-e^{-u}}{u}\right]\,dv. \tag{6.13}$$

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

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

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

The crucial step occurs in the second line. As discussed in Section A.2, we may 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 $u > 1$. Then the integral in the exponent is elementary and the asymptotic behavior follows straightforwardly. More precisely, the asymptotic behavior of $\int_0^t du\,\frac{1-e^{-u}}{u}$ is $\ln t + \gamma + t^{-1}e^{-t} + \ldots$, where $\gamma = 0.577215\ldots$ is Euler's constant. Thus

$$\rho(\infty) - \rho(t) \to t^{-1}\,e^{-2\gamma} \qquad t \to \infty;$$

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

6.2   Combinatorial Approach for Adsorption

Enumeration of dimer configurations

Flory originally determined the jamming coverage for dimer adsorption by a combinatorial method that we now present to contrast with the kinetic approach. In the combinatorial method, we write a recursion for the jamming density on a finite interval of length L in terms of jamming densities on shorter intervals. Let A_L be the average number of occupied sites in all final jammed states for dimer adsorption. 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 $L \geq 2$, the coverage obeys the recurrence

$$A_L = \frac{1}{L-1} \sum_{j=1}^{L-1} (A_{j-1} + 2 + A_{L-j-1})$$

$$= 2 + \frac{2}{L-1} \sum_{j=1}^{L-2} A_j, \tag{6.14}$$

with $A_0 = A_1 = 0$. 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. In the second line, we use the fact the two sums are identical. A crucial element of this recursion is the implicit assumption that dimers are added one at a time. Thus the final state will be the same as the jamming density that was obtained previously by the master equation description of the dimer deposition.

To solve for A_L we introduce the generating function $A(x) = \sum_{L=2}^{\infty} A_L x^{L-2}$, multiply Eq. (6.14) by $(L-1)\,x^{L-2}$, and sum over all L. The left-hand side is $\sum_2^{\infty} (L-1)\,x^{L-2}\,A_L = \frac{d(xA)}{dx}$. For the second term on the right-hand side, we interchange the order of summations (in close analogy with the interchange of integration order discussed on page 79) to give

$$2 \sum_{L=2}^{\infty} x^{L-2} \sum_{j=0}^{L-2} A_j = 2 \sum_{j=0}^{\infty} A_j \sum_{L=j+2}^{\infty} x^{L-2}$$

$$= 2 \sum_{j=0}^{\infty} A_j \frac{x^j}{1-x}$$

$$= \frac{2x^2}{1-x} A(x),$$

so that the recurrence (6.14) can now be recast as the differential equation

$$\frac{d}{dx}(xA) = \frac{2}{(1-x)^2} + \frac{2x^2}{1-x} A, \tag{6.15}$$

subject to the initial condition $A(x = 0) = A_2 = 2$. The solution to Eq. (6.15) is

$$A(x) = \frac{1 - e^{-2x}}{x(1-x)^2} = 2 + 2x + \frac{10}{3}x^2 + 4x^3 + \frac{74}{15}x^4 + \cdots, \tag{6.16}$$

and we can now 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.

What is the meaning of these numbers? For example, consider $A_4 = \frac{10}{3}$, the average number of occupied sites on a 4-site chain. This value 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.

As $L \to \infty$, we can obtain the series 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

$$A(x) = \sum_{2}^{\infty} \rho L \, x^{L-2} = \frac{\rho}{x} \frac{d}{dx} \sum_{L=2}^{\infty} x^L$$
$$= \frac{\rho}{x(1-x)^2} (2x - x^2). \tag{6.17}$$

Comparing Eqs. (6.16) and (6.17) as $x \to 1$, we find $\rho = 1 - e^{-2} = 0.864\,664\ldots$, thus recovering the Flory result (6.1).

Phase space and broken ergodicity

A basic tenet of the microcanonical ensemble in equilibrium statistical physics is that of *equal a priori probability* — each microstate is realized with the same probability. This feature is termed *ergodicity* and it allows us to make the equivalence between the formal ensemble average of statistical mechanics and the time average in a real equilibrium system. Systems with jammed configurations do not fit into this picture as they do not uniformly sample the state space of all configurations. This phenomenon is known as *broken ergodicity*. Irreversible adsorption is an ideal setting to understand broken ergodicity because all states can be readily computed.

Let's start by counting 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. These jammed configurations can be divided 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 F_L is determined by the recurrence

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

We write this Fibonacci-like recurrence in terms of the generating function and use the boundary conditions $F_0 = F_1 = F_2 = 1$ to give

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

Formally, F_L is the Lth term in the generating function. For 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:

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

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

$$F_L \sim A\zeta^L, \tag{6.18}$$

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 and there is an extensive packing entropy, $S = \ln F_L \sim L \ln \zeta$.

Next, we determine the number of configurations with a specified coverage. 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 $\lfloor (L+1)/3 \rfloor \leq N \leq \lfloor L/2 \rfloor$ for the configuration to actually be jammed, with $\lfloor x \rfloor$ 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. Each such string corresponds to a distinct jammed state. Since a vacancy can appear between any 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

$$F_{L,N} = \binom{N+1}{L-2N}, \tag{6.19}$$

and the total number of configurations with any number of dimers in the allowed range 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 two leading terms in the Stirling formula $\ln x! \sim x \ln x - x$. In this approximation, the total number of fixed-density configurations also grows exponentially with the system size, $F_{L,\rho} \sim e^{Lf(\rho)}$, with

$$f(\rho) = \frac{\rho}{2} \ln \frac{\rho}{2} - (1-\rho)\ln(1-\rho) - \left(\frac{3\rho}{2} - 1\right)\ln\left(\frac{3\rho}{2} - 1\right). \tag{6.20}$$

Because $F_{L,\rho}$ grows exponentially with L, $f(\rho)$ is asymptotically dominated by its most probable value. Setting $f' = 0$ leads to $4\rho(1-\rho)^2 = (3\rho - 2)^3$, whose solution gives the asymptotic equilibrium density $\rho_{\rm eq} = 0.823991\ldots$. Expanding f about $\rho_{\rm eq}$, the density dependence of the number of jammed configurations approaches the Gaussian

$$F_{L,N} \simeq \frac{F_L}{\sqrt{2\pi\Delta^2}} e^{-(\rho - \rho_{\rm eq})^2/2\Delta^2}), \tag{6.21}$$

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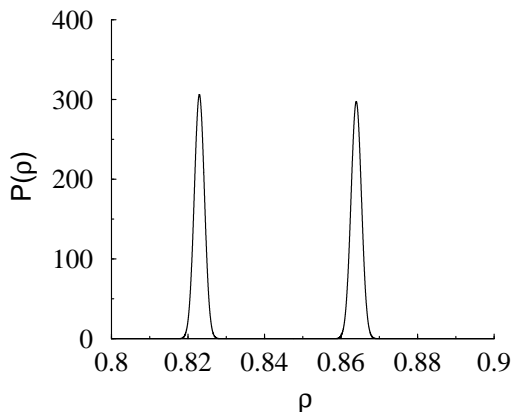

Figure 6.6: The equilibrium distribution (left) and jamming distribution (right) for a system of size $L = 10^4$.

The equilibrium probability distribution and the distribution of jammed states have the same functional form, except that their peak locations are different: $\rho_{\rm jam} \neq \rho_{\rm eq}$! 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.

6.3 Correlations and Fluctuations

The relation $\rho = 1 - E_1$ is a simple example of expressing a fundamental physical quantity (the coverage) in terms of the empty interval probabilities E_m. As we now show, the empty interval probabilities contain much more information about the substrate occupancy, such as spatial correlation functions between occupied sites and fluctuations in surface coverage. Let's denote the probability of an arbitrary configuration by $\mathcal{P}[\cdots]$. Thus, for example, $E_2 = \mathcal{P}[\circ\circ]$, where again the states of the sites external to the string are not specified. With this notation, $\rho = \mathcal{P}[\bullet] = 1 - E_1$ is the consequence of the conservation statement $\mathcal{P}[\circ] + \mathcal{P}[\bullet] = 1$. Other conservation statements, such as

$$\mathcal{P}[\circ\circ] + \mathcal{P}[\circ\bullet] = \mathcal{P}[\circ] \quad \text{or} \quad \mathcal{P}[\circ\circ] + \mathcal{P}[\circ\bullet] + \mathcal{P}[\bullet\circ] + \mathcal{P}[\bullet\bullet] = 1$$

express the probability of any configuration of occupied sites in terms of probabilities of empty configurations. For simple configurations, these probabilities can be expressed only 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

$$\mathcal{P}[\underbrace{\circ\cdots\circ}_{m}\bullet] = E_m - E_{m+1}, \tag{6.22}$$

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

$$V_m = \mathcal{P}[\bullet\underbrace{\circ\cdots\circ}_{m}\bullet] = E_m - 2E_{m+1} + E_{m+2}. \tag{6.23}$$

A fundamental characterization of correlations between occupied sites is the *pair correlation function C_j*

$$C_j \equiv \langle n_0\, n_j \rangle - \langle n_0 \rangle \langle n_j \rangle. \tag{6.24}$$

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

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

where $\times$ denotes a site whose state is unspecified. As we now show, to determine correlation functions such as C_j, we need configurations that include disconnected empty configurations. We thus 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 the configuration that consists of two empty clusters of at least i and at least k sites that surround $j-1$ sites of unspecified states. Then $E_{i,1,k} = E_{i+k}$, where the latter quantity is the empty interval probability. For 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 (6.2):

$$\begin{aligned}
\frac{dE_{i,j,k}}{dt} = &-(i-1)E_{i,j,k} - E_{i+1,j,k} - E_{i+1,j-1,k} \\
&- (k-1)E_{i,j,k} - E_{i,j,k+1} - E_{i,j-1,k+1},
\end{aligned} \tag{6.25}$$

for $i, k \geq 1$ and $j \geq 2$. The consecutive terms in the first 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 second line are counterparts for the empty k-string. To solve this master equation, we generalize the ansatz (6.4) to:

$$E_{i,j,k}(t) = e^{-(i+k-2)t}\,\Psi_j(t) \quad \text{for} \quad i, k \geq 1, \tag{6.26}$$

where $\Psi_j(t) \equiv E_{1,j,1}$, to simplify the above master equations to:

$$\frac{d\Psi_j}{dt} = -2e^{-t}[\Psi_j + \Psi_{j-1}], \tag{6.27}$$

for $j \geq 2$, while for $j = 1$, $\Psi_1 = E_2$. Equations (6.27) are recursive and solvable by introducing the generating function $\Psi(x,t) = \sum_{j=2}^{\infty} x^j \Psi_j(t)$ to recast (6.27) into

$$\frac{\partial \Psi(x,t)}{\partial t} = -2e^{-t} \left[(1+x)\Psi(x,t) + x^2 E_2(t) \right]. \tag{6.28}$$

The initial condition is $\Psi_j(t = 0) = 1$, or $\Psi(x,0) = x^2(1-x)^{-1}$. Solving (6.28) subject to this initial condition and expanding the solution in a Taylor series in x we obtain (for $j \geq 2$):

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

We now exploit these results to compute the pair correlation C_j in Eq. (6.24). Using the conservation statements

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

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:

$$C_1 = E_2 - (E_1)^2, \qquad C_j = -E_1 \left[\frac{(\ln E_1)^j}{2 \cdot j!} + \sum_{k \geq j+1} \frac{(\ln E_1)^k}{k!} \right] \quad j > 1. \tag{6.29}$$

In the jammed state $E_1(\infty) = e^{-2}$, so that 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 is much faster than typical exponential decay of correlations in many equilibrium systems with short-range interactions, such as a system of hard disks.

6.4   Adsorption in Higher Dimensions

Most applications of irreversible adsorption involve two-dimensional substrates. It is natural to begin with the irreversible adsorption of elementary objects such as disks, squares, rectangles, and sticks as a prelude to real systems, such as proteins and latex particles. To get a feeling for numbers, the jamming coverages for random sequential adsorption of various elementary objects in two dimensions are listed in Table 6.2. These coverages strongly depend on the shape of the object. An exact analysis of adsorption is generally not possible in higher dimensions, and one has to resort to approximations and numerical simulations. The one-dimensional theory still serves as a useful guide, however, because the evolution of the coverage has the same qualitative features 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, in which each site is connected to exactly z other sites in tree structure (Fig. 6.7). For dimer adsorption on the Bethe

| object	substrate	ρ_{jam}
unoriented dimers	square lattice	0.9068
2×2 squares	square lattice	0.74788
(aligned) squares	continuum	0.562009
disks	continuum	0.5472

Table 6.2: Jamming coverages for various objects in two dimensions.

lattice, 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. Because these clusters have a tree structure, it is easy to count the "boundary" configurations that enter into the master equations.

The probability E_m that all sites in such a cluster remain vacant during adsorption of dimers satisfies the master equation [compare with Eq. (6.2)]

$$\frac{dE_m}{dt} = -(m-1)E_m - [(z-2)m+2]E_{m+1}, \tag{6.30}$$

for $m \geq 1$, with the initial conditions $E_m(0) = 1$. The first term on the right accounts for deposition events in which the dimer lands somewhere within the cluster. The number of available locations for such "interior" adsorption events is just the number of bonds in the cluster. Since any cluster has a tree topology, 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 cluster perimeter sites — sites that adjoin the cluster, but are not part of the cluster itself (Fig. 6.7). For a cluster of 2 sites, the number of perimeter sites is $2(z-1)$. When a site is added to the cluster, 1 perimeter site is lost, but $(z-1)$ perimeter sites are gained. Continuing this counting for a cluster of m sites, the number of perimeter sites is $zm - 2(z-1)$.
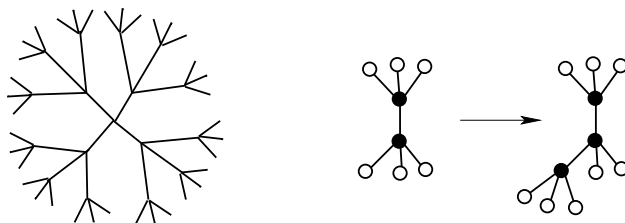
Figure 6.7: (Left) First three generations of a Bethe lattice with coordination number $z = 4$. (Right) Counting perimeter sites (circles) starting with a connected cluster of $m = 2$ and 3 sites (dots).

To solve the master equation (6.30), 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

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

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

$$E_m(t) = e^{-(m-1)t}\left[(z-1) - (z-2)\,e^{-t}\right]^{-m-2/(z-2)}. \tag{6.31}$$

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

$$\rho_{\mathrm{jam}} = 1 - (z-1)^{-z/(z-2)}. \tag{6.32}$$

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, $1 - \rho_{\mathrm{jam}} \sim z^{-1}$. Amusingly, the Bethe lattice provides a good

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

A second look at almost exponential solutions

Consider a master equation with the generic form

$$\frac{dE_m}{dt} = \lambda(m + \alpha)E_m + \mu(m + \beta)E_{m+1}, \tag{6.33}$$

that encompasses Eq. (6.30). Again, the almost exponential ansatz provides an easy route to the solution. Let's assume a solution of the form

$$E_m = \Phi(t)[\varphi(t)]^m. \tag{6.34}$$

Substituting into Eq. (6.33) and then dividing by E_m gives

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

This result shows the utility of the ansatz (6.34), as the above equation divides naturally into terms linear in m and terms independent of m.

From the terms linear in m, we have

$$\frac{\dot{\varphi}}{\varphi} = \lambda + \mu\varphi, \tag{6.35}$$

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

$$\frac{\dot{\Phi}}{\Phi} = \lambda\alpha + \mu\beta\varphi, \tag{6.36}$$

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

The crucial point is that the factor φ^m in the original ansatz separates the initial set of equations (6.34) into two equations: one linear in m and one independent of m.

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

$$\rho_{\text{jam}} - \rho(t) \sim e^{-\lambda t}. \tag{6.37}$$

As a concrete example, consider the dimer adsorption on the square lattice. At long times, the available spaces that can accommodate additional dimers are few and far between. These "target" regions are small 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. Crucially, the probability to find a vacant cluster on the substrate rapidly decreased with 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

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

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

$$P[\circ\circ] \sim e^{-t}, \qquad P[\circ\,\circ\,\circ] \sim e^{-2t}, \qquad P\begin{bmatrix}\circ\circ\\\circ\circ\end{bmatrix} \sim e^{-4t}. \tag{6.38}$$

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 $d\rho/dt \sim -2P[\circ\circ]$, so that

$$\rho_{\text{jam}} - \rho(t) \sim e^{-t}. \tag{6.39}$$

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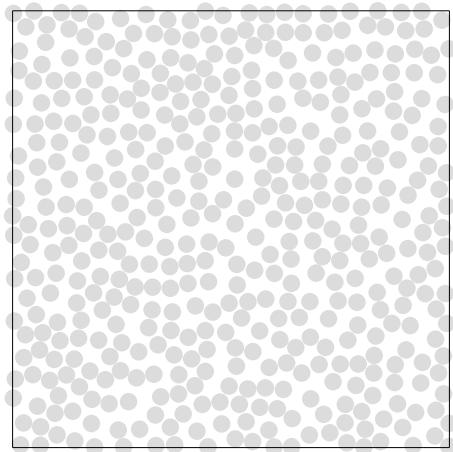
Continuous substrates

Figure 6.8: A jammed state for random sequential adsorption of disks in two dimension.

On continuous substrates, gaps between adjacent adsorbed objects can be arbitrarily small, and this feature leads to a slow algebraic relaxation of the density to the jamming density in which $\rho_{\text{jam}} - \rho(t) \sim t^{-\sigma}$. For car parking in one dimension, we already demonstrated that $\sigma = 1$. Let's derive the corresponding decay for the adsorption of disks in two dimensions (Fig. 6.8). 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, notice that around each disk there is an "exclusion zone" whose radius is twice that of the disk. An incident disk whose center lies within the exclusion zone of any already adsorbed disk cannot adsorb. The target zones of the substrate are the complement of the exclusion zones (Fig. 6.9). In a jammed configuration, no target zones remain even though the adsorbed particles do not completely cover the substrate.

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

$$c(\ell, t) \sim e^{-\ell^2 t}. \tag{6.40}$$

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

$$\rho_{\text{jam}} - \rho(t) \sim \int_0^\infty c(\ell, t)\, d\ell \sim \int_0^\infty e^{-\ell^2 t}\, d\ell \sim t^{-1/2}. \tag{6.41}$$
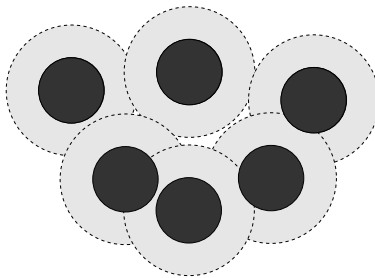
Figure 6.9: Two target areas (white), the exclusion zones (shaded), and the adsorbed disks (dark) near jamming. In the long-time limit only arc-triangular target areas, such as the tiny one on the left, remain.

Because target zones can be arbitrarily small, a power-law decay arises after rescaling the integral. Thus although the probability to find a target zone of a given size vanishes exponentially with time, the average over the sizes of all target zones leads to a power-law tail. This heuristic approach can be straightforwardly extended to arbitrary spatial dimension d. Now the area of a target zone of linear dimension ℓ scales as ℓ^d. Correspondingly, the density of target zones of linear dimension ℓ scales as $c(\ell, t) \sim e^{-\ell^d t}$. The analog of Eq. (6.41) then gives $\rho_{\text{jam}} - \rho(t) \sim t^{-1/d}$ in d dimensions.

We can extend further this argument to determine the approach to jamming for elongated particles, for example, ellipses with a large aspect ratio. Now the notion of a target zone is no longer precise because minimum separation between two adsorbed ellipses depends on their relative orientations. However, as target zones get filled, there is a tendency for a newly-adsorbed ellipse to be oriented with its neighbors. This restriction plays an important role in the adsorption of non-symmetrical objects at long times. Let θ be the range of allowed orientations for an ellipse that is incident on a target zone of linear dimension ℓ. The density of target zones of linear size ℓ will asymptotically evolve according to $\frac{dc}{dt} \propto -\theta \, \ell^2 \, c$. Since the orientational range vanishes in the long-time limit, we make the simplest self-consistent assumption that $\theta = a_1 \ell + a_2 \ell^2 + \cdots$. Then using $\theta \propto \ell$ for small ℓ, the concentration of target areas of linear dimension ℓ is governed by $dc/dt \propto -\ell^3 \, c$. As a result,

$$c(\ell, t) \sim e^{-\ell^3 t} . \tag{6.42}$$

Substituting this form for $c(\ell, t)$ into Eq. (6.41), the relaxation to the jamming coverage is now given by $\rho_{\text{jam}} - \rho(t) \sim t^{-\sigma}$, with $\sigma = 1/3$. Thus the orientational constraint hinders the approach to the jammed state.

For oriented squares, the target areas asymptotically are rectangular and the density $n(x, y, t)$ of target rectangles of size $x \times y$ decays according to $\frac{dc}{dt} = -xy \, c$. Consequently, $c \sim e^{-xy \, t}$, from which

$$
\begin{aligned}
\rho_{\text{jam}} - \rho(t) = \int_0^1 \int_0^1 n(x, y, t) \, dx \, dy &\sim \int_0^1 \frac{1 - e^{-xt}}{xt} \, dx \\
&= t^{-1} \int_0^t \frac{1 - e^{-u}}{u} \, du \\
&\simeq t^{-1} \ln t .
\end{aligned}
\tag{6.43}
$$

Similarly, the approach to jamming for the random sequential adsorption of aligned hypercubes in d dimensions is given by

$$\rho_{\text{jam}} - \rho(t) \sim (\ln t)^{d-1} \, t^{-1}. \tag{6.44}$$

Needles

An particularly intriguing example is the deposition of zero-area, unoriented, identical needles of unit length — the limit of ellipses with a diverging aspect ratio. Here the areal coverage of the substrate vanishes, even though the number of adsorbed particles diverges with time. Early deposition attempts are mostly

successful because the substrate is nearly empty. Thus the number of adsorbed needles starts growing linearly with time and these initial needles have little orientational or positional order. However, when the needle density becomes of the order of 1, previously adsorbed needles strongly constrain both the position and the orientation of subsequent adsorption events. In the long time limit, domains form in which neighboring needles are nearly aligned *and* positionally ordered (Fig. 6.10). 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 domains are well defined, most adsorption attempts fail and the number of adsorbed needles grows sub-linearly with time.
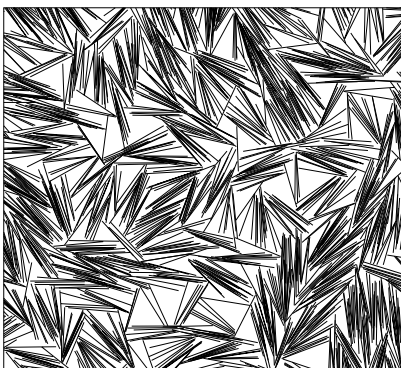

Figure 6.10: Random sequential adsorption of needles in two dimensions.

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 approximately a unit-height trapezoid, with base widths x_1 and $x_2 \approx x_1$. A new needle may adsorb with its bottom end in the range $0 < y_1 < x_1$ and its top end in the range $0 < y_2 < x_2$ (Fig. 6.11). Such an adsorption event divides the trapezoid into two smaller trapezoids with base widths y_1, y_2 and $x_1 - y_1, x_2 - y_2$; this defines a geometric fragmentation process similar to that discussed in Sec. 5.4. We now apply the techniques of that presentation for the needle problem.
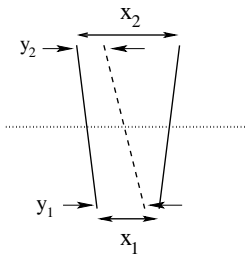

Figure 6.11: Random sequential adsorption of needles in one dimension as the fragmentation of trapezoids.

According to this representation of adsorption as trapezoid fragmentation, the density $c(x_1, x_2)$ of trapezoids with widths $\{x_1, x_2\}$ obeys the master equation

$$\frac{\partial}{\partial t} c(x_1, x_2) = -x_1 x_2 \, c(x_1, x_2) + 2 \int_{x_1}^{\infty} \int_{x_2}^{\infty} c(y_1, y_2) \, dy_1 \, dy_2. \tag{6.45}$$

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

$$\frac{\partial}{\partial t} M(s_1, s_2) = \left(\frac{2}{s_1 s_2} - 1 \right) M(s_1 + 1, s_2 + 1). \tag{6.46}$$

As in rectangular fragmentation, there is an infinite family of hidden conservation laws defined by $s_1^* s_2^* = 2$. Assuming that the Mellin transform has the algebraic time dependence $M(s_1, s_2) \sim t^{-\alpha(s_1,s_2)}$, then Eq. (6.46) gives the recursion $\alpha(s_1 + 1, s_2 + 1) = \alpha(s_1, s_2) + 1$. Using this recursion and the condition $\alpha(s_1^*, s_2^*) = 0$ along the parabola $s_1^* s_2^* = 2$, the exponent $\alpha(s_1, s_2)$ may be determined by the same reasoning as that given in Sec. 5.4, and the result is

$$\alpha(s_1, s_2) = \frac{s_1 + s_2 - \sqrt{(s_1 - s_2)^2 + 8}}{2}. \tag{6.47}$$

One striking consequence of this formula is that the number density of needles $n(t) = M(1, 1)$ varies sublinearly in time:

$$n(t) \sim t^\nu \qquad \text{with} \quad \nu = \sqrt{2} - 1. \tag{6.48}$$

Another basic aspect of needle adsorption is their increasing degree of alignment. We quantify this alignment 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 adjacent needles. This angle is related to the base length 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 $\langle x_1^2 \rangle = \langle x_1^2 \rangle \equiv \langle x^2 \rangle$. Using $\langle x^2 \rangle = M(3, 1)/M(1, 1) \sim t^{-(\alpha(3,1)-\alpha(1,1))}$, the orientational correlation function is then

$$1 - \langle \cos \theta \rangle \sim t^{-\mu} \qquad \text{with} \qquad \mu = 1 + \sqrt{2} - \sqrt{3} = 0.682162\ldots. \tag{6.49}$$

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

While the connection between needle adsorption and rectangular fragmentation involves some leaps of faith and hard-to-justify approximations, we gain in finding a natural way to account for the subtle multiscaling and non-rational exponents that describe needle adsorption.

6.5   Extensions

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

Cooperative Monomer Adsorption

A simple example of a distance-dependent interaction is the irreversible adsorption of monomers in one dimension in which adsorption is forbidden at sites next to already-occupied sites. Suppose that adsorption at 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 can again be treated in terms of empty interval probabilities $E_m(t)$. These probabilities now obey the master equations [compare with Eqs. (6.2)]

$$\frac{dE_1}{dt} = -2rE_2 - (1 - 2r)E_3 \qquad\qquad m = 1$$

$$\frac{dE_m}{dt} = -(m - 2 + 2r)E_m - 2(1 - r)E_{m+1} \qquad m \geq 2. \tag{6.50}$$

The first equation accounts for the disappearance of an empty interval of length 1, an event that occurs with probability $\mathcal{P}[\circ \circ \circ] + 2r\mathcal{P}[\bullet \circ \circ]$. Here $\mathcal{P}[\circ \circ \circ]$ accounts for the loss of an empty site that is surrounded by

empty sites, while $2r\mathcal{P}[\bullet \circ \circ]$ accounts for the loss of an empty site in which one of its neighbors is already occupied. We then use $\mathcal{P}[\circ \circ \circ] = E_3$ and $\mathcal{P}[\bullet \circ \circ] = E_2 - E_3$ [see Eq. (6.22)] to give the first equation. The second equation accounts for the disappearance of an m-site empty interval. In such an interval, the particle can adsorb at $m - 2$ sites in which both neighbors are empty (the factor $(m-2)E_m$). 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 $\mathcal{P}[\bullet \underbrace{\circ \circ \cdots \circ}_{m}] = E_m - E_{m+1}$ [Eq. (6.22)], we obtain the second of Eqs. (6.50).

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. (6.4). Substituting this ansatz into (6.50) gives

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

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 (6.50) and integrating we obtain

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

Hence the surface coverage evolves as

$$\rho(r;t) = \int_0^t \left[2r + (1-2r)\,e^{-u}\right]\,e^{-2ru-2(1-r)(1-e^{-u})}\,du. \tag{6.51}$$

An amazing aspect of this solution is that the behavior for $r = 0$ is not the same as the behavior in the limit $r \to 0$! When $r = 0$, the above integral gives $\rho^0_{\text{jam}} \equiv \rho(0; t = \infty) = (1 - e^{-2})/2$, which is one-half the jamming coverage in dimer adsorption. This result has an intuitive explanation that is illustrated graphically in Fig. 6.12. We define a dual lattice in which each site is halfway between the sites on the original lattice. Then each adsorbed monomer in the cooperative 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 in the original lattice, the jammed density is simply one-half that of the dimer problem, namely, $(1 - e^{-2})/2$.
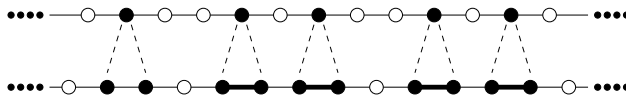

Figure 6.12: Top line: a jammed configuration for cooperative monomer adsorption when $r = 0$, where monomer adsorption requires that both neighbors are unoccupied. Bottom line: corresponding dimer configuration on the dual lattice.

On the other hand the final coverage for non-zero r, no matter how small is $\rho^+_{\text{jam}} \equiv \rho(r \to 0; \infty) = (1 + e^{-2})/2$! Why is there a discontinuity in the jamming coverage for $r \to 0$? Physically, this discontinuity arises because of the wide separation of time scales in the two types of adsorption events that occur for infinitesimal r. In a time of the order of one, $r = 0$ adsorption events occur (adsorption at sites with both neighbors empty) until no further such events are possible. The system then reaches the $r = 0$ jammed state where empty sites can occur singly or in pairs. Then on a much longer time scale (of the order of r^{-1}), one site within each empty pair get filled, e.g., $\bullet \circ \circ \bullet \to \bullet \bullet \circ \bullet$ or $\bullet \circ \circ \bullet \to \bullet \circ \bullet \bullet$. To determine ρ^+_{jam}, 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, $\rho_1 + \rho_2 = \rho_{jam}^0 = (1 - e^{-2})/2$, and also $2\rho_1 + 3\rho_2 = 1$. Solving for ρ_2 gives $\rho_2 = e^{-2}$. After the final infill of one site in all consecutive vacancy pairs, the final jamming density is $\rho_{jam}^+ = (1 - e^{-2})/2 + \rho_2 = (1 + e^{-2})/2$.

Mathematically, the source of the discontinuity is the first term in Eq. (6.51). In the limit $r \to 0$, the leading contribution of this term is

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

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

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

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 where they first land on the substrate. In reality, particles find more stable positions, diffuse, desorb, *etc.* These post-adsorption events are often slow compared to the adsorption. We study the extreme limit where adsorption is infinitely faster than any post-adsorption event; for this limit, we may set the rate of post-adsorption processes to 1 and the adsorption rate to infinity. Thus whenever an adsorbate configuration permits another adsorption event, it occurs instantaneously. This separation of time scales for the two processes simplifies the analysis of this problem.
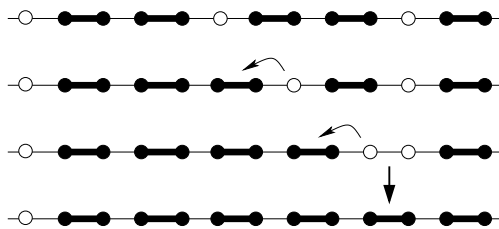

Figure 6.13: Example of mobile adsorbed dimers in one dimension. Each successive row shows the system after a single hopping event. When two holes become adjacent, they are immediately occupied by a dimer.

Suppose that 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 quasi-jammed state in which all empty sites are isolated; we call such sites "holes". Once this state is reached, the dimers adjacent to holes can hop, as illustrated in Fig. 6.13. The hopping of a dimer to the left results in the effective hopping of the hole by 2 steps to the right.

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

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

whose dynamics is well-known (see chapter 9). Here the term diffusion-controlled signifies that diffusion controls the overall reaction rate, since annihilation occurs instantaneously whenever it is possible. Thus we infer that the density of holes decreases as

$$1 - \rho(t) \sim \begin{cases} t^{-1/2} & d = 1; \\ t^{-1} \ln t & d = 2; \\ t^{-1} & d > 2. \end{cases} \tag{6.52}$$

In writing the result for spatial dimension $d > 1$, we make the assumption that the hole motion is asymptotically diffusive when the lattice is nearly completely occupied by randomly-oriented dimers.

We can similarly analyze lattice deposition of trimers. Now holes hop by three lattice sites whenever a trimer hops by one site. When three holes are adjacent they undergo diffusion-controlled ternary annihilation,

$$H + H + H \to \emptyset,$$
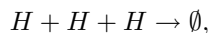
whose dynamics is also known:

$$1 - \rho(t) \sim \begin{cases} t^{-1/2} \sqrt{\ln t} & d = 1; \\ t^{-1/2} & d > 1. \end{cases} \tag{6.53}$$

Here we have glossed over the issues of the shape of the trimer (straight or bent) and their orientation. It seems plausible that these details do not matter in the long-time limit when few holes remain. For the adsorption of diffusing M-mers, the long-time relaxation is controlled by the M-body annihilation

$$\underbrace{H + \cdots + H}_{M} \to \emptyset,$$
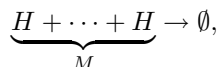
which leads to

$$1 - \rho(t) \sim t^{-1/(M-1)} \qquad M \geq 4. \tag{6.54}$$

Reversible car parking

In real adsorption processes, 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 a gas phase above the substrate, we then have *reversible* adsorption-desorption: molecules adsorb with a rate k_+ and desorb with a rate k_-. While adsorption is subject to the availability of space, desorption events occur independently for each adsorbed molecule. It is fun to think of the monomers as cars that are trying to park along a one-dimensional curb; we ignore the fact that a car needs a little extra room to actually steer into a parking space (Fig. 6.14). From everyday experience, we all know 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, and the car density approaches the limit of perfect packing as the desorption rate goes to zero. This feature is a surprising outcome of the competition between adsorption and desorption. While the steady-state coverage is nearly complete for infinitesimal desorption, the coverage is significantly less than complete for no desorption.
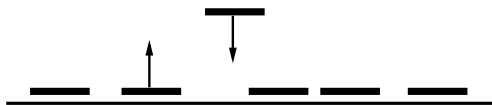

Figure 6.14: Adsorption-desorption of cars. Desorption attempts are always allowed, while the adsorption attempt shown fails because of insufficient parking space.

Another motivation for studying reversible adsorption is its connection to granular compaction. Suppose that identical glass beads are placed into a jar one at a time but randomly. The density of filled space in this bead packing — approximately 0.58 — is known as the *random packing density*. If this bead-filled jar is then vibrated vertically at a suitable intensity and frequency, the density will slowly increase and eventually relax to the *random close-packing density* of approximately 0.68. In experiments, the time scale over which this compaction occurs can be as long as months! Moreover, this random close packing-density is still smaller than the maximal packing fraction of $\pi/\sqrt{18} \approx 0.7405$ for a face-centered cubic lattice sphere pack. This compaction is analogous to adsorption-desorption. After the jar is initially filled, there exist many interstitial empty spaces that are not large enough to accommodate a bead. Because of the vibrations,

occasional local re-arrangements occur that gradually eliminate these empty spaces. As the density increases, re-arrangements become progressively more collective in nature and thus more rare. This slow compaction seems to be captured mathematically in terms of adsorption-desorption.

As a preliminary for the car parking problem, consider the trivial example of adsorbing and desorbing monomers that interact only with single sites on the substrate. The density of adsorbed particles ρ satisfies the Langmuir equation

$$\frac{d\rho}{dt} = -k_-\rho + k_+(1 - \rho), \tag{6.55}$$

in which the total adsorption rate is proportional to the density of empty space and the total desorption rate is proportional to the density of adsorbed monomers. The time dependence of the density is

$$\rho(t) = \rho_\infty + (\rho_0 - \rho_\infty)\,e^{-t/\tau}, \tag{6.56}$$

with the relaxation time τ given by $\tau^{-1} = k_+ + k_-$ and the final coverage $\rho_\infty = k_+/(k_+ + k_-)$ Notice that as $h \equiv k_+/k_- \to \infty$, the asymptotic coverage is $\rho_\infty \approx 1 - h^{-1}$ is reached in a time $\tau \propto h^{-1}$.

For reversible car parking, it is more convenient to work with the density of voids of length x at time t, $V(x,t)$, rather than the density of empty intervals $E(x.t)$. As usual, the strategy is to write and then solve the governing master equations which are:

$$\frac{\partial V(x,t)}{\partial t} = \begin{cases} 2k_+ \displaystyle\int_{x+1}^\infty V(y,t)\,dy - 2k_- V(x,t) & x < 1; \\[2em] 2k_+ \displaystyle\int_{x+1}^\infty V(y,t)\,dy - 2k_- V(x,t) - k_+(x-1)V(x,t) \\[1.5em] \quad + \dfrac{k_-}{\int_0^\infty V(x,t)\,dx} \displaystyle\int_0^{x-1} V(y,t)V(x-y-1,t)\,dy & x > 1. \end{cases} \tag{6.57}$$

Each term 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 in an $x + 1$-void 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 for $x > 1$ is more subtle; it accounts for the creation of an x-void when a car leaves a parking spot that has an empty space of length y at one end of the car and a space $x - y - 1$ at the other end. Thus a void of length x is created by merging voids of length y and $x - y - 1$, together with the unit-length vacated parking spot. The correct 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 equation for the 3-body correlation in terms of higher-body correlations, *ad infinitum*. To break this hierarchy at the simplest level, we invoke the mean-field assumption that the 3-body correlation function for a car to be flanked by voids of length y and $x - y - 1$ is the product of single-void densities. The factor $\int V(x,t)\,dx$ 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 $\rho = \int V(x,t)\,dx$. Also, the mean fraction space occupied by voids and by cars equals 1; thus $1 = \int (x + 1)\,V(x,t)\,dx$. Because each adsorption and desorption event changes the overall density by the same amount, the rate equation for the total density is simply

$$\frac{\partial \rho}{\partial t} = -k_-\rho + k_+ \int_1^\infty (x - 1)\,V(x,t)\,dx, \tag{6.58}$$

which generalizes the Langmuir equation (6.55). The interpretation of this equation is straightforward: with rate $k_-\rho$, a parked car desorbs, while the second term accounts for the parking of a car in a space of length $x > 1$; this same equation can also be obtained by integrating the master equations (6.57) over all lengths.

Most of the interesting behavior about car parking can be easily gleaned by solving the master equations (6.57) in the steady state. Then the equation for $x < 1$ relates the void density to its spatial integral; this

fact suggests an exponential solution $V(x) = Ae^{-\alpha x}$. Substituting this ansatz into the the master equation for $x < 1$ gives the condition

$$h \equiv \frac{k_+}{k_-} = \alpha \, e^{\alpha}. \tag{6.59}$$

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

$$\rho = \int V(x) \, dx = \frac{\alpha}{\alpha+1}, \tag{6.60}$$

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

$$V(x) = \frac{\rho^2}{1-\rho} \, e^{-\rho x/(1-\rho)}. \tag{6.61}$$

From Eqs. (6.59) and (6.60), the limiting behaviors of the steady-state density as a function of the scaled adsorption rate are:

$$\rho(h) \approx \begin{cases} h & h \to 0; \\ 1 - [\ln h]^{-1} & h \to \infty. \end{cases} \tag{6.62}$$

For slow adsorption, excluded-volume effects are negligible and the equilibrium density simply equals the adsorption rate, $\rho \approx h$. 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 ratio of adsorption to desorption rates, $h \approx e^{100}$, is needed! In contrast, for reversible monomer adsorption, a value of $h = 100$ gives a density of 0.99. As mentioned at the beginning of this section, a particularly intriguing feature is that the limiting behavior $\rho(h \to \infty) \to 1$ is distinct from the jamming density $\rho_{\text{jam}} = \rho(h = \infty) = 0.747597\ldots$. The crucial point is that any infinitesimal desorption ($h \to \infty$ but still finite) eventually allows all wasted space to get filled. However, if $h = \infty$ 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 in the limit $h \to \infty$. For this purpose, the *quasi-static* approximation is extremely useful. In later chapters, we will see that this quasi-static approximation provides an easy route to solving a wide variety of slowly-varying phenomena. The basis of this approximation is the observation that car parking rarely succeeds as $h \to \infty$. Consequently, there is sufficient time for the voids to reach a nearly equilibrium state. Thus we use the steady-state exponential void density given by (6.61) in the rate equation (6.58). With this assumption, the density evolves as

$$\frac{d\rho}{dt} = -k_- \rho + k_+ (1-\rho) \, e^{-\rho/(1-\rho)}. \tag{6.63}$$

The linear desorption term has the same form as in the monomer adsorption-desorption problem. However, the adsorption term is modified by the probability that an adsorption event is successful. This effective sticking probability $S(\rho) \equiv e^{-\rho/(1-\rho)}$ 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 the effective sticking probability by the following heuristic argument. Consider a one-dimensional nearly-full parking lot with density $\rho = 1/(1 + \langle x \rangle)$. Here $\langle x \rangle \ll 1$ represents the small average 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. The probability of this cooperative rearrangement of picking cars sequentially and moving them forward by a prescribed amount decays exponentially in the number of cars. Thus the effective sticking probability $S \sim e^{-N} \sim e^{-\rho/(1-\rho)}$.

Finally, we determine the relaxation toward the steady state for $h \to \infty$. In this limiting case, the process is equivalent to a large population of cars are cruising the streets in a predatory manner, looking for parking spots. As soon as a parking spot becomes available it is immediately taken by a nearby cruising car. Technically, this situation is the *desorption-controlled* limit, as desorption limits of the overall reaction. Since any desorption event is immediately followed by at least one adsorption event, the effect of the loss term in Eq. (6.63) is effectively canceled out. Thus we obtain the time dependence of the density by neglecting the

loss term in (6.63). Because the gain term in this equation has been constructed from the steady-state void density, it remains positive for any $\rho < 1$ and therefore builds in a relaxation to the completely-occupied state. To solve the resulting 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 $g \sim \ln(k_+t)$. This gives an extremely slow logarithmic decay law

$$\rho(t) \sim 1 - (\ln k_+t)^{-1}. \tag{6.64}$$

Lateral Adsorption

Our final example is adsorption with lateral relaxation, a process that can be recast as the computer science problem of a hash table construction. To illustrate the basis of the model, consider a gymnasium goer who daily uses a locker room in which all locker use is transient. Which locker should the user choose so that he won't forget his locker after his 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.*, until a vacancy is encountered. As long as the locker room is not too full, this approach provides a quick algorithm to find and remember a vacant locker reliably.
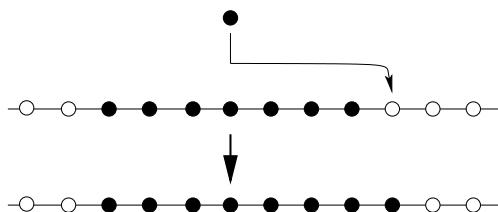

Figure 6.15: A monomer that is incident on an occupied site moves to the right and adsorbs when it first encounters a vacancy.

This search process can be viewed as the following adsorption problem. If an incoming particle is incident on an occupied part of the substrate, the particle moves laterally one site at a time along the substrate and absorbs when a vacancy is first encountered (Fig. 6.15). For convenience, we set the deposition rate equal to 1, while the subsequent search for a vacancy occurs at infinite rate. By construction, each deposition attempt is successful, so that the coverage $\rho(t) = t$ and the system is completely filled at $t = 1$. We now determine the distribution of voids as a function of time by studying the evolution of the empty interval probabilities $E_m(t)$.

The exact master equation for E_m involves
satisfy the approximate master equation

$$\frac{dE_m}{dt} = -mE_m - (E_m - E_{m+1}) \langle m \rangle, \tag{6.65}$$

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 second term accounts for adsorption in an m-interval in which the left boundary site occupied. Here the empty interval gets filled when a monomer is transported along a string of occupied sites until the empty interval is encountered. We have made the mean-field approximation that there is no correlation between the sizes of the island of occupied sites and the adjacent empty interval. With this assumption, the joint probability for an empty interval of length m and the size of the adjacent island may be written as a product of one-body quantities.

The master equation (6.65) still looks formidable because it does not appear to be 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

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

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 island density 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 (6.65), and using the above connection between $\langle m \rangle$ and $E_1 - E_2$ and t, we reduce the infinite set of differential equations (6.65) 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:

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

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

$$\frac{dI_1}{dt} = -\left(3 + \frac{tV_1}{I^2}\right)I_1 + \sum_{n=2}^{\infty}(n-2)V_n$$

$$\frac{dI_m}{dt} = -\left(m + 2 + \frac{tV_1}{I^2}\right)I_m + \left(1 - \frac{V_1}{I}\right)(m+1)I_{m-1} + \frac{V_1}{I^2}\sum_{n=1}^{m-2}(n+1)I_n I_{m-n-1} \qquad m \geq 2. \quad (6.66)$$

(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. (6.65).

Equations (6.66) are recursive and can be solved accordingly. For instance, we get $I_1 = (1-t)t\,e^{-2t}$ and $I_2 = \frac{3}{2}(1-t)t^2 e^{-3t}$ leading to the conjectural behavior $I_m = a_m(1-t)t^m e^{-(m+1)t}$. This ansatz indeed solves the problem if for $m \geq 2$ the amplitudes satisfy

$$ma_m = (m+1)a_{m-1} + \sum_{n=1}^{m-2}(n+1)a_n a_{m-n-1}. \quad (6.67)$$

It is convenient to set $a_0 = 1$; then (6.67) holds for $m = 1$ since it gives $a_1 = a_0 = 1$. With the help of the generating $a(x) = \sum_{m\geq 0} a_m x^m$, we recast the recurrence (6.67) into the differential equation

$$\frac{da}{dx} = a^2 + xa\,\frac{da}{dx}. \quad (6.68)$$

Note that the scale transformation $x \to \lambda x$, $a \to \lambda^{-1}a$ leaves Eq. (6.68) 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

$y = \sum a_m x^{m+1}$. 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. (6.69) 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

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

6.6   Notes

The first equation (6.1) 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 48). The jamming coverage for the car parking model was found by Alfred Rényi (1958) 49. In 60s, several people (particularly Cohen, Keller, Reiss, Widom) recognized the advantages of the evolution approach. Earlier exact results are reviewed and systematized in 50. More recent reviews 51; 52; 7; 53 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 54.

The subject of sections 6.1–6.1 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 55). In sections 6.4 and 6.5 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. 56; 39 for discussion of (6.44). The deposition of needles is due to Tarjus and Viot 58. The connection with diffusion-controlled annihilation was recognized by Privman and co-workers (see 59), the parking lot model 60 is actively investigated due to success in explaining several features of granular materials.

Problems

Section 6.1

1. Compute the total density of voids and the density of islands.

2. Suppose that dimers adsorb onto a one-dimensional partly filled lattice. Consider the initial state where each lattice is independently occupied with probability ρ_0. Compute the jamming coverage.

3. Solve the car parking model if initially there is a density λ of randomly distributed sizeless defects.

Section 6.2

4. Suppose that dimers adsorb onto a one-dimensional lattice of length L. Starting with expression (6.16) for the generating function of the coverage, compute the average jamming coverage.

Section 6.3

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

6. Compute the structure factor $S(q) \equiv \sum e^{iqm} C_m$.

7. Define the probabilities for filled strings of length m, F_m, and for islands of length m, I_m:

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

Show that the island probability is the discrete second derivative of the filled string probability,

$$I_m = F_m - 2F_{m+1} + F_{m+2}, \tag{6.69}$$

8. For $m \leq 3$, use conservation statements to find the following relation between F_m and the empty interval probabilities E_m:

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

Notice that 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 $3 < m < 7$, express F_m in terms of E_j and the probability for two disconnected empty intervals $E_{i,j,k}$. For F_5, for example,

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