model, as we do for binary alloys.

Coin flips and Markov chains, *Unicycle*, and *Red and green bacteria* discuss the behavior and peculiarities of nonequilibrium Markov chains. *Detailed balance* reformulates this condition in an elegant fashion involving only the transition rates. *Metropolis* explores the most commonly applied Monte Carlo method, and in *Implementing Ising* you write your own heat-bath and Metropolis algorithms. *Wolff* and *Implementing Wolff* analyze a powerful and subtle cluster-flip algorithm.

In small systems like biological cells, the numbers of reacting molecules can be so small that number fluctuations can be important; *Stochastic cells* and *Repressilator* develop Monte Carlo methods (the Gillespie algorithm) for stochastic simulations of chemical reactions in these systems. *Entropy increases! Markov chains* shows that the free energy of a Markov chain decreases with time. *Metastability and Markov* introduces a Markov process (continuous time and space) to describe escape over a barrier.

Ising low temperature expansion and *2D Ising cluster expansion* introduce the technology of calculating free energies and magnetizations via sums of cluster diagrams.

Hysteresis and avalanches introduces the nonequilibrium noise of magnets exposed to external fields, and *Hysteresis algorithms* introduces an efficient $O(N \log N)$ algorithm for evolving the model. *Fruit flies and Markov* explores equilibrium and nonequilibrium models of insect behavior, and *Kinetic proofreading* implements an explanation for the high-fidelity transcription of DNA in our cells. Finally, *NP-completeness and satisfiability* explores the most challenging class of problems in computer science, and find a phase transition at which the truly difficult cases congregate.

(8.1) **The Ising model.**[29] (Computation) @

You will need a two-dimensional square-lattice Ising model simulation.

The Ising Hamiltonian is (eqn 8.1):

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i, \tag{8.20}$$

where $S_i = \pm 1$ are spins on a square lattice, and the sum $\sum_{\langle ij \rangle}$ is over the four nearest-neighbor bonds (each pair summed once). It is conventional to set the coupling strength $J = 1$ and Boltzmann's constant $k_B = 1$, which amounts to measuring energies and temperatures in units of J. The constant H is called the external field, and $\mathbf{M} = \sum_i S_i$ is called the magnetization. Our simulation does not conserve the number of spins up, so it is not a natural simulation for a binary alloy. You can think of it as a grand canonical ensemble, or as a model for extra atoms on a surface exchanging with the vapor above.

Play with the simulation. At high temperatures, the spins should not be strongly correlated. At low temperatures the spins should align all parallel, giving a large magnetization.

Roughly locate T_c, the largest temperature where there is a net magnetization (distant spins remain parallel on average) at $H = 0$. Explore the behavior by gradually lowering the temperature from just above T_c to just below T_c; does the behavior gradually change, or jump abruptly (like water freezing to ice)? Explore the behavior at $T = 2$ (below T_c) as you vary the external field $H = \pm 0.1$ up and down through the phase boundary at $H = 0$ (Fig. 8.5). Does the behavior vary smoothly in that case?

(8.2) **Ising fluctuations and susceptibilities.**[30] (Computation) ③

The partition function for the Ising model is $Z = \sum_n \exp(-\beta E_n)$, where the states n run over all 2^N possible configurations of the Ising spins (eqn 8.1), and the free energy $F = -kT \log Z$.

(a) *Show that the average of the magnetization M equals $-(\partial F/\partial H)|_T$.* (Hint: Write out the sum for the partition function and take the derivative.) *Derive the formula for the susceptibility $\chi_0 = (\partial M/\partial H)|_T$ in terms of $\langle (M - \langle M \rangle)^2 \rangle = \langle M^2 \rangle - \langle M \rangle^2$.* (Hint: Remember our derivation of formula 6.13 $\langle (E - \langle E \rangle)^2 \rangle = k_B T^2 C$.)

Now test this using the Ising model simulation. Notice that the program outputs averages of several quantities: $\langle |m| \rangle$, $\langle (m - \langle m \rangle)^2 \rangle$, $\langle e \rangle$, $\langle (e - \langle e \rangle)^2 \rangle$. In simulations, it is standard to measure $e = E/N$ and $m = M/N$ *per spin* (so that the plots do not depend upon system size); you will need to rescale properties appropriately to make comparisons with formulæ written for the energy and magnetization of the *system as a whole*. You can change the system size and decrease the graphics refresh rate (number of sweeps per draw) to speed your averaging. Make sure to equilibrate before starting to average!

(b) Correlations and susceptibilities: numerical. *Check the formulæ for C and χ from part (a)*

[29] Ising simulation software can be found at [28].
[30] Ising simulation software can be found at [28].

at $H = 0$ and $T = 3$, by measuring the fluctuations and the averages, and then changing by $\Delta H = 0.02$ or $\Delta T = 0.1$ and measuring the averages again. Check them also for $T = 2$, where $\langle M \rangle \neq 0$.[31]

There are systematic series expansions for the Ising model at high and low temperatures, using Feynman diagrams (see Section 8.3). The first terms of these expansions are both famous and illuminating.

Low-temperature expansion for the magnetization. At low temperatures we can assume all spins flip alone, ignoring clusters.

(c) *What is the energy for flipping a spin antiparallel to its neighbors? Equilibrate at a relatively low temperature $T = 1.0$, and measure the magnetization. Notice that the primary excitations are single spin flips. In the low-temperature approximation that the flipped spins are dilute (so we may ignore the possibility that two flipped spins touch or overlap), write a formula for the magnetization. (Remember, each flipped spin changes the magnetization by 2.) Check your prediction against the simulation.* (Hint: See eqn 8.19.)

The magnetization (and the specific heat) are exponentially small at low temperatures because there is an *energy gap* to spin excitations in the Ising model,[32] just as there is a gap to charge excitations in a semiconductor or an insulator.

High-temperature expansion for the susceptibility. At high temperatures, we can ignore the coupling to the neighboring spins.

(d) *Calculate a formula for the susceptibility of a free spin coupled to an external field. Compare it to the susceptibility you measure at high temperature $T = 100$ for the Ising model, say, $\Delta M/\Delta H$ with $\Delta H = 1$. (Why is $H = 1$ a small field in this case?)*

Your formula for the high-temperature susceptibility is known more generally as Curie's law.

(8.3) **Coin flips and Markov.** (Mathematics) ⓟ

A physicist, testing the laws of chance, flips a coin repeatedly until it lands tails.

(a) *Treat the two states of the physicist ("still flipping" and "done") as states in a Markov chain. The current probability vector then is $\vec{\rho} = \begin{pmatrix} \rho_{\text{flipping}} \\ \rho_{\text{done}} \end{pmatrix}$. Write the transition matrix $\mathcal{P}$, giving the time evolution $\mathcal{P} \cdot \vec{\rho}_n = \vec{\rho}_{n+1}$, assuming that the coin is fair.*

(b) *Find the eigenvalues and right eigenvectors of $\mathcal{P}$. Which eigenvector is the steady state ρ^*? Call the other eigenvector $\widetilde{\rho}$. For convenience, normalize $\widetilde{\rho}$ so that its first component equals one.*

(c) *Assume an arbitrary initial state is written $\rho_0 = A\rho^* + B\widetilde{\rho}$. What are the conditions on A and B needed to make ρ_0 a valid probability distribution? Write ρ_n as a function of A, B, ρ^*, and $\widetilde{\rho}$.*

(8.4) **Red and green bacteria.**[33] (Mathematics, Biology) ②

A growth medium at time $t = 0$ has 500 red bacteria and 500 green bacteria. Each hour, each bacterium divides in two. A color-blind predator eats exactly 1,000 bacteria per hour.[34]

(a) *After a very long time, what is the probability distribution for the number α of red bacteria in the growth medium?*

(b) *Roughly how long will it take to reach this final state?* (Assume either that one bacterium reproduces and then one is eaten every 1/1,000 of an hour, or that at the end of each hour all the bacteria reproduce and then 1,000 are consumed. My approach was to treat it as a random walk with an α-dependent step size.)

(c) *Assume that the predator has a 1% preference for green bacteria (implemented as you choose). Roughly how much will this change the final distribution?*

[31] Be sure to wait until the state is equilibrated before you start! Below T_c this means the state should not have red and black domains, but be all in one ground state. You may need to apply a weak external field for a while to remove stripes at low temperatures.

[32] Not all real magnets have a gap; if there is a spin rotation symmetry, one can have gapless *spin waves*, which are like sound waves except twisting the magnetization rather than wiggling the atoms.

[33] Adapted from author's graduate admission to candidacy exam, Princeton University, Fall 1977.

[34] This question is purposely open-ended, and rough answers to parts (b) and (c) within a factor of two are perfectly acceptable. Numerical and analytical methods are both feasible.

(8.5) **Detailed balance.** @
In an equilibrium system, for any two states α and β with equilibrium probabilities ρ^*_α and ρ^*_β, detailed balance states (eqn 8.14) that

$$P_{\beta\Leftarrow\alpha}\rho^*_\alpha = P_{\alpha\Leftarrow\beta}\rho^*_\beta, \tag{8.21}$$

that is, the equilibrium flux of probability from α to β is the same as the flux backward from β to α. (Again, here and in eqn 8.22, we do not sum over repeated indices.) It is both possible and elegant to reformulate the condition for detailed balance so that it does not involve the equilibrium probabilities. Consider three states of the system, α, β, and γ.
(a) *Assume that each of the three types of transitions among the three states satisfies detailed balance. Eliminate the equilibrium probability densities to derive*[35]

$$P_{\alpha\Leftarrow\beta}P_{\beta\Leftarrow\gamma}P_{\gamma\Leftarrow\alpha} = P_{\alpha\Leftarrow\gamma}P_{\gamma\Leftarrow\beta}P_{\beta\Leftarrow\alpha}. \tag{8.22}$$

Viewing the three states α, β, and γ as forming a circle, you have derived a relationship between the rates going clockwise and the rates going counter-clockwise around the circle.
Can we show the converse to part (a), that if every triple of states in a Markov chain satisfies the condition 8.22 then it satisfies detailed balance? Given the transition matrix P, can we construct a probability density $\boldsymbol{\rho}^*$ which makes the probability fluxes between all pairs of states equal?
In most problems, most of the rates are zero: the matrix P is sparse, connecting only nearby states. This makes the cyclic condition for detailed balance stricter than Equation 8.22. (Detailed balance demands that the forward and reversed products for cycles of *all* lengths must be equal, the *Kolmogorov criterion*.) There are N^3 equations in Equation 8.22 (α, β, and γ each running over all N states), and we need to solve for N unknowns $\boldsymbol{\rho}^*$. But in a sparse matrix most of these "triangle" conditions tell us only that $0 = 0$. However, if we assume that the transition matrix has enough positive entries, the three-state cyclic eqn 8.22 is enough to construct the stationary state $\boldsymbol{\rho}^*$ from P, satisfying detailed balance (eqn 8.21).
(b) *Suppose P is the transition matrix for some Markov chain satisfying the condition 8.22 for every triple of states α, β, and γ. Assume for simplicity that there is a state α_0 with nonzero transition rates from all other states δ.*[36] *Construct a probability density $\boldsymbol{\rho}^*$ that demonstrates that P satisfies detailed balance (eqn 8.21).* (Hint: Assume you know $\rho^*_{\alpha_0}$; use some of the eqns 8.21 to write a formula for each of the other $N-1$ elements ρ^*_δ that ensures detailed balance for the pair. Then solve for $\rho^*_{\alpha_0}$ to make the probability distribution normalized. Use the cyclic condition eqn 8.22 to show that this candidate stationary state $\boldsymbol{\rho}^*$ satisfies detailed balance for any two states β and δ.)

(8.6) **Metropolis.** (Mathematics, Computation) @
The heat-bath algorithm described in the text thermalizes one spin at a time. Another popular choice is the Metropolis algorithm, which also flips a single spin at a time:

(1) Pick a spin at random;
(2) Calculate the energy $\Delta\mathbf{E}$ for flipping the spin;
(3) If $\Delta\mathbf{E} < 0$ flip it; if $\Delta\mathbf{E} > 0$, flip it with probability $\mathrm{e}^{-\beta\,\Delta\mathbf{E}}$.

Show that Metropolis satisfies detailed balance. Note that it is ergodic and Markovian (no memory), and hence that it will lead to thermal equilibrium. Is Metropolis more efficient than the heat-bath algorithm (fewer random numbers needed to get to equilibrium)?

(8.7) **Implementing Ising.**[37] (Computation) ④
In this exercise, we will implement a simulation of the two-dimensional Ising model on a square lattice using the heat-bath and Metropolis algorithms.
The heat-bath algorithm flips spins one at a time, putting them into equilibrium with their neighbors: it is described in detail in Section 8.1.
(a) *Implement the heat-bath algorithm for the Ising model. Do not recalculate the exponentials for the transition probabilities for each spin flip! Instead, create an array* `heatBathProbUp[nUp]` *to store the probability that a spin will be set to* $+1$ *given that* `nUp` *of its neighbors are currently*

[35] Note that, as in eqn 8.21, we do *not* sum over repeated indices here; this equation must hold for all triples of states α, β, and γ. Hence these form N^3 equations for the N^2 variables $P_{\alpha\Leftarrow\beta}$.
[36] See *regular matrices*, note 20 on p. 225.
[37] Computational hints can be found at the book website [182].

pointing up (equal to +1); recalculate it whenever the external field or temperature is changed. Explore the resulting behavior (say, as in Exercise 8.1).

The Metropolis algorithm also flips one spin at a time, but it always flips spins if the net energy decreases: it is described in detail in Exercise 8.6.

(b) *Implement the Metropolis algorithm for the Ising model. Here you will want to set up an array* `MetropolisProbUp[s,nUp]` *storing the probability that a spin which currently has value* `s` *will be set to* +1 *if* `nUp` *of its neighbors are currently up. Is Metropolis noticeably faster than the heat-bath algorithm?*

The Metropolis algorithm is always faster to equilibrate than the heat-bath algorithm, but is never a big improvement. Other algorithms can be qualitatively faster in certain circumstances (see Exercises 8.8 and 8.9).

(8.8) **Wolff.**[38] (Mathematics, Computation) @

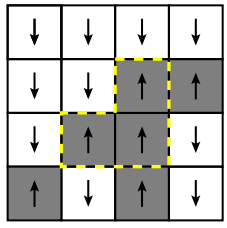

Fig. 8.9 Cluster flip: before. The region inside the dotted line is flipped in one Wolff move. Let this configuration be A. Let the cluster being flipped be C (bounded by the dotted line). Notice that the boundary of C has $n\uparrow = 2$, $n\downarrow = 6$.

Near the critical point T_c where the system develops a magnetization, any single-spin-flip dynamics becomes very slow (the *correlation time* diverges). Wolff [214], building on ideas of Swendsen and Wang [193], came up with a clever method to flip whole clusters of spins.

Find a Wolff simulation (e.g., [28]). Run at $T_c = 2/\log(1+\sqrt{2})$ using the Metropolis algorithm for a 512×512 system or larger; watch the slow growth and long persistence times of the larger clusters. This is *critical slowing down*. Now change to the Wolff algorithm, and see how much faster the large clusters rearrange. Take single Wolff steps: many will almost completely rearrange the pattern.

The *correlation time* is roughly the time it takes a system, begun at one particular configuration in the equilibrium ensemble, to move to an uncorrelated configuration. We measure the correlation time in *sweeps*. A sweep in a $N \times N$ system will attempt to flip N^2 spins.

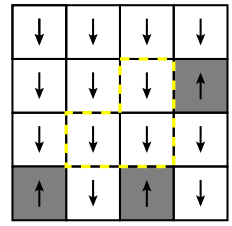

Fig. 8.10 Cluster flip: after. Let this configuration be B. Notice that the cluster has been flipped.

(a) *Change to a smaller system size (perhaps 128×128), and visually estimate the correlation time for the Metropolis algorithm.* (For small sizes, periodic boundary conditions will make the Ising model appear magnetized. Estimate the number of sweeps you need to scramble the largest islands, not to flip the magnetization. Doing many sweeps between redraws will speed things up, and the pauses will help you to count.) *Estimate the correlation time for Wolff (taking single steps). Is the speedup significant?*

How does the Wolff cluster flip method work?

(1) Pick a spin at random, remember its direction $D = \pm 1$, and flip it.

(2) For each of the four neighboring spins, *if* it is in the direction D, flip it with probability p.

(3) For each of the new flipped spins, recursively flip their neighbors as in (2).

Because with finite probability you can flip any spin, the Wolff algorithm is ergodic. As a cluster flip it is Markovian. Let us see that it satisfies detailed balance, when we pick the right value of p for the given temperature. Define $n_\uparrow$ and $n_\downarrow$ to count the number of cluster edges (dotted lines in Figs. 8.9 and 8.10) that are adjacent to external spins pointing up and down, respectively.

[38] Hints for the computations can be found at the book website [182].

(b) *Show for the two configurations in Figs. 8.9 and 8.10 that* $E_B - E_A = 2(n_\uparrow - n_\downarrow)J$. *Argue that this will be true for flipping any cluster of up-spins to down-spins.*
The cluster flip can start at any site α in the cluster C. The ratio of rates $\Gamma_{A\to B}/\Gamma_{B\to A}$ depends upon the number of times the cluster chose *not* to grow on the boundary. Let P_α^C be the probability that the cluster grows internally from site α to the cluster C (ignoring the moves which try to grow outside the boundary). Then

$$\Gamma_{A\to B} = \sum_\alpha P_\alpha^C (1-p)^{n_\uparrow}, \tag{8.23}$$

$$\Gamma_{B\to A} = \sum_\alpha P_\alpha^C (1-p)^{n_\downarrow}, \tag{8.24}$$

since the cluster must refuse to grow $n_\uparrow$ times when starting from the up-state A, and $n_\downarrow$ times when starting from B.
(c) *What value of p lets the Wolff algorithm satisfy detailed balance at temperature T?*
See [144, sections 4.2–3] for more details on the Wolff algorithm, and [98] for the Wolff algorithm for other models including external fields.

(8.9) **Implementing Wolff.**[39] (Computation) ④
In this exercise, we will implement the Wolff algorithm of Exercise 8.8.
Near the critical temperature T_c for a magnet, the equilibration becomes very sluggish: this is called *critical slowing-down*. This sluggish behavior is faithfully reproduced by the single-spin-flip heat-bath and Metropolis algorithms. If one is interested in equilibrium behavior, and not in dynamics, one can hope to use fancier algorithms that bypass this sluggishness, saving computer time.
(a) *Run the two-dimensional Ising model (either from the book website or from your solution to Exercise 8.7) near* $T_c = 2/\log(1+\sqrt{2})$ *using a single-spin-flip algorithm. Start in a magnetized state, and watch the spins rearrange until roughly half are pointing up. Start at high temperatures, and watch the up- and down-spin regions grow slowly. Run a large enough system that you get tired of waiting for equilibration.*
The Wolff algorithm flips large clusters of spins at one time, largely bypassing the sluggishness near T_c. It is described in detail in Exercise 8.8. The Wolff algorithm can be generalized to systems with external fields [98].
(b) *Implement the Wolff algorithm. A recursive implementation works only for small system sizes on most computers. Instead, put the spins that are destined to flip on a list* `toFlip`. *You will also need to keep track of the sign of the original triggering spin.*
While there are are spins `toFlip`,
  if the first spin remains parallel to the original,
    flip it, and
    for each neighbor of the flipped spin,
      if it is parallel to the original spin,
        add it to `toFlip` with probability p.
(c) *Estimate visually how many Wolff cluster flips it takes to reach the equilibrium state at* T_c. *Is Wolff faster than the single-spin-flip algorithms? How does it compare at high temperatures?*
(d) *Starting from a random configuration, change to a low temperature* $T = 1$ *and observe the equilibration using a single-spin flip algorithm. Compare with your Wolff algorithm.* (See also Exercise 12.3.) *Which reaches equilibrium faster? Is the dynamics changed qualitatively?*

(8.10) **Stochastic cells.**[40] (Biology, Computation) ④
Living cells are amazingly complex mixtures of a variety of complex molecules (RNA, DNA, proteins, lipids, ...) that are constantly undergoing reactions with one another. This complex of reactions has been compared to computation; the cell gets input from external and internal sensors, and through an intricate series of reactions produces an appropriate response. Thus, for example, receptor cells in the retina "listen" for light and respond by triggering a nerve impulse. The kinetics of chemical reactions are usually described using differential equations for the concentrations of the various chemicals, and rarely are statistical fluctuations considered important. In a cell, the numbers of molecules of a given type can be rather small; indeed, there is (often) only one copy of the relevant part of DNA for a given reaction. It is an important question whether and when we may describe the dynamics inside the cell using continuous concentration variables, even though the actual numbers of molecules are always integers.

[39] Hints for the computations can be found at the book website [182].
[40] This exercise and the associated software were developed in collaboration with Christopher Myers. Computational hints can be found at the book website [182].