OXFORD
UNIVERSITY PRESS
Great Clarendon Street, Oxford OX2 6DP
Oxford University Press is a department of the University of Oxford.
It furthers the University's objective of excellence in research, scholarship,
and education by publishing worldwide in
Oxford New York
Athens Auckland Bangkok Bogotá Buenos Aires Cape Town
Chennai Dar es Salaam Delhi Florence Hong Kong Istanbul Karachi
Kolkata Kuala Lumpur Madrid Melbourne Mexico City Mumbai Nairobi
Paris São Paulo Shanghai Singapore Taipei Tokyo Toronto Warsaw
with associated companies in Berlin Ibadan

Published in the United States
by Oxford University Press Inc., New York

First published 1999
Reprinted (with corrections) 2001

A catalogue record for this book is available from the British Library
Library of Congress Cataloging in Publication Data
(Data available)
ISBN 0 19 851796 3 (Hbk)
ISBN 0 19 851797 1 (Pbk)
Printed in India by Thomson Press

Monte Carlo Methods in Statistical Physics

M. E. J. NEWMAN
Santa Fe Institute

and

G. T. BARKEMA
Institute for Theoretical Physics
Utrecht University

CLARENDON PRESS • OXFORD

1

Introduction

This book is about the use of computers to solve problems in statistical physics. In particular, it is about **Monte Carlo methods**, which form the largest and most important class of numerical methods used for solving statistical physics problems. In this opening chapter of the book we look first at what we mean by statistical physics, giving a brief overview of the discipline we call **statistical mechanics**. Whole books have been written on statistical mechanics, and our synopsis takes only a few pages, so we must necessarily deal only with the very basics of the subject. We are assuming that these basics are actually already familiar to you, but writing them down here will give us a chance to bring back to mind some of the ideas that are most relevant to the study of Monte Carlo methods. In this chapter we also look at some of the difficulties associated with solving problems in statistical physics using a computer, and outline what Monte Carlo techniques are, and why they are useful. In the last section of the chapter, purely for fun, we give a brief synopsis of the history of computational physics and Monte Carlo methods.

1.1 Statistical mechanics

Statistical mechanics is primarily concerned with the calculation of properties of condensed matter systems. The crucial difficulty associated with these systems is that they are composed of very many parts, typically atoms or molecules. These parts are usually all the same or of a small number of different types and they often obey quite simple equations of motion so that the behaviour of the entire system can be expressed mathematically in a straightforward manner. But the sheer number of equations—just the magnitude of the problem—makes it impossible to solve the mathematics exactly. A standard example is that of a volume of gas in a container. One litre of, say, oxygen at standard temperature and pressure consists of about 3×10^{22} oxygen molecules, all moving around and colliding with one another and the walls of the container. One litre of air under the same conditions contains the same number of molecules, but they are now a mixture of oxygen, nitrogen, carbon dioxide and a few other things. The atmosphere of the Earth contains 4×10^{21} litres of air, or about 1×10^{44} molecules, all moving around and colliding with each other and the ground and trees and houses and people. These are large systems. It is not feasible to solve Hamilton's equations for these systems because there are simply too many equations, and yet when we look at the macroscopic properties of the gas, they are very well-behaved and predictable. Clearly, there is something special about the behaviour of the solutions of these many equations that "averages out" to give us a predictable behaviour for the entire system. For example, the pressure and temperature of the gas obey quite simple laws although both are measures of rather gross average properties of the gas. Statistical mechanics attempts to side-step the problem of solving the equations of motion and cut straight to the business of calculating these gross properties of large systems by treating them in a probabilistic fashion. Instead of looking for exact solutions, we deal with the probabilities of the system being in one state or another, having this value of the pressure or that—hence the name *statistical* mechanics. Such probabilistic statements turn out to be extremely useful, because we usually find that for large systems the range of behaviours of the system that are anything more than phenomenally unlikely is very small; all the reasonably probable behaviours fall into a narrow range, allowing us to state with extremely high confidence that the real system will display behaviour within that range. Let us look at how statistical mechanics treats these systems and demonstrates these conclusions.

The typical paradigm for the systems we will be studying in this book is one of a system governed by a Hamiltonian function H which gives us the total energy of the system in any particular state. Most of the examples we will be looking at have discrete sets of states each with its own energy, ranging from the lowest, or ground state energy E_0 upwards, E_1, E_2, $E_3 \ldots$, possibly without limit. Statistical mechanics, and the Monte Carlo methods we will be introducing, are also applicable to systems with continuous energy spectra, and we will be giving some examples of such applications.

If our Hamiltonian system were all we had, life would be dull. Being a Hamiltonian system, energy would be conserved, which means that the system would stay in the same energy state all the time (or if there were a number of degenerate states with the same energy, maybe it would make transitions between those, but that's as far as it would get).[1] However, there's another component to our paradigm, and that is the **thermal reservoir**. This is an external system which acts as a source and sink of heat, constantly exchanging energy with our Hamiltonian system in such a way as always to push the temperature of the system—defined as in classical thermodynamics—towards the temperature of the reservoir. In effect the reservoir is a weak perturbation on the Hamiltonian, which we ignore in our calculation of the energy levels of our system, but which pushes the system frequently from one energy level to another. We can incorporate the effects of the reservoir in our calculations by giving the system a **dynamics**, a rule whereby the system changes periodically from one state to another. The exact nature of the dynamics is dictated by the form of the perturbation that the reservoir produces in the Hamiltonian. We will discuss many different possible types of dynamics in the later chapters of this book. However, there are a number of general conclusions that we can reach without specifying the exact form of the dynamics, and we will examine these first.

Suppose our system is in a state μ. Let us define $R(\mu \to \nu)\,dt$ to be the probability that it is in state ν a time dt later. $R(\mu \to \nu)$ is the **transition rate** for the transition from μ to ν. The transition rate is normally assumed to be time-independent and we will make that assumption here. We can define a transition rate like this for every possible state ν that the system can reach. These transition rates are usually all we know about the dynamics, which means that even if we know the state μ that the system starts off in, we need only wait a short interval of time and it could be in any one of a very large number of other possible states. This is where our probabilistic treatment of the problem comes in. We define a set of weights $w_\mu(t)$ which represent the probability that the system will be in state μ at time t. Statistical mechanics deals with these weights, and they represent our entire knowledge about the state of the system. We can write a **master equation** for the evolution of $w_\mu(t)$ in terms of the rates $R(\mu \to \nu)$ thus:[2]

$$\frac{\mathrm{d}w_\mu}{\mathrm{d}t} = \sum_\nu \bigl[w_\nu(t)R(\nu \to \mu) - w_\mu(t)R(\mu \to \nu)\bigr]. \tag{1.1}$$

The first term on the right-hand side of this equation represents the rate at which the system is undergoing transitions into state μ; the second term is the rate at which it is undergoing transitions out of μ into other states. The probabilities $w_\mu(t)$ must also obey the sum rule

$$\sum_\mu w_\mu(t) = 1 \tag{1.2}$$

[1] For a classical system which has a continuum of energy states there can be a continuous set of degenerate states through which the system passes, and an average over those states can sometimes give a good answer for certain properties of the system. Such sets of degenerate states are said to form a **microcanonical ensemble**. The more general case we consider here, in which there is a thermal reservoir causing the energy of the system to fluctuate, is known as a **canonical ensemble**.

[2] The master equation is really a set of equations, one for each state μ, although people always call it *the* master equation, as if there were only one equation here.

for all t, since the system must always be in *some* state. The solution of Equation (1.1), subject to the constraint (1.2), tells us how the weights w_μ vary over time.

And how are the weights w_μ related to the macroscopic properties of the system which we want to know about? Well, if we are interested in some quantity Q, which takes the value Q_μ in state μ, then we can define the **expectation** of Q at time t for our system as

$$\langle Q \rangle = \sum_\mu Q_\mu w_\mu(t). \tag{1.3}$$

Clearly this quantity contains important information about the real value of Q that we might expect to measure in an experiment. For example, if our system is definitely in one state τ then $\langle Q \rangle$ will take the corresponding value Q_τ. And if the system is equally likely to be in any of perhaps three states, and has zero probability of being in any other state, then $\langle Q \rangle$ is equal to the mean of the values of Q in those three states, and so forth. However, the precise relation of $\langle Q \rangle$ to the observed value of Q is perhaps not very clear. There are really two ways to look at it. The first, and more rigorous, is to imagine having a large number of copies of our system all interacting with their own thermal reservoirs and whizzing between one state and another all the time. $\langle Q \rangle$ is then a good estimate of the number we would get if we were to measure the instantaneous value of the quantity Q in each of these systems and then take the mean of all of them. People who worry about the conceptual foundations of statistical mechanics like to take this "many systems" approach to defining the expectation of a quantity.[3] The trouble with it however is that it's not very much like what happens in a real experiment. In a real experiment we normally only have one system and we make all our measurements of Q on that system, though we probably don't just make a single instantaneous measurement, but rather integrate our results over some period of time. There is another way of looking at the expectation value which is similar to this experimental picture, though it is less rigorous than the many systems approach. This is to envisage the expectation as a *time average* of the quantity Q. Imagine recording the value of Q every second for a thousand seconds and taking the average of those one thousand values. This will correspond roughly to the quantity calculated in Equation (1.3) as long as the system passes through a representative selection of the states in the probability distribution w_μ in those thousand seconds. And if we make ten thousand measurements of Q instead of one thousand, or a million or more, we will get an increasingly accurate fit between our experimental average and the expectation $\langle Q \rangle$.

Why is this a less rigorous approach? The main problem is the question of what we mean by a "representative selection of the states". There is no guarantee that the system will pass through anything like a representative sample of the states of the system in our one thousand seconds. It could easily be that the system only hops from one state to another every ten thousand seconds, and so turns out to be in the same state for all of our one thousand measurements. Or maybe it changes state very rapidly, but because of the nature of the dynamics spends long periods of time in small portions of the state space. This can happen for example if the transition rates $R(\mu \to \nu)$ are only large for states of the system that differ in very small ways, so that the only way to make a large change in the state of the system is to go through very many small steps. This is a very common problem in a lot of the systems we will be looking at in this book. Another potential problem with the time average interpretation of (1.3) is that the weights $w_\mu(t)$, which are functions of time, may change considerably over the course of our measurements, making the expression invalid. This can be a genuine problem in both experiments and simulations of non-equilibrium systems, which are the topic of the second part of this book. For equilibrium systems, as discussed below, the weights are by definition not time-varying, so this problem does not arise.

Despite these problems however, this time-average interpretation of the expectation value of a quantity is the most widely used and most experimentally relevant interpretation, and it is the one that we will adopt in this book. The calculation of expectation values is one of the fundamental goals of statistical mechanics, and of Monte Carlo simulation in statistical physics, and much of our time will be concerned with it.

1.2 Equilibrium

Consider the master equation (1.1) again. If our system ever reaches a state in which the two terms on the right-hand side exactly cancel one another for all μ, then the rates of change dw_μ/dt will all vanish and the weights will all take constant values for the rest of time. This is an **equilibrium** state. Since the master equation is first order with real parameters, and since the variables w_μ are constrained to lie between zero and one (which effectively prohibits exponentially growing solutions to the equations) we can see that all systems governed by these equations must come to equilibrium in the end. A large part of this book will be concerned with Monte Carlo techniques for simulating equilibrium systems and in this section we develop some of the important statistical mechanical concepts that apply to these systems.

The transition rates $R(\mu \to \nu)$ appearing in the master equation (1.1)

[3] In fact the word *ensemble*, as in the "canonical ensemble" which was mentioned in a previous footnote, was originally introduced by Gibbs to describe an ensemble of *systems* like this, and not an ensemble of, say, molecules, or any other kind of ensemble. These days however, use of this word no longer implies that the writer is necessarily thinking of a many systems formulation of statistical mechanics.

do not just take *any* values. They take particular values which arise out of the thermal nature of the interaction between the system and the thermal reservoir. In the later chapters of this book we will have to choose values for these rates when we simulate thermal systems in our Monte Carlo calculations, and it is crucial that we choose them so that they mimic the interactions with the thermal reservoir correctly. The important point is that we know *a priori* what the equilibrium values of the weights w_μ are for our system. We call these equilibrium values the **equilibrium occupation probabilities** and denote them by

$$p_\mu = \lim_{t\to\infty} w_\mu(t). \tag{1.4}$$

It was Gibbs (1902) who showed that for a system in thermal equilibrium with a reservoir at temperature T, the equilibrium occupation probabilities are

$$p_\mu = \frac{1}{Z}\,\mathrm{e}^{-E_\mu/kT}. \tag{1.5}$$

Here E_μ is the energy of state μ and k is Boltzmann's constant, whose value is $1.38\times10^{-23}\ \mathrm{J\,K^{-1}}$. It is conventional to denote the quantity $(kT)^{-1}$ by the symbol β, and we will follow that convention in this book. Z is a normalizing constant, whose value is given by

$$Z = \sum_\mu \mathrm{e}^{-E_\mu/kT} = \sum_\mu \mathrm{e}^{-\beta E_\mu}. \tag{1.6}$$

Z is also known as the **partition function**, and it figures a lot more heavily in the mathematical development of statistical mechanics than a mere normalizing constant might be expected to. It turns out in fact that a knowledge of the variation of Z with temperature and any other parameters affecting the system (like the volume of the box enclosing a sample of gas, or the magnetic field applied to a magnet) can tell us virtually everything we might want to know about the macroscopic behaviour of the system. The probability distribution (1.5) is known as the **Boltzmann distribution**, after Ludwig Boltzmann, one of the pioneers of statistical mechanics. For a discussion of the origins of the Boltzmann distribution and the arguments that lead to it, the reader is referred to the exposition by Walter Grandy in his excellent book *Foundations of Statistical Mechanics* (1987). In our treatment we will take Equation (1.5) as our starting point for further developments.

From Equations (1.3), (1.4) and (1.5) the expectation of a quantity Q for a system in equilibrium is

$$\langle Q\rangle = \sum_\mu Q_\mu p_\mu = \frac{1}{Z}\sum_\mu Q_\mu\,\mathrm{e}^{-\beta E_\mu}. \tag{1.7}$$

For example, the expectation value of the energy $\langle E\rangle$, which is also the quantity we know from thermodynamics as the internal energy U, is given by

$$U = \frac{1}{Z}\sum_\mu E_\mu\,\mathrm{e}^{-\beta E_\mu}. \tag{1.8}$$

From Equation (1.6) we can see that this can also be written in terms of a derivative of the partition function:

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial\log Z}{\partial\beta}. \tag{1.9}$$

The specific heat is given by the derivative of the internal energy:

$$C = \frac{\partial U}{\partial T} = -k\beta^2\frac{\partial U}{\partial\beta} = k\beta^2\frac{\partial^2\log Z}{\partial\beta^2}. \tag{1.10}$$

However, from thermodynamics we know that the specific heat is also related to the entropy:

$$C = T\frac{\partial S}{\partial T} = -\beta\frac{\partial S}{\partial\beta}, \tag{1.11}$$

and, equating these two expressions for C and integrating with respect to β, we find the following expression for the entropy:

$$S = -k\beta\frac{\partial\log Z}{\partial\beta} + k\log Z. \tag{1.12}$$

(There is in theory an integration constant in this equation, but it is set to zero under the convention known as the third law of thermodynamics, which fixes the arbitrary origin of entropy by saying that the entropy of a system should tend to zero as the temperature does.) We can also write an expression for the (Helmholtz) free energy F of the system, using Equations (1.9) and (1.12):

$$F = U - TS = -kT\log Z. \tag{1.13}$$

We have thus shown how U, F, C and S can all be calculated directly from the partition function Z. The last equation also tells us how we can deal with other parameters affecting the system. In classical thermodynamics, parameters and constraints and fields interacting with the system each have conjugate variables which represent the response of the system to the perturbation of the corresponding parameter. For example, the response of a gas system in a box to a change in the confining volume is a change in the pressure of the gas. The pressure p is the conjugate variable to the parameter V. Similarly, the magnetization M of a magnet changes in response to the applied magnetic field B; M and B are conjugate variables. Thermodynamics tells us that we can calculate the values of conjugate variables from derivatives of the free energy:

$$p = -\frac{\partial F}{\partial V}, \tag{1.14}$$

$$M = \frac{\partial F}{\partial B}. \tag{1.15}$$

Thus, if we can calculate the free energy using Equation (1.13), then we can calculate the effects of parameter variations too.

In performing Monte Carlo calculations of the properties of equilibrium systems, it is sometimes appropriate to calculate the partition function and then evaluate other quantities from it. More often it is better to calculate the quantities of interest directly, but many times in considering the theory behind our simulations we will return to the idea of the partition function, because in principle the entire range of thermodynamic properties of a system can be deduced from this function, and any numerical method that can make a good estimate of the partition function is at heart a sound method.

1.2.1 Fluctuations, correlations and responses

Statistical mechanics can tell us about other properties of a system apart from the macroscopic ones that classical equilibrium thermodynamics deals with such as entropy and pressure. One of the most physically interesting classes of properties is **fluctuations** in observable quantities. We described in the first part of Section 1.1 how the calculation of an expectation could be regarded as a time average over many measurements of the same property of a single system. In addition to calculating the mean value of these many measurements, it is often useful also to calculate their standard deviation, which gives us a measure of the variation over time of the quantity we are looking at, and so tells us quantitatively how much of an approximation we are making by giving just the one mean value for the expectation. To take an example, let us consider the internal energy again. The mean square deviation of individual, instantaneous measurements of the energy away from the mean value $U = \langle E \rangle$ is

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2. \tag{1.16}$$

We can calculate $\langle E^2 \rangle$ from derivatives of the partition function in a way similar to our calculation of $\langle E \rangle$:

$$\langle E^2 \rangle = \frac{1}{Z} \sum_\mu E_\mu^2 e^{-\beta E_\mu} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}. \tag{1.17}$$

So

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left[\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right]^2 = \frac{\partial^2 \log Z}{\partial \beta^2}. \tag{1.18}$$

Using Equation (1.10) to eliminate the second derivative, we can also write this as

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{C}{k\beta^2}. \tag{1.19}$$

And the standard deviation of E, the RMS fluctuation in the internal energy, is just the square root of this expression.

This result is interesting for a number of reasons. First, it gives us the magnitude of the fluctuations in terms of the specific heat C or alternatively in terms of $\log Z = -\beta F$. In other words we can calculate the fluctuations entirely from quantities that are available within classical thermodynamics. However, this result could never have been derived within the framework of thermodynamics, since it depends on microscopic details that thermodynamics has no access to. Second, let us look at what sort of numbers we get out for the size of the energy fluctuations of a typical system. Let us go back to our litre of gas in a box. A typical specific heat for such a system is $1\,\mathrm{J\,K^{-1}}$ at room temperature and atmospheric pressure, giving RMS energy fluctuations of about 10^{-18} J. The internal energy itself on the other hand will be around 10^2 J, so the fluctuations are only about one part in 10^{20}. This lends some credence to our earlier contention that statistical treatments can often give a very accurate estimate of the expected behaviour of a system. We see that in the case of the internal energy at least, the variation of the actual value of U around the expectation value $\langle E \rangle$ is tiny by comparison with the kind of energies we are considering for the whole system, and probably not within the resolution of our measuring equipment. So quoting the expectation value gives a very good guide to what we should expect to see in an experiment. Furthermore, note that, since the specific heat C is an extensive quantity, the RMS energy fluctuations, which are the square root of Equation (1.19), scale like $\sqrt{V}$ with the volume V of the system. The internal energy itself on the other hand scales like V, so that the relative size of the fluctuations compared to the internal energy decreases as $1/\sqrt{V}$ as the system becomes large. In the limit of a very large system, therefore, we can ignore the fluctuations altogether. For this reason, the limit of a large system is called the **thermodynamic limit**. Most of the questions we would like to answer about condensed matter systems are questions about behaviour in the thermodynamic limit. Unfortunately, in Monte Carlo simulations it is often not feasible to simulate a system large enough that its behaviour is a good approximation to a large system. Much of the effort we put into designing algorithms will be aimed at making them efficient enough that we can simulate the largest systems possible in the available computer time, in the hope of getting results which are at least a reasonable approximation to the thermodynamic limit.

What about fluctuations in other thermodynamic variables? As we discussed in Section 1.2, each parameter of the system that we fix, such as a volume or an external field, has a conjugate variable, such as a pressure or a magnetization, which is given as a derivative of the free energy by an equation such as (1.14) or (1.15). Derivatives of this general form are produced by terms in the Hamiltonian of the form $-XY$, where Y is a "field" whose value we fix, and X is the conjugate variable to which it couples. For example, the effect of a magnetic field on a magnet can be accounted for by a magnetic energy term in the Hamiltonian of the form $-MB$, where M is the magnetization of the system, and B is the applied magnetic field. We can write the expectation value of X in the form of Equations (1.14) and (1.15) thus:

$$\langle X\rangle = \frac{1}{\beta Z}\sum_\mu X_\mu \mathrm{e}^{-\beta E_\mu} = \frac{1}{\beta Z}\frac{\partial}{\partial Y}\sum_\mu \mathrm{e}^{-\beta E_\mu}, \tag{1.20}$$

since E_μ now contains the term $-X_\mu Y$ which the derivative acts on. Here X_μ is the value of the quantity X in the state μ. We can then write this in terms of the free energy thus:

$$\langle X\rangle = \frac{1}{\beta}\frac{\partial \log Z}{\partial Y} = -\frac{\partial F}{\partial Y}. \tag{1.21}$$

This is a useful technique for calculating the thermal average of a quantity, even if no appropriate field coupling to that quantity appears in the Hamiltonian. We can simply make up a fictitious field which couples to our quantity in the appropriate way—just add a term to the Hamiltonian anyway to allow us to calculate the expectation of the quantity we are interested in—and then set the field to zero after performing the derivative, making the fictitious term vanish from the Hamiltonian again. This is a very common trick in statistical mechanics.

Another derivative of $\log Z$ with respect to Y produces another factor of X_μ in the sum over states, and we find

$$-\frac{1}{\beta}\frac{\partial^2 F}{\partial Y^2} = \frac{1}{\beta}\frac{\partial\langle X\rangle}{\partial Y} = \langle X^2\rangle - \langle X\rangle^2, \tag{1.22}$$

which we recognize as the mean square fluctuation in the variable X. Thus we can find the fluctuations in all sorts of quantities from second derivatives of the free energy with respect to the appropriate fields, just as we can find the energy fluctuations from the second derivative with respect to β. The derivative $\partial\langle X\rangle/\partial Y$, which measures the strength of the response of X to changes in Y is called the **susceptibility** of X to Y, and is usually denoted by χ:

$$\chi \equiv \frac{\partial\langle X\rangle}{\partial Y}. \tag{1.23}$$

Thus the fluctuations in a variable are proportional to the susceptibility of that variable to its conjugate field. This fact is known as the **linear response theorem** and it gives us a way to calculate susceptibilities within Monte Carlo calculations by measuring the size of the fluctuations of a variable.

Extending the idea of the susceptibility, and at the same time moving a step further from the realm of classical thermodynamics, we can also consider what happens when we change the value of a parameter or field at one particular position in our system and ask what effect that has on the conjugate variable at other positions. To study this question we will consider for the moment a system on a lattice. Similar developments are possible for continuous systems like gases, but most of the examples considered in this book are systems which fall on lattices, so it will be of more use to us to go through this for a lattice system here. The interested reader might like to develop the corresponding theory for a continuous system as an exercise.

Let us then suppose that we now have a field which is spatially varying and takes the value Y_i on the i^{th} site of the lattice. The conjugate variables to this field[4] are denoted x_i, and the two are linked via a term in the Hamiltonian $-\sum_i x_i Y_i$. Clearly if we set $Y_i = Y$ and $x_i = X/N$ for all sites i, where N is the total number of sites on the lattice, then this becomes equal once more to the homogeneous situation we considered above. Now in a direct parallel with Equation (1.20) we can write the average value of x_i as

$$\langle x_i\rangle = \frac{1}{Z}\sum_\mu x_i^\mu \mathrm{e}^{-\beta E_\mu} = \frac{1}{\beta}\frac{\partial \log Z}{\partial Y_i}, \tag{1.24}$$

where x_i^μ is the value of x_i in state μ. Then we can define a generalized susceptibility χ_{ij} which is a measure of the response of $\langle x_i\rangle$ to a variation of the field Y_j at a different lattice site:

$$\chi_{ij} = \frac{\partial\langle x_i\rangle}{\partial Y_j} = \frac{1}{\beta}\frac{\partial^2 \log Z}{\partial Y_i \partial Y_j}. \tag{1.25}$$

Again the susceptibility is a second derivative of the free energy. If we make the substitution $Z = \sum_\mu \mathrm{e}^{-\beta E_\mu}$ again (Equation (1.6)), we see that this is also equal to

$$\begin{aligned}\chi_{ij} &= \frac{\beta}{Z}\sum_\mu x_i^\mu x_j^\mu \mathrm{e}^{-\beta E_\mu} - \beta\left[\frac{1}{Z}\sum_\mu x_i^\mu \mathrm{e}^{-\beta E_\mu}\right]\left[\frac{1}{Z}\sum_\nu x_j^\nu \mathrm{e}^{-\beta E_\nu}\right]\\ &= \beta(\langle x_i x_j\rangle - \langle x_i\rangle\langle x_j\rangle) = \beta G_c^{(2)}(i,j).\end{aligned} \tag{1.26}$$

[4] We use lower-case x_i to denote an intensive variable. X by contrast was extensive, i.e., its value scales with the size of the system. We will use this convention to distinguish intensive and extensive variables throughout much of this book.

The quantity $G_c^{(2)}(i,j)$ is called the **two-point connected correlation function** of x between sites i and j, or just the connected correlation, for short. The superscript (2) is to distinguish this function from higher order correlation functions, which are discussed below. As its name suggests, this function is a measure of the correlation between the values of the variable x on the two sites; it takes a positive value if the values of x on those two sites fluctuate in the same direction together, and a negative one if they fluctuate in opposite directions. If their fluctuations are completely unrelated, then its value will be zero. To see why it behaves this way consider first the simpler **disconnected correlation function** $G^{(2)}(i,j)$ which is defined to be

$$G^{(2)}(i,j) \equiv \langle x_i x_j \rangle. \tag{1.27}$$

If the variables x_i and x_j are fluctuating roughly together, around zero, both becoming positive at once and then both becoming negative, at least most of the time, then all or most of the values of the product $x_i x_j$ that we average will be positive, and this function will take a positive value. Conversely, if they fluctuate in opposite directions, then it will take a negative value. If they sometimes fluctuate in the same direction as one another and sometimes in the opposite direction, then the values of $x_i x_j$ will take a mixture of positive and negative values, and the correlation function will average out close to zero. This function therefore has pretty much the properties we desire of a correlation function, and it can tell us a lot of useful things about the behaviour of our system. However, it is not perfect, because we must also consider what happens if we apply our field Y to the system. This can have the effect that the mean value of x at a site $\langle x_i \rangle$ can be non-zero. The same thing can happen even in the absence of an external field if our system undergoes a phase transition to a **spontaneously symmetry broken state** where a variable such as x spontaneously develops a non-zero expectation value. (The Ising model of Section 1.2.2, for instance, does this.) In cases like these, the disconnected correlation function above can have a large positive value simply because the values of the variables x_i and x_j are always either both positive or both negative, even though this has nothing to do with them being correlated to one another. The *fluctuations* of x_i and x_j can be completely unrelated and still the disconnected correlation function takes a non-zero value. To obviate this problem we define the connected correlation function as above:

$$\begin{aligned} G_c^{(2)}(i,j) &\equiv \langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle \\ &= \big\langle (x_i - \langle x_i \rangle) \times (x_j - \langle x_j \rangle) \big\rangle. \end{aligned} \tag{1.28}$$

When the expectations $\langle x_i \rangle$ and $\langle x_j \rangle$ are zero and x_i and x_j are just fluctuating around zero, this function is exactly equal to the disconnected correlation function. But when the expectations are non-zero, the connected correlation function correctly averages only the fluctuations about those expectations—the term we subtract exactly takes care of any trivial contribution arising because of external fields or spontaneous symmetry breaking. If such trivial contributions are the only reason why $G^{(2)}$ is non-zero then $G_c^{(2)}$ will be zero, which is what we would like. If it is not zero, then we have a genuine correlation between the fluctuations of x_i and x_j.

Although they are not often used in the sorts of systems we will be studying in this book and we will not have call to calculate their values in any of the calculations we will describe here, it is worth mentioning, in case you ever need to use them, that there are also higher-order connected correlation functions, defined by generalizing Equation (1.25) like this:

$$\begin{aligned} G_c^{(3)}(i,j,k) &= \frac{1}{\beta^3} \frac{\partial^3 \log Z}{\partial Y_i \partial Y_j \partial Y_k}, \\ G_c^{(4)}(i,j,k,l) &= \frac{1}{\beta^4} \frac{\partial^4 \log Z}{\partial Y_i \partial Y_j \partial Y_k \partial Y_l}, \end{aligned} \tag{1.29}$$

and so on. These are measures of the correlation between simultaneous fluctuations on three and four sites respectively. For a more detailed discussion of these correlation functions and other related ones, see for example Binney *et al.* (1992).

1.2.2 An example: the Ising model

To try to make all of this a bit more concrete, we now introduce a particular model which we can try these concepts out on. That model is the Ising model, which is certainly the most thoroughly researched model in the whole of statistical physics. Without doubt more person-hours have been spent investigating the properties of this model than any other, and although an exact solution of its properties in three dimensions still eludes us, despite many valiant and increasingly sophisticated attempts, a great deal about it is known from computer simulations, and also from approximate methods such as series expansions and ϵ-expansions. We will spend three whole chapters of this book (Chapters 3, 4 and 10) discussing Monte Carlo techniques for studying the model's equilibrium and non-equilibrium properties. Here we will just introduce it briefly and avoid getting too deeply into the discussion of its properties.

The Ising model is a model of a magnet. The essential premise behind it, and behind many magnetic models, is that the magnetism of a bulk material is made up of the combined magnetic dipole moments of many atomic spins within the material. The model postulates a lattice (which can be of any geometry we choose—the simple cubic lattice in three dimensions is a common choice) with a magnetic dipole or spin on each site. In the Ising model these spins assume the simplest form possible, which is not particularly realistic, of scalar variables s_i which can take only two values ±1, representing up-pointing or down-pointing dipoles of unit magnitude. In a real magnetic material the spins interact, for example through exchange interactions or RKKY interactions (see, for instance, Ashcroft and Mermin 1976), and the Ising model mimics this by including terms in the Hamiltonian proportional to products $s_i s_j$ of the spins. In the simplest case, the interactions are all of the same strength, denoted by J which has the dimensions of an energy, and are only between spins on sites which are nearest neighbours on the lattice. We can also introduce an external magnetic field B coupling to the spins. The Hamiltonian then takes the form

$$H = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_i s_i, \tag{1.30}$$

where the notation $\langle ij \rangle$ indicates that the sites i and j appearing in the sum are nearest neighbours.[5] The minus signs here are conventional. They merely dictate the choice of sign for the interaction parameter J and the external field B. With the signs as they are here, a positive value of J makes the spins want to line up with one another—a ferromagnetic model as opposed to an anti-ferromagnetic one which is what we get if J is negative—and the spins also want to line up in the same direction as the external field—they want to be positive if $B > 0$ and negative if $B < 0$.

The states of the Ising system are the different sets of values that the spins can take. Since each spin can take two values, there are a total of 2^N states for a lattice with N spins on it. The partition function of the model is the sum

$$Z = \sum_{s_1=\pm1} \sum_{s_2=\pm1} \ldots \sum_{s_N=\pm1} \exp\Big[\beta J \sum_{\langle ij \rangle} s_i s_j + \beta B \sum_i s_i\Big]. \tag{1.31}$$

To save the eyes, we'll write this in the shorter notation

$$Z = \sum_{\{s_i\}} \mathrm{e}^{-\beta H}. \tag{1.32}$$

If we can perform this sum, either analytically or using a computer, then we can apply all the results of the previous sections to find the internal energy, the entropy, the free energy, the specific heat, and so forth. We can also calculate the mean magnetization $\langle M \rangle$ of the model from the partition function using Equation (1.15), although as we will see it is usually simpler to evaluate $\langle M \rangle$ directly from an average over states:

$$\langle M \rangle = \Big\langle \sum_i s_i \Big\rangle. \tag{1.33}$$

Often, in fact, we are more interested in the mean magnetization per spin $\langle m \rangle$, which is just

$$\langle m \rangle = \frac{1}{N} \Big\langle \sum_i s_i \Big\rangle. \tag{1.34}$$

(In the later chapters of this book, we frequently use the letter m alone to denote the average magnetization per spin, and omit the brackets $\langle \ldots \rangle$ around it indicating the average. This is also the common practice of many other authors. In almost all cases it is clear from the context when an average over states is to be understood.)

We can calculate fluctuations in the magnetization or the internal energy by calculating derivatives of the partition function. Or, as we mentioned in Section 1.2.1, if we have some way of calculating the size of the fluctuations in the magnetization, we can use those to evaluate the **magnetic susceptibility**

$$\frac{\partial \langle M \rangle}{\partial B} = \beta(\langle M^2 \rangle - \langle M \rangle^2). \tag{1.35}$$

(See Equation (1.22).) Again, it is actually more common to calculate the magnetic susceptibility per spin:

$$\chi = \frac{\beta}{N}(\langle M^2 \rangle - \langle M \rangle^2) = \beta N(\langle m^2 \rangle - \langle m \rangle^2). \tag{1.36}$$

(Note the leading factor of N here, which is easily overlooked when calculating χ from Monte Carlo data.) Similarly we can calculate the specific heat per spin c from the energy fluctuations thus:

$$c = \frac{k\beta^2}{N}(\langle E^2 \rangle - \langle E \rangle^2). \tag{1.37}$$

(See Equation (1.19).)

We can also introduce a spatially varying magnetic field into the Hamiltonian thus:

$$H = -J \sum_{\langle ij \rangle} s_i s_j - \sum_i B_i s_i. \tag{1.38}$$

This gives us a different mean magnetization on each site:

$$\langle m_i \rangle = \langle s_i \rangle = \frac{1}{\beta} \frac{\partial \log Z}{\partial B_i}, \tag{1.39}$$

[5] This notation is confusingly similar to the notation for a thermal average, but unfortunately both are sufficiently standard that we feel compelled to use them here. In context it is almost always possible to tell them apart because one involves site labels and the other involves physical variables appearing in the model.

and allows us to calculate the connected correlation function

$$G_c^{(2)}(i,j) = \frac{1}{\beta^2}\frac{\partial^2 \log Z}{\partial B_i \partial B_j}. \tag{1.40}$$

When we look at the equilibrium simulation of the Ising model in Chapters 3 and 4, all of these will be quantities of interest, and relations like these between them give us useful ways of extracting good results from our numerical data.

1.3 Numerical methods

While the formal developments of statistical mechanics are in many ways very elegant, the actual process of calculating the properties of a particular model is almost always messy and taxing. If we consider calculating the partition function Z, from which, as we have shown, a large number of interesting properties of a system can be deduced, we see that we are going to have to perform a sum over a potentially very large number of states. Indeed, if we are interested in the thermodynamic limit, the sum is over an infinite number of states, and performing such sums is a notoriously difficult exercise. It has been accomplished exactly for a number of simple models with discrete energy states, most famously the Ising model in two dimensions (Onsager 1944). This and other exact solutions are discussed at some length by Baxter (1982). However, for the majority of models of interest today, it has not yet proved possible to find an exact analytic expression for the partition function, or for any other equivalent thermodynamic quantity. In the absence of such exact solutions a number of approximate techniques have been developed including series expansions, field theoretical methods and computational methods. The focus of this book is on the last of these, the computational methods.

The most straightforward computational method for solving problems in statistical physics is to take the model we are interested in and put it on a lattice of finite size, so that the partition function becomes a sum with a finite number of terms. (Or in the case of a model with a continuous energy spectrum it becomes an integral of finite dimension.) Then we can employ our computer to evaluate that sum (or integral) numerically, by simply evaluating each term in turn and adding them up. Let's see what happens when we apply this technique to the Ising model of Section 1.2.2.

If we were really interested in tackling an unsolved problem, we might look at the Ising model in three dimensions, whose exact properties have not yet been found by any method. However, rather than jump in at the deep end, let's first look at the two-dimensional case. For a system of a given linear dimension, this model will have fewer energy states than the three-dimensional one, making the sum over states simpler and quicker to perform, and the model has the added pedagogical advantage that its behaviour has been solved exactly, so we can compare our numerical calculations with the exact solution. Let's take a smallish system to start with, of 25 spins on a square lattice in a 5 × 5 arrangement. By convention we apply periodic boundary conditions, so that there are interactions between spins on the border of the array and the opposing spins on the other side. We will also set the external magnetic field B to zero, to make things simpler still.

With each spin taking two possible states, represented by ±1, our 25 spin system has a total of $2^{25} = 33\,554\,432$ possible states. However, we can save ourselves from summing over half of these, because the system has up/down symmetry, which means that for every state there is another one in which every spin is simply flipped upside down, which has exactly the same energy in zero magnetic field. So we can simplify the calculation of the partition function by just taking one out of every pair of such states, for a total of 16 777 216 states, and summing up the corresponding terms in the partition function, Equation (1.6), and then doubling the sum.[6]

In Figure 1.1 we show the mean magnetization per spin and the specific heat per spin for this 5 × 5 system, calculated from Equations (1.10) and (1.34). On the same axes we show the exact solutions for these quantities on an infinite lattice, as calculated by Onsager. The differences between the two are clear, and this is precisely the difference between our small finite-sized system and the infinite thermodynamic-limit system which we discussed in Section 1.2.1. Notice in particular that the exact solution has a non-analytic point at about $kT = 2.3J$ which is not reproduced even moderately accurately by our small numerical calculation. This point is the so-called "critical temperature" at which the length-scale ξ of the fluctuations in the magnetization, also called the "correlation length", diverges. (This point is discussed in more detail in Section 3.7.1.) Because of this divergence of the length-scale, it is never possible to get good results for the behaviour of the system at the critical temperature out of any calculation performed on a finite lattice—the lattice is never large enough to include all of the important physics of the critical point. Does this mean that calculations on finite lattices are useless? No, it certainly does not. To start with, at temperatures well away from the critical point the problems are much less severe, and the numerical calculation and the exact solution agree better,

[6] If we were really serious about this, we could save ourselves further time by making use of other symmetries too. For example the square system we are investigating here also has a reflection symmetry and a four-fold rotational symmetry (the symmetry group is C_4), meaning that the states actually group into sets of 16 states (including the up–down symmetry pairs), all of which have the same energy. This would reduce the number of terms we have to evaluate to 2 105 872. (The reader may like to ponder why this number is not exactly $2^{25}/16$, as one might expect.) However, such efforts are not really worthwhile, since, as we will see very shortly, this direct evaluation of the partition function is not a promising method for solving models.

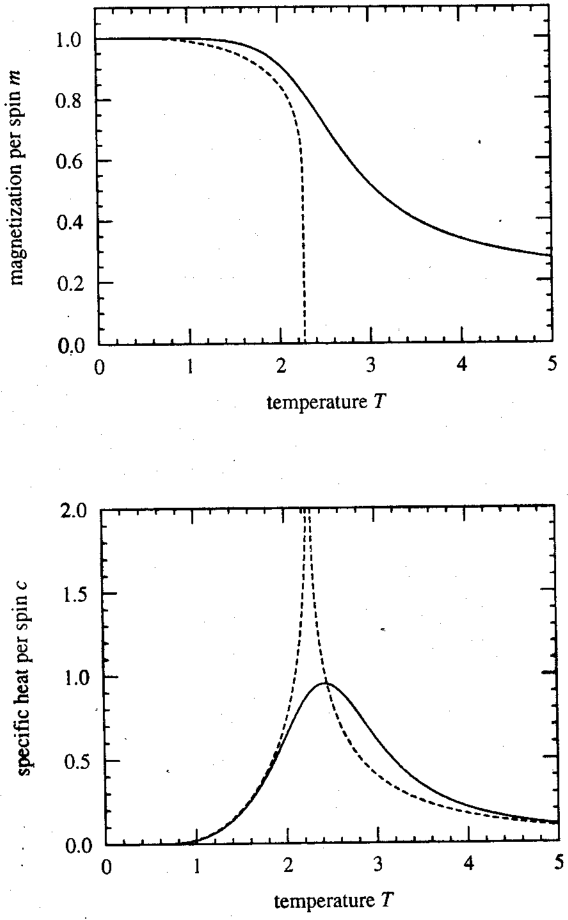

FIGURE 1.1 Top: the mean magnetization per spin m of a 5×5 Ising model on a square lattice in two dimensions (solid line) and the same quantity on an infinitely big square lattice (dashed line). Bottom: the specific heat per spin c for the same two cases.

as we can see in the figure. If we are interested in physics in this regime, then a calculation on a small lattice may well suffice. Second, the technique of "finite size scaling", which is discussed in Section 8.3, allows us to extrapolate results for finite lattices to the limit of infinite system size, and extract good results for the behaviour in the thermodynamic limit. Another technique, that of "Monte Carlo renormalization", discussed in Section 8.4, provides us with a cunning indirect way of calculating some of the features of the critical regime from just the short length-scale phenomena that we get out of a calculation on a small lattice, even though the direct cause of the features that we are interested in is the large length-scale fluctuations that we mentioned.

However, although these techniques can give answers for the critical properties of the system, the accuracy of the answers they give still depends on the size of the system we perform the calculation on, with the answers improving steadily as the system size grows. Therefore it is in our interest to study the largest system we can. However, the calculation which appears as the solid lines in Figure 1.1 took eight hours on a moderately powerful computer. The bulk of this time is spent running through the terms in the sum (1.6). For a system of N spins there are 2^N terms, of which, as we mentioned, we only need actually calculate a half, or 2^{N-1}. This number increases exponentially with the size of the lattice, so we can expect the time taken by the program to increase very rapidly with lattice size. The next size of square lattice up from the present one would be 6×6 or $N = 36$, which should take about $2^{36-1}/2^{25-1} = 2048$ times as long as the previous calculation, or about two years. Clearly this is an unacceptably long time to wait for the answer to this problem. If we are interested in results for any system larger than 5×5, we are going to have to find other ways of getting them.

1.3.1 Monte Carlo simulation

There is essentially only one known numerical method for calculating the partition function of a model such as the Ising model on a large lattice, and that method is Monte Carlo simulation, which is the subject of this book. The basic idea behind Monte Carlo simulation is to simulate the random thermal fluctuation of the system from state to state over the course of an experiment. In Section 1.1 we pointed out that for our purposes it is most convenient to regard the calculation of an expectation value as a time average over the states that a system passes through. In a Monte Carlo calculation we directly simulate this process, creating a model system on our computer and making it pass through a variety of states in such a way that the probability of it being in any particular state μ at a given time t is equal to the weight $w_\mu(t)$ which that state would have in a real system.

In order to achieve this we have to choose a dynamics for our simulation—a rule for changing from one state to another during the simulation—which results in each state appearing with exactly the probability appropriate to it. In the next chapter we will discuss at length a number of strategies for doing this, but the essential idea is that we try to simulate the physical processes that give rise to the master equation, Equation (1.1). We choose a set of rates $R(\mu \to \nu)$ for transitions from one state to another, and we choose them in such a way that the equilibrium solution to the corresponding master equation is precisely the Boltzmann distribution (1.5). Then we use these rates to choose the states which our simulated system passes through during the course of a simulation, and from these states we make estimates of whatever observable quantities we are interested in.

The advantage of this technique is that we need only sample quite a small fraction of the states of the system in order to get accurate estimates of physical quantities. For example, we do not need to include every state of the system in order to get a decent value for the partition function, as we would if we were to evaluate it directly from Equation (1.6). The principal disadvantage of the technique is that there are statistical errors in the calculation due to this same fact that we don't include every state in our calculation, but only some small fraction of the states. In particular this means that there will be statistical noise in the partition function. Taking the derivative of a noisy function is always problematic, so that calculating expectation values from derivatives of the partition function as discussed in Section 1.2 is usually not a good way to proceed. Instead it is normally better in Monte Carlo simulations to calculate as many expectations as we can directly, using equations such as (1.34). We can also make use of relations such as (1.36) to calculate quantities like susceptibilities without having to evaluate a derivative.

In the next chapter we will consider the theory of Monte Carlo simulation in equilibrium thermal systems, and the rest of the first part of the book will deal with the design of algorithms to investigate these systems. In the second part of the book we look at algorithms for non-equilibrium systems.

1.4 A brief history of the Monte Carlo method

In this section we outline the important historical developments in the evolution of the Monte Carlo method. This section is just for fun; feel free to skip over it to the next chapter if you're not interested.

The idea of Monte Carlo calculation is a lot older than the computer. The name "Monte Carlo" is relatively recent—it was coined by Nicolas Metropolis in 1949—but under the older name of "statistical sampling" the method has a history stretching back well into the last century, when numerical calculations were performed by hand using pencil and paper and perhaps a slide-rule. As first envisaged, Monte Carlo was not a method for solving problems in physics, but a method for estimating integrals which could not be performed by other means. Integrals over poorly-behaved functions and integrals in high-dimensional spaces are two areas in which the method has traditionally proved profitable, and indeed it is still an important technique for problems of these types. To give an example, consider the function

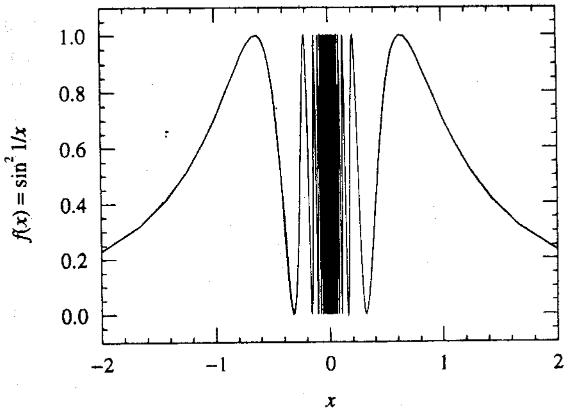

FIGURE 1.2 The pathological function $f(x) \equiv \sin^2 \frac{1}{x}$, whose integral with respect to x, though hard to evaluate analytically, can be evaluated in a straightforward manner using the Monte Carlo integration technique described in the text.

$$f(x) \equiv \sin^2 \frac{1}{x} \tag{1.41}$$

which is pictured in Figure 1.2. The values of this function lie entirely between zero and one, but it is increasingly rapidly varying in the neighbourhood of $x = 0$. Clearly the integral

$$I(x) \equiv \int_0^x f(x')\,\mathrm{d}x' \tag{1.42}$$

which is the area under this curve between 0 and x, takes a finite value somewhere in the range $0 < I(x) < x$, but it is not simple to calculate this value exactly because of the pathologies of the function near the origin. However, we can make an estimate of it by the following method. If we choose a random real number h, uniformly distributed between zero and x, and another v between zero and one and plot on Figure 1.2 the point for which these are the horizontal and vertical coordinates, the probability that

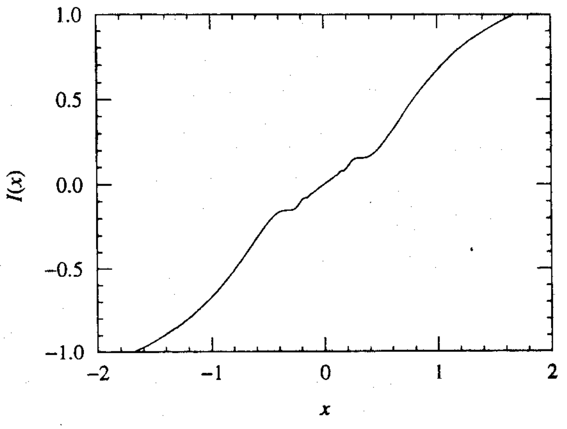

FIGURE 1.3 The function $I(x)$, calculated by Monte Carlo integration as described in the text.

$I(x)/x$ ← area of

this point will be below the line of $f(x)$ is just $I(x)/x$. It is easy to determine whether the point is in fact below the line: it is below it if $h < f(v)$. Thus if we simply pick a large number N of these random points and count up the number M which fall below the line, we can estimate $I(x)$ from

$$I(x) = \lim_{N\to\infty} \frac{Mx}{N}. \tag{1.43}$$

You can get an answer accurate to one figure by taking a thousand points, which would be about the limit of what one could have reasonably done in the days before computers. Nowadays, even a cheap desktop computer can comfortably run through a million points in a few seconds, giving an answer accurate to about three figures. In Figure 1.3 we have plotted the results of such a calculation for a range of values of x. The errors in this calculation are smaller than the width of the line in the figure.[7]

A famous early example of this type of calculation is the experiment known as "Buffon's needle" (Dörrie 1965), in which the mathematical constant π is determined by repeatedly dropping a needle onto a sheet of paper ruled with evenly spaced lines. The experiment is named after Georges-Louis Leclerc, Comte de Buffon who in 1777 was the first to show that if we throw a needle of length l completely at random onto a sheet of paper ruled with lines a distance d apart, then the chances that the needle will fall so as to

intersect one of the lines is $2l/\pi d$, provided that $d \geq l$. It was Laplace in 1820 who then pointed out that if the needle is thrown down N times and is observed to land on a line M of those times, we can make an estimate of π from

$$\pi = \lim_{N\to\infty} \frac{2Nl}{Md}. \tag{1.44}$$

(Perhaps the connection between this and the Monte Carlo evaluation of integrals is not immediately apparent, but it will certainly become clear if you try to derive Equation (1.44) for yourself, or if you follow Dörrie's derivation.) A number of investigators made use of this method over the years to calculate approximate values for π. The most famous of these is Mario Lazzarini, who in 1901 announced that he had calculated a value of 3.1415929 for π from an experiment in which a $2\frac{1}{2}$ cm needle was dropped 3408 times onto a sheet of paper ruled with lines 3 cm apart. This value, accurate to better than three parts in ten million, would be an impressive example of the power of the statistical sampling method were it not for the fact that it is almost certainly faked. Badger (1994) has demonstrated extremely convincingly that, even supposing Lazzarini had the technology at his disposal to measure the length of his needle and the spaces between his lines to a few parts in 10^7 (a step necessary to ensure the accuracy of Equation (1.44)), still the chances of his finding the results he did were poorer than three in a million; Lazzarini was imprudent enough to publish details of the progress of the experiment through the 3408 castings of the needle, and it turns out that the statistical "fluctuations" in the numbers of intersections of the needle with the ruled lines are much smaller than one would expect in a real experiment. All indications are that Lazzarini forged his results. However, other, less well known attempts at the experiment were certainly genuine, and yielded reasonable figures for π: 3.1596 (Wolf 1850), 3.1553 (Smith 1855). Apparently, performing the Buffon's needle experiment was for a while quite a sophisticated pastime amongst Europe's intellectual gentry.

With the advent of mechanical calculating machines at the end of the nineteenth century, numerical methods took a large step forward. These machines increased enormously the number and reliability of the arithmetic operations that could be performed in a numerical "experiment", and made the application of statistical sampling techniques to research problems in physics a realistic possibility for the first time. An early example of what was effectively a Monte Carlo calculation of the motion and collision of the molecules in a gas was described by William Thomson (later Lord Kelvin) in 1901. Thomson's calculations were aimed at demonstrating the truth of the equipartition theorem for the internal energy of a classical system. However, after the fashion of the time, he did not perform the laborious analysis himself, and a lot of the credit for the results must go to Thomson's

[7] In fact there exist a number of more sophisticated Monte Carlo integration techniques which give more accurate answers than the simple "hit or miss" method we have described here. A discussion can be found in the book by Kalos and Whitlock (1986).

secretary, William Anderson, who apparently solved the kinetic equations for more than five thousand molecular collisions using nothing more than a pencil and a mechanical adding machine.

Aided by mechanical calculators, numerical methods, particularly the method of finite differences, became an important tool during the First World War. The authors recently heard the intriguing story of the Herculean efforts of French mathematician Henri Soudée, who in 1916 calculated firing tables for the new 400 mm cannons being set up at Verdun, directly from his knowledge of the hydrodynamic properties of gases. The tables were used when the cannons were brought to bear on the German-occupied Fort de Douaumont, and as a result the fort was taken by the allies. Soudée was later honoured by the French. By the time of the Second World War the mechanical calculation of firing angles for large guns was an important element of military technology. The physicist Richard Feynman tells the story of his employment in Philadelphia during the summer of 1940 working for the army on a mechanical device for predicting the trajectories of planes as they flew past (Feynman 1985). The device was to be used to guide anti-aircraft guns in attacking the planes. Despite some success with the machine, Feynman left the army's employ after only a few months, joking that the subject of mechanical computation was too difficult for him. He was shrewd enough to realize he was working on a dinosaur, and that the revolution of electronic computing was just around the corner. It was some years however before that particular dream would become reality, and before it did Feynman had plenty more chance to spar with the mechanical calculators. As a group leader during the Manhattan Project at Los Alamos he created what was effectively a highly pipelined human CPU, by employing a large number of people armed with Marchant mechanical adding machines in an arithmetic assembly line in which little cards with numbers on were passed from one worker to the next for processing on the machines. A number of numerical calculations crucial to the design of the atomic bomb were performed in this way.

The first real applications of the statistical sampling method to research problems in physics seem to have been those of Enrico Fermi, who was working on neutron diffusion in Rome in the early 1930s. Fermi never published his numerical methods—apparently he considered only the results to be of interest, not the methods used to obtain them—but according to his influential student and collaborator Emilio Segrè those methods were, in everything but name, precisely the Monte Carlo methods later employed by Ulam and Metropolis and their collaborators in the construction of the hydrogen bomb (Segrè 1980).

So it was that when the Monte Carlo method finally caught the attention of the physics community, it was again as the result of armed conflict. The important developments took place at the Los Alamos National Laboratory

in New Mexico, where Nick Metropolis, Stanislaw Ulam and John von Neumann gathered in the last months of the Second World War shortly after the epochal bomb test at Alamagordo, to collaborate on numerical calculations to be performed on the new ENIAC electronic computer, a mammoth, room-filing machine containing some 18 000 triode valves, whose construction was nearing completion at the University of Pennsylvania. Metropolis (1980) has remarked that the technology that went into the ENIAC existed well before 1941, but that it took the pressure of America's entry into the war to spur the construction of the machine.

It seems to have been Stan Ulam who was responsible for reinventing Fermi's statistical sampling methods. He tells of how the idea of calculating the average effect of a frequently repeated physical process by simply simulating the process over and over again on a digital computer came to him whilst huddled over a pack of cards, playing patience[8] one day. The game he was playing was "Canfield" patience, which is one of those forms of patience where the goal is simply to turn up every card in the pack, and he wondered how often on average one could actually expect to win the game. After abandoning the hopelessly complex combinatorics involved in answering this question analytically, it occurred to him that you could get an approximate answer simply by playing a very large number of games and seeing how often you win. With his mind never far from the exciting new prospect of the ENIAC computer, the thought immediately crossed his mind that he might be able to get the machine to play these games for him far faster than he ever could himself, and it was only a short conceptual leap to applying the same idea to some of the problems of the physics of the hydrogen bomb that were filling his work hours at Los Alamos. He later described his idea to John von Neumann who was very enthusiastic about it, and the two of them began making plans to perform actual calculations. Though Ulam's idea may appear simple and obvious to us today, there are actually many subtle questions involved in this idea that a physical problem with an exact answer can be approximately solved by studying a suitably chosen random process. It is a tribute to the ingenuity of the early Los Alamos workers that, rather than plunging headlong into the computer calculations, they considered most of these subtleties right from the start.

The war ended before the first Monte Carlo calculations were performed on the ENIAC. There was some uncertainty about whether the Los Alamos laboratory would continue to exist in peacetime, and Edward Teller, who was leading the project to develop the hydrogen bomb, was keen to apply the power of the computer to the problems of building the new bomb, in order to show that significant work was still going on at Los Alamos. Von Neumann developed a detailed plan of how the Monte Carlo method could be

[8] Also called "solitaire" in the USA.

implemented on the ENIAC to solve a number of problems concerned with neutron transport in the bomb, and throughout 1947 worked with Metropolis on preparations for the calculations. They had to wait to try their ideas out however, because the ENIAC was to be moved from Philadelphia where it was built to the army's Ballistics Research Laboratory in Maryland. For a modern computer this would not be a problem, but for the gigantic ENIAC, with its thousands of fragile components, it was a difficult task, and there were many who did not believe the computer would survive the journey. It did, however, and by the end of the year it was working once again in its new home. Before von Neumann and the others put it to work on the calculations for the hydrogen bomb, Richard Clippinger of the Ballistics Lab suggested a modification to the machine which allowed it to store programs in its electronic memory. Previously a program had to be set up by plugging and unplugging cables at the front of the machine, an arduous task which made the machine inflexible and inconvenient to use. Von Neumann was in favour of changing to the new "stored program" model, and Nick Metropolis and von Neumann's wife, Klari, made the necessary modifications to the computer themselves. It was the end of 1947 before the machine was at last ready, and Metropolis and von Neumann set to work on the planned Monte Carlo calculations.

The early neutron diffusion calculations were an impressive success, but Metropolis and von Neumann were not able to publish their results, because they were classified as secret. Over the following two years however, they and others, including Stan Ulam and Stanley Frankel, applied the new statistical sampling method to a variety of more mundane problems in physics, such as the calculation of the properties of hard-sphere gases in two and three dimensions, and published a number of papers which drew the world's attention to this emerging technique. The 1949 paper by Metropolis and Ulam on statistical techniques for studying integro-differential equations is of interest because it contained in its title the first use of the term "Monte Carlo" to describe this type of calculation. Also in 1949 the first conference on Monte Carlo methods was held in Los Alamos, attracting more than a hundred participants. It was quickly followed by another similar meeting in Gainesville, Florida.

The calculations received a further boost in 1948 with the arrival at Los Alamos of a new computer, humorously called the MANIAC. (Apparently the name was suggested by Enrico Fermi, who was tiring of computers with contrived acronyms for names—he claimed that it stood for "Metropolis and Neumann Invent Awful Contraption". Nowadays, with all our computers called things like XFK-23/z we would no doubt appreciate a few pronounceable names.) Apart from the advantage of being in New Mexico rather than Maryland, the MANIAC was a significant technical improvement over the ENIAC which Presper Eckert (1980), its principal architect, refers to as a "hastily built first try". It was faster and contained a larger memory (40 kilobits, or 5 kilobytes in modern terms). It was built under the direction of Metropolis, who had been lured back to Los Alamos after a brief stint on the faculty at Chicago by the prospect of the new machine. The design was based on ideas put forward by John von Neumann and incorporated a number of technical refinements proposed by Jim Richardson, an engineer working on the project. A still more sophisticated computer, the MANIAC 2, was built at Los Alamos two years later, and both machines remained in service until the late fifties, producing a stream of results, many of which have proved to be seminal contributions to the field of Monte Carlo simulation. Of particular note to us is the publication in 1953 of the paper by Nick Metropolis, Marshall and Arianna Rosenbluth, and Edward and Mici Teller, in which they describe for the first time the Monte Carlo technique that has come to be known as the Metropolis algorithm. This algorithm was the first example of a thermal "importance sampling" method, and it is to this day easily the most widely used such method. We will be discussing it in some detail in Chapter 3. Also of interest are the Monte Carlo studies of nuclear cascades performed by Antony Turkevich and Nick Metropolis, and Edward Teller's work on phase changes in interacting hard-sphere gases using the Metropolis algorithm.

The exponential growth in computer power since those early days is by now a familiar story to us all, and with this increase in computational resources Monte Carlo techniques have looked deeper and deeper into the subject of statistical physics. Monte Carlo simulations have also become more accurate as a result of the invention of new algorithms. Particularly in the last twenty years, many new ideas have been put forward, of which we describe a good number in the rest of this book.

Problems

1.1 "If a system is in equilibrium with a thermal reservoir at temperature T, the probability of its having a total energy E varies with E in proportion to $e^{-\beta E}$." True or false?

1.2 A certain simple system has only two energy states, with energies E_0 and E_1, and transitions between the two states take place at rates $R(0 \to 1) = R_0 \exp[-\beta(E_1 - E_0)]$ and $R(1 \to 0) = R_0$. Solve the master equation (1.1) for the probabilities w_0 and w_1 of occupation of the two states as a function of time with the initial conditions $w_0 = 0$, $w_1 = 1$. Show that as $t \to \infty$ these solutions tend to the Boltzmann probabilities, Equation (1.5).

1.3 A slightly more complex system contains N distinguishable particles, each of which can be in one of two boxes. The particles in the first box have energy $E_0 = 0$ and the particles in the second have energy E_1, and particles