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David P. Landau and Kurt Binder
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1 Introduction

1.1 WHAT IS A MONTE CARLO SIMULATION?

In a Monte Carlo simulation we attempt to follow the 'time dependence' of a model for which change, or growth, does not proceed in some rigorously predefined fashion (e.g. according to Newton's equations of motion) but rather in a stochastic manner which depends on a sequence of random numbers which is generated during the simulation. With a second, different sequence of random numbers the simulation will not give identical results but will yield values which agree with those obtained from the first sequence to within some 'statistical error'. A very large number of different problems fall into this category: in percolation an empty lattice is gradually filled with particles by placing a particle on the lattice randomly with each 'tick of the clock'. Lots of questions may then be asked about the resulting 'clusters' which are formed of neighboring occupied sites. Particular attention has been paid to the determination of the 'percolation threshold', i.e. the critical concentration of occupied sites for which an 'infinite percolating cluster' first appears. A percolating cluster is one which reaches from one boundary of a (macroscopic) system to the opposite one. The properties of such objects are of interest in the context of diverse physical problems such as conductivity of random mixtures, flow through porous rocks, behavior of dilute magnets, etc. Another example is diffusion limited aggregation (DLA) where a particle executes a random walk in space, taking one step at each time interval, until it encounters a 'seed' mass and sticks to it. The growth of this mass may then be studied as many random walkers are turned loose. The 'fractal' properties of the resulting object are of real interest, and while there is no accepted analytical theory of DLA to date, computer simulation is the method of choice. In fact, the phenomenon of DLA was first discovered by Monte Carlo simulation!

Considering problems of statistical mechanics, we may be attempting to sample a region of phase space in order to estimate certain properties of the model, although we may not be moving in phase space along the same path which an exact solution to the time dependence of the model would yield. Remember that the task of equilibrium statistical mechanics is to calculate thermal averages of (interacting) many-particle systems: Monte Carlo simulations can do that, taking proper account of statistical fluctuations and their

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effects in such systems. Many of these models will be discussed in more detail in later chapters so we shall not provide further details here. Since the accuracy of a Monte Carlo estimate depends upon the thoroughness with which phase space is probed, improvement may be obtained by simply running the calculation a little longer to increase the number of samples. Unlike in the application of many analytic techniques (e.g. perturbation theory for which the extension to higher order may be prohibitively difficult), the improvement of the accuracy of Monte Carlo results is possible not just in principle but also in practice!

1.2 WHAT PROBLEMS CAN WE SOLVE WITH IT?

The range of different physical phenomena which can be explored using Monte Carlo methods is exceedingly broad. Models which either naturally or through approximation can be discretized can be considered. The motion of individual atoms may be examined directly; e.g. in a binary (AB) metallic alloy where one is interested in interdiffusion or unmixing kinetics (if the alloy was prepared in a thermodynamically unstable state) the random hopping of atoms to neighboring sites can be modeled directly. This problem is complicated because the jump rates of the different atoms depend on the locally differing environment. Of course, in this description the quantum mechanics of atoms with potential barriers in the eV range is not explicitly considered, and the sole effect of phonons (lattice vibrations) is to provide a 'heat bath' which provides the excitation energy for the jump events. Because of a separation of time scales (the characteristic times between jumps are orders of magnitude larger than atomic vibration periods) this approach provides very good approximation. The same kind of arguments hold true for growth phenomena involving macroscopic objects, such as DLA growth of colloidal particles; since their masses are orders of magnitude larger than atomic masses, the motion of colloidal particles in fluids is well described by classical, random Brownian motion. These systems are hence well suited to study by Monte Carlo simulations which use random numbers to realize random walks. The motion of a fluid may be studied by considering 'blocks' of fluid as individual particles, but these blocks will be far larger than individual molecules. As an example, we consider 'micelle formation' in lattice models of microemulsions (water–oil–surfactant fluid mixtures) in which each surfactant molecule may be modeled by two 'dimers' on the lattice (two occupied nearest neighbor sites on the lattice). Different effective interactions allow one dimer to mimic the hydrophilic group and the other dimer the hydrophobic group of the surfactant molecule. This model then allows the study of the size and shape of the aggregates of surfactant molecules (the micelles) as well as the kinetic aspects of their formation. In reality, this process is quite slow so that a deterministic molecular dynamics simulation (i.e. numerical integration of Newton's second law) is not feasible. This example shows that part of the 'art' of simulation is the appropriate choice (or invention!) of a suitable (coarse-grained) model. Large collections of interacting classical particles are directly amenable to Monte Carlo simulation, and the behavior of interacting quantized particles is being studied either by transforming the system into a pseudo-classical model or by considering permutation properties directly. These considerations will be discussed in more detail in later chapters. Equilibrium properties of systems of interacting atoms have been extensively studied as have a wide range of models for simple and complex fluids, magnetic materials, metallic alloys, adsorbed surface layers, etc. More recently polymer models have been studied with increasing frequency; note that the simplest model of a flexible polymer is a random walk, an object which is well suited for Monte Carlo simulation. Furthermore, some of the most significant advances in understanding the theory of elementary particles have been made using Monte Carlo simulations of lattice gauge models.

1.3 WHAT DIFFICULTIES WILL WE ENCOUNTER?

1.3.1 Limited computer time and memory

Because of limits on computer speed there are some problems which are inherently not suited to computer simulation at this time. A simulation which requires years of cpu time on whatever machine is available is simply impractical. Similarly a calculation which requires memory which far exceeds that which is available can be carried out only by using very sophisticated programming techniques which slow down running speeds and greatly increase the probability of errors. It is therefore important that the user first consider the requirements of both memory and cpu time *before* embarking on a project to ascertain whether or not there is a realistic possibility of obtaining the resources to simulate a problem properly. Of course, with the rapid advances being made by the computer industry, it may be necessary to wait only a few years for computer facilities to catch up to your needs. Sometimes the tractability of a problem may require the invention of a new, more efficient simulation algorithm. Of course, developing new strategies to overcome such difficulties constitutes an exciting field of research by itself.

1.3.2 Statistical and other errors

Assuming that the project can be done, there are still potential sources of error which must be considered. These difficulties will arise in many different situations with different algorithms so we wish to mention them briefly at this time without reference to any specific simulation approach. All computers operate with limited word length and hence limited precision for numerical values of any variable. Truncation and round-off errors may in some cases lead to serious problems. In addition there are statistical errors which

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arise as an inherent feature of the simulation algorithm due to the finite number of members in the 'statistical sample' which is generated. These errors must be estimated and then a 'policy' decision must be made, i.e. should more cpu time be used to reduce the statistical errors or should the cpu time available be used to study the properties of the system under other conditions. Lastly there may be systematic errors. In this text we shall not concern ourselves with tracking down errors in computer programming – although the practitioner must make a special effort to eliminate any such errors! – but with more fundamental problems. An algorithm may fail to treat a particular situation properly, e.g. due to the finite number of particles which are simulated, etc. These various sources of error will be discussed in more detail in later chapters.

1.4 WHAT STRATEGY SHOULD WE FOLLOW IN APPROACHING A PROBLEM?

Most new simulations face hidden pitfalls and difficulties which may not be apparent in early phases of the work. It is therefore often advisable to begin with a relatively simple program and use relatively small system sizes and modest running times. Sometimes there are special values of parameters for which the answers are already known (either from analytic solutions or from previous, high quality simulations) and these cases can be used to test a new simulation program. By proceeding in this manner one is able to uncover which are the parameter ranges of interest and what unexpected difficulties are present. It is then possible to refine the program and then to increase running times. Thus *both* cpu time and human time can be used most effectively. It makes little sense of course to spend a month to rewrite a computer program which may result in a total saving of only a few minutes of cpu time. If it happens that the outcome of such test runs shows that a new problem is not tractable with reasonable effort, it may be desirable to attempt to improve the situation by redefining the model or redirect the focus of the study. For example, in polymer physics the study of short chains (oligomers) by a given algorithm may still be feasible even though consideration of huge macromolecules may be impossible.

1.5 HOW DO SIMULATIONS RELATE TO THEORY AND EXPERIMENT?

In many cases theoretical treatments are available for models for which there is no perfect physical realization (at least at the present time). In this situation the only possible test for an approximate theoretical solution is to compare with 'data' generated from a computer simulation. As an example we wish to mention recent activity in growth models, such as diffusion limited aggregation, for which a very large body of simulation results already exists but for which extensive experimental information is just now becoming

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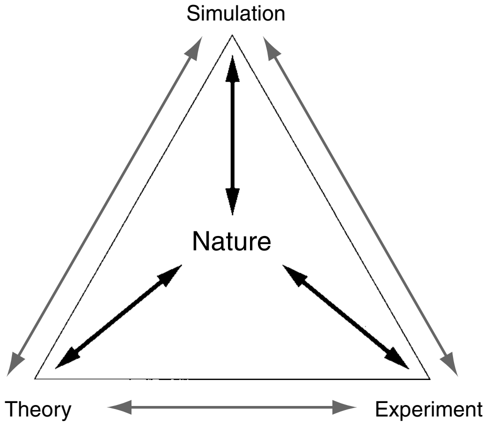

Fig. 1.1 Schematic view of the relationship between theory, experiment, and computer simulation.

available. It is not an exaggeration to say that interest in this field was created by simulations. Even more dramatic examples are those of reactor meltdown or large scale nuclear war: although we want to know what the results of such events would be, we do not want to carry out experiments! There are also real physical systems which are sufficiently complex that they are not presently amenable to theoretical treatment. An example is the problem of understanding the specific behavior of a system with many competing interactions and which is undergoing a phase transition. A model Hamiltonian which is believed to contain all the essential features of the physics may be proposed, and its properties may then be determined from simulations. If the simulation (which now plays the role of theory) disagrees with experiment, then a new Hamiltonian must be sought. An important advantage of the simulations is that different physical effects which are simultaneously present in real systems may be isolated and, through separate consideration by simulation, may provide a much better understanding. Consider, for example, the phase behavior of polymer blends – materials which have ubiquitous applications in the plastics industry. The miscibility of different macromolecules is a challenging problem in statistical physics in which there is a subtle interplay between complicated enthalpic contributions (strong covalent bonds compete with weak van der Waals forces, and Coulombic interactions and hydrogen bonds may be present as well) and entropic effects (configurational entropy of flexible macromolecules, entropy of mixing, etc.). Real materials are very difficult to understand because of various asymmetries between the constituents of such mixtures (e.g. in shape and size, degree of polymerization, flexibility, etc.). Simulations of simplified models can 'switch off' or 'switch on' these effects and thus determine the particular consequences of each contributing factor. We wish to emphasize that the aim of simulations is not to provide better 'curve fitting' to experimental data than does analytic theory. The goal is to create an understanding of physical properties and processes which is as complete as possible, making use of the perfect control of 'experimental' conditions in the 'computer experiment' and of the possibility to examine every aspect of system configurations in detail. The desired result is then the elucidation of the physical mechanisms that are responsible for the observed phenomena. We therefore view the relationship between theory, experiment, and simulation to be similar to those of the vertices of a triangle, as shown in Fig. 1.1: each is distinct, but each is strongly connected to the other two.

1.6 PERSPECTIVE

The Monte Carlo method has had a considerable history in physics. As far back as 1949 a review of the use of Monte Carlo simulations using 'modern computing machines' was presented by Metropolis and Ulam (1949). In addition to giving examples they also emphasized the advantages of the method. Of course, in the following decades the kinds of problems they discussed could be treated with far greater sophistication than was possible in the first half of the twentieth century, and many such studies will be described in succeeding chapters. Now, Monte Carlo simulations are reaching into areas that are far afield of physics. In succeeding chapters we will also provide the reader with a taste of what is possible with these techniques in other areas of investigation. It is also quite telling that there are now several software products on the market that perform simple Monte Carlo simulations in concert with widely distributed spreadsheet software on PCs.

With the rapidly increasing growth of computer power which we are now seeing, coupled with the steady drop in price, it is clear that computer simulations will be able to rapidly increase in sophistication to allow more subtle comparisons to be made. Even now, the combination of new algorithms and new high performance computing platforms has allowed simulations to be performed for more than 10^6 (in special cases exceeding 3×10^{11} (Kadau *et al.*, 2006)) particles (spins). As a consequence it is no longer possible to view the system and look for 'interesting' phenomena without the use of sophisticated visualization techniques. The sheer volume of data that we are capable of producing has also reached unmanageable proportions. In order to permit further advances in the interpretation of simulations, it is likely that the inclusion of intelligent 'agents' (in the computer science sense) for steering and visualization, along with new data structures, will be needed. Such topics are beyond the scope of the text, but the reader should be aware of the need to develop these new strategies.

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2 Some necessary background

2.1 THERMODYNAMICS AND STATISTICAL MECHANICS: A QUICK REMINDER

2.1.1 Basic notions

In this chapter we shall review some of the basic features of thermodynamics and statistical mechanics which will be used later in this book when devising simulation methods and interpreting results. Many good books on this subject exist and we shall not attempt to present a complete treatment. This chapter is hence *not* intended to *replace* any textbook for this important field of physics but rather to 'refresh' the reader's knowledge and to draw attention to notions in thermodynamics and statistical mechanics which will henceforth be assumed to be known throughout this book.

2.1.1.1 Partition function

Equilibrium statistical mechanics is based upon the idea of a partition function which contains all of the essential information about the system under consideration. The general form for the partition function for a classical system is

$$Z = \sum_{\text{all states}} e^{-\mathcal{H}/k_{\text{B}}T}, \tag{2.1}$$

where $\mathcal{H}$ is the Hamiltonian for the system, T is the temperature, and k_{B} is the Boltzmann constant. The sum in Eqn. (2.1) is over all possible states of the system and thus depends upon the size of the system and the number of degrees of freedom for each particle. For systems consisting of only a few interacting particles the partition function can be written down exactly with the consequence that the properties of the system can be calculated in closed form. In a few other cases the interactions between particles are so simple that evaluating the partition function is possible.

Example

Let us consider a system with N particles each of which has only two states, e.g. a non-interacting Ising model in an external magnetic field H, and which has the Hamiltonian

$$\mathcal{H} = -H \sum_i \sigma_i, \tag{2.2}$$

where $\sigma_i = \pm 1$. The partition function for this system is simply

$$Z = \left(e^{-H/k_\mathrm{B}T} + e^{+H/k_\mathrm{B}T}\right)^N, \tag{2.3}$$

where for a single spin the sum in Eqn. (2.1) is only over two states. The energies of the states and the resultant temperature dependence of the internal energy appropriate to this situation are pictured in Fig. 2.1.

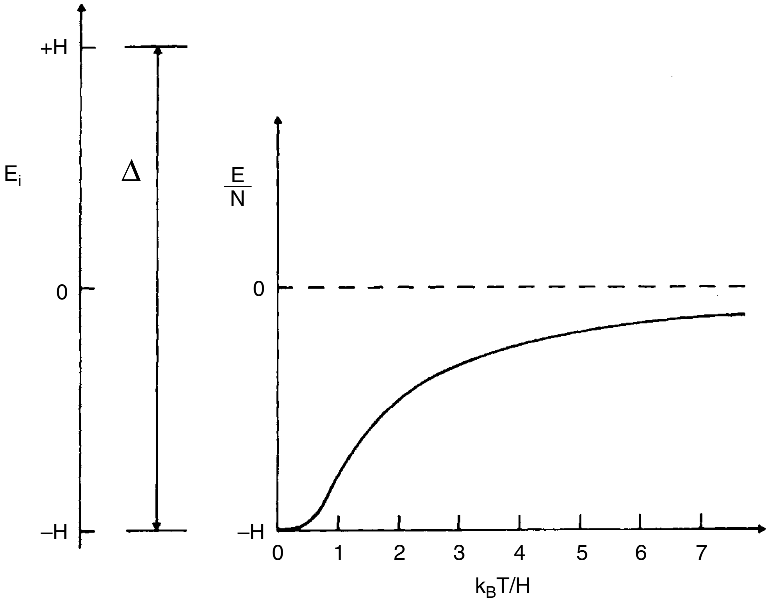

Fig. 2.1 (left) Energy levels for the two level system in Eqn. (2.2); (right) internal energy for a two level system as a function of temperature.

Problem 2.1 Work out the average magnetization per spin, using Eqn. (2.3), for a system of N non-interacting Ising spins in an external magnetic field. [Solution $M = -(1/N)\partial F/\partial H, F = -k_\mathrm{B}T \ln Z \Rightarrow M = \tanh(H/k_\mathrm{B}T)$]

There are also a few examples where it is possible to extract exact results for very large systems of interacting particles, but in general the partition function cannot be evaluated exactly. Even enumerating the terms in the partition function on a computer can be a daunting task. Even if we have only 10 000 interacting particles, a very small fraction of Avogadro's number, with only two possible states per particle, the partition function would contain $2^{10\,000}$

terms! The probability of any particular state of the system is also determined by the partition function. Thus, the probability that the system is in state μ is given by

$$P_\mu = e^{-\mathcal{H}(\mu)/k_\mathrm{B}T}/Z, \tag{2.4}$$

where $\mathcal{H}(\mu)$ is the Hamiltonian when the system is in the μth state. As we shall show in succeeding chapters, the Monte Carlo method is an excellent technique for estimating probabilities, and we can take advantage of this property in evaluating the results.

2.1.1.2 Free energy, internal energy, and entropy

It is possible to make a direct connection between the partition function and thermodynamic quantities and we shall now briefly review these relationships. The free energy of a system can be determined from the partition function (Callen, 1985) from

$$F = -k_\mathrm{B}T \ln Z \tag{2.5}$$

and all other thermodynamic quantities can be calculated by appropriate differentiation of Eqn. (2.5). This relation then provides the connection between statistical mechanics and thermodynamics. The internal energy of a system can be obtained from the free energy via

$$U = -T^2 \partial(F/T)/\partial T. \tag{2.6}$$

By the use of a partial derivative we imply here that F will depend upon other variables as well, e.g. the magnetic field H in the above example, which are held constant in Eqn. (2.6). This also means that if the internal energy of a system can be measured, the free energy can be extracted by appropriate integration, assuming, of course, that the free energy is known at some reference temperature. We shall see that this fact is important for simulations which do not yield the free energy directly but produce instead values for the internal energy. Free energy differences may then be estimated by integration, i.e. from $\Delta(F/T) = \int d(1/T)U$.

Using Eqn. (2.6) one can easily determine the temperature dependence of the internal energy for the non-interacting Ising model, and this is also shown in Fig. 2.1. Another important quantity, the entropy, measures the amount of disorder in the system. The entropy is defined in statistical mechanics by

$$S = -k_\mathrm{B} \ln P, \tag{2.7}$$

where P is the probability of occurrence of a state. The entropy can be determined from the free energy from

$$S = -(\partial F/\partial T)_{V,N}. \tag{2.8}$$

2.1.1.3 Thermodynamic potentials and corresponding ensembles

The internal energy is expressed as a function of the extensive variables, S, V, N, etc. There are situations when it is appropriate to replace some of these variables by their conjugate intensive variables, and for this purpose additional thermodynamic potentials can be defined by suitable Legendre transforms of the internal energy; in terms of liquid–gas variables such relations are given by:

$$F = U - TS, \tag{2.9a}$$

$$H = U + pV, \tag{2.9b}$$

$$G = U - TS + pV, \tag{2.9c}$$

where F is the Helmholtz free energy, H is the enthalpy, and G is the Gibbs free energy. Similar expressions can be derived using other thermodynamic variables, e.g. magnetic variables. The free energy is important since it is a minimum in equilibrium when T and V are held constant, while G is a minimum when T and p are held fixed. Moreover, the difference in free energy between any two states does not depend on the path between the states. Thus, in Fig. 2.2 we consider two points in the p–T plane. Two different paths which connect points 1 and 2 are shown; the difference in free energy between these two points is identical for both paths, i.e.

$$F_2 - F_1 = \int_{\text{path I}} dF = \int_{\text{path II}} dF. \tag{2.10}$$

The multidimensional space in which each point specifies the complete microstate (specified by the degrees of freedom of all the particles) of a system is termed ‘phase space’. Averages over phase space may be constructed by considering a large number of identical systems which are held at the same fixed conditions. These are called ‘ensembles’. Different ensembles are relevant for different constraints. If the temperature is held fixed, the set of systems is said to belong to the ‘canonical ensemble’ and there will be some distribution of energies among the different systems. If instead the energy is fixed, the ensemble is termed the ‘microcanonical’ ensemble. In the first two

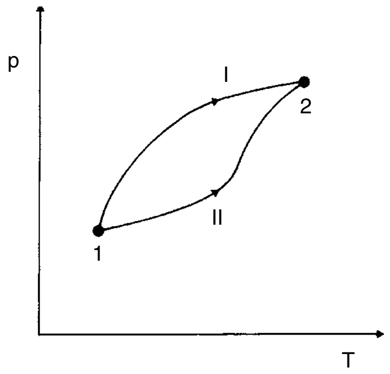

Fig. 2.2 Schematic view of different paths between two different points in thermodynamic p–T space.