

A Guide to
**Monte Carlo Simulations in
Statistical Physics**

David P. Landau

Center for Simulational Physics, The University of Georgia

Kurt Binder

Institut für Physik, Johannes-Gutenberg-Universität Mainz



PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE
The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS
The Edinburgh Building, Cambridge CB2 2RU, UK
40 West 20th Street, New York, NY 10011-4211, USA
477 Williamstown Road, Port Melbourne, VIC 3207, Australia
Ruiz de Alarcón 13, 28014 Madrid, Spain
Dock House, The Waterfront, Cape Town 8001, South Africa
<http://www.cambridge.org>

© David P. Landau and Kurt Binder 2000

This book is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without
the written permission of Cambridge University Press.

First published 2000
Reprinted 2002

Printed in the United Kingdom at the University Press, Cambridge

Typeface Ehrhardt 10.25/12.5pt *System* Advent 3B2 [KW]

A catalogue record for this book is available from the British Library

Library of Congress Cataloging in Publication data
Landau, David P.

A guide to Monte Carlo simulations in statistical physics / David P. Landau, Kurt Binder.
p. cm.

Includes index.

ISBN 0 521 65314 2 (hardbound)

1. Monte Carlo method. 2. Statistical physics. I. Binder, K. (Kurt), 1944–. II. Title.

QC174.85.M64L36 2000

530.13–dc21 99-38308CIP

ISBN 0 521 65314 2 hardback
ISBN 0 521 65366 5 paperback

Contents

Preface	xi
1 Introduction	1
1.1 What is a Monte Carlo simulation?	1
1.2 What problems can we solve with it?	2
1.3 What difficulties will we encounter?	3
1.3.1 Limited computer time and memory	3
1.3.2 Statistical and other errors	3
1.4 What strategy should we follow in approaching a problem?	4
1.5 How do simulations relate to theory and experiment?	4
2 Some necessary background	7
2.1 Thermodynamics and statistical mechanics: a quick reminder	7
2.1.1 Basic notions	7
2.1.2 Phase transitions	13
2.1.3 Ergodicity and broken symmetry	24
2.1.4 Fluctuations and the Ginzburg criterion	25
2.1.5 A standard exercise: the ferromagnetic Ising model	25
2.2 Probability theory	27
2.2.1 Basic notions	27
2.2.2 Special probability distributions and the central limit theorem	29
2.2.3 Statistical errors	30
2.2.4 Markov chains and master equations	31
2.2.5 The ‘art’ of random number generation	32
2.3 Non-equilibrium and dynamics: some introductory comments	39
2.3.1 Physical applications of master equations	39
2.3.2 Conservation laws and their consequences	40
2.3.3 Critical slowing down at phase transitions	43
2.3.4 Transport coefficients	45
2.3.5 Concluding comments	45
References	46
3 Simple sampling Monte Carlo methods	48
3.1 Introduction	48
3.2 Comparisons of methods for numerical integration of given functions	48

3.2.1	Simple methods	48
3.2.2	Intelligent methods	50
3.3	Boundary value problems	51
3.4	Simulation of radioactive decay	53
3.5	Simulation of transport properties	54
3.5.1	Neutron transport	54
3.5.2	Fluid flow	55
3.6	The percolation problem	56
3.6.1	Site percolation	56
3.6.2	Cluster counting: the Hoshen–Kopelman algorithm	59
3.6.3	Other percolation models	60
3.7	Finding the groundstate of a Hamiltonian	60
3.8	Generation of ‘random’ walks	61
3.8.1	Introduction	61
3.8.2	Random walks	62
3.8.3	Self-avoiding walks	63
3.8.4	Growing walks and other models	65
3.9	Final remarks	66
	References	66
4	Importance sampling Monte Carlo methods	68
4.1	Introduction	68
4.2	The simplest case: single spin-flip sampling for the simple Ising model	69
4.2.1	Algorithm	70
4.2.2	Boundary conditions	74
4.2.3	Finite size effects	77
4.2.4	Finite sampling time effects	90
4.2.5	Critical relaxation	98
4.3	Other discrete variable models	105
4.3.1	Ising models with competing interactions	105
4.3.2	q -state Potts models	109
4.3.3	Baxter and Baxter–Wu models	110
4.3.4	Clock models	112
4.3.5	Ising spin glass models	112
4.3.6	Complex fluid models	113
4.4	Spin-exchange sampling	114
4.4.1	Constant magnetization simulations	114
4.4.2	Phase separation	115
4.4.3	Diffusion	117
4.4.4	Hydrodynamic slowing down	119
4.5	Microcanonical methods	119
4.5.1	Demon algorithm	119
4.5.2	Dynamic ensemble	120
4.5.3	Q2R	120
4.6	General remarks, choice of ensemble	121

4.7 Statics and dynamics of polymer models on lattices	121
4.7.1 Background	121
4.7.2 Fixed length bond methods	122
4.7.3 Bond fluctuation method	123
4.7.4 Polymers in solutions of variable quality: θ -point, collapse transition, unmixing	124
4.7.5 Equilibrium polymers: a case study	127
4.8 Some advice	130
References	130
5 More on importance sampling Monte Carlo methods for lattice systems	133
5.1 Cluster flipping methods	133
5.1.1 Fortuin–Kasteleyn theorem	133
5.1.2 Swendsen–Wang method	134
5.1.3 Wolff method	137
5.1.4 ‘Improved estimators’	138
5.2 Specialized computational techniques	139
5.2.1 Expanded ensemble methods	139
5.2.2 Multispin coding	139
5.2.3 N -fold way and extensions	140
5.2.4 Hybrid algorithms	142
5.2.5 Multigrid algorithms	142
5.2.6 Monte Carlo on vector computers	143
5.2.7 Monte Carlo on parallel computers	143
5.3 Classical spin models	144
5.3.1 Introduction	144
5.3.2 Simple spin-flip method	144
5.3.3 Heatbath method	146
5.3.4 Low temperature techniques	147
5.3.5 Over-relaxation methods	147
5.3.6 Wolff embedding trick and cluster flipping	148
5.3.7 Hybrid methods	149
5.3.8 Monte Carlo dynamics vs. equation of motion dynamics	150
5.3.9 Topological excitations and solitons	150
5.4 Systems with quenched randomness	154
5.4.1 General comments: averaging in random systems	154
5.4.2 Random fields and random bonds	157
5.4.3 Spin glasses and optimization by simulated annealing	158
5.5 Models with mixed degrees of freedom: Si/Ge alloys, a case study	163
5.6 Sampling the free energy and entropy	164
5.6.1 Thermodynamic integration	164
5.6.2 Groundstate free energy determination	166
5.6.3 Estimation of intensive variables: the chemical potential	166
5.6.4 Lee–Kosterlitz method	167

5.6.5	Free energy from finite size dependence at T_c	167
5.7	Miscellaneous topics	168
5.7.1	Inhomogeneous systems: surfaces, interfaces, etc.	168
5.7.2	Other Monte Carlo schemes	173
5.7.3	Finite size effects: a review and summary	174
5.7.4	More about error estimation	175
5.7.5	Random number generators revisited	176
5.8	Summary and perspective	178
	References	179
6	Off-lattice models	182
6.1	Fluids	182
6.1.1	NVT ensemble and the virial theorem	182
6.1.2	NpT ensemble	185
6.1.3	Grand canonical ensemble	189
6.1.4	Subsystems: a case study	192
6.1.5	Gibbs ensemble	197
6.1.6	Widom particle insertion method and variants	200
6.2	‘Short range’ interactions	202
6.2.1	Cutoffs	202
6.2.2	Verlet tables and cell structure	202
6.2.3	Minimum image convention	202
6.2.4	Mixed degrees of freedom reconsidered	203
6.3	Treatment of long range forces	203
6.3.1	Reaction field method	203
6.3.2	Ewald method	204
6.3.3	Fast multipole method	204
6.4	Adsorbed monolayers	205
6.4.1	Smooth substrates	205
6.4.2	Periodic substrate potentials	206
6.5	Complex fluids	207
6.6	Polymers: an introduction	210
6.6.1	Length scales and models	210
6.6.2	Asymmetric polymer mixtures: a case study	216
6.6.3	Applications: dynamics of polymer melts; thin adsorbed polymeric films	219
6.7	Configurational bias and ‘smart Monte Carlo’	224
	References	227
7	Reweighting methods	230
7.1	Background	230
7.1.1	Distribution functions	230
7.1.2	Umbrella sampling	230
7.2	Single histogram method: the Ising model as a case study	233
7.3	Multi-histogram method	240
7.4	Broad histogram method	240
7.5	Multicanonical sampling	241

7.5.1	The multicanonical approach and its relationship to canonical sampling	241
7.5.2	Near first order transitions	243
7.5.3	Groundstates in complicated energy landscapes	244
7.5.4	Interface free energy estimation	245
7.6	A case study: the Casimir effect in critical systems	246
	References	248
8	Quantum Monte Carlo methods	250
8.1	Introduction	250
8.2	Feynman path integral formulation	252
8.2.1	Off-lattice problems: low-temperature properties of crystals	252
8.2.2	Bose statistics and superfluidity	258
8.2.3	Path integral formulation for rotational degrees of freedom	259
8.3	Lattice problems	261
8.3.1	The Ising model in a transverse field	261
8.3.2	Anisotropic Heisenberg chain	263
8.3.3	Fermions on a lattice	266
8.3.4	An intermezzo: the minus sign problem	269
8.3.5	Spinless fermions revisited	271
8.3.6	Cluster methods for quantum lattice models	274
8.3.7	Decoupled cell method	275
8.3.8	Handscomb's method	276
8.3.9	Fermion determinants	277
8.4	Monte Carlo methods for the study of groundstate properties	278
8.4.1	Variational Monte Carlo (VMC)	279
8.4.2	Green's function Monte Carlo methods (GFMC)	280
8.5	Concluding remarks	283
	References	283
9	Monte Carlo renormalization group methods	286
9.1	Introduction to renormalization group theory	286
9.2	Real space renormalization group	290
9.3	Monte Carlo renormalization group	291
9.3.1	Large cell renormalization	291
9.3.2	Ma's method: finding critical exponents and the fixed point Hamiltonian	293
9.3.3	Swendsen's method	294
9.3.4	Location of phase boundaries	296
9.3.5	Dynamic problems: matching time-dependent correlation functions	297
	References	298
10	Non-equilibrium and irreversible processes	299
10.1	Introduction and perspective	299
10.2	Driven diffusive systems (driven lattice gases)	299
10.3	Crystal growth	301

10.4 Domain growth	304
10.5 Polymer growth	306
10.5.1 Linear polymers	306
10.5.2 Gelation	306
10.6 Growth of structures and patterns	308
10.6.1 Eden model of cluster growth	308
10.6.2 Diffusion limited aggregation	308
10.6.3 Cluster–cluster aggregation	311
10.6.4 Cellular automata	311
10.7 Models for film growth	312
10.7.1 Background	312
10.7.2 Ballistic deposition	313
10.7.3 Sedimentation	314
10.7.4 Kinetic Monte Carlo and MBE growth	315
10.8 Outlook: variations on a theme	317
References	318
11 Lattice gauge models: a brief introduction	320
11.1 Introduction: gauge invariance and lattice gauge theory	320
11.2 Some technical matters	322
11.3 Results for $Z(N)$ lattice gauge models	322
11.4 Compact $U(1)$ gauge theory	323
11.5 $SU(2)$ lattice gauge theory	324
11.6 Introduction: quantum chromodynamics (QCD) and phase transitions of nuclear matter	325
11.7 The deconfinement transition of QCD	327
References	330
12 A brief review of other methods of computer simulation	332
12.1 Introduction	332
12.2 Molecular dynamics	332
12.2.1 Integration methods (microcanonical ensemble)	332
12.2.2 Other ensembles (constant temperature, constant pressure, etc.)	336
12.2.3 Non-equilibrium molecular dynamics	339
12.2.4 Hybrid methods (MD + MC)	339
12.2.5 <i>Ab initio</i> molecular dynamics	339
12.3 Quasi-classical spin dynamics	340
12.4 Langevin equations and variations (cell dynamics)	343
12.5 Lattice gas cellular automata	344
References	345
13 Outlook	346
Appendix: listing of programs mentioned in the text	348
Index	379

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

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 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.

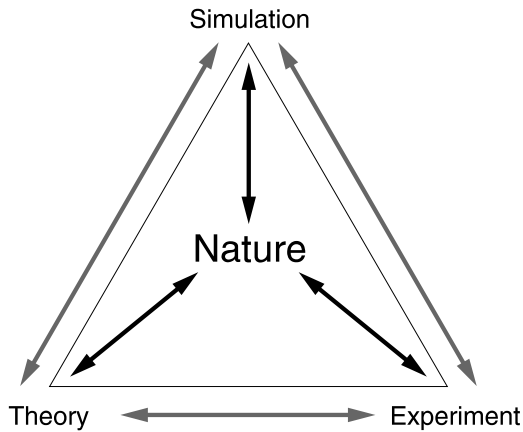
I.4 WHAT STRATEGY SHOULD WE FOLLOW IN APPROACHING A PROBLEM?

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.

I.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 aggrega-

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



tion, for which a very large body of simulation results already exists but for which extensive experimental information is just now becoming 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.

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 increase rapidly in sophistication to allow more subtle comparisons to be made.