Chapter 1

Introduction

(Pre)history of Computer Simulation

It usually takes decades rather than years before a fundamentally new invention finds widespread application. For computer simulation, the story is rather different. Computer simulation started as a tool to exploit the electronic computing machines that had been developed during and after the Second World War. These machines had been built to perform the very heavy computation involved in the development of nuclear weapons and code breaking. In the early 1950s, electronic computers became partly available for nonmilitary use and this was the beginning of the discipline of computer simulation. W. W. Wood [1] recalls: "When the Los Alamos MANIAC became operational in March 1952, Metropolis was interested in having as broad a spectrum of problems as possible tried on the machine, in order to evaluate its logical structure and demonstrate the capabilities of the machine."

The strange thing about computer simulation is that it is also a discovery, albeit a delayed discovery that grew slowly after the introduction of the technique. In fact, *discovery* is probably not the right word, because it does not refer to a new insight into the working of the natural world but into our description of nature. Working with computers has provided us with a new metaphor for the laws of nature: they carry as much (and as little) information as algorithms. For any nontrivial algorithm (i.e., loosely speaking, one that cannot be solved analytically), you cannot predict the outcome of a computation simply by looking at the program, although it often is possible to make precise statements about the general nature (e.g., the symmetry) of the result of the computation. Similarly, the basic laws of nature as we know them have the unpleasant feature that they are expressed in terms of equations we cannot solve exactly, except in a few very special cases. If we wish to study the motion of more than two interacting bodies, even the relatively

simple laws of Newtonian mechanics become essentially unsolvable. That is to say, they cannot be solved analytically, using only pencil and the back of the proverbial envelope. However, using a computer, we can get the answer to any desired accuracy. Most of materials science deals with the properties of systems of many atoms or molecules. *Many* almost always means more than two; usually, very much more. So if we wish to compute the properties of a liquid (to take a particularly nasty example), there is no hope of finding the answer exactly using only pencil and paper.

Before computer simulation appeared on the scene, there was only one way to predict the properties of a molecular substance, namely by making use of a theory that provided an approximate description of that material. Such approximations are inevitable precisely because there are very few systems for which the equilibrium properties can be computed exactly (examples are the ideal gas, the harmonic crystal, and a number of lattice models, such as the two-dimensional Ising model for ferromagnets). As a result, most properties of real materials were predicted on the basis of approximate theories (examples are the van der Waals equation for dense gases, the Debye-Hückel theory for electrolytes, and the Boltzmann equation to describe the transport properties of dilute gases). Given sufficient information about the intermolecular interactions, these theories will provide us with an estimate of the properties of interest. Unfortunately, our knowledge of the intermolecular interactions of all but the simplest molecules is also quite limited. This leads to a problem if we wish to test the validity of a particular theory by comparing directly to experiment. If we find that theory and experiment disagree, it may mean that our theory is wrong, or that we have an incorrect estimate of the intermolecular interactions, or both.

Clearly, it would be very nice if we could obtain essentially exact results for a given model system without having to rely on approximate theories. Computer simulations allow us to do precisely that. On the one hand, we can now compare the calculated properties of a model system with those of an experimental system: if the two disagree, our model is inadequate; that is, we have to improve on our estimate of the intermolecular interactions. On the other hand, we can compare the result of a simulation of a given model system with the predictions of an approximate analytical theory applied to the same model. If we now find that theory and simulation disagree, we know that the *theory* is flawed. So, in this case, the computer simulation plays the role of the experiment designed to test the theory. This method of screening theories before we apply them to the real world is called a *computer experiment*. This application of computer simulation is of tremendous importance. It has led to the revision of some very respectable theories, some of them dating back to Boltzmann. And it has changed the way in which we construct new theories. Nowadays it is becoming increasingly rare that a theory is applied to the real world before being tested by computer simula-

$\rho k_B T$	P
1	1.03 ± 0.04
2	1.99 ± 0.03
3	2.98 ± 0.05
4	4.04 ± 0.03
5	5.01 ± 0.04

Table 1.1: Simulated equation of state of an ideal gas

tion. The simulation then serves a twofold purpose: it gives the theoretician a feeling for the physics of the problem, and it generates some "exact" results that can be used to test the quality of the theory to be constructed. Computer experiments have become standard practice, to the extent that they now provide the first (and often the last) test of a new theoretical result.

But note that the computer as such offers us no understanding, only numbers. And, as in a real experiment, these numbers have statistical errors. So what we get out of a simulation is never directly a theoretical relation. As in a real experiment, we still have to extract the useful information. To take a not very realistic example, suppose we were to use the computer to measure the pressure of an ideal gas as a function of density. This example is unrealistic because the volume dependence of the ideal-gas pressure has, in fact, been well known since the work of Boyle and Gay-Lussac. The Boyle-Gay-Lussac law states that the product of volume and pressure of an ideal gas is constant. Now suppose we were to measure this product by computer simulation. We might, for instance, find the set of experimental results in Table 1.1. The data suggest that P equals $\rho k_B T$, but no more than that. It is left to us to infer the conclusions.

The early history of computer simulation (see, e.g., ref. [2]) illustrates this role of computer simulation. Some areas of physics appeared to have little need for simulation because very good analytical theories were available (e.g., to predict the properties of dilute gases or of nearly harmonic crystalline solids). However, in other areas, few if any exact theoretical results were known, and progress was much hindered by the lack of unambiguous tests to assess the quality of approximate theories. A case in point was the theory of dense liquids. Before the advent of computer simulations, the only way to model liquids was by mechanical simulation [3–5] of large assemblies of macroscopic spheres (e.g., ball bearings). Then the main problem becomes how to arrange these balls in the same way as atoms in a liquid. Much work on this topic was done by the famous British scientist J. D. Bernal, who built and analyzed such mechanical models for liquids. Actually, it would be fair to say that the really tedious work of analyzing the resulting three-dimensional structures was done by his research students, such as the unfor-

tunate Miss Wilkinson whose research assignment was to identify all distinct local packing geometries of plastic foam spheres: she found that there were at least 197. It is instructive to see how Bernal built some of his models. The following quote from the 1962 Bakerian lecture describes Bernal's attempt to build a ball-and-spoke model of a liquid [5]:

> ...I took a number of rubber balls and stuck them together with rods of a selection of different lengths ranging from 2.75 to 4 inch. I tried to do this in the first place as casually as possible, working in my own office, being interrupted every five minutes or so and not remembering what I had done before the interruption. However,....

Subsequent models were made, for instance, by pouring thousands of steel balls from ball bearings into a balloon. It should be stressed that these mechanical models for liquids were in some respects quite realistic. However, the analysis of the structures generated by mechanical simulation was very laborious and, in the end, had to be performed by computer anyway.

In view of the preceding, it is hardly surprising that, when electronic computers were, for the first time, made available for unclassified research, numerical simulation of dense liquids was one of the first problems to be tackled. In fact, the first simulation of a liquid was carried out by Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller on the MANIAC computer at Los Alamos [6], using (or, more properly, introducing) the Metropolis Monte Carlo (MC) method. The name *Monte Carlo simulation* had been coined earlier by Metropolis and Ulam (see Ref. [7]), because the method makes heavy use of computer-generated random numbers. Almost at the same time, Fermi, Pasta, and Ulam [8] performed their famous numerical study of the dynamics of an anharmonic, one-dimensional crystal. The first proper Molecular Dynamics (MD) simulations were reported in 1956 by Alder and Wainwright [9] at Livermore, who studied the dynamics of an assembly of hard spheres. The first MD simulation of a model for a "real" material was reported in 1959 (and published in 1960) by the group led by Vineyard at Brookhaven [10], who simulated radiation damage in crystalline Cu (for a historical account, see [11]). The first MD simulation of a real liquid (argon) was reported in 1964 by Rahman at Argonne [12]. After that, computers were increasingly becoming available to scientists outside the US government labs, and the practice of simulation started spreading to other continents [13–16]. Much of the methodology of computer simulations has been developed since then, although it is fair to say that the basic algorithms for MC and MD have hardly changed since the 1950s.

The most common application of computer simulations is to predict the properties of materials. The need for such simulations may not be immediately obvious. After all it is much easier to measure the freezing point of water than to extract it from a computer simulation. The point is, of course, that

it is easy to measure the freezing point of water at 1 atmosphere but often very difficult and therefore expensive to measure the properties of real materials at very high pressures or temperatures. The computer does not care: it does not go up in smoke when you ask it to simulate a system at 10,000 K. In addition, we can use computer simulation to predict the properties of materials that have not yet been made. And finally, computer simulations are increasingly used in data analysis. For instance, a very efficient technique for obtaining structural information about macromolecules from 2D-NMR is to feed the experimental data into a Molecular Dynamics simulation and let the computer find the structure that is both energetically favorable and compatible with the available NMR data.

Initially, such simulations were received with a certain amount of skepticism, and understandably so. Simulation did not fit into the existing idea that whatever was not experiment had to be theory. In fact, many scientists much preferred to keep things the way they were: theory for the theoreticians and experiments for the experimentalists and no computers to confuse the issue. However, this position became untenable, as is demonstrated by the following autobiographical quote of George Vineyard [11], who was the first to study the dynamics of radiation damage by numerical simulation:

> ...In the summer of 1957 at the Gordon Conference on Chemistry and Physics of Metals, I gave a talk on radiation damage in metals .... After the talk there was a lively discussion .... Somewhere the idea came up that a computer might be used to follow in more detail what actually goes on in radiation damage cascades. We got into quite an argument, some maintaining that it wasn't possible to do this on a computer, others that it wasn't necessary. John Fisher insisted that the job could be done well enough by hand, and was then goaded into promising to demonstrate. He went off to his room to work. Next morning he asked for a little more time, promising to send me the results soon after he got home. After about two weeks, not having heard from him, I called and he admitted that he had given up. This stimulated me to think further about how to get a high-speed computer into the game in place of John Fisher. ...

Finally, computer simulation can be used as a purely exploratory tool. This sounds strange. One would be inclined to say that one cannot "discover" anything by simulation because you can never get out what you have not put in. Computer discoveries, in this respect, are not unlike mathematical discoveries. In fact, before computers were actually available this kind of numerical charting of unknown territory was never considered.

The best way to explain it is to give an explicit example. In the mid-1950s, one of the burning questions in statistical mechanics was this: can crystals form in a system of spherical particles that have a harsh short-range

repulsion, but no mutual attraction whatsoever? In a very famous computer simulation, Alder and Wainwright [17] and Wood and Jacobson [18] showed that such a system does indeed have a first-order freezing transition. This is now accepted wisdom, but at the time it was greeted with skepticism. For instance, at a meeting in New Jersey in 1957, a group of some 15 very distinguished scientists (among whom were 2 Nobel laureates) discussed the issue. When a vote was taken as to whether hard spheres can form a stable crystal, it appeared that half the audience simply could not believe this result. However, the work of the past 30 years has shown that harsh repulsive forces really determine the structural properties of a simple liquid and that attractive forces are in a sense of secondary importance.

Suggested Reading

As stated at the outset, the present book does not cover all aspects of computer simulation. Readers who are interested in aspects of computer simulation not covered in this book are referred to one of the folowing books

- Allen and Tildesley, *Computer Simulation of Liquids* [19]

- Haile, *Molecular Dynamics Simulations: Elementary Methods* [20]

- Landau and Binder, *A Guide to Monte Carlo Simulations in Statistical Physics* [21]

- Rapaport, *The Art of Molecular Dynamics Simulation* [22]

- Newman and Barkema, *Monte Carlo Methods in Statistical Physics* [23]

Also of interest in this context are the books by Hockney and Eastwood [24], Hoover [25,26], Vesely [27], and Heermann [28] and the book by Evans and Morriss [29] for the theory and simulation of transport phenomena. The latter book is out of print and has been made available in electronic form.[1]

A general discussion of Monte Carlo sampling (with examples) can be found in Koonin's *Computational Physics* [30]. As the title indicates, this is a textbook on computational physics in general, as is the book by Gould and Tobochnik [31]. In contrast, the book by Kalos and Whitlock [32] focuses specifically on the Monte Carlo method. A good discussion of (quasi) random-number generators can be found in *Numerical Recipes* [33], while Ref. [32] gives a detailed discussion of tests for random-number generators. A discussion of Monte Carlo simulations with emphasis on techniques relevant for atomic and molecular systems may be found in two articles by Valleau and Whittington in *Modern Theoretical Chemistry* [34,35]. The books by Binder [36,37] and Mouritsen [38] emphasize the application of MC simulations to discrete systems, phase transitions and critical phenomena. In addition, there exist several very useful proceedings of summer schools [39–42] on computer simulation.

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[1]See http://rsc.anu.edu.au/~evans/evansmorrissbook.htm