

Chapter 12

Computer Simulation

12.1. BEGINNINGS

In late 1945, a prototype digital electronic computer, the Electronic Numerical Integrator and Calculator, (ENIAC) designed to compute artillery firing tables, began operation in America. There were many ‘analogue computers’ before ENIAC, there were primitive digital computers that were not programmable, and of course 19th-century computers, calculating engines, were purely mechanical. It is sometimes claimed that ‘the world’s first fully operational computer’ was EDSAC, in Cambridge, England, in 1949 (because the original ENIAC was programmed by pushing plugs into sockets and throwing switches, while EDSAC had a stored electronic program). However that may be, computer simulation in fact began on ENIAC, and one of the first problems treated on this machine was the projected thermonuclear bomb; the method used was the Monte Carlo (MC) approach.

The story of this beginning of computer simulation is told in considerable detail by Galison (1997) in an extraordinary book which is about the evolution of particle physics and also about the evolving nature of ‘experimentation’. The key figure at the beginning was John von Neumann, the Hungarian immigrant physicist whom we have already met in Chapter 1. In 1944, when the Manhattan Project at Los Alamos was still in full swing, he recognised that the hydrodynamical issues linked to the behaviour of colliding shock-waves were too complex to be treated analytically, and he worked out (in Galison’s words) “an understanding of how to transform coupled differential equations into difference equations which, in turn, could be translated into language the computer could understand”. The computer he used in 1944 seems to have been a punched-card device of the kind then used for business transactions. Galison spells out an example of this computational prehistory. Afterwards, within the classified domain, von Neumann had to defend his methods against scepticism that was to continue for a long time. Galison characterises what von Neumann did at this time as “carving out... a zone of what one might call *mesoscopic physics* perched precariously between the macroscopic and the microscopic”.

In view of the success of von Neumann’s machine-based hydrodynamics in 1944, and at about the time when the fission bomb was ready, some scientists at Los Alamos were already thinking hard about the possible design of a fusion bomb. Von Neumann invited two of them, Nicholas Metropolis and Stanley Frankel, to try to model the immensely complicated issue of how jets from a fission device might initiate thermonuclear reactions in an adjacent body of deuterium. Metropolis linked

up with the renowned Los Alamos mathematician, Stanislaw Ulam, and they began to sketch what became the Monte Carlo method, in which random numbers were used to decide for any particle what its next move should be, and then to examine what proportion of those moves constitute a “success” in terms of an imposed criterion. In their first public account of their new approach, Metropolis and Ulam (1949) pointed out that they were occupying the uncharted region of mechanics between the classical mechanician (who can only handle a very few bodies together) and the statistical mechanician, for whom Avogadro’s huge Number is routine. The “Monte Carlo” name came from Ulam; it is sometimes claimed that he was inspired to this by a favourite uncle who was devoted to gambling. (A passage in a recent book (Hoffmann 1998) claims that in 1946, Ulam was recovering from a serious illness and played many games of solitaire. He told his friend Vázsonyi: “After spending a lot of time trying to estimate the odds of particular card combinations by pure combinatorial calculations, I wondered whether a more practical method than abstract thinking might not be to lay the cards out say one hundred times and simply observe and count the number of successful plays... I immediately thought of problems of neutron diffusion and other questions of mathematical physics...”).

What von Neumann and Metropolis first did with the new technique, as a try-out, with the help of others such as Richard Feynman, was to work out the neutron economy in a fission weapon, taking into account all the different things – absorption, scattering, fission initiation, each a function of kinetic energy and the object being collided with – that can happen to an individual neutron. Galison goes on to spell out the nature of this proto-simulation. Metropolis’s innovations, in particular, were so basic that even today, people still write about using the “Metropolis algorithm”.

A simple, time-honoured illustration of the operation of the Monte Carlo approach is one curious way of estimating the constant π . Imagine a circle inscribed inside a square of side a , and use a table of random numbers to determine the cartesian coordinates of many points constrained to lie anywhere at random within the square. The ratio of the number of points that lies inside the circle to the total number of points within the square $\approx \pi a^2 / 4a^2 = \pi/4$. The more random points have been put in place, the more accurate will be the value thus obtained. Of course, such a procedure would make no sense, since π can be obtained to any desired accuracy by the summation of a mathematical series... i.e., analytically. But once the simulator is faced with a complex series of particle movements, analytical methods quickly become impracticable and simulation, with time steps included, is literally the only possible approach. That is how computer simulation began.

Among the brilliant mathematicians who developed the minutiae of the MC method, major disputes broke out concerning basic issues, particularly the question whether any (determinate) computer-based method is in principle capable of

generating an array of truly random numbers. The conclusion was that it is not, but that one can get close enough to randomness for practical purposes. This was one of the considerations which led to great hostility from some mathematicians to the whole project of computer simulation: for a classically trained pure mathematician, an approximate table of pseudo-random numbers must have seemed an abomination! The majority of theoretical physicists reacted similarly at first, and it took years for the basic idea to become acceptable to a majority of physicists. There was also a long dispute, outlined by Galison: "What *was* this Monte Carlo? How did it fit into the universally recognised division between experiment and theory – a taxonomic separation as obvious to the product designer at Dow Chemical as it was to the mathematician at Cornell?" The arguments went on for a long time, and gradually computer simulation came to be perceived as a form of experiment: thus, one of the early materials science practitioners, Beeler (1970), wrote uncompromisingly: "A computer experiment is a computational method in which physical processes are simulated according to a given set of physical mechanisms". Galison himself thinks of computer simulation as a hybrid "between the traditional epistemic poles of bench and blackboard". He goes in some detail into the search for "computational errors" introduced by finite object size, finite time steps, erroneous weighting, etc., and accordingly treats a large-scale simulation as a "numerical experiment". These arguments were about more than just semantics. Galison asserts baldly that "without computer-based simulation, the material culture of late-20th century microphysics (the subject of his book) is not simply inconvenienced – it does not exist".

Where computer simulation, and the numerical 'calculations' which flow from it, fits into the world of physics – and, by extension, of materials science – has been anxiously discussed by a number of physicists. One comment was by Herman (1984), an early contributor to the physics of semiconductors. In his memoir of early days in the field, he asserts that "during the 1950s and into the 1960s there was a sharp dichotomy between those doing formal solid-state research and those doing computational work in the field. Many physicists were strongly prejudiced against numerical studies. Considerable prestige was attached to formal theory." He goes on to point out that little progress was in fact made in understanding the band theory of solids (essential for progress in semiconductor technology) until "band theorists rolled up their sleeves and began doing realistic calculations on actual materials (by computer), and checking their results against experiment".

Recently, Langer (1999) has joined the debate. He at first sounds a distinct note of scepticism: "...the term 'numerical simulation' makes many of us uncomfortable. It is easy to build models on computers and watch what they do, but it is often unjustified to claim that we learn anything from such exercises." He continues by examining a number of actual simulations and points out, first, the value of

obtaining *multiscale* information “of a kind that is not available by using ordinary experimental or theoretical techniques”. Again, “we are not limited to simulating ‘real’ phenomena. *We can test theories by simulating idealised systems for which we know that every element has exactly the properties we think are relevant* (my emphasis)”. In other words, in classical experimental fashion we can change one feature at a time, spreadsheet-fashion.

These two points made by Langer are certainly crucial. He goes on to point out that for many years, physicists looked down on instrumentation as a mere service function, but now have come to realise that the people who brought in tools such as the scanning tunnelling microscope (and won the Nobel Prize for doing so) “are playing essential roles at the core of modern physics. I hope” (he concludes) “that we’ll be quicker to recognise that computational physics is emerging as an equally central part of our field”. Exactly the same thing can be said about materials science and computer simulation.

Finally, in this Introduction, it is worthwhile to reproduce one of the several current definitions, in the Oxford English Dictionary, of the word ‘simulate’: “To imitate the conditions or behaviour of (a situation or process) by means of a model, especially for the purpose of study or training; specifically, to produce a computer model of (a process)”. The Dictionary quotes this early (1958) passage from a text on high-speed data processing: “A computer can simulate a warehouse, a factory, an oil refinery, or a river system, and if due regard is paid to detail the imitation can be very exact”. Clearly, in 1958 the scientific uses of computer simulation were not yet thought worthy of mention, or perhaps the authors did not know about them.

12.2. COMPUTER SIMULATION IN MATERIALS SCIENCE

In his early survey of ‘computer experiments in materials science’, Beeler (1970), in the book chapter already cited, divides such experiments into four categories. One is the *Monte Carlo approach*. The second is the dynamic approach (today usually named *molecular dynamics*), in which a finite system of N particles (usually atoms) is treated by setting up $3N$ equations of motion which are coupled through an assumed two-body potential, and the set of $3N$ differential equations is then solved numerically on a computer to give the space trajectories and velocities of all particles as function of successive time steps. The third is what Beeler called the *variational approach*, used to establish equilibrium configurations of atoms in (for instance) a crystal dislocation and also to establish what happens to the atoms when the defect moves; each atom is moved in turn, one at a time, in a self-consistent iterative process, until the total energy of the system is minimised. The fourth category of ‘computer experiment’ is what Beeler called a *pattern development*

calculation, used to simulate, say, a field-ion microscope or electron microscope image of a crystal defect (on certain alternative assumptions concerning the true three-dimensional configuration) so that the simulated images can be compared with the experimental one in order to establish which is in fact the true configuration. This has by now become a widespread, routine usage. Another common use of such calculations is to generate predicted X-ray diffraction patterns or nuclear magnetic resonance plots of specific substances, for comparison with observed patterns.

Beeler defined the broad scope of computer experiments as follows: "Any conceptual model whose definition can be represented as a unique branching sequence of arithmetical and logical decision steps can be analysed in a computer experiment. . . The utility of the computer. . . springs mainly from its computational speed." But that utility goes further; as Beeler says, conventional analytical treatments of many-body aspects of materials problems run into awkward mathematical problems; computer experiments bypass these problems.

One type of computer simulation which Beeler did not include (it was only just beginning when he wrote in 1970) was finite-element simulation of fabrication and other production processes, such as for instance rolling of metals. This involves exclusively continuum aspects; 'particles', or atoms, do not play a part.

In what follows, some of these approaches will be further discussed. A very detailed and exhaustive survey of the various basic techniques and the problems that have been treated with them will be found in the first comprehensive text on "computational materials science", by Raabe (1998). Another book which covers the principal techniques in great mathematical detail and is effectively focused on materials, especially polymers, is by Frenkel and Smit (1996).

One further distinction needs to be made, that between 'modelling' and 'simulation'. Different texts favour different usages, but a fairly common practice is to use the term 'modelling' in the way offered in Raabe's book: "It describes the classical scientific method of formulating a simplified imitation of a real situation with preservation of its essential features. In other words, a model describes a part of a real system by using a *similar* but *simpler* structure." Simulation is essentially the putting of numbers into the model and deriving the numerical end-results of letting the model run on a computer. A simulation can never be better than the model on which it relies.

12.2.1 Molecular dynamics (MD) simulations

The simulation of molecular (or atomic) dynamics on a computer was invented by the physicist George Vineyard, working at Brookhaven National Laboratory in New York State. This laboratory, whose 'biography' has recently been published (Crease 1999), was set up soon after World War II by a group of American universities,

initially to foster research in nuclear physics; because radiation damage (see Section 5.1.3) was an unavoidable accompaniment to the accelerator experiments carried out at Brookhaven, a solid-state group was soon established and grew rapidly. Vineyard was one of its luminaries. In 1957, Vineyard, with George Dienes, wrote an influential early book, *Radiation Damage in Solids*. (Crease comments that this book “helped to bolster the image of solid-state physics as a basic branch of physics”.) In 1973, Vineyard became laboratory director.

In 1972, some autobiographical remarks by Vineyard were published at the front of the proceedings of a conference on simulation of lattice defects (Vineyard 1972). Vineyard recalls that in 1957, at a conference on chemistry and physics of metals, he explained the then current analytical theory of the damage cascade (a collision sequence originating from one very high-energy particle). During discussion, “the idea came up that a computer might be applied to follow in more detail what actually goes on in radiation damage cascades”. Some insisted that this could not be done on a computer, others (such as a well-known, argumentative GE scientist, John Fisher) that it was not necessary. 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 two weeks... he admitted that he had given up.” Vineyard then drew up a scheme with an atomic model for copper and a procedure for solving the classical equations of state. However, since he knew nothing about computers he sought help from the chief applied mathematician at Brookhaven, Milton Rose, and was delighted when Rose encouragingly replied that ‘it’s a great problem; this is just what computers were designed for’. One of Rose’s mathematicians showed Vineyard how to program one of the early IBM computers at New York University. Other physicists joined the hunt, and it soon became clear that by keeping track of an individual atom and taking into account only near neighbours (rather than all the N atoms of the simulation), the computing load was roughly proportional to N rather than to N^2 . (The initial simulation looked at 500 atoms.) The first paper appeared in the *Physical Review* in 1960. Soon after, Vineyard’s team conceived the idea of making moving pictures of the results, “for a more dramatic display of what was happening”. There was overwhelming demand for copies of the first film, and ever since then, the task of making huge arrays of data visualisable has been an integral part of computer simulation. Immediately following his mini-autobiography, Vineyard outlines the results of the early computer experiments: Figure 12.1 is an early set of computed trajectories in a radiation damage cascade.

One other remark of Vineyard’s in 1972, made with evident feeling, is worth repeating here: “Worthwhile computer experiments require time and care. The easy understandability of the results tends to conceal the painstaking hours that went into conceiving and formulating the problem, selecting the parameters of a model,

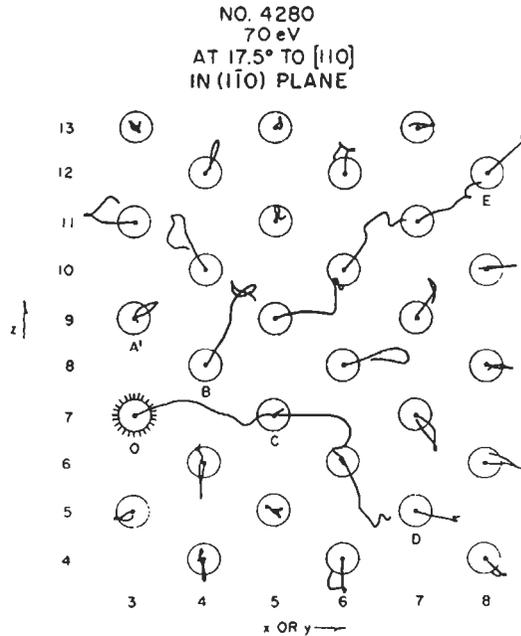


Figure 12.1. Computer trajectories in a radiation damage cascade in iron, reproduced from Erginsoy *et al.* (1964).

programming for computation, sifting and analysing the flood of output from the computer, rechecking the approximations and stratagems for accuracy, and out of it all synthesising physical information". None of this has changed in the last 30 years!

Two features of such dynamic simulations need to be emphasised. One is the limitation, set simply by the finite capacity of even the fastest and largest present-day computers, on the number of atoms (or molecules) and the number of time-steps which can be treated. According to Raabe (1998), the time steps used are 10^{-14} – 10^{-15} s, less than a typical atomic oscillation period, and the sample incorporates 10^3 – 10^9 atoms, depending on the complexity of the interactions between atoms. So, at best, the size of the region simulated is of the order of 1 nm^3 and the time below one nanosecond. This limitation is one reason why computer simulators are forever striving to get access to larger and faster computers.

The other feature, which warrants its own section, is the issue of interatomic potentials.

12.2.1.1 Interatomic potentials. All molecular dynamics simulations and some MC simulations depend on the form of the interaction between pairs of particles (atoms

or molecules). For instance, the damage cascade in Figure 12.1 was computed by a dynamics simulation on the basis of specific interaction potentials between the atoms that bump into each other. When a MC simulation is used to map the configurational changes of polymer chains, the van der Waals interactions between atoms on neighbouring chains need to have a known dependence of attraction on distance. A plot of force vs distance can be expressed alternatively as a plot of potential energy vs distance; one is the differential of the other. Figure 12.2 (Stoneham *et al.* 1996) depicts a schematic, interionic short-range potential function showing the problems inherent in inferring the function across the significant range of distances from measurements of equilibrium properties alone.

Interatomic potentials began with empirical formulations (empirical in the sense that analytical calculations based on them... no computers were being used yet... gave reasonable agreement with experiments). The most famous of these was the Lennard-Jones (1924) potential for noble gas atoms; these were essentially van der Waals interactions. Another is the 'Weber potential' for covalent interactions between silicon atoms (Stillinger and Weber 1985); to take into account the directed covalent bonds, interactions between three atoms have to be considered. This potential is well-tested and provides a good description of both the crystalline and

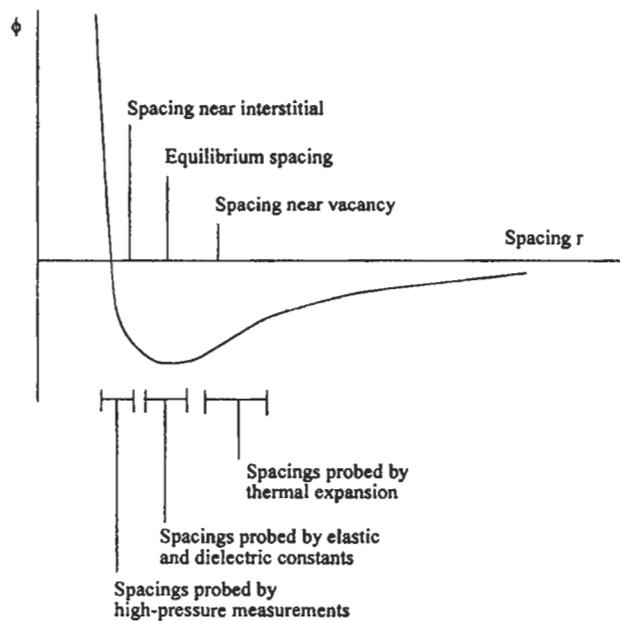


Figure 12.2. A schematic interionic short-range potential function, after Stoneham *et al.* (1996).

the amorphous forms of silicon (which have quite different properties) and of the crystalline melting temperature, as well as predicting the six-coordinated structure of liquid silicon. This kind of test is essential before a particular interatomic potential can be accepted for continued use.

In due course, attempts began to *calculate* from first principles the form of interatomic potentials for different kinds of atoms, beginning with metals. This would quickly get us into very deep quantum-mechanical waters and I cannot go into any details here, except to point out that the essence of the different approaches is to identify different simplifications, since Schrödinger's equation cannot be solved accurately for atoms of any complexity. The many different potentials in use are summarised in Raabe's book (p. 88), and also in a fine overview entitled "the virtual matter laboratory" (Gillan 1997) and in a group of specialised reviews in the *MRS Bulletin* (Voter 1996) that cover specialised methods such as the Hartree-Fock approach and the embedded-atom method. A special mention must be made of density functional theory (Hohenberg and Kohn 1964), an elegant form of simplified estimation of the electron-electron repulsions in a many-electron atom that won its senior originator, Walter Kohn, a Nobel Prize for Chemistry. The idea here is that all that an atom embedded in its surroundings 'knows' about its host is the local electron density provided by its host, and the atom is then assumed to interact with its host exactly as it would if embedded in a homogeneous electron gas which is everywhere of uniform density equal to the local value around the atom considered.

Most treatments, even when intended for materials scientists, of these competing forms of quantum-mechanical simplification are written in terms accessible only to mathematical physicists. Fortunately, a few 'translators', following in the tradition of William Hume-Rothery, have explained the essentials of the various approaches in simple terms, notably David Pettifor and Alan Cottrell (e.g., Cottrell 1998), from whom the formulation at the end of the preceding paragraph has been borrowed.

It may be that in years to come, interatomic potentials can be estimated experimentally by the use of the atomic force microscope (Section 6.2.3). A first step in this direction has been taken by Jarvis *et al.* (1996), who used a force feedback loop in an AFM to prevent sudden springback when the probing silicon tip approaches the silicon specimen. The authors claim that their method means that "force-distance spectroscopy of specific sites is possible – mechanical characterisation of the potentials of specific chemical bonds".

12.2.2 Finite-element simulation

In this approach, continuously varying quantities are computed, generally as a function of time as some process, such as casting or mechanical working, proceeds, by 'discretising' them in small regions, the finite elements of the title. The more

complex the mathematics of the model, the smaller the finite elements have to be. A good understanding of how this approach works can be garnered from a very thorough treatment of a single process; a recent book (Lenard *et al.* 1999) of 364 pages is devoted entirely to hot-rolling of metal sheet. The issue here is to simulate the distribution of pressure across the arc in which the sheet is in contact with the rolls, the friction between sheet and rolls, the torque needed to keep the process going, and even microstructural features such as texture (preferred orientation). The modelling begins with a famous analytical formulation of the problem by Orowan (1943), numerous refinements of this model and the canny selection of acceptable levels of simplification. The end-result allows the mechanical engineering features of the rolling-mill needed to perform a specific task to be estimated.

Finite-element simulations of a wide range of manufacturing processes for metals and polymers in particular are regularly performed. A good feeling for what this kind of simulation can do for engineering design and analysis generally, can be obtained from a popular book on supercomputing (Kaufmann and Smarr 1993).

Finite-element approaches can be supplemented by the other main methods to get comprehensive models of different aspects of a complex engineering domain. A good example of this approach is the recently established Rolls-Royce University Technology Centre at Cambridge. Here, the major manufacturing processes involved in superalloy engineering are modelled: these include welding, forging, heat-treatment, thermal spraying, machining and casting. All these processes need to be optimised for best results and to reduce material wastage. As the Centre's then director, Roger Reed, has expressed it, "if the behaviour of materials can be quantified and understood, then processes can be optimised using computer models". The Centre is to all intents and purposes a virtual factory. A recent example of the approach is a paper by Matan *et al.* (1998), in which the rates of diffusional processes in a superalloy are estimated by simulation, in order to be able to predict what heat-treatment conditions would be needed to achieve an acceptable approach to phase equilibrium at various temperatures. This kind of simulation adds to the databank of such properties as heat-transfer coefficients, friction coefficients, thermal diffusivity, etc., which are assembled by such depositories as the National Physical Laboratory in England.

12.2.3 Examples of simulations of a material

12.2.3.1 Grain boundaries in silicon. The prolonged efforts to gain an accurate understanding of the fine structure of interfaces – surfaces, grain boundaries, interphase boundaries – have featured repeatedly in this book. Computer simulations are playing a growing part in this process of exploration. One small corner of this process is the study of the role of grain boundaries and free surfaces in the

process of melting, and this is examined in a chapter of a book (Phillpot *et al.* 1992). Computer simulation is essential in an investigation of how much a crystalline solid can be overheated without melting *in the absence of surfaces and grain boundaries* which act as catalysts for the process; such simulation can explain the asymmetry between melting (where superheating is not normally found at all) and freezing, where extensive supercooling is common. The same authors (Phillpot *et al.* 1989) began by examining the melting of imaginary crystals of silicon with or without grain boundaries and surfaces (there is no room here to examine the tricks which computer simulators use to make a model pretend that the small group of atoms being examined has no boundaries). The investigators finish up by distinguishing between mechanical melting (triggered by a phonon instability), which is homogeneous, and thermodynamic melting, which is nucleated at extended defects such as grain boundaries. The process of melting starting from such defects can be neatly simulated by molecular dynamics.

The same group (Kebblinski *et al.* 1996), continuing their researches on grain boundaries, found (purely by computer simulation) a highly unexpected phenomenon. They simulated twist grain boundaries in silicon (boundaries where the neighbouring orientations differ by rotation about an axis normal to the boundary plane) and found that if they introduced an amorphous (non-crystalline) layer 0.25 nm thick into a large-angle crystalline boundary, the computed potential energy is lowered. This means that an amorphous boundary is thermodynamically stable, which takes us back to an idea tenaciously defended by Walter Rosenhain a century ago!

12.2.3.2 Colloidal 'crystals'. At the end of Section 2.1.4, there is a brief account of regular, crystal-like structures formed spontaneously by two differently sized populations of hard (polymeric) spheres, typically near 0.5 nm in diameter, depositing out of a colloidal solution. Binary 'superlattices' of composition AB_2 and AB_{13} are found. Experiment has allowed 'phase diagrams' to be constructed, showing the 'crystal' structures formed for a fixed radius ratio of the two populations but for variable volume fractions in solution of the two populations, and a computer simulation (Eldridge *et al.* 1995) has been used to examine how nearly theory and experiment match up. The agreement is not bad, but there are some unexpected differences from which lessons were learned.

The importance of these pseudo-crystals is that their periodicities are similar to those of visible light and they can thus be used like semiconductors in acting on light beams in optoelectronic devices.

12.2.3.3 Grain growth and other microstructural changes. When a deformed metal is heated, it will *recrystallise*, that is to say, a new population of crystal grains will

replace the deformed population, driven by the drop in free energy occasioned by the removal of dislocations and vacancies. When that process is complete but heating is continued then, as we have seen in Section 9.4.1, the mean size of the new grains gradually grows, by the progressive removal of some of them. This process, *grain growth*, is driven by the disappearance of the energy of those grain boundaries that vanish when some grains are absorbed by their neighbours. In industrial terms, grain growth is much less important than recrystallisation, but it has attracted a huge amount of attention by computer modellers during the past few decades, reported in literally hundreds of papers. *This is because the phenomenon offers an admirable testbed for the relative merits of different computational approaches.*

There are a number of variables: the specific grain-boundary energy varies with misorientation if that is fairly small; if the grain-size *distribution* is broad, and if a subpopulation of grains has a pronounced preferred orientation, a few grains grow very much larger than others. (We have seen, Section 9.4.1, that this phenomenon interferes drastically with sintering of ceramics to 100% density.) The metal may contain a population of tiny particles which seize hold of a passing grain boundary and inhibit its migration; the macroscopic effect depends upon both the mean size of the particles and their volume fraction. All this was quantitatively discussed properly for the first time in a classic paper by Smith (1948). On top of these variables, there is also the different grain growth behaviour of thin metallic films, where the surface energy of the metal plays a key part; this process is important in connection with failure of conducting interconnects in microcircuits.

There is no space here to go into the great variety of computer models, both two-dimensional and three-dimensional, that have been promulgated. Many of them are statistical 'mean-field' models in which an average grain is considered, others are 'deterministic' models in which the growth or shrinkage of every grain is taken into account in sequence. Many models depend on the Monte Carlo approach. One issue which has been raised is whether the simulation of grain size *distributions* and their comparison with experiment (using stereology, see Section 5.1.2.3) can be properly used to prove or disprove a particular modelling approach. One of the most disputed aspects is the modelling of the limiting grain size which results from the pinning of grain boundaries by small particles.

The merits and demerits of the many computer-simulation approaches to grain growth are critically analysed in a book chapter by Humphreys and Hatherly (1995), and the reader is referred to this to gain an appreciation of how alternative modelling strategies can be compared and evaluated. A still more recent and very clear critical comparison of the various modelling approaches is by Miodownik (2001).

Grain growth involves no phase transformation, but a number of such transformations have been modelled and simulated in recent years. A recently published overview volume relates some experimental observations of phase

transformations to simulation (Turchi and Gonis 2000). Among the papers here is one describing some very pretty electron microscopy of an order–disorder transformation by a French group, linked to simulation done in cooperation with an eminent Russian-emigré expert on such transformations, Armen Khachaturyan (Le Bouar *et al.* 2000). Figure 12.3 shows a series of micrographs of progressive transformation, in a Co–Pt alloy which have long been studied by the French group, together with corresponding simulated patterns. The transformation pattern here, called a ‘chessboard pattern’, is brought about by internal stresses: a cubic crystal structure (disordered) becomes tetragonal on ordering, and in different domains the unique fourfold axis of the tetragonal form is constrained to lie in orthogonal directions, to accommodate the stresses. The close agreement indicates that the model is close to physical reality... which is always the objective of such modelling and simulation.

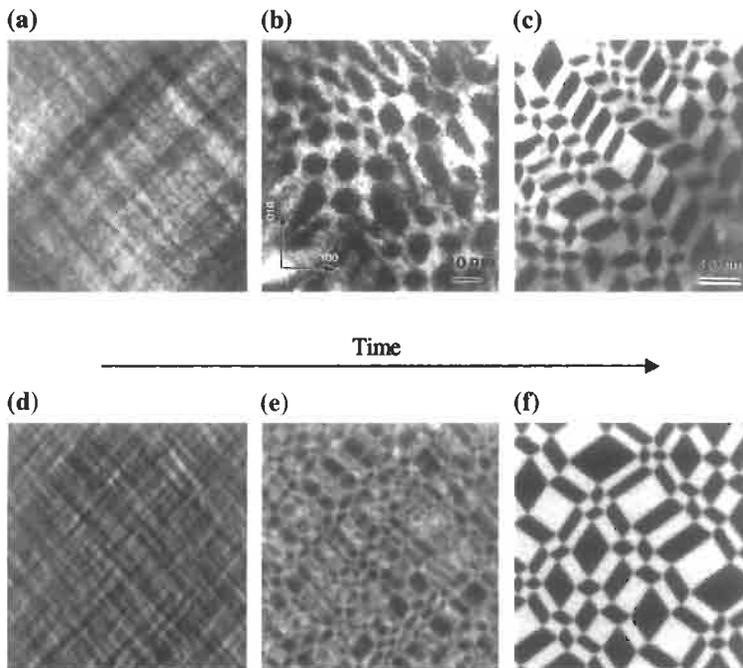
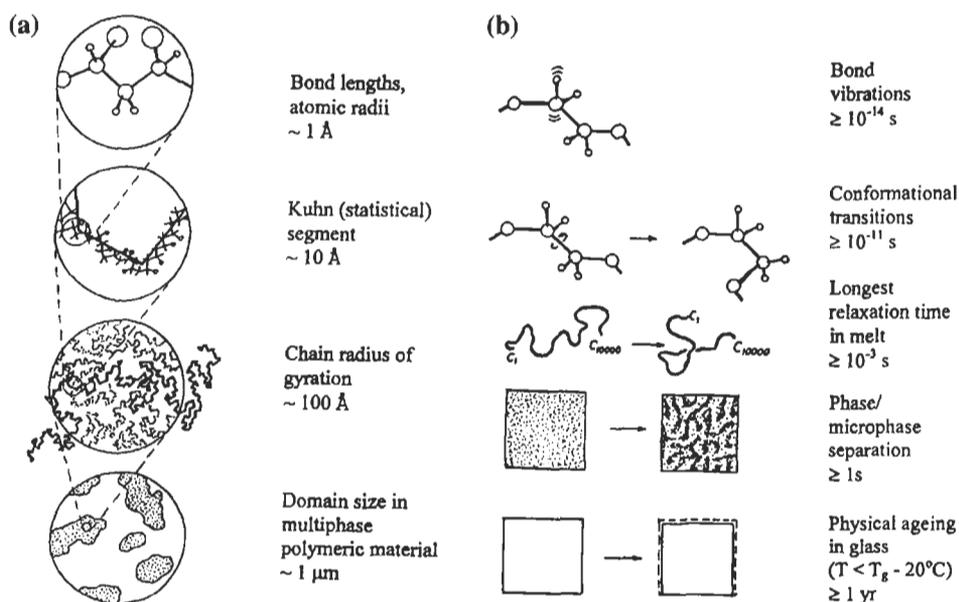


Figure 12.3. Comparison between experimental observations (a–c) and simulation predictions (d–f) of the microstructural development of a ‘chessboard’ pattern forming in a $\text{Co}_{39.5}\text{Pt}_{60.5}$ alloy slowly cooled from 1023 K to (a) 963 K, (b) 923 K and (c) 873 K. The last of these was maintained at 873 K to allow the chessboard pattern time to perfect itself (Le Bouar *et al.* 2000) (courtesy Y. Le Bouar).

12.2.3.4 Computer-modelling of polymers. The properties of polymers are determined by a large range of variables – chemical constitution, mean molecular weight and molecular weight distribution, fractional crystallinity, preferred orientation of amorphous regions, cross-linking, chain entanglement. It is thus no wonder that computer simulation, which can examine all these features to a greater or lesser extent, has found a special welcome among polymer scientists.

The length and time scales that are relevant to polymer structure and properties are shown schematically in Figure 12.4. Bearing in mind the spatial and temporal limitations of MD methods, it is clear that a range of approaches is needed, including quantum-mechanical ‘high-resolution’ methods. In particular, configurations of long-chain molecules and consequences such as rubberlike elasticity depend heavily on MC methods, which can be invoked with “algorithms designed to allow a correspondence between number of moves and elapsed time” (from a review by Theodorou 1994). A further simplification that allows space and time limitations to weigh less heavily is the use of *coarse-graining*, in which “explicit atoms in one or several monomers are replaced by a single particle or *bead*”. This form of words comes from a further concise overview of the “hierarchical simulation approach to



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Figure 12.4. Hierarchy of length scales of structure and time scales of motion in polymers. T_g denotes the glass transition temperature. After Uhlherr and Theodorou (1998) (courtesy Elsevier Science).

structure and dynamics of polymers” by Uhlherr and Theodorou (1998); Figure 12.4 also comes from this overview. Not only structure and properties (including time-dependent ones such as viscosity) of polymers, but also configurations and phase separations of block copolymers, and the kinetics of polymerisation reactions, can be modelled by MC approaches. One issue which has recently received a good deal of attention is the configuration of block copolymers with hydrophobic and hydrophilic ends, where one constituent is a therapeutic drug which needs to be delivered progressively; the hydrophobically ended drug moiety finishes up inside a spherical micelle, protected by the hydrophilically ended outer moiety. Simulation allows the tendency to form micelles and the rate at which the drug is released within the body to be estimated.

The voluminous experimental information about the linkage between structural variables and properties of polymers is assembled in books, notably that by van Krevelen (1990). In effect, such books “encapsulate much empirical knowledge on how to formulate polymers for specific applications” (Uhlherr and Theodorou 1998). What polymer modellers and simulators strive to achieve is to establish more rigorous links between structural variables and properties, to foster more rational design of polymers in future.

A number of computer modelling codes, including an important one named ‘Cerius 2’, have by degrees become commercialised, and are used in a wide range of industrial simulation tasks. This particular code, originally developed in the Materials Science Department in Cambridge in the early 1980s, has formed the basis of a software company and has survived (with changes of name) successive takeovers. The current company name is Molecular Simulations Inc. and it provides codes for many chemical applications, polymeric ones in particular; its latest offering has the ambitious name “Materials Studio”. It can be argued that the ability to survive a series of takeovers and mergers provides an excellent filter to test the utility of a published computer code.

Some special software has been created for particular needs, for instance, lattice models in which, in effect, polymer chains are constrained to lie within particular cells of an imaginary three-dimensional lattice. Such models have been applied to model the spatial distribution of preferred vectors (‘directors’) in liquid-crystalline polymers (e.g., Hobdell *et al.* 1996) and also to study the process of solid-state welding between polymers. In this last simulation, a ‘bead’ on a polymer chain can move by occupying an adjacent vacancy and in this way diffusion, in polymers usually referred to as ‘reptation’, can be modelled; energies associated with different angles between adjacent bonds must be estimated. When two polymer surfaces interpenetrate, a stage is reached when chains wriggle out from one surface and into the contacting surface until the chain midpoints, on average, are at the interface (Figure 12.5). At that stage, adhesion has reached a maximum. Simulation has shown that

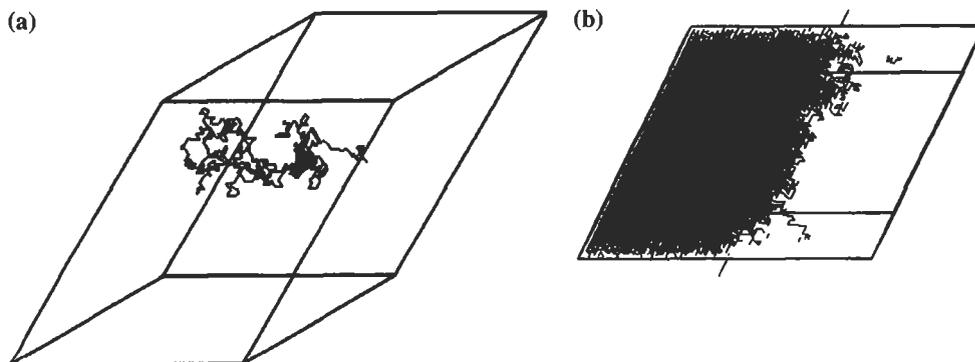


Figure 12.5. (a) Lattice model showing a polymer chain of 200 'beads', originally in a random configuration, after 10,000 Monte Carlo steps. The full model has 90% of lattice sites occupied by chains and 10% vacant. (b) Half of a lattice model containing two similar chain populations placed in contact. The left-hand side population is shown after 50,000 Monte Carlo steps; the short lines show the location of the original polymer interface (courtesy K. Anderson).

the number of effective 'crossovers' achieved in a given time varies as the square root of the mean molecular weight, and has also allowed strength to be predicted as a function of molecular weight, temperature and time (K. Anderson and A.H. Windle, private communication). The procedure for the MC model involved in this simulation is described by Haire and Windle (2001).

Another family of simulations concerns polymeric fibres, which constitute a major industrial sector. Y. Termonia has spent many years at Du Pont modelling the extrusion and tensile drawing of fibres from liquid solution. A recent publication (Termonia 2000) uses an extreme form of coarse-graining to simulate the process; the model starts with an idealised oblique set of mutually orthogonal straight chains with regular entanglement points. This system is deformed at constant temperature and strain rate, by a succession of minute length increments, moving the top row of entanglement points in the draw direction while leaving the bottom row unmoved. The positions of the remaining entanglement points are then readjusted by an iterative relaxation procedure which minimises the net residual force acting on each site. After each strain increment and complete relaxation, each site is 'visited' by an MC lottery (in the author's words), and four processes are allowed to occur, breakage of interchain bonds, slippage of chains through entanglements, chain breakage and final network relaxation. Then the cycle restarts. All this is done for chains of different lengths, i.e., different molecular weights. The model shows how low molecular weights lead to poor drawability and premature fracture, in accord with experiment. Termonia's extrapolation of this simulation, in the same book, to

ultrastrong spider web fibres, where molecular weight *distribution* plays a major part in determining mechanical properties, shows the power of the method.

12.2.3.5 Simulation of plastic deformation. The modelling of plastic deformation in metals presents in stark form the problems of modelling on different length scales. Until recently, dislocations have either been treated as flexible line defects without consideration of their atomic structure, or else the Peierls–Nabarro force tying a dislocation to its lattice has been modelled in terms of a relatively small number of atoms surrounding the core of a dislocation cross-section. There is also a further range of issues which has exercised a distinct subculture of modellers, attempting to predict the behaviour of a polycrystal from an empirical knowledge of the behaviour of single crystals of the same substance. This last is a huge subject (see Section 2.1.6), and I can do no more here than to cite a concise coverage of the issues in Chapter 17 of Raabe's (1998) book and also to refer to *the* definitive treatment in detail, representing many years of work (Kocks *et al.* 1998).

Very recently, the modelling of plastic deformation in terms of the motion, interaction and mutual blocking of dislocations moving under applied stress has entered the mesoscale. Two papers have applied MD methods to this task; instead of treating dislocations as semi-macroscopic objects, the motion of up to 100 million individual atoms around the interacting dislocation lines has been modelled; this is feasible since the timescale for such a simulation can be quite brief. One paper is by Bulatov *et al.* (1998), the other by Zhou *et al.* (1998); each has received an illuminating discussion in the same issues of their respective journals. These two studies follow a first attempt by L.P. Kubin and others in 1992. As P. Gumbsch points out in his discussion of the Zhou paper, these atomistic computations generate such a huge amount of information (some 10^4 configurations of 10^6 atoms each) that "one of the most important steps is to discard most of it, namely, all the atomistic information not directly connected to the *cores* of the dislocations. What is left is a physical picture of the atomic configurations in such a dislocation intersection and even some quantitative information about the stresses required to break the junction". This kind of information overload is a growing problem in modern super simulation, and knowing what to discard, as well as turning pages of numbers into readily assimilable visual displays, are central parts of the simulator's skill.

Baskes (1999) has discussed the "status role" of this kind of modelling and simulation, citing many very recent studies. He concludes that "modelling and simulation of materials at the atomistic, microstructural and continuum levels continue to show progress, but prediction of mechanical properties of engineering materials is still a vision of the future". Simulation cannot (yet) do everything, in spite of the optimistic claims of some of its proponents.

This kind of simulation requires massive computer power, and much of it is done on so-called 'supercomputers'. This is a reason why much recent research of this kind has been done at Los Alamos. In a survey of research in the American national laboratories, the then director of the Los Alamos laboratory, Siegfried Hecker (1990) explains that the laboratory "has worked closely with all supercomputer vendors over the years, typically receiving the serial No. 1 machine for each successive model". He goes on to exemplify the kinds of problems in materials science that these extremely powerful machines can handle.

12.3. SIMULATIONS BASED ON CHEMICAL THERMODYNAMICS

As we have repeatedly seen in this chapter, proponents of computer simulation in materials science had a good deal of scepticism to overcome, from physicists in particular, in the early days. A striking example of sustained scepticism overcome, at length, by a resolute champion is to be found in the history of CALPHAD, an acronym denoting CALculation of PHase Diagrams. The decisive champion was an American metallurgist, Larry Kaufman.

The early story of experimentally determined phase diagrams and of their understanding in terms of Gibbs free energies and of the Phase Rule was set out in Chapter 3, Section 3.1.2. In that same chapter, Hume-Rothery's rationalisation of certain features of phase diagrams in terms of atomic size ratios and electron/atom ratios was outlined (Section 3.3.1.1). Hume-Rothery did use his theories to predict limited features of phase diagrams, solubility limits in particular, but it was a long time before experimentally derived values of free energies of phases began to be used for the prediction of phase diagrams. Some tentative early efforts in that direction were published by a Dutchman, van Laar (1908), but thereafter there was a void for half a century. The challenge was taken up by another Dutchman, Meijering (1957) who seems to have been the first to attempt the calculation of a complete ternary phase diagram (Ni-Cr-Cu) from measured thermochemical quantities from which, in turn, free energies could be estimated. Meijering's work was particularly important in that he recognised that for his calculation to have any claims to accuracy he needed to estimate a value for the free energy (as a function of temperature) of face-centred cubic chromium, a notional crystal structure which was not directly accessible to experiment. This was probably the first calculation of the lattice stability of a potential (as distinct from an actual) phase.

At the time Meijering published his research, Larry Kaufman was working for his doctorate at MIT with a charismatic steel metallurgist, Professor Morris Cohen, and they undertook some simple equilibrium calculations directed at practical problems of the steel industry. From the end of the 1950s, Kaufman directed his

efforts at developing these methods, sustained by two other groups, one in Stockholm, Sweden, run from 1961 by Mats Hillert and another in Sendai, Japan, led by T. Nishizawa. Hillert and Kaufman had studied together at MIT and their interaction over the years was to be crucial to the development of CALPHAD.

At a meeting at Battelle Memorial Institute in Ohio in 1967, Kaufman demonstrated some approximate calculations of binary phase diagrams using an ideal solution model, but met opposition particularly from solid-state physicists who preferred to use first-principles calculations of electronic band structures instead of thermodynamic inputs. For some years, this became the key battle between competing approaches. At about this time, Kaufman began exchanging letters with William Hume-Rothery concerning the best way to represent thermodynamic equilibria. Thereupon, Hume-Rothery, in his capacity as editor of *Progress in Materials Science*, invited Kaufman to write a review about lattice stabilities of phases, which appeared (Kaufman 1969) shortly after Hume-Rothery's death in 1968. Shortly before his death, Hume-Rothery had written to Kaufman to say that he was "not unsympathetic to any theory which promises reasonably accurate calculations of phase boundaries, and saves the immense amount of work which their experimental determination involves", but that he was still sceptical about Kaufman's approach. This extract comes from a full account of the history of CALPHAD in Chapter 2 of a recent book (Saunders and Miodownik 1998). In his short overview, Kaufman took great trouble to counter Hume-Rothery's reservations, and he also gave a fair account of the competing band-theoretical approaches. The imperative need to account for the competition in stability between alternative phases, actual and potential, was central to Kaufman's case.

For the many ensuing stages in CALPHAD's history, including the incorporation of CALPHAD Inc. in 1973, and the practice of organising meetings at which different approaches to formulating Gibbs energies could be reconciled, Saunders and Miodownik's history chapter must be consulted. Effective international cooperation got under way in 1973, with involvement of a number of national laboratories, and numerous published computer codes from around the world such as Thermocalc and Chemsage are now in regular use. From 1976 on, physicists were encouraged to attend CALPHAD meetings in order to assess the feasibility of merging data obtained by thermochemistry with those calculated by first-principles electron-theory methods (Pettifor 1977). CALPHAD's own journal began publication in 1977. Kaufman is still, today, a key participant at the regular CALPHAD meetings.

Kaufman and Bernstein (1970) brought out the first book on phase diagram calculations; there was not another comprehensive treatment till Saunders and Miodownik's book came out in 1998. This last covers the ways of obtaining the thermodynamic input data, ways of dealing with complications such as atomic

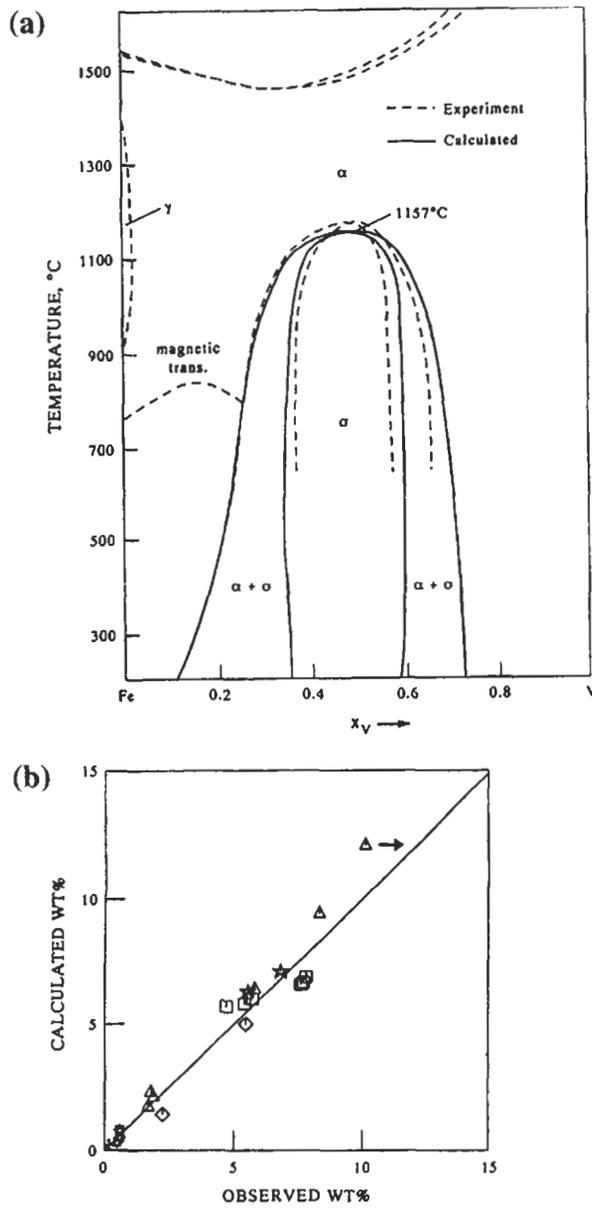


Figure 12.6. (a) Calculated ($\alpha + \sigma$) phase boundary for Fe-V together with experimental boundaries (After Spencer and Putland 1973). (b) Comparison between calculated and experimental values of the concentration of Al, V and Fe in the two phases in Ti-6Al-4V alloy (after Saunders and Miodownik 1998).

ordering and ferromagnetism, and (in particular) many forms of application of CALPHAD. It also describes the crucial methods of critically *optimising* thermodynamic data for incorporation in internationally agreed databases. Figure 12.6(a) shows an early example of a simple binary phase diagram obtained by experiment together with calculated phase boundaries. Figure 12.6(b) shows a plot of observed versus calculated solute concentrations in a standard titanium alloy. It has been an essential part of the gradual acceptance of CALPHAD methods that theory and experiment have been shown to agree well, and progressively better so as methods improved. Indeed, *in all computer modelling and simulation, confidence can only come gradually from a steady series of such comparisons between simulation and experiment.*

Even when the CALPHAD approach had been widely accepted as valid, there was still the problem of the reluctance of newcomers to start using it. Hillert (1980) proposed looking at thermodynamics as a game and to consider how one can learn to play that game well. He went on: "For inspiration, one may first look at another game, the game of chess. The rules are very simple to learn, but it was always very difficult to become a good player. The situation has now changed due to the application of computers. Today there are programmes for playing chess which can beat almost any expert. It seems reasonable to expect that it should also be possible to write programmes for 'playing thermodynamics', programmes which should be almost as good as the very best thermodynamic expert." In other words... for novices, tried and tested commercial software, whether for thermodynamics or for MC or MD, should take the sting out of taking the plunge into computer simulation, and perhaps in the fullness of time such simulations will move out of specialised journals and coteries of specialists and find their way increasingly into mainline journals, and students with first degrees in materials science will be entirely at ease with this kind of activity. Perhaps we are already there.

Today, thermodynamic simulation has broadened out far beyond the calculation of binary and ternary (and even quaternary) phase diagrams. For instance, as explained in the last chapter of Saunders and Miodownik's book, methods have recently been developed to combine diffusional simulations with phase stability simulations in order to obtain estimates of the kinetics of phase transformation. A recent text issued by SGTE, the Scientific Group Thermodata Europe (Hack 1996) includes 24 short chapters instancing applications, in particular, to processing issues. Two examples from Sweden, relating to solidification, include the calculation of solidification paths for a multicomponent system and (severely practical) calculations directed towards the prevention of clogging by premature freezing in a continuous casting process. Another chapter discusses the formulation of a Co-Fe-Ni binder phase for use with a dispersion of tungsten carbide 'hard metal'. A chapter by Per Gustafson in Sweden hinges on computer development of a high-speed (cutting) steel. This last application is reminiscent of a protracted programme of

research at Northwestern University (where materials science started in 1958) by Gregory Olson (e.g. Kuehmann and Olson 1998) to design steels for specially demanding purposes by a sophisticated computer-optimisation program, including extensive use of CALPHAD; some further remarks about this program can be found in Section 4.3.

Very recently, a very detailed report from two groups attending a 1997 meeting on 'Applications of Computational Thermodynamics' has been published (Kattner and Spencer 2000) with presentations of many applications to practical problems, with emphasis on processing methods, including processing of semiconductors and microcircuits. One process modelled here is the deposition of a compound semiconductor from an organometallic precursor, a 'soft chemistry' approach discussed in the preceding chapter.

The CALPHAD approach has been treated here at some length because its history illustrates the strengths and limitations of computer modelling and simulation. The strengths clearly outweigh the limitations, and this is becoming increasingly true throughout the broad spectrum of applications of computers in materials science and engineering.

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Chapter 13

The Management of Data

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