Preface

This monograph presents three main topics, only fragments of which are otherwise covered in textbooks and research treatises: (a) construction of the complete Hamiltonian for crystals, amorphous solids, and liquids, (b) presentation of liquid dynamics theory based on this Hamiltonian, and (c) comparison of theory and experiment over a broad range of properties for crystals and liquids. The work is limited primarily to the elements, but the same principles apply to alloys and compounds. Our presentation is aimed at addressing questions along the lines of: What is our "best" theory for a given property? How accurate is a good theory? What information is gained by a comparison of theory and experiment? How accurate is a good experiment? What small effects need to be accounted for in order to extract the most accurate data from an experiment? The techniques discussed are those which the author has found useful in forty-three years of condensed matter research, and which might be useful to other researchers as well, both theorists and experimentalists.

The condensed matter Hamiltonian consists of four contributions which represent, in order of strongly decreasing overall importance, the groundstate energy with static nuclei, the motion of nuclei, excitation of electrons from their groundstate, and interaction between nuclear motion and electronic excitation. The last two contributions are significant only for metals. All the parameters of the Hamiltonian, the various potentials and interactions, are defined in principle through electronic structure theory, and can be obtained in practice from density functional calculations. Hence the groundstate, and all the excited states, and all the equilibrium statistical mechanical properties, are encoded into a single Hamiltonian function (operator), all whose terms we know in principle how to calculate.

For a crystal, the Hamiltonian is transformed to a set of phonons, plus phonon-phonon interactions (anharmonicity), excited electronic states, and electron-phonon interactions. Once the phonons and electrons are defined, their interactions are completely prescribed, by the unique total Hamiltonian. This internal consistency condition is sometimes of essential importance, but is hardly ever recognized. For elemental crystals, theory and experiment are compared at the highest possible level of accuracy for many properties, with special emphasis on phonon frequencies and thermodynamic entropy. Quantum and classical regimes are identified, temperature and volume effects are separated, anharmonic contributions are assessed, and electronic-excitation and electron-phonon contributions are analyzed.

For a liquid, the underlying picture of the monatomic liquid state is presented. This picture is derived from three properties deduced from experimental data: (a) the melting of an element falls into one of two classes, normal melting in which there is no significant change in the electronic structure, and anomalous melting which is otherwise; (b) the entropy of melting at constant volume is very nearly a universal constant for normal melting; and (c) the specific heat of the liquid at melt corresponds to nearly harmonic motion of the nuclei. From these properties we infer that the potential energy surface seen by the nuclei is composed of a very large number of intersecting nearly-harmonic many-particle valleys, and the nuclear motion consists of oscillations within these valleys, and nearly-instantaneous transits between valleys. The picture is confirmed by computer simulation studies. Theory and experiment are compared for equilibrium statistical mechanical properties of monatomic liquids, and liquid dynamics theory is shown to be reliable and of respectable accuracy in zeroth order, with well-defined higher order corrections remaining to be studied.

We live with an apparently never-ending debate over the interpretation of statistical mechanics. The author has survived discussions of such questions as, "What is the temperature of an atom?" and, "How does the reservoir interact with the systems of an ensemble?" But statistical mechanics is not a mystery whose meaning we must divine, it is rather a tool we make to do useful work. Here we present statistical mechanics in a way that is direct, practical, and as rigorous as any other. We consider a many-atom mechanical system with prescribed Hamiltonian and boundary conditions, intended to represent a real laboratory system, and we calculate macroscopic properties by averaging over the system's phase space, with a weight function. The purpose of the weight function is to enforce constraints. We recover the standard partition-function formulation, in a way that makes it easy to discuss the effects of boundary conditions, and to see what is involved in comparing theory and experiment. We also derive classical statistics as a well-defined regime within quantum statistics, and we discuss statistical averages for a molecular dynamics system. An approximate extension of equilibrium statistical mechanics to metastable states is presented. Equilibrium crystal-crystal and crystal-liquid phase transitions are discussed, and an application to the glass transition is made, to illustrate a nonequilibrium process.

Pseudopotential perturbation theory was developed in the early 1960s, as an approximate electronic structure theory for nearly-free-electron metals. This theory taught the physics community that a quantitative understanding of every equilibrium property of a metal can be achieved through its electronic structure. Though the modern electronic structure paradigm is density functional theory, pseudopotential perturbation theory is still extremely useful. First, this theory is an excellent learning device, since it presents a simple analytic description of all the essential metallic properties, namely Fermi statistics, electron response, exchange-correlation corrections, the electron-ion interaction, the effective ion-ion interaction, and excited electronic states. Second, when calibrated to density functional calculations, or directly to experimental data, pseudopotential perturbation theory gives a highly accurate overall description of a metal. The one-parameter fit to the phonon dispersion curves of Al, done in 1969 and shown in Fig. 5.1, is still a very good model. Fewer parameters means better physics. Our 1968 model for Na is compared with experiment throughout this monograph, to demonstrate what is achievable with a highly accurate Hamiltonian. A detailed formulation of pseudopotential perturbation theory is presented, and is used to illustrate various theoretical topics throughout this work.

This book carries the subtitle *A Guide to Highly Accurate Equations of State*. By equations of state, we mean the complete set of thermodynamic functions for a given material, over a wide range of temperature and pressure. From the analysis presented here, it is clear that we know in principle how to calculate *ab initio* the equation of state of an elemental solid or liquid, to an accuracy on the same order as the accuracy of experimental data. We also know a great deal about the errors associated with various approximations, such as the neglect of anharmonicity, or the neglect of electron-phonon interactions. This level of understanding will allow us to construct condensed matter equations of state of the highest possible accuracy, not only in regions where experimental data are available for calibration, but also in regions where such data are not available.

This monograph is not an "update" of my previous book *Thermodynamics of Crystals* (Wiley, New York, 1972; reprinted by Dover, New York, 1998), since a much broader scope of condensed matter theory is presented here. On the other hand, *Thermodynamics of Crystals* contains much useful information not included here, for example, lattice dynamics of nonprimitive lattices. Here we shall often mention relevant information which can be found in that book, citing only the title and location.

The experimental data tabulated in this monograph are of the highest accuracy available today. Data from unreliable experimental techniques are omitted from consideration. By way of notation, a number in parentheses is a value which *might* be in error, not by a lot, but by a little more than the other numbers in the same column. The parentheses appear because there is a discrepancy in the experimental data base, or because we have resorted to a slight extrapolation somewhere within the data analysis. References to experimental data are generally not given here, but they can be found in the publications cited here, where the data analysis was originally done.

Some comments on notation will be useful. We use the word *structure* with two different meanings, namely (a) as in *electronic structure*, meaning the wave functions and energy levels of the system electrons, and (b) as in *crystal structure*, meaning any stable-equilibrium configuration of the nuclei. To indicate atmospheric pressure we sometimes write $P = 1$ bar, but usually write $P = 0$. *On the order*, or the symbol $\sim$, means within a factor of two or so, while *approximately equal*, or $\approx$, means much closer, and usually indicates an approximation based on a small parameter. The symbol $\doteq$ is used here to denote a relation which we believe to be highly accurate, almost exact.

It is amazing to realize how many people, whose names and faces I remember, have had a positive influence on my work. Perhaps a meaningful expression of appreciation can be achieved by acknowledging the places where this work was carried on: the physics department at Iowa State University, the research groups at Sandia National Laboratories, the theoretical physics department at Ecole Polytechnique Federale de Lausanne, the Commonwealth Scientific and Industrial Research Organization

in Sydney, the physics department at the University of Antwerp, and the theoretical division at Los Alamos National Laboratory. Los Alamos has supported this work for many years on the grounds that it leads to a better understanding of the motion of particles in condensed matter systems, and hence leads to improved equations of state for real materials. During the preparation of this monograph, I have had the benefit of encouragement and valuable insights from James N. Johnson, Brad Clements, John Wills, and Eric Chisolm. Collaboration with Nicolas Bock and Dermot Coffey on electron-phonon interactions has been very helpful. The work of transforming my handwritten pages into book format was done with extraordinary skill by Kay Grady. And always cheerfully, Jo Ann Brown has provided me with communications services.

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