1
Introduction

Thermodynamics provides a universal theory of matter at the macroscopic level and is a consequence of underlying symmetries of nature. Quantities that cannot be destroyed at the microscopic level, due to symmetries and their resulting conservation laws, give rise to the *state variables* upon which the theory of thermodynamics is built.

Statistical physics provides the microscopic foundations of thermodynamics. At the microscopic level, many-body systems have a huge numbers of states available to them and are continually sampling large subsets of these states. The task of statistical physics is to determine the macroscopic (measurable) behavior of many-body systems, given some knowledge of properties of the underlying microscopic states, and to recover the thermodynamic behavior of such systems.

The field of statistical physics has expanded dramatically during the last half-century. New results in quantum fluids, nonlinear chemical physics, critical phenomena, transport theory, and biophysics have revolutionized the subject, and yet these results are rarely presented in a form that students who have little background in statistical physics can appreciate or understand. This book attempts to incorporate many of these subjects into a basic course on statistical physics. It includes, in a unified and integrated manner, the foundations of statistical physics and develops from them most of the tools needed to understand the concepts underlying modern research in the above fields.

There is a tendency in many books to focus on equilibrium statistical mechanics and derive thermodynamics as a consequence. As a result, students do not get the experience of traversing the vast world of thermodynamics and do not understand how to apply it to systems which are too complicated for statistical mechanics. We will begin in Chapter 2, by deriving the equations of state for some simple systems starting from our knowledge, and our ability to count, the underlying microscopic states of those systems. This will give some intuition about the complexity of microscopic behavior underlying the very simple equations of state that emerge in those systems.

In Chapter 3, we provide a thorough grounding in thermodynamics. We review the foundations of thermodynamics and thermodynamic stability theory and devote a large part of the chapter to a variety of applications which do not involve phase transitions, such as the cooling of gases, mixing, osmosis, and chemical

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thermodynamics. Chapter 4 is devoted to the thermodynamics of phase transitions and the use of thermodynamic stability theory in analyzing these phase transitions. We discuss first-order phase transitions in liquid–vapor–solid transitions, with particular emphasis on the liquid–vapor transition and its critical point and critical exponents. We also introduce the Ginzburg–Landau theory of continuous phase transitions and discuss a variety of transitions which involve broken symmetries. And we introduce the critical exponents which characterize the behavior of key thermodynamic quantities as a system approaches its critical point.

Chapters 5 and 6 are devoted entirely to equilibrium statistical mechanics. In Chapter 5, we derive the probability density operator for systems in thermal contact with the outside world but isolated chemically (the *canonical ensemble*). We use the canonical ensemble to derive the thermodynamic properties of a variety of model systems, including semiclassical gases, harmonic lattices and spin systems. We also introduce the concept of scaling of free energies as we approach the critical point and we derive critical exponents from microscopic theory for some particular spin lattices. In Chapter 6, we derive the probability density operator for open systems (the *grand canonical ensemble*), and use it to discuss properties of interacting classical gases, ideal quantum gases, and super-conductors.

Because many-body systems have a finite (but large) number of degrees of freedom, there will always be fluctuations about the average (thermodynamic) behavior. These fluctuations can be measured and give valuable information about decay processes and the hydrodynamic behavior of many-body systems

The discrete nature of matter introduces fluctuations about the average (thermodynamic) behavior of systems. These fluctuations can be measured and give valuable information about decay processes and the hydrodynamic behavior of many-body systems. Therefore, in Chapter 7 we introduce the theory of Brownian motion which is the paradigm theory describing the effect of underlying fluctuations on macroscopic quantities. The relation between fluctuations and decay processes is the content of the so-called fluctuation–dissipation theorem which is derived in this chapter. We also derive Onsager's relations between transport coefficients, and we introduce the mathematics needed to introduce the effect of causality on correlation functions. We conclude this chapter with a discussion of thermal noise in ballistic electron conductors.

Chapter 8 is devoted to hydrodynamic processes for systems near equilibrium. We begin by deriving the Navier–Stokes equations from the symmetry properties of a fluid of point particles, and we use the derived expression for entropy production to obtain the transport coefficients for the system. We use the solutions of the linearized Navier–Stokes equations to predict the outcome of light-scattering experiments. We also derive a general expression for the entropy production in systems and use this theory to describe thermal and chemical transport processes in mixtures, and in electrical circuits. We conclude Chapter 8 with a derivation of hydrodynamic equations for superfluids and consider the types of sound that can exist in such fluids.

In Chapter 9, we derive microscopic expressions for the coefficients of diffusion, shear viscosity, and thermal conductivity, starting both from mean free path arguments and from the Boltzmann and Lorentz–Boltzmann equations. We obtain explicit microscopic expressions for the transport coefficients of a hard sphere gas.

Finally, in Chapter 10 we conclude with the fascinating subject of nonequilibrium phase transitions. We also show how nonlinearities in the rate equations for chemical reaction–diffusion systems lead to nonequilibrium phase transitions which give rise to chemical clocks, nonlinear chemical waves, and spatially periodic chemical structures, while nonlinearities in the Rayleigh–Bénard hydrodynamic system lead to spatially periodic convection cells.

The book contains Appendices with background material on a variety of topics. Appendix A, gives a review of basic concepts from probability theory. Appendix B reviews the theory of exact differentials which is the mathematics underlying thermodynamics. In Appendix we review ergodic theory. Ergodicity is a fundamental ingredient for the microscopic foundations of thermodynamics. In Appendix D, we derive the second quantized formalism of quantum mechanics and show how it can be used in statistical mechanics. Appendix E reviews basic classical scattering theory. Finally, in Appendix F, we give some useful math formulas and data.