

# Thermal Physics: Thermodynamics and Statistical Mechanics for Scientists and Engineers

THIS IS A TABLE OF CONTENTS AND CHAPTER ABSTRACTS FOR MY BOOK THAT  
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# Preface

This book is based on lectures in courses that I taught from 2000-2011 in the Department of Physics at Carnegie Mellon University to undergraduates (mostly juniors and seniors) and graduate students (mostly first and second year). Portions are also based on a course that I taught to undergraduate engineers (mostly juniors) in the Department of Metallurgical Engineering and Materials Science in the early 1970s. It began as class notes but started to be organized as a book in 2004. As a work in progress, I made it available on my web site as a pdf, password protected for use by my students and a few interested colleagues.

It is my version of what I learned from my own research and self-study of numerous books and papers in preparation for my lectures. Prominent among these sources were the books by Fermi [1], Callen [2], Gibbs [3, 4], Lupis [5], Kittel and Kroemer [6], Landau and Lifshitz [7], and Pathria [8, 9] that are listed in the bibliography. Explicit references to these and other sources are made throughout, but the source of much information is beyond my memory.

Initially it was my intent to give an integrated mixture of thermodynamics and statistical mechanics, but it soon became clear that most students had only a cursory understanding of thermodynamics, having encountered only a brief exposure in introductory physics courses. Moreover, I believe that thermodynamics can stand on its own as a discipline based on only a few postulates, or so-called laws, that have stood the test of time experimentally. Although statistical concepts can be used to motivate thermodynamics, it still takes a bold leap to appreciate that thermodynamics is valid, within its intended scope, independent of any statistical mechanical model. As stated by Albert Einstein in Autobiographical Notes (1946), [10]:

“A theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability. Therefore the deep impression which classical thermodynamics made on me. It is the only physical theory of universal content concerning which I am convinced that within the framework of the applicability of its basic concepts, it will never be overthrown.”

Of course thermodynamics only allows one to relate various measurable quantities to one another and must appeal to experimental data to get actual values. In that respect, models based on statistical mechanics can greatly enhance thermodynamics by providing values that are independent of experimental measurements. But in the last analysis, any model must be compatible with the laws of thermodynamics in the appropriate limit of

sufficiently large systems. Statistical mechanics, however, has the potential to treat smaller systems for which thermodynamics is not applicable.

Consequently, I finally decided to present thermodynamics first, with only a few connections to statistical concepts, and then present statistical mechanics in that context. That allowed me to better treat reversible and irreversible processes as well as to give a thermodynamic treatment of such subjects as phase diagrams, chemical reactions and anisotropic surfaces and interfaces that are especially valuable to materials scientists and engineers.

The treatment of statistical mechanics begins with a mathematical measure of disorder, quantified by Shannon in the context of information theory. This measure is put forward as a candidate for the entropy, which is formally developed in the context of the microcanonical, canonical and grand canonical ensembles. Ensembles are first treated from the viewpoint of quantum mechanics, which allows for explicit counting of states. Subsequently, classical versions of the microcanonical and canonical ensembles are presented in which integration over phase space replaces counting of states, but with loss of information unless one establishes the number of states to be associated with a phase space volume by requiring agreement with quantum treatments in the limit of high temperatures. This is counter to the historical development of the subject, which was in the context of classical mechanics. Later in the book I discuss the foundation of the quantum mechanical treatment by means of the density operator to represent pure and statistical (mixed) quantum states.

Throughout the book, a number of example problems are presented, immediately followed by their solutions. This serves to clarify and reinforce the presentation but also allows students to develop problem-solving techniques. For several reasons I did not provide lists of problems for students to solve. Many such problems can be found in textbooks now in print, and most of their solutions are on the internet. I leave it to teachers to assign modifications of some of those problems or, even better, to devise new problems whose solutions cannot yet be found on the internet.

The book also contains a number of appendices, mostly to make it self-contained but also to cover technical items whose treatment in the chapters would tend to interrupt the flow of the presentation.

I view this book as an intermediate contribution to the vast subjects of thermodynamics and statistical mechanics. Its level of presentation is intentionally more rigorous and demanding than in introductory books. Its coverage of statistical mechanics is much less extensive than in books that specialize in statistical mechanics, such as the recent third edition of Pathria's book, now authored by Pathria and Beale [9], that contains several new and advanced topics. I suspect the present book will be useful for scientists, particularly physicists and chemists, as well as engineers, particularly materials, chemical, and mechanical engineers. If used as a textbook, many advanced topics can be omitted to suit a one- or two-semester undergraduate course. If used as a graduate text, it could easily provide for a one- or two-semester course. The level of mathematics needed in most parts of the book is advanced calculus, particularly a strong grasp of functions of several variables, partial derivatives, and infinite series as well as an elementary knowledge of differential equations and their solutions. For the treatment of anisotropic surfaces and



interfaces, necessary relations of differential geometry are presented in an appendix. For the statistical mechanics part, an appreciation of stationary quantum states, including degenerate states, is essential, but the calculation of such states is not needed. In a few places, I use the notation of the Dirac vector space, bras and kets, to represent quantum states, but always with reference to other representations; the only exceptions are Chapter 26, Quantum Statistics, where the Dirac notation is used to treat the density operator, and Appendix I, where creation and annihilation operators are treated.

I had originally planned to include some of my own research on the thermodynamics of inhomogeneously stressed crystals and a few more chapters on the statistical mechanical aspects of phase transformations. Treatment of the liquid state, foams, and very small systems are other possibilities. I do not address many-body theory, which I leave to other works. There is an introduction to Monte Carlo simulation at the end of Chapter 27, which treats the Ising model. The renormalization group approach is described briefly but not covered in detail. Perhaps I will address some of these topics in later writings, but for now I would like to disseminate what is finished rather than add to the already considerable bulk of the product.

Over the years that I shared versions of this book with students, I received some valuable feedback that stimulated revision or augmentation of topics. I thank all those students. A few faculty at other universities used versions for self-study in connection with courses they taught, and also gave me some valuable feedback. I thank these colleagues as well. Nevertheless, I alone am responsible for any misconceptions or outright errors that remain and would be grateful to anyone who would bring them to my attention.

There are other people I could thank individually for contributing in some way to the writing of this book but I will not attempt to present such a list. I would, however, like to thank my wife Carolyn for her patience and encouragement and her meticulous proofreading. She is an attorney, not a scientist, but the logic and intellect she brought to the task resulted in my rewriting a number of obtuse sentences and even correcting a number of embarrassing typos and inconsistent notation in the equations. Finally, I thank Carnegie Mellon University for providing me with an intellectual home and the freedom to undertake this work.

Robert F. Sekerka  
Pittsburgh, PA



**Part I**  
**Thermodynamics**



**Part II**  
**Statistical Mechanics**





**Part III**  
**Appendices**





# Appendix J

## Chapter and Appendix Abstracts

### J.1 Chapter 1, Introduction

Thermal physics deals with macroscopic systems containing an enormous number of particles. Equilibrium states can be characterized by a small number of state variables such as the number of particles, volume, pressure, and temperature. We seek to relate and compute values of properties of such systems, for example heat capacity, compressibility, and coefficient of thermal expansion. Thermodynamics can relate such properties based on a few laws that govern changes of state variables of a system when work is done on that system or energy is exchanged by heat transfer. An alternative is to use statistical mechanics to compute average properties of models of many-particle systems. The concept of temperature is introduced empirically based on thermal expansion, especially for an ideal gas thermometer. We classify state variables as extensive or intensive and review quantitatively the concepts of kinetic and potential energy in classical mechanics. Elementary kinetic theory is used to relate to temperature and pressure of an ideal gas.

#### J.1.1 Keywords for Chapter 1

thermodynamics, statistical mechanics, macroscopic state variables, extensive variable, intensive variable, temperature, pressure, ideal gas, kinetic energy, potential energy

### J.2 Chapter 2, First Law of Thermodynamics

The first law of thermodynamics is stated in terms of the existence of an extensive function of state called the internal energy. For a chemically closed system, the internal energy changes when energy is added by heat transfer or work is done by the system. Heat and work are not state variables because they depend on a process. Reversible quasistatic work can be done by a system by using pressure to change its volume very slowly. Heat capacities are defined as the amount of energy needed to cause temperature change at constant volume or pressure. Processes are illustrated for an ideal gas whose energy depends only on temperature. Sudden volume changes can result in irreversible work during which pressure is undefined. We define an auxiliary state function known as enthalpy to relate

to processes at constant pressure. Phase transformations such as melting involve enthalpy changes that liberate latent heat.

### J.2.1 Keywords for Chapter 2

internal energy, state function, heat transfer, quasistatic work, heat capacity, reversible isothermal expansion, irreversible expansion, enthalpy, latent heat

## J.3 Chapter 3, Second Law of Thermodynamics

The second law of thermodynamics is stated as the existence of an extensive function of state called the entropy that can only increase for an isolated system. Equilibrium is reached at maximum entropy. Reciprocal absolute temperature is defined as entropy change with energy. Entropy is additive for a composite system. Heat added to a chemically closed system increases entropy by an amount greater than the ratio of the heat to the absolute temperature for an irreversible process; entropy equals that ratio for a reversible process. We relate entropy to its historical roots including other postulates and the Carnot cycle for an ideal gas. The second law plus the first law establish a fundamental equation to calculate entropy changes as a function of state. Reversible and irreversible expansion of an ideal gas are illustrated. Enthalpy and entropy changes are calculated for an isobaric melting of ice. Entropy is related to quantum microstates of a system via probability of a macrostate.

### J.3.1 Keywords for Chapter 3

entropy, absolute temperature defined, composite system, irreversible change, equilibrium criterion, Carnot cycle, fundamental equation, calculated entropy, quantum microstates, probability, Boltzmann constant

## J.4 Chapter 4, Third Law of Thermodynamics

According to the third law of thermodynamics, the entropy of a system in internal equilibrium approaches a constant independent of phase as the absolute temperature tends to zero. This constant value is taken to be zero for a non-degenerate ground state, in accord with statistical mechanics. Independence of phase is illustrated by extrapolation due to Fermi of the entropy of gray and white tin as the temperature is reduced to absolute zero. The third law is based on the postulate of Nernst to explain empirical rules for equilibrium of chemical reactions as absolute zero is approached. As a consequence of the third law, the following quantities vanish at absolute zero: heat capacity, coefficient of thermal expansion, and ratio of thermal expansion to isothermal compressibility.

### J.4.1 Keywords for Chapter 4

zero of entropy, absolute zero temperature, phase independence, vanishing heat capacities, vanishing expansion coefficient, Nernst chemical reaction postulate

## J.5 Chapter 5, Open Systems

Open systems exchange particles with their environment in addition to work and heat. This exchange entails energy transfer. Internal energy becomes a function of entropy, volume and moles of particles; its partial derivative with particle mole number is called chemical potential. This is extended to multicomponent systems. The chemical potential of an ideal gas depends on temperature and the logarithm of pressure, with fugacity replacing pressure for real gases. Maxwell relations result by equating mixed partial derivatives and relate measurable physical quantities. Euler's theorem of homogeneous functions formalizes relationships of extensive and intensive variables, allows integration of fundamental differentials (Euler equation), and connects differentials of intensive variables (Gibbs-Duhem equation). Mole fractions define composition of multicomponent systems. Legendre transformations are developed and used to define new potentials such as Helmholtz and Gibbs free energies. Partial molar quantities are calculated by the method of intercepts. Entropy of a chemical reaction is introduced.

### J.5.1 Keywords for Chapter 5

chemical potential, ideal gas, fugacity, Euler equation, Gibbs-Duhem equation, Legendre transformations, mole fractions, partial molar quantities, method of intercepts

## J.6 Chapter 6, Equilibrium and Thermodynamic Potentials

The equilibrium criterion of maximum entropy for an isolated system is used to derive the equivalent criterion of minimum internal energy at constant entropy. Alternative equilibrium criteria for chemically closed systems are derived for other conditions and thermodynamic potentials: minimum Helmholtz free energy for constant temperature and no external work; minimum enthalpy for constant pressure or minimum Gibbs free energy for constant temperature and pressure, both with no external work in excess of that against the external pressure. For an open system at constant temperature, constant chemical potentials, and no external work, the Kramers potential is a minimum at equilibrium. According to any of these criteria, the conditions for mutual equilibrium of heterogeneous systems are uniformity of temperature, pressure, and chemical potentials of each chemical component. We also derive the Gibbs phase rule that bounds the number of macroscopic degrees of freedom, depending on the number of phases in mutual equilibrium.

### J.6.1 Keywords for Chapter 6

equilibrium criteria, entropy equivalent, internal energy, Helmholtz free energy, enthalpy, Gibbs free energy, Kramers potential, mutual heterogeneous equilibrium, uniform potentials, Gibbs phase rule

## J.7 Chapter 7, Requirements for Stability

We investigate whether a homogeneous system is stable with respect to breakup into a composite system of two or more homogeneous subsystems. Criteria to avoid breakup lead to requirements for the dependence of the entropy and thermodynamic potentials on their natural variables. For stability, the entropy must be a concave function of its natural variables (all extensive) and the internal energy must be a convex function of its natural variables (all extensive). The thermodynamic potentials (Helmholtz, enthalpy, Gibbs, Kramers) must be convex functions of their extensive variables and concave functions of their intensive variables. Properties of Legendre transformations are used to derive the stability requirements for intensive variables. Local stability criteria depend on the signs of second order partial derivatives. When these stability criteria are violated, there can be locally unstable regions and metastable regions that are locally stable but globally unstable. Then transformations can occur. Principles of Le Chatlier and Le Chatlier-Braun elucidate the approach to equilibrium.

### J.7.1 Keywords for Chapter 7

concave functions, convex functions, required functional dependence, globally stable, locally stable, metastable

## J.8 Chapter 8, Monocomponent Phase Equilibria

Phase equilibria for a monocomponent system require uniformity of temperature, pressure and chemical potential. In the temperature-pressure plane, single-phase regions are separated from one another by two-phase coexistence curves that meet at the triple point where all three phases, crystalline solid, liquid, and vapor, are in mutual equilibrium. The Clapeyron differential equation depends on the ratio of enthalpy change to volume change and describes the coexistence curves that can be approximated by the Clausius-Clapeyron equation for ideal vapors. The solid-vapor coexistence curve ends at a critical point; at larger pressures or temperatures there is no distinction between these phases. The chemical potential is continuous at the coexistence curves but its slope versus temperature or pressure is discontinuous. We develop equations for the thermodynamic functions and sketch them versus temperature and pressure. Finally we discuss phase equilibria in the volume-pressure plane where two phases in equilibrium are separated by a miscibility gap in volume.

**J.8.1 Keywords for Chapter 8**

single-phase region, two-phase coexistent curves, triple point, Clapeyron equation, Clausius-Clapeyron equation, vapor pressure, Arrhenius form, critical point, miscibility gap

**J.9 Chapter 9, Two-Phase Equilibrium for a van der Waals Fluid**

The van der Waals model of a fluid exhibits a liquid-vapor phase transition. Isotherms in the volume-pressure plane depend on a parameter accounting for the finite size of molecules and another for molecular interactions. Below a critical temperature, the pressure of an isotherm is not monotonic. The locus of its maximum and minimum has an inverted U-shape and is called the spinodal curve. Volumes inside the spinodal curve represent unstable fluid. For volumes just outside the spinodal the fluid becomes metastable. For volumes beyond another inverted U-shaped curve there are two stable phases, a liquid and a vapor, separated by a miscibility gap. The Helmholtz free energy as a function of volume is investigated by the chord and common tangent constructions to calculate the miscibility gap. Isotherms of the Gibbs free energy as a function of pressure can be multiple-valued and display cusps. The miscibility gap obeys an equal-area construction due to Maxwell.

**J.9.1 Keywords for Chapter 9**

liquid-vapor phase transition, non-monotonic isotherms, spinodal curve, miscibility gap, non-convex Helmholtz energy, chord construction, common tangent construction, Maxwell construction

**J.10 Chapter 10, Binary Solutions**

A binary solution constitutes two chemical components mutually dissolved on an atomic scale. We study its molar Gibbs free energy as a function of mole fraction at various temperatures and fixed pressure. Chemical potentials are calculated by the method of intercepts. Below a critical temperature, the common tangent construction demonstrates equilibrium between two phases having different mole fractions that lie on a curve that bounds a miscibility gap. Ideal solutions are those whose components do not interact energetically and whose entropy compared to unmixed components is due only to random configuration of the components; they have no miscibility gap. An ideal solid solution and an ideal liquid solution, however, are separated by a lens-shaped miscibility gap for temperatures between melting points of the pure components. A regular solution based on a mean-field model allows components to have energetic interactions; repulsive interactions result in a miscibility gap and a spinodal curve below a critical temperature in the composition-temperature plane.

### J.10.1 Keywords for Chapter 10

mutual solubility, ideal solution, spinodal curve, chemical potentials, method of intercepts, common tangent construction, miscibility gap, phase diagram, lens-shaped gap, regular solution

## J.11 Chapter 11, External Forces and Rotating Coordinate Systems

We derive equilibrium criteria in the presence of conservative external forces. For a chemically closed isothermal system with constant volume, equilibrium requires virtual variations of the Helmholtz free energy plus the external potential to be positive. For a uniform gravitational field, use of the calculus of variations shows that the gravitational chemical potential, which is the chemical potential per unit mass plus the product of the gravitational acceleration and height, is constant for each component. Pressure increases with height and the composition changes with height, so such systems are not homogeneous. For a mixture of ideal gases and binary liquids, the segregation of chemical components with height is small for samples of laboratory size. For the non-uniform gravitational field in the atmosphere of the Earth, there can be larger segregation. Rotating systems are treated by equivalence to gravitational forces; a fast centrifuge causes significant segregation. For applied electric fields, the electrochemical potential of ions is constant.

### J.11.1 Keywords for Chapter 11

conservative external forces, gravitational chemical potential, inhomogeneous pressure, gravitational segregation, centrifuge, electrochemical potential

## J.12 Chapter 12, Chemical Reactions

Chemical reactions entail making or breaking of bonds, so energy is conserved for an isolated system. Reactions at constant volume or pressure exchange heat with the environment by change of internal energy or enthalpy, respectively. Reaction extent is measured by a progress variable; reactions progress until equilibrium is reached or some component is depleted. We define standard states of components and heats of formation of compounds. Affinity is defined as the decrease of Gibbs free energy per unit progress variable; its sign determines the direction of the reaction such that entropy is produced. Change of enthalpy per unit progress variable determines whether the reaction is endothermic or exothermic. At equilibrium the affinity is zero. Equilibrium conditions are expressed by equating a function of temperature and pressure called the 'equilibrium constant' to a reaction product that depends on activities and fugacities of chemical components. Special cases include reaction products that can be approximated in terms of partial pressures of ideal gases.

**J.12.1 Keywords for Chapter 12**

progress variable, affinity, entropy production, endothermic, exothermic, standard states, equilibrium constant, activity, fugacity, reaction product

**J.13 Chapter 13, Thermodynamics of Fluid-Fluid Interfaces**

Surfaces or interfaces of discontinuity where phases meet are modeled by a Gibbs dividing surface of zero thickness. The differences between extensive variables of an actual system and one in which phases are uniform up to the dividing surface are defined to be surface excess quantities that depend on location of the dividing surface. The excess Kramers potential divided by surface area is independent of location and called the surface free energy or surface tension. The Gibbs adsorption equation governs segregation of surface components. The Cahn layer model is used to represent physically meaningful surface excess quantities by determinants. Curved interfaces can exert forces that cause pressure jumps between adjacent phases. We derive conditions for equilibrium at contact lines where three interfaces meet. Shapes of liquid surfaces under forces due to gravity and surface tension, including sessile drops and bubbles, are computed by solving differential equations.

**J.13.1 Keywords for Chapter 13**

Gibbs dividing surface, surface excess quantities, surface free energy, interfacial free energy, surface tension, Cahn layer model, Gibbs adsorption equation, contact lines, sessile drops, sessile bubbles

**J.14 Chapter 14, Thermodynamics of Solid-Fluid Interfaces**

Solid-fluid interfaces differ from fluid-fluid interfaces because a solid can be strained elastically. Surface area can change by stretching and by addition of new surface, each process giving rise to surface stress. Interfacial energy and adsorption can be referenced to the area of either the unstrained crystal surface or its actual strained surface. Interfacial free energy of crystal-fluid interfaces is anisotropic, consistent with crystal symmetry, and can be described by a vector field known as the xi-vector; its normal component is the surface free energy and its tangential component measures the change of energy with surface orientation. A small crystal can acquire an equilibrium shape that has facets and missing orientations and minimizes its surface energy. This shape can be computed from the Wulff construction or the xi-vector. A large crystal surface can develop facets to minimize its energy. We derive Herring's formula for the equilibrium potential on a curved crystal surface.



### **J.14.1 Keywords for Chapter 14**

surface strain, surface stress, anisotropic interfacial energy, xi-vector, equilibrium shape, Wulff construction, surface faceting, Herring formula

## **J.15 Chapter 15, Entropy and Information**

Since the 1800s and the work of Clausius and Boltzmann, it was believed that the entropy function, which can only increase for an isolated system, was a measure of a state of greater probability, a more disordered state in which information is lacking. In 1948, Shannon developed a quantitative measure of information in the context of communication theory. Shannon's measure is a function of an abstract set of probabilities and provides a quantitative measure of disorder. It is maximum when all probabilities are the same, in which case it becomes equal to Boltzmann's formula for the entropy within a multiplicative constant. This provides us with a modern basis for the microcanonical ensemble in the next chapter. We give a demonstration of Boltzmann's eta theorem for an ideal gas based on a statistical analysis of elastic collisions of hard spheres. Boltzmann's eta function decreases as time increases. Its negative is the dynamical equivalent of Shannon's measure of disorder.

### **J.15.1 Keywords for Chapter 15**

entropy, communication theory, Shannon information function, maximum disorder, Boltzmann eta theorem

## **J.16 Chapter 16, Microcanonical Ensemble**

An ensemble is a collection of microstates that are compatible with a specified macrostate of a thermodynamic system. The microcanonical ensemble represents an isolated system having fixed energy. For that ensemble, the fundamental assumption of statistical mechanics is that every compatible stationary quantum microstate is equally probable. Properties of a system in a macrostate are calculated by averaging its values over the ensemble microstates. The entropy is assumed to be proportional to the logarithm of the number of compatible microstates as proposed by Boltzmann and in agreement with the disorder function of information theory. The proportionality constant is known as Boltzmann's constant. Temperature, pressure and chemical potential are calculated from partial derivatives of the entropy. The ensemble is illustrated for two-state subsystems, harmonic oscillators, an ideal gas with Gibbs correction factor, and a multicomponent ideal gas. The entropy of mixing of ideal gases is calculated.

### **J.16.1 Keywords for Chapter 16**

ensemble, stationary quantum microstate, Boltzmann entropy, Boltzmann constant, two-state subsystem, harmonic oscillator, ideal gas, Gibbs correction factor, multicomponent

ideal gas, entropy of mixing

## J.17 Chapter 17, Classical Microcanonical Ensemble

Classical many-particle systems are governed by continuous variables, the positions and momenta of all particles in multi-dimensional phase space. Total energy depends on these variables and is called the Hamiltonian. Hamilton's equations govern dynamics. According to Liouville's theorem, the time rate of change of the density of a given set of particles in phase space is independent of time. For a system in equilibrium, this will be true if the density depends only on the Hamiltonian. The classical microcanonical ensemble is obtained by assuming that this density is uniform in the volume of phase space available to the system for a narrow band of energies; it plays the same role as the assumption of equal probability of microstates for the quantum ensemble. The entropy is calculated within an additive constant by assuming it to be proportional to the logarithm of available phase space. We illustrate this ensemble for an ideal gas and three-dimensional harmonic oscillators.

### J.17.1 Keywords for Chapter 17

phase space, Hamiltonian, Hamilton's equations, Liouville's theorem, phase space density, available phase space, uniform probability density

## J.18 Chapter 18, Distinguishable Particles with Negligible Interaction Energies

We derive a simplified version of the canonical ensemble developed in the next chapter. We treat a system of identical particles that can be distinguished, perhaps by position in a solid. We derive a statistical distribution of particles, each in a quantum state, by maximizing the number of ways they can be distributed among quantum states, subject to the constraint of constant total energy. This results in a most probable distribution. The probability of occupation of a given quantum state is proportional to its Boltzmann factor, the exponential of the negative of the energy of that state divided by a thermal energy. The thermal energy is the product of temperature and Boltzmann's constant. The sum of all Boltzmann factors is called the partition function and is used to determine thermodynamic functions. Examples include two-state subsystems, harmonic oscillators, and rotations of a rigid diatomic molecule. Results are used to model heat capacities of solids and blackbody (cavity) radiation.

### J.18.1 Keywords for Chapter 18

distinguishable particles, most probable distribution, Boltzmann factor, partition function, rigid rotator, heat capacity, blackbody radiation, Stefan-Boltzmann constant

## J.19 Chapter 19, Canonical Ensemble

The canonical ensemble applies to a system held at constant temperature. Two derivations are based on the microcanonical ensemble by putting a system of interest in contact with a heat reservoir to form an isolated system. A third derivation employs the most probable distribution of ensemble members. The probability of a system being in a given stationary quantum state is proportional to its Boltzmann factor. We calculate dispersion of energy relative to its average. The sum of Boltzmann factors gives a system partition function that relates to Helmholtz free energy. For a system composed of independent but distinguishable subsystems with negligible interaction energies, the system partition function factors. For such subsystems of identical particles, we recover the simplified ensemble of the preceding chapter. We treat an ideal gas and explore its Maxwell-Boltzmann distribution of velocities. Paramagnetism is treated both classically and quantum mechanically and compared. The partition function is related to the density of states by a Laplace transform.

### J.19.1 Keywords for Chapter 19

heat reservoir, system Boltzmann factor, system partition function, Helmholtz free energy, factorization theorem, energy dispersion, Maxwell-Boltzmann distribution, paramagnetism, adiabatic demagnetization, density of states

## J.20 Chapter 20, Classical Canonical Ensemble

The classical canonical ensemble employs a probability density function in phase space in which the energy in the Boltzmann factor for a quantum system is replaced by the classical Hamiltonian. The classical partition function is the integral of that Boltzmann factor over phase space. One can artificially divide the classical partition function by a factor containing powers of Planck's constant to get results that agree with quantum mechanics at high temperatures. We illustrate this for an ideal gas and compute effusion from a small hole. The law of Dulong and Petit is derived for a harmonic potential. We compute classical averages of canonical coordinates and momenta. We derive the virial theorem for time averages and use it to treat a non-ideal gas with particle interactions calculated by using a pair distribution function. We discuss the use of canonical transformations in calculating partition functions and calculate the partition function for a rotating polyatomic molecule by using Jacobians.

### J.20.1 Keywords for Chapter 20

probability density function, phase space integral, classical partition function, ideal gas effusion, law of Dulong and Petit, classical averages, virial theorem, pair distribution function, canonical transformation, rotating polyatomic molecule

## J.21 Chapter 21, Grand Canonical Ensemble

The grand canonical ensemble applies to a system at constant temperature and chemical potential; its number of particles is not fixed. We derive it from the microcanonical ensemble by contact with heat and particle reservoirs to form an isolated system. The probability of a system having a specified number of particles and being in a given stationary quantum state is proportional to its Gibbs factor, the product of a Boltzmann factor and a factor exponential in the number of particles. Summing all Gibbs factors gives the grand partition function that relates to the Kramers potential. We calculate dispersion of particle number and energy. The grand partition function factors for independent subsystems, dilute sites, and ideal Fermi and Bose gases whose distribution functions are derived. We treat a classical ideal gas with internal nuclear and electronic structure and molecules that can rotate and vibrate. A pressure ensemble is derived and used to treat point defects in crystals.

### J.21.1 Keywords for Chapter 21

grand partition function, Gibbs factor, particle number dispersion, Kramers potential, dilute systems, Fermi-Dirac distribution, Bose-Einstein distribution, ideal gas internal structure, pressure ensemble, crystal point defects

## J.22 Chapter 22, Entropy for a General Ensemble

We use the method of the most probable distribution to show that the entropy for a general ensemble can be expressed by the maximum value of the disorder function of information theory, derived in Chapter 15, subject to the set of constraints appropriate to the ensemble. We illustrate this in detail for a grand canonical ensemble with two kinds of particles. We treat a number of other ensembles practically by inspection, including an ensemble that relates to a Massieu function that is the Legendre transform of the entropy. By using a degeneracy factor to sum over energy levels, particle numbers, and volumes, we show that all ensembles can be related in a similar way to their associated thermodynamic functions, as observed by Hill.

### J.22.1 Keywords for Chapter 22

most probable distribution, maximum disorder, ensemble constraints, degeneracy factor, density of distribution functions

## J.23 Chapter 23, Unified Treatment of Ideal Fermi, Bose and Classical Gases

We give a unified treatment of ideal Fermi, Bose and classical gases for temperatures sufficiently large that energy levels can be treated as a quasi-continuous. Sums can be

converted to integrals over a density of quantum states to evaluate thermodynamic functions. Pressure is equal to two-thirds of the energy density for all three gases. Relevant integrals can be represented by series expansions if the absolute activity is less than unity, which is always the case for bosons. For fermions, larger values of the absolute activity can be handled by an asymptotic expansion. Virial expansions for the pressure of these ideal gases are power series in the ratio of the actual concentration to the quantum concentration. For absolute activity less than unity, the deviation from ideal gas behavior is practically linear in that ratio, less pressure for bosons and more for fermions. Formulae for the heat capacity of these gases at constant volume are calculated in terms of several integrals.

### **J.23.1 Keywords for Chapter 23**

quasi-continuous energies, density of states, series expansions, asymptotic expansions, absolute activity, virial expansions, heat capacity

## **J.24 Chapter 24, Bose Condensation**

Below a critical temperature, occupation of the ground state of a Bose gas becomes comparable to occupation of all excited states. This Bose condensation increases with decreasing of temperature and affects thermodynamic functions. Only particles in excited states contribute to the pressure, internal energy and entropy. Pressure remains equal to two-thirds of the energy density and becomes independent of molar volume. Heat capacity per particle is zero at zero temperature and rises to a sharp maximum at the critical temperature; with further increase of temperature it decreases to the constant value of a classical ideal gas. Its graph somewhat resembles the Greek letter lambda. A similar behavior occurs in helium with mass number four at its so-called lambda-point, although helium is not ideal because its atoms attract. We explore condensate regions that are bounded by an isentrope in the volume-temperature and volume-pressure planes.

### **J.24.1 Keywords for Chapter 24**

critical temperature, ground state condensation, excited states, lambda-point, condensate region, isentropic boundary

## **J.25 Chapter 25, Degenerate Fermi Gas**

Even at absolute zero, the Pauli exclusion principle forces fermions into high energy states, a degenerate gas. States fill to the Fermi energy, equivalent to about 50,000 Kelvin for a free electron gas. At laboratory temperatures, small excitation into higher energy states is calculated by using an asymptotic Sommerfeld expansion. Heat capacity is linear in temperature and typically 100 times smaller than for a classical gas. A magnetic field can split spin states, resulting in weak Pauli paramagnetism; its effect on orbits causes Landau

diamagnetism. Heating enables electron escape by thermionic emission, also affected by electric fields and radiation. Semiconductors have densities of states with a forbidden energy band. Electrons in intrinsic semiconductors can be thermally excited to a conduction band above a band gap leaving empty states called holes in the valence band. This results in electrical conductivity that can be enhanced by dopants called donors and acceptors that provide states that are easier to excite.

### J.25.1 Keywords for Chapter 25

Pauli exclusion principle, Fermi energy, Sommerfeld expansion, Pauli paramagnetism, Landau diamagnetism, thermionic emission, band gap, intrinsic semiconductor, donor, acceptor

## J.26 Chapter 26, Quantum Statistics

Two types of averaging occur in quantum statistical mechanics, the first for pure quantum mechanical states and the second for a statistical ensemble of pure states. We define and exhibit the properties of density operators and their density matrix representation for both pure and statistical states. For equilibrium states, a statistical density operator depends only on stationary quantum states. We exhibit it in the energy representation for the microcanonical, canonical and grand canonical ensembles; its use is illustrated for an ideal gas and the harmonic oscillator. Density matrices for spin 1/2 are expressed in terms of a polarization vector and Pauli spin matrices and related to vectors called spinors. Symmetric wave functions for bosons and antisymmetric wave functions for fermions are constructed from single-particle quantum states in terms of occupation numbers by using permutation operators, or Slater determinants for fermions. Weighting factors for states are contrasted for bosons, fermions and distinguishable classical particles.

### J.26.1 Keywords for Chapter 26

pure state, statistical state, density operator, density matrix, Pauli spin matrices, polarization vector, occupation numbers, symmetric boson states, antisymmetric fermion states, weighting factors

## J.27 Chapter 27, Ising Model

Cooperative phenomena are introduced via the simple Ising model in which spins having two states occupy a lattice and interact with nearest neighbors and an applied magnetic field. We study this model in the mean field approximation. Correlations among spin states are neglected, so each spin interacts with a self-consistent mean field. With no applied magnetic field, the model predicts ordering of spins below some critical temperature for lattices of all dimensionalities, 1,2,3..., and enables properties such as heat capacity and magnetic susceptibility to be calculated. Exact solutions for a one-dimensional lattice show

no ordering transition; the mean field model fails badly in that case but otherwise shows reasonable trends. Exact solutions exist in two dimensions and show ordering. Better approximate solutions (Boethe cluster model) or numerical solutions can be obtained for lattices of all dimensionalities. We introduce Monte Carlo simulation for numerical solution of the Ising model as well as for models involving interacting classical particles.

### **J.27.1 Keywords for Chapter 27**

spin interactions, correlations, mean field model, ordering, critical temperature, heat capacity, magnetic susceptibility, exact solutions, Monte Carlo simulation, interacting classical particles

## **J.28 Appendix A, Stirling's Approximation**

We state Stirling's approximation for the logarithms of factorials of large numbers and for the factorials themselves. We present some numerical examples and an elementary motivation by using a staircase to approximate the graph of a logarithm. Then we discuss Stirling's asymptotic series for the gamma function. We contrast asymptotic series and convergent series.

### **J.28.1 Keywords for Appendix A**

approximation of factorials, gamma function, asymptotic series, convergent series

## **J.29 Appendix B, Use of Jacobians to Convert Partial Derivatives**

Most thermodynamic properties can be expressed in terms of partial derivatives. Jacobians are determinants that provide a systematic and powerful way to convert partial derivatives for a certain variable set to partial derivatives with respect to a different variable set, and hence to other physical properties. Useful properties of determinants are reviewed, especially the fact that they multiply formally like fractions. Examples related to thermodynamics include: relationship of heat capacity at constant volume to that at constant pressure; ratio of those heat capacities to the ratio of compressibility at constant entropy to that at constant temperature; and relationship of isentropic thermal expansion to isothermal thermal expansion.

### **J.29.1 Keywords for Appendix B**

Jacobian determinants, Jacobian multiplication, isentropic compressibility, isentropic thermal expansion, compressibility ratio

## J.30 Appendix C, Differential Geometry of Surfaces

We introduce methods for calculation of the xi-vector used to measure anisotropy of crystal surface free energy. A vector formulation of differential geometry is presented for a parametric representation of a surface. Normal and tangential vectors and their reciprocal vectors are used to derive general formulae for mean and Gaussian surface curvatures. Differential operators such as surface gradient, divergence and curl are defined. We derive a general formulation for the variation of a surface normal for small changes in the surface. The surface divergence theorem is presented. Divergence of the xi-vector is calculated for a general surface and in a Monge representation. This methodology is used to derive a generalization of Herring's formula for surface chemical potential and for a variational approach to surface equilibrium shape.

### J.30.1 Keywords for Appendix C

xi-vector, anisotropy, mean curvature, Gaussian curvature, surface differential operators, surface divergence theorem, divergence of xi-vector, generalized Herring formula, variational formulation

## J.31 Appendix D, Equilibrium of Two-State Systems

We use the microcanonical ensemble to make a detailed study of the equilibrium of a composite system consisting of two-state subsystems, each having a number of spin 1/2 particles. The multiplicity function of the combined system is a sum over products of the multiplicity functions of the subsystems that conserve total energy. That sum is dominated by its largest terms; we evaluate it approximately by converting to two Gaussian integrals whose integrands are sharp peaks having a narrow region of overlap. We demonstrate explicitly how the logarithm of the product of subsystem multiplicity functions, evaluated at their peaks, is equal to that for the combined system, provided that sub-extensive terms are negligible. This demonstrates the degree to which entropy of the subsystems is additive.

### J.31.1 Keywords for Appendix D

composite system, spin one-half, multiplicity functions, dominant terms, Gaussian integrals, overlap integral, entropy additivity

## J.32 Appendix E, Aspects of Canonical Transformations

We use a variational method due to Courant to derive the necessary and sufficient conditions for a general canonical transformation that can depend on time in terms of Lagrange brackets. These transformation conditions can be described by a matrix that is a member



of the symplectic group and has a Jacobian of magnitude unity. This knowledge enables the conversion of integral expressions for the classical canonical partition function to be evaluated by making any convenient canonical transformation. For restricted canonical transformations that are independent of time, we derive a simplified set of conditions and show that they are compatible with the general necessary and sufficient conditions.

### **J.32.1 Keywords for Appendix E**

general canonical transformation, conditions, Lagrange brackets, symplectic matrix, unit Jacobian, restricted canonical transformation

## **J.33 Appendix F, Rotation of Rigid Bodies**

We express the moment of inertia of a rigid body by a moment of inertia tensor. Angular momentum and kinetic energy of a body that rotates about an axis through its center of mass is related to moment of inertia and an axial rotation vector. Time derivatives are evaluated in a fixed reference frame. In a rotating coordinate system, the inertia tensor can be expressed by three constant principal values. Fixed and rotating coordinates are related by a matrix that depends on three Euler angles that can be related to an axial rotation vector. The Hamiltonian of a rotating body, expressed in Euler angles and principal moments of inertia, can be used to calculate canonical momenta of a polyatomic molecule. We derive the quantum states for a diatomic molecule having three principal moments of inertia.

### **J.33.1 Keywords for Appendix F**

rigid body, moment of inertia, inertia tensor, angular momentum, rotating coordinates, Euler angles, canonical momenta, polyatomic molecule, diatomic molecule quantum states

## **J.34 Appendix G, Thermodynamic Perturbation Theory**

We develop approximate methods for calculation of canonical partition functions when the Hamiltonian is the sum of an unperturbed Hamiltonian plus a small perturbation. For the classical case, the Boltzmann factor for the perturbation is expanded to second order and evaluated by averaging with respect to the probabilities associated with the unperturbed Hamiltonian. The Helmholtz free energy has a first order correction equal to the average of the perturbation and a negative second order correction proportional to its variance. For the quantum case, one approximates the energy eigenstates by using second order quantum perturbation theory and sums the resulting Boltzmann factors. The second order correction to the Helmholtz free energy is again negative and proportional to the variance of the perturbation if the splittings of unperturbed energies are small compared to the thermal energy.

### J.34.1 Keywords for Appendix G

perturbed Hamiltonian, expanded Boltzmann factor, averaged perturbation, perturbation variance

## J.35 Appendix H, Selected Mathematical Relations

Alternative definitions of Bernoulli numbers and polynomials are presented. The Euler-Maclaurin sum formula that relates sums to integrals is presented in general form with a remainder term. Specialization leads to an approximation for an infinite sum of terms by an integral plus a series whose coefficients are Bernoulli numbers. Use of that sum formula is illustrated for approximate evaluation of the partition function for a rigid linear rotator and calculation of its heat capacity at high temperatures. We also derive a sum formula for an infinite sum of terms that depend on half integers and test its use to obtain an approximate partition function for a harmonic oscillator for which an exact evaluation is possible.

### J.35.1 Keywords for Appendix H

Bernoulli numbers, Bernoulli polynomials, Euler-Maclaurin sum formula, rigid linear rotator

## J.36 Appendix I, Creation and Annihilation Operators

We express the Hamiltonian for a one-dimensional harmonic oscillator in terms of creation and annihilation operators. The commutation relation for such operators is the same as for boson operators and is used to find eigenvalues for their product, which is a Hermitian number operator. We show by purely algebraic manipulations that the eigenvalues of these number operators are integers. Eigenvectors for larger integers can be created by successive operations of creation operators on an eigenvector with eigenvalue zero. We discuss fermion operators that obey anti-commutation relations and explore the states of their number operators, whose only eigenvalues are zero and one. Number operators for both boson and fermion operators are extended to many-particle systems whose eigenvectors can be created by successive operation on a vacuum state having eigenvalue zero.

### J.36.1 Keywords for Appendix I

creation operator, annihilation operator, number operator, bosons, fermions, eigenstates, vacuum state



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