SECOND EDITION

STATISTICAL MECHANICS

KERSON HUANG

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FROM THE PREFACE TO THE FIRST EDITION

This book is an outgrowth of a year course in statistical mechanics that I have been giving at the Massachusetts Institute of Technology. It is directed mainly to graduate students in physics.

In this book the starting point of statistical mechanics is taken to be certain phenomenological postulates, whose relation to quantum mechanics I try to state as clearly as I can, and whose physical consequences I try to derive as simply and directly as I can.

Before the subject of statistical mechanics proper is presented, a brief but self-contained discussion of thermodynamics and the classical kinetic theory of gases is given. The order of this development is imperative, from a pedagogical point of view, for two reasons. First, thermodynamics has successfully described a large part of macroscopic experience, which is the concern of statistical mechanics. It has done so not on the basis of molecular dynamics but on the basis of a few simple and intuitive postulates stated in everyday terms. If we first familiarize ourselves with thermodynamics, the task of statistical mechanics reduces to the explanation of thermodynamics. Second, the classical kinetic theory of gases is the only known special case in which thermodynamics can be derived nearly from first principles, i.e., molecular dynamics. A study of this special case will help us understand why statistical mechanics works.

A large part of this book is devoted to selected applications of statistical mechanics. The selection is guided by the interest of the topic to physicists, its value as an illustration of calculating techniques, and my personal taste.

To read the first half of the book the reader needs a good knowledge of classical mechanics and some intuitive feeling for thermodynamics and kinetic theory. To read the second half of the book he needs to have a working knowledge of quantum mechanics. The mathematical knowledge required of the reader does not exceed what he should have acquired in his study of classical mechanics and quantum mechanics.

KERSON HUANG

Cambridge, Massachusetts
February 1963

PREFACE

This book is intended for use as a textbook for a one-year graduate course in statistical mechanics, and as a reference book for workers in the field.

Significant changes and additions have been made at various places in the text and in the problems to make the book more instructive. The general approach remains the same as that stated in the preface to the first edition.

The most substantive change is the addition of the last three chapters on the Landau-Wilson approach to critical phenomena. I hope that these chapters will provide the uninitiated reader with an introduction to this fascinating and important subject, which has developed since the first edition of this book.

To make room for the additions, I have omitted or abridged some of the original material, notably the sections on many-body theory and "rigorous" statistical mechanics, which by now have become separate fields.

All the material in this book probably cannot be covered in a one-year course (even if that were deemed desirable). It might be helpful, therefore, to list the chapters that form the "hard core" of the book. They are the following: Chapters 3, 4, 6, 7, 8, 11, 12 (excepting 3.5, 7.6, 7.7, 7.8).

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CONTENTS

PART A THERMODYNAMICS AND KINETIC THEORY 1

CHAPTER 1 THE LAWS OF THERMODYNAMICS 3

1.1 Preliminaries 3
1.2 The First Law of Thermodynamics 7
1.3 The Second Law of Thermodynamics 9
1.4 Entropy 14
1.5 Some Immediate Consequences of the Second Law 19
1.6 Thermodynamic Potentials 22
1.7 The Third Law of Thermodynamics 25

CHAPTER 2 SOME APPLICATIONS OF THERMODYNAMICS 31

2.1 Thermodynamic Description of Phase Transitions 31
2.2 Surface Effects in Condensation 35
2.3 Van der Waals Equation of State 38
2.4 Osmotic Pressure 43
2.5 The Limit of Thermodynamics 48

CHAPTER 3 THE PROBLEM OF KINETIC THEORY 52

3.1 Formulation of the Problem 52
3.2 Binary Collisions 56
3.3 The Boltzmann Transport Equation 60
3.4 The Gibbsian Ensemble 62
3.5 The BBGKY Hierarchy 65

CHAPTER 4 THE EQUILIBRIUM STATE OF A DILUTE GAS 73

4.1 Boltzmann's *H* Theorem 73
4.2 The Maxwell-Boltzmann Distribution 75
4.3 The Method of the Most Probable Distribution 79
4.4 Analysis of the *H* Theorem 85
4.5 The Poincaré Cycle 90

CHAPTER 5 TRANSPORT PHENOMENA 93

5.1 The Mean Free Path 93
5.2 Effusion 95
5.3 The Conservation Laws 96
5.4 The Zero-Order Approximation 100
5.5 The First-Order Approximation 104

5.6 Viscosity **108**
5.7 Viscous Hydrodynamics **111**
5.8 The Navier-Stokes Equation **113**
5.9 Examples in Hydrodynamics **117**

PART B STATISTICAL MECHANICS **125**

CHAPTER 6 CLASSICAL STATISTICAL MECHANICS **127**

6.1 The Postulate of Classical Statistical Mechanics **127**
6.2 Microcanonical Ensemble **130**
6.3 Derivation of Thermodynamics **135**
6.4 Equipartition Theorem **136**
6.5 Classical Ideal Gas **138**
6.6 Gibbs Paradox **140**

CHAPTER 7 CANONICAL ENSEMBLE AND GRAND CANONICAL ENSEMBLE **143**

7.1 Canonical Ensemble **143**
7.2 Energy Fluctuations in the Canonical Ensemble **145**
7.3 Grand Canonical Ensemble **149**
7.4 Density Fluctuations in the Grand Canonical Ensemble **152**
7.5 The Chemical Potential **154**
7.6 Equivalence of the Canonical Ensemble and the Grand Canonical Ensemble **157**
7.7 Behavior of $W(N)$ **161**
7.8 The Meaning of the Maxwell Construction **163**

CHAPTER 8 QUANTUM STATISTICAL MECHANICS **171**

8.1 The Postulates of Quantum Statistical Mechanics **171**
8.2 Density Matrix **174**
8.3 Ensembles in Quantum Statistical Mechanics **176**
8.4 The Third Law of Thermodynamics **178**
8.5 The Ideal Gases: Microcanonical Ensemble **179**
8.6 The Ideal Gases: Grand Canonical Ensemble **185**
8.7 Foundations of Statistical Mechanics **189**

CHAPTER 9 GENERAL PROPERTIES OF THE PARTITION FUNCTION **193**

9.1 The Darwin-Fowler Method **193**
9.2 Classical Limit of the Partition Function **199**
9.3 Singularities and Phase Transitions **206**
9.4 The Lee-Yang Circle Theorem **210**

CHAPTER 10 APPROXIMATE METHODS **213**

10.1 Classical Cluster Expansion **213**
10.2 Quantum Cluster Expansion **220**
10.3 The Second Virial Coefficient **224**
10.4 Variational Principles **228**
10.5 Imperfect Gases at Low Temperatures **230**

CHAPTER 11 FERMI SYSTEMS **241**

11.1 The Equation of State of an Ideal Fermi Gas **241**
11.2 The Theory of White Dwarf Stars **247**
11.3 Landau Diamagnetism **253**
11.4 The De Haas-Van Alphen Effect **260**
11.5 The Quantized Hall Effect **261**
11.6 Pauli Paramagnetism **267**
11.7 Magnetic Properties of an Imperfect Gas **272**

CHAPTER 12 BOSE SYSTEMS **278**

12.1 Photons **278**
12.2 Phonons in Solids **283**
12.3 Bose-Einstein Condensation **286**
12.4 An Imperfect Bose Gas **294**
12.5 The Superfluid Order Parameter **298**

PART C SPECIAL TOPICS IN STATISTICAL MECHANICS **305**

CHAPTER 13 SUPERFLUIDS **307**

13.1 Liquid Helium **307**
13.2 Tisza's Two-Fluid Model **311**
13.3 The Bose-Einstein Condensate **313**
13.4 Landau's Theory **315**
13.5 Superfluid Velocity **317**
13.6 Superfluid Flow **321**
13.7 The Phonon Wave Function **325**
13.8 Dilute Bose Gas **329**

CHAPTER 14 THE ISING MODEL **341**

14.1 Definition of the Ising Model **341**
14.2 Equivalence of the Ising Model to Other Models **344**
14.3 Spontaneous Magnetization **348**
14.4 The Bragg-Williams Approximation **352**
14.5 The Bethe-Peierls Approximation **357**
14.6 The One-Dimensional Ising Model **361**

CHAPTER 15 THE ONSAGER SOLUTION **368**

15.1 Formulation of the Two-Dimensional Ising Model **368**
15.2 Mathematical Digression **374**
15.3 The Solution **378**

CHAPTER 16 CRITICAL PHENOMENA **392**

16.1 The Order Parameter **392**
16.2 The Correlation Function and the Fluctuation-Dissipation Theorem **394**
16.3 Critical Exponents **396**
16.4 The Scaling Hypothesis **399**
16.5 Scale Invariance **403**
16.6 Goldstone Excitations **406**
16.7 The Importance of Dimensionality **407**

CHAPTER 17 THE LANDAU APPROACH **416**

17.1 The Landau Free Energy **416**
17.2 Mathematical Digression **418**
17.3 Derivation in Simple Models **420**
17.4 Mean-Field Theory **422**
17.5 The Van der Waals Equation of State **426**
17.6 The Tricritical Point **428**
17.7 The Gaussian Model **434**
17.8 The Ginzburg Criterion **437**
17.9 Anomalous Dimensions **438**

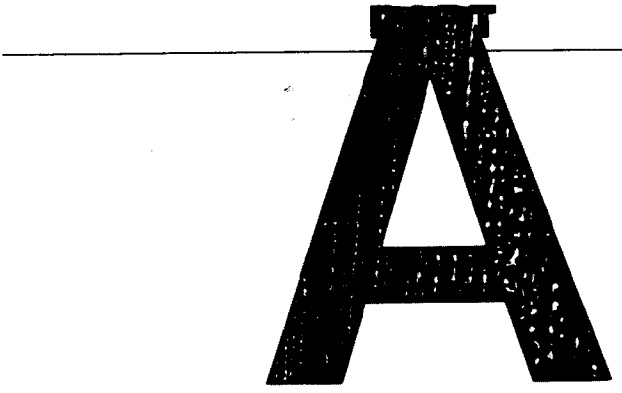
CHAPTER 18 RENORMALIZATION GROUP **441**

18.1 Block Spins **441**
18.2 The One-Dimensional Ising Model **443**
18.3 Renormalization-Group Transformation **446**
18.4 Fixed Points and Scaling Fields **449**
18.5 Momentum-Space Formulation **452**
18.6 The Gaussian Model **455**
18.7 The Landau-Wilson Model **458**

APPENDIX *N*-BODY SYSTEM OF IDENTICAL PARTICLES **468**

A.1 The Two Kinds of Statistics **468**
A.2 *N*-Body Wave Functions **470**
A.3 Method of Quantized Fields **477**
A.4 Longitudinal Sum Rules **484**

INDEX **497**



THERMODYNAMICS AND KINETIC THEORY

CHAPTER 1

THE LAWS OF THERMODYNAMICS

1.1 PRELIMINARIES

Thermodynamics is a phenomenological theory of matter. As such, it draws its concepts directly from experiments. The following is a list of some working concepts which the physicist, through experience, has found it convenient to introduce. We shall be extremely brief, as the reader is assumed to be familiar with these concepts.

(*a*) A *thermodynamic system* is any macroscopic system.

(*b*) *Thermodynamic parameters* are measurable macroscopic quantities associated with the system, such as the pressure P, the volume V, the temperature T, and the magnetic field H. They are defined experimentally.

(*c*) A *thermodynamic state* is specified by a set of values of all the thermodynamic parameters necessary for the description of the system.

(*d*) *Thermodynamic equilibrium* prevails when the thermodynamic state of the system does not change with time.

(*e*) The *equation of state* is a functional relationship among the thermodynamic parameters for a system in equilibrium. If P, V, and T are the thermodynamic parameters of the system, the equation of state takes the form

$$f(P,V,T)=0$$

which reduces the number of independent variables of the system from three to two. The function f is assumed to be given as part of the specification of the system. It is customary to represent the state of such a system by a point in the three-dimensional P-V-T space. The equation of state then defines a surface in this space, as shown in Fig. 1.1. Any point lying on this surface represents a state in equilibrium. In

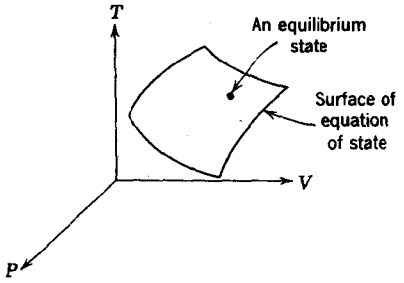


Fig. 1.1 Geometrical representation of the equation of state.

thermodynamics a state automatically means a state in equilibrium unless otherwise specified.

(*f*) A *thermodynamic transformation* is a change of state. If the initial state is an equilibrium state, the transformation can be brought about only by changes in the external condition of the system. The transformation is *quasi-static* if the external condition changes so slowly that at any moment the system is approximately in equilibrium. It is *reversible* if the transformation retraces its history in time when the external condition retraces its history in time. A reversible transformation is quasi-static, but the converge is not necessarily true. For example, a gas that freely expands into successive infinitesimal volume elements undergoes a quasi-static transformation but not a reversible one.

(*g*) The *P-V diagram* of a system is the projection of the surface of the equation of state onto the *P-V* plane. Every point on the *P-V* diagram therefore represents an equilibrium state. A reversible transformation is a continuous path on the *P-V* diagram. Reversible transformations of specific types give rise to paths with specific names, such as *isotherms*, *adiabatics*, etc. A transformation that is not reversible cannot be so represented.

(*h*) The concept of *work* is taken over from mechanics. For example, for a system whose parameters are P, V, and T, the work dW done by a system in an infinitesimal transformation in which the volume increases by dV is given by

$$dW = P\,dV$$

(*i*) *Heat* is what is absorbed by a homogeneous system if its temperature increases while no work is done. If ΔQ is a small amount of the heat absorbed, and ΔT is the small change in temperature accompanying the absorption of heat, the *heat capacity* C is defined by

$$\Delta Q = C\Delta T$$

The heat capacity depends on the detailed nature of the system and is given as a part of the specification of the system. It is an experimental fact that, for the same ΔT, ΔQ is different for different ways of heating

up the system. Correspondingly, the heat capacity depends on the manner of heating. Commonly considered heat capacities are C_V and C_P, which respectively correspond to heating at constants V and P. Heat capacities per unit mass or per mole of a substance are called *specific heats*.

(*j*) A *heat reservoir*, or simply *reservoir*, is a system so large that the gain or loss of any finite amount of heat does not change its temperature.

(*k*) A system is *thermally isolated* if no heat exchange can take place between it and the external world. Thermal isolation may be achieved by surrounding a system with an *adiabatic wall*. Any transformation the system can undergo in thermal isolation is said to take place adiabatically.

(*l*) A thermodynamic quantity is said to be *extensive* if it is proportional to the amount of substance in the system under consideration and is said to be *intensive* if it is independent of the amount of substance in the system under consideration. It is an important empirical fact that to a good approximation thermodynamic quantities are either extensive or intensive.

(*m*) The *ideal gas* is an important idealized thermodynamic system. Experimentally all gases behave in a universal way when they are sufficiently dilute. The ideal gas is an idealization of this limiting behavior. The parameters for an ideal gas are pressure P, volume V, temperature T, and number of molecules N. The equation of state is given by Boyle's law:

$$\frac{PV}{N} = \text{constant} \qquad \text{(for constant temperature)}$$

The value of this constant depends on the experimental scale of temperature used.

(*n*) The equation of state of an ideal gas in fact defines a temperature scale, the *ideal-gas temperature* T:

$$PV = NkT$$

where

$$k = 1.38 \times 10^{-16} \text{ erg/deg}$$

which is called Boltzmann's constant. Its value is determined by the conventional choice of temperature intervals, namely, the Centigrade degree. This scale has a universal character because the ideal gas has a universal character. The origin $T = 0$ is here arbitrarily chosen. Later we see that it actually has an absolute meaning according to the second law of thermodynamics.

To construct the ideal-gas temperature scale we may proceed as follows. Measure PV/Nk of an ideal gas at the temperature at which water boils and at

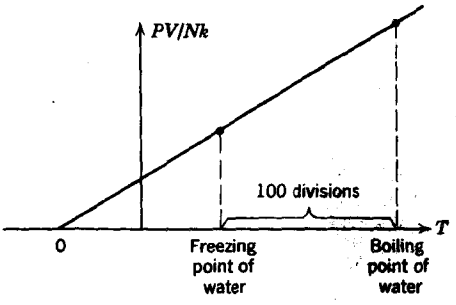


Fig. 1.2 The ideal-gas temperature scale.

which water freezes. Plot these two points and draw a straight line through them, as shown in Fig. 1.2. The intercept of this line with the abscissa is chosen to be the origin of the scale. The intervals of the temperature scale are so chosen that there are 100 equal divisions between the boiling and the freezing points of water. The resulting scale is the Kelvin scale (K). To use the scale, bring anything whose temperature is to be measured into thermal contact with an ideal gas (e.g., helium gas at sufficiently low density), measure PV/Nk of the ideal gas, and read off the temperature from Fig. 1.2. An equivalent form of the equation of state of an ideal gas is

$$PV = nRT$$

where n is the number of moles of the gas and R is the gas constant:

$$\begin{aligned} R &= 8.315 \text{ joule/deg} \\ &= 1.986 \text{ cal/deg} \\ &= 0.0821 \text{ liter-atm/deg} \end{aligned}$$

Its value follows from the value of Boltzmann's constant and Avogadro's number:

$$\text{Avogadro's number} = 6.205 \times 10^{23} \text{ atoms/mol}$$

Most of these concepts are properly understood only in molecular terms. Here we have to be satisfied with empirical definitions.

In the following we introduce thermodynamic laws, which may be regarded as mathematical axioms defining a mathematical model. It is possible to deduce rigorous consequences of these axioms, but it is important to remember that this model does not rigorously correspond to the physical world, for it ignores the atomic structure of matter, and will thus inevitably fail in the atomic domain. In the macroscopic domain, however, thermodynamics is both powerful and useful. It enables one to draw rather precise and far-reaching conclusions from a few seemingly commonplace observations. This power comes from the implicit assumption that the equation of state is a regular function, for which the thermodynamic laws, which appear to be simple and naive at first sight, are in fact enormously restrictive.

1.2 THE FIRST LAW OF THERMODYNAMICS

In an *arbitrary* thermodynamic transformation let ΔQ denote the net amount of heat absorbed by the system and ΔW the net amount of work done by the system. The first law of thermodynamics states that the quantity ΔU, defined by

$$\Delta U = \Delta Q - \Delta W \tag{1.1}$$

is the same for all transformations leading from a given initial state to a given final state.

This immediately defines a state function U, called the internal energy. Its value for any state may be found as follows. Choose an arbitrary fixed state as reference. Then the internal energy of any state is $\Delta Q - \Delta W$ in *any* transformation which leads from the reference state to the state in question. It is defined only up to an arbitrary additive constant. Empirically U is an extensive quantity. This follows from the saturation property of molecular forces, namely, that the energy of a substance is doubled if its mass is doubled.

The experimental foundation of the first law is Joule's demonstration of the equivalence between heat and mechanical energy—the feasiblity of converting mechanical work completely into heat. The inclusion of heat as a form of energy leads naturally to the inclusion of heat in the statement of the conservation of energy. The first law is precisely such a statement.

In an infinitesimal transformation, the first law reduces to the statement that the differential

$$dU = dQ - dW \tag{1.2}$$

is exact. That is, there exists a function U whose differential is dU; or, the integral $\int dU$ is independent of the path of the integration and depends only on the limits of integration. This property is obviously not shared by dQ or dW.

Given a differential of the form $df = g(A, B)\,dA + h(A, B)\,dB$, the condition that df be exact is $\partial g/\partial B = \partial h/\partial A$. Let us explore some of the consequences of the exactness of dU. Consider a system whose parameters are P, V, T. Any pair of these three parameters may be chosen to be the independent variables that completely specify the state of the system. The other parameter is then determined by the equation of state. We may, for example, consider $U = U(P, V)$. Then*

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \tag{1.3}$$

The requirement that dU be exact immediately leads to the result

$$\frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial P}\right)_V\right]_P = \frac{\partial}{\partial P}\left[\left(\frac{\partial U}{\partial V}\right)_P\right]_V \tag{1.4}$$

The following equations, expressing the heat absorbed by a system during an infinitesimal reversible transformation (in which $dW = P\,dV$), are easily ob-

*The symbol $(\partial U/\partial P)_V$ denotes the partial derivative of U with respect to P, with V held constant.

tained by successively choosing as independent variables the pairs (P, V), (P, T), and (V, T):

$$dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV \tag{1.5}$$

$$dQ = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP \tag{1.6}$$

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \tag{1.7}$$

Called dQ equations, these are of little practical use in their present form, because the partial derivatives that appear are usually unknown and inaccessible to direct measurement. They will be transformed to more useful forms when we come to the second law of thermodynamics.

It can be immediated deduced from the dQ equations that

$$C_V \equiv \left(\frac{\Delta Q}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{1.8}$$

$$C_P \equiv \left(\frac{\Delta Q}{\Delta T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{1.9}$$

where $H = U + PV$ is called the enthalpy of the system.

We consider the following examples of the application of the first law.

(a) *Analysis of Joule's Free-Expansion Experiment.* The experiment in question concerns the free expansion of an ideal gas into a vacuum. The initial and final situations are illustrated in Fig. 1.3.

Experimental Finding. $T_1 = T_2$.

Deductions. $\Delta W = 0$, since the gas performs no work on its external surrounding. $\Delta Q = 0$, since $\Delta T = 0$. Therefore, $\Delta U = 0$ by the first law.

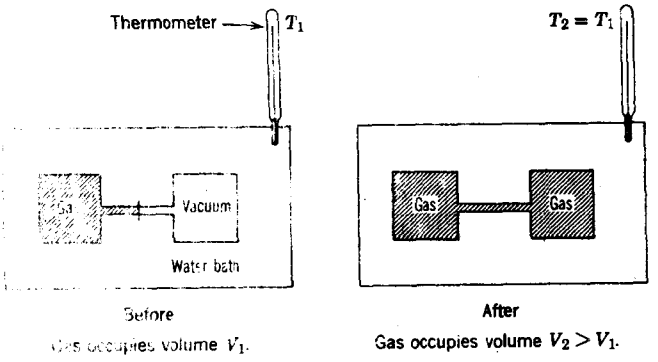


Fig. 1.3 Joule's free-expansion experiment.