

STATISTICAL
MECHANICS

STATISTICAL MECHANICS

PREFACE

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.

The purpose of the book is to teach statistical mechanics as an integral part of theoretical physics, a discipline that aims to describe all natural phenomena on the basis of a single unifying theory. This theory, at present, is quantum mechanics.

This does not mean that the sole concern of this book is the derivation of statistical mechanics from quantum mechanics, because such a pre-occupation would not serve the purpose of teaching. Furthermore, such a derivation does not at present exist.

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.

Certain passages in the book set in reduced type may be omitted on first reading. At the end of most chapters a set of problems is included. They are designed to illustrate or to extend the discussion given in the text. The serious reader should consider them to be an integral part of the book.

The material in this book probably cannot be completely covered in a year's study. It might be helpful, therefore, to give a list of chapters that form the "hard core" of the book. They are the following: Chapters 3, 4, 7, 8 (possibly excluding Sections 8.5, 8.6, and 8.7), 9, 11, and 12.

KERSON HUANG

Cambridge, Massachusetts
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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 B . 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

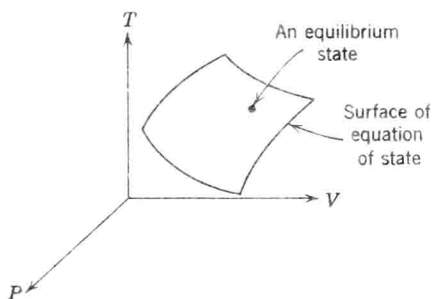


Fig. 1.1. Geometrical representation of the equation of state.

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 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 converse 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

$$dW = P dV$$

Generalization to other cases is obvious.

(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 constant 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:

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

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 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 ($^{\circ}\text{K}$). 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:

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

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

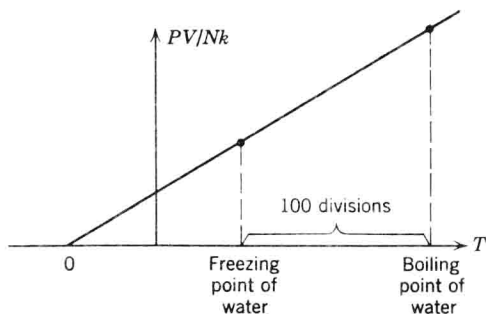


Fig. 1.2. The ideal-gas temperature scale.

important to remember that this model may not rigorously correspond to the physical world; the thermodynamic laws may not be rigorous consequences of the molecular laws, which we take to be the fundamental laws of the physical world. The thermodynamic laws, then, are introduced only as phenomenological statements that conveniently summarize macroscopic experience. As such, they must be at least approximately true for the physical world. The relation between thermodynamic laws and molecular laws is discussed later, in kinetic theory.

Thermodynamics, as a mathematical model, can be axiomatized, in the best tradition of mathematics. Nevertheless, in view of the foregoing discussion, such a formulation contributes little to the understanding of physics.

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

$$\Delta U = \Delta Q - \Delta W \quad (1.1)$$

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 feasibility 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

$$dU = dQ - dW \quad (1.2)$$

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*

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

The requirement that dU be exact immediately leads to the result

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

The following equations, expressing the heat absorbed by a system during an infinitesimal reversible transformation (in which $dW = P dV$), are easily obtained by successively choosing as independent variables the pairs (P, V) , (P, T) , and (V, T) :

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

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

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

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 immediately deduced from the dQ equations that

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

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

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

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