of this particle, indicating the regions of this space which are accessible to the particle.

**2.2** Consider a system consisting of two weakly interacting particles, each of mass $m$ and free to move in one dimension. Denote the respective position coordinates of the two particles by $x_1$ and $x_2$, their respective momenta by $p_1$ and $p_2$. The particles are confined within a box with end walls located at $x = 0$ and $x = L$. The total energy of the system is known to lie between $E$ and $E + \delta E$. Since it is difficult to draw a four-dimensional phase space, draw separately the part of the phase space involving $x_1$ and $x_2$ and that involving $p_1$ and $p_2$. Indicate on these diagrams the regions of phase space accessible to the system.

**2.3** Consider an ensemble of classical one-dimensional harmonic oscillators.

(*a*) Let the displacement $x$ of an oscillator as a function of time $t$ be given by $x = A \cos(\omega t + \varphi)$. Assume that the phase angle $\varphi$ is equally likely to assume any value in its range $0 < \varphi < 2\pi$. The probability $w(\varphi)\, d\varphi$ that $\varphi$ lies in the range between $\varphi$ and $\varphi + d\varphi$ is then simply $w(\varphi)\, d\varphi = (2\pi)^{-1}\, d\varphi$. For any fixed time $t$, find the probability $P(x)\, dx$ that $x$ lies between $x$ and $x + dx$ by summing $w(\varphi)\, d\varphi$ over all angles $\varphi$ for which $x$ lies in this range. Express $P(x)$ in terms of $A$ and $x$.

(*b*) Consider the classical phase space for such an ensemble of oscillators, their energy being known to lie in the small range between $E$ and $E + \delta E$. Calculate $P(x)\, dx$ by taking the ratio of that volume of phase space lying in this energy range *and* in the range between $x$ and $x + dx$ to the total volume of phase space lying in the energy range between $E$ and $E + \delta E$ (see Fig. 2·3·1). Express $P(x)$ in terms of $E$ and $x$. By relating $E$ to the amplitude $A$, show that the result is the same as that obtained in part (*a*).

**2.4** Consider an isolated system consisting of a large number $N$ of very weakly interacting localized particles of spin $\frac{1}{2}$. Each particle has a magnetic moment $\mu$ which can point either parallel or antiparallel to an applied field $H$. The energy $E$ of the system is then $E = -(n_1 - n_2)\mu H$, where $n_1$ is the number of spins aligned parallel to $H$ and $n_2$ the number of spins aligned antiparallel to $H$.

(*a*) Consider the energy range between $E$ and $E + \delta E$ where $\delta E$ is very small compared to $E$ but is microscopically large so that $\delta E \gg \mu H$. What is the total number of states $\Omega(E)$ lying in this energy range?

(*b*) Write down an expression for $\ln \Omega(E)$ as a function of $E$. Simplify this expression by applying Stirling's formula in its simplest form (A·6·2).

(*c*) Assume that the energy $E$ is in a region where $\Omega(E)$ is appreciable, i.e., that it is not close to the extreme possible values $\pm N\mu H$ which it can assume. In this case apply a Gaussian approximation to part (*a*) to obtain a simple expression for $\Omega(E)$ as a function of $E$.

**2.5** Consider the infinitesimal quantity

$$A\, dx + B\, dy \equiv đF$$

where $A$ and $B$ are both functions of $x$ and $y$.

(*a*) Suppose that $đF$ is an exact differential so that $F = F(x,y)$. Show that $A$ and $B$ must then satisfy the condition

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$$

(*b*) If $đF$ is an exact differential, show that the integral $\int đF$ evaluated along *any* closed path in the $xy$ plane must vanish.

**2.6** Consider the infinitesimal quantity

$$(x^2 - y)\, dx + x\, dy \equiv đF \qquad (1)$$

(*a*) Is this an exact differential?

(*b*) Evaluate the integral $\int đF$ between the points (1,1) and (2,2) of Fig. 2·11·1 along the straight-line paths connecting the following points:

$$(1,1) \to (1,2) \to (2,2)$$
$$(1,1) \to (2,1) \to (2,2)$$
$$(1,1) \to (2,2)$$

(*c*) Suppose that both sides of (1) are divided by $x^2$. This yields the quantity $đG = đF/x^2$. Is $đG$ an exact differential?

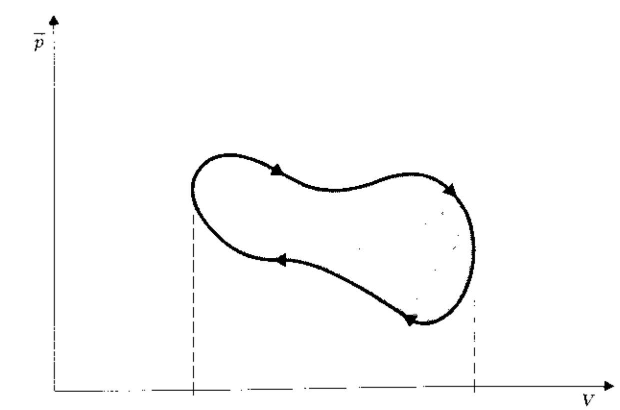
(*d*) Evaluate the integral $\int đG$ along the three paths of part (*b*).

**2.7** Consider a particle confined within a box in the shape of a cube of edges $L_x = L_y = L_z$. The possible energy levels of this particle are then given by (2·1·3).

(*a*) Suppose that the particle is in a given state specified by particular values of the three integers $n_x$, $n_y$, and $n_z$. By considering how the energy of this state must change when the length $L_x$ of the box is changed quasistatically by a small amount $dL_x$, show that the force exerted by the particle in this state on a wall perpendicular to the $x$ axis is given by $F_x = -\partial E/\partial L_x$.

(*b*) Calculate explicitly the force per unit area (or pressure) on this wall. By averaging over all possible states, find an expression for the mean pressure on this wall. (Exploit the property that the average values $\overline{n_x^2} = \overline{n_y^2} = \overline{n_z^2}$ must all be equal by symmetry.) Show that this mean pressure can be very simply expressed in terms of the mean energy $\bar{E}$ of the particle and the volume $V = L_x L_y L_z$ of the box.

**2.8** A system undergoes a quasi-static process which appears in a diagram of mean pressure $\bar{p}$ versus volume $V$ as a closed curve. (See diagram. Such a process is called "cyclic" since the system ends up in a final macrostate which is identical to its initial macrostate.) Show that the work done by the system is given by the area contained within the closed curve.




**2.9** The tension in a wire is increased quasi-statically from $F_1$ to $F_2$. If the wire has length $L$, cross-sectional area $A$, and Young's modulus $Y$, calculate the work done.

**2.10** The mean pressure $\bar{p}$ of a thermally insulated amount of gas varies with its volume $V$ according to the relation

$$\bar{p}V^{\gamma} = K$$

where $\gamma$ and $K$ are constants. Find the work done by this gas in a quasistatic process from a macrostate with pressure $\bar{p}_i$ and volume $V_i$ to one with pressure $\bar{p}_f$ and volume $V_f$. Express your answer in terms of $\bar{p}_i$, $V_i$, $\bar{p}_f$, $V_f$, and $\gamma$.

**2.11** In a quasi-static process $A \rightarrow B$ (see diagram) in which no heat is exchanged with the environment, the mean pressure $\bar{p}$ of a certain amount of gas is found to change with its volume $V$ according to the relation

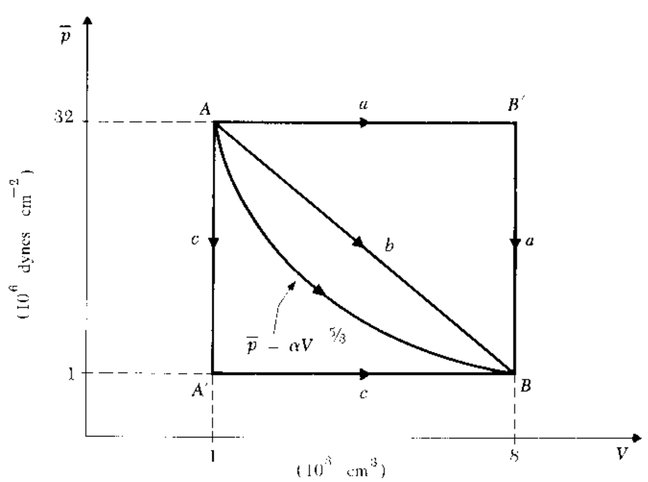
$$\bar{p} = \alpha V^{-5/3}$$

where $\alpha$ is a constant. Find the quasi-static work done and the net heat absorbed by this system in each of the following three processes, all of which take the system from macrostate $A$ to macrostate $B$.

(*a*) The system is expanded from its original to its final volume, heat being added to maintain the pressure constant. The volume is then kept constant, and heat is extracted to reduce the pressure to $10^6$ dynes cm$^{-2}$.

(*b*) The volume is increased and heat is supplied to cause the pressure to decrease linearly with the volume.

(*c*) The two steps of process (*a*) are performed in the opposite order.




# Statistical thermodynamics

THE FUNDAMENTAL statistical postulate of equal a priori probabilities can be used as the basis of the entire theory of systems in equilibrium. In addition, the hypothesis mentioned at the end of Sec. 2·3 (and based on the assumed validity of the $H$ theorem) also makes a statement about isolated systems not in equilibrium, asserting that these tend to approach ultimate equilibrium situations (characterized by the uniform statistical distribution over accessible states which is demanded by the fundamental postulate).

In this chapter we shall show how these basic statements lead to some very general conclusions concerning all macroscopic systems. The important results and relationships thus established constitute the basic framework of the discipline of "equilibrium statistical mechanics" or, as it is sometimes called, "statistical thermodynamics." Indeed, the major portion of this book will deal with systems in equilibrium and will therefore be an elaboration of the fundamental ideas developed in this chapter.

## IRREVERSIBILITY AND THE ATTAINMENT OF EQUILIBRIUM

## 3·1 *Equilibrium conditions and constraints*

Consider an isolated system whose energy is specified to lie in a narrow range. As usual, we denote by $\Omega$ the number of states accessible to this system. By our fundamental postulate we know that, in equilibrium, such a system is equally likely to be found in any one of these states.

We recall briefly what we mean by "accessible states." There are in general some specified conditions which the system is known to satisfy. These act as constraints which limit the number of states in which the system can possibly be found without violating these conditions. The accessible states are then all the states consistent with these constraints.

The constraints can be described more quantitatively by specifying the evaluated for the mean energy $E = \bar{E}$ of the gas. Here the right side is only a function of $E$, but *not* of $V$. Thus it follows that, for an ideal gas $\beta = \beta(\bar{E})$

or

$$\bar{E} = \bar{E}(T) \tag{3·12·11}$$

Hence one reaches the important conclusion that the mean energy of an ideal gas depends only on its temperature and is independent of its volume. This result is physically plausible. An increase in volume of the container increases the mean distance between the molecules and thus changes, in general, their mean potential energy of mutual interaction. But in the case of an *ideal* gas this interaction energy is negligibly small, while the kinetic and internal energies of the molecules do not depend on the distances between them. Hence the total energy of the gas remains unchanged.

## SUGGESTIONS FOR SUPPLEMENTARY READING

The following books give a statistical discussion somewhat similar to the one of this text:


C. Kittel: "Elementary Statistical Physics," secs. 1–10, John Wiley & Sons, Inc., New York, 1958.

R. Becker: "Theorie der Wärme," secs. 32–35, 45, Springer-Verlag, Berlin, 1955. (A good book, but in German.)

L. Landau and E. M. Lifshitz: "Statistical Physics," secs. 1–13, Addison-Wesley, Reading, Mass., 1963.


The following books are good introductions to classical thermodynamics from a completely macroscopic point of view:


M. W. Zemansky: "Heat and Thermodynamics," 4th ed, McGraw-Hill Book Company, New York, 1957.

E. Fermi: "Thermodynamics," Dover Publications, New York, 1957.

H. B. Callen: "Thermodynamics," John Wiley & Sons, Inc., New York, 1960. (More sophisticated in approach than the preceding books.)


## PROBLEMS



**3.1** A box is separated by a partition which divides its volume in the ratio 3:1. The larger portion of the box contains 1000 molecules of Ne gas; the smaller, 100 molecules of He gas. A small hole is punctured in the partition, and one waits until equilibrium is attained.

(*a*) Find the mean number of molecules of each type on either side of the partition.

(*b*) What is the probability of finding 1000 molecules of Ne gas in the larger portion and 100 molecules of He gas in the smaller (i.e., the same distribution as in the initial system)?

**3.2** Consider a system of $N$ localized weakly interacting particles, each of spin $\frac{1}{2}$ and magnetic moment $\mu$, located in an external magnetic field $H$. This system was already discussed in Problem 2.4.

(*a*) Using the expression for $\ln \Omega(E)$ calculated in Problem 2.4*b* and the definition $\beta = \partial \ln \Omega / \partial E$, find the relation between the absolute temperature $T$ and the total energy $E$ of this system.

(*b*) Under what circumstances is $T$ negative?

(*c*) The total magnetic moment $M$ of this system is related to its energy $E$. Use the result of part (*a*) to find $M$ as a function of $H$ and the absolute temperature $T$.

**3.3** Consider two spin systems $A$ and $A'$ placed in an external field $H$. System $A$ consists of $N$ weakly interacting localized particles of spin $\frac{1}{2}$ and magnetic moment $\mu$. Similarly, system $A'$ consists of $N'$ weakly interacting localized particles of spin $\frac{1}{2}$ and magnetic moment $\mu'$. The two systems are initially isolated with respective total energies $bN\mu H$ and $b'N'\mu'H$. They are then placed in thermal contact with each other. Suppose that $|b| \ll 1$ and $|b'| \ll 1$ so that the simple expressions of Problem 2.4*c* can be used for the densities of states of the two systems.

(*a*) In the most probable situation corresponding to the final thermal equilibrium, how is the energy $\tilde{E}$ of system $A$ related to the energy $\tilde{E}'$ of system $A'$?

(*b*) What is the value of the energy $\tilde{E}$ of system $A$?

(*c*) What is the heat $Q$ absorbed by system $A$ in going from the initial situation to the final situation when it is in equilibrium with $A'$?

(*d*) What is the probability $P(E)\,dE$ that $A$ has its final energy in the range between $E$ and $E + dE$?

(*e*) What is the dispersion $(\Delta^*E)^2 \equiv \overline{(E - \bar{E})^2}$ of the energy $E$ of system $A$ in the final equilibrium situation?

(*f*) What is the value of the relative energy spread $|\Delta^*E/\bar{E}|$ in the case when $N' \gg N$?

**3.4** Suppose that a system $A$ is placed into thermal contact with a heat reservoir $A'$ which is at an absolute temperature $T'$ and that $A$ absorbs an amount of heat $Q$ in this process. Show that the entropy increase $\Delta S$ of $A$ in this process satisfies the inequality $\Delta S \geq Q/T'$, where the equals sign is only valid if the initial temperature of $A$ differs infinitesimally from the temperature $T'$ of $A'$.

**3.5** A system consists of $N_1$ molecules of type 1 and $N_2$ molecules of type 2 confined within a box of volume $V$. The molecules are supposed to interact very weakly so that they constitute an ideal gas mixture.

(*a*) How does the total number of states $\Omega(E)$ in the range between $E$ and $E + \delta E$ depend on the volume $V$ of this system? You may treat the problem classically.

(*b*) Use this result to find the equation of state of this system, i.e., to find its mean pressure $\bar{p}$ as a function of $V$ and $T$.

**3.6** A glass bulb contains air at room temperature and at a pressure of 1 atmosphere. It is placed in a chamber filled with helium gas at 1 atmosphere and at room temperature. A few months later, the experimenter happens to read in a journal article that the particular glass of which the bulb is made is quite permeable to helium, although not to any other gases. Assuming that equilibrium has been attained by this time, what gas pressure will the experimenter measure inside the bulb when he goes back to check?