CHAPTER

The first law of thermodynamics

1.1 MACROSCOPIC PHYSICS

Statistical physics is devoted to the study of the physical properties of macroscopic systems, i.e. systems consisting of a very large number of atoms or molecules. A piece of copper weighing a few grams or a litre of air at atmospheric pressure and room temperature are examples of macroscopic systems. In general the number of particles in such a system will be of the order of magnitude of Avogadro's number $N_0 = 6 \times 10^{23}$. Even if one knows the law of interaction between the particles, the enormousness of Avogadro's number precludes handling a macroscopic system in the way in which one would treat a simple system—say planetary motion according to classical mechanics or the hydrogen molecule according to quantum mechanics. One can never obtain experimentally a complete microscopic* specification of such a system, i.e. a knowledge of some 10^{23} coordinates. Even if one were given this initial information, one would not be able to solve the equations of motion; some 10^{23} of them!

In spite of the enormous complexity of macroscopic bodies when viewed from an atomistic viewpoint, one knows from everyday experience as well as from precision experiments that macroscopic bodies obey quite definite

*'Microscopic' is here used in contrast to 'macroscopic'. It means a complete atomistic specification.

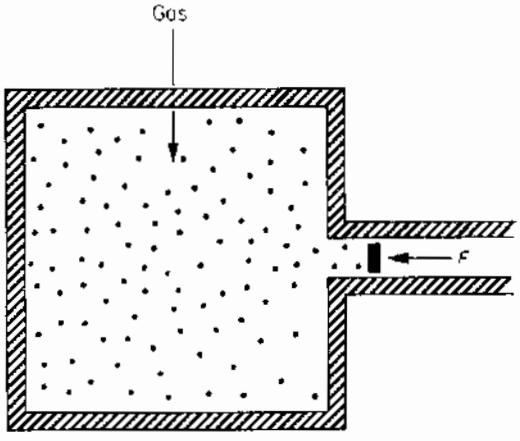


Fig. 1.1. Gas exerting pressure on movable piston, balanced by external applied force F.

laws. Thus when a hot and a cold body are put into thermal contact temperature equalization occurs; water at standard atmospheric pressure always boils at the same temperature (by definition called 100 °C); the pressure exerted by a dilute gas on a containing wall is given by the ideal gas laws. These examples illustrate that the laws of macroscopic bodies are quite different from those of mechanics or electromagnetic theory. They do not afford a complete microscopic description of a system (e.g. the position of each molecule of a gas at each instant of time). They provide certain macroscopic observable quantities, such as pressure or temperature. These represent averages over microscopic properties. Thus the macroscopic laws are of a statistical nature. But because of the enormous number of particles involved, the fluctuations which are an essential feature of a statistical theory turn out to be extremely small. In practice they can only be observed under very special conditions. In general they will be utterly negligible, and the statistical laws will in practice lead to statements of complete certainty.

To illustrate these ideas consider the pressure exerted by a gas on the walls of a containing vessel. We measure the pressure by means of a gauge attached to the vessel. We can think of this gauge as a freely movable piston to which a variable force F is applied, for example by means of a spring (Fig. 1.1). When the piston is at rest in equilibrium the force F balances the pressure P of the gas: $P = F/A$ where A is the area of the piston.

In contrast to this macroscopic determination of pressure consider how the pressure actually comes about.* According to the kinetic theory the

*For a detailed derivation of the pressure of a perfect gas from kinetic theory, see Flowers and Mendoza,[16] section 5.1.2, R. Becker,[2] section 24, or Present,[11] Chapter 2.

molecules of the gas are undergoing elastic collisions with the walls. The pressure due to these collisions is certainly not a strictly constant time-independent quantity. On the contrary the instantaneous force acting on the piston is a rapidly fluctuating quantity. By the pressure of the gas we mean the average of this fluctuating force over a time interval sufficiently long for many collisions to have occurred in this time. We may then use the steady-state velocity distribution of the molecules to calculate the momentum transfer per unit area per unit time from the molecules to the wall, i.e. the pressure. The applied force F acting on the piston can of course only approximately balance these irregular impulses due to molecular collisions. On average the piston is at rest but it will perform small irregular vibrations about its equilibrium position as a consequence of the individual molecular collisions. These small irregular movements are known as Brownian motion (Flowers and Mendoza,[26] section 4.4.2). In the case of our piston, and generally, these minute movements are totally unobservable. It is only with very small macroscopic bodies (such as tiny particles suspended in a liquid) or very sensitive apparatus (such as the very delicate suspension of a galvanometer—see section 7.9.1) that Brownian motion can be observed. It represents one of the ultimate limitations on the accuracy of measurements that can be achieved.

There are two approaches to the study of macroscopic physics. Historically the oldest approach, developed mainly in the first half of the 19th century by such men as Carnot, Clausius, William Thomson (the later Lord Kelvin), Robert Mayer and Joule, is that of classical thermodynamics. This is based on a small number of basic principles—the laws of thermodynamics—which are deductions from and generalizations of a large body of experiments on macroscopic systems. They are phenomenological laws, justified by their success in describing macroscopic phenomena. They are not derived from a microscopic picture but avoid all atomic concepts and operate exclusively with macroscopic variables, such as pressure, volume, temperature, describing the properties of systems in terms of these. Of course, the avoidance of atomic concepts severely limits the information that thermodynamics can provide about a system. In particular, the equation of state (e.g. for an ideal gas: $PV = RT$) which relates the macroscopic variables and which distinguishes one system from another must be derived from experiment. But there are many situations where a microscopic description is not necessary or not practicable and where thermodynamics proves its power to make far-reaching deductions of great generality.*

The second approach to macroscopic physics is that of statistical mechanics. This starts from the atomic constitution of matter and endeavours to derive

*For a superb if not easy account of classical thermodynamics, showing its aesthetic appeal, logical structure and power, see the book by Pippard.[9]

the laws of macroscopic bodies from the atomic properties. This line of approach originated in Maxwell's kinetic theory of gases which led to the profound works of Boltzmann and of Gibbs. There are two aspects to statistical mechanics. One aim is to *derive* the thermodynamic laws of macroscopic bodies from the laws governing their atomic behaviour. This is a fascinating but very difficult field. Nowadays one has a fairly general understanding of the underlying physics but most physicists working in the field would probably agree that no real proofs exist. In this book we shall not consider these aspects of statistical mechanics and shall only give arguments which make the thermodynamic laws plausible from the microscopic viewpoint.

The second objective of statistical mechanics is to derive the properties of a macroscopic system—for example, its equation of state—from its microscopic properties. Essentially this is done by averaging over unobservable microscopic coordinates leaving only macroscopic coordinates such as the volume of a body, as well as other macroscopic variables, such as temperature or specific heat, which have no counterpart in mechanics and which represent averages over unobservable microscopic coordinates.

This division of macroscopic physics into thermodynamics and statistical mechanics is largely of historical origin. We shall not follow this development. Instead we shall emphasize the unity of the subject, showing how the two aspects illuminate each other, and we shall use whichever is more appropriate.

1.2 SOME THERMAL CONCEPTS

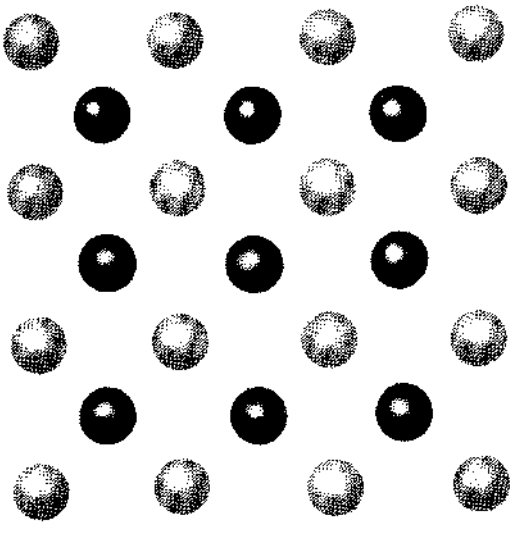
Some of the variables which were introduced in the last section to describe a macroscopic system, such as its volume or pressure, have a direct meaning in terms of mechanical concepts, e.g. one can measure the pressure of gas in a container by means of a mercury manometer. However, some of the concepts are quite foreign to mechanics. Of these the one most basic to the whole of statistical thermodynamics is that of temperature. Originally temperature is related to the sensations of 'hot' and 'cold'. The most remarkable feature of temperature is its tendency to equalization: i.e. if a hot and a cold body are put into thermal contact, the hot body cools down and the cold body warms up until both bodies are at the same temperature. This equalization is due to a net flow of energy from the hotter to the colder body. Such a flow of energy is called a flow of heat. When this flow of heat ceases, the two bodies are in thermal equilibrium. The basic fact of experience which enables one to compare the temperatures of two bodies by means of a third body is that if two bodies are each in thermal equilibrium with a third body they are also in thermal equilibrium with each other. This statement is sometimes referred to as the zeroth law of thermodynamics. To measure temperature, one can utilize any convenient property of matter which depends

on its degree of hotness, such as the electric resistance of a platinum wire, the volume (i.e. length in a glass capillary) of a mass of mercury, the pressure of a given mass of gas contained in a fixed volume. For each of these thermometers one can then define a Celsius (centigrade) scale by calling the temperatures of the ice and steam points* 0 °C and 100 °C and interpolating linearly for other temperatures. It turns out that these different temperature scales do not agree exactly (except at the fixed points, of course). They depend on the particular thermometer used. We shall see presently that this arbitrariness is removed by the second law of thermodynamics which enables one to define an *absolute temperature scale*, i.e. one which is independent of the experimental arrangement used for measuring the temperature. The physical meaning of the absolute temperature is revealed by statistical mechanics. It turns out to be a measure of the energy associated with the molecular, macroscopically unobserved, motions of a system.

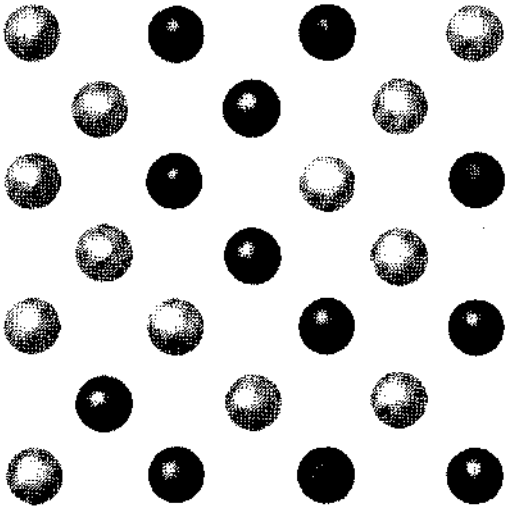
Above we considered temperature equilibrium. More generally, let us consider an isolated system. This system may be in a state containing all sorts of pressure differences, temperature gradients, inhomogeneities of density, concentrations, etc. A system in such a state is of course not in equilibrium. It will change with time as such processes as pressure equalization, thermal conduction, diffusion, etc., occur. Left to itself, the system eventually reaches a state in which all these pressure gradients, etc., have disappeared and the system undergoes no further macroscopically observable changes. We call such a state an *equilibrium state*. Of course, this is not static equilibrium. Sufficiently refined experiments will show up the thermal motions, a typical example being Brownian motion. The time that a system requires to reach equilibrium depends on the processes involved. In general there will be several mechanisms, as we have seen; each will possess its own characteristic relaxation time. After a time long compared to all relaxation times the system will be in equilibrium.

On the other hand there are frequently situations where the relaxation time for a particular process is very long compared with the time for which a system is observed. One can then ignore this process altogether. It occurs too slowly to be of any consequence. In many cases the relaxation time is for practical purposes infinite. Consider a binary alloy, for example β-brass which consists of Cu and Zn atoms in equal numbers. At sufficiently low temperatures, the stable equilibrium configuration of the atoms is one where they are ordered in a regular mosaic-like pattern in the crystal lattice. No such ordering occurs at high temperatures. The two situations are schematically illustrated for a two-dimensional model lattice in Figs. 1.2(a) and (b). If such an

*The ice point is defined as the temperature at which pure ice coexists in equilibrium with air-saturated water at a pressure of one standard atmosphere. The steam point is the temperature at which pure water and pure steam coexist in equilibrium at a pressure of one standard atmosphere.



(*a*) Ordered



(*b*) Disordered

Fig. 1.2. Schematic two-dimensional model of a binary alloy: (*a*) in ordered state, (*b*) in disordered state.

alloy is rapidly cooled from a high to a low temperature, the atoms get 'frozen' into their instantaneous disordered pattern. This is a metastable state but the rate of migration of the atoms at the low temperature is so small that for practical purposes the disorder will persist for all times.

In β-brass the Cu and Zn atoms each form a simple cubic lattice, the two lattices being interlocked so that each Cu atom is at the centre of a cube formed by 8 Zn atoms, and vice versa. There is an attractive force between the Cu and Zn atoms. At low temperatures this attraction dominates over the comparatively feeble thermal motion resulting in an ordered state, but at high temperatures the thermal agitation wins. The ordering shows up as extra diffraction lines in x-ray diffraction, since the two types of atom will scatter x-rays differently.

We have discussed relaxation times in order to explain what is meant by equilibrium. The calculation of how long it takes for equilibrium to establish itself, and of non-equilibrium processes generally, is extremely difficult. We shall not consider such questions in this book but shall exclusively study the properties of systems in equilibrium without inquiring how they reached equilibrium. But we shall of course require a criterion for characterizing an equilibrium state. The second law of thermodynamics provides just such a criterion.

The description of a system is particularly simple for equilibrium states. Thus for a fluid not in equilibrium it may be necessary to specify its density at every point in space as a function of time, whereas for equilibrium the density is uniform and constant in time. The equilibrium state of a system is fully determined by a few macroscopic variables. These variables then determine all other macroscopic properties of the system. Such properties which depend only on the state of a system are called *functions of state*. The state of a homogeneous fluid is fully determined by its mass M, volume V, and pressure P. Its temperature T is then a function of state determined by these, i.e.

$$T=f(P,V,M) \ . \tag{1.1}$$

Eq. (1.1) is called the equation of state of the fluid. Of course, we could have chosen other independent variables to specify the state of the fluid, for example M, V and T, and found P from Eq. (1.1).

In our discussion of a fluid we tacitly assumed the characteristic property of a fluid: that its thermodynamic properties are independent of its shape. This makes a fluid a very simple system to discuss. More complicated systems require a larger number of parameters to determine a unique state and lead to a more complicated equation of state. This mode of description of a system breaks down if its state depends not only on the instantaneous values of certain parameters but also on its previous history, i.e. in the case of

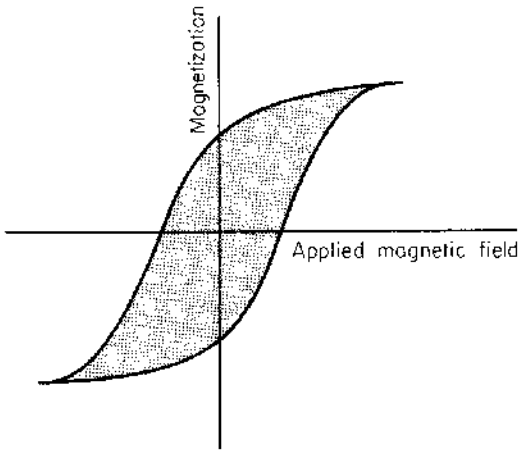


Fig. 1.3. Hysteresis in a ferromagnetic material.

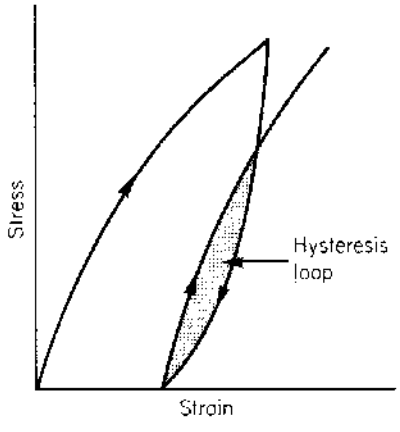


Fig. 1.4. Stress-strain relationship in a solid showing the hysteresis loop.

hysteresis effects such as occur in ferromagnetic materials or the plastic deformation of solids. In the former example the magnetization is not a unique function of the applied magnetic field (Fig. 1.3); in the latter, the strain is not a unique function of the applied stress (Fig. 1.4).*

In general the equation of state of a substance is very complicated. It must be found from experiment and does not allow a simple analytic representation. The perfect (or ideal) gas is an exception. For real gases, at sufficiently

*The elastic example is discussed by Flowers and Mendoza,[26] section 9.1.1, and more fully by A. H. Cottrell,[25] section 4.4.

low pressures, the pressure and volume of a fixed mass of gas are very nearly related by

$$PV = \text{const.} \tag{1.2}$$

at a given temperature. An equation such as (1.2), relating different states of a system, all at the *same* temperature, is called an *isotherm*. A perfect gas is defined to be a fluid for which the relation (1.2) holds *exactly* for an isotherm, i.e. a perfect gas represents an extrapolation to zero pressure from real gases. We can use this to define a (perfect) gas temperature scale T by the relation

$$T \propto \lim_{P \to 0} PV \ . \tag{1.3}$$

The gas temperature scale is then completely determined if we fix *one* point on it *by definition*. This point is taken as the triple point of water, i.e. the temperature at which ice, water and water vapour coexist in equilibrium. The reason for this choice is that the triple point corresponds to a unique temperature and pressure of the system (see section 8.3). The triple point temperature T_{tr} was chosen so that the size of the degree on the gas scale equals as nearly as possible the degree Celsius, i.e. according to the best available measurements there should be a temperature difference of 100 degrees between the steam and ice points. This criterion led to

$$T_{tr} \equiv 273.16\,\text{K} \tag{1.4}$$

being internationally adopted in 1954 as the *definition* of the triple point. (Very accurate measurements, in the future, of the steam and ice points on this temperature scale may result in their temperature difference being not *exactly* 100 degrees.) In Eq. (1.4) we have written K (kelvin) in anticipation of the fact that the gas scale will turn out to be identical with the absolute thermodynamic temperature scale. (Older notations for K are deg. or °K.) Any other absolute temperature is then, in principle, determined from Eqs. (1.3) and (1.4). The temperature of the ice point becomes 273.15 K.

The constant of proportionality, still missing in Eq. (1.3), is determined from accurate measurements with gas thermometers. For one mole (we shall always use the gram-mole) of gas one finds that

$$PV = RT \tag{1.5}$$

with the gas constant R having the value

$$R = 8.31\ \text{J mol}^{-1}\,\text{K}^{-1} \ . \tag{1.6}$$

From Avogadro's number

$$N_0 = 6.02 \times 10^{23} \text{ molecules/mole} \ , \tag{1.7}$$

we can calculate Boltzmann's constant k, i.e. the gas constant per molecule

$$k \equiv R/N_0 = 1.38 \times 10^{-23} \text{ J/K} \ . \tag{1.8}$$

The equation of state of a perfect gas consisting of N molecules can then be written

$$PV = NkT \ . \tag{1.9}$$

The physically significant quantity in this equation is the energy kT. Under classical conditions, i.e. when the theorem of equipartition of energy holds (see, for example, section 7.9.1 below, or Flowers and Mendoza,[26] sections 5.3 and 5.4.4), kT is of the order of the energy of one molecule in a macroscopic body at temperature T. By contrast, Boltzmann's constant is merely a measure of the size of the degree Celsius. At $T = 290$ K (room temperature)

$$kT = 4.0 \times 10^{-21} \text{ J} = \tfrac{1}{40} \text{ eV} \tag{1.10}$$

where we introduced the electron-volt (eV):

$$\begin{aligned} 1 \text{ eV} &= 1.60 \times 10^{-19} \text{ J} \\ &= 1.60 \times 10^{-12} \text{ erg} \ . \end{aligned} \tag{1.11}$$

The electron-volt is a reasonably-sized unit of energy on the atomic scale. For example, the ionization energy of atoms varies from about 4 eV to about 24 eV; the cohesive energy of solids varies from about 0.1 eV to about 10 eV per molecule, depending on the type of binding force.

1.3 THE FIRST LAW

We shall now consider the application of the universally valid principle of conservation of energy to macroscopic bodies. The new feature, which makes this different from merely a very complicated problem in mechanics, is that we do not want to describe the system on the microscopic scale, i.e. in terms of the individual molecular motions. This is of course impossibly complicated. Instead we want to describe the motion associated with these internal degrees of freedom in terms of macroscopic parameters.

Consider a system enclosed in walls impervious to heat transmission. Such walls are called adiabatic walls. (In practice one uses a dewar flask to obtain these conditions.) We can change the state of such a thermally isolated system by doing work on it. There is overwhelming experimental evidence that for a change from a definite state 1 to another definite state 2 of the system the same amount of work W is required irrespective of the mechanism used to perform the work or the intermediate states through which the system passes. Historically the earliest precise evidence comes from Joule's work, published in 1843, on the mechanical equivalent of heat. He produced given changes of state in a thermally isolated liquid in different ways. These included vigorously stirring the liquid with a paddle-wheel driven by weights (Fig. 1.5) and supplying electrical work by inserting a resistor carrying a current in the liquid (Fig. 1.6). The work done on the system—known in the first case from the motion of the weights, in the second from the current through the resistor and the potential drop across it—is the same in both cases.

We can hence define a *function of state* E, such that for a change from a state 1 to a state 2 of a *thermally isolated system* the work done on the system equals the change in E:

$$W = \Delta E \equiv E_2 - E_1 \ . \tag{1.12}$$

E is called the energy of the system. Except for an arbitrary choice of the zero of the energy scale (i.e. of the energy of a standard reference state) Eq. (1.12) determines the energy of any other state.

Suppose we now consider changes of state of the system no longer thermally isolated. It turns out that we can in general still effect the same change from state 1 to state 2 of the system but in general the work W done on the system does not equal the increase in energy ΔE of the system. We define the deficit

$$Q = \Delta E - W \tag{1.13}$$

as the heat supplied *to* the system. Eq. (1.13) is the general statement of the first law of thermodynamics. It is the law of conservation of energy applied to processes involving macroscopic bodies. The concept of heat, as introduced here, has all the properties associated with it from calorimetry experiments, etc. These are processes in which no work is done, the temperature changes being entirely due to heat transfer.

Let us consider how the energy E of a given state of a macroscopic system subdivides. (For definiteness you might think of the system as a gas or a crystal.) According to the laws of mechanics, the energy E is the sum of two contributions: (i) the energy of the macroscopic mass motion of the system, (ii) the internal energy of the system.

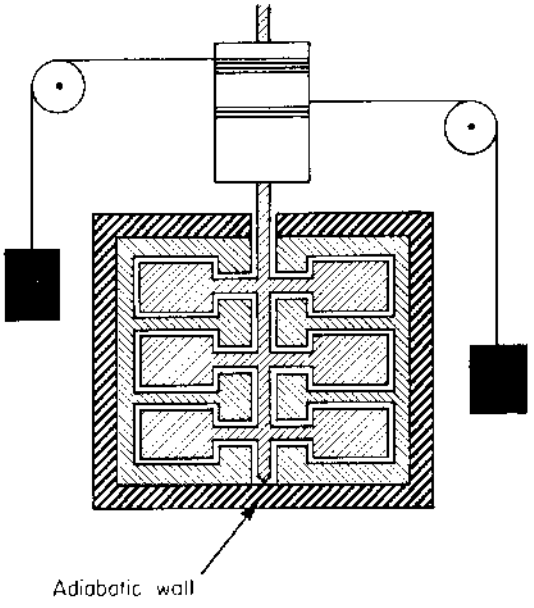


Fig. 1.5. Schematic picture of Joule's paddle-wheel experiment. A system for doing mechanical work on the liquid in the calorimeter.

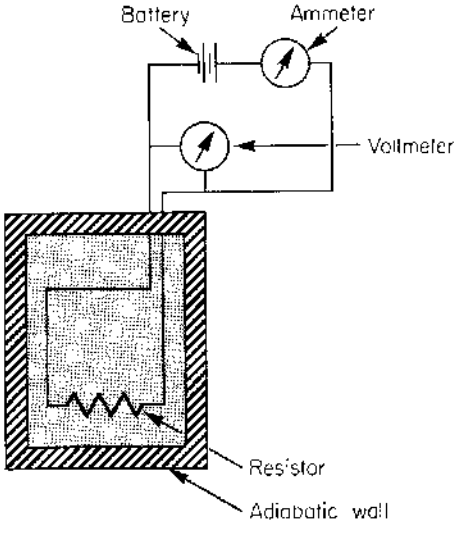


Fig. 1.6. A system for doing electrical work on the liquid in the calorimeter.

The energy of the mass motion consists of the kinetic energy of the motion of the centre of mass of the system, plus any potential energy which the system might possess due to the presence of an external field of force. For example, the system might be in a gravitational field. In statistical physics one is usually interested in the internal properties of systems, not in their macroscopic mass motion. Usually we shall be considering systems at rest and the potential energy of any external fields will be unimportant so that we shall not distinguish between the energy and the internal energy of a system.

The internal energy of a system is the energy associated with its internal degrees of freedom. It is the kinetic energy of the molecular motion (in a frame of reference in which the system is at rest) plus the potential energy of interaction of the molecules with each other. In an ideal gas at rest the internal energy is the sum of the kinetic energies of the translational motions of the molecules plus the internal energies of the molecules due to their rotations, etc. In a crystal the internal energy consists of the kinetic and potential energies of the atoms vibrating about their equilibrium positions in the crystal lattice. Thus the internal energy is the energy associated with the 'random' molecular motion of the system. We shall see later that the temperature of a system is a measure of its internal energy, which is therefore also called the thermal energy of the system.

The internal energy of a system is a function of state. For a fluid we could write $E=E(P,T)$ or $E=E(V,T)$, depending on which independent variables we choose to specify the state of the fluid. (We have suppressed the dependence on the mass of the fluid in these expressions for E as we shall usually be considering a constant mass, i.e. size of system, and are only interested in the variation of the other variables. In most cases the dependence on the size is trivial.) Thus for the change of a system from a state 1 to a state 2, ΔE in Eq. (1.13) is the difference of two energies, E_1 and E_2, for these two states as given by Eq. (1.12). By contrast Q and W are *not* changes in functions of state. There exists *no* function of state 'heat of a system' such that the system has a definite 'heat' in state 1 and a definite 'heat' in state 2, with Q the difference of these 'heats'. Similarly there exists *no* function of state 'work of a system' such that the system has a definite 'work' in state 1 and a definite 'work' in state 2, with W the difference of these 'works'. It follows that there is no conservation of 'heat' by itself, nor conservation of 'work' by itself. We only have conservation of energy, given by Eq. (1.13). *Work and heat flow are different forms of energy transfer.* The physical distinction between these two modes is that work is energy transfer via the macroscopically observable degrees of freedom of a system, whereas heat flow is the direct energy transfer between microscopic, i.e. internal, degrees of freedom. For examples of these two modes of energy transfer we again consider a gas. If the gas is contained in a thermally isolated cylinder, closed off at one end by a movable piston (Fig. 1.7), then work can be done on

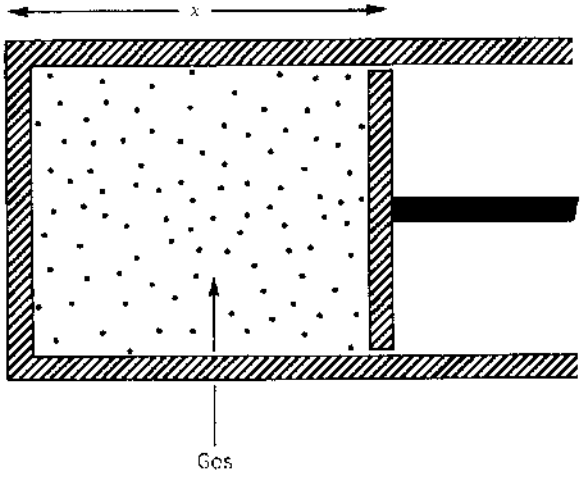


Fig. 1.7. Adiabatic compression of a gas.

the gas by compressing it. The macroscopic degree of freedom here corresponds to the position coordinate x of the piston. During the compression the gas is warmed up. From the molecular standpoint this warming up comes about because in elastic collisions with the moving piston the molecules gain energy which, as a result of subsequent collisions between molecules, is shared by all of them. Next assume that the gas is contained in a vessel with fixed walls and that there exists a temperature gradient in the gas. If we consider an element of area normal to this gradient, then a net transport of energy occurs across this area. This is the process of thermal conduction in the gas. Its explanation on the molecular scale is that molecules traversing this element of area from opposite sides possess different kinetic energies on average, corresponding to the different temperatures which exist in the regions from which those molecules came (for details, see Flowers and Mendoza,[26] Chapter 6, or Present,[11] Chapter 3).

Eq. (1.13) expresses the conservation of energy for finite changes. For infinitesimal changes we correspondingly write

$$\mathrm{d}E = đQ + đW \ . \tag{1.14}$$

Here $\mathrm{d}E$ is the infinitesimal change in the energy of the system, brought about by an infinitesimal amount of work $đW$ and an infinitesimal heat transfer $đQ$. We write $đW$ and $đQ$ (*not* $\mathrm{d}W$ and $\mathrm{d}Q$) to emphasize that, as discussed, these infinitesimal quantities are *not* changes in functions of state.

For a change from a definite state 1 to a definite state 2, ΔE is determined and hence, from Eq. (1.13), so is $(Q+W)$; but not Q and W separately.

Q and W depend on *how* the change from state 1 to state 2 takes place, i.e. *on the particular path taken by the process*. (Corresponding statements hold for infinitesimal changes.) Of course, for adiabatic changes, $Q=0$, the work is determined by initial and final states only, as we saw in Eq. (1.12). Similarly for a change involving no work ($W=0$), the heat transfer Q is determined. But these are the exceptions.

Of particular importance are *reversible changes*. For a process to be reversible it must be possible to reverse its direction by an infinitesimal change in the applied conditions. For a process to be reversible two conditions must be satisfied: (i) it must be a quasistatic process; (ii) there must be no hysteresis effects.

A *quasistatic* process is defined as a succession of equilibrium states of the system. Thus it represents an idealization from reality. For, to produce actual changes one must always have pressure differences, temperature differences, etc. But by making these sufficiently small one can ensure that a system is arbitrarily close to equilibrium at any instant. Strictly speaking, processes must occur infinitely slowly under these conditions. But in practice a process need only be slow compared to the relevant relaxation times in order that it may be considered quasistatic.

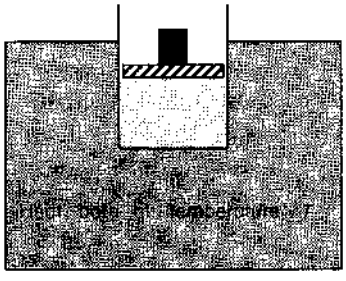


Fig. 1.8. Isothermal compression of a gas.

The importance of reversible processes is that for these the work performed on the system is well defined by the properties of the system. Consider the isothermal compression of a gas contained in a cylinder closed off by a piston (Fig. 1.8). To ensure isothermal compression (i.e. at constant temperature) the cylinder is placed in thermal contact with a *heat bath* at temperature T. By a heat bath we mean a body whose heat capacity is *very large* compared to that of the system it serves. Because of its large heat capacity, the temperature of the heat bath stays constant in spite of heat exchange with the system. The system is then also at the same constant temperature when in thermal equilibrium with the heat bath. To perform the compression quasistatically, the weight on the piston must be increased in a large number of very small increments. After each step we must wait for thermal and

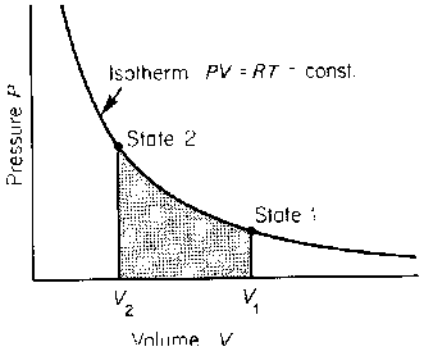


Fig. 1.9. The isotherm of an ideal gas. The shaded area is the work W done on the gas in compressing it isothermally from volume V_1 to V_2, Eq. (1.16).

mechanical equilibrium to establish itself. At any instant the pressure of the gas is then given from the equation of state in terms of the volume V, temperature T and mass M of gas. Let us consider one mole of an ideal gas. The locus of equilibrium states along which the quasistatic compression occurs is then given by the perfect gas law, Eq. (1.5), with T the temperature of the heat bath. This isotherm is plotted on the (P, V) diagram in Fig. 1.9. The work done on the gas in compressing it from V to $V+\mathrm{d}V$ is

$$\mathrm{d}W = -P\mathrm{d}V \; ; \tag{1.15a}$$

for compression one has $\mathrm{d}V<0$, making $đW>0$. In a finite change from volume V_1 to V_2 the work done on the system is

$$W = -\int_{V_1}^{V_2} P\mathrm{d}V = RT\ln\frac{V_1}{V_2} \; . \tag{1.16}$$

The significance of carrying changes out slowly becomes clear if we consider a fast change, such as a sudden compression of the gas in Fig. 1.8. We may imagine the piston initially clamped in a fixed position with a weight resting on it which exerts a pressure P_0 on the piston, which exceeds the gas pressure P. If the piston is unclamped and the volume of gas changes by $\mathrm{d}V(<0)$, then the work done by the weight on the system is $đW = -P_0\mathrm{d}V$; from $P_0>P$ it follows that (remember $\mathrm{d}V<0$!)

$$\mathrm{d}W > -P\mathrm{d}V \; . \tag{1.15b}$$

This inequality also holds for a sudden expansion of the gas, for example by suddenly lifting the piston. This produces a rarefaction of gas near the

piston initially, and the work done by the gas ($-đW$) during this expansion is less than the work which would be done by the gas during a slow expansion for which the gas pressure would be uniform: $(-đW) < P\,dV$, in agreement with Eq. (1.15b). An extreme example of this kind of process is the expansion of a gas into a vacuum (see the end of this section). In this case no work is done by the gas ($-đW = 0$), but $P\,dV$ is of course positive. In these sudden volume changes of the gas, pressure gradients are produced. The equalization of such gradients through mass flow of the gas is of course an irreversible process. (This point is discussed further in section 2.1.)

In order that the work done on the system (Fig. 1.8) in compressing the gas from volume V to $V+dV$ be given by Eq. (1.15a), there must be no frictional forces between cylinder and piston. Only in this way is there equality between the applied pressure P_0 due to the weight and the pressure P of the gas: $P_0 = P$. Only in this case is the work done on the system by the applied pressure ($đW = -P_0\,dV$) equal to $-P\,dV$. If there is friction then in compressing the gas the applied pressure P_0 must be greater than the gas pressure P, in order to overcome the frictional forces, and the work performed $đW$ exceeds $-P\,dV$, i.e. we have again obtained the inequality (1.15b). This inequality also holds for the expansion of the gas when there is friction. This relation between the applied pressure P_0 and the pressure P of the gas is illustrated in Fig. 1.10. The dashed curve shows the gas pressure P, the continuous curves the applied pressure P_0 for compression and for expansion. When there is no friction ($P_0 = P$) the two continuous curves coalesce on top of the dashed curve. If we carry out the cycle ABCDA by first

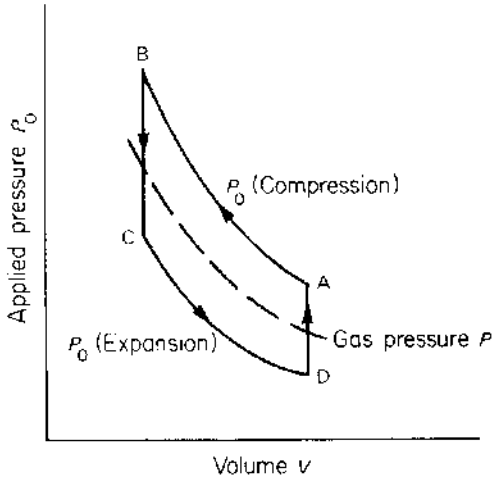


Fig. 1.10. Relation between applied pressure P_0 and volume V of a gas.

compressing and then expanding the gas, then the applied force has done a net amount of work on the system which is positive and is given by the area of the cycle ABCDA. This work is converted into thermal energy due to the friction, i.e. it produces a temperature rise. With the arrangement shown in Fig. 1.8 this thermal energy is of course passed on to the heat bath. The path ABCDA has the features of a hysteresis curve, similar to the cases illustrated in Figs. 1.3 and 1.4. All such hysteretic processes are irreversible. On reversing the external conditions, the system won't traverse the original path in the reverse direction but will follow a new path. It is only for a reversible process that the work done on the system can be expressed in terms of the parameters of state of the system; in the above example in terms of P and V.

We can sum up our conclusions about work in reversible and irreversible processes in the relations

$$đW \geqslant -P\mathrm{d}V \tag{1.15c}$$

where $đW$ is the work done on the system by external agencies while P and V are parameters of state of the system. The equality sign holds for reversible changes, the 'greater than' sign for irreversible changes.

Although the work done in a reversible change is well-defined, it does depend on the path, i.e. the intermediate states of the process. Thus we could join the states 1 and 2 in Fig. 1.9 by many paths other than the isotherm shown. Two such paths are shown in Fig. 1.11(*a*). The work done in going from state 1 to state 2 via paths A or B is given by the areas under the two curves respectively. For curve A

$$W_{\mathrm{A}} = -\int_{V_1,\,(\text{path A})}^{V_2} P\mathrm{d}V$$

and similarly for path B. The work depends on the path. This result is put differently in Fig. 1.11(*b*). Consider the cyclic process: from state 1 via path A to state 2 and then via path B′ (which is the reverse of path B of Fig. 1.11(*a*)) back to state 1. The work done on the system in this cycle is represented by the shaded area of Fig. 1.11(*b*) and is given by

$$-\oint P\mathrm{d}V = W_{\mathrm{A}} - W_{\mathrm{B}} \neq 0 \ .$$

Thus the work around a complete cycle does not vanish. In contrast the change in internal energy around any complete cycle does vanish,

$$\oint \mathrm{d}E = 0 \ ,$$

because at *any* point on the path (e.g. at 1 in Fig. 1.11(*b*)) E has a definite value. *This distinction is characteristic of a function of state.*

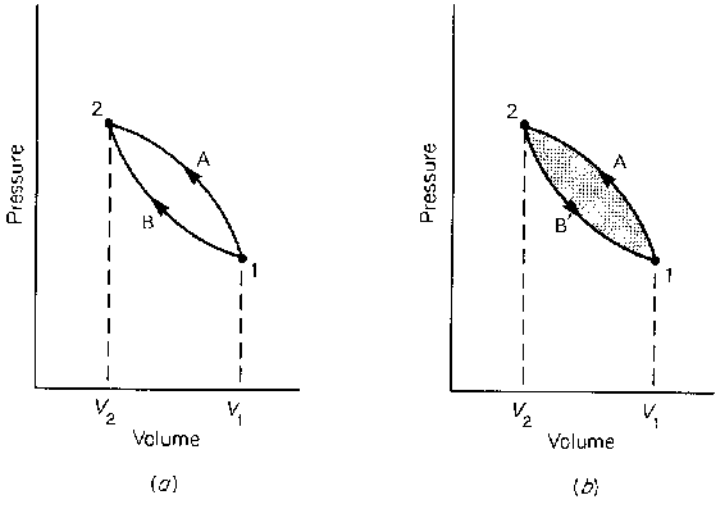


Fig. 1.11. (*a*) The work done in going from 1 to 2 along different paths. (*b*) The net work done in the cyclic process shown is given by the shaded area.

Having considered the work term in Eq. (1.14) we shall next look at the heat term in that equation. Combining it with Eq. (1.15a)—i.e. we are still considering a fluid—the first law, for *a reversible change*, becomes

$$đQ = \mathrm{d}E + P\mathrm{d}V \ . \tag{1.17}$$

From this equation we get the heat capacities. (We shall prefer the term heat capacity to the term specific heat which will be reserved for heat capacity per unit mass.) We shall consider one mole of fluid and so get molar heat capacities. Since $đQ$ does not define a state function, the heat capacity depends on the mode of heating the system.

The heat capacity at constant volume is given by

$$C_V = \left(\frac{đQ}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \ , \tag{1.18a}$$

i.e. it is the ratio of the quantity of heat $đQ$ to the temperature change $\mathrm{d}T$ which this produces, the volume V of the system being kept constant. In the last expression in Eq. (1.18a), we must think of E as a function of V and T: $E = E(V, T)$.

The heat capacity at constant pressure is similarly defined by

$$C_P = \left(\frac{đQ}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{1.18b}$$

where we now think of both E and V as functions of P and T: these are the appropriate independent variables for *this* problem.

To conclude this section we apply Eqs. (1.18) to a perfect gas. For this purpose we must use the fact that for a perfect gas the internal energy E depends only on the temperature:

$$E=E(T) \ . \tag{1.19}$$

The explanation of this is that in a perfect gas the volume occupied by the molecules and their mutual interactions are negligible, so the mean spacing between molecules cannot matter.

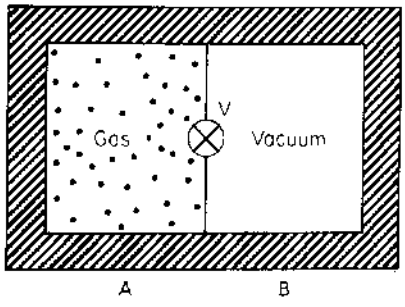


Fig. 1.12. Free expansion of a completely isolated gas from compartment A to compartment B via valve V.

The experimental evidence for Eq. (1.19) comes from Joule's experiment. Consider the expansion of a gas into a vacuum. This is schematically illustrated in Fig. 1.12. Initially compartment A contains the gas, compartment B vacuum. The entire system is totally isolated. The valve V is opened and the gas expands into compartment B. Eventually the gas is again in a state of equilibrium. Under the conditions of this experiment no work is done on the system and no heat enters it: $W=Q=0$. Hence from the first law, the internal energy of the gas remains unchanged: $\Delta E=0$. For a real gas this free expansion leads to a small temperature drop due to the work done against the cohesive forces in the gas. At low pressures (i.e. under ideal gas conditions) this temperature change becomes negligible. Hence an ideal gas is defined by two conditions: (i) it satisfies the equation of state (1.9): $PV=NkT$; (ii) its internal energy is independent of P and V, and depends on T only, Eq. (1.19): $E=E(T)$.

It follows from Eqs. (1.18) and (1.19) that for a perfect gas

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = R \ , \tag{1.20}$$

where the last step follows from the equation of state (1.5).

We have so far considered work done by a hydrostatic pressure on a fluid. In general other forms of work may occur. In writing down the first law (1.14) one must allow for *all* these forms of work. Correspondingly one then defines other heat capacities with the appropriate parameters held constant.

★ 1.4 MAGNETIC WORK

For the study of the magnetic properties of matter, one requires the expression for the work of magnetizing a material. We shall now derive this. We shall consider a process in which an initially unmagnetized sample of material is magnetized by applying a magnetic field to it. This can be done in various ways. For example, we might place the sample inside a solenoid in which a current is gradually switched on, or we might move the sample into the field of the solenoid in which a constant current is maintained. In either case we end up with the magnetized sample *situated in the external applied field*. We shall consider these two procedures in turn, starting with the stationary sample inside the solenoid.

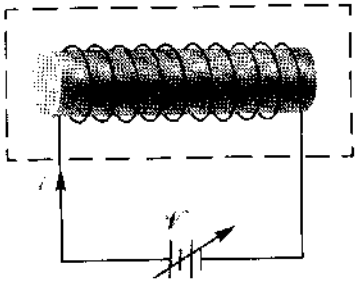


Fig. 1.13. Magnetization of a material inside a solenoid.

Consider a solenoid of length L, cross-sectional area A, and n turns per unit length. We shall assume the magnetic field inside the solenoid uniform* and that the coil has zero resistance. A current i in the solenoid produces a uniform magnetic intensity $\mathscr{H}$ parallel to the axis of the solenoid given by

$$\mathscr{H} = ni \ . \tag{1.21}$$

(We are using SI units.) It follows from Ampère's law that, with the specimen inside the solenoid (Fig. 1.13), the magnetic intensity for a given current i

*Pippard[9] gives an ingenious proof which avoids this assumption. It leads to the same result as we shall obtain.

is still given by Eq. (1.21).* Since the magnetic field $\mathscr{B}$ is parallel to the axis of the solenoid, the total magnetic flux through the solenoid is given by

$$\Phi = A(nL)\mathscr{B} \ . \tag{1.22}$$

A change of flux induces an E.M.F. of magnitude $\mathscr{V}$ given by

$$\mathscr{V} = \frac{\mathrm{d}\Phi}{\mathrm{d}t} = A(nL)\frac{\mathrm{d}\mathscr{B}}{\mathrm{d}t} \tag{1.23}$$

in the circuit. Correspondingly during a time interval $\mathrm{d}t$ the battery does work $đW_1$ on the system in driving the current against this induced E.M.F., given by

$$đW_1 = \mathscr{V} i \ \mathrm{d}t \ . \tag{1.24}$$

The system here consists of the solenoid and the specimen. In Fig. 1.13 the system is marked off by the dashed lines. When compressing a gas (Fig. 1.7) the analogously defined system—on which the external agency does work—consists of cylinder, piston and gas. We rewrite Eq. (1.24) by substituting for i and $\mathscr{V}$ from Eqs. (1.21) and (1.23), and using the fact that $\mathscr{B}$ and $\mathscr{H}$ are parallel:

$$đW_1 = V\mathscr{H} \cdot \mathrm{d}\mathscr{B} \tag{1.25}$$

where $V = AL$. We now write

$$\mathscr{B} = \mu_0(\mathscr{H} + \mathscr{I}) \ , \tag{1.26}$$

where $\mathscr{H}$ is the applied magnetic field intensity (1.21) and $\mathscr{I}$ is the magnetization (magnetic moment per unit volume) of the specimen. Eq. (1.25) then becomes

$$\mathrm{d}W_1 = \mathrm{d}(V\tfrac{1}{2}\mu_0\mathscr{H}^2) + V\mu_0\mathscr{H} \cdot \mathrm{d}\mathscr{I} \ , \tag{1.27}$$

which can also be written

$$đW_1 = \mathrm{d}\left(\int \tfrac{1}{2}\mu_0\mathscr{H}^2 \,\mathrm{d}V\right) + \int (\mu_0\mathscr{H} \cdot \mathrm{d}\mathscr{I})\mathrm{d}V \ . \tag{1.28}$$

*The electromagnetic theory which is used in this section will be found in most standard textbooks on the subject; for example, in I. S. Grant and W. R. Phillips, *Electromagnetism* (Manchester Physics Series), Wiley, Chichester, England, 1975.

Pippard has shown that Eq. (1.28) also holds if the fields depend on position. If the specimen is situated in a homogeneous magnetic field $\mathscr{H}$ and possesses a magnetic moment

$$\mathscr{M} = \int \mathscr{I}\, \mathrm{d}V \,, \tag{1.29}$$

we can rewrite Eq. (1.28) as

$$\mathrm{d}W_1 = \mathrm{d}\left(\int \tfrac{1}{2}\mu_0 \mathscr{H}^2\, \mathrm{d}V \right) + \mu_0 \mathscr{H} \cdot \mathrm{d}\mathscr{M} \,. \tag{1.30}$$

Eq. (1.30) is our final result. It gives the work done by the battery in an infinitesimal change of the solenoid current. As this current is increased, the battery does work to increase the vacuum field energy

$$E_{\mathrm{vac}} = \int \tfrac{1}{2}\mu_0 \mathscr{H}^2\, \mathrm{d}V \tag{1.31}$$

i.e. E_{vac} is the energy stored in the magnetic field of the solenoid in the absence of the sample. The first term in Eq. (1.30) represents this work. The second term in (1.30) therefore represents *all* other changes in energy of the system due to work having been done on it. We shall analyse this further later in this section.

Before doing so, we shall consider a second way of magnetizing a sample, namely by moving it from far away into the field of the solenoid in which a constant current i is maintained. In the above analysis of the stationary sample, we were able to treat the magnetic field as uniform. For a large-sized sample, it may not be justified to treat the field as uniform throughout the motion of the sample. To overcome this difficulty, we shall consider a small sample. (For a large sample, one would first consider individual volume elements of the sample and then integrate over the volume of the sample.) For a small sample, the magnetic field due to the solenoid is approximately uniform over the sample. We shall move the sample along the solenoid axis,

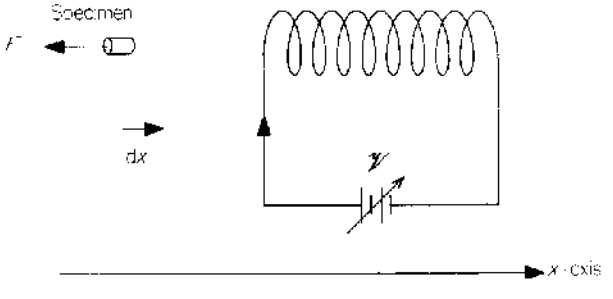


Fig. 1.14. Magnetizing a specimen by bringing it up to a current-carrying solenoid.

taken as the x-axis, through the distance dx towards the solenoid (Fig. 1.14). A small sample, positioned at x, will experience an attractive force

$$\mu_0 \mathscr{M}(x) \cdot \frac{d\mathscr{H}(x)}{dx}$$

towards the solenoid. Here $\mathscr{M}(x)$ is the magnetic moment of the sample when situated at x, and $\mathscr{H}(x)$ is the magnetic field intensity at x due to the solenoid. In order to carry out the process quasistatically, we apply a balancing force

$$F = -\mu_0 \mathscr{M}(x) \cdot \frac{d\mathscr{H}(x)}{dx}$$

to the sample (see Fig. 1.14). For example, the sample might lift a weight as it is pulled into the field of the solenoid. In moving the sample through dx, the applied force F does work

$$đW = F dx = -\mu_0 \mathscr{M}(x) \cdot d\mathscr{H}(x) \ . \tag{1.32}$$

This expression does not represent the total work done in this process. Moving the magnetized sample produces a change of magnetic flux through the solenoid. Thus an E.M.F. $\mathscr{V}$ is induced in the solenoid, and the battery must do work against this E.M.F. to maintain a *constant* current i. This work is given by

$$đW' = i\mathscr{V}\, dt = i d\Phi$$

where $d\Phi$ is the change in flux through the solenoid due to the sample being moved through dx. Since the solenoid current is kept constant in this process the self-flux of the solenoid is constant, and we shall take $\Phi = \Phi(x)$ as the flux through the solenoid due to the sample, situated at x. Also, since i is constant, we can write the last expression

$$đW' = d(i\Phi) \ . \tag{1.33}$$

Now the flux Φ through the solenoid due to the sample does not depend on the detailed structure of the sample but only on its magnetic moment $\mathscr{M}$. We shall assume that the sample has the shape of a cylinder of cross-sectional area A_m, with a magnetization current i_m circulating around its curved surface. The magnetic moment of the sample is then given by

$$\mathscr{M} = \mathbf{A}_m i_m \ , \tag{1.34}$$

the direction of the vector area $\mathbf{A}_m$ being defined by the right-hand screw sense of the circulating current i_m.

We can express $(i\Phi)$ in Eq. (1.33) in terms of the magnetic moment $\mathscr{M}$ in the following way. Let M be the mutual inductance of the solenoid and the equivalent elementary current loop by which we represented the sample. In terms of M, the flux through the solenoid due to the sample is given by

$$\Phi = Mi_{\mathrm{m}} \tag{1.35}$$

and the flux through the current loop due to the solenoid by

$$\mu_0 \mathscr{H} \cdot \mathbf{A}_{\mathrm{m}} = Mi \ . \tag{1.36}$$

It follows from the last equation and Eq. (1.34) that

$$Mii_{\mathrm{m}} = \mu_0 \mathscr{H} \cdot \mathscr{M} \ , \tag{1.37}$$

and hence from (1.35) that

$$i\Phi = \mu_0 \mathscr{H} \cdot \mathscr{M} \ . \tag{1.38}$$

Note that in deriving Eq. (1.38) we did not have to assume that the field due to the sample is uniform over the volume of the solenoid.

Substituting Eq. (1.38) in Eq. (1.33) gives

$$\mathrm{d}W' = \mathrm{d}(\mu_0 \mathscr{H} \cdot \mathscr{M}) \ . \tag{1.39}$$

Adding Eqs. (1.32) and (1.39), we obtain for the total work done in moving the sample through $\mathrm{d}x$

$$\mathrm{d}W_2 = \mathrm{d}W + \mathrm{d}W' = \mu_0 \mathscr{H}(x) \cdot \mathrm{d}\mathscr{M}(x) \ . \tag{1.40}$$

Eq. (1.40) is our final result for the work done in this second way of magnetizing the sample. Comparison with the corresponding result (1.30) for the first method shows that these results are consistent as in the second method the solenoid current, and hence the vacuum field, are held constant, so that E_{vac} does not change.

In analysing magnetic work further, we shall for simplicity restrict ourselves to the case of uniform fields and a uniformly magnetized sample, i.e. to the magnetization of the stationary sample filling the solenoid, which we considered above.* The work done by the battery in this magnetization process is obtained by integrating Eq. (1.30):

*This analysis can be extended to non-uniform fields, and the results which are derived below can be shown to hold in the more general case. The general derivation, on which our more specialized treatment is based, has been given by A. J. Hillel and P. J. Buttle (private communication). See also J. R. Waldram,[19] chapter 15, for a treatment based on the same point of view.

$$W_1 = \int \tfrac{1}{2}\mu_0 \mathscr{H}^2 \, \mathrm{d}V + \int \mu_0 \mathscr{H} \cdot \mathrm{d}\mathscr{M} \tag{1.41a}$$

or, on integrating the second integral by parts,

$$W_1 = \int \tfrac{1}{2}\mu_0 \mathscr{H}^2 \, \mathrm{d}V + \mu_0 \mathscr{H} \cdot \mathscr{M} - \int \mathscr{M} \cdot \mu_0 \mathrm{d}\mathscr{H} \, . \tag{1.41b}$$

To interpret the expressions (1.41), we go back to the general expression for the energy stored in a magnetic field $\mathscr{B}$:

$$E_{\mathrm{mag}} = \frac{1}{2\mu_0} \int \mathscr{B}^2 \mathrm{d}V \, . \tag{1.42}$$

With

$$\mathscr{B} = \mu_0(\mathscr{H} + \mathscr{I}) \, , \tag{1.26}$$

the integral in Eq. (1.42) breaks up into three terms

$$E_{\mathrm{mag}} = \int \tfrac{1}{2}\mu_0 \mathscr{H}^2 \mathrm{d}V + \int \tfrac{1}{2}\mu_0 \mathscr{I}^2 \mathrm{d}V + \int \mu_0 \mathscr{H} \cdot \mathscr{I} \mathrm{d}V \, . \tag{1.43}$$

These three terms admit a simple interpretation. The first term is just the vacuum field energy (1.31). The second term does not depend on the applied field $\mathscr{H}$ but only on the magnetization $\mathscr{I}$ of the sample, i.e. it represents a magnetic self-energy of the sample. To interpret the third term, we remind the reader that just as $\mathscr{H}$ is the magnetic field intensity originating from the free currents (in our case the solenoid current), so $\mathscr{I}$ is the magnetic field intensity due to the magnetization currents.* Thus the third term in Eq. (1.43) represents a *mutual field energy* due to the superposition of the fields originating from the solenoid and from the magnetized sample. For the case of a uniform applied field, which we are considering, we have from Eq. (1.29) that this mutual field energy reduces to

$$\int \mu_0 \mathscr{H} \cdot \mathscr{I} \mathrm{d}V = \mu_0 \mathscr{H} \cdot \mathscr{M} \, . \tag{1.44}$$

This result can also be understood if we consider a single dipole of the sample, which we again represent by an elementary current loop, placed in the field of the solenoid. The magnetic energy can be written in the usual way as

$$E_{\mathrm{mag}} = \tfrac{1}{2} L i^2 + \tfrac{1}{2} L_{\mathrm{m}} i_{\mathrm{m}}^2 + M i i_{\mathrm{m}}$$

*It is these statements which hold for uniform fields only, necessitating a more indirect treatment for non-uniform fields.

where L and L_m are the self-inductances of the solenoid and of the current loop, M is the mutual inductance of the solenoid and the loop, and i and i_m are the solenoid and loop currents. The three terms in the last equation correspond to the vacuum field energy, the magnetic self-energy and the mutual field energy in Eq. (1.43). We see from Eq. (1.37) that the mutual field energy Mii_m reduces to $\mu_0 \mathscr{H} \cdot \mathscr{M}$, in agreement with Eq. (1.44).

We now use Eq. (1.43) to interpret Eq. (1.41b) for the work done by the battery in magnetizing the sample and establishing the fields. The first term on the right-hand side of Eq. (1.41b) is just the work done in establishing the vacuum field. From Eq. (1.44), we recognize the second term in Eq. (1.41b) as the work done in generating the mutual field energy. Hence the third term in (1.41b) is the work done in magnetizing the sample, *exclusive of establishing the mutual field energy*.

In studying a magnetic system, we usually subtract off the vacuum field energy, i.e. we do not count the vacuum field energy as part of the system. This still leaves two possibilities, depending on whether we include the mutual field energy (1.44) as part of the system or not. If it is excluded, we see from Eq. (1.41b) that the magnetic work in an infinitesimal change is given by

$$đW = -\mathscr{M} \cdot \mu_0 \mathrm{d}\mathscr{H} . \tag{1.45}$$

If we *in*clude it as part of the system, we obtain from Eq. (1.41a) for the magnetic work in an infinitesimal change

$$đW_1 = \mu_0 \mathscr{H} \cdot \mathrm{d}\mathscr{M} . \tag{1.46}$$

We next consider the first law of thermodynamics, i.e. we take into account that we can change the energy of a system by doing work on it or by heat transfer. We note first of all that the expressions (1.45) and (1.46) for the infinitesimal work are generally valid. However, we want to use these in the first law (1.14) and we want the infinitesimal work to be defined by the parameters of state of the system. We know from section 1.3 that for this to be the case we must restrict ourselves to reversible processes, i.e. to processes which are quasistatic and which do not involve hysteresis effects. This means that we must exclude ferromagnetic materials from our discussion. We require that the magnetization is a single-valued function of the applied magnetic field.

Above we had two different expressions for the magnetic work and correspondingly we obtain two different forms for the first law (1.14). If the mutual field energy as well as the vacuum field energy are *not* counted as part of the system, the magnetic work is given by Eq. (1.45) and the first law becomes

$$\mathrm{d}E = đQ - \mathscr{M} \cdot \mu_0 \mathrm{d}\mathscr{H} . \tag{1.47}$$

Alternatively, if E' is the energy of the system includng the mutual field energy, but still excluding the vacuum field energy, then

$$E' = E + \mu_0 \mathscr{H} \cdot \mathscr{M} \ , \tag{1.48}$$

whence Eq. (1.47) becomes

$$\mathrm{d}E' = đQ + \mu_0 \mathscr{H} \cdot \mathrm{d}\mathscr{M} \ . \tag{1.49}$$

This is in agreement with the expression (1.46) for the work in this case. We shall see later that in statistical physics, i.e. from the microscopic point of view, it is more natural and useful not to count the mutual field energy as part of the system and to employ Eqs. (1.45) and (1.47).

Strictly speaking, statements of the first law must contain terms corresponding to *all* types of work of which the system is capable. Thus the right-hand sides of Eqs. (1.47) and (1.49) should be augmented by a term $-P\mathrm{d}V$ corresponding to volume changes, as in Eq. (1.17). Frequently one particular work term dominates so that the others can be omitted. For example, in studying magnetic properties of solids, volume changes are generally unimportant.

Analogously to the definitions of heat capacities at constant volume and at constant pressure from Eq. (1.17), we can define heat capacities at constant magnetization, $C_{\mathscr{M}}$, and at constant magnetic field strength, $C_{\mathscr{H}}$,

$$C_{\mathscr{M}} = \left(\frac{đQ}{\partial T} \right)_{\mathscr{M}} \ , \tag{1.50}$$

$$C_{\mathscr{H}} = \left(\frac{đQ}{\partial T} \right)_{\mathscr{H}} \ . \tag{1.51}$$

From the expressions of the first law of a magnetic system, these heat capacities can be expressed in various ways. For example, Eqs. (1.51) and (1.47) lead to

$$C_{\mathscr{H}} = \left(\frac{\partial E}{\partial T} \right)_{\mathscr{H}} \ . \tag{1.52}$$

SUMMARY

In this summary we collect together those definitions and equations from this chapter with which the reader may not have been familiar and which will be used frequently later on.

Quasistatic (p. 15) A quasistatic process is defined as a succession of equilibrium states.

Reversible (p. 15) A process is reversible if it is possible to reverse its direction by an infinitesimal change in the applied conditions. For a process to be reversible it must be quasistatic and there must be no hysteresis effects.

The first law

(i) Generally:

$$\Delta E = Q + W \ . \tag{1.13}$$

(ii) For infinitesimal changes:

$$\mathrm{d}E = \đ Q + \đ W \ . \tag{1.14}$$

(In these equations, only the energy E is a function of state.)

Work done on a fluid in an infinitesimal change:

$$\đ W \geqslant -P\mathrm{d}V \tag{1.15c}$$

where the $=$ and $>$ signs apply to reversible and irreversible changes respectively.

Heat bath (p. 15) is a system at a definite temperature whose heat capacity is so large compared with that of another system that when the two systems are put into thermal contact the temperature of the heat bath remains essentially constant.

PROBLEMS 1

1.1 Show that for a quasistatic adiabatic process in a perfect gas, with constant specific heats,

$$PV^{\gamma} = \text{const.}$$

($\gamma \equiv C_P/C_V$).

1.2 The molar energy of a monatomic gas which obeys van der Waals' equation is given by

$$E = \frac{3}{2}RT - \frac{a}{V} \ ,$$

where V is the molar volume at temperature T, and a is a constant. Initially one mole of the gas is at the temperature T_1 and occupies a volume V_1. The gas is allowed to expand adiabatically into a vacuum so that it occupies a total volume V_2. What is the final temperature of the gas?

1.3 Calculate the work done on 1 mole of a perfect gas in an adiabatic quasistatic compression from volume V_1 to V_2.

1.4 The enthalpy H is defined by $H \equiv E + PV$. Express the heat capacity at constant pressure in terms of H.

1.5 One mole of a perfect gas performs a quasistatic cycle which consists of the following four successive stages: (i) from the state (P_1, V_1) at constant pressure

to the state (P_1, V_2), (ii) at constant volume to the state (P_2, V_2), (iii) at constant pressure to the state (P_2, V_1), (iv) at constant volume back to the initial state (P_1, V_1). Find the work done on the gas in the cycle and the heat absorbed by the gas in the cycle.

1.6 The same as problem 1.5 with the four stages of the cycle: (i) at constant volume from (T_1, V_1) to (T_2, V_1), (ii) isothermally to (T_2, V_2), (iii) at constant volume to (T_1, V_2), (iv) isothermally back to (T_1, V_1).

1.7 Calculate the change in internal energy when 1 mole of liquid water at 1 atm and 100 °C is evaporated to water vapour at the same pressure and temperature, given that the molar volumes of the liquid and the vapour under these conditions are 18.8 cm^3/mol and 3.02×10^4 cm^3/mol, and that the latent heat of evaporation is 4.06×10^4 J/mol.