

Section 1

Introduction to Classical Thermodynamics

1.1 Introduction – Macroscopic and microscopic descriptions

Any system may be described *macroscopically* or *microscopically* (G pp. 1-4, F pp. xi-xii).

The *macroscopic* description considers the system as a whole. The system is characterised, in equilibrium, by a relatively small number of variables e.g. pressure, volume, temperature, internal energy, entropy. The state of a system described in this way is referred to as a *macrostate*. The macrostate of a system can be changed in two principal ways: we can do work on the system and/or heat can flow in. (The macrostate would also change if particles flowed into or out of the system.) The general rules governing these macroscopic variables and their inter-relationships is the subject of thermodynamics.

The *microscopic* description considers the detailed microscopic nature of the system. At this level the system is characterised by a large number of variable which specify the state of the microscopic entities that make it up. For example, classically the state of a gas is given at any instant by the position and momentum of each particle. So for N particles we need $6N$ variables. This is a very large number; for 1cm^3 of gas at STP, N is of order 10^{19} . The state of a system described in this way is referred to as a *microstate*. The positions and momenta of the particles, and thus the microstate, evolves with time according to the laws of mechanics. Practically, we could never hope to perform such a calculation!

In the *quantum mechanical* description a microstate will correspond to the system having a given wave function. The microstate will be specified by a set of quantum numbers for the system.

In specifying microstates of a system we note that the energy of each atom may take on a continuous or a discrete set of values. In equilibrium there will be a certain distribution of atoms among these energy levels. This distribution will tell us how many atoms have, on average, energy in the range E to $E + dE$. This probabilistic description is enough to determine the macroscopic thermodynamic variables. This is the subject of statistical mechanics: to connect a probabilistic microscopic mechanical description of a system to the macroscopic thermodynamic description.

Historically the two most important figures in the unification of thermal physics and mechanics were Boltzmann and Gibbs..

Here we will review some fundamental macroscopic concepts. You should read the first three chapters of Finn for more details.

1.2 Systems and Variables

A *system* is separated from its surroundings by *walls*. In general we consider closed systems that do not exchange matter with their surroundings. Walls can then be classified into two types

- *Adiabatic*: no heat can pass through the wall.
- *Diathermal*: heat can pass through the wall.

Two systems we will use a lot are

- an isolated system surrounded by an adiabatic wall (*an adiabatic system*)
- a system in contact with a heat bath *via* a diathermal wall (*an isothermal system*).

A system is described by *thermodynamic variables*. These are of two kinds: *extensive* and *intensive*.

Intensive variables are independent of the size of a system and they can vary throughout the system (i.e. they can be defined locally). Examples are pressure, temperature, density.

Extensive variables scale with the size of the system, and are proportional to its volume, if other conditions are kept constant. Examples are volume (obviously!), numbers of particles, mass, internal energy.

The appropriate variables depend on the particular system. Examples are given below. Extensive and intensive variables tend to come in pairs (*conjugate variables*). The incremental work done on a body is (it turns out) the product of an intensive variable and the increment in the conjugate extensive variable $dW = Xdx$.

Conjugate variables:

system	intensive variable	extensive variable
generalised	generalised force X	generalised displacement x
fluid	pressure p	volume V
wire	tension \mathcal{F}	length l
film	surface tension γ	area A

We will see that the incremental increase in energy of a body due to the flow of heat may also be expressed in the same way

all systems	temperature T	entropy S .
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End of lecture 1

1.3 Thermodynamic Equilibrium

1.3.1 Equilibrium

The concept of equilibrium is fundamental to thermodynamics.

In equilibrium the thermodynamic properties (i.e. the macroscopic physical properties) are constant throughout the system and they do not vary with time.

Imagine an isolated cylinder of gas with a piston at one end. Rapidly move the piston so as to expand the gas. Then the gas will be in a chaotic state; there may be a shock wave associated with the turbulent flow of the gas and the intensive variables such as temperature, pressure and density will be non-uniform and changing. After waiting a sufficiently long time the gas will achieve internal

equilibrium (in the microscopic view we know this happens because of collisions between the gas molecules). In the equilibrium state the temperature, pressure and density are constant throughout the gas and they do not vary subsequently in time, so long as the system is not disturbed.

It is equilibrium states which are able to be described by a small number of macroscopic variables. In this course we shall be concerned exclusively with equilibrium states.

1.3.2 Thermodynamic state

A thermodynamic (macro)state is specified by the appropriate choice of state variables.

For example for a gas p , V , T are possible state variables. But they cannot be chosen independently because they are related by the *equation of state*. For an ideal gas of N atoms $pV = NkT$ (the ideal gas law). So we have three variables and one constraint, leading to two independent variables.

In other words you only need to fix say V and T . Then the state of the gas (comprising N atoms) is determined. If you want to know the pressure in this state then plug the values of V and T into the equation of state.

1.3.3 Functions of state

We will encounter a number of quantities which are uniquely determined by the thermodynamic state of the system. These are called *functions of state*. An example is the internal energy E . The state is fixed by the pair V , T (or p , T or p , V). Since E is a function of state it is determined by V , T . Mathematically it is a function of two variables and this may be written $E(V, T)$. Other examples of functions of state we will encounter are entropy S , enthalpy H , Helmholtz free energy F , and Gibbs free energy G .

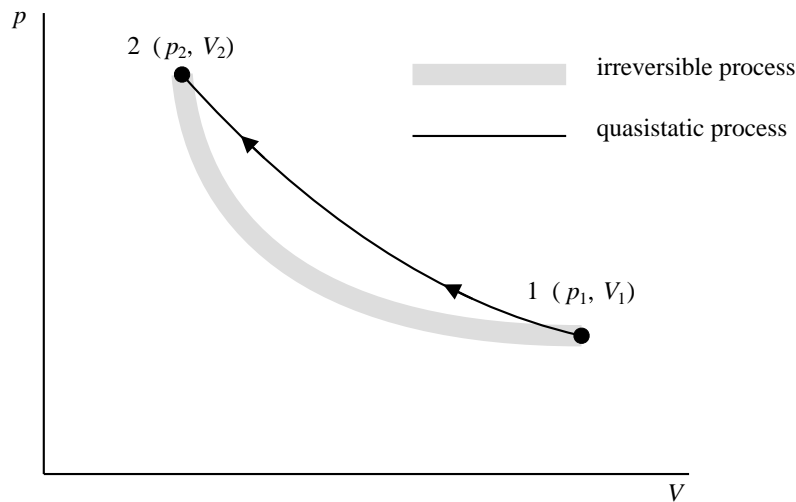
These must be distinguished from other quantities which are *not* functions of state. For example the work done on a system and the heat flowing into a system are not functions of state.

1.3.4 Reversible processes

You might think that a system sitting at thermodynamic equilibrium is not that interesting. Indeed historically the development of thermodynamics was driven by the need to understand the operation of steam engines. Essentially these involve a sequence of processes in which the thermodynamic state of a gas is changed.

Well, steam engines are rather complicated. So let's do the usual trick of the physicist: simplify and idealise. Consider a process in which the system goes from one equilibrium state to another. We will continue to use a gas as our workhorse example of a physical system, but of course the ideas apply to any system with the appropriate choice of state variables.

So for a gas, the end points of the process, the initial and the final states are specified by the state variables. Here we use pressure and volume. The initial state 1 is (p_1, V_1) and the final state 2 is (p_2, V_2) . We can represent these on a two-dimensional plot called an indicator diagram.



Indicator diagram

Suppose the change from 1 to 2 is accomplished sufficiently slowly (by moving the piston very slowly) so that at each stage of the process the gas is in equilibrium. Such a process passing through a succession of equilibrium states is called *quasistatic*. Only in this case may it be represented by a trajectory on the indicator diagram.

Now suppose that no dissipative forces such as friction are present (these may be reduced to insignificance by moving the piston very slowly). Then the direction of the process can be reversed by an infinitesimal change in the force bringing it about; in our example this is the pressure differential across the piston.

This then leads us to the notion of a *reversible process*: one which is quasistatic and for which no dissipative forces are present.

In a reversible process the system can be moved from 1 to 2; this process can be reversed and the system returned to 1. Thus the state of the system and the rest of the world are left unchanged when the system returns to its original state (an alternative definition).

Important examples of reversible processes are:

- *Reversible adiabatic process*. Here, complying with the above conditions the state of the thermally isolated system is changed. No heat may enter or leave. Later on we shall see that for such a process the entropy is constant (the process is called *isentropic*)
- *Reversible isothermal process*. During this process the system is in thermal contact with a heat bath with which it can exchange heat energy. The temperature is constant and equal to that of the bath.

1.3.5 Cyclic processes

When a system passes through a sequence of states, ending up back in its original state, such a process is called a *cyclic process*. Clearly a cyclic process is described by a closed curve on an indicator diagram. Cyclic processes have a close connection with *functions of state*, since these will all be at their original values at the end of the cycle. Other variables, such as the work done on a substance during such a cycle or the heat input/output will change.

- Satisfy yourself that the work done on a fluid is given by the area of the closed curve of the p, V indicator diagram.

Cyclic processes may be used to make general deductions about non- functions of state, such as the interconversion of heat and energy. Thus Carnot deduced that the efficiency of a steam engine did not depend on the working substance.

1.3.6 Temperature, thermal equilibrium and the zeroth law of thermodynamics

We need to clean up our ideas a little on thermal equilibrium between systems and how this leads to the concept of temperature. Two volumes of gas each in internal equilibrium are placed in thermal contact. In general they will not be in thermal equilibrium with each other. Thus the states of the two samples of gas will change, as observed by changing pressures, for example. When no further change takes place thermal equilibrium has been achieved. The two systems are then said to be at the same temperature.

Thus we assert that *all* systems possess a common property called *temperature*. This is the property of a system that determines whether it is in thermal equilibrium with other systems. This view is encapsulated by the zeroth law of thermodynamics (F pp. 4-5).

Zeroth law of thermodynamics: *If two systems are separately in thermal equilibrium with a third then they are in thermal equilibrium with each other.*

1.3.7 Temperature scales

You should be familiar with the Celsius scale and the ideal gas scale. These are covered in Finn, chapter 1. Read this.

The ideal gas temperature scale is based on the equation of state of an ideal gas $pV = NkT$. We shall see that this temperature is identical to that defined on the Kelvin / thermodynamic scale. It is also equivalent to statistical temperature, which arises from a microscopic treatment of systems. These equivalences will be demonstrated later on in the course.

Thus the temperature which crops up in all the equations of this course is called *absolute temperature*. Absolute zero, $T = 0$, corresponds to $-273.15\text{ }^\circ\text{C}$. Absolute zero is unattainable, but you can get infinitesimally close to it in principle. This result follows from the *third law of thermodynamics*, covered later in the course.

This is the province of ultralow temperature physics, one of the research areas of this department. It is the low energy frontier of physics where new discoveries await the intrepid explorer. The record low temperature for a system in internal thermal equilibrium is held by colleagues at the University of Lancaster: $7\mu\text{K}$ in a brush of metal wires. In other systems you can play tricks to cool only parts to temperatures of a few nK. You can also have negative temperatures, but these are hotter than $T = \infty$. Confused?!..... well stay tuned!

End of lecture 2

1.4 The First Law of Thermodynamics

There is a function of state called the *internal energy*, E . When a system is taken from one equilibrium state 1 to another 2, the change in internal energy ΔE is given by the sum of the work done *on* the system ΔW and the heat flowing *into* the system ΔQ :

$$\Delta E = \Delta W + \Delta Q \quad \text{where} \quad \Delta E = E_2 - E_1.$$

(Note the sign convention for ΔW and ΔQ)

This law is a statement of the equivalence of heat and work. It is the principle of conservation of energy generalised to thermal systems. Heating is thus nothing more than the flow of energy into a system from its surroundings.

From a modern perspective we see the first law simply as a statement of the conservation of energy. But historically it was important since there was uncertainty about the nature of heat (there was the caloric theory, phlogiston theory, etc.). When formulated, the first law was telling people simply that heat is another form of energy.

The complete conversion of work into heat is possible and it is allowed by the first law. This was what Joule spent so much of his time investigating, with paddles in water.

The complete conversion of heat into work is not possible *in a cyclic process*. (It is possible in a “single shot” process e.g. the reversible isothermal expansion of an ideal gas against a piston). Although allowed by the first law, the continuous conversion of heat into work is forbidden by the second law of thermodynamics.

Historically the first law followed from the experiments of Joule, who demonstrated that for a thermally isolated system ($\Delta Q = 0$) the work necessary to perform a given change in its thermodynamic state (for example increase the temperature by one degree) does not depend on how the work is done or the choice of path between the states. This led to the introduction of internal energy E as a function of state.

In the case of a non-adiabatic process ΔE is no longer equal to ΔW . The difference (heat ΔQ) is the non-mechanical exchange of energy of the system with the surroundings, arising from a temperature difference.

Note importantly that $\Delta E = \Delta W + \Delta Q$ *applies to both reversible and irreversible changes*.

For an infinitesimal change we have $dE = \delta W + \delta Q$. The bars in the differentials δW , δQ are to emphasise that we are not taking the differential of a function, W and Q are not functions of state. δW and δQ are *inexact differentials*, they represent infinitesimal quantities only.

1.5 Work

See Finn pp22-33.

1.5.1 Expression for work

So far we have considered work and heat in general terms. However an expression for the work done on a system in a process may be given in terms of the particular state variables appropriate to that system, *if the process is reversible*.

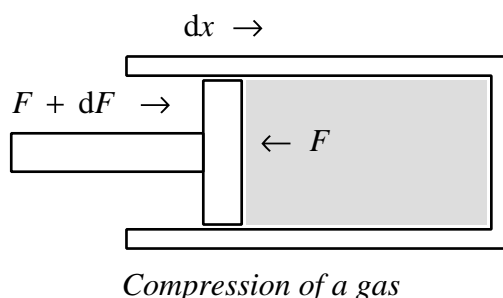
In some cases we can use the fact that work = force \times distance. Thus in an infinitesimal change $dW = F dx$. Since in general F is a function of x , we should write $dW = F(x) dx$. The work done in a process in which x is changed by a finite amount, from x_1 to x_2 is then given by

$$W = \int_{x_1}^{x_2} F(x) dx.$$

1.5.2 An example: work done on a gas

Consider the work done in reversibly compressing a gas.

The force exerted by the gas, of pressure p , on the piston, of area A , is pA (pressure = force per unit area remember?).



To hold the piston stationary we must exert a force $F = pA$. To move the piston in by dx we increase the force F by an infinitesimal amount dF . The piston is frictionless so it moves!

The incremental work done is $dW = (F + dF) dx = Fdx = pAdx$. But the volume of the gas has changed by $dV = -Adx$ (the volume has decreased). So $dW = -pdV$ is the expression for the work done on the gas. *Note the sign convention – work done on a system is positive; this is important.* This is an exact differential, but don't forget we are dealing with the special case of a reversible compression.

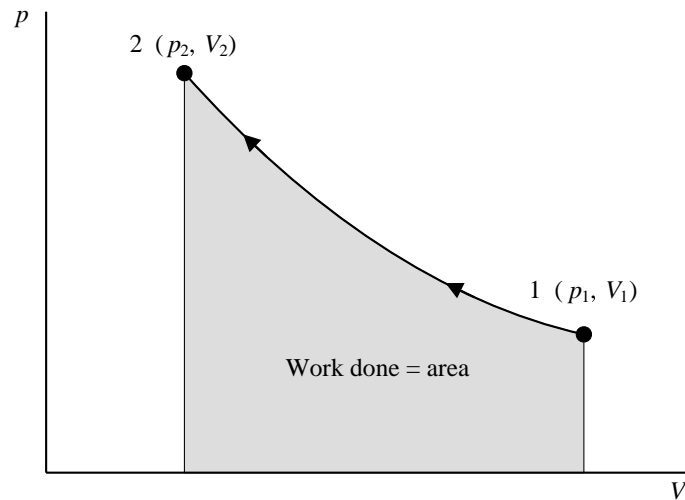
So you only do work on a gas if you change its volume – remember that!

In a finite quasistatic volume change (all intermediate states equilibrium states) from volume V_1 to V_2 :

$$W = - \int_{V_1}^{V_2} p(V) dV.$$

Remember as the volume is decreased the pressure will go up, i.e. the pressure is a function of volume, *so we must do an integral.*

The result will depend on the *conditions* under which the compression is performed. This determines the form of $p(V)$ (that is the path of the process, as represented on an indicator diagram). And the area under that path is the work.



Work done in compressing a fluid

Clearly the area depends on the path; work is not a function of state.

For an ideal gas (as an exercise prove these expressions for W):

- Isothermal compression: $pV = NkT = \text{constant}$ so $p \propto V^{-1}$. Hence in a compression from V_1 to V_2 , $W = NkT \ln V_1 / V_2$.
- Adiabatic compression: $pV^\gamma = \text{constant}$. Then $W = (\gamma - 1)^{-1} [p_2V_2 - p_1V_1]$.

For a compressible solid or fluid see Finn p32.

1.5.3 Other examples of expressions for work

(These are discussed in all the books, see Finn 28-31)

Stretching a wire under tension (\mathcal{F}): $dW = \mathcal{F}dx$.

Increasing the surface area of a liquid film: $dW = \gamma dA$, where γ is the surface tension (usually independent of A).

End of lecture 3