

## Lecture 9

### Classical Thermodynamics

In this section we will develop the essential ideas of energy, relation between energy, heat and work done, how much work can you get out of a quantity of heat, engines, entropy etc. This section is purely dedicated to classical thermodynamics.

#### The internal energy

The development of the principle of conservation of energy has been one of the most significant achievements in the evolution of physics. The present form of the principle was not discovered in one magnificent stroke of insight but was slowly and laboriously developed over two and a half century. The first recognition of a conservation principle, by Leibniz in 1693, referred only to the sum of kinetic and potential energy of a simple mechanical mass point in the terrestrial (earth) gravitational field. As additional types of

systems were considered, the conservation principle failed repeatedly. But, it was found that the conservation principle was revived by the addition of a new mathematical term — a new kind of energy. For example, in charged systems, the addition of the Coulomb interaction energy ( $K \frac{q_1 q_2}{r^0}$ ) and eventually the energy of the electron magnetic field. Then in 1905 Einstein extended the principle to the relativistic region, adding terms like relativistic rest-mass energy and so on. The principle of conservation of energy is now seen as a reflection of the fact that the fundamental laws are the same as it is now, as they were years before, and will be so in future. In more technical terms, conservation of energy is a consequence of the symmetry of action ( $t \rightarrow t + \text{constant}$ ) in classical mechanics, dating back to Noether's theorem. Energy conservation is one of the most fundamental, general and significant principles in physical theory.

Since macroscopic systems are agglomeration of an enormous number of electrons and nuclei, interacting with complex and definite forces, which are subject to the energy conservation principle, we can conclude that macroscopic systems have definite and precise energies, and are subject to energy conservation principle. That is, we now accept the existence of a well defined energy in a thermo-dynamic system, which is a manifestation of a conservation law, which is highly developed, tested to an extreme precision, and of complete generality at the atomic level. From the historical point of view, the existence of the conservative macroscopic total energy was demonstrated by purely macroscopic means, since atomic picture was still not there. It was done by Count Rumford, Humphy Davy, Sadi Carnot, Robert Mayer, James Joule and few more. These experiments and logical explanations done by these scientists justifies our postulate of the existence of the conservative energy function.

Only the differences in energy, rather than the absolute values of energy has physical ~~mean~~  
significance, either at atomic level or in macroscopic systems. This is due to the fact that, there are potential energies involved. And, absolute value of potential energy doesn't have any physical significance. Then, it is true for <sup>total</sup> energy as well. Therefore, we can arbitrarily adopt a particular state of a system as a fiducial state, the energy of which is arbitrarily chosen to be zero. The energy of the system in any other state, relative to the energy in fiducial state, is then called the thermodynamic internal energy  $U$ .

### Thermodynamic equilibrium

A system in thermodynamics is whatever part of the universe we want to study. Near the system are its surrounding. We already developed the idea of thermal equilibrium, that, a system is in thermal equilibrium when its macroscopic observables (such as pressure, temperature etc.) are no longer changing with time.

time. That is, the time average of these quantities are same over some period of time. A system in thermal equilibrium having a particular set of macroscopic observables characterizes the equilibrium macrostate of the system. We will call the macrostate simply state later.

To be more elaborate, macroscopic systems often have some memory effect of their recent history. For example, a stirred cup of tea continues to swirl within the cup. But memory eventually fades, turbulence damp out and systems tend to subside to very simple state, independent of their past specific history. In some cases the evolution towards simple state is rapid, in some case slow. But all systems have a tendency to evolve toward states in which properties are determined by intrinsic factors and not by previously applied external influences. Such simple states are by definition time independent and are called the equilibrium states. Thermodynamics seeks to describe such equilibrium states to which the systems eventually evolves. Such equilibrium states will be characterized by a set of observables such as  $U$ ,  $V$ , mole number  $n$  etc. As one studies more complicated systems, one needs to

introduce more new variables.

However, a persistent problem of experimentalists is to find whether a system is in equilibrium or not, since thermodynamic analysis can only be applied to equilibrium states. In cases, it can be tough. If a system that is not in equilibrium is analyzed on the basis of thermodynamic formalism, inconsistencies appear, and the predicted results are at variance with the experimental results. This discrepancy can be considered as an *a posteriori* criterion for the detection of non-equilibrium states.

In reality, few systems are in absolute and true equilibrium. In absolute equilibrium, all radioactive materials would have decayed to most stable isotopes, which would take cosmic times. Such processes, which takes cosmic times to complete, can generally be ignored. A system that has completed relevant processes of evolution and can be described by small number of parameter, can be considered for applications of thermodynamics.

In practice, the criterion for equilibrium is circular. Operationally, a system is in equilibrium if its properties are consistently described by thermodynamics. However, thermodynamics is applied to describe equilibrium states. This circular character is not different from mechanics. A particle of known mass in a known gravitational field might be expected to follow a particular trajectory. If it doesn't, it doesn't mean that we reject the theory of mechanics, it just that there are additional forces (like electromagnetic) are present. Thus the existence of the electric charge and associated related electric force is not known ~~predictions~~ a priori. It is inferred only by circular reasoning, that the dynamical ~~predictions~~ predictions are incorrect, unless the electric contribution of the force is taken into account. Mechanical/dynamical theory is completely correct to a particular situation if it yields successful predictions.

## Walls and constraints

A description of thermodynamic system requires the specification of the "walls" that separate the system from its surroundings and provides us with boundary conditions. It is by the means of the walls

that's the extensive parameters are altered and  
thermodynamic processes are initiated.

The processes arising by manipulation of the walls are associated with a redistribution of some quantity among various systems or among various portions of the same system. A formal classification of wall thermodynamic walls is then based on permitting or preventing of such quantities. For example, consider that two systems are separated by a closed (no hole), rigid ~~cylinder~~ piston of some shape. If the piston is rigidly fixed in one position, then this wall (piston) ~~permits~~ prevents the re-distribution of volume between the two systems. The piston here constitutes a wall which is ~~non-~~restrictive w.r.t. volume. However, if the piston was moveable, it would have been non-restrictive w.r.t. volume.

There are walls which are restrictive w.r.t. energy. An essential prerequisite for the measurability of energy is the existence of such walls. From practical experience, one would find that, keeping an ice cube in a summer day inside a steel box melts it. But, if we enforce a different type of box of different materials, the melting slows down. And there are some materials with

which we can effectively stop the melting of the ice cube. This type of walls are restrictive with respect to heat, and are called adiabatic walls. The walls that permits flow of heat are called diathermal walls. There are walls of this type (if we enclose the whole ice cube and no machine inside) that are restrictive w.r.t. both work and heat, so they are restrictive to energy. A system enclosed by a wall that is restrictive with respect to energy, volume and particles, is said to be a closed system.

The existence of different types of walls confirms that energy is macroscopically controllable. It can be trapped by restrictive walls and manipulated by diathermal walls. We can now proceed about the measurability of energy, or to be more precise, energy differences and

Consider a system within an adiabatic and impermeable (do not permit exchange of particles) wall. Then, the only type of energy transfer can be through the means of work. We can calculate amount of work from the theory of mechanics. If work is done

by compressing/expanding of a gas by moving a piston, work done is simply force times the displacement. We can also calculate work done in any different scenario. Then, if work is done on such system, the energy difference between the states is simply the work done on the system. So, by employing adiabatic walls, the internal energy relative to a reference state can be measured by only measuring the mechanical work done. In this way, we can ~~not~~ always find the energy difference between two equilibrium states.

Now, energy difference can be created by another mean — any presence of heat flux. But how do we calculate that? Consider, some specified process takes a system from its initial state A to final state B. The process might involve work done ~~by body~~ as well as heat flux. We want to know how much was contributed by them individually. How do we do that? Well, contribution from work done is calculable from mechanics. If we somehow know the internal energy difference  $\Delta U_{AB} = U_B - U_A$ , then the

This is a definition of heat

contribution from heat is simply  $(\Delta U_{AB} - \text{work done})$ .

And, we can calculate  $\Delta U_{AB}$  through only ~~heat~~ calculation of work done. We employ some adiabatic wall, take the same system from A to B, but here only through mechanical work, and that gives us  $\Delta U_{AB} = U_B - U_A$ ! And, we are done.

So, even if a system goes from state A to state B, the amount of work done and heat can independently vary from 0 to  $\Delta U_{AB}$ . However, the sum of the ~~is~~ work done and heat flux is always equal to  $\Delta U_{AB}$ .

$$\therefore \Delta U_{AB} = \Delta Q + \Delta W$$

If one contemplates infinitesimal changes, the small increment of internal energy is denoted by ~~dU~~  $dU$ , where the small amount of work done ~~and~~ on the system and absorbed heat is given by respectively  $dW$  and  $dQ$ .

$$\boxed{\therefore dU = dQ + dW} \quad \text{--- (1)}$$

where  $d$  denotes inexact differentials. It does not designate any difference between works or heat. It makes no sense to talk about work or

or heat in a particular state of a system. So, they are not differences.

Equation (i) is the first law of thermodynamics.

### Exact and inexact differentials

Consider a purely mathematical problem where  $F(x, y)$  is some function of two independent variables  $x$  and  $y$ . So, the value of  $x$  and  $y$  is determined if the value of  $F$ . If one goes to a neighbouring point  $(x+dx, y+dy)$  from  $(x, y)$ , the infinitesimal change in  $F$  is,

$$dF = F(x+dx, y+dy) - F(x, y)$$

But, we can also write,

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy$$

where  $\frac{\partial}{\partial x}$  and  $\frac{\partial}{\partial y}$  denotes the partial derivatives. To see why the previous line is true, think about this. The infinitesimal change in  $F$  between  $(x+dx, y+dy)$  and  $(x, y)$  can be found by adding the change of  $F$  while you move from  $x$  to  $x+dx$  keeping  $y$  constant with the change in  $F$  when you move from  $y$  to  $y+dy$  keeping  $x$  constant. (for infinitesimal changes  $dx$  and  $dy$ )

$$\therefore dF = \{F(x+dx, y) - F(x)\} + \{F(x, y+dy) - F(y)\}$$

Now,

$$\frac{\partial F}{\partial x} = \frac{F(x+dx, y) - F(x)}{dx} \quad \text{--- (i)}$$

$$\text{and } \frac{\partial F}{\partial y} = \frac{F(x, y+dy) - F(y)}{dy} \quad \text{--- (ii)}$$

Using (i) and (ii) we can clearly write,

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = M(x, y) dx + N(x, y) dy$$

$dF$  here is an ordinary differential. If one now goes from  $(x_i, y_i)$  to  $(x_f, y_f)$ , the total change is given by,

$$\Delta F = F_f - F_i = \int_i^f dF = \int_i^f \left( \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy \right)$$

Since the left hand side is only functions of initial and final points, the integral is independent of specific path taken. Thus, the change in energy

$$\Delta E = \int_{i \rightarrow f}^f dE \quad \text{is independent of the}$$

path taken (distribution of work and heat), and only depends on the states i and f.  $dE$  is then an exact differential.

On the other hand, consider an infinitesimal quantity,

$$dG = M'(x,y) dx + N'(x,y) dy \rightarrow (III)$$

Although  $dG$  is infinitesimal, it is not guaranteed that there exists some function  $G(x,y)$  such that  $dG = G(x+dx, y+dy) - G(x,y)$  is equal to (III). Equivalently, it is not true that upon performing the integral,  $\int dG = \int (M' dx + N' dy)$  is independent of the path used ~~and~~ and given  $\Delta G_{\text{path}}$ . Such a differential is called inexact differential, and is denoted by  $d$  or  $\delta$ .

It turns out that, for a differential to be exact,  $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$  (Argue why this is true).

$$dF = 3y^2 dx + 6xy dy$$

Say,

the actual function is then found by,

The

$$\begin{aligned} F &= \int 3y^2 dx \quad \text{or} \quad F = \int 6xy dy \\ &= 3xy^2 + C \\ &= \frac{6xy^2}{2} + C \\ &= 3xy^2 + C \end{aligned}$$

$$\text{However, if } dF = 8y^2 dx + 12xy dy$$

Then

$$\begin{aligned} F &= \int 3y^2 dx \quad \text{or} \\ &= 3xy^2 + C \end{aligned}$$

$$\begin{aligned} F &= \int 12xy dy \\ &= 6xy^2 + C \end{aligned}$$

Now, in this case, we see, there is no such function  $F$  such that the differential is satisfied. Such a differential is then called the inexact differential.

### Different examples

1. Say,  $\begin{aligned} df &= 3x \, dy + 2y \, dx \\ dg &= x \, dy + 2y \, dx \end{aligned}$  } None of them are exact differentials

However,  $dh = df + dg = 3x \, dy + 3y \, dx$

is an exact differential. So, it's possible to find an exact differential by adding two inexact differentials.

2. Say,  $df = 3x^2 \, dx + 4y^3 \, dy$

$$\therefore F = \int 3x^2 \, dx = x^3 + C \quad \text{or} \quad f = \int 4y^3 \, dy = y^4 + C$$

Your first instinct might say the differential is inexact. However, if you construct  $F = x^3 + y^4 + C$ , then you see that the differential is actually exact.

So, whenever you have,

$$df = M(x) \, dx + N(y) \, dy$$

that is,  $M$  is only a function of  $x$ ,  $N$  is only a function of  $y$ , the differential is exact.

The exact differentials depend only on the endpoints, where the inexact differentials depends on the particular path.

### Functions of state

A function of state is any physical quantity that has a well defined value for each equilibrium state of a system. Thus, at thermal equilibrium, these variables have no time dependence. Examples are - pressure, volume, temperature, internal energy etc. Examples of not function of state variables are - work, heat, position ~~of~~ and momentum of a specific particle etc.

Functions of states are then by definition exact variables. If a function of state is  $f$ , ~~is~~ and the system is described by parameters

$\vec{x} = (x_1, x_2, \dots)$ , then,

$$\Delta f = \int_{\vec{x}_i}^{\vec{x}_f} df = f(x_f) - f(x_i)$$

that is, it depends on only the particular state, and not how we got there. For example, you can raise the temperature either by doing

work on a system, or by adding heat, or by doing both of them, to reach the same temperature. However, there is no notion of work or heat in a particular state, rather, these are processes. And they do depend on path.

If we choose a function  $f = xy$ , so that,

$$df = d(xy) = xdy + ydx$$

If  $(x,y)$  changes from  $(0,0)$  to  $(1,1)$ , then the

change in  $f$  is given by,

$$\Delta f = \int_{(0,0)}^{(1,1)} df = \int_{(0,0)}^{(1,1)} d(xy) = xy \Big|_{(0,0)}^{(1,1)} = (1 \times 1) - (0 \times 0) = 1$$

It is independent of how you get to  $(1,1)$  from  $(0,0)$ .

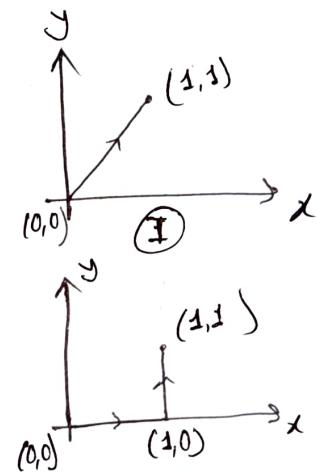
Check that it is the same in the two paths shown in the figures.

However, if you choose a differential,

$$dg = ydx$$

$$\text{Then: Path I: } \Delta g = \int_{(0,0)}^{(1,1)} ydx = \int_{(0,0)}^{(1,1)} xdx$$

$$= \frac{x^2}{2} \Big|_0^1 = \frac{1}{2}$$



$$\text{Path II: } \Delta g = \int_0^1 0 \cdot dx + \int_{0,1}^1 1 dx = 1$$

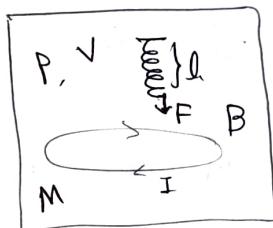
And they are different!

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If  $x = V$  and  $y = P$ , then  $f = PV$  which relates to temperature  $T$  (since  $PV = nRT$ ), and it hence  $T$  is a function of state. However,  $\delta q = \delta PV$ , which is the negative of work done on the system in  $\delta W$ , which is then not a function of state.

### A general system

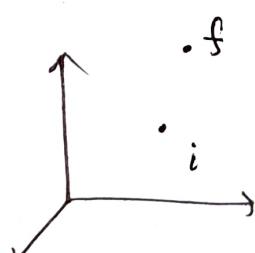
Consider a system containing gas, a spring, a current carrying loop that will create magnetic field and so on.



When the system is in equilibrium, we can measure the values of the variables precisely. However, consider, for example, you suddenly apply some force on the spring such that the spring's linearity gets disturbed, or it starts vibrating, so that its end position is not stable. You can't measure the values precisely. In terms of gaseous system, if you suddenly push the piston to compress the gas, it might create a shock-wave, the density of the gas, pressure, temperature etc. becomes non-uniform through the

system, and you do not have any precise measurement of these quantities. You have to wait for some time (relaxation time  $\tau$ , that depends on particular system) until the system comes to equilibrium when you can make measurements and measure the values of the variables.

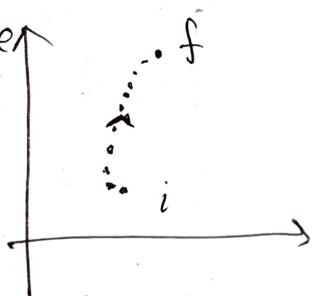
So, only when the system is in equilibrium, you can have precise values of the parameters ( $P, V, l, \beta, M$  etc.) and you can denote these values as a point in some  $n$ -dimensional configuration space that is created by these parameters, say, the system was in some initial state ~~in~~<sup>at</sup> equilibrium, which is denoted by a point  $i$  (we just have drawn three coordinates, but you get the idea). After some process, it reaches a different state (at equilibrium again), which is denoted by a point  $f$ . But you can't show a path how it got there, because there were no precise values during the non-equilibrium period.



Thermodynamics applies to equilibrium, and you can just denote denote these two points, nothing in between.

### Quasi-static process

Since we can deal with quantities in equilibrium only, how can we deal with thermodynamic process - say compressing a box of ~~at~~ gas or adding heat to it. Physicist came up with the idea of quasi-static process. In this process, you basically perform the operation so slowly, that the system is always very close to equilibrium. To be slow enough to be quasi-static, it implies that one proceeds slowly compared to relaxation time  $\tau$ . In such case, you proceed slowly, & so they point slowly traverse a path and roughly create a line from  $i$  to  $f$ .



Now, if the external parameters are  $x_1, x_2, \dots, x_n$ , then we can write the internal energy as,

$$U = U(x_1, x_2, \dots, x_n)$$

When the values of the parameters are changed, the internal energy changes. If a parameter infinitesimally changes from  $x_a$  to  $x_a + dx_a$ , then,

$$dU = \frac{\partial U}{\partial x_a} dx_a$$

The work done on the system is then also,

$$dW = \frac{\partial U}{\partial x_a} dx_a = J_a dx_a$$

where  $J_a$  is called the generalized force (conjugate to the generalized displacement  $dx_a$ ). If  $x_a$  is an actual displacement, then  $J_a$  is just the normal force.

For changes of all variables,

$$dW = \sum_{a=1}^n J_a dx_a$$

### Quasi-static work done by pressure

Consider that we have only one external parameter of significance, the volume  $V$  of the system. The work done on the system for changing the volume from  $V$  to  $V + dV$  is then given by simply corresponding force times displacement. If the gas is in a cylinder, the pressure of the area is  $P$ , area is  $A$ , and an infinitesimal displacement

of the piston is  $dx$ , then,

$$\delta W = (P \cdot A) dx = P(A dx) = P dV$$

However, since volume is decreasing, to define the work done on the system be positive, we choose,

$$\delta W = -P dV$$

$$\Rightarrow \cancel{dU} = -P dV$$

$$\therefore P = \frac{\partial U}{\partial V}$$

So,  $P$  is a generalized force, conjugated to volume  $V$ .