Contents

1 Introduction

Statistical mechanics is the art of turning the microscopic laws of physics into a description of Nature on a macroscopic scale. Suppose you've got theoretical physics cracked. Suppose you know all the fundamental laws of Nature, the properties of the elementary particles and the forces at play between them. How can you turn this knowledge into an understanding of the world around us? More concretely, if I give you a box containing 1023 particles and tell you their mass, their charge, their interactions, and so on, what can you tell me about the stuff in the box?

There's one strategy that definitely won't work: writing down the Schr¨odinger equation for $10^2$3 particles and solving it. That's typically not possible for 23 particles, let alone $10^2$3. What's more, even if you could find the wavefunction of the system, what would you do with it? The positions of individual particles are of little interest to anyone. We want answers to much more basic, almost childish, questions about the contents of the box. Is it wet? Is it hot? What colour is it? Is the box in danger of exploding? What happens if we squeeze it, pull it, heat it up? How can we begin to answer these kind of questions starting from the fundamental laws of physics?

For centuries from the 1600s to the 1900s scientists were discovering laws of physics that govern different substances. There are many hundreds of these laws, mostly named after their discovers. Boyle's law and Charles's law relate pressure, volume and temperature of gases (they are usually combined into the ideal gas law); the Stefan-Boltzmann law tells you how much energy a hot object emits; Wien's displacement law tells you the colour of that hot object; the Dulong-Petit law tells you how much energy it takes to heat up a lump of stuff; Curie's law tells you how a magnet loses its magic if you put it over a flame; and so on and so on. Yet we now know that these laws aren't fundamental. In some cases they follow simply from Newtonian mechanics and a dose of statistical thinking. In other cases, we need to throw quantum mechanics into the mix as well. But in all cases, we're going to see how derive them from first principles

A large part of this course will be devoted to figuring out the interesting things that happen when you throw 10^23 particles together. One of the recurring themes will be that $10^23 \neq 1$. More is different: there are key concepts that are not visible in the underlying laws of physics but emerge only when we consider a large collection of particles. One very simple example is temperature. This is not a fundamental concept: it doesn't make sense to talk about the temperature of a single electron. But it would be impossible to talk about physics of the everyday world around us without mention of temperature. This illustrates the fact that the language needed to describe physics on one scale is very different from that needed on other scales. We'll see several similar emergent quantities in this course, including the phenomenon of phase transitions where the smooth continuous laws of physics conspire to give abrupt, discontinuous changes in the structure of matter.

Historically, the techniques of statistical mechanics proved to be a crucial tool for understanding the deeper laws of physics. Not only is the development of the subject intimately tied with the first evidence for the existence of atoms, but quantum mechanics itself was discovered by applying statistical methods to decipher the spectrum of light emitted from hot objects. (We will study this derivation in Section 3). However, physics is not a finished subject. There are many important systems in Nature from high temperature superconductors to black holes which are not yet understood at a fundamental level. The information that we have about these systems concerns their macroscopic properties and our goal is to use these scant clues to deconstruct the underlying mechanisms at work. The tools that we will develop in this course will be crucial in this task.

2 Basic concepts

Few definitions to start with

1. A system that is completely isolated from all outside influences is said to be contained in adiabatic walls. We will also refer to such systems as insulated
2. Walls that are not adiabatic are said to be diathermal and two systems separated by a diathermal wall are said to be in thermal contact. A diathermal wall is still a wall which means that it neither moves, nor allows particles to transfer from one system to the other. However, it is not in any other way special and it will allow heat to be transmitted between systems. If in doubt, think of a thin sheet of metal.

3. An isolated system, when left alone for a suitably long period of time, will relax to a state where no further change is noticeable. This state is called equilibrium

For a gas, the only two variables that we need to specify are pressure P and volume V : if you know the pressure and volume, then all other quantities - colour, smell, viscosity, thermal conductivity all are fixed. For other systems, further (or different) variables may be needed to describe their macrostate. Common examples are surface tension and area for a film; magnetic field and magnetization for a magnet; electric field and polarization for a dielectric. In what follows we'll assume that we're dealing with a gas and use P and V to specify the state. Everything that we say can be readily extended to more general settings.

In the case of a magnetic solid the appropriate variables are the magnetic field H, the magnetization M, and the temperature T. In more complicated situations, such as when a liquid is in contact with its vapor, additional variables may be needed: such as the volume of both liquid and gas V_L, V_a, the interfacial area A, and surface tension σ. If the thermodynamic variables are independent of time, the system is said to be in a steady state.

2.1 System

Any macroscopic material body could be considered as a thermodynamic system. Macroscopic system means a system composed of atoms or molecules of the order of one Avogadro number $\left(N_A \approx 6.022 \times 10^{23}\right)$ per mole. The examples of thermo- dynamic system could be a wire under tension, a liquid film, a gas in a cylinder, radiation, a solid material, magnetic material, dielectrics, and many others. The thermodynamic systems should have a boundary which separates the systems from the surroundings. Consider a drop of liquid as a thermodynamic system. The surface of the liquid is the boundary between the liquid and air. In the language of thermodynamics, the boundary is considered as a wall. This has been demonstrated in the following Figure.

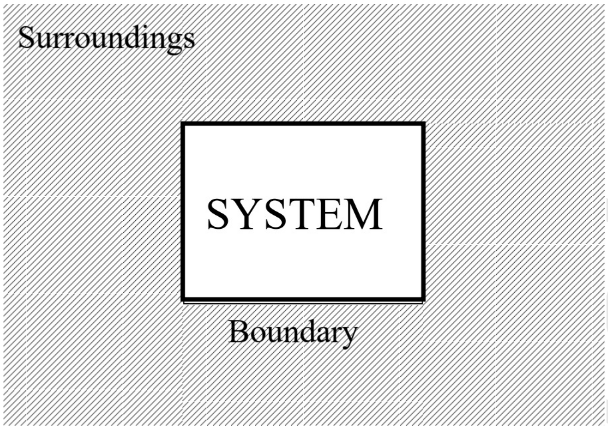

Figure 2.1: Schematic representation of a thermodynamic system. The shaded area is the surroundings or the universe. The thick line represents the boundary. The central white space is the system.

The nature of the wall classifies the thermodynamic system in different categories.

(i) If the wall is such that energy or matter (atoms or molecules) cannot be exchanged between the system and its surroundings, then the system is called isolated. Total energy E, and total number of particles N are conserved for this system.

(ii) The wall is such that only energy could be exchanged between the system and the surroundings. If the system is in thermal contact with a heat bath in the surroundings, heat energy will be exchanged however total number of particles will remain constant. This system is known as closed system.

(iii) If the wall is porous, then, beside energy, matter (atoms or molecules) can also be exchanged between the system and the surroundings. If the system is in contact with a heat bath as well as with a particle reservoir, heat energy and number of particles both will be exchanged. Neither energy nor number of particles is conserved in this system. The system is called an open system.

2.2 Parameters

Thermodynamic parameters are measurable macroscopic physical quantities of a system. Consider a gas in a cylinder. Measurable physical quantities are the pressure (P), temperature (T) and the volume (V) of the gas.

These physical quantities are called thermodynamic parameters or thermodynamic variables. The thermodynamic variables are macroscopic in nature. They are divided in two categories, intensive and extensive parameters.

Extensive quantities are proportional to the amount of matter present - V, U, N, total magnetization etc

Intensive quantities are independent of the amount of matter present - P, T, μ magnetic field etc.

Every intensive parameter has a corresponding independent extensive parameter. They form a conjugate pair of thermodynamic variables. Since they are independent of each other, one could be changed without effecting the other. Keeping the pressure constant the volume of the gas can be changed and vice versa.

A partial list of conjugate thermodynamic parameters are given in Table

System	Intensive parameter	Extensive parameter
Wire	Tension (τ)	Length (L)
Liquid film	Surface tension (γ)	Surface area (A)
Fluid	Pressure (P)	Surface area (A)
Charged particles	Electric potential (ϕ)	Electric charge (q)
Magnetic material	Magnetic field (B)	Total magnetization ($\mathbf{M}$)
Dielectrics	External electric field (E)	Electric polarization ($\mathbf{P}$)

For each system, there always exists one more pair of conjugate intensive and extensive parameters. They are temperature (T) and entropy (S). Temperature is the other intensive parameter and entropy is the corresponding conjugate extensive parameter.

2.3 Thermodynamic State

Position and momentum coordinates are used to specify the state of a particle in mechanics. Similarly, the state of a thermodynamic system can be specified by the given values of a set of thermodynamic parameters. For example, the state of a fluid system can be specified by the pressure P, volume V, and temperature T and specified as (P, V, T). For an dielectric of polarization P at temperature T under an external electric field $\mathbf{E}$, the state is defined by $(\mathbf{E}, \mathbf{P}, T)$. For a magnetic system the state can be given by (M, B, T). For every thermodynamic systems there always exists three suitable thermodynamic parameters to specify the state of the system. It is important to notice that thermodynamic parameters are all macroscopic measurable quantities. On the other hand, microscopic quantities like position or momentum of the constituent particles are not used for specifying the state of a thermodynamic system.

2.4 equilibrium

The equilibrium condition in mechanics is defined as: in absence of external forces, if a particle is slightly displaced from its stable equilibrium position it will come back to its original position after some time.

Consider a thermodynamic system like gas in a cylinder. Suppose the gas is in a state defined by the given thermodynamic parameter values (P, V, T). The downward force (W) due to the weight of the piston is just balanced by the upward force exerted by the pressure (P) of the gas, and the system is in equilibrium. If the piston is slightly depressed and released, it will oscillate around the equilibrium position for some time and slowly come to rest at the original equilibrium position. It means that if a small external force is applied to the system and released, the system would come back to the thermodynamic state it was in originally, i.e., the values of all the extensive and intensive parameters would recover.

This definition is very similar to the definition of equilibrium given in mechanics and known as mechanical equilibrium of a thermodynamic system. Apart from mechanical equilibrium, the system should have thermal and chemical equilibrium as well to achieve thermodynamic equilibrium of a system.

Consider an isolated system with two partial systems. Initially each of them are in equilibrium at different temperatures. Temperature at all points of each system are the same. They are now taken into thermal contact, only exchange of heat and no exchange of matter, with each other. Heat would flow from the system of higher temperature to the system of lower temperature until uniform temperature is attained throughout the combined system. The system is then in thermal equilibrium. Experience shows, all systems which are in thermal equilibrium with a given system are also in thermal equilibrium with each other. This principle defines the temperature of a thermodynamic system and known as zeroth law of thermodynamics. Hence systems which are in thermal equilibrium with each other have a common intensive property, i.e., temperature.

Suppose the system is a mixture of several different chemical components. When the composition of the system remain fixed and definite, the system is said to be in chemical equilibrium. Generally, chemical equilibrium takes a long time to achieve. Sometimes the system appears to be in chemical equilibrium, having fixed amount of components but the chemical reaction may continue with an extremely slow reaction rate. The mechanical equilibrium therefore refers to uniformity of pressure, the thermal equilibrium refers to uniformity of temperature and the chemical equilibrium refers to the constancy of chemical composition. If there exist in the system gradients of macroscopic parameters such as pressure, temperature, density, etc such a state of the system is referred as a non-equilibrium state. A system which satisfies all possible equilibrium conditions is said to be in thermodynamic equilibrium. Thermodynamic equilibrium is thus correspond to the situation when the thermodynamic state does not change with time.

$$\begin{aligned} T &= \text{ const. } \rightarrow \text{ Thermal equilibrium} \\ P &= \text{ const. } \rightarrow \text{ Mechanical equilibrium} \\ \mu &= \text{ const. } \rightarrow \text{ Chemical equilibrium} \end{aligned}$$

2.5 Equation of State

In equilibrium the state variables are not all independent and are connected by equations of state. The role of statistical mechanics is the derivation, from microscopic interactions, of such equations of state. Simple examples are the ideal gas law,

$$PV - Nk_BT = 0$$

where N is the number of molecules in the system and k_B is Boltzmann's constant; the van der Waals equation,

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) - Nk_BT = 0$$

where $a,\ b$ are constants; the virial equation of state

$$P - \frac{Nk_BT}{V}\left[1 + \frac{NB_2(T)}{V} + \frac{N^2B_3(T)}{V^2} + \dots\right] = 0$$

where the functions $B_2(T), B_3(T)$ are called virial coefficients; and in the case of a paramagnet, the Curie law,

$$M - \frac{CH}{T} = 0$$

where C is a constant called the Curie constant. These equations of states are approximations, and we shall use them primarily to illustrate various principles. The virial equation of state is, in principle, exact, but calculation of more than a few of the virial coefficients is very difficult.

3 Thermodynamic transformation

A thermodynamic transformation is a change of state. If one or more of the parameters of a system are changed, the state of the system changes. It is said that the system is undergoing a transformation or process. The transformation is generally from an initial equilibrium state to a final equilibrium state. Thermodynamic processes are classified into two groups (i) irreversible and (ii) reversible.

3.1 irreversible process

The water from the slopes of the Himalayas flows down the Ganges into the Indian Ocean. The water in the Indian Ocean will never go back to the hill on itself even if the total energy loss during the down flow producing heat and sound energy is supplied back to the water at the Ocean. This means that the work done in the forward process is not equal to the work done in the backward process. Such natural flow of liquid downward is spontaneous and is irreversible.

Almost all natural spontaneous processes are irreversible, just reversing the direction of the process it is not possible to get back the initial state. Consider free expansion of a gas. It does no work during the free expansion however to compress it back to the original volume a large amount of work has to be performed on the gas. A pendulum without a driving force will by itself cease to swing after some time, since its mechanical energy is transformed into heat by friction. The reverse process, that a pendulum starts swing by itself while the surroundings cool, has never been occurred. It is characteristic of irreversible processes that they proceed over non-equilibrium states dissipating energy in various forms during the transformation from one state to the other. Ferromagnets are magnetized by applying external magnetic field. If the external filed is reduced the magnetization curve does not follow the original path and forms a hysteresis loop because during magnetization the system dissipates energy in the form of heat and sound.

3.2 reversible process

In a reversible process, the change of states occurs only over equilibrium intermediate states. That is to say, all steps between the final and initial states are in equilibrium during a reversible process. A reversible process is then an idealization. Because, if a system is in thermodynamic equilibrium, the parameters should not change with time. On the contrary, in order to change the state one needs to change the parameter values. However, a reversible process could be realized in a quasi static manner.

In a quasi static process, infinitesimal change in the parameter values are made sufficiently slowly compared to the relaxation time of the system. Relaxation time is the time required for a system to pass from a non-equilibrium state to an equilibrium state. Thus, if the process rate is considerably less than the rate of relaxation, there will be enough time for the parameters to equalize over the entire system and the system could be considered at equilibrium.

The process will represent a continuous succession of equilibrium states infinitely close to each other and could be considered as a reversible process, reversing the direction of the process one could reach to the initial state from the final state following the same path. The reversible change could be performed under different conditions. Consider a thermally insulated system where no heat exchange is possible, any process under this condition is an adiabatic process. Reversible adiabatic process are also known as iso-entropic process. If a system undergoes a change keeping temperature constant, it is called an isothermal process, it is an isochoric process if volume kept constant and it is an isobaric process if pressure remains constant.

4 Work Heat Internal energy

4.1 Work

Work appears during a change in state. The definition of work in thermodynamics is borrowed from mechanics and it is given by

$$\delta W = -\vec{F} \cdot \overrightarrow{d\ell} \tag{4.1}$$

where $\vec{F}$ is the force acting on the system during a small displacement $\overrightarrow{d\ell}$. The negative sign is a convention in thermodynamics and it is decided by the fact that: work done by the system is negative and work done on the system is positive. In mechanics, doing work the potential or kinetic energy of the system is changed. Similarly, work is equivalent to energy exchange in thermodynamics. Energy exchange is positive if it is added to a system and it is negative if it is subtracted from a system. Note that, only macroscopic work is considered here, and not on an atomic level.

Consider a gas enclosed in a cylinder at an equilibrium thermodynamic state (P, V, T). Assuming that there is no friction between the piston and the cylinder, the force acting on the gas, i.e., the weight on the piston, is $F = PA$

where A is the cross sectional area of the piston. In order to compress the volume by an infinitesimal amount dV, the piston is pushed down by an infinitesimal amount $d\ell$. The corresponding work done is

$$\delta W = -\vec{F} \cdot \overrightarrow{d\ell} = PAd\ell = -PdV \tag{4.2}$$

since pressure is acting in a direction opposite to the displacement and $Ad\ell = -dV$ during compression. The same definition is also valid for expansion. In case of expansion, the pressure will act in the same direction of the displacement and $Ad\ell = dV$

Thus, work is the product of an intensive state quantity (pressure) and the change of an extensive state quantity (volume). One could easily verify that the same definition can be applied to the other thermodynamic systems. For example, in case of dielectrics and magnetic materials, in order to change the electric polarization $\mathbf{P}$ or magnetization $\mathbf{M}$ by a small amount $d\mathbf{P}$ or $d\mathbf{M}$ in presence of electric field $\mathbf{E}$ or magnetic field $\mathbf{H}$, the amount of work has to be performed on the systems are

$$\delta W = \mathbf{E} \cdot d\mathbf{P} \qquad \text{or} \qquad \delta W = \mathbf{B} \cdot d\mathbf{M} \tag{4.3}$$

where E and B are the intensive parameters and P and M are extensive parameters. In order to change the particle number by dN, one should add particles those have energy comparable to the mean energy of other particles otherwise equilibrium will be lost. Let us define

$$\delta W = \mu dN \tag{4.4}$$

as the work necessary to change the particle number by dN. The intensive field quantity μ is called the chemical potential and represents the resistance of the system against adding particles.

However, this definition is only valid for an infinitesimal displacement because the pressure changes during the change of volume. To calculate the total work done then one needs to know the equation of state $P = f(V, T)$ and the nature of the process. For a reversible process, the total work done can be obtained just by integrating δW from the initial to the final state

$$W = \int_1^2 \delta W = -\int_1^2 P(V,T)dV \tag{4.5}$$

In a reversible cyclic path, the work done is then zero. since the work depends on the process or the path of integration, it is then an inexact differential. Notice that, the above definition is only for reversible process. In an irreversible process (sudden expansion or compression of gas), the work needed to change the state is always larger than the work needed to change the state in a reversible way, $\delta W_{irr} \geq \delta W_{rev}$ In other words, for reversible process one requires the least work or the system produces the most work, while for a irreversible process a part of the work is always converted into heat which is radiated out of the system.

4.2 Heat

Heat, another form of energy, is the measure of the temperature of a system. Let us define

$$\delta Q = CdT \tag{4.6}$$

where δQ is a small amount of heat which causes the increase in the temperature by dT of a system. The proportionality constant C is called the total heat capacity of the system. Though work and heat are just different form of energy transfer, the main difference between work and heat is that work is energy transfer via the macroscopic observable degrees of freedom of a system, whereas heat is the direct energy transfer between microscopic, i.e., internal degrees of freedom. For example, consider gas in a thermally isolated cylinder with a piston. In order to compress the gas, work has to be performed on the gas by changing the macroscopic coordinate, the position of the piston.

On the other hand, the warming up of the gas during the compression is due to the elastic collisions of the gas molecules with the moving piston. The energy gained in elastic collisions with the moving piston is shared between all other molecules by subsequent molecular collisions. Moreover, work can be easily transformed into heat but heat cannot be wholly converted into work. In order to convert heat into work one always needs a thermodynamic engine. Heat always flows from a hotter body to a colder body. Heat is an extensive quantity.

Therefore, the total heat capacity C is also an extensive quantity, since temperature is an intensive parameter. However, the specific heat c defined as $c = C/m$ where m is the mass of the substance, is an intensive quantity. It is also possible to define the specific heat on a molar basis,

$C = nc_{mol}$, with $n = N/N_A$ where N is the total number of particles and N_A is the Avogadro number. The quantity c_{mol} is the molar specific heat. The heat capacity may depend on the external conditions under which heat is transferred to the system. It matters whether a measurement is performed at constant pressure or at constant volume. The corresponding specific heats are

$$c_P = \frac{1}{m}\left(\frac{\delta Q}{dT}\right)_P, \qquad \text{and} \qquad c_V = \frac{1}{m}\left(\frac{\delta Q}{dT}\right)_V \tag{4.7}$$

They are known as specific heat at constant pressure and specific heat at constant volume respectively.

4.3 Internal energy

Let us consider the energy E of a given state of a macroscopic system. According to the laws of mechanics, the energy E is the sum of (i) the energy of the macroscopic mass motion of the system, and (ii) the internal energy of the system.

The energy of the mass motion consists of the kinetic energy of the motion of the center of mass of a system, plus the potential energy due to the presence of an external force field. In thermodynamics, we are interested in the internal properties of the system and not in their macroscopic mass motion. Usually the stationary systems are considered and the potential energy due to any external field becomes unimportant. Thus, energy in thermodynamics means the internal energy. 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 plus the potential energy of the molecular interaction. In an ideal gas, the internal energy is the sum of the translational kinetic energy of the gas molecules due to their random motion plus the rotational kinetic energy due to their rotations, etc. In a crystal, the internal energy consists of the kinetic and potential energy 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 atoms or molecules or the constituent particles of the system. However, in thermodynamics it is not our interest to calculate internal energy from microscopic interaction. Internal energy will be considered here as a thermodynamic potential.

5 Laws of thermodynamics

5.1 First Law

The principle of conservation of energy is of fundamental importance in Physics. The first law is a law of conservation of energy in thermodynamics. The principle of conservation of energy is valid in all dimensions, i.e., in macroscopic as well as in microscopic dimensions. Therefore, in thermodynamics one should consider conservation between work done (W) which may be performed by or on a system, heat exchange (Q) with the surroundings and the change in internal energy (E).

Suppose there is an isolated system, no heat exchange, and some work ΔW is performed on the system. There is then an increase in the internal energy ΔE of the system. The conservation of energy demands

$$\Delta E = \Delta W \tag{5.1}$$

Suppose instead of doing work on a system, an amount of heat ΔQ is exchanged with the surroundings which raises the internal energy by ΔE and one has

$$\Delta E = \Delta Q \tag{5.2}$$

The first law says that the change in the internal energy ΔE for an arbitrary (reversible or irreversible) change of state is given by the sum of work done ΔW and heat exchange ΔQ with the surroundings. One thus writes

$$\Delta E = \Delta W + \Delta Q \tag{5.3}$$

This is called the first law.

The work done and the heat exchange with the surroundings in a small change in state depend on the way in which the procedure takes place. They are then not exact differentials. On the other hand, the change in internal energy is independent of the way the procedure takes place and depends only on the initial and final state of the system. The internal energy is therefore an exact differential. In order to distinguish the exact and inexact differentials in case of infinitesimal change of state, the following notations are used

$$dE = \delta W + \delta Q \tag{5.4}$$

since the internal energy E depends only on the macroscopic state of the system, it is then a state function. For a state function, the infinitesimal change dE is always a total differential. Since dE is a total differential and path independent, for a cyclic process where a system comes back to its initial state after passing through a series of changes of state, the following equation is always true.

$$\oint dE = 0 \tag{5.5}$$

Now, one can write the differential form of the first law in different context:

Fluid system: $dE = \delta Q - PdV$ Strained wire:

$$dE = \delta Q + \tau dL$$

Surface film: $dE = \delta Q + \gamma dA$ Magnetic materials:

$$dE = \delta Q + BdM$$

The definitions of heat capacities can be rewritten in terms of energy now. Consider one mole of a fluid and the first law for the fluid can be written as

$$\delta Q = dE + PdV \tag{5.6}$$

Since Q is not a state function, the heat capacity depends on the mode of heating the system and one has heat capacities at constant volume and constant pressure. The molar heat capacity at constant volume is then given by

$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{5.7}$$

The energy is then a function V and $T: \quad E = E(V,T)$. The molar heat capacity at constant pressure then can be written as

$$C_P = \left(\frac{\delta Q}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{5.8}$$

The energy E in this case is a function P and $T: \quad E = E(p,T)$. If the considered fluid is an ideal gas for which the specific heat is a constant, the volume occupied by the molecules and their mutual interactions are negligible, the internal energy E is function of temperature T only $E = E(T)$.

5.2 Carnot engine

Consider one mole of monatomic ideal gas as working substance. In the Carnot process, the working substance is taken back to its original state through four successive reversible steps as illustrated in a p V diagram in Figure 5.2

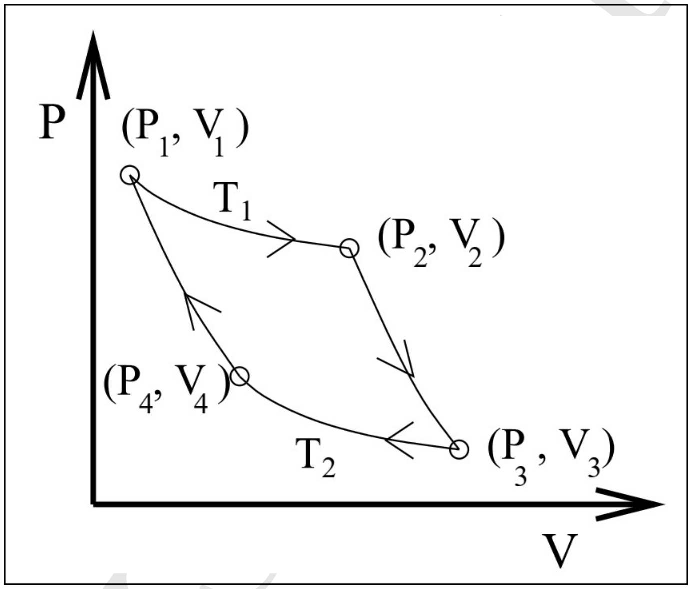

Figure 5.1: Carnot cycle for an ideal gas

Step 1: Isothermal expansion from volume V_1 to volume V_2 at constant temperature T_1. For the isotherm, $P_1V_1 = P_2V_2 = RT_1$ where R is the universal gas constant. since $E = E(T)$ for ideal gas,

$$\Delta E_1 = \Delta W_1 + \Delta Q_1 = 0$$

$$\implies \quad \Delta Q_1 = -\Delta W_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right) \tag{5.9}$$

since $V_2 > V_1$, then $\Delta Q_1 > 0$, i.e., the amount of heat ΔQ_1 is absorbed by the gas from the surroundings.

Step 2: Adiabatic expansion of the gas from V_2 to V_3. The temperature decreases from T_1 to $T_2 \left(T_1 > T_2\right)$. The equation of state is $V_3/V_2 = \left(T_1/T_2\right)^{3/2}$. since $\Delta Q = 0$

$$\Delta E_2 = \Delta W_2 = C_V \left(T_2 - T_1\right) \tag{5.10}$$

Step 3: Isothermal compression from V_3 to V_4 at temperature T_2. The equation of state is: $P_3V_3 = P_4V_4 = RT_2$. Again one has,

$$\begin{aligned} \Delta E_3 &= \Delta W_3 + \Delta Q_2 = 0 \\ \implies \quad \Delta Q_2 &= -\Delta W_3 = -RT_2 \ln\left(\frac{V_3}{V_4}\right) \end{aligned} \tag{5.11}$$

since $V_3 > V_4, \Delta Q_2 < 0$, the amount of heat is released by the gas.

Step 4: Adiabatic compression from V_4 to V_1. Here temperature increases from T_2 to T_1 and the equation of state is $V_1/V_4 = (T_2/T_1)^{3/2}$. since $\Delta Q = 0$

$$\Delta E_4 = \Delta W_4 = C_V\,(T_1 - T_2) = -\Delta W_2 \tag{5.12}$$

The net change in internal energy $\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 = 0$ as it is expected. Consider the amount of heat exchanged during the isothermal processes:

$$\Delta Q_1 = RT_1 \ln\left(\frac{V_2}{V_1}\right) \quad \text{and} \quad \Delta Q_2 = -RT_2 \ln\left(\frac{V_3}{V_4}\right) \tag{5.13}$$

During the adiabatic processes, one has combining the equation of states

$$V_3/V_2 = V_4/V_1 \quad \Longrightarrow \quad V_2/V_1 = V_3/V_4 \tag{5.14}$$

This implies

$$\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} = 0 \tag{5.15}$$

If the Carnot's cycle is made of a large number of infinitesimal steps, the above equation modifies to

$$\oint \frac{\delta Q}{T} = 0 \tag{5.16}$$

This is not only true for Carnot's cycle but also true for any reversible cyclic process. Suppose that the state of a thermodynamic system is changed from state 1 to state 2 along a path C_1 and the system is taken back to the initial state along another reversible path C_2, as shown in Figure 5.2. Thus, $1 - C_1 - 2C_2 - 1$ forms a closed reversible cycle and one has

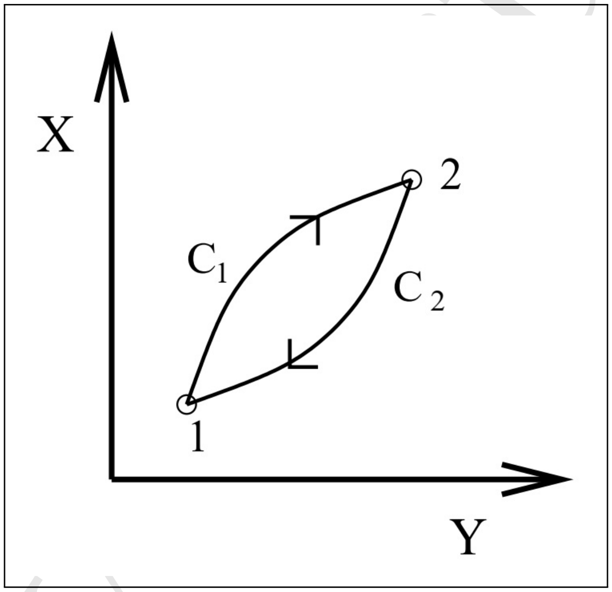

Figure 5.2: A reversible cyclic process on a XY diagram where X and Y form a conjugate pair of thermodynamic variables.

$$\oint_{1C_12C_21} \frac{\delta Q}{T} = 0 \quad \text{or} \quad \int_1^2 \left(\frac{\delta Q}{T}\right)_{C_1} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{C_2} = 0 \tag{5.17}$$

Since, the paths are reversible, one also has

$$\int_2^1 \left(\frac{\delta Q}{T}\right)_{C_2} = -\int_1^2 \left(\frac{\delta Q}{T}\right)_{C_2} \tag{5.18}$$

so hence

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_{C_1} = \int_1^2 \left(\frac{\delta Q}{T}\right)_{C_2} \tag{5.19}$$

Thus the integral $\int \delta Q/T$ is path independent, *i.e.*, independent of the process of heating or cooling the system. The integral depends only on the initial and final states of the system and thus represents a state function whose total differential is $\delta Q/T$. since heat is an extensive quantity, this state function, say S, is also extensive whose conjugate intensive parameter is temperature T. This extensive state function is the entropy S and defined as

$$dS = \frac{\delta Q}{T} \quad \text{and} \quad S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \tag{5.20}$$

Note that, only entropy difference could be measure, not the absolute entropy. The statistical mechanical definition of entropy will be given in the section of statistical mechanics.

5.3 Second Law

The second law of thermodynamics introduces the entropy S as an extensive state variable and states that for an infinitesimal reversible process at temperature T, the heat given to the system is

$$\left.đQ\right|_{rev} = TdS$$

while for an irreversible process

$$\left.đQ\right|_{irrev} \leq TdS$$

If we are only interested in thermodynamic equilibrium states we can use $\left.đQ\right|_{rev} = TdS$ and treat the entropy S as the generalized displacement which is coupled to the 'force' T. The above formulation of the second law is due to Gibbs

We present next two equivalent statements of the second law of thermodynamics. The Kelvin version is:

There exists no thermodynamic process whose sole effect is to extract a quantity of heat from a

system and to convert it entirely to work.

The equivalent statement of Clausius is:

No process exists in which the sole effect is that heat flows from a reservoir at a given temperature to a reservoir at a higher temperature.

A corollary of these statements is that the most efficient engine operating between two reservoirs at temperatures T_1 and T_2 is the Carnot engine.

The first law of thermodynamics tells us about the conservation of energy in a thermodynamic process during its change of state. The second law tells us about the direction of a natural process in an isolated system. The entropy $S = \delta Q_{rev}/T$ is the amount of heat reversibly exchanged with the surroundings at temperature T. since the amount of heat δQ_{irr} exchanged in an irreversible process is always less than that of δQ_{rev} exchanged in a reversible process, it is then always true that

$$\delta Q_{irr} < \delta Q_{rev} = TdS \tag{5.21}$$

For an isolated system, $\delta Q_{rev} = 0$. Therefore, in an isolated system the entropy is constant in thermodynamic equilibrium and it has an extremum since $dS = 0$.

It is found that in every situation this extremum is a maximum. All irreversible processes in isolated system which lead to equilibrium are then governed by an increase in entropy and the equilibrium will be reestablished only when the entropy will assume its maximum value. This is the second law of thermodynamics.

Any change of state from one equilibrium state to another equilibrium state in an isolated system will occur naturally if it corresponds to an increase in entropy.

For reversible process the entropy change is zero.

$$dS = 0 \tag{5.22}$$

and for irreversible processes the entropy change is always positive

$$dS > 0 \tag{5.23}$$

Note that, entropy could be negative if there is heat exchange with the surroundings i.e., the system is not an isolated system. It is positive only for an isolated system.

The first law for reversible changes now can be rewritten in terms of entropy:

Fluid system:	$dE = TdS - PdV$	Strained wire:	$dE = T$
Surface film:	$dE = TdS + \gamma dA$	Magnetic materials:	$dE = T$

If there is exchange of energy of several different forms, the first law should take a form

$$dE = TdS - PdV + HdM + \mu dN + \cdots \tag{5.24}$$

5.4 Third Law

The third law of thermodynamics deals with the entropy of a system as the absolute temperature tends to zero. It is already seen that

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \tag{5.25}$$

and one can only measure the entropy difference between two states. The absolute value of entropy for a given thermodynamic states remains undetermined because of the arbitrary additive constant depending on the choice of the initial state. The third law enables us to determine the additive constant appearing in the definition of entropy. It states that: the entropy of every system at absolute zero can always be taken equal to zero,

$$\lim_{T \to 0} S = 0 \tag{5.26}$$

The zero temperature entropy is then independent of any other properties like volume or pressure of the system. It is generally believed that the ground state at $T = 0$ is a single non-degenerate state. It is therefore convenient to choose this nondegenerate state at $T = 0$ as the standard initial state in the definition of entropy and one could set the entropy of the standard state equal to zero. The entropy of any state A of the system is now defined, including the additive constant, by the integral

$$S(A) = \int_{T=0}^{A} \frac{\delta Q}{T} \tag{5.27}$$

where the integral is taken along a reversible transformation from $T = 0$ state (lower limit) to the state A. since $dQ = C(T)dT$, the entropy of a system at temperature T can also be given as

$$S = \int_0^T \frac{C_V(T)}{T} dT \quad \text{or} \quad S = \int_0^T \frac{C_P(T)}{T} dT \tag{5.28}$$

when the system is heated at constant volume or constant pressure. As a consequence of the third law $S(0) = 0$, the heat capacities C_V or C_P at $T = 0$ must be equal to zero otherwise the above integrals will diverge at the lower limit. Thus, one concludes

$$C_V \quad \text{or} \quad C_P \to 0 \quad \text{as} \quad T \to 0 \tag{5.29}$$

The results are in agreement with the experiments on the specific heats of solid