

## Properties of a system

Any characteristic of a system is called a property. Some familiar properties are pressure  $P$ , temperature  $T$ , volume  $V$ , and mass  $m$ .

Properties are considered to be either intensive or extensive. Intensive properties are those that are independent of the mass of a system, such as temperature, pressure and density. Extensive properties are those whose values depend on the size - or extent - of the system. Total mass, total volume, and total momentum are some examples of extensive properties.

Generally, uppercase letters are used to denote extensive properties (with  $m$  being a major exception), and lowercase letters are used for intensive properties (with pressure  $P$  and temperature  $T$  being the obvious exceptions).

Extensive properties per unit mass are called specific properties. Some examples of specific properties are specific volume ( $v = \frac{V}{m}$ ) and specific total energy ( $e = \frac{E}{m}$ ). Specific properties are intensive properties.

### Concept of continuum

From the macroscopic viewpoint, we are always concerned with volumes which are very large compared to molecular dimensions. Even a very small volume of a system is assumed to contain a large number of molecules so that a property value is meaningful and can be assigned to it. Disregarding the behaviour of individual molecules, matter is here treated as continuous. Let us consider the mass  $\delta m$  in a volume  $\delta V$  surrounding the point  $P$ . The ratio  $\frac{\delta m}{\delta V}$  is the average mass density of the system (Fig. 2.2).

within the volume  $\delta V$ . We suppose that at first  $\delta V$  is rather large, and is subsequently shrunk about the point P. If we plot  $\delta m/\delta V$  against  $\delta V$ , the average density tends to approach an asymptote as  $\delta V$  increases (Fig. 2.2). However, when  $\delta V$  becomes so small as to contain relatively few molecules the average density fluctuates substantially with time as molecules pass into and out of the volume in random motion, and so it is impossible to speak of a definite value of  $\delta m/\delta V$ . The smallest volume which may be regarded as continuous is  $\delta V'$ . The density  $\rho$  of the system at a point is thus defined as

$$\rho = \lim_{\delta V \rightarrow \delta V'} \frac{\delta m}{\delta V} \quad (1)$$

Similarly, the fluid velocity at a point P is defined as the instantaneous velocity of the centre of gravity of the continuous volume  $\delta V'$ .

The concept of continuum loses validity when the mean free path of the molecules approaches the order of magnitude of the dimensions of the vessel, as, for instance, in highly rarefied gases encountered in high vacuum technology, in rocket flights at high altitudes and in electron tubes. In most engineering applications, however, the assumption of a continuum is valid and convenient, and goes hand in hand with the macroscopic point of view.

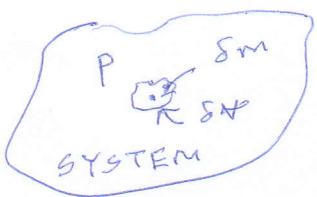


Fig. 2.1

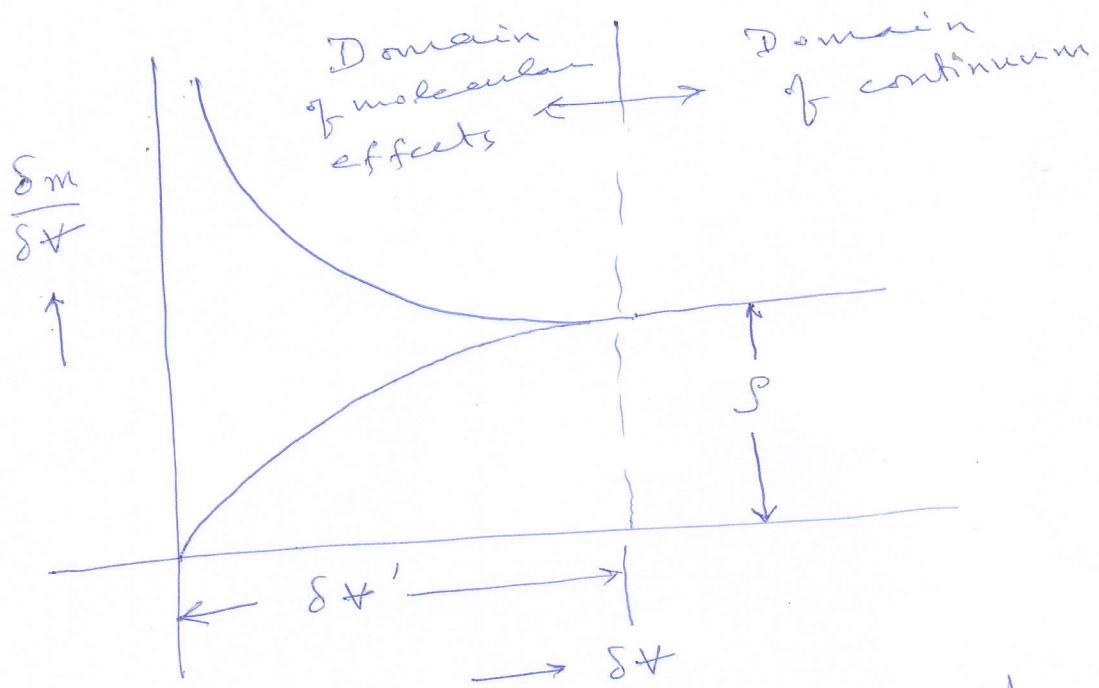


Fig. 2.2 Definition of the macroscopic property, density

### State and Equilibrium

Consider a system not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition, or the state of the system. At a given state, all the properties of a system have fixed values. If a value of even one property changes, the

state will change to a different one. In Fig. 2.3 a system is shown at two different states.

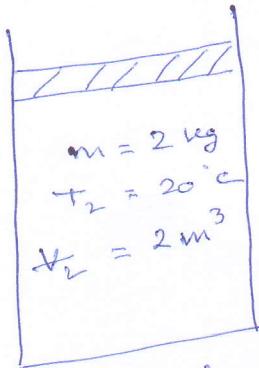
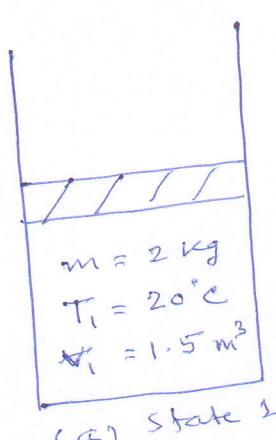


Fig. 2.3

A system at two different states

Thermodynamics deals with equilibrium states. The word equilibrium implies a state of balance. In an equilibrium state there are no unbalanced potential (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from the surroundings.

There are many types of equilibrium, and a system is not in thermodynamic equilibrium under the conditions of equilibrium unless all the relevant types of equilibrium are satisfied. For example, a system is in thermal equilibrium if the temperature is same throughout the entire system. Mechanical equilibrium is related to pressure, a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time. The variation of pressure as a result of gravity in most thermodynamic systems is relatively small and usually disregarded.

If a system involves two phases, it is in phase equilibrium when the mass of each phase reaches an equilibrium level and stays there. Finally, a system is in chemical equilibrium if its chemical composition does not change with time, that is, no chemical reactions occur. A system will not be in equilibrium unless all the relevant equilibrium criteria are satisfied.

## The State Postulate

The number of properties required to fix the state of a system is given by the state postulate:

The state of a simple compressible substance is completely specified by two independent, intensive properties.

A system is called a simple system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects.

The state postulate requires that the two properties specified be independent to fix the state. Two properties are independent if one property can be varied while the other one is held constant. Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system.

Temperature and pressure, however, are independent properties for single phase systems, but are dependent properties for multiphase systems. At sea level (P = 1 atm), water boils at 100°C, but on a mountain top where the pressure is lower, water boils at a lower temperature. That is,  $T = f(P)$  during a phase change process; thus, temperature and pressure are not sufficient to fix the state of a two-phase system.

### Processes and Cycles

Any change that a system undergoes from one equilibrium state to another is called a process, and the series of states through which a system passes during a process is called the path of the process (Fig. 2.4). To describe a process completely, one should specify the initial and final states of the process, as well as the path it follows, and the interactions with the surroundings.

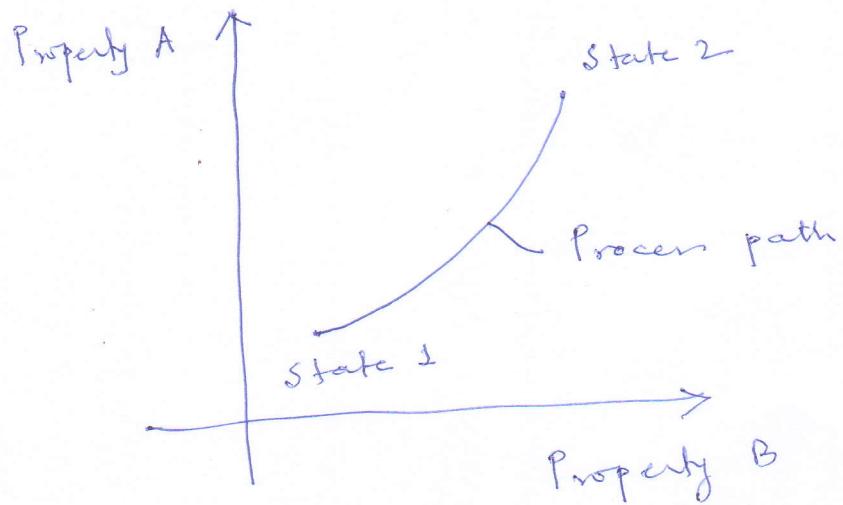
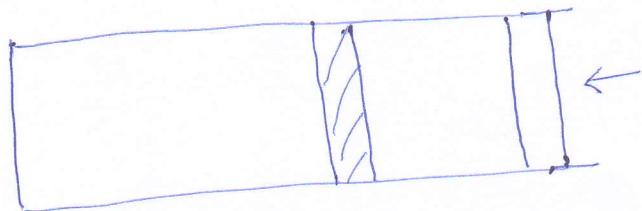


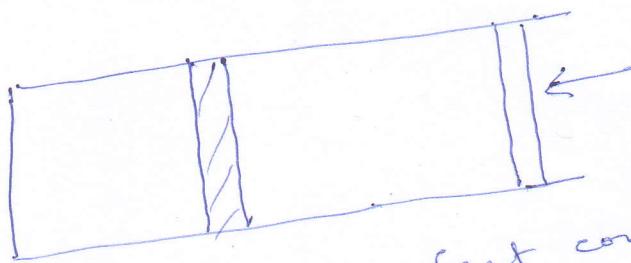
Fig. 2.4 A process between states 1 and 2 and the process path

When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a quasi-static, or quasi-equilibrium process. A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

This is illustrated in Fig. 2.5.



(a) slow compression  
(quasi-equilibrium)



(b) very fast compression  
(nonquasi-equilibrium)

Fig. 2.5 Quasi-equilibrium  
and nonquasi-equilibrium  
processes

When a gas in a piston-cylinder device is compressed suddenly, the molecules near the face of the piston will not have enough time to escape and they will have to pile up in a small region in front of the piston, thus creating a high pressure-region. Because of this pressure difference, the system can no longer be said to be in equilibrium, and this makes the entire process non quasi-equilibrium. However, if the piston moves slowly, the molecules will have sufficient time to redistribute and there will not be a molecular pile up in front of the piston. As a result, the pressure inside the cylinder will always be nearly uniform and will rise at the same rate at all locations. Since equilibrium is maintained at all times, this is a quasi-equilibrium process.

It should be pointed out that a quasiequilibrium process is an idealized process and is not a true representation of an actual process. But many actual processes closely approximate it, and they can be modelled as quasiequilibrium with negligible error. Engineers are interested in quasiequilibrium processes for two reasons. First, they are easy to analyze; second, work-producing devices deliver the most work when they operate on quasiequilibrium processes. Therefore, quasiequilibrium processes serve as standards to which actual processes can be compared.

Fig. 2.6 shows the  $P-H$  diagram of a compression process of a gas.

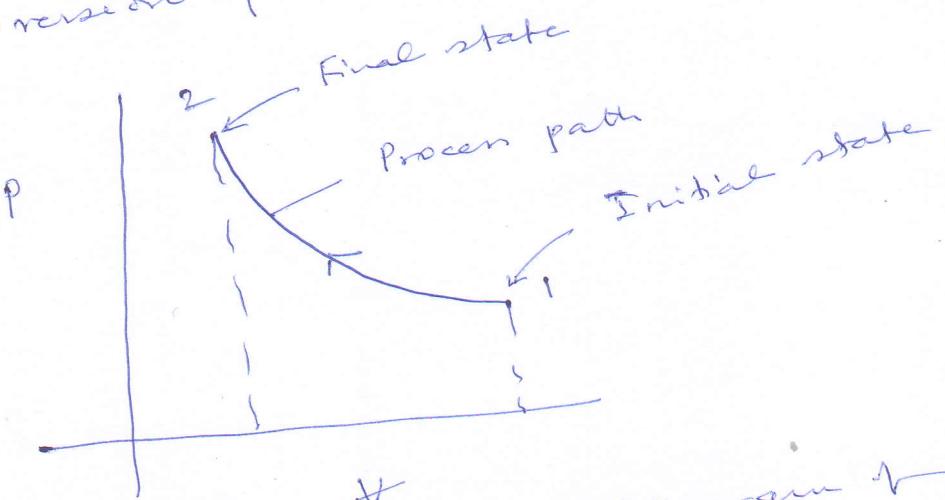


Fig. 2.6 The  $P-H$  diagram for a compression process

Note that process path indicates a series of equilibrium states through which the system passes during a process and has significance for process and has significance for quasi-equilibrium process only. For non quasi-equilibrium processes, we are not able to characterize the entire system by a single state, and thus we cannot speak of a process path for a system as a whole. A non quasi-equilibrium process is denoted by a dashed line between the initial and final states instead of a solid line.

The prefix iso- is often used to designate a process for which a particular property remains constant. An isothermal process, for example, is a process during which the temperature  $T$  remains constant; an isobaric process is a process during which the pressure  $P$  remains constant; and an isochoric (or isometric) process is a process during which the specific volume  $v$  remains constant.

A system is said to have undergone a cycle if it returns to its initial state at the end of the process. That is, for a cycle the initial and final states are identical (Fig. 2-7)

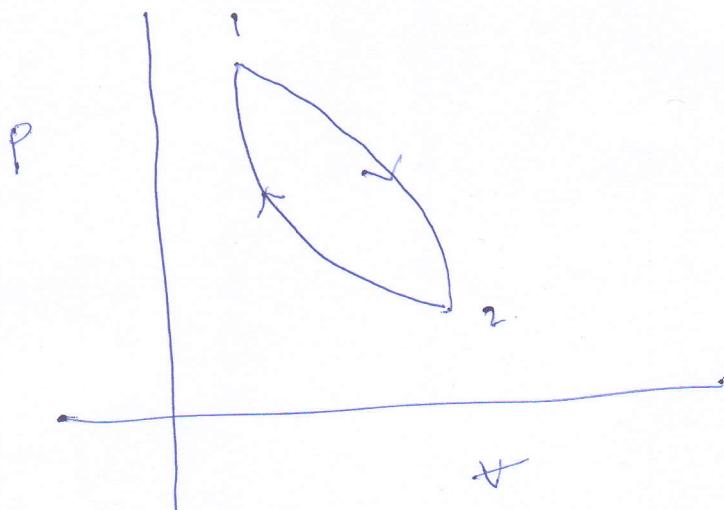


Fig. 2-7 A cycle