For isothermal change of state (T = Const, N = Const)

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change of entropy $S_f - S_i = NK \ln\left(V_f/V_i\right)$

$$S = NK \ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}NK$$

$$= NK\left[\ln V + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right)\right] + \frac{3}{2}NK$$

As temperature remain constant total energy also remain constant since $\left(E = \frac{3}{2}nRT\right)$.

$$\therefore S_f - S_i = NK\ln V_f - NK\ln V_i = NK\ln\left(V_f/V_i\right)$$

Therefore entropy of the ideal gas becomes

$$S = NK\ln V + \frac{3}{2}NK\left[1 + \ln\left(\frac{2\pi mKT}{h^2}\right)\right] \quad \left[\because E = \frac{3}{2}NKT\right]$$

~~if~~ If we increase the size of the system by a factor α keeping the intensive variables (like particle density $\frac{N}{V}$) unchanged, i.e

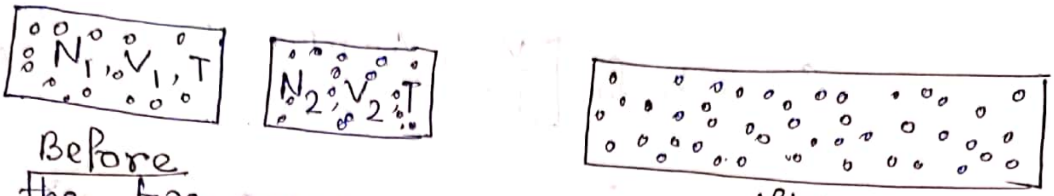
$N \to \alpha N$

$V \to \alpha V$

$E \to \alpha E$

Then entropy should also increase by an amount α being an extensive variable. But the term $\ln V$ affects the result adversely. That means our ~~expes~~ expression of entropy makes S an intensive variable which is quite un-physical.

Gibbs Paradox :- Let us take two ideal gas 1 and 2. both being initially at the same temperature T.



now the two gases are mixed at the same temperature T.

Before mixing, Entropy of individual gas

$$S_i = N_i k \ln V_i + \frac{3}{2} N_i k \left[1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right] \quad \text{------} ①$$

$i = 1, 2$

After mixing, Entropy of the Gas mixture

$$S_T = \sum_{i=1}^{2} \left[N_i k \ln V + \frac{3}{2} N_i k \left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\}\right]$$

$V = V_1 + V_2$ total volume

∴ Increase in the entropy

$$\Delta S = S_T - \sum_{i=1}^{2} S_i$$

$$= k\left[N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2}\right]$$

= +ve (since it is an irreversible process)

As, we have kept the intensive variable unchanged ∴ particle density remain unchanged

i.e. $n_1 = n_2 = n$, $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}$

$$\therefore \frac{V_1+V_2}{V_1} = \frac{N_1+N_2}{N_1} \quad \text{and} \quad \frac{V_1+V_2}{V_2} = \frac{N_1+N_2}{N_2}$$

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$$\therefore \Delta S = K\left[N_1 \ln\frac{N_1+N_2}{N_1} + N_2 \ln\frac{N_1+N_2}{N_2}\right]$$

$$\therefore \Delta S > 0$$

So far it seems all right. as we know for irriversable process $\Delta S > 0$

But if we consider the mixing of two samples of the same gas. Entropy of the individual samples is given by equation(1) with $m_i = m$ (say). And the entropy after mixing

$$S_T = \sum_{i=1}^{2}\left[K N_i \ln V + \frac{3}{2} N_i K\left\{1+\ln\left(\frac{2\pi m K T}{h^2}\right)\right\}\right]$$

$$= NK\ln V + \frac{3}{2}NK\left\{1+\ln\left(\frac{2\pi m K T}{h^2}\right)\right\} \quad \left[\begin{array}{l}\text{where}\\ N = N_1+N_2\end{array}\right]$$

$$\therefore \Delta S = K\left[N_1 \ln\frac{N_1+N_2}{N_1} + N_2 \ln\frac{N_1+N_2}{N_2}\right] > 0$$

But this ~~os~~ result is unaceeptable because mixing of two samples of ~~same~~ the same gas with common initial temperature and common initial particale density is clearly a reversable process, ~~b~~ for we can simply re insert the partioning wall into the system and we get the systems which are present before mixing. There fore the result should be

$$\Delta S = 0$$

Thus, the expression of entropy as derived makes the entropy a intensive variable and gives the entropy of mixing for two sample of same gas positive, which are quite unphysical.

This paradoxial situation can be avoided if expression of entropy is diminished (subtracted) by a term $K\ln(N!)$. This remedy is proposed by Gibbs to avoid the paradox.

$$\therefore\ S(N,V,E) = NK\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}NK - K\ln(N!)$$

$$= NK\ln\left[\frac{V}{h^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}NK - K\left[N\ln N - N\right]$$

$$\therefore\ S = NK\ln\left(\frac{V}{N}\right) + \frac{3}{2}NK\left\{\frac{5}{3} + \ln\left(\frac{2\pi mKT}{h^2}\right)\right\} \quad \text{——} ②$$

[$\ln N! = N\ln N - N$ Stirling approximation]

~~If Now the size of the system increased~~

If we now mix two samples of the same gas at temperature T. entropy of mixing

$$\Delta S = K\left[(N_1+N_2)\ln\left(\frac{V_1+V_2}{N_1+N_2}\right) - N_1\ln\left(\frac{V_1}{N_1}\right) - N_2\ln\left(\frac{V_2}{N_2}\right)\right]$$

Since the particle densities of the samples are equal

i.e. $$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1+V_2}$$

$\therefore \Delta S = 0$

Also using the expression ② it can be shown that

$$\Delta S \text{ (for irreversible process)} = K\left[N_1 \ln\frac{N_1+N_2}{N_1} + N_2 \ln\frac{N_1+N_2}{N_2}\right]$$

Thus the paradox of ~~g~~ Gibbs is thereby resolved.

And the equation ② is generally refered to as Sackur - Tetrode equation.

If now the size of the system is increased by an amount α then from the relation

$$S = NK\ln\left(\frac{V}{N}\right) + \frac{3}{2}NK\left[\frac{5}{3} + \ln\left(\frac{2\pi mKT}{h^2}\right)\right]$$

we see that S also increases by the amount α. That means S becomes an extensive variable.

☒ As of we noted that for a given macro state (N, V, E) a statistical system at any time t is equally likely to be in any one of an extremely large no. of distinct micro-states. As time passes, the system continually switches from one microstate to another. therefore, ~~Af~~ after a reasonabale span of time all we ~~obes~~ observes is a behavioral average over the variety of micro states through which the system passes.

From here, ~~oo~~ we will study about ensemble.

Ensemble :- An ensemble is defined as collection of a large number of microscopically identical but essentially independent systems. By the term microscopically identical we mean that each of the system constituting an ensemble satisfies the same macroscopic condition (e.g volume, Energy, total no. of particles etc). By the term independent systems we mean that systems constituting an ensemble are mutually non-interacting.

Simply ensemble means given system along with a large number of mental copies of it.

Phase space of a classical system :- In classical statistical mechanics, the microscopic state of the system is described by specifying the position ($\vec{r}$) and momenta ($\vec{p}$) of all the particles in the system. For a system of N. molecules, each having f degrees of freedom, the complete specification of dynamical state is given by f co-ordinates and f conjugate momenta. The state is termed as the phases of the system. These $2f$ quantities constituting the phase can be represented geometrically by a point (phase point) in a $2f$ dimensional space called μ- space or phase space.

defined by these limits.

Now, if we consider an ensemble of systems (i.e., the given system, along with a large number of mental copies of it) then, at any time t, the various members of the ensemble will be in all sorts of possible microstates; indeed, each one of these microstates must be consistent with the given macrostate that is supposed to be common to all members of the ensemble. In the phase space, the corresponding picture will consist of a swarm of representative points, one for each member of the ensemble, all lying within the "allowed" region of this space. As time passes, every member of the ensemble undergoes a continual change of microstates; correspondingly, the representative points constituting the swarm continually move along their respective trajectories. The overall picture of this movement possesses some important features that are best illustrated in terms of what we call a *density function* $\rho(q,p;t)$.[1] This function is such that, at any time t, the number of representative points in the "volume element" $(d^{3N}q\,d^{3N}p)$ around the point (q,p) of the phase space is given by the product $\rho(q,p;t)d^{3N}q\,d^{3N}p$. Clearly, the density function $\rho(q,p;t)$ symbolizes the manner in which the members of the ensemble are distributed over all possible microstates at different instants of time. Accordingly, the *ensemble average* $\langle f\rangle$ of a given physical quantity $f(q,p)$, which may be different for systems in different microstates, would be given by

$$\langle f\rangle = \frac{\int f(q,p)\rho(q,p;t)d^{3N}q\,d^{3N}p}{\int \rho(q,p;t)d^{3N}q\,d^{3N}p}. \tag{3}$$

The integrations in (3) extend over the whole of the phase space; however, it is only the populated regions of the phase space ($\rho \neq 0$) that really contribute. We note that, in general, the ensemble average $\langle f\rangle$ may itself be a function of time.

An ensemble is said to be *stationary* if ρ does not depend explicitly on time, that is, at all times

$$\frac{\partial\rho}{\partial t} = 0. \tag{4}$$

---

[1] Note that (q,p) is an abbreviation of $(q_i,p_i) \equiv (q_1,\ldots,q_{3N},p_1,\ldots,p_{3N})$.

Clearly, for such an ensemble the average value $\langle f\rangle$ of *any* physical quantity $f(q,p)$ will be independent of time. Naturally, a stationary ensemble qualifies to represent a system in *equilibrium*. To determine the circumstances under which equation (4) may hold, we have to make a rather detailed study of the movement of the representative points in the phase space.

2.2 Liouville's theorem and its consequences

Consider an arbitrary "volume" ω in the relevant region of the phase space and let the "surface" enclosing this volume be denoted by σ; see Figure 2.1. Then, the rate at which the number of representative points in this volume increases with time is written as

$$\frac{\partial}{\partial t}\int_{\omega}\rho\, d\omega, \tag{1}$$

where $d\omega \equiv (d^{3N}q\, d^{3N}p)$. On the other hand, the *net* rate at which the representative points "flow" out of ω (across the bounding surface σ) is given by

$$\int_{\sigma}\rho\boldsymbol{v}\cdot\hat{\boldsymbol{n}}\, d\sigma; \tag{2}$$

here, $\boldsymbol{v}$ is the velocity vector of the representative points in the region of the surface element $d\sigma$ while $\hat{\boldsymbol{n}}$ is the (outward) unit vector normal to this element. By the divergence theorem, (2) can be written as

$$\int_{\omega}\mathrm{div}(\rho\boldsymbol{v})d\omega; \tag{3}$$

of course, the operation of divergence here means

$$\mathrm{div}(\rho\boldsymbol{v}) \equiv \sum_{i=1}^{3N}\left\{\frac{\partial}{\partial q_i}(\rho\dot{q}_i)+\frac{\partial}{\partial p_i}(\rho\dot{p}_i)\right\}. \tag{4}$$

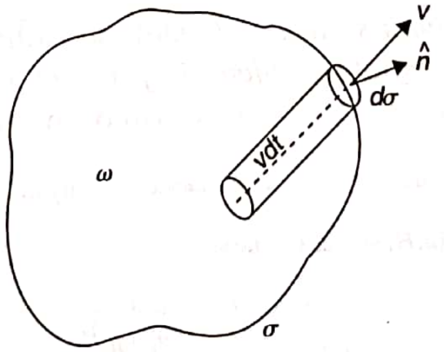

FIGURE 2.1 The "hydrodynamics" of the representative points in the phase space.

In view of the fact that there are no "sources" or "sinks" in the phase space and hence the total number of representative points remains conserved,[2] we have, by (1) and (3),

$$\frac{\partial}{\partial t}\int_{\omega} \rho \, d\omega = -\int_{\omega} \operatorname{div}(\rho \boldsymbol{v}) d\omega, \tag{5}$$

that is,

$$\int_{\omega} \left\{ \frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) \right\} d\omega = 0. \tag{6}$$

Now, the necessary and sufficient condition that integral (6) vanish for all arbitrary volumes ω is that the integrand itself vanish *everywhere* in the relevant region of the phase space. Thus, we must have

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \boldsymbol{v}) = 0, \tag{7}$$

which is the *equation of continuity* for the swarm of the representative points.

Combining (4) and (7), we obtain

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) + \rho \sum_{i=1}^{3N}\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) = 0. \tag{8}$$

The last group of terms vanishes identically because, by the equations of motion, we have, for all i,

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i, p_i)}{\partial q_i \partial p_i} \equiv \frac{\partial^2 H(q_i, p_i)}{\partial p_i \partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i}. \tag{9}$$

Further, since $\rho \equiv \rho(q, p; t)$, the remaining terms in (8) may be combined to form the "total" time derivative of ρ, with the result that

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0. \tag*{(10)^3}$$

Equation (10) embodies *Liouville's theorem* (1838). According to this theorem, the "local" density of the representative points, *as viewed by an observer moving with a representative point*, stays constant in time. Thus, the swarm of the representative points moves in

---

[2] This means that in the ensemble under consideration neither are any new members being added nor are any old ones being removed.

[3] We recall that the *Poisson bracket* $[\rho, H]$ stands for the sum

$$\sum_{i=1}^{3N}\left(\frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right),$$

which is identical to the group of terms in the middle of (8).

the phase space in essentially the same manner as an incompressible fluid moves in the physical space!

A distinction must be made, however, between equation (10) on one hand and equation (2.1.4) on the other. While the former derives from the basic mechanics of the particles and is therefore *quite generally* true, the latter is only a requirement for equilibrium which, in a given case, may or may not be satisfied. The condition that ensures simultaneous validity of the two equations is clearly

$$[\rho, H] = \sum_{i=1}^{3N} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0. \tag{11}$$

Now, one possible way of satisfying (11) is to assume that ρ, which is already assumed to have no explicit dependence on time, is *independent* of the coordinates (q, p) as well, that is,

$$\rho(q, p) = \text{const.} \tag{12}$$

over the relevant region of the phase space (and, of course, is zero everywhere else). Physically, this choice corresponds to an ensemble of systems that at *all* times are *uniformly* distributed over all possible microstates. The ensemble average (2.1.3) then reduces to

$$\langle f \rangle = \frac{1}{\omega} \int_{\omega} f(q, p) d\omega; \tag{13}$$

here, ω denotes the total "volume" of the relevant region of the phase space. Clearly, in this case, *any* member of the ensemble is equally likely to be in *any* one of the various possible microstates, inasmuch as *any* representative point in the swarm is equally likely to be in the neighborhood of *any* phase point in the allowed region of the phase space. This statement is usually referred to as the postulate of "equal *a priori* probabilities" for the various possible microstates (or for the various volume elements in the allowed region of the phase space); the resulting ensemble is referred to as the *microcanonical ensemble*.

A more general way of satisfying (11) is to assume that the dependence of ρ on (q, p) comes only through an explicit dependence on the Hamiltonian $H(q, p)$, that is,

$$\rho(q, p) = \rho[H(q, p)]; \tag{14}$$

condition (11) is then identically satisfied. Equation (14) provides a class of density functions for which the corresponding ensemble is stationary. In Chapter 3 we shall see that the most natural choice in this class of ensembles is the one for which

$$\rho(q, p) \propto \exp[-H(q, p)/kT]. \tag{15}$$

The ensemble so defined is referred to as the *canonical ensemble*.

2.3 The microcanonical ensemble

In this ensemble the macrostate of a system is defined by the number of molecules N, the volume V, and the energy E. However, in view of the considerations expressed in Section 1.4, we may prefer to specify a range of energy values, say from $(E-\frac{1}{2}\Delta)$ to $(E+\frac{1}{2}\Delta)$, rather than a sharply defined value E. With the macrostate specified, a choice still remains for the systems of the ensemble to be in *any one* of a large number of possible microstates. In the phase space, correspondingly, the representative points of the ensemble have a choice to lie *anywhere* within a "hypershell" defined by the condition

$$\left(E-\frac{1}{2}\Delta\right) \le H(q,p) \le \left(E+\frac{1}{2}\Delta\right). \tag{1}$$

The volume of the phase space enclosed within this shell is given by

$$\omega = \int' d\omega \equiv \int' \left(d^{3N}q\, d^{3N}p\right), \tag{2}$$

where the primed integration extends only over that part of the phase space which conforms to condition (1). It is clear that ω will be a function of the parameters N, V, E, and Δ.

Now, the microcanonical ensemble is a collection of systems for which the density function ρ is, at all times, given by

$$\left.\begin{array}{ll} \rho(q,p) = \text{const.} & \text{if } \left(E-\frac{1}{2}\Delta\right) \le H(q,p) \le \left(E+\frac{1}{2}\Delta\right) \\ 0 & \text{otherwise} \end{array}\right\}. \tag{3}$$

Accordingly, the expectation value of the number of representative points lying in a volume element $d\omega$ of the relevant hypershell is simply proportional to $d\omega$. In other words, the *a priori* probability of finding a representative point in a given volume element $d\omega$ is the same as that of finding a representative point in an equivalent volume element $d\omega$ located *anywhere* in the hypershell. In our original parlance, this means an equal *a priori* probability for a given member of the ensemble to be in *any one* of the various possible microstates. In view of these considerations, the ensemble average $\langle f \rangle$, as given by equation (2.2.13), acquires a simple physical meaning. To see this, we proceed as follows.

Since the ensemble under study is a stationary one, the ensemble average of any physical quantity f will be independent of time; accordingly, taking a time average thereof will not produce any new result. Thus

$\langle f \rangle \equiv$ the ensemble average of f

$=$ the time average of (the ensemble average of f).

Now, the processes of time averaging and ensemble averaging are completely independent, so the order in which they are performed may be reversed without causing any change in the value of $\langle f \rangle$. Thus

$$\langle f \rangle = \text{the ensemble average of (the time average of } f).$$

Now, the time average of any physical quantity, taken over a sufficiently long interval of time, must be the same for *every* member of the ensemble, for after all we are dealing with only *mental copies* of a given system.[4] Therefore, taking an ensemble average thereof should be inconsequential, and we may write

$$\langle f \rangle = \text{the long-time average of } f,$$

where the latter may be taken over *any* member of the ensemble. Furthermore, the long-time average of a physical quantity is all one obtains by making a measurement of that quantity on the given system; therefore, it may be identified with the value one expects to obtain through experiment. Thus, we finally have

$$\langle f \rangle = f_{\text{exp}}. \tag{4}$$

This brings us to the most important result: *the ensemble average of any physical quantity f is identical to the value one expects to obtain on making an appropriate measurement on the given system.*

The next thing we look for is the establishment of a connection between the mechanics of the microcanonical ensemble and the thermodynamics of the member systems. To do this, we observe that there exists a direct correspondence between the various microstates of the given system and the various locations in the phase space. The volume ω (of the allowed region of the phase space) is, therefore, a direct measure of the multiplicity Γ of the microstates accessible to the system. To establish a numerical correspondence between ω

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[4] To provide a *rigorous* justification for this assertion is not trivial. One can readily see that if, for any particular member of the ensemble, the quantity f is averaged only over a *short* span of time, the result is bound to depend on the relevant "subset of microstates" through which the system passes during that time. In the phase space, this will mean an averaging over only a "part of the allowed region." However, if we employ instead a sufficiently long interval of time, the system may be expected to pass through *almost* all possible microstates "without fear or favor"; consequently, the result of the averaging process would depend only on the macrostate of the system, and not on a subset of microstates. Correspondingly, the averaging in the phase space would go over *practically* all parts of the allowed region, again "without fear or favor." In other words, the representative point of our system will have traversed each and every part of the allowed region *almost* uniformly. This statement embodies the so-called *ergodic theorem* or *ergodic hypothesis*, which was first introduced by Boltzmann (1871). According to this hypothesis, the trajectory of a representative point passes, in the course of time, through *each and every* point of the relevant region of the phase space. A little reflection, however, shows that the statement as such requires a qualification; we better replace it by the so-called *quasiergodic hypothesis*, according to which the trajectory of a representative point traverses, in the course of time, *any neighborhood of any point* of the relevant region. For further details, see ter Haar (1954, 1955), Farquhar (1964).

Now, when we consider an ensemble of systems, the foregoing statement should hold for every member of the ensemble; thus, *irrespective of the initial (and final) states* of the various systems, the long-time average of any physical quantity f should be the same for every member system.

and Γ, we need to discover a *fundamental volume* ω_0 that could be regarded as "equivalent to one microstate." Once this is done, we may say that, asymptotically,

$$\Gamma = \omega/\omega_0. \tag{5}$$

The thermodynamics of the system would then follow in the same way as in Sections 1.2–1.4, namely through the relationship

$$S = k \ln \Gamma = k \ln(\omega/\omega_0), \quad \text{etc.} \tag{6}$$

The basic problem then consists in determining ω_0. From dimensional considerations, see (2), ω_0 must be in the nature of an "angular momentum raised to the power $3N$." To determine it exactly, we consider certain simplified systems, both from the point of view of the phase space and from the point of view of the distribution of quantum states.

Intensive property :- It is a physical quantity whose value does not depend on the amount of the substance. In thermal equilibrium temperature of a system is the same as the temperature of any part of it. If the system is divided that does not change its temperature.

Extensive Property :- It is a physical quantity whose value depend on the size of the system. ~~It depe~~ Mass of a sample is extensive property, it depends on the amount of the ~~syst~~, substance.
Magnitude of the Extensive quantity is additive ~~for~~ of subsystems

If An Extensive quantity is divided by another Extensive quantity then Resultant will be Intensive quantity.

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