

## Equilibrium distribution

We have seen that a microstate of an ideal gas is specified by a set of values of all the  $3N$  position coordinates and  $3N$  momentum coordinates  $(x_1, p_{x_1}), (y_1, p_{y_1}), (z_1, p_{z_1}), \dots, (y_N, p_{y_N}), (z_N, p_{z_N})$  of all the  $N$  molecules. However, a macrostate of the gas is specified by the total energy  $E$  of all the gas molecules. Clearly many distinct microstates may correspond to the same macrostate. For instance an ideal gas consisting of free particles, all the microstates whose momentum coordinates satisfy

$$p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2 + \dots + p_{z_N}^2 = E \quad (1)$$

would correspond to the same macrostate with energy value  $E$ . The number of microstates corresponding to that macrostate is thermodynamic probability  $W(E)$  of that macrostate.

We will now derive a condition that thermodynamic probability of any macrostate must obey. We will use this condition to derive an explicit form for thermodynamic probability as a function of energy. For this purpose we will make use of an important empirical fact about the thermodynamic probability when different parts of the ideal gas are at thermal equilibrium.

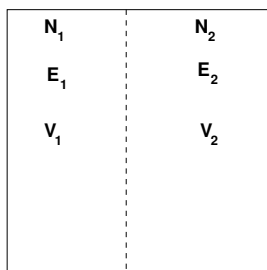


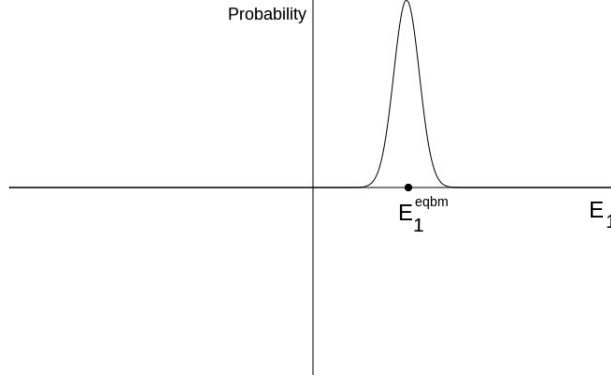
Figure 1: Two subsystems of an isolated system

Consider a thermodynamic system consisting of an ideal gas in a box of volume  $V$  that is thermally isolated from its surroundings. Let the total number of gas molecules be  $N$  with a total energy  $E$ . Consider two subsystems 1 and 2 obtained by an imaginary partition of the above system as indicated in the figure. Let the subsystem 1 have a volume  $V_1$ , number of molecules  $N_1$ , a total energy  $E_1$  and the corresponding numbers for subsystem 2 be  $V_2$ ,  $N_2$  and  $E_2$  respectively. Here  $N_1$  and  $N_2$  are taken to be sufficiently large so as to treat each of the subsystems thermodynamic. Clearly

$$N_1 + N_2 = N \quad E_1 + E_2 = E \quad V_1 + V_2 = V \quad (2)$$

Since the partition between the subsystems is not actual, the particles can cross over from one side to the other. It is clear that the numbers  $N_1$ ,  $N_2$  and the energies  $E_1$ ,  $E_2$  tend to vary with time.

If we leave the entire box undisturbed for sufficiently long time, the gas in subsystem 1 will interact with that in 2 and finally reach an *equilibrium* when the average energy exchanged between subsystems 1 and 2 is zero. Let  $E_1^{(eqbm)}$  and  $E_2^{(eqbm)}$  be the energies of subsystem 1 and 2 at equilibrium. Once it reaches equilibrium variations in energy of subsystem 1 from its  $E_1^{(eqbm)}$  will be very rare and very small. Same holds true for subsystem 2 because even at equilibrium, the total energy must remain same,  $E_1^{(eqbm)} + E_2^{(eqbm)} = E$ . If we plot the probability of finding subsystem 1 for various values of its energy  $E_1$  we get



Therefore we can conclude that  $E_1^{(eqbm)}$  is the most probable value for  $E_1$ . In other words, the probability as a function of energy must have a maximum at  $E_1 = E_1^{(eqbm)}$ .

The probability  $P(E_1)$  of a macrostate must be proportional to the number of ways in which that macrostate can be realized. Now this is precisely thermodynamic probability  $W(E_1)$  of that macrostate, ie., the number of microstates associated with that macrostate. Therefore

$$\begin{aligned} P(E_1) &\propto W(E_1) \\ P(E_1) &= cW(E_1) \end{aligned} \quad (3)$$

where  $c$  is the constant of proportionality. For subsystem 2 we can similarly obtain

$$P'(E_2) = cW'(E_2) \quad (4)$$

We have two independent subsystems 1 and 2. Thus subsystem 1 can assume any one of the microstates allowed to it independent of what microstate subsystem 2 is in. Then we can see that the probability for subsystem 1 to have energy  $E_1$  and 2 to have energy  $E_2$  is

$$P(E_1, E_2) = P(E_1)P'(E_2) = c c' W(E_1)W'(E_2) \quad (5)$$

At equilibrium, we expect the above probability to have a maximum as a function of  $E_1$ . Thus

$$\left. \frac{dP(E_1, E_2)}{dE_1} \right|_{E_1=E_1^{(eqbm)}} = 0 \quad (6)$$

If  $P(E_1, E_2)$  has a maximum at  $E_1 = E_1^{(eqbm)}$ , then  $\ln P(E_1, E_2)$  also must have a maximum at the same value of energy. Finding

$$\ln P(E_1, E_2) = \ln(c c') + \ln W(E_1) + \ln W'(E_2) \quad (7)$$

we get

$$\frac{d}{dE_1} \ln P(E_1, E_2) = \frac{1}{W(E_1)} \frac{dW(E_1)}{dE_1} + \frac{dE_2}{dE_1} \frac{1}{W(E_2)} \frac{dW(E_2)}{dE_2} \quad (8)$$

From eqn (3) we get  $\frac{dE_2}{dE_1} = -1$ , which converts the RHS of eqn (8) into

$$\frac{1}{W(E_1)} \frac{W(E_1)}{dE_1} - \frac{1}{W(E_2)} \frac{W(E_2)}{dE_2} \quad (9)$$

Since we have a maximum for  $\ln P(E_1, E_2)$  at  $E_1 = E_1^{(eqbm)}$

$$\left. \frac{d \ln P(E_1, E_2)}{dE_1} \right|_{E_1=E_1^{(eqbm)}} = 0 \quad (10)$$

$$\Rightarrow \left. \frac{1}{W(E_1)} \frac{W(E_1)}{dE_1} \right|_{E_1=E_1^{(eqbm)}} = \left. \frac{1}{W(E_2)} \frac{W(E_2)}{dE_2} \right|_{E_2=E_2^{(eqbm)}} \quad (11)$$

Note that since  $E$  is still a constant  $E_2^{(eqbm)} = E - E_1^{(eqbm)}$ . From the above we can conclude that different subsystems that are at thermal equilibrium with respect to each other will have their thermodynamic probability satisfy

$$\frac{1}{W(E)} \frac{W(E)}{dE} = \beta, \text{ a constant} \quad (12)$$

From experiment we know that, at thermal equilibrium, different subsystems of a system must have the *same temperature*  $T$ . Thus the quantity in eqn (12) must be a constant for a constant temperature. In other words it must be a function of temperature. We will find this function below.

It is useful to note another aspect of eqn (12). If we integrate the equation we get

$$W(E) = C e^{\beta E} \quad (13)$$

where  $C$  is the constant of integration.

This means the number of microstates associated with the macrostate with energy  $E$  grows exponentially fast. But according to the principle of equipartition of probability, all microstates corresponding to a given macrostate have the same probability. Thus any microstate corresponding to the macrostate with energy  $E$  must have a probability

$$p_{micro}(E) = \frac{1}{W(E)} = \frac{1}{C} e^{-\beta E} \quad (14)$$

The exponential function  $e^{-\beta E}$  of energy is known as Boltzmann factor. The value of constant of integration  $C$  is not yet determined, hence it remains arbitrary in eqn (14).

As the number of possible ways of achieving a given value of energy increases, the disorder of that system increases. The degree of disorder in the system is measured in terms of the entropy  $S$ . Entropy has the feature that it is additive. For the subsystems, considered in figure (1) this means that the net entropy of the system  $S$  is the sum of the entropy  $S_1$  of the subsystem 1 and  $S_2$  that of the subsystem 2.

The number of possible ways of achieving a given value of energy is the thermodynamic probability  $W(E)$ . For the subsystems 1 & 2 in figure (1), we know that the thermodynamic probability for subsystem 1 can have energy  $E_1$  and subsystem 2 can have energy  $E_2$  is the product  $W(E_1) W(E_2)$  of their individual thermodynamic probabilities. Thus the thermodynamic probability is multiplicative, and not additive. We can create an additive quantity from this if we consider the logarithm of  $W(E)$ .

$$\ln (W(E_1) W(E_2)) = \ln W(E_1) + \ln W(E_2)$$

This implies the entropy must be proportional to the logarithm of the thermodynamic probabilities,  $S(E) \propto \ln W(E)$

$$\Rightarrow S(E) = k_B \ln W(E) \tag{15}$$

where constant of proportionality  $k_B$  is the Boltzmann's constant with value (in SI units)  $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ .