

Lecture 6

Recap from the last class

We talked about two systems A_1 and A_2 being in equilibrium. We assumed A_1 has an energy E_1 and A_2 has an energy E_2 such that,

$$E_1 + E_2 = E = \text{constant} \Rightarrow E_2 = E - E_1$$

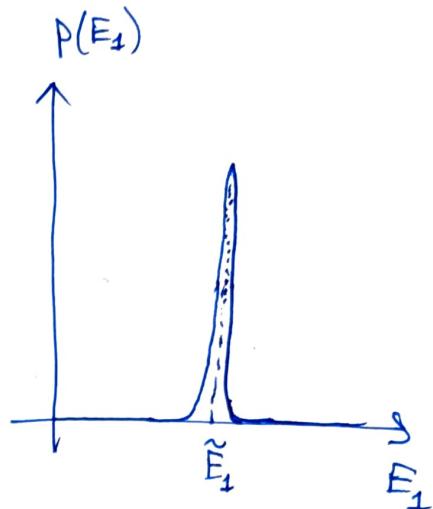
where E is the total energy of the system. At equilibrium, our fundamental postulate asserted that all the microstates are equally likely. So, the probability $P(E_1)$ that the system A_1 has an energy of E_1 is proportional to the total number of microstates of the combined system, Ω .

$$\therefore P(E_1) = C \Omega(E_1) = C \Omega_1(E_1) \Omega_2(E_2)$$

which we described in the last class.

Now, the number of microstates increases exponentially with energy. So, $\Omega_1(E_1)$ and $\Omega_2(E_2)$ are rapidly increasing functions of their respective energies. But if E_1 increases, E_2 decreases. So, as E_1 increases, $\Omega_1(E_1)$ increases rapidly and $\Omega_2(E_2)$ decreases rapidly. The product of an increasingly rapidly function with a rapidly decreasing function exhibits a sharp maximum.

So, we are going to get a sharp maximum for $P(E_1)$ (and similarly for $P(E_2)$) at a particular energy, say \tilde{E}_1 . This is shown in the graph.



We basically calculated for the condition of maximum of this graph. We found that, the maximum will occur for the condition,

$$\frac{d \ln \Omega_1(E_1)}{d E_1} = \frac{d \ln \Omega_2(E_2)}{d E_2} \quad \text{--- (1)}$$

We defined $\beta = \frac{1}{k_B T} = \frac{d \ln \Omega}{d E}$, as the Boltzmann factor, which has a dimension of reciprocal of energy.

$\therefore \frac{d \ln \Omega_1}{d E_1} \Big|_{\tilde{E}_1} = \frac{d \ln \Omega_2}{d E_2} \Big|_{\tilde{E}_2}$. $\beta_1(\tilde{E}_1) = \beta_2(\tilde{E}_2)$ and so, $T_1 = T_2$. Because maxima the probability is maximized. One defines the entropy as $S = k_B \ln \Omega$, so that, the energies at these energies parameter T is defined as -

$$\frac{1}{T} = \frac{d S}{d E}$$

and (1) is written as, $\frac{d S_1}{d E_1} = \frac{d S_2}{d E_2}$.

Correspondingly, if $\Omega_1(E_1) \Omega_2(E_2) = \text{max.}$, then,

$$\ln \Omega_1(E_1) + \ln \Omega_2(E_2) = \text{max.}$$

$\therefore S_1 + S_2 = \text{maximum}$

in equilibrium for $P(E)$ to be maximum.

So, if the systems are brought to thermal contact, the equilibrium will be achieved, and in that case system A_1 will mostly at an energy \tilde{E}_1 and system A_2 will be at an energy \tilde{E}_2 . There will be small fluctuations in their energy, but they will be such that the mean values of the energy of A_1 and A_2 are \tilde{E}_1 and \tilde{E}_2 respectively.

If two systems initially with energy E_1^i and E_2^i are bought into thermal contact, then they will exchange energy and reach equilibrium. Say, the final energies are E_1^f and E_2^f . The energy changes are given by,

$$Q_1 = E_1^f - E_1^i \quad \text{and} \quad Q_2 = E_2^f - E_2^i$$

The conservation of energy suggests that,

$$E_1^i + E_2^i = E_1^f + E_2^f \Rightarrow E_2^f - E_2^i = E_1^i - E_1^f$$

$$\Rightarrow \cancel{E_2^f - E_2^i} + \cancel{E_1^f - E_1^i} = 0$$

$$\therefore Q_2 = -Q_1$$

So, if Q_1 is positive, Q_2 is negative and vice versa. Negative Q just means heat is given off. So, if one system absorbs heat, another system must give off the heat.

By definition, we call the system that absorbs heat a "colder" object and the object that gives off heat, a "hotter" object.

There can be two situations —

(i) The initial energies are such that $\beta_1(E_1^i) = \beta_2(E_2^i)$, and correspondingly $T_1 = T_2$. In this case, the maximum probability is already achieved and they are in equilibrium. So, no heat transfer happens.

(ii) The energies are such that $\beta_1(E_1^i) \neq \beta_2(E_2^i)$ and hence transfer of heat energy will occur ~~not~~ until the condition of equilibrium, that is maximum probability is achieved. When this is achieved, $\beta_1(E_1^f) = \beta_2(E_2^f)$.

Concept of temperature

Say, we have three systems — A, B and C. We know, A and B will remain in equilibrium when they are brought into thermal contact if $\beta_A = \beta_B$. Similarly, B and C will be in ~~the~~ equilibrium if $\beta_B = \beta_C$. We can then conclude, $\beta_A = \beta_C$, which means A and C will be in thermal equilibrium. This is basically the statement of the zeroth law of thermodynamics.

The zeroth law of thermodynamics makes it possible to use a test system, called thermometer. It allows measurements that allows us to conclude whether two systems are in equilibrium or not. There are two specifications

(i) Since thermometer is also a system, it has many characterizing macroscopic parameter. Call it ν , and say, it varies appreciably when it is in contact with other systems. This parameter is called a thermometric parameter of M .

(ii) The system M is much smaller than the systems which are to be tested. This is necessary since we need the energy transfer to be minimum such that not much of the systems change.

One example of a thermometric parameter is the mercury in a glass tube. The resistance of a conductor is another one. The pressure of a gas in a bulb keeping volume constant corresponds to another thermometer.

If you place M in contact with a system, the thermometric property, such as height of mercury will change. If this change is same for A and B, they are in equilibrium. One can also build

up a scale using the value of ν . The

Value of β is by definition called the "temperature" when the system and M is in thermal equilibrium. According to this definition, temperature can be length, pressure, resistance etc. If we take this definition, then we can say -

Two systems will remain in equilibrium when placed in thermal contact if and only if they have the same temperature.

Since at equilibrium of thermometer M and system A, the parameter β is same, so, $\beta_m = \beta_A$. If one uses a different thermometer M', even then, $\beta'_m = \beta_A$. So, if β is used as a thermometric parameter, any thermometer yields the same ~~for~~ β , that is same temperature. This is called the absolute temperature.

One can use a reference point to make a scale of the absolute temperature $T_0 = (\beta K_B)^{-1}$, by exploiting the thermometric properties of thermometers. Such a scale is the Kelvin scale, in which the unit of temperature is K (kelvin). Boltzmann constant K_B then has an unit of $J K^{-1}$ and is given by,

$$K_B = 1.38 \times 10^{-23} \text{ J/K.}$$

Ensembles

In a given statistical description of a system, one always has some information available about the physical situation under consideration. The representative ensemble is then constructed in such a way that all the systems in the ensemble satisfy conditions consistent with given information about the system. Since there can be a variety of physical situations, there can be a corresponding number of ensembles.

We will talk about two out of the three most useful ensembles. These ensembles are -

- (i) Microcanonical ensemble: An ensemble of systems whose energy is fixed and can't exchange energy.
- (ii) Canonical ensemble: An ensemble of systems where the systems can exchange energy with other objects but not particles.
- (iii) Grand canonical ensemble: An ensemble of systems where the systems can exchange energy and particles with other objects surrounding them.

Micro-canonical ensemble

An isolated system that can't exchange energy represents a situation of fundamental importance. Even, whenever we are dealing with two systems in thermal contact, we can always consider the combined system as an isolated system. An isolated system of this kind consists of a given number of particles N , volume V and energy E . Probability arguments are then made with reference to an ensemble of such systems where all of them consists this N, V and E .

In microcanonical ensemble, all the microstates corresponds to the same energy E , since energy exchange is not possible. Fundamental postulate then asserts that all the microstates are equally probable. So, the probability of a particular microstate π occurring is given by,

$$P_\pi(E) = \frac{1}{\Omega(E)}$$

accessible

where $\Omega(E)$ is the total number of microstates with energy E of the system.

The idea of temperature that we derived before was using the idea of microcanonical ensemble. So, in this ensemble, temperature is a derived quantity, where energy

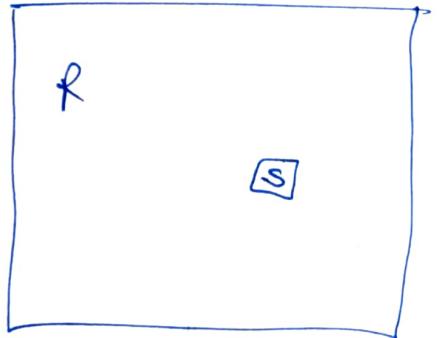
is fixed and given.

Canonical ensemble

This ensemble consists of systems that can exchange energy with a large reservoir, called the heat bath/ reservoir. Heat reservoirs are some ideal systems that has an infinite heat capacity. So, taking some heat or giving some is not going to change its temperature. In thermodynamics, we often deal with systems that are connected to heat reservoirs. So, canonical ensemble is much more of physical interest than the microcanonical one. Also, in canonical ensemble, the temperature is fixed, rather than the energy. So, we have an ensemble of systems having fixed N , V and T .

Consider a very small system S compared to a large heat reservoir R , where S is in thermal contact with R . The heat reservoir is big both in size, number of particles and so in degrees of

freedom) as compared to our system. For example, it can be a bottle of ~~water~~ juice in a pool (pool is reservoir, bottle is system), or a distinguishable microscopic system, like a single atom at some lattice site of a solid (solid acts as a reservoir). After the interaction takes place, the reservoir and the system come to an equilibrium temperature T . We ask the question, under the conditions of equilibrium, what is the probability ~~that~~ P_r of finding the system in "any one" of the microstates with energy ~~is~~ E_r ?



We already discussed that at equilibrium, the system can take a value of energy from a large spectrum. Even at equilibrium, there are exchange of energies between the reservoir and the system. It's just that, the net average exchange of heat energy is zero.

Now, the total energy of the reservoir-system is,

$$E_{\text{tot}} = E_R + E_r \Rightarrow E_R = E_{\text{tot}} - E_r$$

Now, since the microstate of the system is specified, that is, in the definite state r , the reservoir can be

in any of its accessible microstates $\Omega_R(E_R)$. So, the total number of microstates of the combined system is $= \Omega_R(E_R) \times 1 = \Omega_R(E_R) = \Omega_R(E_{\text{tot}} - E_R)$. The combined system can be considered as an isolated system and we can use fundamental postulate. The probability of occurrence that S is in a microstate r is simply proportional to the ^{number of} accessible microstates to the whole system.

$$\therefore P_r = C \Omega_R(E_{\text{tot}} - E_R)$$

Now, since the system S is much smaller in comparison to reservoir and the whole system, $E_R \ll E_{\text{tot}}$ for all practical values of E_R . We can then approximate P_r by expanding the slowly varying logarithm of $\Omega_R(E_{\text{tot}} - E_R)$ about the value $E_R = E_{\text{tot}}$.

Taylor expansion of a function $f(x)$ around a point $x=a$ is given by,

$$f(x) = f(a) + \frac{1}{1!} \left. \frac{df(x)}{dx} \right|_{x=a} (x-a) + \frac{1}{2!} \left. \frac{d^2f(x)}{dx^2} \right|_{x=a} (x-a)^2 + \dots$$

Here, you know the value of the function at $x=a$ and all its derivatives and calculate $f(x)$ at a particular x . If on the other hand, you knew $f(x)$ at x , and wanted to find $f(x-a)$, that is the value of the function at a point $x-a$, knowing the value at x , you just

Replace a by x and x by $x-a$.

$$\therefore f(x-a) = f(x) + \frac{1}{1!} \frac{df(x-a)}{dx(x-a)} (x-a-x) + \frac{1}{2!} \frac{d^2f(x-a)}{dx^2(x-a)^2} (x-a-x)^2 + \dots$$

$$\therefore f(x-a) = f(x) + \frac{1}{1!} \frac{df(x-a)}{dx(x-a)} (-a) + \frac{1}{2!} \frac{d^2f(x-a)}{dx^2(-a)^2} (-a)^2 + \dots$$

$$\therefore \ln S_R(E_{\text{tot}} - E_n) = \ln S_R(E_{\text{tot}}) + \left. \frac{dS_R}{dE_R} \right|_{E_R} \frac{d \ln S_R(E_{\text{tot}} - E_n)}{dE_R} (-E_n) + O(E_n^2)$$

We can neglect the higher order term since $E_R = E_{\text{tot}}$ and $E_n \ll E_{\text{tot}}$.

$$\therefore \ln S_R(E_{\text{tot}} - E_n) = \ln S_R(E_{\text{tot}}) + - \left. \frac{d \ln S_R}{dE_R} \right|_{E_{\text{tot}}} E_n$$

$$\Rightarrow \ln S_R(E_{\text{tot}} - E_n) = \ln S_R(E_{\text{tot}}) - \frac{E_n}{k_B T}$$

where we used the definition $\beta = \frac{1}{k_B T} = \left. \frac{d \ln S_R}{dE_R} \right|_{E_{\text{tot}}}$ evaluated at a fixed energy E_{tot} . It is the constant temperature characterizing the heat reservoir. Physically, it means the reservoir R is so large compared to S that its temperature remains the same by whatever small amount of energy it gives to S .

$$\therefore \ln S_R(E_{\text{tot}} - E_n) = \ln S_R(E_{\text{tot}}) e^{-\frac{E_n}{k_B T}}$$

$$\therefore S_R(E_{\text{tot}} - E_n) = S_R(E_{\text{tot}}) e^{-\frac{E_n}{k_B T}}$$

$$\therefore P_n = C S_R(E_{\text{tot}}) e^{-\frac{E_n}{k_B T}}$$

$$\boxed{\therefore P_n = C' e^{-\frac{E_n}{k_B T}}} \rightarrow \begin{aligned} &\text{lets write it as,} \\ &P(E_n) = C' e^{-\frac{E_n}{k_B T}} \end{aligned}$$

where we introduced a new constant $C' = C S_R(E_{\text{tot}})$.

The constant of probability can be found by the normalization condition,

$$\sum_{i=1}^N P(E_i) = 1$$

$$\Rightarrow C' \sum_{i=1}^N e^{-\frac{E_i}{k_B T}} = 1 \quad \therefore C' = \frac{1}{\sum_{i=1}^N e^{-\frac{E_i}{k_B T}}}$$

$$\therefore P(E_n) = \frac{e^{-\frac{E_n}{k_B T}}}{\sum_{i=1}^N e^{-\frac{E_i}{k_B T}}}$$

where the sum runs over all possible energies. The distribution is called the Boltzman distribution and the normalization factor is called the partition function Z .

$$\therefore Z = \sum_{i=1}^N e^{-\frac{E_i}{k_B T}}$$

The factor $e^{-\frac{E_n}{k_B T}} = e^{-\beta E_n}$ is called the Boltzman factor.

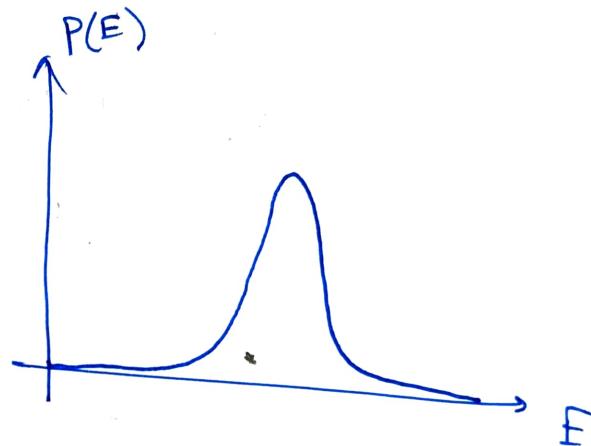
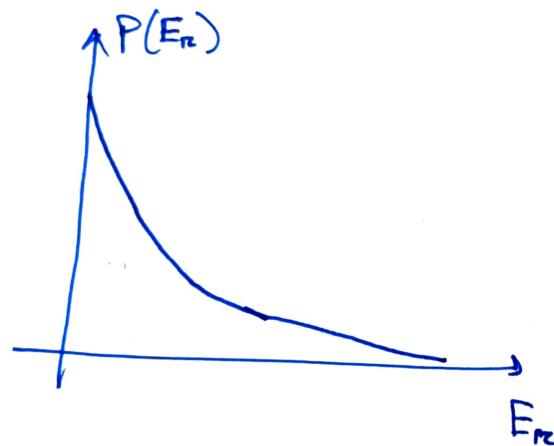
This probability is for finding S in a particular state with energy E_n . The probability that the energy of S is E , is the sum over all the states having energy E .

$$\therefore P(E) = C \Omega(E) e^{-\beta E}$$

where $\Omega(E)$ is the number of microstates having energy E . Since $\Omega(E)$ is rapidly increasing

if A is a large system

function of E and $e^{-\beta E}$ is rapidly decreasing function of E , $P(E)$ will have a maximum.



The system has a reasonable chance of achieving an energy $E_n < k_B T$. But the probability exponentially decreases for $E_n > k_B T$.