PHY202: Statistical Physics

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I'm made these notes after following the lectures by Prof. Susskind

1   *Entropy*

We define Entropy as follows:

> **Definition 1.1** (Entropy). *Suppose a system can take values from set $\mathcal{S} = \{x_1, x_2, x_3, \ldots x_n\}$, with probability of x_i being $\mu(x_i)$. Then the (Boltzmann) entropy S is defined as*
>
> $$S = -k_b \sum_i \mu(x_i) \log(\mu(x_i))$$

Entropy can be thought of as the amount of ignorance/uncertainity that you have. It's obvious that if probability is 1 or 0 the you are 100% sure that a particular result will be observed or not observed.

> **Assumption 1.1.**   *If S_a and S_b be respective entropies for system A and B. Then*
>
> $$S_{\text{net}} = S_a + S_b$$

Using above assumption, if we have N identical systems then the net entropy of the system is given as $S = -Nk_b \sum \mu_i \log(\mu_i)$

1.2   *On existence of Entropy*

Does entropy exists? Or is it just a mathematial formalism?

I'll try to answer it it in my own way. But for that I need to make an assumption, and it's a fairly good assumption. Let me give an example to support my argument, suppose we are given an experiment of tossing a fair coin, let say n number of times, and we are asked to count probabilities of number of getting a head or tails.

Since, the above experiment follows a Binomial distribution, we know that most number of times we are getting equal number of heads and tails (*because number of arrangement given equal number of heads and tails is the most*). So, the assumption that we'll make is:

> **Assumption 1.2.**   *Given a constraint on a system, in equilibrium, the system will exist in the state with maximum number of configurations (or microstates). And state is consistent with the constraint.*

We'll see in Microcanonical Ensemble, the constrain on the system is energy E, volume V and N the number of particles.

Let $\Omega(E, V, N)$ denote the possible number of microstates of the system. Let's sub-divide this system into two non-interacting parts, call A and B. So, we have:

$$\Omega(E, V, N) = \Omega_A(E_A, V_A, N_A)\Omega_B(E_B, V_B, N_B)$$
$$E = E_A + E_B$$
$$V = V_A + V_B$$
$$N = N_A + N_B$$

Since, by assumption 1.2 we need to maximize the Ω. So,

$$\frac{\partial \Omega}{\partial E} = 0$$
$$\frac{\partial(\Omega_A \Omega_B)}{\partial E} = 0$$

Since, E is constant, we can formulate the whole argument in terms of either E_A or E_B.

$$\frac{\partial(\Omega_A(E_A)\Omega_B(E - E_A))}{\partial E_A} = 0$$
$$\frac{\partial(\Omega_A(E_A))}{\partial E_A}\Omega_B(E - E_A) - \frac{\partial(\Omega_B(E - E_A))}{\partial E_A}\Omega_A(E_A) = 0$$
$$\frac{1}{\Omega_A(E_A)}\frac{\partial(\Omega_A(E_A))}{\partial E_A} = \frac{1}{\Omega_B(E - E_A)}\frac{\partial(\Omega_B(E - E_A))}{\partial E_A}$$
$$\frac{\partial \log(\Omega_A(E_A))}{\partial E_A} = \frac{\partial \log(\Omega_B(E - E_A))}{\partial E_A}$$

We define the quantity $k_b \log(\Omega)$ [1]and "Entropy" and denote it be S.

$$S = k_b \log(\Omega)$$

> [1] the factor k_b has something to do with units

Hence, the entropy comes before any of the physical quantities like pressure, temperature etc. We'll see in the next section, that how the two definition of Entropy are related.

2   *Microcanonical Ensemble*

In *Microcanonical Ensemble* [2] we consider an isolated system with N particles and energy E in a volume V. By definition, such a system exchanges neither particles nor energy with the surroundings.

> [2] An **ensemble** is a large number of points in the phase space that can be described by a density function $\mu(x, p)$

Let a system consist of N particles, for which each particle can have M configurations [3]. Also, if a particle is in i^{th} state then let the energy associated with that particle be ϵ_i.

For this system the total energy $E = \sum n_i \epsilon_i$, where n_i denotes the number of particles in state (*or configuration i*). Hence the constrain equations on the system are:

$$E = \sum n_i \epsilon_i$$
$$\sum n_i = N$$

In the thermodynamic limit of Statistical mechanics we usually assume N and V to be very large (i.e $N, V \to \infty$) such that $\rho = \frac{N}{V}$ is constant. In such case, we can assume that the number of particle in each state increases proportional to N. Let probability of finding particle in i^{th} configuration being μ_i and by the definition of probability we have $\mu_i = \lim_{N \to \infty} \frac{n_i}{N}$ or $n_i = \mu_i N$.

Now, we can reformulate the above constrain equations in terms of probability. And we have

$$\sum \mu_i = 1 \Longleftrightarrow \sum n_i = N$$
$$\sum_i N\mu_i \epsilon_i = E \Longleftrightarrow \sum_i \mu_i \epsilon_i = \epsilon \qquad \text{1}$$

We define $\epsilon = \frac{E}{N} = \langle E \rangle$ as average energy per particle.

Let Ω be the number of possible microstates of the system [4]. If you know some basics combinatorics, then for our case Ω is give as

$$\Omega = \frac{N!}{\Pi n_i!}$$
$$\log(\Omega) = \log(N!) - \sum \log(n_i!)$$

Now we need to introduce *Stirling's Approximation*, it says for large N

$$N! \sim e^{-N} N^N$$
$$log(N!) \sim N \log(N) - N$$

Therefore we have,

$$\log(\Omega) = N \log(N) - N - \sum n_i \log(n_i) + \sum n_i$$
$$\log(\Omega) = N \log(N) - N - \sum n_i \log(n_i) + N$$
$$\log(\Omega) = N \log(N) - \sum N\mu_i \log(N) - \sum N\mu_i \log(\mu_i)$$
$$\log(\Omega) = N \log(N) - N \log(N) \sum \mu_i - \sum N\mu_i \log(\mu_i)$$
$$\log(\Omega) = -N \sum \mu_i \log(\mu_i)$$

Buy assumption 1.1 observe that $\boxed{S = k_b \log(\Omega) = -Nk_b \sum \mu_i \log(\mu_i)}$.

Hence, entropy of the system can also be defined as $S = k_b \log(\Omega)$[5]. Also, note that $-k_b \sum \mu_i \log(\mu_i)$ is the entropy associated with each particle.

3   Boltzmann Distribution

In statistical mechanics and mathematics, a Boltzmann distribution (also called Gibbs distribution) is a probability distribution or probability measure that gives the probability that a system will be in a certain state as a function of that state's energy and the temperature of the system.

We'll try to derive the Boltzmann distribution from Microcanonical ensemble. The Boltzmann distribution is the distribution that maximizes the entropy $S = -k_b \sum \mu_i \log(\mu_i)$ or equivalently $S = -\sum \mu_i \log(\mu_i)$

We need to find the probability distribution of the system under the given constrains, such that the entropy is maximum Hence, we would use Lagrange multiplier.

Let

$$F(\{\mu_i\}) = -\sum \mu_i \log(\mu_i) + \alpha(1 - \sum \mu_i) + \beta(\epsilon - \sum \mu_i \epsilon_i)$$
$$= -\sum \mu_i \log(\mu_i) + \alpha G(\{\mu_i\}) + \beta G'(\{\mu_i\})$$

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where $G'(\{\mu_i\}) = 0$ & $G(\{\mu_i\}) = 0$ are constrain equations[6].

To maximize, differentiate (2) w.r.t μ_i and equate to 0, we get

$$\frac{dF}{d\mu_i} = -\log(\mu_i) - 1 - \alpha - \beta\epsilon_i = 0$$

$$\mu_i = e^{-1-\alpha}e^{-\beta\epsilon}$$

$$\boxed{\mu_i(\vec{r}, \vec{p}) = \frac{e^{-\beta\epsilon_i(\vec{r},\vec{p})}}{z}}$$

where $z = e^{1+\alpha}$. z is called the *partition function*. **NOTICE, THE DEPENDENCE OF ENERGY ON PHASE SPACE**

Substitute μ_i in above equations and you will see that

$$\sum \mu_i = 1 \iff \boxed{z(\beta) = \sum e^{-\beta\epsilon_i}}$$
$$\sum \epsilon_i \mu_i = \epsilon \iff \sum \epsilon_i e^{-\beta\epsilon_i} = z\epsilon$$

Also, observe that

$$\frac{\partial z(\beta)}{\partial \beta} = -\sum \epsilon_i e^{-\beta\epsilon_i} = -z\epsilon$$

$$\boxed{\frac{\partial \log(z)}{\partial \beta} = -\epsilon}$$

[6] there was no need for them but, it looks trippy, and that's how mathematicians do it.

Let's look at how does the Entropy looks like. We had

$$S = -k_b \sum \mu_i \log(\mu_i)$$

$$= -\frac{k_b}{z} \sum \{e^{-\beta \epsilon_i} \log(e^{-\beta \epsilon_i}) - e^{-\beta \epsilon_i} \log(z)\}$$

$$= \frac{k_b}{z} \sum \{e^{-\beta \epsilon_i} \beta \epsilon_i) + e^{-\beta \epsilon_i} \log(z)\}$$

$$= \beta k_b \sum \frac{e^{-\beta \epsilon_i}}{z} \epsilon_i + k_b \log(z) \sum \frac{e^{-\beta \epsilon_i}}{z}$$

$$\boxed{S = k_b \beta \epsilon + k_b \log(z)}$$

We define (*stastical definition of temperature*) temperature as [7]

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

So,

$$\frac{1}{T} = \frac{\partial S}{\partial \epsilon} = k_b \beta$$

$$\beta = \frac{1}{k_b T}$$

So, finally everything unveils it self and we get

1.

$$\mu_i = \frac{e^{\frac{-\epsilon_i}{k_b T}}}{z}$$

$$z(T) = \sum_i e^{\frac{-\epsilon_i}{k_b T}}$$

$$\epsilon = -\frac{\partial \log(z)}{\partial \beta} = k_B T^2 \frac{\partial \log(z)}{\partial T}$$

$$S = \frac{\epsilon}{T} + k_b \log(z)$$

3.1 *Relation to thermodynamic variables*

We know variance is defined as :

$$\langle (\Delta X)^2 \rangle = \left\langle (X - \langle X \rangle)^2 \right\rangle$$

$$= \langle X^2 \rangle - (\langle X \rangle)^2$$

We calculate:

$$\langle E \rangle = \epsilon = -\frac{\partial \log(z)}{\partial \beta}$$

$$\langle E \rangle = \frac{1}{z} \sum_i e^{-\beta E_i} E_i^2$$

$$= \frac{1}{z} \frac{\partial^2 z}{\partial^2 \beta}$$

So, $\langle(\Delta E)^2\rangle$ is:

$$\langle(\Delta E)^2\rangle = \frac{1}{z}\frac{\partial^2 z}{\partial^2 \beta} - \left(-\frac{1}{z}\frac{\partial z}{\partial \beta}\right)^2$$

$$= \frac{\partial^2 \log(z)}{\partial^2 \beta} + \left(\frac{1}{z}\frac{\partial z}{\partial \beta}\right)^2 - \left(\frac{1}{z}\frac{\partial z}{\partial \beta}\right)^2$$

$$= \frac{\partial^2 \log(z)}{\partial^2 \beta}$$

$$= -\frac{\partial \langle E\rangle}{\partial \beta}$$

or we can write it as

$$\langle(\Delta E)^2\rangle = -\frac{\partial \langle E\rangle}{\partial \beta}$$

$$= -\frac{\partial \langle E\rangle}{\partial T}\frac{\partial T}{\partial \beta}$$

$$= k_b T^2 \frac{\partial \langle E\rangle}{\partial T}$$

$$= k_b T^2 C_v$$

or

$$\boxed{C_v = \frac{1}{k_b T^2}\langle(\Delta E)^2\rangle}$$

where C_v is the heat capacity at constant volume[8].

Observe that:

$$A = E - TS = -k_b T \log(z)$$

where A is the helmholtz free energy[9].

We define pressure P to be:

$$P = -\left.\frac{\partial E}{\partial V}\right|_S = -\left.\frac{\partial A}{\partial V}\right|_T$$

$$\boxed{P = k_b T \left(\frac{\partial \log(z)}{\partial V}\right)_T}$$

[8] it's heat capacity at "constant volume" because we are talking about Microcanonical ensemble.

[9] it's the definition

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3.2   *Meaning of Partition Function

Source: Wikipedia

It may not be obvious why the partition function, as we have defined it above, is an important quantity. First, consider what goes into it. The partition function is a function of the temperature T and the microstate energies $\epsilon_1, \epsilon_2, \epsilon_3$, etc. The microstate energies are determined by other thermodynamic variables, such as the number of particles and the volume, as well as microscopic quantities like the mass of the constituent particles. This dependence on microscopic variables is the central point of statistical mechanics. With a model

of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamic properties of the system.

The partition function can be related to thermodynamic properties because it has a very important statistical meaning. The probability μ_i that the system occupies microstate i is

$$\mu_i = \frac{1}{z}e^{-\beta\epsilon_i}$$

Thus, as shown above, the partition function plays the role of a normalizing constant (note that it does not depend on i), ensuring that the probabilities sum up to one:

$$\sum_i \mu_i = \frac{1}{z}\sum_i e^{-\beta\epsilon_i} = \frac{1}{z}z = 1$$

This is the reason for calling z the "partition function": it encodes how the probabilities are partitioned among the different microstates, based on their individual energies. The letter z stands for the German word *Zustandssumme*, "sum over states". The usefulness of the partition function stems from the fact that it can be used to relate macroscopic thermodynamic quantities to the microscopic details of a system through the derivatives of its partition function. Finding the partition function is also equivalent to performing a Laplace transform of the density of states function from the energy domain to the β domain, and the inverse Laplace transform of the partition function reclaims the state density function of energies.

4   The Ideal Gas

4.1   Introduction

Suppose a system is made of N sub-systems (*particles*) with negligible interaction energy, that is, we can assume the particles are essentially non-interacting. If the partition functions of the sub-systems are $\zeta_1, \zeta_2, \ldots \zeta_N$, respectively then the partition function of the entire system is the product of the individual partition functions:

$$z = \prod_{j=1}^{N} \zeta_j.$$

If the sub-systems have the same physical properties, then their partition functions are equal, $\zeta_1, \zeta_2, \ldots \zeta_N$, in which case

$$z = \zeta^N$$

However, there is a well-known exception to this rule. If the subsystems are actually identical particles, in the quantum mechanical sense that they are impossible to distinguish even in principle, the total partition function must be divided by a $N!$[10]:

$$z = \frac{\zeta^N}{N!}$$

While this may seem like a strange requirement, it is actually necessary to preserve the existence of a thermodynamic limit for such systems. This is known as the Gibbs paradox.

4.2   *The partition function for ideal gas*

If you have taken an introductory probability theory course, then you may know in continuous case, PMF (probability mass function) is replaced by PDF (probability density function).

In classical mechanics, the position and momentum variables of a particle can vary continuously, so the set of microstates is actually uncountable. In classical statistical mechanics, it is rather inaccurate to express the partition function as a sum of discrete terms. In this case we must describe the partition function using an integral rather than a sum.

We'll assume the systen to be non-interacting. The partion function for single particle (assuming it to a subsystem) is defined as[11]:

$$\zeta = \frac{1}{h^3} \int_p \int_x e^{-\beta E(x,p)} d^3x d^3p$$

For non-interating particles energy is due to momentum only. So, it implies:

$$\zeta = \frac{1}{h^3} \int_p \int_x e^{-\beta \frac{p^2}{2m}} d^3x d^3p$$

$$= \frac{1}{h^3} \int_x d^3x \int_p e^{-\beta \frac{p^2}{2m}} d^3p \qquad \text{a}$$

$$= \frac{V}{h^3} \int_p e^{-\beta \frac{p^2}{2m}} d^3p$$

observe that $p^2 = p_x^2 + p_y^2 + p_z^2$ and $d^3p = dp_x dp_y dp_z$. We'll make an assumption

> **Assumption 4.1** (Equipartition theorem).   *Energy is distributed equally among all the degrees of freedom. In other words if total energy is E and there are d degree of freedom. Then each degree of freedom contains $\frac{E}{d}$ amount of energy.*

The above form of p^2 becomes $p^2 = 3\bar{p}^2$ and $d^3p = (d\bar{p})^3$. And equation **??** becomes

$$\zeta = \frac{V}{h^3} \int_p e^{-\beta \frac{p^2}{2m}} d^3p$$

$$= \frac{V}{h^3} \left(\int_p e^{-\beta \frac{p^2}{2m}} d\bar{p} \right)^3$$

$$\zeta = \frac{V}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}$$

Hence, we have taken an ideal gas consisting of identical N particles. The partition function for the whaole system is

$$z = \frac{(\zeta)^N}{N!}$$

$$z = \frac{V^N}{h^{3N} N!} \left(\frac{2\pi m}{\beta} \right)^{3N/2}$$

$$\log(z) = N \log(V) + \frac{3N}{2} \log(2\pi m) - \frac{3N}{2} \log(\beta) - \log(N!) - 3N \log(h)$$

Energy for the system is

$$E = -\frac{\partial \log(z)}{\partial \beta}$$

$$= \frac{3N}{2\beta}$$

$$\boxed{E = \frac{3N}{2} k_b T}$$

Don't forget the Pressure from equation (i):

$$P = k_b T \left(\frac{\partial \log(z)}{\partial V} \right)_T$$

$$P = k_b T \frac{N}{V} \implies \boxed{PV = Nk_b T}$$