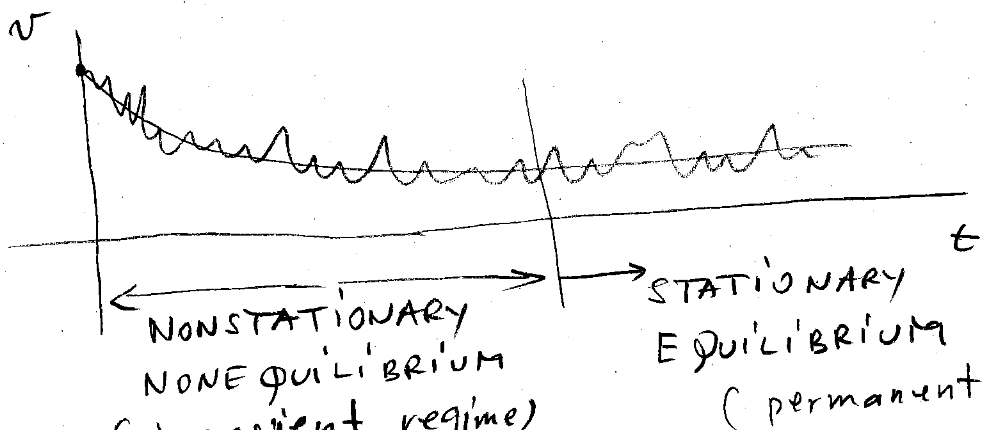
Lecture

Equilibrium Statistical Mechanics



In the <u>stationary state</u> there is a STATIONARY or EQUILIBRIUM PROBABILITY DISTRIBUTION

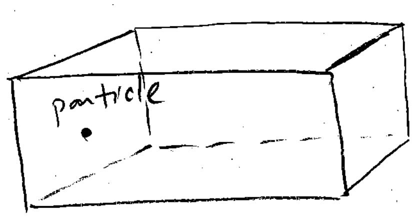
$$P(v)$$ time is not present!

<u>Goal</u>: find P

<u>Method</u> We will find P basend on a very general principle

Principle of maximization of our lack of knowledge

<u>Example</u>

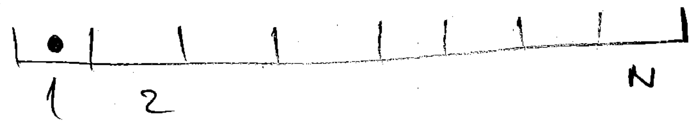


what is the probability that a particle is in a specified subvolume of the Volume?

All subvolumes are equiprobable
this statement maximize our lack of knowledge

We need a measure of our lack of knowledge

(1)



How many questions we need to ask to find the particle (we do not see the particle).

$$2^{\#\text{ questions}} = N$$

$$\underbrace{\#\text{ questions}}_{\text{our initial lack of knowledge}} = \log_2 N$$

so lack of knowledge $\sim \ln N = -\ln \frac{1}{N}$

But the probability for the particle to be in any one of the boxes is

$$p = \frac{1}{N}$$

this is the only information we have. So

$$\boxed{\text{lack of knowledge} \sim -\ln p}$$

② Now the boxes are grouped

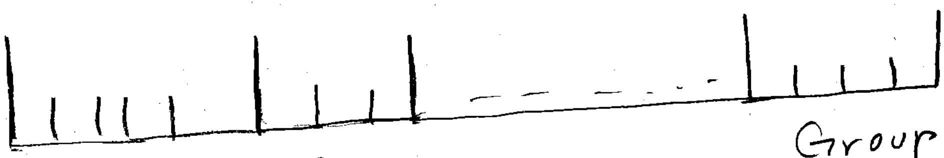


Figure 1

We <u>know</u> the probabilities

p_1 — to be in Group 1

p_2 — to be in Group 2

⋮

p_k — to be in Group k

First step is to choose at random a group lets say Group m, and then ask

$-\ln p_m$

questions. The <u>average</u> lack on knowlege will be thus

$p_1 \cdot$ (# questions Group 1) + p_2 (# questions Group 2) + $+ \cdots +$ p_k (# questions Group k) =

$= p_1(-\ln p_1) + p_2(-\ln p_2) + \cdots + p_k(-\ln p_k)$

This lack of knowledge, given <u>ONLY</u> the probabilities $p_1, p_2, \ldots, p_k$ is called ENTROPY

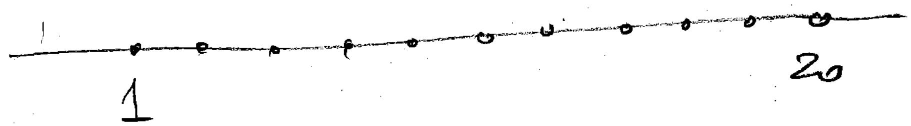
$$\boxed{S = -k_B \sum_{j=1}^{k} p_j \ln p_j}$$

This formula is general. It is not restricted or connected with Figure 1

The principle of maximization of the lack of knowledge or the maximisation of the entropy is:

Now you do not know $p_1, p_2, \dots, p_K$. You can find them by requiring that the entropy is maximum.

<u>Example</u>. A particle can be in any of the 20 possible states.



Find $p_1, \dots, p_{20}$.

Maximize

$$S = -k_B \sum_{j=1}^{20} p_j \ln p_j$$

We have a constrain

$$\sum_{j=1}^{20} p_j = 1$$

so not all $p_1, p_2, \dots, p_{20}$ are independent

Express

$$p_{20} = 1 - p_1 - \dots - p_{19}$$

so

$$k_B^{-1} \cdot S = -\sum_{j=1}^{19} p_j \ln p_j - (1 - p_1 - \dots - p_{19}) \ln (1 - p_1 - \dots - p_{19})$$

Now all $p_1, \dots, p_{19}$ are independent so we can maximize S by imposing

$$\frac{\partial S}{\partial p_1} = 0, \ \ldots, \quad \frac{\partial S}{\partial p_{19}} = 0$$

$$k_B^{-1} \cdot \frac{\partial S}{\partial p_1} = -\ln p_1 - 1 - (-1)\ln(1 - p_1 - \cdots - p_{19}) - $$
$$- (1 - p_1 - \cdots - p_{19}) \frac{-1}{1 - p_1 - \cdots - p_{19}} = 0$$

So $\ln p_1 = \ln(1 - p_1 - \cdots - p_{19})$

$$\boxed{p_1 = 1 - p_1 - \cdots - p_{19}}$$

For $p_2, p_3, \ldots, p_{19}$ we will get

$$p_2 = 1 - p_1 - \cdots - p_{19}$$
$$\vdots$$
$$p_{19} = 1 - p_1 - \cdots - p_{19}$$

that is $\boxed{p_1 = p_2 = \cdots = p_{19}}$

and thus all p_i are equal with $\frac{1}{20}$.

the distribution which will maximize the entropy (our lack of knowledge) is the uniform distribution.

Canonical Distribution

The physical system has a set of states indexed by the index $j = 1, 2, \dots, m$

$$\boxed{\text{state index } j}$$

For each state we have a level of energy

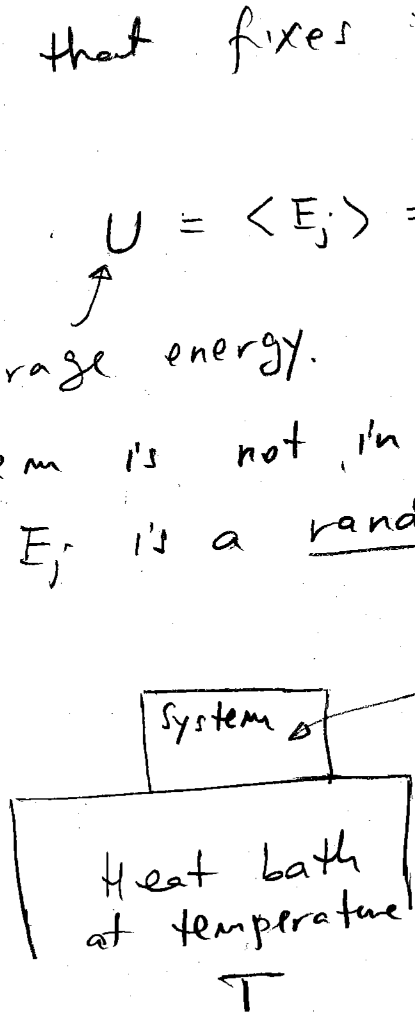
$$\boxed{E_j}$$

The system is in contact with a big heat bath that fixes the system's <u>average energy</u>

$$\underset{\substack{\uparrow \\ \text{average energy.}}}{U} = \langle E_j \rangle = p_1 E_1 + \dots + p_m E_m$$

The system is not in a fixed energy E_j.
The energy E_j is a <u>random variable</u>

The volume V is fixed
The number of particles inside is fixed at N.



We want to find the conditional probability

$$p(j \mid T, V, N)$$

The probability that the system is in the state j, given the temperature of the heat bath, the volume of the system and the number of particles.

<u>Solution</u>

Maximize the entropy

$$S = -k_B \sum_{j=1}^{m} p_j \ln p$$

subjected to two constraints

$$\sum_{j=1}^{m} p_j = 1$$

$$\sum_{j=1}^{m} p_j E_j = U$$ given in terms of the temperature T the volume V and the particle number N.

<u>Problem</u>: How to maximize under constraints? Answer: Lagrange Multipliers

We need to maximize

$$F = S - \alpha' \sum_{\text{states}} p_j - \beta \sum_{\text{states}} p_j E_j$$

with α and β the Lagrange multipliers

$$\frac{\partial F}{\partial p_j} = \frac{\partial S}{\partial p_j} + k_B \alpha - k_B \beta E_j = k_B(-\ln p_j - 1 - \alpha - \beta E_j) = 0$$

we introduce k_B here for algebraic convenience only.

$$\boxed{p_j = e^{-1-\alpha-\beta E_j}}$$

From constraints we need to find α and β

$$\begin{cases} \sum p_j = 1 \\ \sum p_j E_j = U \end{cases}$$

$$\sum e^{-1-\alpha-\beta E_j} = 1$$

$$\sum E_j e^{-1-\alpha-\beta E_j} = U$$

So $$e^{1+\alpha} = \sum_{\text{all}} e^{-\beta E_j}$$

So $$\boxed{p_j = \frac{e^{-\beta E_j}}{\sum_{\text{states}} e^{-\beta E_j}}}$$

Canonical distribution

The parameter β is the solution to the equation

$$U = \sum_{\text{states}}' p_j E_j = \frac{\sum_{\text{states}} E_j e^{-\beta E_j}}{\sum_{\text{states}}' e^{-\beta E_j}}$$

The meaning of β

It is hard to solve for β in term of the average energy U. However we can relate the average energy with the entropy S (which is also an average, the average of $-\ln p_i$)

$$k_B^{-1} S = -\sum_{\text{states}}' p_j \ln p_j =$$

$$= -\sum_{\text{states}} \frac{e^{-\beta E_j}}{Z} \ln\left(\frac{e^{-\beta E_j}}{Z}\right) =$$

$$\boxed{Z = \sum_{\text{states}} e^{-\beta E_j}}$$

$$= \frac{1}{Z} \sum_{\text{states}}' \beta E_j e^{-\beta E_j} + \frac{1}{Z} \sum_{\text{states}}' e^{-\beta E_j} \ln Z =$$

$$= \beta \frac{1}{Z} \sum_{\text{states}} E_j e^{-\beta E_j} + \ln Z = \beta U + \ln Z$$

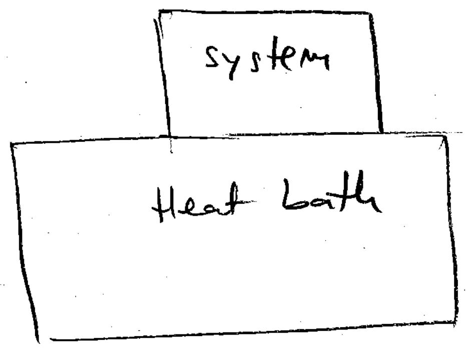
So

$$k_B^{-1} S = \beta U + \ln Z$$

$$\boxed{-k_B \ln Z = k_B \beta U - S} \qquad (*)$$

From thermodynamics we know that

$$\Delta U = \underset{\substack{\uparrow \\ \text{heat} \\ \text{exchange}}}{\delta Q} + \underset{\substack{\uparrow \\ \text{work} \\ \text{exchange}}}{\delta W}$$



and

$$\Delta S = \frac{\delta Q_{rev}}{T}$$

so $\Delta U = T \Delta S + \delta W$

or

$$\boxed{\delta W = \Delta U - T \Delta S} \qquad (**)$$

We maintain a constant volume for our system so $\delta W = 0$. Then

$$\Delta U = T \Delta S$$

From $(*)$ we get that a variation in $k_B \beta U - S$ relates ΔU with $\frac{1}{k_B \beta} \Delta S$.

So

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

Thus

$$\boxed{\beta = \frac{1}{k_B T}}$$

<u>Conclusion</u>

$$p_j = \frac{e^{-\frac{E_j}{k_B T}}}{Z}$$

$$Z = \sum_{\text{states}} e^{-\frac{E_j}{k_B T}}$$

$$-k_B T \ln Z = U - TS$$

It is very good to show the variables $\boxed{T, V, N}$

$$Z(T, V, N) = \sum_{\text{states}} e^{-\frac{E_j}{k_B T}}$$

$$\underbrace{-k_B T \ln Z(T, V, N)}_{\text{Notation } F(T,V,N)} = U(T, V, N) - T\,S(T, V, N)$$

Name — Thermodynamic potential