

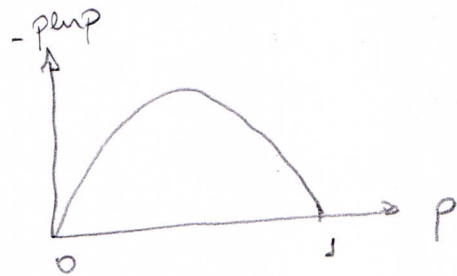
Entropy and etc.

Given any probability distribution P_m , we define its entropy as

$$S = -k_B \sum_m P_m \ln P_m \quad (1)$$

In thermodynamics this is called the Gibbs entropy. In probability theory it goes by the name of Shannon entropy and they define it without the k_B .

The entropy is a measure of the disorder of the distribution. To see that, note how S is a sum of functions like $-p \ln p$ where $p \in [0, 1]$. This function looks like this



It is zero when $p = 0$ or $p = 1$. Thus, if we have a deterministic distribution, $P_m = 1$ and $P_m = 0$ for $m \neq m$, the entropy will be zero

$$S = 0 \text{ for a deterministic distribution}$$

(2)

The entropy is a maximum when all probabilities are equal,

$$P_m = \frac{1}{\Omega} \quad \Omega = \text{const} \quad (3)$$

This is called the maximally disordered configuration.

In this case

$$S = -k_B \sum_m \frac{1}{\Omega} \ln(1/\Omega) = -k_B \frac{1}{\Omega} \Omega \ln(1/\Omega)$$

since $\sum_m 1 = \Omega$ by definition. Thus

$$S = k_B \ln \Omega \quad (4)$$

I will leave for you as an exercise to show that this (3) is indeed the distribution which maximizes S . The calculation is very similar to one we will do later in Eq (23).

Thus, in summary, the entropy is zero when there is order and maximum when there is maximum disorder. It therefore serves as a measure of the disorder of the distribution.

Entropy for thermal states

The entropy (S) is a quantity that can be defined for any probability distribution. But for thermal states it acquires a special significance.

Assume

$$P_m = \frac{e^{-\beta E_m}}{Z} \quad (5)$$

Then

$$\ln P_m = -\beta E_m - \ln Z$$

so Eq (5) becomes

$$S = k_B \beta \underbrace{\sum_m E_m P_m}_U + k_B \ln Z \underbrace{\sum_m P_m}_1$$

Thus, with the definitions

$$U = \sum_m E_m P_m \quad (6)$$

$$F = -k_B T \ln Z \quad (7)$$

we get

$$S = \frac{U - F}{T} \quad (8)$$

This relates the entropy of a thermal state as being the difference between the energy and the free energy.