What is the disorder of this two state system, $S(p_1, p_2)$?

Consider N copies of the two state system.
By additivity of S we want the disorder of this joint system of N copies to be

$$(*) \qquad S = N\, S(p_1, p_2)$$

Now in any given sample of the N copy system, M of the systems will be in state 1, while $N-M$ are in state 2. The prob for this will be given by the binomial distribution

$$P_M = \frac{N!}{M!\,(N-M)!}\, p_1^M\, p_2^{N-M} \quad \leftarrow \text{prob} \begin{cases} M \text{ in state } 1 \\ (N-M) \text{ in state } 2 \end{cases}$$

For N large, this probability is <u>very</u> strongly peaked about the average $M = Np_1$. We have

average # systems in state 1 $\quad \langle n_1 \rangle = N p_1$

standard deviation of # in state 1 $\quad \sqrt{\langle n_1^2\rangle - \langle n_1\rangle^2} = \sqrt{N p_1 p_2}$

so relative width of distribution is $\dfrac{\sqrt{\langle n_1^2\rangle - \langle n_1\rangle^2}}{\langle n_1\rangle} \sim \dfrac{1}{\sqrt{N}}$

$\to 0$ as $N \to \infty$.

$\Rightarrow$ as N gets large we almost always find the system of N copies with Np_1 in state 1 and Np_2 in state 2.

How many ways are there to choose which Np_1 of the N two level sub-systems are in state 1?

There are $\dfrac{N!}{(Np_1)!\,(Np_2)!}$ ways $\quad (Np_2 = N(1-p))$

each of these ways are <u>equally likely</u>!

$\Rightarrow$ the entropy of the N copy system is

$$S = k \ln\left[\frac{N!}{(Np_1)!\,(Np_2)!}\right]$$ log of # equally likely states!

$$= k\left[\ln N! - \ln (Np_1)! - \ln (Np_2)!\right]$$

use Stirling formula

$$= k\left[N\ln N - N - Np_1 \ln Np_1 + Np_1 - Np_2 \ln Np_2 + Np_2\right]$$

use $Np_1 + Np_2 = N$ as $p_1 + p_2 = 1$

$$= kN\left[\ln N - p_1 \ln N - p_1 \ln p_1 - p_2 \ln N - p_2 \ln p_2\right]$$

$$\Rightarrow S = kN\left[-p_1 \ln p_1 - p_2 \ln p_2\right]$$ since $p_1 + p_2 = 1$

But by (*) we expect $S = N\,S(p_1, p_2)$

$$\Rightarrow \quad S(p_1, p_2) = -k\left[p_1 \ln p_1 + p_2 \ln p_2\right]$$

Similarly, if our system had m possible states, with probabilities $p_1, p_2, \ldots, p_m$, and we took N copies of this m level system, the joint system would have Np_1 subsystems in state 1, Np_2 in state 2, ..., Np_m in state m. The number of equally likely ways to divide the N subsystems this way is

$$\frac{N!}{(Np_1)!\,(Np_2)!\cdots(Np_m)!}$$

and so a similar line of argument results in

$$S(p_1, \cdots p_m) = -k\left[p_1 \ln p_1 + p_2 \ln p_2 + \cdots + p_m \ln p_m\right]$$

$$\boxed{S(\{p_i\}) = -k \sum_i p_i \ln p_i}$$

Defines our measure of the disorder of the prob distribution p_i. We see it agrees with what we found for the entropy in both canonical and microcanonical ensembles.

But now we will use it to <u>derive</u> the microcanonical and the canonical ensembles!

S above agrees with the desired properties (1) and (2).
$S = 0$ if any $p_i = 1$ and all others are zero.
We soon see that S is max if all p_i are equal.

We can now use the above as our <u>definition</u> of entropy and <u>define equilibrium</u> as the prob distribution that maximizes S, subject to whatever constraints may exist on the distribution. Each such constraint represents some "information" we have about the system.

<u>microcanonical ensemble</u> - each state i has an energy E_i

We have $p_i = 0$ for $E_i \neq E$, $p_i \neq 0$ for $E_i = E$

Considering only those states i with $E_i = E$, we now want to maximize S over these non-zero p_i.

We want to maximize $S = -k \sum_i p_i \ln p_i$
subject to the constraint $\sum_i p_i = 1$ (normalization of probabilities)

Use method of Lagrange multipliers

$\Rightarrow$ maximize in an <u>unconstrained</u> way

$$S + k\lambda \sum_i p_i$$

where λ is the Lagrange multiplier - we then determine the value of λ by imposing the constraint. So if there are N states of energy E, the maximization gives

$$0 = \frac{\partial}{\partial p_i}\left(S + k\lambda \sum_i p_i\right) = \frac{\partial}{\partial p_i}\left(-k \sum_j \left(p_j \ln p_j - \lambda p_j\right)\right)$$

$$\Rightarrow \quad p_i\left(\frac{1}{p_i}\right) + \ln p_i - \lambda = 0$$

$$1 + \ln p_i - \lambda = 0$$

$$p_i = e^{\lambda - 1} \quad \text{same for all } i$$

$\Rightarrow$ distribution that maximizes S is equally likely states

$$\sum_i p_i = N e^{\lambda-1} = 1 \Rightarrow \lambda = 1 + \ln(1/N) = 1 - \ln N$$

$$\Rightarrow p_i = e^{\lambda-1} = e^{-\ln N} = \frac{1}{N} \quad \text{as expected}$$

$\Rightarrow$ in microcanonical ensemble at energy E, all states with energy E are equally likely.

Canonical Ensemble

Now any E_i is allowed, but we have the constraint that the average energy $\langle E \rangle$ is fixed $\Rightarrow \sum_i p_i E_i = \langle E \rangle$ is fixed. We still have the constraint that $\sum_i p_i = 1$. Thus the maximization requires two Lagrange multipliers.

$$0 = \frac{\partial}{\partial p_i}\left(-k \sum_j \left[p_j \ln p_j - \lambda p_j + \beta p_j E_j \right]\right)$$

$$\Rightarrow 0 = 1 + \ln p_i - \lambda + \beta E_i$$

$$p_i = e^{\lambda-1} e^{-\beta E_i}$$

Normalization $\Rightarrow \sum_i p_i = e^{\lambda-1} \sum_i e^{-\beta E_i} = 1$

$$\Rightarrow e^{\lambda-1} = \frac{1}{\sum_i e^{-\beta E_i}}$$

$$\Rightarrow \boxed{p_i = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}}}$$

Determine β by condition that

$$\frac{\sum_i e^{-\beta E_i} E_i}{\sum_i e^{-\beta E_i}} = \langle E \rangle \quad \text{fixed average energy}$$

If we interpret $\beta = \frac{1}{k_B T}$, we recover the canonical distribution!

More generally if we had any quantity X constraind, ie X_i is value in state i, and average value $\langle X \rangle = \sum_i p_i X_i$ is fixed, then

$$p_i = \frac{e^{-\beta X_i}}{\sum_j e^{-\beta X_j}}$$ gives maximum S consistent with the constraint.

β determined by requiring $$\frac{\sum_i X_i e^{-\beta X_i}}{\sum_j e^{-\beta X_j}} = \langle X \rangle$$ gives the desired value of $\langle X \rangle$.

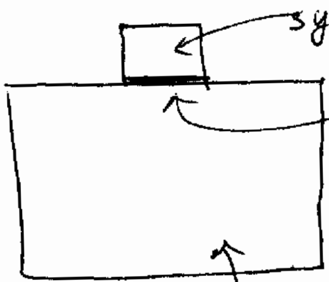
We can use the definition

$$S = -k_B \sum_i p_i \ln p_i$$

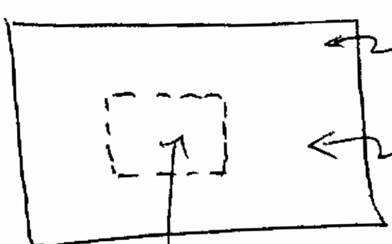
more generally than for systems in equilibrium in the thermodynamic limit. It can be used just as well for systems of finite size, and for systems out of equilibrium.

Grand Canonical Ensemble

Consider a system of interest which is in contact with both a thermal <u>and</u> a particle reservoir



One way such a situation may arise physically is if the "system of interest" is just a certain volume immersed in a much larger volume of the same "stuff", and the walls ~~at~~ around the "system of interest" are just our mental constructs



system of interest is some interior region of the gas. Dashed lines are mental construct - not physical walls! The energy E and number of particles N in the region of interest are not fixed but fluctuate as energy + particles flow between the region and the rest of the gas.

The reservoir is so large, that no matter how much energy or particles the system of interest transfers to it, its temperature T_R and chemical potential μ_R do not change — this is what we mean by it being a reservoir.

We see this as we argued before. If heat $dQ = TdS$ is transfered to the reservoir then the change in T_R is

$$\Delta T_R = \frac{\partial T_R}{\partial S_R} dS = \left(\frac{\partial^2 E_R}{\partial S_R^2}\right) dS \sim \frac{N}{N_R} T_R \quad \text{as } E_R, S_R \sim N_R$$

$dS \sim N$ at most

so if $N \ll N_R$, $\Delta T_R \ll T_R$

Similarly, if dN is transfered to the reservoir

$$\Delta \mu_R = \frac{\partial \mu_R}{\partial N_R} dN = \left(\frac{\partial^2 E_R}{\partial N_R^2}\right) dN \sim \frac{N}{N_R} \mu_R \quad \text{as } E_R, N_R \sim N_R$$

and $dN \sim N$ at most

so if $N \ll N_R$, $\Delta \mu_R \ll \mu_R$

So we regard T_R and μ_R of the reservoir as fixed

Now because the "system of interest" is in equilib with the reservoir, we have $T = T_R$, and $\mu = \mu_R$

Now $N + N_R = N_T$ is fixed, $E + E_R = E_T$ is fixed
V, V_R are fixed

Similar to what we had for the canonical ensemble, the density of states for the total system of reservoir + system of interest is

$$g_T(E_T, V, V_R, N_T) = \int dE \sum_N g(E,V,N)\, g_R(E_T - E, V_R, N_T - N)$$

or for the number of states $\Omega = g\Delta$ (Δ is small energy interval as before)

$$\Omega_T(E_T, V, V_R, N_T) = \int \frac{dE}{\Delta} \sum_N \Omega(E,V,N)\, \Omega_R(E_T - E, V_R, N_T - N)$$

$$= \int \frac{dE}{\Delta} \sum_N \Omega(E,V,N)\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

probability density for system to have E and N is proportional to the number of states (of the total system) that have the system with E and N

$$P(E,N) \propto \frac{\Omega}{\Delta}(E,V,N)\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

expand

$$S_R(E_T - E, V_R, N_T - N) \simeq S_R(E_T, V_R, N_T) + \frac{\partial S_R}{\partial E_R}(-E_R) + \left(\frac{\partial S_R}{\partial N_R}\right)(-N)$$

$$= S_R - \frac{E}{T} + \frac{\mu N}{T}$$

$$P(E,N) \propto \frac{\Omega}{\Delta}(E,V,N)\, e^{-(E - \mu N)/k_B T}$$

Normalize

$$p(E,N) = \frac{\frac{\Omega}{\Delta}(E,V,N)\, e^{-(E-\mu N)/k_B T}}{\sum_N \int \frac{dE}{\Delta}\, \Omega(E,V,N)\, e^{-E/k_B T}\, e^{\mu N/k_B T}}$$