Grand Canonical distribution

(another name $T-\mu$ distribution)

The original derivation of the canonical distribution was this:

maximize $$S = -k \sum_j P_j \ln P_j$$

with constraints
$$\langle E \rangle = \sum_j E_j \cdot P_j$$

given

$$1 = \sum_j P_j$$

We used the Lagrange multipliers α and β

$$S - k\beta \left(\sum_j E_j \cdot P_j \right) - k\alpha \left(\sum_j P_j \right)$$

In this way we introduced temperature

$$\beta = \frac{1}{kT}$$

The microcononical distribution can be introduced using the same approach but now E should be fixed, because the system is isolated. So maximize

$$S = -k \sum_j P_j \ln P_j$$

with only one constraint

$$1 = \sum_j P_j$$

We obtain that all P_j are equal (we say that the states for an isolated system are equiprobable). Notice that we have only α as a Lagrange multplier

$$S - k\alpha\left(\sum_j P_j\right)$$

and thus β is not present. We cannot speak about a temperature (the system is isolated). However, the microcononical distribution can appear as an approximation of the cononical distribution. In this approximation we speak about a temperature.

Following the same logic as above we can construct other probability distributions by adding more constraints, which depend on the particular physical situation. For example, if the system is in contact with a heat bath (which fixes the temperature) and in contact with a source of particles (so the number of particles is not fixed any more) we have the following problem.

Find P_j such that

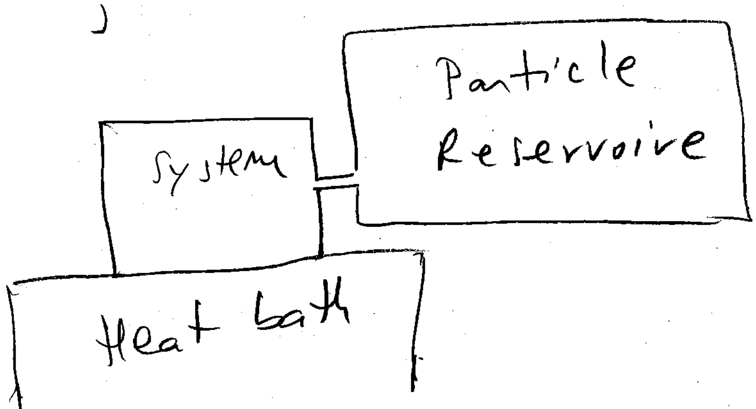
$$S = -k \sum_j P_j \ln P_j$$

is maximum, and

$$1 = \sum_j P_j$$

The average energy is given $\rightarrow$ $$\langle E \rangle = \sum_j E_j P_j$$

The average number of particle in the system is given $\rightarrow$ $$\langle N \rangle = \sum_j N_j P_j$$



We have three Lagrange multipliers

$$S - k\alpha\left(\sum_j P_j\right) - k\beta\left(\sum_j E_j P_j\right) - k\gamma\left(\sum_j N_j P_j\right)$$

the multiplier β is determined by the heat bath

the multiplier μ is determined by the particle reservoire

The solution to this problem is

$$P_j = \frac{e^{-\beta E_j - \gamma N_j}}{\Lambda}$$

$$\Lambda = \sum_j e^{-\beta E_j - \gamma N_j}$$

Grand Canonical Distribution

From the Grand partition function we can compute (similar with Canonical distribution) the average energy and the average number of particles. The logic in this approach is that the temperature T is known (fixed by the heat bath) and γ is know (fixed by the particle reservoire)

We have

$$\langle N \rangle = -\left(\frac{\partial \ln \Delta}{\partial \gamma}\right)_\beta$$

$$\langle E \rangle = -\left(\frac{\partial \ln \Delta}{\partial \beta}\right)_\gamma$$

Also we can find the variation in the internal energy $U \equiv \langle E \rangle$

$$dU = \sum_j E_j dP_j + \sum_j P_j dE_j =$$

$$= \sum_j -\frac{1}{\beta}\left(\ln \Delta + \gamma N_j + \ln P_j\right) dP_j + \sum_j P_j dE_j =$$

$$= -\frac{1}{\beta} \ln \Delta \underbrace{\sum_j dP_j}_{\substack{=0 \text{ from} \\ \sum_j P_j = 1}} - \underbrace{\frac{\gamma}{\beta} \sum_j N_j dP_j}_{} - \frac{1}{\beta} \sum_j (\ln P_j) dP_j +$$

$$+ \sum_j P_j dE_j = \overbrace{-\frac{\gamma}{\beta}\sum_j d(N_j P_j) - \frac{\gamma}{\beta}\sum_j P_j dN_j}^{} -$$

$$-\frac{1}{\beta}\sum_j (\ln P_j) dP_j + \sum_j P_j dE_j$$

$$dU = -\frac{\gamma}{\beta}\, d\langle N\rangle - \frac{\gamma}{\beta}\sum_j{}' P_j\, dN_j +$$

$$\underbrace{+\, T\, dS}\; + \sum_j{}' P_j\, dE_j$$

because it equals $-\frac{1}{\beta}\sum_j (\ln P_j)\, dP_j$ like in the Canonical distribution

$$dU = T\, dS' - \frac{\gamma}{\beta}\, d\langle N\rangle - \frac{\gamma}{\beta}\sum_j{}' P_j\, \underbrace{dN_j} + \sum_j{}' P_j\, dE_j$$

The number of particles N_j (in state j) is usual independant on the thermodynamic parameters like the B field or Volume of the system.

We will take $dN_j = 0$

Remember that dE_j depends on B or volume, so $dE_j \neq 0$.

Thus

$$dU = \boxed{T\,dS} \boxed{- \frac{\gamma}{\beta} d\langle N\rangle + \sum_j{}' P_j\, dE_j}$$

Heat exchange Work exchanged

The meaning of $-\frac{\gamma}{\beta} d\langle N\rangle$: If the average number of particles changes ($d\langle N\rangle \neq 0$) the internal energy varies with

$$-\frac{\gamma}{\beta} d\langle N\rangle.$$

We want to express the part of work due to the variation of $\langle N\rangle$ using a simpler notation. For this we change notation

$$\mu \overset{\text{definition}}{=} -\frac{\gamma}{\beta}$$

chemical potential

$$\boxed{dU = T\,dS + \mu\, d\langle N\rangle + \sum_j P_j\, dE_j}$$

This change of notation does not mean that μ is positive all the time. The sign of μ for an ideal gas is in fact negative, as we will see in future lectures.

Heat exchange $= T\,dS$

Work exchange $= \mu\, d\langle N\rangle + \sum_j P_j\, dE_j$

The chemical potential μ is fixed by the particle reservoire.

$$\boxed{\begin{aligned} P_j &= \frac{e^{-\beta E_j + \beta\mu N_j}}{\Lambda} \\ \Lambda &= \sum_j e^{-\beta E_j + \beta\mu N_j} \end{aligned}}$$

Grand canonical distribution

$$\langle N \rangle = \frac{1}{\beta}\left(\frac{\partial \ln \Lambda}{\partial \mu}\right)_{\beta}$$

$$U = -\left(\frac{\partial \ln \Lambda}{\partial \beta}\right)_{\mu} + \mu \langle N \rangle$$

$$-kT \ln \Lambda = U - TS - \mu \langle N \rangle$$