Lecture 14 - Grand canonical ensemble

What's Important:

- weakly interacting systems
- entropy and probability
- grand canonical ensemble

Text: Reif

Secs. 6.7 and 6.8 on approximation techniques can be read independently.

Weakly interacting systems

If two systems A and A' are weakly interacting, then their combined energy will be approximately equal to the sum of their individual energies:

$$E_{rs}{}^{o} = E_r + E'_s + [\textit{no interaction energy}]$$

In the absence of a interaction piece, the partition function of the whole system separates into a product of individual partition functions

$$\begin{aligned} Z^{o} &= \Sigma_{rs}\exp(-\beta E_{rs}{}^{o}) \\ &= \Sigma_r \exp(-\beta E_r{}^{o})\ \Sigma_s \exp(-\beta E_s{}^{o}) \\ &= Z \bullet Z'. \end{aligned} \qquad (14.1)$$

Lastly, quantities such as energy and entropy which depend on ln$Z$, are additive according to Eq. (14.1).

Entropy and probability

In terms of the partition function, the entropy is written as

$$S = k_B(\ln Z + \beta \bar{E}). \qquad (14.2)$$

The mean energy can be expressed in terms of Boltzmann factors or, after dividing by the partition function

$$\bar{E} = \sum_r P_r E_r$$

where P_r is the probability of the state being in state r,

$$P_r = \frac{e^{-\beta E_r}}{Z} \qquad (14.3)$$

Thus,

$$S = k_B(\ln Z + \beta \sum_r P_r E_r) = k_B(\ln Z + \sum_r P_r \beta E_r) \qquad (14.4)$$

Now, Eq. (14.4) can be rearranged to read

$$\ln(P_r Z) = -\beta E_r$$

which permits Eq. (14.3) to be recast as

$$S = k_B \left[\ln Z - \sum_r P_r \ln(P_r Z) \right]$$

$$= k_B \left[\ln Z - \sum_r P_r \ln(P_r) - \sum_r P_r \ln Z \right]$$

$$= k_B \left[\ln Z - \sum_r P_r \ln P_r - \ln Z \sum_r P_r \right]$$

where the last line follows because ln$Z$ is a constant. Now, the sum of the probabilities must equal unity,

$$\Sigma_r P_r = 1,$$

so

$$S = k_B \left[\ln Z - \sum_r P_r \ln P_r - \ln Z \right]$$

or (14.5)

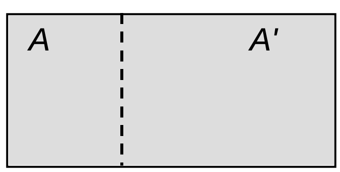
$$S = -k_B \sum_r P_r \ln P_r$$

Eq. (14.5) is a very useful alternative to the definition of S in terms of the partition function or the number of accessible states:

$$S = k_B (\ln Z + \beta \bar{E}) \qquad \text{or} \qquad S = k_B \ln \Omega.$$

Grand canonical ensemble

Although most of the systems we deal with can be described by the canonical ensemble (*NVT* or *NPT*), many situations of interest do **not** have fixed particle number N. Such systems are free to exchange particles with their surroundings. Consider, as usual, two systems A and A' which are allowed to come into contact *via* a porous wall, with no change in total volume:

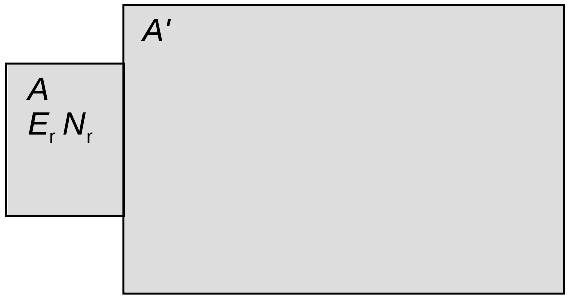


The presence of a porous wall, rather than a moveable piston, means that the systems cannot do work on each other (local PV has no meaning). What the system has is:

energy exchange $E^o = E + E'$ = constant → common temperature

particle exchange $N^o = N + N'$ = constant → common chemical potential.

The "Bolzmann factor" for a chemical potential can be determined in the same way that the factor was determined for the canonical ensemble with a temperature. Imagine two systems *A* and *A′*, where *A′* is not only a heat reservoir, but also a particle reservoir:



A particular "state" in *A* is now characterized by its energy E_r and particle number N_r. For every state (E_r ,N_r), there are Ω′ states in reservoir *A′*, where

$$\Omega' = (E^o\text{-}E_r\,,\,N^o\text{-}N_r).$$

Hence, the probability of system *A′* having (E_r ,N_r) is

$$P(E_r\,,N_r) \quad \Omega'(E^o\text{-}E_r\,,\,N^o\text{-}N_r).$$

Next, we perform the usual expansion of lnΩ′ around E^o, N^o, assuming

$$E_r << E^o \qquad N_r << N^o.$$

That is

$$\ln\Omega'(E^o - E_r, N^o - N_r) = \ln\Omega'(E^o, N^o) + \frac{\partial \ln\Omega'}{\partial E'}(-E_r) + \frac{\partial \ln\Omega'}{\partial N'}(-N_r)\ldots \quad (14.6)$$

where we have used

$$\Delta E' = \text{-}E_r \qquad\qquad \Delta N' = \text{-}N_r$$

Define

$$\beta \equiv \frac{\partial \ln\Omega'}{\partial E'} \qquad \alpha \equiv \frac{\partial \ln\Omega'}{\partial N'}$$

so that Eq. (14.6) becomes

$$\Omega'(E^o - E_r, N^o - N_r) = \Omega'(E^o, N^o)e^{-\beta E_r - \alpha N_r}$$

after exponentiating. Hence, the generalized Boltzmann factor is

$$P_r \quad e^{-\beta E_r - \alpha N_r} \qquad (14.7)$$

Averages can be constructed from this weighting as usual:

$$\bar{E} = \frac{\sum_r E_r e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

$$\overline{N} = \frac{\sum_r N_r e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r - \alpha N_r}}$$

where the sums are unrestricted, since essentially all E_r , N_r combinations are accessible from the reservoir.

Finally, note that it is conventional to make the replacement

$$\alpha = -\beta\mu,$$

where μ is the chemical potential.