Appendix C extra - Grand canonical ensemble

The grand canonical ensemble is the least restrictive of the commonly used ensembles in statistical mechanics. It is not found in the textbook solely because of the mathematics necessary to establish its form. For example, the critical micelle concentration in Chap. 5 should really be calculated with the grand canonical ensemble. We present the ensemble here for completeness, establishing its properties through the partition function Z.

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:

$$E_{\alpha\beta}{}^{o} = E_{\alpha} + E'_{\beta} + [\textit{no interaction energy}]$$

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

$$\begin{aligned} Z^{o} &= \Sigma_{\alpha\beta}\exp(-ßE_{\alpha\beta}{}^{o}) \\ &= \Sigma_{\alpha}\exp(-ßE_{\alpha}{}^{o})\ \Sigma_{\beta}\exp(-ßE_{\beta}{}^{o}) \\ &= Z \bullet Z'. \end{aligned} \qquad \text{(Cx5.1)}$$

Lastly, quantities such as energy and entropy which depend on ln$Z$, are additive according to Eq. (Cx5.1).

Entropy and probability

In terms of the partition function, the entropy can be written as

$$S = k_B(\ln Z + ß\overline{E}). \qquad \text{(Cx5.2)}$$

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

$$\overline{E} = \sum_{\alpha} P_{\alpha} E_{\alpha},$$

where P_{α} is the probability of the state being in state α,

$$P_{\alpha} = \frac{e^{-ßE_{\alpha}}}{Z}. \qquad \text{(Cx5.3)}$$

Thus,

$$S = k_B(\ln Z + ß\sum_{\alpha} P_{\alpha} E_{\alpha}) = k_B(\ln Z + \sum_{\alpha} P_{\alpha} ßE_{\alpha}) \qquad \text{(Cx5.4)}$$

Now, Eq. (Cx5.4) can be rearranged to read

$$\ln(P_\alpha Z) = -ßE_\alpha$$

which permits Eq. (Cx5.3) to be recast as

$$S = k_B\left[\ln Z - \sum_\alpha P_\alpha \ln(P_\alpha Z)\right]$$
$$= k_B\left[\ln Z - \sum_\alpha P_\alpha \ln(P_\alpha) - \sum_\alpha P_\alpha \ln Z\right]$$
$$= k_B\left[\ln Z - \sum_\alpha P_\alpha \ln P_\alpha - \ln Z \sum_\alpha P_\alpha\right]$$

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

$$\Sigma_\alpha P_\alpha = 1,$$

so

$$S = k_B\left[\ln Z - \sum_\alpha P_\alpha \ln P_\alpha - \ln Z\right]$$

or (Cx5.5)

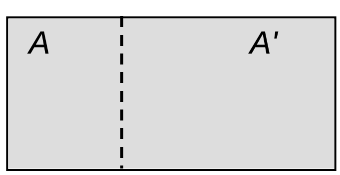
$$S = -k_B \sum_\alpha P_\alpha \ln P_\alpha$$

Eq. (Cx5.5) is a very useful alternative to the definition of S in terms of the partition function or the number of accessible states:

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

Grand canonical ensemble

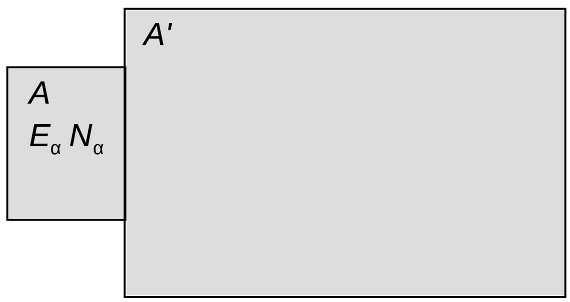
Although most of the systems we deal with can be described by the canonical ensemble (*NVT* or *NPT*), many situations of interest do **not** have fixed particle number *N*. Such systems are free to exchange particles with their surroundings. Consider, as usual, two systems *A* and *A'* which are allowed 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_α and particle number N_α. For every state (E_α ,N_α), there are Ω' states in reservoir *A′*, where

$$\Omega' = (E^o\text{-}E_\alpha\, ,\, N^o\text{-}N_\alpha).$$

Hence, the probability of system *A′* having (E_α ,N_α) is

$$P(E_\alpha ,N_\alpha) \quad \Omega'(E^o\text{-}E_\alpha\, ,\, N^o\text{-}N_\alpha).$$

Next, we perform the usual expansion of $\ln\Omega'$ around E^o, N^o, assuming

$$E_\alpha << E^o \qquad N_\alpha << N^o.$$

That is

$$\ln\Omega'(E^o - E_\alpha, N^o - N_\alpha) = \ln\Omega'(E^o, N^o) + \frac{\partial \ln\Omega'}{\partial E'}(-E_\alpha) + \frac{\partial \ln\Omega'}{\partial N'}(-N_\alpha)\ldots \quad \text{(Cx5.6)}$$

where we have used

$$\Delta E' = -E_\alpha \qquad\qquad \Delta N' = -N_\alpha$$

Define

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

so that Eq. (Cx5.6) becomes

$$\Omega'(E^o - E_\alpha, N^o - N_\alpha) = \Omega'(E^o, N^o)\, e^{-\beta E_\alpha + \beta\mu N_\alpha}$$

after exponentiating. Hence, the generalized Boltzmann factor is

$$P_\alpha \quad e^{-\beta E_\alpha + \beta\mu N_\alpha} \qquad \text{(Cx5.7)}$$

Averages can be constructed from this weighting as usual:

$$\bar{E} = \frac{\sum_\alpha E_\alpha e^{-\beta E_\alpha + \beta\mu N_\alpha}}{\sum_\alpha e^{-\beta E_\alpha + \beta\mu N_\alpha}}$$

$$\bar{N} = \frac{\sum_\alpha N_\alpha e^{-\beta E_\alpha + \beta\mu N_\alpha}}{\sum_\alpha e^{-\beta E_\alpha + \beta\mu N_\alpha}}$$

where the sums are unrestricted, since essentially all E_α , N_α combinations are accessible from the reservoir.