Appendix C extra - Ensembles

In the previous section, a numerical example illustrated how the interaction of a system affected the occupancy of its sites. We chose an arbitrary numerical degeneracy for a two-state system in isolation, then showed how the occupation probability changed when the system was placed in thermal contact with another system and a constraint was placed on the energy of the combined system. This demonstrated how the occupational probability of states in a system depends on the nature of its contact (if any) with other systems.

In statistical mechanics, systems are classified according to the mechanism of contact with their surroundings, of which three categories are commonly encountered. We will now give a synopsis of each type of ensemble, and then describe one of these in a little more detail, namely the canonical ensemble.

Ensembles in brief

1. *Microcanonical ensemble*
This system sits in splendid isolation, exhanging nothing with its environment. Among its attributes:

- particle **N**umber, **V**olume and **E**nergy are all fixed; hence *NVE* ensemble
- the system lies in some small energy range E to $E + \Delta E$, with all states α in the range equally accessible

Defining P_α as the probability of finding the system in state α, one finds

$$
\begin{array}{ll}
P_\alpha = 0 & E_\alpha > E + \Delta E \\
P_\alpha = \text{constant} & E \leq E_\alpha \leq E + \Delta E \\
P_\alpha = 0 & E_\alpha < E
\end{array}
$$

2. *Canonical ensemble*
Here, the system is in thermal contact with a heat reservoir, which is assumed to have much more energy than the system itself. The ensemble is characterized by

- fixed particle **N**umber, **V**olume and **T**emperature; hence *NVT* ensemble
- variable energy, because of its interaction with the reservoir
- all states are accessible, with varying probability.

As will be established momentarily, the probability of occupying state α is

$$P_\alpha \quad \exp(-ßE_\alpha)$$

or

$$P_\alpha = \frac{e^{-ßE_\alpha}}{\sum_\alpha e^{-ßE_\alpha}}$$

A closely related ensemble has fixed **P**ressure, rather than fixed volume, and is called the *isobaric-isothermal ensemble* or *NPT*

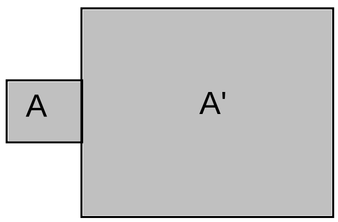
3. *Grand canonical ensemble*
This ensemble is the least restrictive of the three, being able to exchange both energy and particles with a reservoir. It is described by

- fixed chemical potential (**μ**), **V**olume and **T**emperature; hence μVT
- fluctuating particle number and energy
- all states are accessible, with varying probability:

  $P_\alpha \quad \exp(-\beta E_\alpha + \beta\mu N_\alpha)$.

Canonical ensemble (*NVT*)

The *NVT* ensemble is one which is free to exchange energy (but nothing else) with a heat reservoir, which is assumed to be sufficiently large that any transfer of energy does not change its temperature. Pictorially, *A* is the system and *A′* is the reservoir



Hence, at equilibrium, the temperature of the system is determined by the temperature of the heat reservoir:

$$\beta = \frac{\partial \ln\Omega'}{\partial E'} \qquad \text{(Cx3.1)}$$

What is the probability of finding the small system *A* in a state with energy E_α? For every state α, there are 1 x $\Omega'(E^o - E_\alpha)$ states of the combined system $A + A'$, where

$$E' = E^o - E_\alpha.$$

Thus, the probability of $A+A'$ having system *A* in state α is

$$P_\alpha = C\,\Omega'(E^o - E_\alpha). \qquad \text{(Cx3.2)}$$

Since $E_\alpha << E^o$, then $\ln\Omega'$ can be expanded in a Taylor series around E^o:

$$\ln\Omega'(E^o - E_\alpha) = \ln\Omega'(E^o) + \left.\frac{\partial \ln\Omega'}{\partial E'}\right|_{E^o} (-E_\alpha) + ...$$

which becomes, after using Eq. (Cx3.1) for the temperature

$$\Omega'(E^o - E_\alpha) = \Omega'(E^o) e^{-\beta E_\alpha} \,. \qquad \text{(Cx3.3)}$$

Now, the first term on the right-hand side can be absorbed into the constant *C* of Eq. (Cx3.2) to yield

$$P_\alpha = C e^{-ßE_\alpha}, \qquad \text{(Cx3.4)}$$

where exp($-ßE_\alpha$) is the Boltzmann factor. The normalization constant in Eq. (Cx3.4) is simply determined by summing over the accessible states, to give:

$$P_\alpha = \frac{e^{-ßE_\alpha}}{\sum_\alpha e^{-ßE_\alpha}} \qquad \text{(Cx3.5)}$$

For an observable *y*, the mean value can be determined from P_α through

$$\bar{y} = \sum_\alpha y_\alpha P_\alpha = \frac{\sum_\alpha y_\alpha e^{-ßE_\alpha}}{\sum_\alpha e^{-ßE_\alpha}} \qquad \text{(Cx3.6)}$$

where y_α is the value of *y* in the state α.