4.1: The Canonical Ensemble

Examples of "systems" and "baths":

- Bottle of wine/a swimming pool.
- Sample of gas/laboratory temperature control apparatus.
- One ideal gas molecule/sample of gas.
- But not one interacting gas molecule/sample of gas. (The Boltzmann distribution is for systems within ensembles, not for molecules within systems.)

We denote a microstate by x. Exactly what is meant by a microstate will depend upon circumstances. For a system of point particles it means specifying all the positions and momenta. For a spin system it means specifying the "up" or "down" state of each spin. We'll see other examples later.

I'll try to use different letters for microscopic and macroscopic (thermodynamic) quantities. For example $H(\mathrm{x})$ versus E (the thermodynamic energy is $E=\langle H(\mathrm{x})\rangle$; $\mathcal{M}(x)$ versus $M=\langle\mathcal{M}(\mathrm{x})\rangle$.

Summary

The canonical ensemble in general:

The probability that the system is in the microstate x is proportional to the "Boltzmann factor"

$$e^{-H(x)/k_BT}. \tag{4.1.1}$$

The normalization factor is called the "partition function" or "sum over all states" (German "Zustandsumme"):

$$Z(T,V,N)=\sum_{\text{microstates } x} e^{-H(\mathrm{x})/k_BT}. \tag{4.1.2}$$

(Note that Z is independent of x.) Thus the probability that the system is in microstate x is

$$\frac{e^{-H(\mathrm{x})/k_BT}}{Z(T,V,N)}. \tag{4.1.3}$$

The connection to thermodynamics is that the Helmholtz free energy is

$$F(T,V,N)=-k_BT\ln Z(T,V,N). \tag{4.1.4}$$

Note that in finding Z we sum over all microstates: the low-energy ones, the high-energy ones, the "orderly" ones (e.g. all atoms heading west, or all atoms heading east), the "disorderly" ones (e.g. atoms heading in scattered directions).

The canonical ensemble for a pure classical monatomic fluid:

The probability that the system is in the microstate Γ is proportional to the "Boltzmann factor"

$$e^{-H(\Gamma)/k_BT}. \tag{4.1.5}$$

Writing out all the normalizations correctly gives: the probability that the system is in some microstate within the phase space volume element $d\Gamma$ about Γ is

$$\frac{e^{-H(\Gamma)/k_BT}}{N!h_0^{3N}Z(T,V,N)}d\Gamma, \tag{4.1.6}$$

where the partition function is

$$Z(T,V,N)=\frac{1}{N!h_0^{3N}}\int e^{-H(\Gamma)/k_BT}d\Gamma. \tag{4.1.7}$$

(The integral runs over all of phase space.) This is an example of "partition function", namely the partition function for a pure classical monatomic fluid. It does not apply to mixtures, to crystals, to the ideal paramagnet. In contrast, the definition of "partition function" is equation (4.2), the "sum over all states" of the Boltzmann factor.