5.3: The partition function and relation to thermodynamics

In principle, we should derive the isothermal-isobaric partition function by coupling our system to an infinite thermal reservoir as was done for the canonical ensemble and also subject the system to the action of a movable piston under the influence of an external pressure P. In this case, both the temperature of the system and its pressure will be controlled, and the energy and volume will fluctuate accordingly.

However, we saw that the transformation from E to T between the microcanonical and canonical ensembles turned into a Laplace transform relation between the partition functions. The same result holds for the transformation from V to T. The relevant "energy" quantity to transform is the work done by the system against the external pressure P in changing its volume from $V=0$ to V, which will be PV. Thus, the isothermal-isobaric partition function can be expressed in terms of the canonical partition function by the Laplace transform:

$$\Delta(N,P,T) = \frac{1}{V_0}\int_0^\infty dV e^{-\beta PV} Q(N,V,T)$$

where V_0 is a constant that has units of volume. Thus,

$$\Delta(N,P,T) = \frac{1}{V_0 N! h^{3N}}\int_0^\infty dV \int d\mathrm{x} e^{-\beta(H(\mathrm{x})+PV)}$$

The Gibbs free energy is related to the partition function by

$$G(N,P,T) = -\frac{1}{\beta}\ln\Delta(N,P,T)$$

This can be shown in a manner similar to that used to prove the $A=-(1/\beta)\ln Q$. The differential equation to start with is

$$G = A + PV = A + P\frac{\partial G}{\partial P}$$

Other thermodynamic relations follow:

Volume:

$$V = -kT\left(\frac{\partial \ln\Delta(N,P,T)}{\partial P}\right)_{N,T}$$

Enthalpy:

$$\bar{H} = \langle H(\mathrm{x}) + PV\rangle = -\frac{\partial}{\partial\beta}\ln\Delta(N,P,T)$$

Heat capacity at constant pressure

$$C_P = \left(\frac{\partial \bar{H}}{\partial T}\right)_{N,P} = k\beta^2\frac{\partial^2}{\partial\beta}\ln\Delta(N,P,T)$$

Entropy:

S	$=$	$-\left(\frac{\partial G}{\partial T}\right)_{N,P}$	
	$=$	$k\ln\Delta(N,P,T)+\frac{\bar{H}}{T}$	

The fluctuations in the enthalpy $\Delta\bar{H}$ are given, in analogy with the canonical ensemble, by

$$\Delta\bar{H} = \sqrt{kT^2 C_P}$$

so that

$$\frac{\Delta \bar{H}}{\bar{H}} = \frac{\sqrt{kT^2 C_P}}{\bar{H}}$$

so that, since C_P and $\bar{H}$ are both extensive, $\Delta \bar{H}/\bar{H} \sim 1/\sqrt{N}$ which vanish in the thermodynamic limit.