6.2: Partition Functions

Consider two canonical systems, 1 and 2, with particle numbers N_1 and N_2, volumes V_1 and V_2 and at temperature T. The systems are in chemical contact, meaning that they can exchange particles. Furthermore, we assume that $N_2 \gg N_1$ and $V_2 \gg V_1$ so that system 2 is a particle reservoir. The total particle number and volume are

$$V = V_1 + V_2$$

$$N = N_1 + N_2$$

The total Hamiltonian $H(x, N)$ is

$$H(x, N) = H_1(x_1, N_1) + H_2(x_2, N_2)$$

If the systems *could not* exchange particles, then the canonical partition function for the whole system would be

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int dx \, e^{-\beta(H_1(x_1, N_1) + H_2(x_2, N_2))}$$

$$= \frac{N_1! N_2!}{N!} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T)$$

where

$$Q_1(N_1, V_1, T) = \frac{1}{N_1! h^{3N_1}} \int dx \, e^{-\beta H_1(x_1, N_1)}$$

$$Q_2(N_2, V_2, T) = \frac{1}{N_2! h^{3N_2}} \int dx \, e^{-\beta H_2(x_2, N_2)}$$

However, N_1 and N_2 are *not* fixed, therefore, in order to sum over all microstates, we need to sum over all values that N_1 can take on subject to the constraint $N = N_1 + N_2$. Thus, we can write the canonical partition function for the whole system as

$$Q(N, V, T) = \sum_{N_1=0}^{N} f(N_1, N) \frac{N_1! N_2!}{N!} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T)$$

where $f(N_1, N_2)$ is a function that weights each value of N_1 for a given N.

Thus,

- $f(0, N)$ is the number of configurations with 0 particles in V_1 and N particles in V_2.
- $f(1, N)$ is the number of configurations with 1 particles in V_1 and $N - 1$ particles in V_2.
- etc.

Determining the values of $f(N_1, N)$ amounts to a problem of counting the number of ways we can put N identical objects into 2 baskets. Thus,

$$f(0, N) = 1$$

$$f(1, N) = N$$

$$= \frac{N!}{1!(N-1)!}$$

$$f(2, N) = \frac{N(N-1)}{2}$$

$$= \frac{N!}{2!(N-2)!}$$

etc. or generally,

$$f(N_1, N) = \frac{N!}{N_1!(N - N_1)!} = \frac{N!}{N_1! N_2!}$$

which is clearly a classical degeneracy factor. If we were doing a purely classical treatment of the grand canonical ensemble, then this factor would appear in the sum for $Q(N, V, T)$, however, we always include the *ad hoc* quantum correction $\frac{1}{N!}$ in the expression for the canonical partition function, and we see that these quantum factors will exactly cancel the classical degeneracy factor, leading to the following expression:

$$Q(N, V, T) = \sum_{N_1=0}^{N} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T)$$

which expresses the fact that, in reality, the various configurations are not distinguishable from each other, and so each one should count with equal weighting. Now, the distribution function $\rho(x)$ is given by

$$\rho(x, N) = \frac{\frac{1}{N! h^{3N}} e^{-\beta H(x,N)}}{Q(N, V, T)}$$

which is chosen so that

$$\int dx \, \rho(x, N) = 1$$

However, recognizing that $N_2 \approx N$, we can obtain the distribution for $\rho_1(x_1, N_1)$ immediately, by integrating over the phase space of system 2:

$$\rho_1(x_1, N_1) = \frac{1}{Q(N, V, T)} \frac{1}{N_1! h^{3N_1}} e^{-\beta H_1(x_1,N_1)} \frac{1}{N_2! h^{3N_2}} \int dx_2 e^{-\beta H_2(x_2,N_2)}$$

where the $\frac{1}{N_1! h^{3N_1}}$ prefactor has been introduced so that

$$\sum_{N_1=0}^{N} \int dx_1 \, \rho(x_1, N_1) = 1$$

and amounts to the usual *ad hoc* quantum correction factor that must be multiplied by the distribution function for each ensemble to account for the identical nature of the particles. Thus, we see that the distribution function becomes

$$\rho_1(x_1, N_1) = \frac{Q_2(N_2, V_2, T)}{Q(N, V, T)} \frac{1}{N_1! h^{3N_1}} e^{-\beta H_1(x_1,N_1)}$$

Recall that the Hemlholtz free energy is given by

$$A = -\frac{1}{\beta} \ln Q$$

Thus,

$$Q(N, V, T) = e^{-\beta A(N,V,T)}$$
$$Q_2(N_2, V_2, T) = e^{-\beta A(N_2,V_2,T)} = e^{-\beta A(N-N_1,V-V_1,T)}$$

or

$$\frac{Q_2(N_2, V_2, T)}{Q(N, V, T)} = e^{-\beta(A(N-N_1,V-V_1,T)-A(N,V,T))}$$

But since $N \gg N_1$ and $V \gg V_1$, we may expand:

$$A(N - N_1, V - V_1, T) = A(N, V, T) - \frac{\partial A}{\partial N} N_1 - \frac{\partial A}{\partial V} V_1 + \cdots$$
$$= A(N, V, T) - \mu N_1 + P V_1 + \cdots$$

Therefore the distribution function becomes

$$\rho_1(x_1, N_1) = \frac{1}{N_1! h^{3N_1}} e^{\beta \mu N_1} e^{-\beta P V_1} e^{-\beta H_1(x_1,N_1)} = \frac{1}{N_1! h^{3N_1}} \frac{1}{e^{\beta P V_1}} e^{\beta \mu N_1} e^{-\beta H_1(x_1,N_1)} \tag{6.2.1}$$

Dropping the "1" subscript, we have

$$\rho(x, N) = \frac{1}{e^{\beta PV}} \left[\frac{1}{N! h^{3N}} e^{\beta \mu N} e^{-\beta H(x, N)} \right]$$

We require that $\rho(x, N)$ be normalized:

$\sum_{N=0}^{\infty} \int dx \, \rho(x, N) = 1$

$\frac{1}{e^{\beta PV}} \left[\sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} e^{\beta \mu N} \int dx \, e^{-\beta H(x, N)} \right] = 1$

Now, we define the grand canonical partition function

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} e^{\beta \mu N} \int dx \, e^{-\beta H(x, N)}$$

Then, the normalization condition clearly requires that

$$\mathcal{Z}(\mu, V, T) = e^{\beta PV}$$

$$\ln \mathcal{Z}(\mu, V, T) = \frac{PV}{kT}$$

Therefore PV is the free energy of the grand canonical ensemble, and the entropy $S(\mu, V, T)$ is given by

$$S(\mu, V, T) = \left(\frac{\partial (PV)}{\partial T} \right)_{\mu, V} = k \ln \mathcal{Z}(\mu, V, T) - k\beta \left(\frac{\partial}{\partial \beta} \ln \mathcal{Z}(\mu, V, T) \right)_{\mu, V}$$

We now introduce the **fugacity** ζ defined to be

$$\zeta = e^{\beta \mu}$$

Then, the grand canonical partition function can be written as

$$\mathcal{Z}(\zeta, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \zeta^N \int dx \, e^{-\beta H(x, N)}$$

$$= \sum_{N=0}^{\infty} \zeta^N Q(N, V, T)$$

which allows us to view the grand canonical partition function as a function of the thermodynamic variables ζ, V and T.

Other thermodynamic quantities follow straightforwardly:

$$\frac{\partial}{\partial \mu} = \frac{\partial \zeta}{\partial \zeta} = \beta \zeta \frac{\partial}{\partial \zeta}$$

Thus,

$$\langle N \rangle = \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T)$$