2.4: Equilibrium ensembles

An equilibrium ensemble is one for which there is no explicit time-dependence in the phase space distribution function, $\frac{\partial f}{\partial t} = 0$. In this case, Liouville's equation reduces to

$$\{f, H\} = 0$$

which implies that $f(x)$ must be a pure function of the Hamiltonian

$$f(x) = F(H(x))$$

The specific form that $F(H(x))$ has depends on the specific details of the ensemble.

The integral over the phase space distribution function plays a special role in statistical mechanics:

$$F = \int dx F(H(x)) \tag{2.4.1}$$

It is known as the partition function and is equal to the number of members in the ensemble. That is, it is equal to the number of microstates that all give rise to a given set of macroscopic observables. Thus, it is the quantity from which all thermodynamic properties are derived.

If a measurement of a macroscopic observable $A(x)$ is made, then the value obtained will be the ensemble average:

$$\langle A \rangle = \frac{1}{F} \int dx A(x) F(H(x)) \tag{2.4.2}$$

Equations 2.4.1 and 2.4.2 are the central results of ensemble theory, since they determine all thermodynamic and other observable quantities.