

3.2: The Partition Function

Consider two systems (1 and 2) in thermal contact such that

- $N_2 \gg N_1$
- $E_2 \gg E_1$
- $N = N_1 + N_2$
- $E = E_1 + E_2$
- $\dim(x_1) \gg \dim(x_2)$

and the total Hamiltonian is just

$$H(x) = H_1(x_1) + H_2(x_2)$$

Since system 2 is infinitely large compared to system 1, it acts as an infinite heat reservoir that keeps system 1 at a constant temperature T without gaining or losing an appreciable amount of heat, itself. Thus, system 1 is maintained at canonical conditions, N, V, T .

The full partition function $\Omega(N, V, E)$ for the combined system is the microcanonical partition function

$$\Omega(N, V, E) = \int dx \delta(H(x) - E) = \int dx_1 dx_2 \delta(H_1(x_1) + H_2(x_2) - E)$$

Now, we define the distribution function, $f(x_1)$ of the phase space variables of system 1 as

$$f(x_1) = \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E)$$

Taking the natural log of both sides, we have

$$\ln f(x_1) = \ln \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E)$$

Since $E_2 \gg E_1$, it follows that $H_2(x_2) \gg H_1(x_1)$, and we may expand the above expression about $H_1 = 0$. To linear order, the expression becomes

$$\begin{aligned} \ln f(x_1) &= \ln \int dx_2 \delta(H_2(x_2) - E) + H_1(x_1) \frac{\partial}{\partial H_1(x_1)} \ln \int dx_2 \delta(H_1(x_1) + H_2(x_2) - E) \Big|_{H_1(x_1)=0} \\ &= \ln \int dx_2 \delta(H_2(x_2) - E) - H_1(x_1) \frac{\partial}{\partial E} \ln \int dx_2 \delta(H_2(x_2) - E) \end{aligned}$$

where, in the last line, the differentiation with respect to H_1 is replaced by differentiation with respect to E . Note that

$$\begin{aligned} \ln \int dx_2 \delta(H_2(x_2) - E) &= \frac{S_2(E)}{k} \\ \frac{\partial}{\partial E} \ln \int dx_2 \delta(H_2(x_2) - E) &= \frac{\partial}{\partial E} \frac{S_2(E)}{k} = \frac{1}{kT} \end{aligned}$$

where T is the common temperature of the two systems. Using these two facts, we obtain

$$\begin{aligned} \ln f(x_1) &= \frac{S_2(E)}{k} - \frac{H_1(x_1)}{kT} \\ f(x_1) &= e^{\frac{S_2(E)}{k}} e^{-\frac{H_1(x_1)}{kT}} \end{aligned}$$

Thus, the distribution function of the canonical ensemble is

$$f(x) \propto e^{-\frac{H(x)}{kT}}$$

The prefactor $e^{\frac{S_2(E)}{k}}$ is an irrelevant constant that can be disregarded as it will not affect any physical properties.

The normalization of the distribution function is the integral:

$$\int dx e^{\frac{-H(x)}{kT}} \equiv Q(N, V, T)$$

where $Q(N, V, T)$ is the canonical partition function. It is convenient to define an inverse temperature $\beta = \frac{1}{kT}$. $Q(N, V, T)$ is the canonical partition function. As in the microcanonical case, we add in the *ad hoc* quantum corrections to the classical result to give

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

The thermodynamic relations are thus,

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