Chapter 8

Canonical Ensemble (E, V, N)

3. Microcanonical ensemble of the combined system

Since the combined system A is isolated, the distribution function in the combined phase space is given by the microcanonical distribution function $\rho(q,p)$,

$$\rho(q,p)=\frac{\delta\left(E-H(q,p)\right)}{\int dq\,dp\,\delta\left(E-H(q,p)\right)}, \qquad \int dq\,dp\;\delta(E-H)=\Omega(E), \tag{1}$$

$$\boxed{\rho(q,p)=\frac{\delta(E-H)}{\Omega(E)}}$$

where $\Omega(E)$ is the density of phase space.

Calculation of A_2. It is not the distribution function $\rho(q,p)$ of the total system A that we are interested in, but the distribution function ρ_1 of the small system A_1. One hence needs to trace out A_2:

$$\rho_1\left(q(1), p(1)\right) = \int dq(2)\,dp(2)\;\rho$$

$$= \frac{\int dq(2)\,dp(2)\,\delta\left(E-(H_1+H_2)\right)}{\Omega(E)} = \frac{\Omega_2\left(E-H_1\right)}{\Omega(E)} \tag{2}$$

where $\Omega_2\left(E_2\right) = \Omega_2\left(E-H_1\right)$ is the phase space density of A_2.

Small E_1 expansion. Now, we make use of the fact that A_1 is a much smaller system than A_2 and therefore the energy E_1 given by H_1 is much smaller than the energy of the combined system:

$$E_1 \ll E$$

In this case, we can approximate (2) by expanding the slowly varying logarithm of $\Omega_2\left(E_2\right) = \Omega_2\left(E-H_1\right)$ around the $E_2 = E$ as

$$\ln\Omega_2\left(E_2\right) = \ln\Omega_2\left(E-H_1\right) \simeq \ln\Omega_2\left(E\right) - \left[\frac{\partial \ln\Omega_2}{\partial E_2}\right]_{E_2=E} H_1 + ... \tag{3}$$

and neglect the higher-order terms since $H_1 = E_1 \ll E$.

Derivatives of the entropy. Using,

$$S = k_B \ln\left(\frac{\Gamma\left(E,V,N\right)}{\Gamma_0}\right) = k_B \ln\left(\frac{\Omega\left(E\right)\Delta}{\Gamma_0}\right) \tag{4}$$

where Δ is the width of the energy shell, we find that derivatives of the entropy like

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{\partial \ln\Omega\left(E\right)}{\partial E} \tag{5}$$

can be taken with respect to the logarithm of the phase space density $\Omega\left(E\right)$.

Boltzmann Factor

Using (5) for the larger system A_2 we may rewrite (3) as

$$\Omega_2\left(E-H_1\right) = \exp\left[\ln\Omega_2\left(E\right) - \left.\frac{\partial \ln\Omega_2\left(E_2\right)}{\partial E_2}\right|_{E_2=E} H_1 + ...\right]$$

$$= \Omega_2\left(E\right)\exp\left[-\frac{H_1}{k_B T_2}\right]$$

The temperature T_2 of the heat reservoir A_2 by whatever small amount of energy the large system A_2 gives to the small system A_1. Both systems are thermally coupled, such that $T_1 = T_2 = T$. We hence find with (2).

$$\rho_1\left(q(1), p(1)\right) = \frac{\Omega_2}{\Omega(E)} e^{-\frac{H_1}{k_B T}} \propto e^{-\frac{H_1}{k_B T}} \quad (6)$$

The factor $\exp\left[-H_1/\left(k_B T\right)\right]$ is called the *Boltzmann factor*.