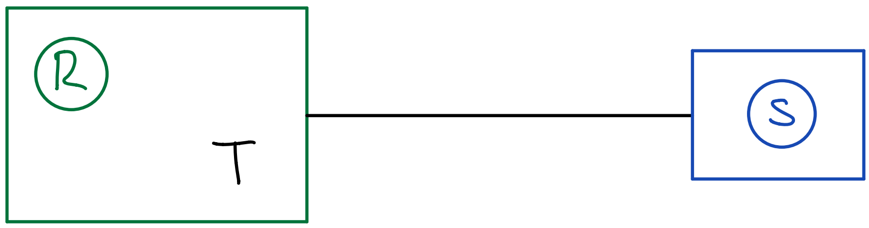
Canonical ensemble



$$E_0 = E_R - E_S$$

$P_j = c\,\Omega_R(E_0 - E_j) \longrightarrow$ Probability of S being in j

$E := E_R \longrightarrow \Omega_R(E) =: \#$ of microscopic accessible states of the reservoir with energy $E = E_0 - E_j$

$E \gg E_j \;\; ; \forall j.$

$$\rightarrow \ln(P_j) = \ln(c) + \ln(\Omega_R(E_0)) + \left[\frac{\partial}{\partial E}\ln(\Omega_R(E))\right]_{E=E_0} \overset{E-E_0}{\overset{=}{(-E_j)}}$$

$$+ \frac{1}{2}\left[\frac{\partial^2}{\partial E^2}\ln(\Omega_R(E))\right]_{E=E_0}(-E_j)^2 + \ldots$$

but $\frac{\partial}{\partial E}\ln(\Omega_R(E)) = \frac{1}{K_B T} \;\; \rightarrow T$ is the reservoir temperature

$$\frac{\partial^2}{\partial E^2}\ln(\Omega_R(E)) = \frac{1}{K_B}\frac{\partial}{\partial E}\left(\frac{1}{T}\right) \rightarrow 0$$

The temperature of R does not change.

then

$$\ln(P_j) = \text{constant} - \frac{1}{K_B T}E_j$$

Finally,

$$P_j = \frac{\exp(-\beta E_j)}{\sum_k \exp(-\beta E_k)}$$

The probability must be normalized

$$K_B T = \frac{1}{\beta}.$$

Canonical ensemble.

let us define

$$Z := \sum_j \exp(-\beta E_j) \;\; \rightarrow \text{Partition function.}$$

$$= \sum_{\epsilon} \Omega(\epsilon) \exp(-\beta \epsilon).$$

$$Z = \sum_{\epsilon} \exp\left[\ln(\Omega(\epsilon)) - \beta\epsilon\right] = \sum_{\epsilon} \exp\left[\frac{S}{K_B} - \frac{\epsilon}{K_B T}\right]$$

$$= \sum_{\epsilon} \exp\left[\frac{1}{K_B T}(TS - \epsilon)\right] \sim \exp\left[-\beta \min_{\epsilon}\{\epsilon - TS(\epsilon)\}\right]$$

$Z \longrightarrow \exp(-\beta F) \longrightarrow F$ is the Helmholtz free energy.

$$F = F(T, v, N) \longrightarrow -\frac{1}{\beta}\ln(Z(T, V, N))$$

In the thermodynamic limit we get

$$f(T, v) = -\frac{1}{\beta} \lim_{\substack{V, N \to +\infty \\ \frac{V}{N} = v}} \frac{1}{N} \ln(Z(T, V, N))$$ Helmholtz free energy per particle.

In the phase space

$$\rho(q, p) = \frac{1}{Z} \exp\{-\beta \mathcal{H}_s(q, p)\}$$ s is the system in equilibrium with the reservoir.

$$Z = \int \exp\{-\beta \mathcal{H}_s(q, p)\} \, dq \, dp$$

$$\langle E_j \rangle = \frac{\sum_j E_j \exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)} = -\frac{\partial}{\partial\beta}\ln(Z).$$

$$-\frac{\partial}{\partial\beta}\ln(Z) = \frac{\partial}{\partial\beta}\left(\frac{1}{K_B T} F\right) = \frac{\partial}{\partial\beta}(\beta U - TS\beta)$$

$$= \frac{\partial}{\partial\beta}\left[\beta\left(U - \frac{S}{K_B}\right)\right] = U$$

$$\langle (E_j - \langle E_j \rangle)^2 \rangle = \langle E_j^2 \rangle - \langle E_j \rangle^2$$

$$= \frac{1}{Z}\sum_j E_j^2 \exp(-\beta E_j) - \left[\frac{1}{Z}\sum_j E_j \exp(-\beta E_j)\right]^2$$

then,

$$\langle (E_j - \langle E_j \rangle)^2 \rangle = \frac{\partial}{\partial \beta}\left[\frac{1}{z}\frac{\partial z}{\partial \beta}\right] = \frac{\partial}{\partial \beta}\left[\frac{\partial \ln(z)}{\partial \beta}\right] = -\frac{\partial}{\partial \beta}\langle E_j \rangle$$

$$= -\frac{\partial U}{\partial \beta} = K_\beta T^2 \frac{\partial U}{\partial T} = N K_B T^2 c_v > 0$$

therefore, $c_v > 0$

$$\frac{\langle (E_j - \langle E_j \rangle)^2 \rangle^{1/2}}{\langle E_j \rangle} = \frac{\sqrt{N K_B T^2 c_v}}{N u} \sim \frac{1}{\sqrt{N}}$$

In phase transitions c_v is large.