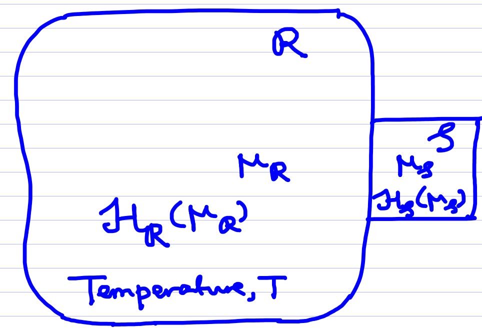
A system $\mathcal{S}$ is in contact with a reservoir $\mathcal{R}$ at temperature $T$ such that the wall(s) connecting the two is:
- Diathermal $\longrightarrow$ Exchange of heat allowed
- Fixed $\longrightarrow$ No work
- Impermeable $\longrightarrow$ No particle exchange




$p_{T,\vec{x}}(\mu)$ of various microstates of $\mathcal{S}$. ?

$\mathcal{R}\oplus\mathcal{S}$ belongs to a microcanonical ensemble of energy $E_{tot} \gg E_{\mathcal{S}}$.

Joint prob. of microstates $\mu_{\mathcal{S}}\otimes\mu_{\mathcal{R}}$ is:

$$p(\mu_{\mathcal{S}}\otimes\mu_{\mathcal{R}}) = \frac{1}{\Omega_{\mathcal{S}\oplus\mathcal{R}}(E_{tot})} \times \begin{cases} 1 & \text{if } \mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}})+\mathcal{H}_{\mathcal{R}}(\mu_{\mathcal{R}}) = E_{tot} \\ 0 & \text{otherwise} \end{cases}$$

The unconditional probability for microstates of $\mathcal{S}$ is
$$p(\mu_{\mathcal{S}}) = \sum_{\{\mu_{\mathcal{R}}\}} p(\mu_{\mathcal{S}}\otimes\mu_{\mathcal{R}})$$

i.e., once $\mathcal{S}$ is specified, the sum is restricted to microstates of reservoir with energy $E_{tot} - \mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}})$.

$$p(\mu_{\mathcal{S}}) = \frac{\Omega_{\mathcal{R}}(\mathcal{H}_{\mathcal{R}}(\mu_{\mathcal{R}}))}{\Omega_{\mathcal{S}\oplus\mathcal{R}}(\mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}})+\mathcal{H}_{\mathcal{R}}(\mu_{\mathcal{R}}))}.$$

$$= \frac{\Omega_{\mathcal{R}}(E_{tot} - \mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}}))}{\Omega_{\mathcal{S}+\mathcal{R}}(E_{tot})}$$

$$\propto \exp\left[\frac{1}{k_B} S_{\mathcal{R}}(E_{tot} - \mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}}))\right].$$

But $S_{\mathcal{R}}(E_{tot} - \mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}})) = S_{\mathcal{R}}(E_{tot}) - \mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}})\frac{\partial S_{\mathcal{R}}}{\partial E_{\mathcal{R}}} + (\;)\frac{\partial^2 S_{\mathcal{R}}}{\partial E_{\mathcal{R}}^2} - + \cdots$

$$= S_{\mathcal{R}}(E_{tot}) - \frac{\mathcal{H}_{\mathcal{S}}(\mu_{\mathcal{S}})}{T}.$$ For a 'good' reservoir.

$$\therefore\ p_{T,\vec{x}}(\mu) = \frac{e^{-\beta\mathcal{H}(\mu)}}{\sum_{\{\mu\}} e^{-\beta\mathcal{H}\{\mu\}}}$$

where, $\sum_{\{\mu\}} e^{-\beta\mathcal{H}(\mu)} = Z(T,\vec{x})$ is called the partition function.

$$\underbrace{p(\mu_S)} = C\,\Omega_R(\underbrace{E_{tot}}_{E_0} - \underbrace{\mathcal{H}_S(\mu_S)}_{E_j}).$$

$$p_j = C\,\Omega_R(E_0 - E_j).$$

$E_j$ : energy of $S$ in microstate $j$

$\Omega_R(E)$ : number of accessible microstates of thermal reservoir $R$ with energy $E = E_0 - E_j$.

Also, $E_j \ll E_0\ \forall j$ (large reservoir).

$$\therefore\ \ln p_j = \ln C + \ln\Omega_R(E_0 - E_j).$$

$$= \ln C + \ln\Omega_R(E_0) + \left(\frac{\partial \ln\Omega_R(E)}{\partial E}\right)_{E=E_0}(-E_j)$$

$$+ \left(\frac{\partial^2 \ln\Omega_R(E)}{\partial E^2}\right)_{E=E_0}\frac{(-E_j)^2}{2!} + \cdots$$

But $\left(\frac{\partial \ln\Omega_R}{\partial E}\right)_{E=E_0} = \frac{1}{k_BT}$ & higher derivatives are zero (for a reservoir).

$$\therefore\ \ln p_j = \text{const.} - \frac{E_j}{k_BT}. \Rightarrow p_j = \text{const.}\, e^{-E_j/k_BT}$$

But $\sum_j p_j = 1 \Rightarrow \text{const.} = \frac{1}{\sum_j e^{-E_j/k_BT}}$.

Using $\beta = \frac{1}{k_BT}$,

$$\Rightarrow p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}. \quad \text{where, } E_j \equiv \mathcal{H}_S(\mu_S)$$

& $Z = \sum_j e^{-\beta E_j}$ "Zustandsumme"

Partition function (sum over states)

## Different notations

$$p_j = \frac{\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)}$$

$$p(\mu) = \frac{\exp(-\beta \mathcal{H}(\mu))}{\sum_{\{\mu\}} \exp(-\beta \mathcal{H}(\mu))}$$

$\{\mu\}$: microstates.

$j$: microstate label

For phase space point $(q, p)$, the probability density is:

$$\rho(q,p) = \frac{\exp(-\beta \mathcal{H}(q,p))}{Z}.$$

where, $Z = \int dq\, dp \exp\left(-\beta \mathcal{H}(q,p)\right)$.

## Degenerate case

If $\exists$ multiple energy levels with same energy value,

$$Z = \sum_j \exp(-\beta E_j) = \sum_E \Omega(E) \exp(-\beta E).$$

$$= \sum_E \exp\left(\frac{k_B \ln\Omega}{k_B} - \beta E\right)$$

$\left\{ \begin{array}{l} \Omega(E): \\ \#\text{ of microstates} \\ \text{with energy } E \end{array} \right.$

$$= \sum_E \exp\left[-\beta(E - TS)\right]. \qquad \because S = k_B \ln\Omega.$$

$$= \sum_E \exp\left(-\beta F(E)\right).$$

Maximum contribution to this sum is at the most probable value of $E \, (= E^*)$.

$$\therefore F(E^*) \approx -k_B T \ln Z. \qquad E^* = \langle E_j \rangle.$$

"Essence" of entropy S.

$$F = -\frac{1}{\beta}\ln Z .$$

$$\therefore S = -\left(\frac{\partial F}{\partial T}\right) = -\left(\frac{\partial \beta}{\partial T}\right)\left(\frac{\partial F}{\partial \beta}\right).$$

$$= \frac{1}{k_B T^2}\left(\frac{\partial F}{\partial \beta}\right) = -\frac{1}{k_B T^2}\frac{\partial}{\partial \beta}\left(\frac{1}{\beta}\ln Z\right).$$

$$= -\frac{1}{k_B T^2}\left[-\frac{1}{\beta^2}\ln Z + \frac{1}{\beta}\frac{\partial \ln Z}{\partial \beta}\right].$$

$$\because \quad p_j = \frac{1}{Z}e^{-\beta E_j}$$

$$\Rightarrow E_j = -\frac{1}{\beta}\ln(p_j Z)$$

$$\Rightarrow S = -\frac{1}{k_B T^2}\left[-\frac{1}{\beta^2}\ln Z + \frac{1}{\beta}\frac{\partial}{\partial \beta}\ln \sum_j e^{-\beta E_j}\right]$$

$$= -\frac{1}{k_B T^2}\left[-\frac{1}{\beta^2}\ln Z - \frac{1}{\beta Z}\sum_j E_j e^{-\beta E_j}\right].$$

$$= -\frac{1}{k_B T^2}\left[-\frac{1}{\beta^2}\ln Z + \frac{1}{\beta Z}\sum_j \frac{p_j Z}{\beta}\ln(p_j Z)\right].$$

$$= -\frac{1}{k_B T^2}\left[-\frac{1}{\beta^2}\ln Z + \frac{1}{\beta^2}\left(\sum_j p_j\right)\ln Z + \frac{1}{\beta^2}\sum_j p_j \ln p_j\right]$$

$$= -k_B \sum_j p_j \ln p_j .$$

$$\boxed{S = -k_B \sum_j p_j \ln p_j}$$

## Generator of cumulants

$$\langle E_j \rangle = \sum_j E_j \, p(j)$$

$$= \frac{1}{Z} \sum_j E_j \exp(-\beta E_j)$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$= -\frac{\partial \ln Z}{\partial \beta} = \text{mean.}$$

Now, $$\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \frac{\partial \ln Z}{\partial \beta}$$

$$= \frac{\partial}{\partial \beta} \left[ \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right].$$

$$= \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2.$$

$$= \frac{1}{Z} \sum_j E_j^2 \exp(-\beta E_j) - \left( \frac{\partial \ln Z}{\partial \beta} \right)^2.$$

$$= \langle E_j^2 \rangle - \langle E_j \rangle^2.$$

$$= \text{variance} = \sigma.$$

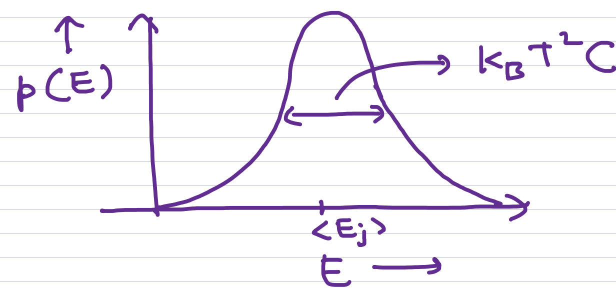
In general, $n^{th}$ cumulant is given by, $\langle E_j^n \rangle = (-1)^n \left( \frac{\partial}{\partial \beta} \right)^n \ln Z$.

$$\text{Mean} = -\frac{\partial \ln Z}{\partial \beta} = \langle E_j \rangle = U.$$

$$\text{Variance} = \langle E_j^2 \rangle - \langle E_j \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

$$= \frac{\partial}{\partial \beta}\left(\frac{\partial \ln Z}{\partial \beta}\right) = -\frac{\partial U}{\partial \beta}.$$

$$= -\left(\frac{\partial U}{\partial T}\right) / \left(\frac{\partial \beta}{\partial T}\right) = k_B T^2 C \geq 0.$$




C : Heat capacity

# Examples

## 1. Einstein solid

Consider N localized and noninteracting quantum one dimensional harmonic oscillators with fundamental frequency $\omega$ in contact with a thermal reservoir at temperature T.

The microscopic states of this system are characterized by a set of quantum numbers $\{n_1, n_2, \ldots, n_N\}$ where, $n_j$ is the label for $j^{th}$ oscillator.

$$E(\{n_j\}) = \sum_{j=1}^{N} (n_j + \tfrac{1}{2})\hbar\omega .$$

$\therefore$ Canonical partition function is given by,

$$Z = \sum_{\{n_j\}} \exp(-\beta E(\{n_j\})).$$

$$= \sum_{n_1, \ldots, n_N} \exp\left[-\sum_{j=1}^{N} (n_j + \tfrac{1}{2})\beta\hbar\omega\right].$$

As there are no interaction terms, the above sum factorizes leading to,

$$Z = \left\{\sum_{n=0}^{\infty} \exp\left[-(n+\tfrac{1}{2})\beta\hbar\omega\right]\right\}^N = Z_1^N$$

s.t., $$Z_1 = \sum_{n=0}^{\infty} \exp\left[-(n+\tfrac{1}{2})\hbar\omega\right] = \frac{\exp\left[-\frac{1}{2}\beta\hbar\omega\right]}{1-\exp\left[-\beta\hbar\omega\right]}$$

Notes:

- $f = -\frac{1}{\beta} \lim_{N\to\infty} \frac{1}{N} \ln Z$
  $= \frac{1}{2}\hbar\omega + k_B T \ln\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right].$
- $s = -\frac{\partial f}{\partial T} = -k_B \ln\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right] + k_B \left(\frac{\hbar\omega}{k_B T}\right) \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right]}.$
- $c = T\frac{\partial s}{\partial T} = k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right]^2}$

Internal energy per oscillator as a function of temperature is,

$$u = -\frac{1}{N}\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}.$$

$$\therefore\ U = N\left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}\right].$$

## 2. Two level systems

N two-state systems in thermal equilibrium with a reservoir at temperature T.

The single particle states have energies $\epsilon_1 = 0$ & $\epsilon_2 = \epsilon > 0$.

Introduce a variable $t_j$ associated with the $j^{th}$ particle $(j = 1, 2, \dots, N)$

s.t., $j = \begin{cases} 0 & \text{if particle } j \text{ has zero energy.} \\ 1 & \text{if particle } j \text{ has energy } \epsilon. \end{cases}$

$\therefore$ Canonical partition function can be written as

$$Z = \sum_{\{t_j\}} \exp(-\beta E\{t_j\}) = \sum_{\{t_j\}} \exp\left(-\sum_{j=1}^{N} \beta\epsilon t_j\right)$$

$$= \sum_{t_1,\dots,t_N} \exp\left(-\sum_{j=1}^{N} \beta\epsilon t_j\right).$$

$$= Z_1^N$$

where, $Z_1 = \sum_t \exp(-\beta\epsilon t) = 1 + \exp(-\beta\epsilon).$

Alternatively,

$$Z = \sum_E \Omega(E,N) \exp(-\beta E)$$

$$= \sum_{\substack{N_1, N_2 = 0 \\ N_1 + N_2 = N}}^{N} \frac{N!}{N_1!\, N_2!} \exp(-\beta\epsilon N_2)$$

$\begin{cases} N_1 \text{ with } \epsilon_1 = 0. \\ N_2 \text{ with } \epsilon_2 = \epsilon > 0 \end{cases}$

$$= [1 + \exp(-\beta\epsilon)]^N = Z_1^N.$$

Notes:

- $f = f(T) = -\frac{1}{\beta} \lim_{N\to\infty} \frac{1}{N} \ln Z$

$$= -k_B T \ln\left[1 + \exp\left(-\frac{\epsilon}{k_B T}\right)\right].$$

- $s = -\frac{\partial f}{\partial T}$

$$= k_B \ln\left[1 + \exp\left(-\frac{\epsilon}{k_B T}\right)\right] + \frac{\epsilon}{T} \frac{\exp(-\epsilon/k_B T)}{[1 + \exp(-\epsilon/k_B T)]^2}.$$

- $c = T\frac{\partial s}{\partial T} = k_B \left(\frac{\epsilon}{k_B T}\right)^2 \frac{\exp(-\epsilon/k_B T)}{\left[1 + \exp\left(-\frac{\epsilon}{k_B T}\right)\right]^2}.$

- Using $f = u - Ts$

$$\Rightarrow u = \frac{\epsilon \exp(-\epsilon/k_B T)}{1 + \exp(-\epsilon/k_B T)}.$$