Examples :

① Consider N classical spins S_i which take two values $S_i = \pm 1$. If the Hamiltonian is $H = h \sum_{i=1}^{N} S_i$, what is the probability of the configuration where all $S_i = +1$ at temperature β^{-1} ?

Ans: Energy of the configuration where all $S_i = +1$:

$$E = Nh$$

Partition f^n $Z = \sum_c e^{-\beta h \sum_{i=1}^{N} S_i}$

$$= \sum_{S_1, S_2 \cdots S_N} e^{-\beta h \sum_i S_i} = \sum_{S_1} e^{-\beta h S_1} \sum_{S_2} e^{-\beta h S_2} \cdots \sum_{S_N} e^{-\beta h S_N}$$

$$= \left[e^{-\beta h} + e^{\beta h} \right]^N$$

$\Rightarrow$ Probability for all $s_i = +1$

$$= \frac{e^{-\beta N h}}{\left[e^{-\beta h} + e^{\beta h} \right]^N}.$$

As expected, the probability $\to +1$ as $\beta \to \infty$ (i.e. $T \to 0$) if $h > 0$, and probability $\to 0$ as $\beta \to \infty$ if $h < 0$.

② In this same model, what is the probability of finding zero energy at a temperature β^{-1}?

Ans: Zero energy states correspond to $N_\uparrow = N_\downarrow = \frac{N}{2}$.

$$\Rightarrow \text{Probability} = \frac{e^{-\beta \times 0}}{Z(\beta)} \times \#\text{ of states with } E=0$$

$$= \frac{{}^N C_{N/2}}{Z(\beta)} \simeq \frac{2^N}{\left[e^{\beta h} + e^{-\beta h}\right]^N}$$

As one may note, this probability $\to 1$ as $\beta \to 0$. This is because at $\beta = 0$ (infinite temperature) almost all states have zero energy.

③ Consider a single particle in a box with volume V. The probability of finding the particle at momentum $\vec{p} = \left[\frac{\beta}{2\pi m}\right]^{3/2} e^{-\frac{\beta p^2}{2m}}$, exactly as we found in microcanonical ensemble.

Quantum Mechanical Canonical Ensemble

Probability P_n for n'th eigenstate $|E_n\rangle$

$$= \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{e^{-\beta E_n}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

Correspondingly, expectation value of any operator $\hat{O}$ at temperature β^{-1}

$$= \sum_n \langle E_n | \hat{O} E_n \rangle P_n$$

$$= \frac{\sum_n e^{-\beta E_n} \langle E_n | \hat{O} | E_n \rangle}{\sum_n e^{-\beta E_n}}$$

$$= \mathrm{Tr}\left[e^{-\beta \hat{H}} \hat{O} \right] / \mathrm{Tr}\left[e^{-\beta \hat{H}} \right]$$

Correspondingly, the quantum mechanical partition f^n is:

$$\boxed{Z = \sum_n e^{-\beta E_n} = \mathrm{Trace}\left(e^{-\beta H} \right)}$$

There are two ways to arrive at above equations

- By maximizing entropy subject to the constraint that energy is fixed.

$$S^* = \underbrace{-\sum_n P(E_n) \log P(E_n)}_{S = \text{Shannon entropy}}$$
$$- \lambda_1 \left[\left(\sum_n P(E_n) E_n \right) - E \right]$$
$$- \lambda_2 \sum_n \left[P(E_n) - 1 \right]$$

where $\lambda_{1,2}$ are lagrange multipliers.

We need to extremize over $P(E_n), \lambda_1, \lambda_2$.

$$\Rightarrow \delta S = - \sum_n \delta P(E_n) - \sum_n \left[\log P(E_n) \right] \delta P(E_n)$$
$$- \lambda_1 \sum_n \delta P(E_n) E_n - \lambda_2 \sum_n \delta P(E_n)$$
$$- \delta\lambda_1 \left[\sum_n P(E_n) E_n - E \right] - \delta\lambda_2 \sum_n \left[P(E_n) - 1 \right]$$
$$= 0$$

Collecting terms proportional to $\delta P(E_n)$ and setting them to zero $\Rightarrow$

$$-1 - \log P(E_n) - \lambda_1 E_n - \lambda_2 = 0$$

$$\Rightarrow \quad P(E_n) \propto e^{-\lambda_1 E_n}$$

Normalizing, $P(E_n) = \dfrac{e^{-\lambda_1 E_n}}{\sum_n e^{-\lambda_1 E_n}}$

One might guess that $\lambda_1 = \beta$. To see this, note that for a small variation in energy δE, $\delta S^* = 0$

$$\Rightarrow \quad \delta S = \lambda_1 \, \delta E$$

$$\Rightarrow \quad \lambda_1 = \beta \quad \text{since} \quad \beta = \frac{\delta S}{\delta E}$$

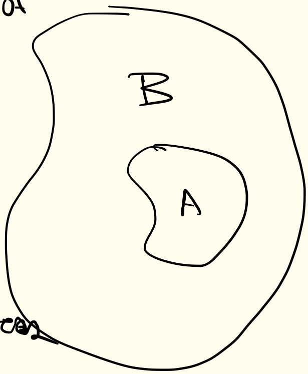
This argument works also for classical systems.

– Quantum Canonical Ensemble from ergodicity (Heuristic).

Similar to the argument for classical derivation using ergodicity, one expects that an eigenstate for the full system takes the form

eigenstate of H_A eigenstate of H_B

$$|E\rangle = \sum C_{ij}\, |E^i\rangle_A \otimes |E^j\rangle_B \; \delta(E^i + E^j - E)$$



where C_{ij} are random Gaussian variables. This gaurantees that all states with total energy E contribute equally. From this, the reduced

Partition Function and Free Energy

Lets calculate $Z = \sum_c e^{-\beta E(c)}$ within saddle point approximation.

$$Z = \sum_c e^{-\beta E(c)}$$

$$= \sum_E \underbrace{e^{S(E)}}_{\#\text{ of config. with energy } E} e^{-\beta E} = \int dE\, e^{S(E) - \beta E}$$

Since both $S(E)$ and E are extensive, one can perform the above integral within saddle point.

$$Z \simeq e^{S(E^*) - \beta E^*}$$

where $\left.\frac{\partial S}{\partial E}\right|_{E^*} = \beta \Rightarrow Z$ get's contribution primarily from states that correspond to the temperature β, as expected. E^* is indeed the expectation value of the Hamiltonian at temperature β:

$$\langle H \rangle_\beta = \frac{\sum_c E(c)\, e^{-\beta E(c)}}{\sum_c e^{-\beta E(c)}}$$

$$= \frac{\int dE\, E\, e^{S(E) - \beta E}}{\int dE\, e^{S(E) - \beta E}}$$

$$= \frac{E^*\, e^{S(E^*) - \beta E^*}}{e^{S(E^*) - \beta E^*}} = E^*$$

We will henceforth denote $\langle H \rangle_\beta$ by just E, and drop the asterisk. This is the thermodynamic energy E at temperature β^{-1}.

$$\Rightarrow \quad Z(\beta) = e^{-\beta[E - TS]}$$

$$= e^{-\beta F}$$

where we have <u>defined</u> a new variable F, called <u>Helmholtz free energy</u>, as

$$\boxed{F = E - TS}$$

The differential dF satisfies

$$\begin{aligned} dF &= dE - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -SdT - PdV. \end{aligned}$$

Above, we used $dE = TdS - PdV$ assuming the particle number is fixed i.e. $dN = 0$.

More generally, one can also change energy of the system not just by heat (TdS) or work $(-PdV)$, but also by adding particles to the system. Defining the chemical potential μ as the energy added per particle at fixed volume and entropy,

$$dE = TdS - PdV + \mu dN$$

$$\Rightarrow \boxed{dF = -SdT - PdV + \mu dN}.$$

Systems in equilibrium have same temperature ($\sim$ thermal equilibrium), pressure ($\sim$ mechanical equilibrium) and chemical potential ($\sim$ chemical equilibrium).

Implication of Extensivity of Energy

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

Differentiating w.r.t. λ and using chain rule,

$$\frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda}$$

$$+ \frac{\partial E(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = E(S, V, N)$$

$$\Rightarrow \quad \frac{1}{\lambda}\left[\left.\frac{\partial E}{\partial S}\right|_{V,N} S + \left.\frac{\partial E}{\partial V}\right|_{S,N} V + \left.\frac{\partial E}{\partial N}\right|_{S,V} N\right] = E(S, V, N)$$

Setting $\lambda = 1$

$$\Rightarrow \quad \boxed{E(S, V, N) = TS - PV + \mu N}$$

$$\Rightarrow \quad \boxed{\begin{aligned} F(T, V, N) &= E - TS \\ &= -PV + \mu N. \end{aligned}}$$

Energy Fluctuations in Canonical Ensemble

Probability $P(E_0)$ of finding energy E_0

$$\propto e^{-\beta E_0} e^{S(E_0)}$$

$$= e^{-g(E_0)}$$

where $g(E_0) = -\beta[E_0 - T S(E_0)]$ is sharply peaked at $E_0 = \langle H \rangle \overset{\text{def}}{=} E$ as discussed above.

By Taylor expanding, one can quantify how sharply peaked the energy is.

$$g(E_0) = g(E) + \cancel{\frac{\partial g}{\partial E_0}\Big|_{E_0=E}}^{\,0} (E_0 - E) + \frac{1}{2}\frac{\partial^2 g}{\partial E_0^2}\Big|_E (E-E_0)^2$$

$$\Rightarrow \quad P(E_0) \propto e^{\frac{1}{2}\frac{\partial^2 S}{\partial E_0^2}\big|_{E_0=E}(E-E_0)^2}$$

$$\frac{\partial^2 S}{\partial E_0^2} = \frac{\partial}{\partial E_0}\left(\frac{\partial S}{\partial E_0}\right) = \frac{\partial}{\partial E_0}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{\partial T}{\partial E_0}$$

$$= -\frac{1}{T^2}\frac{1}{C_V}$$

where C_V is the specific heat at constant volume.

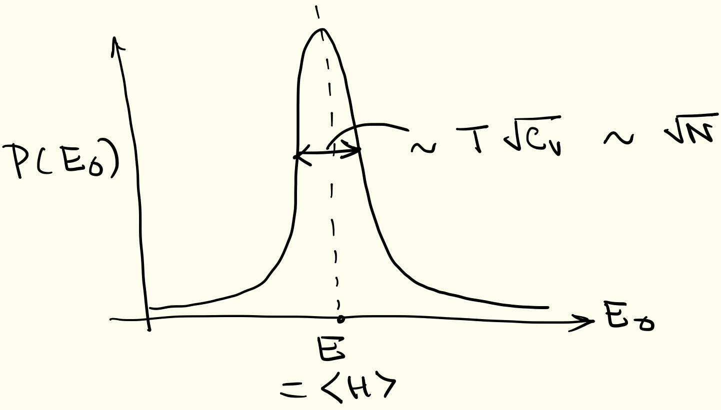
$$\Rightarrow \quad P(E_0) \propto e^{-(E-E_0)^2/2(\delta E)^2}$$

where $(\delta E)^2 = T^2 C_v$ is the variance corresponding to energy fluctuations.

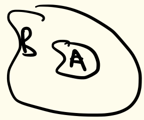
Since $C_v = \dfrac{\partial E}{\partial T}$ is extensive $\sim N$.

$$\Rightarrow \quad |\delta E| \sim \sqrt{N}$$

$$\Rightarrow \quad \frac{|\delta E|}{E} \sim \frac{1}{\sqrt{N}}$$ $\Rightarrow$ relative fluctuations are small, and distributed in a Gaussian manner as shown above.



What if the subsystem is not small compared to the total system?



$V_A = O(V_B)$

See pset-2.

A slightly different view:

$$\langle \hat{H} \rangle = E = -\frac{\partial Z}{Z\,\partial \beta}$$

$$C_v = \frac{\partial E}{\partial T} = -\beta^2 \frac{\partial E}{\partial \beta} = +\beta^2 \frac{\partial^2 Z}{Z\,\partial \beta^2} - \frac{\beta^2}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

$$= \beta^2 \left[\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2 \right]$$

$$= \beta^2 (\delta E)^2$$

$$\Rightarrow \quad (\delta E)^2 = C_v T^2$$