Appendix[+]: Functional form of $\mathcal{P}(E_i)$ around peak value

Recall:

$\mathcal{P}(E_i)$ = Prob. of finding the system in an energy level of energy E_i

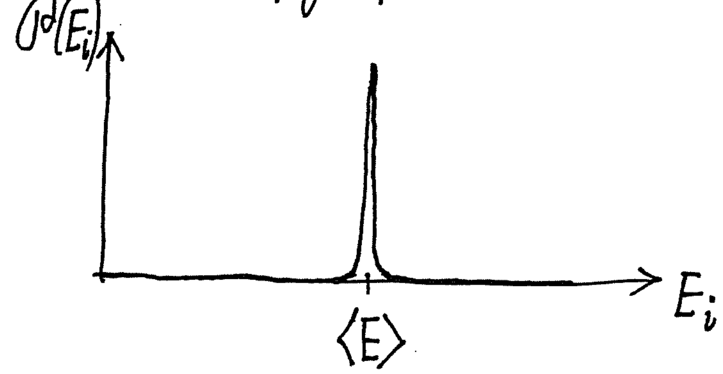
$$= W_S(E_i) \cdot \frac{W_B(E_0 - E_i)}{W}$$

[from postulate that microstates are equally probable]

In terms of temperature T:

$$\mathcal{P}(E_i) = W_S(E_i)\, \frac{e^{-E_i/kT}}{Z}$$

We know that $\mathcal{P}(E_i)$ is sharply peaked at the mean energy



Question: What is the form of $\mathcal{P}(E_i)$ around its peak?

[+] Optional

$$\mathcal{P}(E_i) = W_S(E_i)\, \frac{e^{-E_i/kT}}{Z}$$

Formally, one can locate where $\mathcal{P}(E)$ peaks by $\dfrac{d\mathcal{P}(E)}{dE} = 0$.

We may as well work on $\ln \mathcal{P}(E)$.

$$\ln \mathcal{P}(E) = \ln W_S(E) - \frac{E}{kT} - \ln Z$$

$$\frac{\partial \ln \mathcal{P}(E)}{\partial E} = \frac{\partial \ln W_S(E)}{\partial E} - \frac{1}{kT}$$

Let $\mathcal{P}(E)$ peak at $E = \bar{E}$. $\bar{E}$ is determined by

$$\left.\frac{\partial \ln W_S(E)}{\partial E}\right|_{E=\bar{E}} = \frac{1}{kT}$$

OR

$$\boxed{\left.\frac{1}{k}\frac{\partial S(E)}{\partial E}\right|_{E=\bar{E}} = \frac{1}{kT} \quad \text{an equation to solve for } \bar{E}}$$

Note:
- "Same" equation $\dfrac{\partial S}{\partial E} = \dfrac{1}{T}$ as in microcanonical ensemble
- But now T is given, the equation $\left.\dfrac{\partial S(E)}{\partial E}\right|_{E=\bar{E}} = \dfrac{1}{T}$ determines $\bar{E}$.

- $\bar{E}$ is where $\mathcal{P}(E)$ peaks
- To find the form around $\bar{E}$, expand $\mathcal{P}(E)$ around $\bar{E}$.

<u>Work on $\ln \mathcal{P}(E)$:</u>

$$\ln \mathcal{P}(E) = \ln W_s(E) - \frac{E}{kT} - \ln Z$$

Expand around $E = \bar{E}$:

$$\ln \mathcal{P}(E) = \ln W_s(\bar{E}) - \frac{\bar{E}}{kT} - \ln Z$$

$$+ \cancel{\left(\frac{\partial \ln W_s(E)}{\partial E} - \frac{1}{kT}\right)\bigg|_{E=\bar{E}}} \cdot (E-\bar{E}) \quad \to 0 \text{ (by eqn. for } \bar{E})$$

$$+ \frac{1}{2}\frac{\partial^2 \ln W_s(E)}{\partial E^2}\bigg|_{E=\bar{E}} \cdot (E-\bar{E})^2 + \underbrace{\cdots}_{\text{ignore! } (E \approx \bar{E})}$$

$$= \left[\ln W_s(\bar{E}) - \frac{\bar{E}}{kT} - \ln Z\right] + \frac{1}{2k}\frac{\partial^2 S}{\partial E^2}\bigg|_{E=\bar{E}} \cdot (E-\bar{E})^2$$

<u>Aside:</u> $$\frac{\partial^2 \ln W_s(E)}{\partial E^2} = \frac{1}{k}\frac{\partial^2 S}{\partial E^2}$$

$\because S(E,V,N) = k \ln W_s(E)$

Recall: $\dfrac{\partial S}{\partial E} = \dfrac{1}{T}$ in microcanonical ensemble and thus $T = T(E,V,N)$

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

(C_V: heat capacity)

$$\therefore \frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 C_V}$$

$$\therefore \ln \mathcal{P}(E) = \left[\ln W_s(\bar{E}) - \frac{\bar{E}}{kT} - \ln Z\right] - \frac{1}{2kT^2 C_V} \cdot (E-\bar{E})^2$$

$$\Rightarrow \mathcal{P}(E) = \underbrace{\frac{W_s(\bar{E})\, e^{-\bar{E}/kT}}{Z}}_{\substack{\text{peak value of } \mathcal{P}(E) \text{ at } \bar{E} \\ \text{(just a constant)}}} \cdot \underbrace{e^{-\frac{(E-\bar{E})^2}{2kT^2 C_V}}}_{} \quad \text{for } E \text{ close to } \bar{E}$$

- a gaussian distribution!
- Variance $\sigma_E^2 = kT^2 C_V$ (C_V extensive $\sim N$)
- $\bar{E} = \langle E \rangle$ (extensive $\sim N$)
- $\dfrac{\sigma_E}{\bar{E}} \sim \dfrac{1}{\sqrt{N}} \Rightarrow$ extremely sharp for macroscopic systems

- For a macroscopic system, it is (almost) always that the system is observed to have $E=\bar{E}$.

Thus, as a by-product,

$$\underset{\substack{\uparrow \\ \text{always}}}{\mathcal{P}(\bar{E}) = 1} = \underbrace{W_s(\bar{E})}_{e^{S(E)/k}} \frac{e^{-\bar{E}/kT}}{Z}$$

$$= \frac{1}{Z} e^{-\frac{(\bar{E}-TS(E))}{kT}}$$

$$\Rightarrow \quad Z = e^{-\frac{(\bar{E}-TS(E))}{kT}} = e^{-F/kT}$$

$$\therefore \quad F = -kT \ln Z$$

a result already known.

This is, yet, another way to connect Z (microscopic quantity) to F (macroscopic quantity)