Boltzmann Distribution

The well-known Botlzmann distribution is a direct consequence of the P.E.A.P.P.. It can be straight-forwardly deriveed by considering a small system in thermal contact with a reservoir of constant temperature. We will motivate this physically.

Canonical Ensemble

We are often interested in the thermal properties of a small system in equilibirum with a large system, say the heat capacity of a pebble on a large table surrounded by a roomful of air. To be more specific, consider a ginormous isolated system in thermal equilibrium. Suppose we are only interested a very small subsystem. P.E.A.P.P. cannot be applied to the subsystem directly, but can be applied to the entire system. Call the number of accessible states of the subsystem Γ_s, and that of the reset of the system Γ_R, where R stands for reservoir. The total number of accessible states of the combined isolated system is simply a product $\Gamma = \Gamma_s\Gamma_R$ by counting. If we *only allow energy exchange* between the subsystem and the reservoir, then the set of states the subsystem can access is known as the **canonical ensemble**. The number of accessible states is controlled by the energy of the subsystem E, but it is no longer constant as in the microcanonical ensemble. Assuming the total energy of the combined isolated system is E_o, then

$$\Gamma(E) = \Gamma_s(E)\Gamma_R(E_o - E) \approx \Gamma_R(E_o - E) = \sum_{n=0}^{\infty} \frac{(-E)^n}{n!} \left(\left.\frac{\partial^n \Gamma}{\partial E^n}\right|_{E=E_o} \right). \tag{1}$$

The approximation in (1) is that the reservoir is so large that any multiplicative factor looks like 1, i.e. only order-of-magnitude changes matter. The last equality is given by Taylor expansion, where we assume Γ is analytic at E_0. One may say that $\Gamma_s(E) = 1$ if the subsystem has no internal degrees of freedom. However, this is not quite true, because the actually vaue of $\Gamma_s(E)$ depends on the level of coarse-graining of energy $E \sim E \pm \delta E$. By P.E.A.P.P., the ratio of probabilities of subsystem having energies E_1, E_2 is

$$\frac{P(E_1)}{P(E_2)} = \frac{\Gamma(E_1)}{\Gamma(E_2)} \approx \frac{\Gamma_R(E_o - E_1)}{\Gamma_R(E_o - E_2)} = \frac{\sum\limits_{n=0}^{\infty} \frac{(-E_1)^n}{n!} \left(\left.\frac{\partial^n \Gamma}{\partial E^n}\right|_{E=E_o} \right)}{\sum\limits_{n=0}^{\infty} \frac{(-E_2)^n}{n!} \left(\left.\frac{\partial^n \Gamma}{\partial E^n}\right|_{E=E_o} \right)}. \tag{2}$$

Now we use the reservoir property again to evaluate the derivative $\frac{\partial^n \Gamma}{\partial E^n}$. Recall $S(E) \equiv k_B \ln \Gamma(E)$ and $\frac{\partial S}{\partial E} = \frac{1}{T}$. If we assume the reservoir is so large that its temperature T is constant, then

$$\frac{\partial S}{\partial E} = \frac{1}{T} \Rightarrow k_B \frac{1}{\Gamma}\frac{\partial \Gamma}{\partial E} = \frac{1}{T} \Rightarrow \frac{\partial \Gamma}{\partial E} = \frac{\Gamma}{k_B T} \Rightarrow \frac{\partial^n \Gamma}{\partial E^n} = \frac{\Gamma}{(k_B T)^n}. \tag{3}$$

Therefore (2) reduces to

$$\frac{P(E_1)}{P(E_2)} = \frac{\sum\limits_{n=0}^{\infty} \frac{1}{n!}(-\frac{E_1}{k_B T})^n}{\sum\limits_{n=0}^{\infty} \frac{1}{n!}(-\frac{E_2}{k_B T})^n} = \frac{e^{-E_1/k_B T}}{e^{-E_2/k_B T}}. \tag{4}$$

By normalization of probability distribution

$$\boxed{P(E) = \frac{e^{-E/k_BT}}{\sum\limits_i e^{-E_i/k_BT}}}, \tag{5}$$

where i enumerate all accessible quantum states of the subsystem.

Most textbooks presents (2) in terms of entropy as

$$\frac{P(E_1)}{P(E_2)} = \frac{e^{S_R(E_o-E_1)/k_B}}{e^{S_R(E_o-E_2)/k_B}} = \frac{e^{S_R(E_o)/k_B-E_1/k_BT}}{e^{S_R(E_o)/k_B-E_2/k_BT}} = \frac{e^{-E_1/k_BT}}{e^{-E_2/k_BT}}. \tag{6}$$

While this is a cleaner derivation, it can mislead one to think the expression is not exact because the middle step looks like a Taylor expansion of $S(E)$ to first order in E. This expression is actually exact because $\frac{\partial S}{\partial E} = \frac{1}{T}$ which is constant for the reservoir, so $\frac{\partial^n S}{\partial E^n} = 0$, $\forall n > 1$.

Grand Canonical Ensemble

Suppose we allow both energy and particle transfer between the subsystem and the reservoir. Then the set of states the subsystem can access is known as the **grand canonical ensemble**

$$\begin{aligned}
\frac{P(E_1)}{P(E_2)} &= \exp\frac{1}{k_B}\left\{S_R(E_o - E_1, N_o - N_1) - S(E_o - E_2, N_o - N_2)\right\} \\
&= \exp\left\{-\frac{E_1}{k_B}\frac{\partial S}{\partial E} - \frac{N_1}{k_B}\frac{\partial S}{\partial N} + \frac{E_2}{k_B}\frac{\partial S}{\partial E} + \frac{N_2}{k_B}\frac{\partial S}{\partial N}\right\} \\
&= \exp\left\{-\frac{E_1}{k_B}\cdot\frac{1}{T} - \frac{N_1}{k_B}\cdot\frac{-\mu}{T} + \frac{E_2}{k_B}\cdot\frac{1}{T} + \frac{N_2}{k_B}\cdot\frac{-\mu}{T}\right\} \\
&= \exp\left\{-\frac{E_1 - \mu N_1}{k_BT}\right\} / \exp\left\{-\frac{E_2 - \mu N_2}{k_BT}\right\}. \qquad (7)
\end{aligned}$$

Again, by normalization of probability distribution

$$\boxed{P(E,N) = \frac{e^{-(E-\mu N)/k_BT}}{\sum\limits_i e^{-(E_i-\mu N_i)/k_BT}}}. \tag{8}$$

We understand (8) is exact because both $\frac{\partial S}{\partial E} = \frac{1}{T}$ and $\frac{\partial S}{\partial N} = -\frac{\mu}{T}$ are constant.