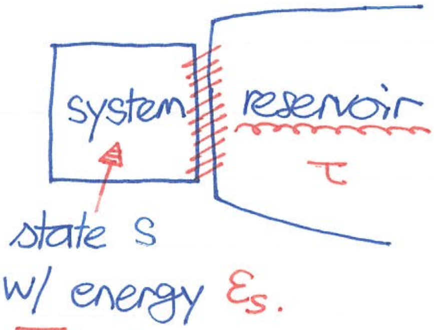
HH0059 Boltzmann Factor

For a statistical system in thermal equilibrium with a very large system (referred as reservoir), the probability to find the system in quantum state s is

$$\boxed{P_s \propto e^{-\varepsilon_s/\tau}}$$

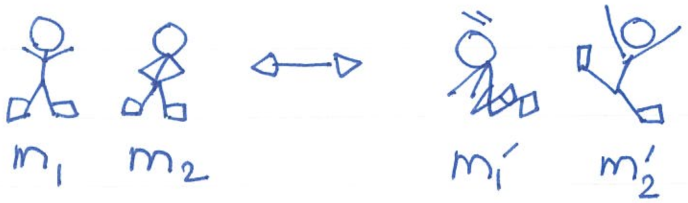
where ε_s is the energy of the state.



We will explain and derive the Boltzmann factor in the notes. Let us first turn to an interesting social phenomena exhibting Boltzmann distribution first.

⟨I⟩ Boltzmnan distribution in liberal economy

Assuming the total money is conserved (just an approximation),



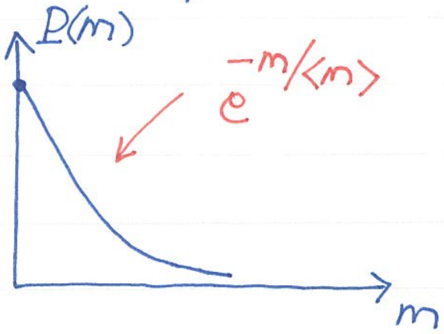
$$m_1 + m_2 = m_1' + m_2'$$

After many social competitions equilibrium is reached.

Following Einstein's idea of detail balance, all reversible processes are equally probable.

$$\boxed{P(m_1)P(m_2) = P(m_1')P(m_2')}$$

It's straightforward to find the probability distribution in equilibrium $\rightarrow$ $P(m) \propto e^{-m/\langle m \rangle}$



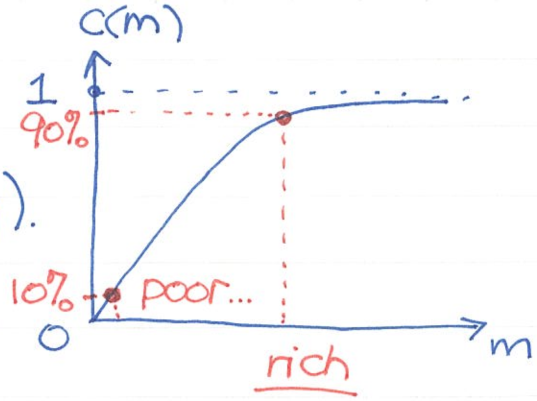
Normalization of $P(m)$ fixes the constant:

$$\boxed{P(m) = \frac{1}{\tau} e^{-m/\tau}}$$

where $\tau = \langle m \rangle$ is the average income.

To estimate the rich/poor disparity, it's convenient to introduce the accumulated distribution $C(m)$.

$$C(m) \equiv \int_0^m P(m')\,dm' = 1 - e^{-m/\tau}$$



$$C(m_{poor}) = 10\% \rightarrow m_{poor} = \tau \log(10/9).$$

$$C(m_{rich}) = 90\% \rightarrow m_{rich} = \tau \log(10).$$

$$\text{Disparity ratio} \equiv \frac{m_{rich}}{m_{poor}} = \frac{\cancel{\tau}\log(10)}{\cancel{\tau}\log(10/9)} \approx 21.85$$ the price for liberal economy.

Note. In Taiwan, the disparity ratio is 28.36 (before tax) and 24.95 (after tax), according to data collected in 2009.

⟨2⟩ Derivation of Boltzmann factor.

Consider a system $\mathcal{S}$ in thermal equilibrium with a reservoir $\mathcal{R}$.

$$\boxed{g = \sum_E g_s(E) \cdot g_R(U_0 - E)}$$ where U_0 is the total energy.

According to the fundamental assumption, each state of the WHOLE system $(\mathcal{S}+\mathcal{R})$ appears with equal prob. $1/g$. We're interested in the system $\mathcal{S}$ but not the reservoir $\mathcal{R}$ and ask for the probability to find the system in state 1 (with energy ε_1).

$$P(\varepsilon_1) = \frac{1}{g} \cdot g_R(U_0 - \varepsilon_1)$$ Similarly, for state 2, $P(\varepsilon_2) = \dfrac{g_R(U_0-\varepsilon_2)}{g}$

It's not easy to compute g directly but the ratio is

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{g_R(U_0-\varepsilon_1)}{g_R(U_0-\varepsilon_2)} = e^{\sigma_R(U_0-\varepsilon_1) - \sigma_R(U_0-\varepsilon_2)}}$$ $\varepsilon_1, \varepsilon_2 \ll U_0$!

Expand the entropy in Taylor series,

temperature of reservoir.

$$\sigma_R(U_0 - \varepsilon) = \sigma_R(U_0) - \left(\frac{\partial \sigma_R}{\partial U}\right)_{N,V} \cdot \varepsilon + \cdots \cong \sigma_R(U_0) - \frac{1}{\tau}\cdot\varepsilon$$

$$\rightarrow \frac{P(\varepsilon_1)}{P(\varepsilon_2)} = e^{-\frac{1}{\tau}(\varepsilon_1 - \varepsilon_2)} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}$$ i.e. $\boxed{P(\varepsilon_s) \propto e^{-\varepsilon_s/\tau}}$

Boltzmann factor ☺

Note. If one asks a different question: "What's the probability to find the system with energy ε?", the answer is different,

$$P(\varepsilon) \propto \sum_{s'} e^{-\varepsilon_{s'}/\tau} = g(\varepsilon)\, e^{-\varepsilon/\tau}, \quad s' \text{ are states w/ } \varepsilon_{s'} = \varepsilon.$$

The Boltzmann factor $e^{-\varepsilon_s/\tau}$ is somewhat surprising because it means the probability to sit in a lower energy state is always exponentially large. Wouldn't this mean that the system tends to stay in the ground state? This is indeed true! However, $g(\varepsilon)$ usually grows fast and the most probable energy of the system is determined by $g(\varepsilon)\, e^{-\varepsilon/\tau}$, not the Boltzmann factor alone ☺

③ Alternative derivation of Boltzmann factor

Starting from the definition of Shannon entropy σ_I,

$$\boxed{\sigma_I \equiv \sum_s -P_s \log P_s} \quad \text{with the constraint } \sum_s P_s = 1$$

Maximize σ_I with the constraint by Lagarange multiplier.

$$\sigma^* = \sigma_I + \lambda\left(\sum_s P_s - 1\right), \quad \frac{\partial \sigma^*}{\partial P_s} = 0 \longrightarrow -\log P_s - 1 + \lambda = 0$$

It is easy to see that $P_s = e^{\lambda - 1} = \text{const}$ — all states appear with equal probability ⟵ just the fundamental assumption!

Now consider another situation with two constraints.

$$\sum_s P_s = 1, \quad \sum_s P_s \varepsilon_s = U$$

Now we need two Lagarange multipliers to do the job.

$$\sigma^* = \sigma_I + \lambda_1\left(\sum_s P_s - 1\right) + \lambda_2\left(\sum_s P_s \varepsilon_s - U\right)$$

$$\frac{\partial \sigma^*}{\partial P_s} = 0 \longrightarrow -\log P_s - 1 + \lambda_1 + \lambda_2 \varepsilon_s = 0$$

The solution is $P_s = e^{\lambda_1 - 1} e^{\lambda_2 \varepsilon_s}$ some rewriting $e^{\lambda_1 - 1} \to \frac{1}{Z}$, $\lambda_2 \to -1/\tau$

The probability distribution is $\boxed{P_s = \frac{1}{Z} e^{-\varepsilon_s/\tau}}$ ← temperature

partition function

The above result indicates the Boltzmann factor can be viewed as the consequence of entropy maximization with the energy constraint.

Because all probabilities add up to unity, $\sum_s P_s = 1$, one finds

$$Z = \sum_s e^{-\varepsilon_s/\tau}$$ ← partition function, will learn more about it later.

In fancy jargons, one can say that temperature τ and partition function Z are Lagarange multipliers for energy and probability constraints when maximizing entropy σ.

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