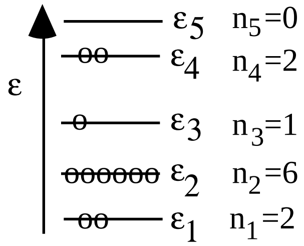
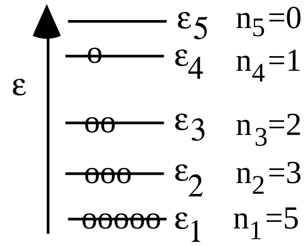
Boltzman Distribution and the Most Probable Distribution



$$N = \sum_i n_i$$

$$\varepsilon = \sum_i n_i E_i$$

sum over all states, i



$$U\text{-}U(0) = \frac{\sum n_i E_i}{\sum n_i}$$

for most probable distribution

$$W = \frac{N!}{n_1!\, n_2!\, n_3! \ldots}$$

$$\ln W = \ln N! - \sum \ln n_i!$$

$$d(\ln W) = \sum \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i$$

Constraints: $dN = dn_1 + dn_2 + dn_3 + \ldots = \sum dn_i = 0$

$d\varepsilon = E_1\, dn_1 + E_2\, dn_2 + \quad = 0$

$$0 = \sum \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i + \alpha \sum dn_i - \beta \sum E_i\, dn_i$$

α and β undetermined multipliers

$$0 = \sum \left(\left(\frac{\partial \ln W}{\partial n_i}\right) + \alpha - \beta E_i \right) dn_i$$

now n_i's are independent!

$$\left(\frac{\partial \ln W}{\partial n_i}\right) + \alpha - \beta E_i = 0$$

Sterling's Formula: $\ln x! = x \ln x - x$

$$\ln W = N \ln N - N - \sum (n_j \ln n_j - n_j)$$

$\sum n_i = N$ *so* $\ln W = N \ln N - \sum n_j \ln n_j$

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = -\left(n_i \frac{\partial \ln n_i}{\partial n_i} + \ln n_i \right)$$

$$= -\left(n_i \frac{1}{n_i} + \ln n_i \right)$$

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = -\left(\ln n_i + 1\right) \cong -\ln n_i$$

$$-\ln n_i + \alpha - \beta E_i = 0$$

$$\ln n_i = \alpha - \beta E_i$$

$$n_i = e^{\alpha - \beta E_i} = e^{\alpha} e^{-\beta E_i}$$

$$N = \sum_i n_i = \sum_i e^{\alpha} e^{-\beta E_i} = e^{\alpha} \sum_i e^{-\beta E_i}$$

$$e^{\alpha} = \frac{N}{\sum_i e^{-\beta E_i}}$$

$$Q = \sum_i e^{-\beta E_i}$$ Q = partition function = number of accessible states

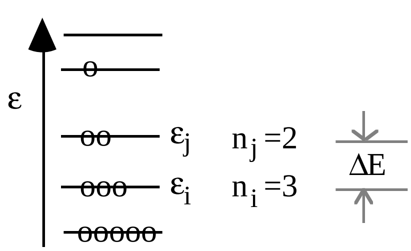
---

$$n_i = \frac{N}{Q} e^{-E_i/kT}$$ n_i = number of systems in energy state E_i

---

$$\frac{n_i}{N} = \frac{e^{-E_i/kT}}{Q}$$ probability of finding a system in energy state E_i

---



$$\frac{n_j}{n_i} = \frac{e^{-E_j/kT}}{e^{-E_i/kT}} = e^{-(E_j - E_i)/kT}$$

$$\frac{n_j}{n_i} = e^{-\Delta E/kT}$$