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Now apply equilibrium condition.

$$dF = du - Tds \quad \text{at const. } T$$
$$= d\langle E \rangle - Tds$$

Note $\sum_{j=1}^{t} P_j = 1$, so $\sum_{j=1}^{t} dP_j = 0$

$$dF = du - Tds = d\langle E \rangle - Tds + \alpha \sum_{j=1}^{t} dP_j = 0$$

$$\Rightarrow dF = \sum_{j=1}^{t} \left(E_j + KT(1 + \ln P_j^*) + \alpha \right] dP_j^* = 0$$

P_j^* : prob. of "j" state at eq.

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$$\ln p_j^* = -\frac{E_j}{kT} - \frac{\alpha}{kT} - 1$$

$$p_j^* = e^{-E_j/kT} \cdot e^{[-\alpha/kT - 1]}$$

$$\sum_{j=1}^{t} e^{-E_j/kT} e^{[-\frac{\alpha}{kT} - 1]} = \sum_{j=1}^{t} p_j^* = 1$$

more general: $p_j^* = \dfrac{e^{-E_j/kT}}{\sum_{j=1}^{t} e^{-E_j/kT}} = \dfrac{e^{-E_j/kT}}{Q}$

— Boltzmann distribution for energy.

$$\beta = \frac{1}{kT}$$

as $E_j \downarrow$, $p_j \uparrow$

understanding Q.

2 limiting regimes

- $T \to 0$. low T. or $E_j \to \infty$ ①
- $T \to \infty$. high T or $E_j \to 0$ ②

regime ①: $\dfrac{E_j}{kT} \xrightarrow{j=1} \infty \Rightarrow e^{-E_j/kT} = 0$

Boltzmann factor

$$Q = 1 + \sum_{j=2}^{t} e^{-E_j/kT} \quad (E_1 = 0) \ ?$$

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$P_j = \frac{e^{-E_j/kT}}{Q}$ — $j=1$ ground state $P_j = 1$; $j \neq 1$ excited state $P_j = 0$

regime ②. $T \to \infty$ or $E_j \to 0$.

$$\frac{E_j}{kT} \to 0, \quad e^{-E_j/kT} \to 1.$$

$$Q = 1 + 1 + 1 \cdots = t.$$

for all P_j, $P_j = \frac{1}{t}$.

all energy levels are equally populated.

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