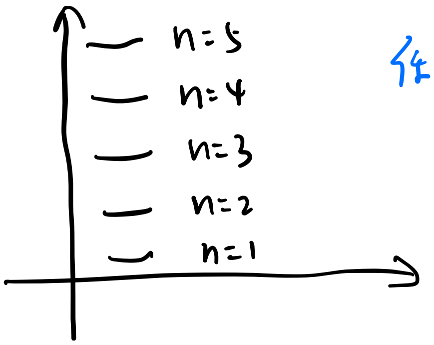
玻尔兹曼分布：



孤立体系中（与外界无物质、能量交换）

任一粒子在能级上的分布 $\{n_i\}$ 权重为

$$W = \frac{N!}{\prod_i n_i!}$$

由摘取最大项原理，以最可几分布权重代替体系总微观状态数：$\ln\Omega \simeq \ln W$

平衡态要求孤立系统的熵值最大 $(S = k\ln\Omega \simeq k\ln W)$

此时问题转化为：

在粒子数、总能量不变的情况下，求 $k\ln\frac{N!}{\prod_i n_i!}$ 最大值

$\Rightarrow$ 典型拉格朗日求约束极值问题

$$\begin{cases} \sum_i n_i = N & \longrightarrow \text{粒子数约束} \\ \sum_i \varepsilon_i n_i = E & \longrightarrow \text{能量约束} \end{cases}$$

} 孤立体系

构造 $\mathcal{L}(\{n_i\}, \alpha, \beta) = \ln\frac{N!}{\prod_i n_i!} - \alpha\left(\sum_i n_i - N\right) - \beta\left(\sum_i n_i\varepsilon_i - E\right)$

$$\frac{\partial\mathcal{L}}{\partial\alpha} = \sum_i n_i - N = 0, \quad \frac{\partial\mathcal{L}}{\partial\beta} = \sum_i \varepsilon_i n_i - E = 0$$

$$\frac{\partial\mathcal{L}}{\partial n_i} = \frac{\partial\, \ln N! + \alpha N + \beta E}{\partial n_i} + \frac{\partial\, -\sum_i \ln n_i! - \alpha\sum n_i - \beta\sum n_i\varepsilon_i}{\partial n_i}$$

$$= \frac{\partial}{\partial n_i}\left(-\ln n_i! - \alpha n_i - \beta n_i\varepsilon_i\right)$$

n_i也许在高能级不够大？影响应该不大

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

$$= \left(-\ln n_i - 1 + 1 - \alpha - \beta\varepsilon_i\right) = 0$$

$$\therefore \quad \ln n_i + \alpha + \beta\varepsilon_i = 0, \quad n_i = \frac{1}{e^{+\alpha} e^{+\beta\varepsilon_i}}$$

$\therefore$ 解得 $\{n_i\}$ 分布为 $n_i^* = \dfrac{1}{e^{\alpha} e^{\beta\varepsilon_i}}$.

由 $\sum_i n_i^* = e^{-\alpha} \sum_i e^{-\beta\varepsilon_i} = N.$ $\quad -[\ln N - \ln \sum_i e^{-\beta\varepsilon_i}$

$$\therefore \quad e^{-\alpha} = N \Big/ \sum_i e^{-\beta\varepsilon_i}, \quad \alpha = -\ln \frac{N}{\sum_i e^{-\beta\varepsilon_i}}$$

$$\therefore \quad n_i^* = e^{-\alpha} \cdot e^{-\beta\varepsilon_i} = \frac{N e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$$

到此已经出现 Boltzmann 分布的雏形. 下证 $\beta = \dfrac{1}{kT}$

$$S = k\ln W^* = k(N\ln N - \sum_i n_i \ln n_i)$$

代入 $\ln n_i^* = -\alpha - \beta\varepsilon_i$, 则.

$$S = k[N\ln N - \sum_i n_i^*(-\alpha - \beta\varepsilon_i)]$$

$$= k[N\ln N + \alpha\sum_i n_i^* + \beta\sum n_i^* \varepsilon_i]$$

$$= k[N\ln N + \alpha N + \beta E) \qquad \xrightarrow{\alpha = -\ln N + \ln\sum_i e^{-\beta\varepsilon_i}}$$

$$= k[N\ln N - N\ln N + N\ln\sum_i e^{-\beta\varepsilon_i} + \beta E]$$

$$= k[N\ln(\sum_i e^{-\beta\varepsilon_i}) + \beta E]$$

$$= S(N, E, \beta) \overset{\star}{=} S(N, E, V).$$

这里推导出 S 是 N, E, β 的函数，而经典里 S 是 N, E, V 的函数，故此处可令 $\beta = \beta(E, V)$

$$dS = \left(\frac{\partial S}{\partial N}\right)_{E,\beta} dN + \left(\frac{\partial S}{\partial E}\right)_{N,\beta} dE + \left(\frac{\partial S}{\partial \beta}\right)_{N,E} d\beta$$

$$= \left(\frac{\partial S}{\partial N}\right)_{E,V} dN + \left(\frac{\partial S}{\partial E}\right)_{N,\beta} dE + \left(\frac{\partial S}{\partial \beta}\right)_{N,E} \left(\frac{\partial \beta}{\partial E}\right)_{V,N} dE$$

$$+ \left(\frac{\partial S}{\partial \beta}\right)_{N,E} \left(\frac{\partial \beta}{\partial V}\right)_{E,N} dV$$

$$dS = \left(\frac{\partial S}{\partial N}\right)_{E,V} dN + \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV.$$

$$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial S}{\partial E}\right)_{N,\beta} + \left(\frac{\partial S}{\partial \beta}\right)_{N,E} \left(\frac{\partial \beta}{\partial E}\right)_{N,V}$$

其中 $$\left(\frac{\partial S}{\partial \beta}\right)_{N,E} = k \frac{\partial (N \ln \sum_i e^{-\beta \varepsilon_i} + \beta E)}{\partial \beta}$$

$$= k\left(\frac{N \sum_i -\varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}} + E\right)$$

即 $$\left(\frac{\partial S}{\partial \beta}\right)_{N,E} = k\left(E - N \frac{\sum_i \varepsilon_i e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}\right)$$

代入 $e^{-\alpha} = N / \sum_i e^{-\beta \varepsilon_i}$

$$\left(\frac{\partial S}{\partial \beta}\right)_{N,E} = k\left(E - \sum_i \varepsilon_i e^{-\alpha - \beta \varepsilon_i}\right)$$

$$= k\left(E - \sum_i \varepsilon_i n_i^*\right) \overset{\star}{=} 0$$

$$\therefore \quad \left(\frac{\partial S}{\partial E}\right)_{V,N} = \left(\frac{\partial S}{\partial E}\right)_{\beta,N}$$

$$\Downarrow \quad \frac{1}{T}$$

$$\therefore \quad \left(\frac{\partial S}{\partial E}\right)_{\beta,N} = \frac{1}{T} = k\beta.$$

$$\therefore \quad \beta = \frac{1}{kT}.$$

到此、证得 Boltzmann 分布:

$$n_i^* = \frac{N e^{-\varepsilon_i/kT}}{\sum_i e^{-\varepsilon_i/kT}}$$ (不含简并度)