最可几分布

N_0个原子分配到 $\varepsilon_1^{N_1}$ 和 $\varepsilon_2^{N_2}$ 两个能级上

$$W(N_1, N_2) = \frac{N_0!}{N_1!\,(N_0-N_1)!}$$

$$H = \varepsilon_1 N_1 + \varepsilon_2 (N_0 - N_1)$$

$$S = k_B \ln \frac{N_0!}{N_1!\,(N_0-N_1)!} \approx k_B \left[N_0 \ln N_0 - N_1 \ln N_1 - (N_0-N_1)\ln(N_0-N_1) \right]$$

$$G = H - TS$$

$$0 = \frac{\partial G}{\partial N_1} = [\varepsilon_1 + k_B T \ln N_1] - [\varepsilon_2 + k_B T \ln(N_0 - N_1)]$$

$$\frac{N_2}{N_1} = \frac{N_0 - N_1}{N_1} = \frac{\exp\left(-\frac{\varepsilon_2}{k_B T}\right)}{\exp\left(-\frac{\varepsilon_1}{k_B T}\right)}$$

$$\frac{N_1}{N_0} = \frac{\exp\left(-\frac{\varepsilon_1}{k_B T}\right)}{\exp\left(-\frac{\varepsilon_1}{k_B T}\right) + \exp\left(-\frac{\varepsilon_2}{k_B T}\right)}$$

孤立体系/微正则系综

Multiplier 乘子

$$\sum_{i=0} \delta n_i \ln n_i = 0 \qquad 1$$

$$\delta U = \sum_i \varepsilon_i \delta n_i = 0 \qquad \beta$$

$$\delta N = \sum_i \delta n_i = 0 \qquad \alpha$$

$$\sum_i (\ln n_i + \alpha + \beta \varepsilon_i)\delta n_i = 0$$

$$\Rightarrow \ln n_i + \alpha + \beta\varepsilon_i = 0$$

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

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

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

定义配分函数 $Z \equiv \sum_i^r e^{-\beta\varepsilon_i}$

$$n_i = \frac{N}{Z} e^{-\beta\varepsilon_i}$$

$$U = \sum_i^r \varepsilon_i n_i = \Sigma \frac{N}{Z} \varepsilon_i e^{-\beta\varepsilon_i}$$

$$\Sigma \varepsilon_i e^{-\beta\varepsilon_i} = \frac{UZ}{N}$$

$$S = k \ln \Omega = k(N \ln N - \Sigma \varepsilon_i \ln n_i)$$

$$n_i \ln n_i = \frac{N}{Z} e^{-\beta\varepsilon_i}\left(\ln \frac{N}{Z} - \beta\varepsilon_i\right)$$

$$S = k\left[N \ln N - \frac{N}{Z}\left(\delta \ln \frac{N}{Z} e^{-\beta\varepsilon_i} - \delta \beta \varepsilon_i e^{-\beta\varepsilon_i}\right)\right]$$

$$= k\left[N \ln N - \ln \frac{N}{Z} \Sigma n_i + \beta U\right]$$

$$= k[N \ln Z + \beta U]$$

$$= kN \ln Z + k\beta U$$

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{kN}{Z} \underbrace{\left[\frac{\partial Z}{\partial U}\right]_V}_{0} + k\beta + kU \underbrace{\left(\frac{\partial \beta}{\partial U}\right)_V}_{0}$$

$$= k\beta$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

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

$$n_i = \frac{N}{Z} \cdot e^{-\frac{\varepsilon_i}{kT}}$$

$Z_i = \sum_i e^{-\frac{\varepsilon_i}{kT}}$ r个能级 N个粒子数

$$\left(\frac{\partial Z}{\partial T}\right)_V = \sum_i \exp\left(-\frac{\varepsilon_i}{kT}\right) \frac{\varepsilon_i}{kT^2}$$

$$= \frac{1}{kT^2} \sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i}{kT}\right)$$

$$U = \sum_i n_i \varepsilon_i = \sum_i \frac{N}{Z} e^{-\frac{\varepsilon_i}{kT}} \varepsilon_i$$

$$= \frac{N}{Z} kT^2 \left(\frac{\partial Z}{\partial T}\right)_V$$

$$S = kN \ln Z + \frac{U}{T} = kN \ln Z + NkT \left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}$$

$$F \equiv U - TS = -kNT \ln Z$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = kNT \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$$

$$H = U + pV = U + VkNT \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$$

$$G = H - TS = kNTV \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} - kNT \ln Z$$

$$= kNT \left[V \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} - \ln Z\right]$$

理想气体(单原子)

$$Z = Z_t \cdot Z_r \cdot Z_v \cdot Z_e \cdot Z_n$$

平动 转动 振动 电子运动 核运动

$$Z_t \cdot Z_e \cdot Z_n$$

$$Z_t = \frac{(2\pi m k T)^{\frac{3}{2}}}{h^3} \cdot V$$

$P =$ 思考

U

$$\left(\frac{\partial U}{\partial T}\right)_V$$