Boltzman假设占据某一状态数是无限的

泡利不相容 不是不限

费米-狄拉克分布

费米子

E_i的状态数为g_i

N_i 占据E_i能级粒子的数目 N_i个粒子分配到g_i个位置

E_i能级 $C_{g_i}^{N_i} = \frac{g_i!}{N_i!(g_i-N_i)!}$

所有 $\Omega = \prod_i C_{g_i}^{N_i}$

$S = k\sum_i[g_i\ln g_i - N_i\ln N_i - (g_i-N_i)\ln(g_i-N_i)]$

待定系数

$$\begin{cases}\sum_i[-\ln N_i + \ln(g_i-N_i)]\delta N_i = 0 & 1\\ \sum E_i\delta N_i = 0 & -\beta\\ \sum \delta N_i = 0 & -\alpha\end{cases}$$

$$\ln\frac{g_i-N_i}{N_i} = \alpha+\beta E_i$$

$$N_i = \frac{g_i}{1+\exp(\alpha+\beta E_i)}$$

$$dS = k\sum_i \ln\left(\frac{g_i-N_i}{N_i}\right)dN_i$$

$$\frac{g_i-N_i}{N_i} = \frac{g_i}{N_i}-1 = \exp(\alpha+\beta E_i)$$

$$dS = k\sum_i(\alpha+\beta E_i)dN_i$$

$$= k\alpha\sum_i dN_i + k\beta\sum_i E_i dN_i$$

$$= k\alpha dN + k\beta dU$$

$F = U - TS$

$dS = -\frac{dF}{T} + \frac{dU}{T}$

$k\beta = \frac{1}{T} \Rightarrow \beta = \frac{1}{kT}$

$k\alpha dN = -\frac{dF}{T}$

$\alpha = -\frac{1}{kT}\frac{dF}{dN} = -\frac{\mu}{kT}$

化学势

F-D分布 $N_i = \frac{g_i}{1+\exp\left(\frac{E_i-\mu}{kT}\right)}$

玻尔兹曼分布

$$N_i = \frac{g_i\exp\left(-\frac{E_i}{kT}\right)}{Z}$$

$$Z = \sum_i g_i\exp\left(-\frac{E_i}{kT}\right)$$

微观则系综下 V,T 相行 $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$

$F = -NkT\ln Z$

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

$Z = \exp\left(-\frac{\mu}{kT}\right)$

Boltzman分布 $N_i = \frac{g_i\exp\left(-\frac{E_i}{kT}\right)}{\exp\left(-\frac{\mu}{kT}\right)} = \frac{g_i}{\exp\left(\frac{E_i-\mu}{kT}\right)}$

玻色-爱因斯坦分布

E_i能级, g_i个, N_i

E_i能级上 $C_{N_i+g_i-1}^{g_i-1} = C_{N_i+g_i-1}^{N_i}$

插入g_i-1个隔板

0 | 000 || 0 共N_i+g_i-1个

g_i N_i-1隔板

$C_5^3 = C_5^2$

近似 $C_{N_i+g_i-1}^{N_i} = \frac{(N_i+g_i-1)!}{N_i!(g_i-1)!}$

$$N_i+g_i-1 \approx N_i+g_i$$

B-E分布 $N_i = \frac{g_i}{\exp\left(\frac{E_i-\mu}{kT}\right)-1}$

对B-E $\Omega_{BE} = \prod\frac{(g_i+n_i-1)!}{n_i!(g_i-1)!}$

对F-D $\Omega_{FD} = \prod\frac{g_i!}{n_i!(g_i-n_i)!}$

对M-B $\Omega_{MB} = N!\prod\frac{g_i^{N_i}}{N_i!}$

Boltzman

当 $n_i \ll g_i$时 $\Omega_{B-E} \approx \Omega_{F-D} \approx \frac{\Omega_{M-B}}{N!}$

热空位浓度

N_{va} 空位 N个原子

$W = \frac{(N+N_{va})!}{N!\,N_{va}!}$

$\Delta S = -Nk\ln\frac{N}{N+N_{va}} - N_{va}k\ln\frac{N_{va}}{N+N_{va}}$

空位形成能→吉布斯自由能 g

$\frac{\partial\Delta G}{\partial N_{va}} = 0$

$\gamma_{va}^{eq} = \exp\left(-\frac{g}{kT}\right)$

$T\to T_m$, $\gamma_{va}\sim 10^{-3}\sim10^{-4}$

$\frac{g}{kT}\cong 8$

能级简并

$\varepsilon_1 \quad \varepsilon_2 \quad \cdots \quad \varepsilon_n$

$N_1 \quad N_2 \quad \cdots \quad N_n$

g_i

$C_N^{N_1}\cdot C_{N-N_1}^{N_2}\,C_{N-N_1-N_2}^{N_3}\cdots = \frac{N!}{\prod_i N_i!}$

再简并 $(C_N^{N_1}\,g_1^{N_1})$ $\quad$ $(\quad)\cdot\prod g_i^{N_i}$

$g_i^{N_i}$

$$\Downarrow$$

$$(C_N^{N_1}\,g_1^{N_1})\cdot(C_{N-N_1}^{N_2}\,g_2^{N_2})\cdots(C_{N-\cdots-N_{i-1}}^{N_i}\,g_i^{N_i})$$