# 基础统计热力学笔记

## Du Jiajie

#### 基础统计热力学笔记

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#### 定位系统和非定位系统

按照统计单位是否可区分:定位系统(定域子系统)和非定位系统(离域子系统)。定位系统粒子可以彼此分辨而非定位系统的粒子不能彼此分辨。

定位系统的微观状态数多于非定位系统、因为非定位系统的粒子不能彼此分辨。

### 近独立粒子系统和非近独立粒子系统

按照统计单位之间有无相互作用:近独立粒子系统和非近独立粒子系统。 近独立粒子系统的粒子之间的相互作用微弱可以忽略不计,非近独立粒子系统的粒子 之间的相互作用能不能忽略,总能量包含粒子的位能(为各粒子坐标 $q_i$ 之函数),即

$$U=\sum_i N_i E_i + U_1(q_1,q_2,\cdots,q_N)$$

# 统计热力学基本假定

- 系统的热力学概率 $\Omega$ 是系统在一定宏观状态下的微态数。根据 $S=k\ln\Omega$ ,可由 $\Omega$  得到熵S。
- 熵函数S = S(U, V, N),因而 $\Omega = \Omega(U, V, N)$ ,期中U为总能量,V为体积,N为分子数。
- 对于(U,V,N)确定的系统,任何可能出现的微观状态具有相同的数学概率,即系统的总微态数为 $\Omega$ ,每一种微观状态出现的概率为 $P=1/\Omega$ 。
- 宏观上看来很短的时间在微观看来是足够长的,因而宏观测得的物理量是很多微观量的平均值,且每一种微观状态提供的微观量在平均值中的贡献相同。
   对于一个力学量,其微观量为B<sub>i</sub>,那么有

$$B = \langle B \rangle = \sum_{i} B_{i} P_{i}$$

$$\sigma_B^2 = \sum_i (B_i - < B >)^2 P_i$$

# Boltzmann统计

#### 定位系统的最概然分布

#### 按照量子态分布

N个**可区分**分子,分子间作用忽略不计,对于(U,V,N)固定系统,分子的能级量子化,为 $\varepsilon_1,\varepsilon_2,\dots,\varepsilon_n$ ,在各能级分布分子数为 $N_1,N_2,\dots,N_n$ ,分布满足

$$N = \sum_i N_i \ U = \sum_i N_i arepsilon_i$$

对于 $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_n$ 各能级分布分子数为 $N_1, N_2, \dots, N_n$ 的分布,相当于N个球分堆为每堆数目分别为 $N_1, N_2, \dots, N_n$ 的堆,由排列组合可知方法数t为

$$egin{aligned} t &= inom{N_1}{N} inom{N_2}{N-N_1} \cdots inom{N_n}{N-\sum\limits_{i=1}^{n-1} N_n} \ &= rac{N!}{(N-N_1)!N_1!} \cdot rac{(N-N_1)!}{(N-N_1-N_2)!N_2!} \cdots rac{(N-\sum\limits_{i=0}^{n-1} N_i)!}{0!N_n!} \ &= rac{N!}{\prod\limits_{i} N_i!} \end{aligned}$$

对于各种分布方法, 求和得到总的微观状态数

$$arOmega = \sum_{\substack{\sum_i N_i = N \ \sum_i N_i arepsilon_i }} t_i = \sum_{\substack{\sum_i N_i = N \ \sum_i N_i arepsilon_i = U}} rac{N!}{\prod\limits_i N_i!}$$

在求和式中,将最大项记作 $t_m$ ,于是有

$$t_m \leq arOmega \leq nt_m \ \ln t_m \leq \ln arOmega \leq \ln t_m + \ln n$$

又 $n \ll t_m$ , 于是 $\ln n \ll \ln t_m$ , 从而(<mark>撷取最大项法</mark>)

$$\ln \Omega \approx \ln t_m$$

任意一项 $t=N!/\sum_i N_i!$ 取对数有

$$\ln t = \ln N! - \sum_i \ln N_i!$$

考虑到 $\ln N \approx N \ln N - N$  (Stirling公式), 于是有

$$\ln t pprox (N \ln N - N) - \sum_i (N_i \ln N_i - N_i)$$

只需要求上式的极值即可。上式存在约束条件

$$N_1+N_2+\cdots N_n=N$$
  $N_1arepsilon_1+N_2arepsilon_2+\cdots N_narepsilon_n=U$ 

构造Lagrange函数

$$L = \ln t + lpha (N_1 + N_2 + \cdots N_n - N) \ + eta (N_1 arepsilon_1 + N_2 arepsilon_2 + \cdots N_n arepsilon_n - U)$$

利用Lagrange乘数法,有

$$egin{aligned} rac{\partial L}{\partial N_1} &= rac{\partial \ln t}{\partial N_1} + lpha + eta arepsilon_1 = 0 \ rac{\partial L}{\partial N_2} &= rac{\partial \ln t}{\partial N_2} + lpha + eta arepsilon_2 = 0 \ & \dots \ rac{\partial L}{\partial N_n} &= rac{\partial \ln t}{\partial N_n} + lpha + eta arepsilon_n = 0 \end{aligned}$$

于是有

$$egin{aligned} rac{\partial \ln t}{\partial N_i} &= - \ln N_i = -lpha - eta arepsilon_i \ & \ln N_i = lpha + eta arepsilon_i \ & N_i = e^{lpha + eta arepsilon_i} \end{aligned}$$

记 $t_m$ 对应的分布为 $N_1^*, N_2^*, \cdots, N_n^*$ , 考虑约束条件

$$egin{aligned} N &= \sum_i N_i^* = \sum_i e^{lpha + eta arepsilon_i} = e^lpha \sum_i e^{eta arepsilon_i} \ lpha &= \ln rac{N}{\sum_i e^{eta arepsilon_i}} = \ln N - \ln \sum_i e^{eta arepsilon_i} \end{aligned}$$

于是

$$N_i^* = e^{lpha} \cdot e^{eta arepsilon_i} = rac{N}{\sum_i e^{eta arepsilon_i}} e^{eta arepsilon_i}$$

考虑 $S = k \ln \Omega$ ,于是

$$egin{aligned} S &= k \ln \Omega pprox k \ln t_m = k \left[ N \ln N - N - \sum_i N_i^* \ln N_i^* + \sum_i N_i^* 
ight] \ &= k \left[ N \ln N - \sum_i N_i^* \ln N_i^* 
ight] \end{aligned}$$

又

$$\ln N_i^* = \alpha + \beta \varepsilon_i$$

进一步化简为

$$egin{aligned} S &= k \left[ N \ln N - \sum_i N_i^* (lpha + eta arepsilon_i) 
ight] \ &= k \left[ N \ln N - lpha \sum_i N_i^* - eta \sum_i N_i^* arepsilon_i 
ight] \ &= k (N \ln N - lpha N - eta U) \end{aligned}$$

因为 $\alpha = \ln N - \ln \sum_{i} e^{\beta \varepsilon_{i}}$ ,于是

$$egin{aligned} S &= k \left[ N \ln N - N \left( \ln N - \ln \sum_i e^{eta arepsilon_i} 
ight) - eta U 
ight] \ &= k N \ln \sum_i e^{eta arepsilon_i} - k eta U \end{aligned}$$

$$\mathrm{d}S = \left(rac{\partial S}{\partial U}
ight)_{eta,N} \mathrm{d}U + \left(rac{\partial S}{\partial eta}
ight)_{U,N} \mathrm{d}eta \ \mathrm{d}eta = \left(rac{\partial eta}{\partial U}
ight)_{V,N} \mathrm{d}U + \left(rac{\partial eta}{\partial V}
ight)_{U,N} \mathrm{d}V$$

于是S关于U得偏导数为

$$\begin{split} \mathrm{d}S &= \left[ \left( \frac{\partial S}{\partial U} \right)_{\beta,N} + \left( \frac{\partial S}{\partial \beta} \right)_{U,N} \left( \frac{\partial \beta}{\partial U} \right)_{V,N} \right] \mathrm{d}U \\ &+ \left( \frac{\partial S}{\partial \beta} \right)_{U,N} \left( \frac{\partial \beta}{\partial V} \right)_{U,N} \mathrm{d}V \\ &\left( \frac{\partial S}{\partial U} \right)_{V,N} = \left( \frac{\partial S}{\partial U} \right)_{\beta,N} + \left( \frac{\partial S}{\partial \beta} \right)_{U,N} \left( \frac{\partial \beta}{\partial U} \right)_{V,N} \end{split}$$

其中

$$\left(rac{\partial S}{\partial U}
ight)_{eta,N} = -keta \quad \left(rac{\partial S}{\partial eta}
ight)_{U,N} = k\left[Nrac{\partial}{\partial eta}\left(\ln\sum_i e^{etaarepsilon_i}
ight) - U
ight]$$

注意此处

$$egin{aligned} Nrac{\partial}{\partialeta}igg(\ln\sum_{i}e^{etaarepsilon_{i}}igg)-U&=Nrac{\sum_{i}arepsilon_{i}e^{etaarepsilon_{i}}}{\sum_{i}e^{etaarepsilon_{i}}}-U\ &=Nrac{e^{lpha}\sum_{i}arepsilon_{i}e^{etaarepsilon_{i}}}{e^{lpha}\sum_{i}e^{etaarepsilon_{i}}}-U&=Nrac{\sum_{i}arepsilon_{i}N_{i}^{st}}{\sum_{i}N_{i}^{st}}-U&=0 \end{aligned}$$

于是偏导数为

$$\left(rac{\partial S}{\partial U}
ight)_{V,N} = \left(rac{\partial S}{\partial U}
ight)_{eta,N} = -keta$$

又因为dU = TdS - pdV, 于是

$$\left(rac{\partial S}{\partial U}
ight)_{V,N} = rac{1}{T}$$
  $eta = -rac{1}{kT}$ 

于是Boltzmann最概然分布为

$$N_i^* = N rac{e^{eta arepsilon_i}}{\sum e^{eta arepsilon_i}} = N rac{e^{-arepsilon_i/kT}}{\sum e^{-arepsilon_i/kT}}$$

于是熵和Helmholtz自由能为

$$S=kN\ln\sum_{i}e^{etaarepsilon_{i}}-keta U=kN\ln\sum_{i}e^{-arepsilon_{i}/kT}+rac{U}{T}, 
onumber \ A=U-TS=-NkT\ln\sum_{i}e^{arepsilon_{i}/kT}$$

#### 按照能级分布

如果存在简并能级,即一个能级对应多个量子态,记简并度为g。

对于N个**可区分**分子的系统,在简并度分别为为 $g_1, g_2, \dots, g_n$ 的能级 $\varepsilon_1, \varepsilon_2, \dots, \varepsilon_n$ 分布有分子数 $N_1, N_2, \dots, N_n$ ,此时方法数为

$$egin{aligned} t &= g_1^{N_1}inom{N_1}{N}g_2^{N_2}inom{N_2}{N-N_1}\cdots g_n^{N_n}inom{N_n}{N-\sum\limits_{i=1}^{n-1}N_n} \ &= rac{g_1^{N_1}N!}{(N-N_1)!N_1!}\cdotrac{g_2^{N_2}(N-N_1)!}{(N-N_1-N_2)!N_2!}\cdotsrac{g_n^{N_n}(N-\sum\limits_{i=0}^{n-1}N_i)!}{0!N_n!} \ &= N!\prod\limits_irac{g_i^{N_i}}{N_i!} \end{aligned}$$

总的微观状态数为

$$\Omega = \sum_{\substack{\sum_i N_i = N \ \sum_i N_i arepsilon_i}} t_i = \sum_{\substack{\sum_i N_i = N \ \sum_i N_i arepsilon_i = U}} \left( N! \prod_i rac{g_i^{N_i}}{N_i!} 
ight)$$

同样采用撷取最大项法,有

$$\ln arOmega pprox \ln t_m = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i!$$

利用Stirling公式近似,有

$$\ln t = N \ln N - N + \sum_i N_i \ln g_i - (\sum_i N_i \ln N_i - N_i)$$

考虑约束条件

$$N_1+N_2+\cdots N_n=N$$
  $N_1arepsilon_1+N_2arepsilon_2+\cdots N_narepsilon_n=U$ 

构造Lagrange函数

$$L = \ln t + lpha (N_1 + N_2 + \cdots N_n - N) \ + eta (N_1 arepsilon_1 + N_2 arepsilon_2 + \cdots N_n arepsilon_n - U)$$

利用Lagrange乘数法,有

$$egin{aligned} rac{\partial L}{\partial N_1} &= rac{\partial \ln t}{\partial N_1} + lpha + eta arepsilon_1 = 0 \ rac{\partial L}{\partial N_2} &= rac{\partial \ln t}{\partial N_2} + lpha + eta arepsilon_2 = 0 \ & \cdots \ rac{\partial L}{\partial N_n} &= rac{\partial \ln t}{\partial N_n} + lpha + eta arepsilon_n = 0 \end{aligned}$$

于是有

$$egin{aligned} rac{\partial \ln t}{\partial N_i} &= \ln g_i - \ln N_i = -lpha - eta arepsilon_i \ & \ln N_i = \ln g_i lpha + eta arepsilon_i \ & N_i = g_i e^{lpha + eta arepsilon_i} \end{aligned}$$

记 $t_m$ 对应的分布为 $N_1^*, N_2^*, \cdots, N_n^*$ ,考虑约束条件

$$egin{aligned} N &= \sum_i N_i^* = \sum_i e^{lpha + eta arepsilon_i} = e^lpha \sum_i g_i e^{eta arepsilon_i} \ lpha &= \ln rac{N}{\sum_i g_i e^{eta arepsilon_i}} = \ln N - \ln \sum_i g_i e^{eta arepsilon_i} \end{aligned}$$

于是

$$N_i^* = g_i e^{lpha} \cdot e^{eta arepsilon_i} = rac{N}{\sum_i g_i e^{eta arepsilon_i}} g_i e^{eta arepsilon_i}$$

考虑 $S = k \ln \Omega$ ,于是

$$egin{aligned} S &= k \ln \Omega pprox k \ln t_m = \ k \left[ N \ln N - N + \sum_i N_i^* \ln g_i - \sum_i N_i^* \ln N_i^* + \sum_i N_i^* 
ight] \ &= k \left[ N \ln N + \sum_i N_i^* \ln g_i - \sum_i N_i^* \ln N_i^* 
ight] \end{aligned}$$

又

$$\ln N_i^* = \ln g_i + \alpha + \beta \varepsilon_i$$

进一步化简为

$$egin{aligned} S &= k \left[ N \ln N + \sum_i N_i^* \ln g_i - \sum_i N_i^* (\ln g_i + lpha + eta arepsilon_i) 
ight] \ &= k \left[ N \ln N + \sum_i N_i^* \ln g_i - (lpha + \ln g_i) \sum_i N_i^* - eta \sum_i N_i^* arepsilon_i 
ight] \ &= k (N \ln N - lpha N - eta U) \end{aligned}$$

因为 $\alpha = \ln N - \ln \sum_i g_i e^{\beta \varepsilon_i}$ ,于是

$$egin{aligned} S &= k \left[ N \ln N - N \left( \ln N - \ln \sum_i g_i e^{eta arepsilon_i} 
ight) - N \ln g_i - eta U 
ight] \ &= k N \ln \sum_i g_i e^{eta arepsilon_i} - N \ln g_i - k eta U \end{aligned}$$

$$\mathrm{d}S = \left(rac{\partial S}{\partial U}
ight)_{eta,N} \mathrm{d}U + \left(rac{\partial S}{\partial eta}
ight)_{U,N} \mathrm{d}eta \ \mathrm{d}eta = \left(rac{\partial eta}{\partial U}
ight)_{V,N} \mathrm{d}U + \left(rac{\partial eta}{\partial V}
ight)_{U,N} \mathrm{d}V$$

于是S关于U得偏导数为

$$\mathrm{d}S = \left[ \left( \frac{\partial S}{\partial U} \right)_{\beta,N} + \left( \frac{\partial S}{\partial \beta} \right)_{U,N} \left( \frac{\partial \beta}{\partial U} \right)_{V,N} \right] \mathrm{d}U$$

$$+ \left( \frac{\partial S}{\partial \beta} \right)_{U,N} \left( \frac{\partial \beta}{\partial V} \right)_{U,N} \mathrm{d}V$$

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

其中

$$\left(rac{\partial S}{\partial U}
ight)_{eta,N} = -keta \quad \left(rac{\partial S}{\partial eta}
ight)_{U,N} = k\left[Nrac{\partial}{\partial eta}\left(\ln\sum_i g_i e^{etaarepsilon_i}
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注意此处

$$egin{aligned} Nrac{\partial}{\partialeta}igg(\ln\sum_{i}g_{i}e^{etaarepsilon_{i}}igg) - U &= Nrac{\sum_{i}arepsilon_{i}g_{i}e^{etaarepsilon_{i}}}{\sum_{i}g_{i}e^{etaarepsilon_{i}}} - U \ &= Nrac{e^{lpha}\sum_{i}arepsilon_{i}e^{etaarepsilon_{i}}}{e^{lpha}\sum_{i}g_{i}e^{etaarepsilon_{i}}} - U &= Nrac{\sum_{i}arepsilon_{i}N_{i}^{st}}{\sum_{i}N_{i}^{st}} - U &= 0 \end{aligned}$$

于是偏导数为

$$\left(rac{\partial S}{\partial U}
ight)_{V,N} = \left(rac{\partial S}{\partial U}
ight)_{eta,N} = -keta$$

又因为dU = TdS - pdV,于是

$$\left(rac{\partial S}{\partial U}
ight)_{V,N} = rac{1}{T}$$
  $eta = -rac{1}{kT}$ 

于是Boltzmann最概然分布为

$$N_i^* = N rac{g_i e^{eta arepsilon_i}}{\sum g_i e^{eta arepsilon_i}} = N rac{g_i e^{-arepsilon_i/kT}}{\sum g_i e^{-arepsilon_i/kT}}$$

于是熵和Helmholtz自由能为

$$S=kN\ln\sum_ig_ie^{etaarepsilon_i}-keta U=kN\ln\sum_ig_ie^{-arepsilon_i/kT}+rac{U}{T} \ A=U-TS=-NkT\ln\sum_ig_ie^{arepsilon_i/kT} \$$

按量子态分布和按能级分布推到过程类似,仅有简并度 $q_i$ 的差异。

#### 非定位系统的最概然分布

对于N个不可区分粒子,方法数变为

$$egin{aligned} t &= rac{1}{N!} g_1^{N_1} inom{N_1}{N} g_2^{N_2} inom{N_2}{N-N_1} \cdots g_n^{N_n} inom{N_n}{N-\sum\limits_{i=1}^{n-1} N_n} \ &= rac{1}{N!} rac{g_1^{N_1} N!}{(N-N_1)! N_1!} \cdot rac{g_2^{N_2} (N-N_1)!}{(N-N_1-N_2)! N_2!} \cdots rac{g_n^{N_n} (N-\sum\limits_{i=0}^{n-1} N_i)!}{0! N_n!} \ &= \prod\limits_i rac{g_i^{N_i}}{N_i!} \end{aligned}$$

总的微观状态数为

$$\Omega = \sum_{\substack{\sum_i N_i = N \ \sum_i N_i \in j}} t_i = \sum_{\substack{\sum_i N_i = N \ \sum_i N_i arepsilon_i = U}} \left(\prod_i rac{g_i^{N_i}}{N_i!}
ight)$$

用同样的处理方法可以得到

$$N_i^* = N rac{g_i e^{-arepsilon_i/kT}}{\sum_i g_i e^{-arepsilon_i/kT}} \ S = k \ln rac{(\sum_i g_i e^{-arepsilon_i/kT})^N}{N!} + rac{U}{T} \ A = U - TS = -kT \ln rac{(\sum_i g_i e^{-arepsilon_i/kT})^N}{N!}$$

### 配分函数

配分函数定义如下

$$q=\sum_i g_i e^{-arepsilon_i/kT}$$

于是最概然分布为

$$N_i^* = N rac{g_i e^{-arepsilon/kT}}{q}$$

#### 配分函数与热力学函数之关系

### 定位系统

1. Helmholtz自由能

$$A = -NkT \ln \sum_i g_i e^{arepsilon_i/kT} = -kT \ln q^N$$

2. 熵

$$S = -igg(rac{\partial A}{\partial T}igg)_{V.N} = -k \ln q^N - NkTigg(rac{\partial \ln q}{\partial T}igg)_{V.N}$$

3. 热力学能

$$U = A + TS = NkT^2igg(rac{\partial \ln q}{\partial T}igg)_{V,N}$$

4. Gibbs自由能

考虑
$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$
,于是

$$G = A + pV = A - Vigg(rac{\partial A}{\partial V}igg)_{T,N} = -kT \ln q^N + NkTVigg(rac{\partial \ln q}{\partial V}igg)_{T,N}$$

5. 焓

$$H = G + TS = NkTVigg(rac{\partial \ln q}{\partial V}igg)_{T,N} + NkT^2igg(rac{\partial \ln q}{\partial T}igg)_{V,N}$$

6. 定容热容

$$C_V = \left(rac{\partial U}{\partial T}
ight)_V$$

#### 非定位系统

1. Helmholtz自由能

$$A = -kT \ln rac{(\sum_i g_i e^{-arepsilon_i/kT})^N}{N!} = -kT \ln rac{q^N}{N!}$$

2. 熵

$$S = -igg(rac{\partial A}{\partial T}igg)_{V,N} = -k\lnrac{q^N}{N!} - NkTigg(rac{\partial \ln q}{\partial T}igg)_{V,N}$$

3. 热力学能

$$U = A + TS = NkT^2igg(rac{\partial \ln q}{\partial T}igg)_{V,N}$$

4. Gibbs自由能

考虑
$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$
,于是

$$G = A + pV = A - Vigg(rac{\partial A}{\partial V}igg)_{T,N} = -kT\lnrac{q^N}{N!} + NkTVigg(rac{\partial \ln q}{\partial V}igg)_{T,N}$$

5. 焓

$$H = G + TS = NkTVigg(rac{\partial \ln q}{\partial V}igg)_{T,N} + NkT^2igg(rac{\partial \ln q}{\partial T}igg)_{V,N}$$

#### 6. 定容热容

$$C_V = \left(rac{\partial U}{\partial T}
ight)_V$$

#### 配分函数的分离

分子的能量包括分子的平动能及分子内部运动能量(转动能、振动能、电子的能量、 核运动的能量)之核,即

$$\varepsilon_i = \varepsilon_{i,t} + \varepsilon_{i,r} + \varepsilon_{i,v} + \varepsilon_{i,e} + \varepsilon_{i,n}$$

总的简并度为各能级简并度的乘积

$$g_i = g_{i,t} \cdot g_{i,r} \cdot g_{i,v} \cdot g_{i,e} \cdot g_{i,n}$$

于是配分函数为

$$q = q_t \cdot q_r \cdot q_v \cdot q_e \cdot q_n$$

#### 原子核配分函数

$$egin{aligned} q_n &= g_{n,0} e^{-arepsilon_{n,0}/kT} + g_{n,1} e^{-arepsilon_{n,1}/kT} + \cdots \ &= g_{n,0} e^{-arepsilon_{n,0}/kT} \left[ 1 + rac{g_{n,1}}{g_{n,0}} e^{-(arepsilon_{n,1} - arepsilon_{n,0})/kT} + \cdots 
ight] \end{aligned}$$

通常原子核能级差较大,第二项及之后可以忽略,又原子核通常处于基态,将原子核基态能量( $\varepsilon_{n,0}$ )选为零,于是

$$q_n = g_{n,0}$$

对于核自旋量子数为 $s_i$ 的原子,其简并度为 $2s_i+1$ ,多原子分子核的配分函数为各原子配分函数的乘积,即

$$q_{n, ext{total}} = \prod_i (2s_i + 1)$$

#### 电子配分函数

$$egin{aligned} q_e &= g_{e,0} e^{-arepsilon_{e,0}/kT} + g_{e,1} e^{-arepsilon_{e,1}/kT} + \cdots \ &= g_{e,0} e^{-arepsilon_{e,0}/kT} \left[ 1 + rac{g_{e,1}}{g_{e,0}} e^{-(arepsilon_{e,1} - arepsilon_{e,0})/kT} + \cdots 
ight] \end{aligned}$$

通常电子处于基态,于是将电子基态能量( $\varepsilon_{e,0}$ )选为零,于是

$$q_e = g_{e,0}$$

#### 平动配分函数

$$arepsilon_{i,t} = rac{h^2}{8m}(rac{n_x^2}{a^2} + rac{n_y^2}{b^2} + rac{n_z^2}{c^2})$$

于是平动配分函数为

$$egin{aligned} q_t &= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left[ -rac{h^2}{8mkT} (rac{n_x^2}{a^2} + rac{n_y^2}{b^2} + rac{n_z^2}{c^2}) 
ight] \ &= \sum_{n_x=1}^{\infty} \exp \left[ -rac{n_x^2 h^2}{8mkTa^2} 
ight] \sum_{n_y=1}^{\infty} \exp \left[ -rac{n_y^2 h^2}{8mkTb^2} 
ight] \sum_{n_z=1}^{\infty} \exp \left[ -rac{n_z^2 h^2}{8mkTc^2} 
ight] \end{aligned}$$

令 $\alpha = h/\sqrt{8mkTa^2}$ ,由于 $\alpha$ 很小,于是

$$egin{aligned} \sum_{n_x=1}^\infty \exp\left[-rac{n_x^2h^2}{8mkTa^2}
ight] &= \sum_{n_x=1}^\infty \exp\left(-lpha^2n_x^2
ight) pprox \int_0^\infty e^{-lpha^2n_x^2}\,\mathrm{d}n_x = rac{\sqrt{\pi}}{2lpha} \ &= \sqrt{rac{2\pi mkT}{h^2}}a \end{aligned}$$

于是平动配分函数

$$q_t = \left(rac{2\pi mkT}{h^2}
ight)^{rac{3}{2}} abc = \left(rac{2\pi mkT}{h^2}
ight)^{rac{3}{2}} V$$

平动配分函数对各热力学函数的贡献(注意Stirling公式近似)

1. 
$$A_t = -kT\lnrac{q_t^N}{N!} = -NkT\ln\left[\left(rac{2\pi mkT}{h^2}
ight)^{rac{3}{2}}V
ight] + NkT\ln N - NkT$$

2. 
$$S_t = -\left(rac{\partial A_t}{\partial T}
ight)_{V,N} = Nk(\lnrac{q_t}{N} + rac{5}{2})$$

3. 
$$U_t = A_t + TS_t = rac{3}{2}NkT$$

$$C_{V,t} = \left(rac{\partial U_t}{\partial T}
ight)_V = rac{3}{2}Nk$$