基础统计热力学笔记

Du Jiajie

统计系统

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

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

统计热力学基本假定

- 系统的热力学概率Ω是系统在一定宏观状态下的微态数。根据$S=k\ln\Omega$，可由Ω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Ω，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_i，那么有

$$B=<B>=\sum_i B_iP_i$$

其涨落可以表示为

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

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$\varepsilon_1,\varepsilon_2,\cdots,\varepsilon_n$，在各能级分布分子数为$N_1,N_2,\cdots,N_n$，分布满足

$$N = \sum_i N_i$$
$$U = \sum_i N_i\varepsilon_i$$

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

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

对于各种分布方法，求和得到总的微观状态数

$$\Omega = \sum_{\substack{\sum_i N_i = N \\ \sum_i N_i\varepsilon_i = U}} t_i = \sum_{\substack{\sum_i N_i = N \\ \sum_i N_i\varepsilon_i = U}} \frac{N!}{\prod\limits_i N_i!}$$

在求和式中，将最大项记作t_m，于是有

$$t_m \leq \mathit{\Omega} \leq n t_m$$
$$\ln t_m \leq \ln \mathit{\Omega} \leq \ln t_m + \ln n$$

又$n \ll t_m$，于是$\ln n \ll \ln t_m$，从而（**撷取最大项法**）

$$\ln \mathit{\Omega} \approx \ln t_m$$

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

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

只需要求上式的极值即可。上式存在约束条件

$$N_1 + N_2 + \cdots N_n = N$$
$$N_1 \varepsilon_1 + N_2 \varepsilon_2 + \cdots N_n \varepsilon_n = U$$

构造Lagrange函数

$$\begin{aligned} L = \ln t + \alpha(N_1 + N_2 + \cdots N_n - N) \\ + \beta(N_1 \varepsilon_1 + N_2 \varepsilon_2 + \cdots N_n \varepsilon_n - U) \end{aligned}$$

利用Lagrange乘数法，有

$$\begin{aligned} \frac{\partial L}{\partial N_1} &= \frac{\partial \ln t}{\partial N_1} + \alpha + \beta \varepsilon_1 = 0 \\ \frac{\partial L}{\partial N_2} &= \frac{\partial \ln t}{\partial N_2} + \alpha + \beta \varepsilon_2 = 0 \\ &\cdots \\ \frac{\partial L}{\partial N_n} &= \frac{\partial \ln t}{\partial N_n} + \alpha + \beta \varepsilon_n = 0 \end{aligned}$$

于是有

$$\begin{aligned} \frac{\partial \ln t}{\partial N_i} = - \ln N_i &= -\alpha - \beta \varepsilon_i \\ \ln N_i &= \alpha + \beta \varepsilon_i \\ N_i &= e^{\alpha + \beta \varepsilon_i} \end{aligned}$$

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

$$N=\sum_i N_i^*=\sum_i e^{\alpha+\beta\varepsilon_i}=e^\alpha\sum_i e^{\beta\varepsilon_i}$$
$$\alpha=\ln\frac{N}{\sum_i e^{\beta\varepsilon_i}}=\ln N-\ln\sum_i e^{\beta\varepsilon_i}$$

于是

$$N_i^*=e^\alpha\cdot e^{\beta\varepsilon_i}=\frac{N}{\sum_i e^{\beta\varepsilon_i}}e^{\beta\varepsilon_i}$$

考虑$S=k\ln\mathit{\Omega}$，于是

$$\begin{aligned}S=k\ln\mathit{\Omega}\approx k\ln t_m&=k\left[N\ln N-N-\sum_i N_i^*\ln N_i^*+\sum_i N_i^*\right]\\&=k\left[N\ln N-\sum_i N_i^*\ln N_i^*\right]\end{aligned}$$

又

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

进一步化简为

$$\begin{aligned}S&=k\left[N\ln N-\sum_i N_i^*(\alpha+\beta\varepsilon_i)\right]\\&=k\left[N\ln N-\alpha\sum_i N_i^*-\beta\sum_i N_i^*\varepsilon_i\right]\\&=k(N\ln N-\alpha N-\beta U)\end{aligned}$$

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

$$\begin{aligned}S&=k\left[N\ln N-N\left(\ln N-\ln\sum_i e^{\beta\varepsilon_i}\right)-\beta U\right]\\&=kN\ln\sum_i e^{\beta\varepsilon_i}-k\beta U\end{aligned}$$

上式$S=S(U,\beta,N)$，又$S=S(U,V,N)$，因而$S=S(U,\beta,N)=S(U,\beta(U,V,N),N)$，于是当$N$一定时，微分得

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

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

$$\left(\frac{\partial S}{\partial U}\right)_{\beta,N}=-k\beta\quad\left(\frac{\partial S}{\partial \beta}\right)_{U,N}=k\left[N\frac{\partial}{\partial\beta}\left(\ln\sum_i e^{\beta\varepsilon_i}\right)-U\right]$$

注意此处

$$N\frac{\partial}{\partial\beta}\left(\ln\sum_i e^{\beta\varepsilon_i}\right)-U=N\frac{\sum_i\varepsilon_i e^{\beta\varepsilon_i}}{\sum_i e^{\beta\varepsilon_i}}-U$$
$$=N\frac{e^{\alpha}\sum_i\varepsilon_i e^{\beta\varepsilon_i}}{e^{\alpha}\sum_i e^{\beta\varepsilon_i}}-U=N\frac{\sum_i\varepsilon_i N_i^*}{\sum_i N_i^*}-U=0$$

于是偏导数为

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

又因为$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$，于是

$$\left(\frac{\partial S}{\partial U}\right)_{V,N}=\frac{1}{T}$$
$$\beta=-\frac{1}{kT}$$

于是Boltzmann最概然分布为

$$N_i^*=N\frac{e^{\beta\varepsilon_i}}{\sum e^{\beta\varepsilon_i}}=N\frac{e^{-\varepsilon_i/kT}}{\sum e^{-\varepsilon_i/kT}}$$

于是熵和Helmholtz自由能为

$$S=kN\ln\sum_i e^{\beta\varepsilon_i}-k\beta U=kN\ln\sum_i e^{-\varepsilon_i/kT}+\frac{U}{T}$$
$$A=U-TS=-NkT\ln\sum_i e^{\varepsilon_i/kT}$$

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$g_1, g_2, \cdots, g_n$的能级$\varepsilon_1, \varepsilon_2, \cdots, \varepsilon_n$分布有分子数$N_1, N_2, \cdots, N_n$，此时方法数为

$$
\begin{aligned}
t &= g_1^{N_1}\binom{N_1}{N} g_2^{N_2}\binom{N_2}{N-N_1}\cdots g_n^{N_n}\binom{N_n}{N-\sum\limits_{i=1}^{n-1}N_n} \\
&= \frac{g_1^{N_1}N!}{(N-N_1)!N_1!}\cdot\frac{g_2^{N_2}(N-N_1)!}{(N-N_1-N_2)!N_2!}\cdots\frac{g_n^{N_n}(N-\sum\limits_{i=0}^{n-1}N_i)!}{0!N_n!} \\
&= N!\prod_i \frac{g_i^{N_i}}{N_i!}
\end{aligned}
$$

总的微观状态数为

$$
\Omega = \sum_{\substack{\sum_i N_i = N \\ \sum_i N_i\varepsilon_i = U}} t_i = \sum_{\substack{\sum_i N_i = N \\ \sum_i N_i\varepsilon_i = U}} \left(N!\prod_i \frac{g_i^{N_i}}{N_i!}\right)
$$

同样采用撷取最大项法，有

$$
\ln \Omega \approx \ln t_m = \ln N! + \sum_i N_i \ln g_i - \sum_i \ln N_i!
$$

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

$$
\begin{gathered}
N_1 + N_2 + \cdots N_n = N \\
N_1\varepsilon_1 + N_2\varepsilon_2 + \cdots N_n\varepsilon_n = U
\end{gathered}
$$

构造Lagrange函数

$$
\begin{aligned}
L = \ln t &+ \alpha(N_1 + N_2 + \cdots N_n - N) \\
&+ \beta(N_1\varepsilon_1 + N_2\varepsilon_2 + \cdots N_n\varepsilon_n - U)
\end{aligned}
$$

利用Lagrange乘数法，有

$$
\begin{gathered}
\frac{\partial L}{\partial N_1}=\frac{\partial \ln t}{\partial N_1}+\alpha+\beta\varepsilon_1=0\\
\frac{\partial L}{\partial N_2}=\frac{\partial \ln t}{\partial N_2}+\alpha+\beta\varepsilon_2=0\\
\cdots\\
\frac{\partial L}{\partial N_n}=\frac{\partial \ln t}{\partial N_n}+\alpha+\beta\varepsilon_n=0
\end{gathered}
$$

于是有

$$
\begin{gathered}
\frac{\partial \ln t}{\partial N_i}=\ln g_i-\ln N_i=-\alpha-\beta\varepsilon_i\\
\ln N_i=\ln g_i\alpha+\beta\varepsilon_i\\
N_i=g_ie^{\alpha+\beta\varepsilon_i}
\end{gathered}
$$

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

$$
\begin{gathered}
N=\sum_i N_i^*=\sum_i e^{\alpha+\beta\varepsilon_i}=e^\alpha\sum_i g_ie^{\beta\varepsilon_i}\\
\alpha=\ln\frac{N}{\sum_i g_ie^{\beta\varepsilon_i}}=\ln N-\ln\sum_i g_ie^{\beta\varepsilon_i}
\end{gathered}
$$

于是

$$
N_i^*=g_ie^\alpha\cdot e^{\beta\varepsilon_i}=\frac{N}{\sum_i g_ie^{\beta\varepsilon_i}}g_ie^{\beta\varepsilon_i}
$$

考虑$S=k\ln\Omega$，于是

$$
\begin{aligned}
S=k\ln\Omega\approx k\ln t_m=\\
k\left[N\ln N-N+\sum_i N_i^*\ln g_i-\sum_i N_i^*\ln N_i^*+\sum_i N_i^*\right]\\
=k\left[N\ln N+\sum_i N_i^*\ln g_i-\sum_i N_i^*\ln N_i^*\right]
\end{aligned}
$$

又

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

进一步化简为

$$
\begin{aligned}
S &= k\left[N\ln N+\sum_i N_i^*\ln g_i-\sum_i N_i^*(\ln g_i+\alpha+\beta\varepsilon_i)\right]\\
&= k\left[N\ln N+\sum_i N_i^*\ln g_i-(\alpha+\ln g_i)\sum_i N_i^*-\beta\sum_i N_i^*\varepsilon_i\right]\\
&= k(N\ln N-\alpha N-\beta U)
\end{aligned}
$$

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

$$
\begin{aligned}
S = k\left[N\ln N-N\left(\ln N-\ln\sum_i g_ie^{\beta\varepsilon_i}\right)-N\ln g_i-\beta U\right]\\
= kN\ln\sum_i g_ie^{\beta\varepsilon_i}-N\ln g_i-k\beta U
\end{aligned}
$$

上式$S=S(U,\beta,N)$，又$S=S(U,V,N)$，因而$S=S(U,\beta,N)=S(U,\beta(U,V,N),N)$，于是当$N$一定时，微分得

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

于是S关于U得偏导数为

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

其中

$$
\left(\frac{\partial S}{\partial U}\right)_{\beta,N}=-k\beta\quad\left(\frac{\partial S}{\partial \beta}\right)_{U,N}=k\left[N\frac{\partial}{\partial\beta}\left(\ln\sum_i g_ie^{\beta\varepsilon_i}\right)-U\right]
$$

注意此处

$$
\begin{aligned}
N\frac{\partial}{\partial\beta}\left(\ln\sum_i g_ie^{\beta\varepsilon_i}\right)-U=N\frac{\sum_i\varepsilon_ig_ie^{\beta\varepsilon_i}}{\sum_i g_ie^{\beta\varepsilon_i}}-U\\
=N\frac{e^\alpha\sum_i\varepsilon_ig_ie^{\beta\varepsilon_i}}{e^\alpha\sum_i g_ie^{\beta\varepsilon_i}}-U=N\frac{\sum_i\varepsilon_iN_i^*}{\sum_i N_i^*}-U=0
\end{aligned}
$$

于是偏导数为

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

又因为$\mathrm{d}U=T\mathrm{d}S-p\mathrm{d}V$，于是

$$\left(\frac{\partial S}{\partial U}\right)_{V,N}=\frac{1}{T}$$

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

于是Boltzmann最概然分布为

$$N_i^*=N\frac{g_ie^{\beta\varepsilon_i}}{\sum g_ie^{\beta\varepsilon_i}}=N\frac{g_ie^{-\varepsilon_i/kT}}{\sum g_ie^{-\varepsilon_i/kT}}$$

于是熵和Helmholtz自由能为

$$S=kN\ln\sum_i g_ie^{\beta\varepsilon_i}-k\beta U=kN\ln\sum_i g_ie^{-\varepsilon_i/kT}+\frac{U}{T}$$

$$A=U-TS=-NkT\ln\sum_i g_ie^{\varepsilon_i/kT}$$

按量子态分布和按能级分布推到过程类似，仅有简并度g_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

$$\begin{aligned}
t&=\frac{1}{N!}g_1^{N_1}\binom{N_1}{N}g_2^{N_2}\binom{N_2}{N-N_1}\cdots g_n^{N_n}\binom{N_n}{N-\sum\limits_{i=1}^{n-1}N_n}\\
&=\frac{1}{N!}\frac{g_1^{N_1}N!}{(N-N_1)!N_1!}\cdot\frac{g_2^{N_2}(N-N_1)!}{(N-N_1-N_2)!N_2!}\cdots\frac{g_n^{N_n}(N-\sum\limits_{i=0}^{n-1}N_i)!}{0!N_n!}\\
&=\prod_i\frac{g_i^{N_i}}{N_i!}
\end{aligned}$$

总的微观状态数为

$$\Omega=\sum_{\substack{\sum_i N_i=N\\\sum_i N_i\varepsilon_i=U}}t_i=\sum_{\substack{\sum_i N_i=N\\\sum_i N_i\varepsilon_i=U}}\left(\prod_i\frac{g_i^{N_i}}{N_i!}\right)$$

用同样的处理方法可以得到

$$N_i^* = N\frac{g_i e^{-\varepsilon_i/kT}}{\sum_i g_i e^{-\varepsilon_i/kT}}$$

$$S = k\ln\frac{(\sum_i g_i e^{-\varepsilon_i/kT})^N}{N!} + \frac{U}{T}$$

$$A = U - TS = -kT\ln\frac{(\sum_i g_i e^{-\varepsilon_i/kT})^N}{N!}$$

配分函数

配分函数定义如下

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

于是最概然分布为

$$N_i^* = N\frac{g_i e^{-\varepsilon/kT}}{q}$$

配分函数与热力学函数之关系

定位系统

1. Helmholtz自由能

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

2. 熵

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = -k\ln q^N - NkT\left(\frac{\partial \ln q}{\partial T}\right)_{V,N}$$

3. 热力学能

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

4. Gibbs自由能

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

$$G=A+pV=A-V\left(\frac{\partial A}{\partial V}\right)_{T,N}=-kT\ln q^N+NkTV\left(\frac{\partial \ln q}{\partial V}\right)_{T,N}$$

5. 焓

$$H=G+TS=NkTV\left(\frac{\partial \ln q}{\partial V}\right)_{T,N}+NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_{V,N}$$

6. 定容热容

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

非定位系统

1. Helmholtz自由能

$$A=-kT\ln\frac{\left(\sum_i g_i e^{-\varepsilon_i/kT}\right)^N}{N!}=-kT\ln\frac{q^N}{N!}$$

2. 熵

$$S=-\left(\frac{\partial A}{\partial T}\right)_{V,N}=-k\ln\frac{q^N}{N!}-NkT\left(\frac{\partial \ln q}{\partial T}\right)_{V,N}$$

3. 热力学能

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

4. Gibbs自由能

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

$$G=A+pV=A-V\left(\frac{\partial A}{\partial V}\right)_{T,N}=-kT\ln\frac{q^N}{N!}+NkTV\left(\frac{\partial \ln q}{\partial V}\right)_{T,N}$$

5. 焓

$$H=G+TS=NkTV\left(\frac{\partial \ln q}{\partial V}\right)_{T,N}+NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_{V,N}$$

6. 定容热容

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

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

$$\begin{aligned} q_n &= g_{n,0} e^{-\varepsilon_{n,0}/kT} + g_{n,1} e^{-\varepsilon_{n,1}/kT} + \cdots \\ &= g_{n,0} e^{-\varepsilon_{n,0}/kT} \left[1 + \frac{g_{n,1}}{g_{n,0}} e^{-(\varepsilon_{n,1}-\varepsilon_{n,0})/kT} + \cdots \right] \end{aligned}$$

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

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

电子配分函数

$$
\begin{aligned}
q_e &= g_{e,0} e^{-\varepsilon_{e,0}/kT} + g_{e,1} e^{-\varepsilon_{e,1}/kT} + \cdots \\
&= g_{e,0} e^{-\varepsilon_{e,0}/kT} \left[1 + \frac{g_{e,1}}{g_{e,0}} e^{-(\varepsilon_{e,1}-\varepsilon_{e,0})/kT} + \cdots \right]
\end{aligned}
$$

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

$$
\varepsilon_{i,t} = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)
$$

于是平动配分函数为

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

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

$$
\begin{aligned}
\sum_{n_x=1}^{\infty} \exp \left[-\frac{n_x^2 h^2}{8mkTa^2} \right] &= \sum_{n_x=1}^{\infty} \exp \left(-\alpha^2 n_x^2 \right) \approx \int_0^{\infty} e^{-\alpha^2 n_x^2} \mathrm{d}n_x = \frac{\sqrt{\pi}}{2\alpha} \\
&= \sqrt{\frac{2\pi mkT}{h^2}} a
\end{aligned}
$$

于是平动配分函数

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

平动配分函数对各热力学函数的贡献（**注意Stirling公式近似**）

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

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

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

4.

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