第七章　几率法
近独立子系组成系统的统计理论

统计基本假设

【一】 等几率假设

孤立系统中，每个可能的微观态出现几率相同

【二】 热力学平衡态是最可几态 ☞Boltzmann 几率法

- ☞ 几率法是 Boltzmann 和 Maxwell 最早发展起来的，主要是用于处理气体。
- ☞ 这种系统中粒子之间的相互作用比较小（$\ll$ 动能等），可以忽略不计。
- ☞ 在此系统中，我们可以把系统的微观态用单粒子微观态表示出来，并通过分布函数得到宏观态和微观态之间的对应关系。
- ☞ 利用等几率假设，得到不同宏观态发生的几率，进一步得到最可几态，也就是热力学平衡态。

7.1 近独立子系组成的系统

- 近独立子系组成的系统
  考虑系统运动时，可以把系统分成不同的子系统，这些子系统之间相互作用可以忽略不计

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i(\boldsymbol{r}_i, \boldsymbol{p}_i) + H_I \simeq \sum_{i=1}^{N} h_i(\boldsymbol{r}_i, \boldsymbol{p}_i)$$

- 子系可以是组成系统的粒子、或者粒子的某个自由度、或者是元激发　　子系 $\Leftrightarrow$ 粒子

$$\hat{H} = \sum_i \frac{\boldsymbol{p}_i^2}{2m} = \sum_i \frac{p_{ix}^2}{2m} + \sum_i \frac{p_{iy}^2}{2m} + \sum_i \frac{p_{iz}^2}{2m}$$

单原子气体

$$\hat{H} = \sum_i \frac{\boldsymbol{p}_i^2}{2M} + \sum_i \frac{\mathbf{L}_i^2}{2I} + \sum_i \hat{h}_{iv}$$

多原子分子气体

$$\hat{H} = \sum_i \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} V(\boldsymbol{r}_{ij}) \simeq E_0 + \sum_{\boldsymbol{q}} \hbar\omega_{\boldsymbol{q}} |n_{\boldsymbol{q}}\rangle\langle n_{\boldsymbol{q}}|$$

声子

近独立子系组成的系统

N 个近独立粒子组成的系统，这些粒子具有相同的运动形式，单粒子的 Hamiltonian 相同，粒子间没有相互作用

$$\hat{H} = \sum_i \hat{h}_i(\hat{\boldsymbol{r}}_i, \hat{\boldsymbol{p}}_i | V, H, \cdots) = \sum_i \hat{h}(\hat{\boldsymbol{r}}_i, \hat{\boldsymbol{p}}_i | V, H, \cdots)$$

- 这里只考虑粒子具有相同的 Hamiltonian，即单组元系统。多组元的话分开来处理。
- $\hat{h}$ 依赖于外界参数，例如系统体积 / 尺寸、磁场、电场等。
- 微观描述：系统的波函数 $|\Psi(\boldsymbol{r}_i, t)\rangle$
  热力学平衡态物理量（特别是能量）不随时间改变
  $\Rightarrow$ 只要考虑物理量（特别是能量）不变的态 $\Rightarrow$ 能量本征态
- 对于无相互作用的系统，粒子之间没有关系，求系统的本征态/波函数时可以通过分离变量，先求出单粒子的本征态/波函数，然后组合出系统本征态/波函数。

无相互作用系统的微观描述：单粒子问题

$$\hat{H} = \sum_i \hat{h}_i = \sum_i \hat{h}(\boldsymbol{r}_i, \boldsymbol{p}_i | V)$$

$$\hat{h}|\psi_s\rangle = \varepsilon_s(V)|\psi_s\rangle$$

态描述，V 为体积，即外界参数

$$= \varepsilon_l(V)|\psi_{l\alpha}\rangle$$

能级描述：$\alpha = 1, 2, \cdot, \omega_l$； ω_l 简并度

$$\langle\psi_s|\psi_{s'}\rangle = \delta_{ss'} \qquad \langle\psi_{l\alpha}|\psi_{l'\alpha'}\rangle = \delta_{ll'}\delta_{\alpha\alpha'}$$

无相互作用系统的微观描述：系统问题

$$\hat{H} = \sum_i \hat{h}_i = \sum_i \hat{h}(\boldsymbol{r}_i, \boldsymbol{p}_i)$$

$$\hat{h}|\psi_s\rangle = \varepsilon_s|\psi_s\rangle = \varepsilon_l|\psi_{l\alpha}\rangle$$

$$\hat{H}|\Psi\rangle = E_s|\Psi\rangle$$

- ☞ 统计假设中微观态的数目指的是系统态，不是单粒子态。单粒子态只不过是得到系统态的手段。
- ☞ 从单粒子态得到系统态时需要考虑粒子全同性
- 非全同粒子：系统本征波函数是单粒子态的简单直积

$$\begin{aligned}|\Psi_S(1,2,\cdots,N)\rangle &= |\psi_{s_1}(1)\rangle \otimes |\psi_{s_2}(2)\rangle \cdots \otimes |\psi_{s_N}(N)\rangle \\ &= |\psi_{s_1}(1)\psi_{s_2}(2)\cdots\psi_{s_N}(N)\rangle \\ &= |\psi_{l_1\alpha_1}(1)\psi_{l_2\alpha_2}(2)\cdots\psi_{l_N\alpha_N}(N)\rangle\end{aligned}$$

$$\hat{H}|\Psi_S\rangle = E_s|\Psi_S\rangle = \sum_i \varepsilon_{s_i}|\Psi_S\rangle = \sum_i \varepsilon_{l_i}|\Psi_S\rangle$$

$$E_S = \sum_i \varepsilon_{s_i} = \sum_i \varepsilon_{l_i}$$

无相互作用系统的微观描述：系统问题

$$\hat{H} = \sum_i \hat{h}_i = \sum_i \hat{h}(\boldsymbol{r}_i, \boldsymbol{p}_i)$$

$$\hat{h}|\psi_s\rangle = \varepsilon_s|\psi_s\rangle = \varepsilon_l|\psi_{l\alpha}\rangle$$

$$\hat{H}|\Psi\rangle = E_s|\Psi\rangle$$

- 全同粒子：系统本征波函数是单粒子波函数简单直积后再对称化（波色子）或者反对称化（费米子）

$$|\Psi_S\rangle = \frac{1}{C}\sum_P (\pm)^P |\psi_{s_1}(1)\psi_{s_2}(2)\cdots\psi_{s_N}(N)\rangle$$

P：交换算符，$N!$ 个

☞ 统计物理的基本假设和方法对所有系统都相同，不依赖于组成系统的粒子遵循的微观规律，也不要考虑粒子是否全同，以及具有什么样的全同性。

- 全同性仅仅体现在从单粒子态构造系统态的方法不一样。

全同和非全同粒子

两个粒子（1,2），两个单粒子态 $|\psi_1\rangle, |\psi_2\rangle$

- 非全同粒子：多粒子态（系统态）无对称性要求

$$|\Psi_1\rangle = |\psi_1(1)\psi_2(2)\rangle \qquad |\Psi_2\rangle = |\psi_2(1)\psi_1(2)\rangle$$

If $|\psi_1\rangle = |\psi_2\rangle$，只有一个多粒子态（系统态）。
If $|\psi_1\rangle \neq |\psi_2\rangle$，有两个不同的多粒子态

- 全同波色子：交换对称的多粒子波函数

$$|\Psi\rangle = \frac{1}{C}[|\psi_1(1)\psi_2(2)\rangle + |\psi_1(2)\psi_2(1)\rangle] = \frac{1}{C}[|\psi_1(1)\psi_2(2)\rangle + |\psi_2(1)\psi_1(2)\rangle]$$

不管 ψ_1 和 ψ_2 是不是相同，都只有一个多粒子态

- 全同费米子：交换反对称的多粒子波函数

$$|\Psi\rangle = \frac{1}{C}[|\psi_1(1)\psi_2(2)\rangle - |\psi_1(2)\psi_2(1)\rangle] = \frac{1}{C}[|\psi_1(1)\psi_2(2)\rangle - |\psi_2(1)\psi_1(2)\rangle]$$

If $\psi_1 = \psi_2$，$|\Psi\rangle = 0$，此多粒子态不存在 ☞ Pauli 不相容原理
If $\psi_1 \neq \psi_2$，有一个多粒子态

系统态（多粒子态）和单粒子态

以前面的 toy model 为例，取 $|\psi_1\rangle = |L\rangle$，表示处于粒子左边的态；$|\psi_2\rangle = |R\rangle$，表示粒子处在右边的态；在 $N = 2$ 时

- 非全同粒子：体系具有四种可能的微观态

$$|\Psi_1\rangle = |\psi_1(1)\psi_1(2)\rangle \qquad |\Psi_4\rangle = |\psi_2(1)\psi_2(2)\rangle$$
$$|\Psi_2\rangle = |\psi_1(1)\psi_2(2)\rangle \qquad |\Psi_3\rangle = |\psi_2(1)\psi_1(2)\rangle$$

在等几率假设下，不同宏观态的几率如下

$$p(N_L = 2, N_R = 0) = \frac{1}{4} \qquad p(N_L = 0, N_R = 2) = \frac{1}{4}$$
$$p(N_L = 1, N_R = 1) = \frac{1}{2}$$

系统态（多粒子态）和单粒子态

- 全同 Boson：体系有三种可能的微观态

$$|\Psi_1\rangle = |\psi_1(1)\psi_1(2)\rangle \qquad |\Psi_3\rangle = |\psi_2(1)\psi_2(2)\rangle$$
$$|\Psi_2\rangle = [|\psi_1(1)\psi_1(2)\rangle + |\psi_2(1)\psi_2(2)\rangle]/\sqrt{2}$$

在等几率假设下，不同宏观态的几率如下

$$p(N_L = 2, N_R = 0) = \frac{1}{3} \qquad p(N_L = 0, N_R = 2) = \frac{1}{3}$$
$$p(N_L = 1, N_R = 1) = \frac{1}{3}$$

- 全同 Fermion：体系只有一种可能的微观态

$$|\Psi_1\rangle = [|\psi_1(1)\psi_1(2)\rangle - |\psi_2(1)\psi_2(2)\rangle]/\sqrt{2}$$

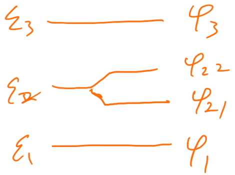
在等几率假设下，不同宏观态的几率如下

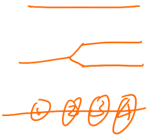
$$p(N_L = 2, N_R = 0) = 0 \qquad p(N_L = 0, N_R = 2) = 0$$
$$p(N_L = 1, N_R = 1) = 1$$

系统态（多粒子态）和单粒子态

经典粒子

Boltzmann

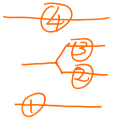




$E = 4\varepsilon_1$

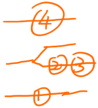
$|4\rangle = |\varphi_1(1)\varphi_1(2)\varphi_1(3)\varphi_1(4)\rangle$

$E = \varepsilon_1 + 2\varepsilon_2 + \varepsilon_3$



$|\varphi_1(1)\varphi_{21}(2)\varphi_{22}(3)\varphi_3(4)\rangle$

$C_4^1 \cdot C_3^1 \cdot C_2^1 \cdot C_1^1 = 4! = 24$



$|\varphi_1(1)\varphi_{21}(2)\varphi_{21}(3)\varphi_3(4)\rangle$

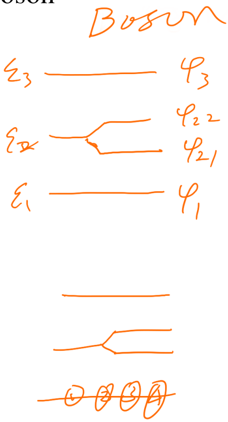
$C_4^1 \cdot C_3^2 \cdot C_1^1 = 12$

$|\varphi_1(1)\varphi_{22}(2)\varphi_{22}(3)\varphi_3(4)\rangle$

$C_4^1 C_3^2 \cdot C_1^1 = 12$

系统态（多粒子态）和单粒子态

Boson

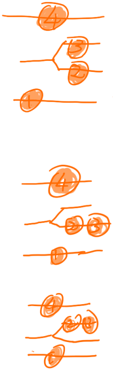


$E = 4\varepsilon_1$

$|4\rangle = |\varphi_1(1)\varphi_1(2)\varphi_1(3)\varphi_1(4)\rangle$

$W = 1$

$E = \varepsilon_1 + 2\varepsilon_2 + \varepsilon_3$



$\{|\varphi_1(1)\varphi_{21}(2)\varphi_{22}(3)\varphi_3(4)\rangle + |\varphi_1(2)\varphi_{21}(1)\varphi_{22}(3)\varphi_3(4)\rangle + \cdots\}/\sqrt{24}$

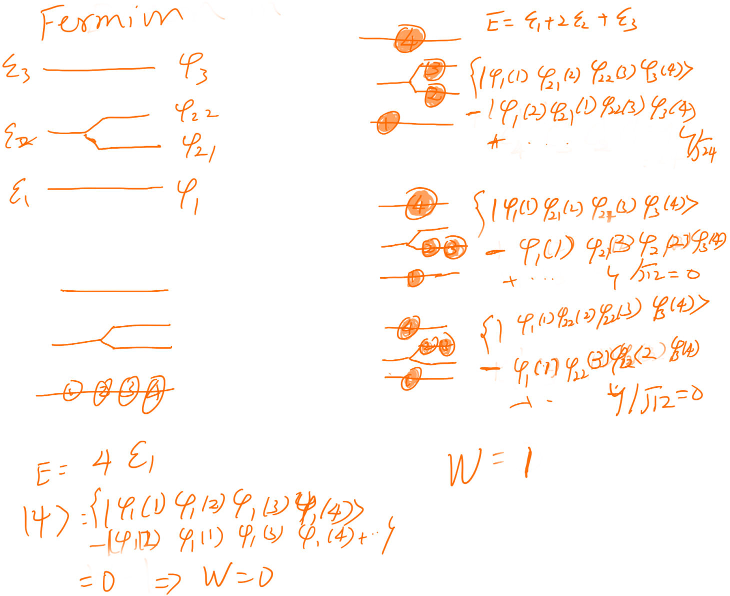
$\{|\varphi_1(1)\varphi_{21}(2)\varphi_{21}(3)\varphi_3(4)\rangle + \varphi_1(2)\varphi_{21}(1)\varphi_{21}(3)\varphi_3(4) + \cdots\}/\sqrt{12}$

$\{|\varphi_1(1)\varphi_{22}(2)\varphi_{22}(3)\varphi_3(4)\rangle + \varphi_1(2)\varphi_{22}(1)\varphi_{22}(3)\varphi_3(4) + \cdots\}/\sqrt{12}$

$W = 3$

系统态（多粒子态）和单粒子态

Fermion



系统态（多粒子态）和单粒子态

- 经典粒子

$$\frac{p(E=4\varepsilon_1)}{p(E=\varepsilon_1+2\varepsilon_2+\varepsilon_3)}=\frac{C_1W(E=4\varepsilon_1)}{C_2W(E=\varepsilon_1+2\varepsilon_2+\varepsilon_3)}=\frac{C_1/C_2}{48}$$

- 全同 Boson

$$\frac{p(E=4\varepsilon_1)}{p(E=\varepsilon_1+2\varepsilon_2+\varepsilon_3)}=\frac{C_1W(E=4\varepsilon_1)}{C_2W(E=\varepsilon_1+2\varepsilon_2+\varepsilon_3)}=\frac{C_1/C_2}{3}$$

- 全同 Fermion

$$\frac{p(E=4\varepsilon_1)}{p(E=\varepsilon_1+2\varepsilon_2+\varepsilon_3)}=\frac{C_1W(E=4\varepsilon_1)}{C_2W(E=\varepsilon_1+2\varepsilon_2+\varepsilon_3)}=0$$

☞ 相同外界条件下，Fermionic 系统处于高能量的可能性 > 经典粒子系统 > Bosonic 系统

分布函数

- 微观描述：系统态、多粒子波函数 $|\Psi\rangle$
- 宏观描述：内能密度 $u(\boldsymbol{r})$，粒子数密度 $\rho(\boldsymbol{r})$，总能量 $\cdots$
- 分布函数：每个态/能级上有几个粒子占据 a_s/a_l

☞ 从分布函数可以得到宏观描述

$$\rho(\boldsymbol{r}) = \langle\Psi|\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{r}_i)|\Psi\rangle = \sum_{i=1}^{N}|\psi_{s_i}(\boldsymbol{r})|^2 = \sum_{s}a_s|\psi_s(\boldsymbol{r})|^2$$

求密度时，不关心具体粒子，只要知道每个态上的粒子数 a_s 即可

$$u(\boldsymbol{r}) = \langle\Psi|\sum_{i=1}^{N}\varepsilon_{s_i}\delta(\boldsymbol{r}-\boldsymbol{r}_i)|\Psi\rangle = \sum_{i=1}^{N}\varepsilon_{s_i}|\psi_{s_i}(\boldsymbol{r})|^2 = \sum_{s}a_s\varepsilon_s|\psi_s(\boldsymbol{r})|^2$$

$$U = \langle\Psi|\hat{H}|\Psi\rangle = \sum_{i=1}\varepsilon_{s_i} = \sum_{s}\varepsilon_s a_s = \sum_{l}\varepsilon_l a_l$$

$$N = \sum_{i}1 = \sum_{s}a_s = \sum_{l}a_l$$

☞不同的分布函数代表不同的宏观态，可以是平衡态，
也可以是非平衡态

7.2 Boltzmann 统计

- ☞ 等几率假设：分布为 $\{a_l\}$ 的宏观态出现几率
  $p(\{a_l\}) \propto \Omega(E,N,V,\{a_l\})$：分布对应的系统微观态数目
- 非全同粒子组成的系统的 $\Omega(E,N,V,\{a_l\})$

$$
\begin{aligned}
\Omega(E,N,V,\{a_l\}) &= C_N^{a_1} C_{N-a_1}^{a_2} \cdots C_{N-a_1-a_2-\cdots-a_{l-1}}^{a_l} \cdots \\
&\quad \times \omega_1^{a_1}\omega_2^{a_2}\cdots\omega_l^{a_l}\cdots \\
&= \frac{N!}{a_1!(N-a_1)!}\frac{(N-a_1)!}{a_2!(N-a_1-a_2)!}\cdots\frac{(N-a_1-a_2-\cdots-a_{l-1}!}{a_l!(N-a_l)!}\cdots \\
&\quad \times \omega_1^{a_1}\omega_2^{a_2}\cdots\omega_l^{a_l}\cdots \\
&= \frac{N!}{a_1!a_2!\cdots a_l!\cdots}\omega_1^{a_1}\omega_2^{a_2}\cdots\omega_l^{a_l}\cdots = \frac{N!}{\prod_l a_l!}\prod_l \omega_l^{a_l}
\end{aligned}
$$

$$
E = \sum_i \varepsilon_{s_i} = \sum_s a_s\varepsilon_s = \sum_l a_l\varepsilon_l
$$

$$
N = \sum_i 1 = \sum_s a_s = \sum_l a_l
$$

热力学平衡态 ⇔ 最可几态

Stirling 公式:
$\ln N! \simeq N\ln N - N$

$$\ln\Omega = \ln N! - \sum_l \ln a_l! + \sum_l a_l \ln\omega_l$$

假设 a_l 很大

$$= N\ln N - N - \sum_l (a_l \ln a_l - a_l) + \sum_l a_l \ln\omega_l$$

$$= (\sum_l a_l)\ln(\sum_l a_l) - \sum_l a_l(\ln a_l - \ln\omega_l)$$

$N = \sum_l a_l$

$\{a_l \to a_l + \delta a_l\}$ $\qquad (x\ln x)' = \ln x + 1$

$$0 = \delta\ln\Omega = [\ln(\sum_l a_l) + 1]\sum_l \delta a_l - \sum_l(\ln a_l + 1 - \ln\omega_l)\delta a_l$$

$$= \sum_l \left[\ln N - \ln\frac{a_l}{\omega_l}\right]\delta a_l$$

$$0 = \delta E = \sum_l \delta a_l \varepsilon_l \qquad 0 = \delta N = \sum_l \delta a_l$$

a_l 不独立

热力学平衡态 ⇔ 最可几态

$$0 = \delta \ln \Omega - \beta \delta E - \tilde{\alpha} \delta N$$

$\tilde{\alpha}, \beta$ 是待定的 Lagrange 乘子；引入 $\tilde{\alpha}, \beta$ 后，a_l 可以认为是独立的

$$= \sum_l \left[\ln N - \ln \frac{a_l}{\omega_l} - \tilde{\alpha} - \beta \varepsilon_l \right] \delta a_l$$

$$\ln \frac{a_l}{\omega_l} = \ln N - \tilde{\alpha} - \beta \varepsilon_l$$

$$\bar{a}_l = N \omega_l e^{-\tilde{\alpha} - \beta \varepsilon_l} = \omega_l e^{\ln N - \tilde{\alpha} - \beta \varepsilon_l} = \omega_l e^{-\alpha - \beta \varepsilon_l}$$

$$\bar{a}_s = e^{-\alpha - \beta \varepsilon_s}$$

$$\alpha = \tilde{\alpha} - \ln N \qquad \tilde{\alpha} = \alpha + \ln N$$

Boltzmann 分布

$$\bar{a}_l = \omega_l e^{-\alpha-\beta\varepsilon_l(V)} \qquad \bar{a}_s = e^{-\alpha-\beta\varepsilon_s(V)}$$

$$E = \sum_l a_l\varepsilon_l = \sum_l \varepsilon_l\omega_l e^{-\alpha-\beta\varepsilon_l} \qquad N = \sum_l \bar{a}_l = \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l}$$

$\alpha(\tilde{\alpha}), \beta$ 二者未知，需要从 E 和 N 两个方程定出，非常麻烦。

$$\overline{\Omega} = \Omega(E, N, \{\overline{a}_l\}) = \frac{N!}{\prod_l \overline{a}_l} \prod_l \omega_l^{\overline{a}_l} = \overline{\Omega}(E, N, V)$$

$$\ln \overline{\Omega} = \ln \overline{\Omega}(E, N, V)$$

$$0 = \delta \ln \overline{\Omega} - \beta\delta E - \tilde{\alpha}\delta N \Rightarrow \beta = \lim_{\delta E\to 0} \left.\frac{\delta \ln \overline{\Omega}}{\delta E}\right|_{\delta N=0} = \left(\frac{\partial \ln \overline{\Omega}}{\partial E}\right)_N$$

$$\Rightarrow \tilde{\alpha} = \lim_{\delta N\to 0} \left.\frac{\delta \ln \overline{\Omega}}{\delta N}\right|_{\delta E=0} = \left(\frac{\partial \ln \overline{\Omega}}{\partial N}\right)_E$$

$$d\ln \overline{\Omega} = \beta dE + \tilde{\alpha} dN \xrightarrow[\text{Legendre 变换}]{\text{特性函数}} \ln Z = \ln Z(\beta, N, V) = \ln \overline{\Omega} - \beta E$$

$$d\ln Z = d(\ln \overline{\Omega} - \beta E) = -E d\beta + \tilde{\alpha} dN$$

配分函数

$$\bar{a}_l = \omega_l e^{-\alpha-\beta\varepsilon_l} \qquad \ln\overline{\Omega} = N\ln N - N - \sum_l \left(\bar{a}_l \ln\bar{a}_l - \bar{a}_l - \bar{a}_l \ln\omega_l\right)$$

$$\ln Z = \ln\overline{\Omega} - \beta E = N\ln N - \sum_l \bar{a}_l \ln\frac{\bar{a}_l}{\omega_l} - \beta\sum_l \bar{a}_l\varepsilon_l - N + \sum_l \bar{a}_l$$

$$= N\ln N - \sum_l \bar{a}_l\left(\ln\frac{\bar{a}_l}{\omega_l} + \beta\varepsilon_l\right)$$

$$= N\ln N - \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l}(-\alpha - \beta\varepsilon_l + \beta\varepsilon_l)$$

$$= N\ln N + \alpha e^{-\alpha}\sum_l \omega_l e^{-\beta\varepsilon_l} = N\ln N + \alpha e^{-\alpha} z$$

单粒子配分函数

$$z = z(\beta, V)$$

$$= \sum_l \omega_l e^{-\beta\varepsilon_l}$$

$$N = \sum_l \bar{a}_l = \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l} = e^{-\alpha}\sum_l \omega_l e^{-\beta\varepsilon_l} = e^{-\alpha} z$$

$$e^{-\alpha} = \frac{N}{z} \qquad \alpha = -\ln\frac{N}{z} = -\ln N + \ln z \qquad \tilde{\alpha} = \alpha + \ln N = \ln z$$

$$\ln Z = N\ln N + N(-\ln N + \ln z) = N\ln z = \ln z^N \Rightarrow$$ 系统配分函数

配分函数

$$\ln \overline{\Omega} = \ln \overline{\Omega}(E, N, V) \qquad\qquad d \ln \overline{\Omega} = \beta dE + \tilde{\alpha} dN$$

$$\ln Z = \ln Z(\beta, N, V) = \ln z^N(\beta, V) \qquad\qquad d \ln Z = -E d\beta + \tilde{\alpha} dN$$

$$z = z(\beta, V) = \sum_l \omega_l e^{-\beta \varepsilon_l(V)} = \sum_s e^{-\beta \varepsilon_s(V)}$$

- 通过 Legendre 变换，使得自变量从 E, N, V 改变为 β, N, V
- 原先需要从 E 和 N 的方程定出 β 和 α（或者 $\tilde{\alpha}$），计算麻烦；变换之后计算相对简单
- 这等价于从能量确定的孤立系统变换为温度确定的封闭系统
- 在研究平衡态物理量时二者没有区别

7.3 物理量

☞ 以后的计算把 $\bar{a}_l/\bar{a}_s$ 直接写成 a_l/a_s

内能 = 最可几态能量

☞热力学中内能是一个唯象的参数，统计物理里给了物理解释

$$U = \overline{E} = \sum_l a_l \varepsilon_l = \sum_l \omega_l e^{-\alpha-\beta\varepsilon_l}\varepsilon_l$$

$$= e^{-\alpha}\sum_l \varepsilon_l \omega_l e^{-\beta\varepsilon_l} = \frac{N}{z}\sum_l \omega_l \left(-\frac{\partial e^{-\beta\varepsilon_l}}{\partial\beta}\right)_V$$

$$= -\frac{N}{z}\left(\frac{\partial}{\partial\beta}\sum_l \omega_l e^{-\beta\varepsilon_l}\right)_V = -\frac{N}{z}\left(\frac{\partial z}{\partial\beta}\right)_V = -N\left(\frac{\partial \ln z}{\partial\beta}\right)_V$$

$$= -\left(\frac{\partial \ln Z}{\partial\beta}\right)_{NV}$$

$$= Nk_BT^2\left(\frac{\partial \ln z}{\partial T}\right)_V = k_BT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{NV} \qquad \boxed{\beta = 1/(k_BT)}$$

压强和熵

$$\delta U = \delta \bar{E} = \sum_l \varepsilon_l(V)\delta a_l + \sum_l a_l \delta\varepsilon_l(V)$$

$=$ 体积不变导致内能变动 $\Rightarrow$ 吸热

$+$ 体积改变导致内能变动 $\Rightarrow$ 做功

$$dU = đQ - đW$$
$$= đQ - p\,dV$$

☞ 能够清晰地把能量改变分为功和热两部分是传统统计物理的一大成就。这使得微观过程和宏观过程有明确的对应关系。目前有很多“量子热力学”、“量子热机”的研究，但这些研究都面对无法明确区分功和热的问题，导致热力学定律对这类系统的适用性存疑。 “Quantum Steampunk”, Halpern

$$p = -\sum_l a_l \left(\frac{\partial \varepsilon_l}{\partial V}\right) = -\sum_l \omega_l e^{-\alpha-\beta\varepsilon_l}\left(\frac{\partial \varepsilon_l}{\partial V}\right) = e^{-\alpha}\sum_l \omega_l \frac{1}{\beta}\left(\frac{\partial}{\partial V}e^{-\beta\varepsilon_l}\right)_\beta$$

$$= \frac{N}{z}\frac{1}{\beta}\left(\frac{\partial}{\partial V}\sum_l \omega_l e^{-\beta\varepsilon_l}\right)_\beta = \frac{N}{z}\frac{1}{\beta}\left(\frac{\partial z}{\partial V}\right)_\beta = \frac{N}{\beta}\left(\frac{\partial \ln z}{\partial V}\right)_\beta = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_{\beta N}$$

$$= N k_B T\left(\frac{\partial \ln z}{\partial V}\right)_T = k_B T\left(\frac{\partial \ln Z}{\partial V}\right)_{TN}$$

$$\boxed{\beta = 1/(k_B T)}$$

压强和熵

$$\delta U = \delta \bar{E} = \sum_l \varepsilon_l(V)\delta a_l + \sum_l a_l \delta\varepsilon_l(V)$$

$$dU = đQ - đW$$

$$= đQ - p\,dV$$

= 体积不变导致内能变动 ⇒ 吸热

\+ 体积改变导致内能变动 ⇒ 做功

$$\beta đQ = \beta \sum_l \varepsilon_l da_l = \sum_l [d(\beta\varepsilon_l a_l) - a_l d(\beta\varepsilon_l)]$$

$$= d(\sum_l \beta\varepsilon_l a_l) - \sum_l a_l d(\beta\varepsilon_l) = d(\beta U) - \sum_l e^{-\alpha}\omega_l e^{-\beta\varepsilon_l} d(\beta\varepsilon_l)$$

$$= d(\beta U) + \frac{N}{z}\sum_l \omega_l d(e^{-\beta\varepsilon_l}) = d(\beta U) + \frac{N}{z} d\left(\sum_l \omega_l e^{-\beta\varepsilon_l}\right)$$

$$= d(\beta U) + \frac{N}{z} dz = d(\beta U + N\ln z)$$

- ☞ $\beta đQ$ 是全微分；类比于 $\frac{1}{T}đQ = dS$ 是全微分 ⇒ $\beta = 1/(k_B T)$
- ☞ 熵

$$\beta đQ = dS/k_B = d[U/(k_B T) + N\ln z] \Rightarrow S = Nk_B \ln z + U/T$$

压强和熵的另外一种推导

$$p = \sum_s a_s \langle \psi_s | -\frac{\partial \hat{h}(V)}{\partial V} | \psi_s \rangle = \sum_s a_s \times \left[-\left(\frac{\partial \varepsilon_s}{\partial V} \right) \right] = \sum_l a_l \left[-\left(\frac{\partial \varepsilon_l}{\partial V} \right) \right]$$

$$= -e^{-\alpha} \sum_l \omega_l e^{-\beta \varepsilon_l} \left(\frac{\partial \varepsilon_l}{\partial V} \right) = \frac{N}{\beta z} \frac{\partial}{\partial V} \left(\sum_l \omega_l e^{-\beta \varepsilon_l} \right)_\beta = \frac{N}{z\beta} \left(\frac{\partial z}{\partial V} \right)_\beta$$

$$= \frac{N}{\beta} \left(\frac{\partial \ln z}{\partial V} \right)_\beta$$

$$\beta đQ = \beta(dU + pdV) = d(\beta U) - U d\beta + \beta p dV$$

$$= d(\beta U) + N \left(\frac{\partial \ln z}{\partial \beta} \right)_V d\beta + N \left(\frac{\partial \ln z}{\partial V} \right)_\beta dV$$

$$= d(\beta U + N \ln z) \qquad \Leftrightarrow \frac{đQ}{T} = dS \Rightarrow \beta = \frac{1}{k_B T}$$

$$\frac{dS}{k_B} = d\left(\frac{U}{k_B T} + N \ln z \right) \Rightarrow S = \frac{U}{T} + N k_B \ln z = k_B \left[N\beta \left(\frac{\partial \ln z}{\partial \beta} \right)_V + N \ln z \right]$$

Boltzmann 关系：$S = k_B \ln \Omega$

$$\ln Z = N \ln z = \ln \overline{\Omega} - \beta E$$

$$\begin{aligned} S &= k_B[\beta U + N \ln z] \\ &= k_B[\beta U + \ln \overline{\Omega} - \beta U] \\ &= k_B \ln \overline{\Omega} \end{aligned}$$

- ☞ 平衡态
  $S = k_B \ln \overline{\Omega} = k_B \ln \Omega(\{\overline{a}_l\})$
- ☞ 可以推广到任意的态
  $S(\{a_l\}) = k_B \ln \Omega(\{a_l\})$
- ☞ 在非平衡态下也可以定义熵
- ☞ 孤立系统平衡态下 $\ln \Omega$ 最大 $\Leftrightarrow$ 孤立系统的平衡态熵最大

自由能

$$S = U/T + Nk_B \ln z = U/T + k_B \ln Z$$

$$F = U - TS = -Nk_B T \ln z = -k_B T \ln Z$$

$$U = -N\left(\frac{\partial \ln z}{\partial \beta}\right)_V = -N\frac{dT}{d(\beta)}\left(\frac{\partial \ln z}{\partial T}\right)_V$$

$$= -\frac{Nk_B}{d(1/T)/dT}\left(\frac{\partial \ln z}{\partial T}\right)_V$$

$$= Nk_B T^2\left(\frac{\partial \ln z}{\partial T}\right)_V$$

$$p = \frac{1}{\beta}\left(\frac{\partial \ln z}{\partial V}\right)_\beta = Nk_B T\left(\frac{\partial \ln z}{\partial V}\right)_T$$

7.4 Boltzmann 因子

$$a_s = \frac{N}{z} e^{-\beta \varepsilon_s} \propto e^{-\beta(\varepsilon_s - \varepsilon_g)} \propto e^{-\beta \Delta \varepsilon_s}$$

- 单粒子态 $|s\rangle$ 被占据的几率：$p_s = a_s/N = (1/z)e^{-\beta \varepsilon_s}$
- 单粒子基态能量 ε_g，对计算 a_s 没有影响，可以取成零。
- 某自由度特征激发能量为 $\Delta\varepsilon$，该自由度被激发的几率 p

$$p \propto e^{-\beta \Delta \varepsilon} = e^{-\Delta \varepsilon / k_B T} = e^{-\Theta / T}$$

$$\Theta = \Delta \varepsilon / k_B$$ 特征温度

- $T \ll \Theta$，$p \sim 0$，基本上所有粒子都处于该自由度的基态，激发态上几乎没有粒子
  ☞ 能量量子化导致自由度冻结，该自由度对系统热力学性质无影响
- $T \gg \Theta$，低能激发态上的 $p \sim 1$，自由度被完全激发
  $\Rightarrow$ 经典结果，满足能量均分原理
- 温度可以当成能量来看待：$k_B T$ ☞ 热力学温标的新定义

☞ 2019.5.20 起，k_B 被定义为：$k_B = 1.380649 \times 10^{-23}$ J/K

几种运动的特征温度

$k_B = 1.380649\times10^{-23}\text{J/K}$,

$T = 1K, k_BT = 8.6\times10^{-5}\text{eV}\simeq 0.1\text{ meV}$

$T = 300K, k_BT = 25.8\text{ meV}$

- 原子中电子运动

$$\varepsilon_n = -\frac{m_e e^4}{8h^2\epsilon_0^2 n^2} = -\frac{1Ry}{n^2} = \frac{-13.6\,eV}{n^2}$$

$\Delta\varepsilon_e \sim 10\,eV$

$\Theta_e = \Delta\varepsilon_e/k_B = 10^5\ K$

$p_{ex} \sim e^{-\Theta_e/T}$ $\qquad p_{ex}(T = 300K) \sim 10^{-168}$

氢原子

$\varepsilon_n = -Ry/n^2 \qquad \omega_n = 2n^2$

$z = \sum_n \omega_n e^{-\beta\varepsilon_n} \to \infty$

$p_g = a_g/N = 1/z \to 0$

$\Rightarrow$ 氢原子处于基态的几率 ~ 0

???????

☞室温附近，原子中电子自由度完全被冻结，对热力学性质没有任何影响

- 双原子振动自由度 $\Theta_v \sim 10^2 - 10^3$ K
- 双原子转动自由度 $\Theta_r \sim 10$ K
- 原子平动自由度 $\Theta_t \sim 10^{-12}$K：氢原子在尺寸为 1mm 盒子中

7.5 两能级系统

☞最简单的体系：没有相互作用的两能级子系组成的系统

$$\hat{h}|0\rangle = 0|0\rangle \qquad \hat{h}|1\rangle = \varepsilon|1\rangle = k_B\Theta|1\rangle$$

$$z = \sum_s e^{-\beta\varepsilon_s} = 1 + e^{-\beta\varepsilon}$$

$$a_0 = \frac{N}{z}e^{-\beta\varepsilon_0} = \frac{N}{1+e^{-\beta\varepsilon}} = \frac{N}{1+e^{-\Theta/T}}$$

$$a_1 = \frac{N}{z}e^{-\beta\varepsilon_1} = \frac{Ne^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} = \frac{Ne^{-\Theta/T}}{1+e^{-\Theta/T}}$$

$$U = a_0\varepsilon_0 + a_1\varepsilon_1 = a_1\varepsilon = N\varepsilon\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}$$

$$= -N\left(\frac{\partial \ln z}{\partial \beta}\right) = Nk_BT^2\left(\frac{\partial \ln z}{\partial T}\right) = \frac{N\varepsilon}{e^{\beta\varepsilon}+1} = \frac{Nk_B\Theta}{e^{\Theta/T}+1}$$

$$C = \left(\frac{\partial U}{\partial T}\right) = Nk_B\left(\frac{\varepsilon}{k_BT}\right)^2\frac{e^{\beta\varepsilon}}{(e^{\beta\varepsilon}+1)^2} = Nk_B\left(\frac{\Theta}{T}\right)^2\frac{e^{\Theta/T}}{(e^{\Theta/T}+1)^2}$$

$$S = \frac{U}{T} + Nk_B\ln z = Nk_B\frac{\Theta/T}{e^{\Theta/T}+1} + Nk_B\ln[1+e^{-\Theta/T}]$$

两能级系统的低温、高温极限

- 低温极限 $T \ll \Theta$

$$a_0 \simeq N \qquad a_1 \simeq Ne^{-\Theta/T} \simeq 0$$

$$U \simeq Nk_B\Theta e^{-\Theta/T} \sim 0$$

$$C \simeq Nk_B(\Theta/T)^2 e^{-\Theta/T} \sim 0$$

$$S \simeq Nk_B(\Theta/T)e^{-\Theta/T} \sim 0$$

$$= k_B \ln \Omega \boxed{\simeq 1}$$

- 高温极限 $T \gg \Theta$

$$z = 1 + e^{-\Theta/T} \simeq 2$$

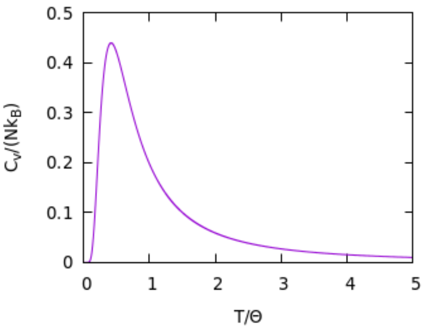
$$a_0 \simeq a_1 \simeq N/2$$

$$U \simeq N\varepsilon/2$$

$$C \simeq Nk_B\left(\frac{\Theta}{2T}\right)^2 \to 0$$

$$S \simeq Nk_B \ln 2$$

$$= k_B \ln \Omega \boxed{\simeq 2^N}$$



☞ Schottky 反常
低温和高温下热容都趋于零，热容随温度出现一个峰。

☞ 峰值位置大体在激发态能级处

- 高温时，每个处在基态和激发态上的几率相同，因此 $\Omega = 2^N$
- 出现 Schottky 反常的原因是系统态数目以及能量有上限。

7.6 单原子气体热容、能量均分原理

把原子看成是个整体，单粒子能量包含核的能量，核外电子能量及其相互作用

$$\hat{h}_t = \frac{\boldsymbol{p}^2}{2m} + u(\boldsymbol{r}) + \sum_{i\in\text{电子}} \left[\frac{\boldsymbol{p}_i^2}{2m_e} + u_e(\boldsymbol{r}_i) - \frac{Ze^2}{\epsilon_0|\boldsymbol{r}_i - \boldsymbol{r}|} + \sum_{j<i} \frac{e^2}{\epsilon_0|\boldsymbol{r}_i - \boldsymbol{r}_j|} \right]$$

电子 $\Delta\varepsilon_e \sim 1 - 10$ eV $\sim 10^{4-5}$ K, 自由度冻结，只要考虑质心平动

$$\hat{h} = \frac{\boldsymbol{p}^2}{2m} + u(\boldsymbol{r}) + E_{eg} \boxed{=0} \qquad u(\boldsymbol{r}) = \begin{cases} 0 & \boldsymbol{r} \in V(L_x, L_y, L_z) \\ \infty & otherwise \end{cases}$$

$$= \frac{p_x^2}{2m} + u(x) + \frac{p_y^2}{2m} + u(y) + \frac{p_z^2}{2m} + u(z)$$

$$\hat{h}|\psi_{n_x,n_y,n_z}\rangle = \varepsilon_{n_x,n_y,n_z}|\psi_{n_x,n_y,n_z}\rangle$$

$$\psi_{n_x}(x) = \langle x|\psi_{n_x}\rangle = \sqrt{\frac{2}{L_x}} \sin\frac{n_x\pi x}{L_y} \qquad \varepsilon_{n_x}^x = \frac{\hbar^2\pi^2 n_x^2}{2mL_x^2} \qquad \cdots$$

$$\psi_{n_xn_yn_z}(\boldsymbol{r}) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$$

$$\varepsilon_{n_xn_yn_z} = \varepsilon_{n_x}^x + \varepsilon_{n_y}^y + \varepsilon_{n_z}^z \qquad n_x, n_y, n_z = 1, 2, 3, \cdots$$

Euler-Maclaurin 公式

求配分函数会涉及到求和，高温的时候可以把它化为求积分的形式，这样计算更为简便。王竹溪,《特殊函数概论》p7

$$f_l = f(a + l \times h) \qquad f_0 = f(a) \qquad f_N = f(b) = f(a + Nh)$$

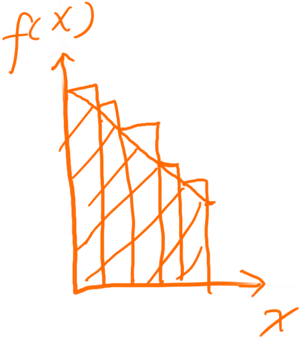
$$\sum_{l=0}^{N} f_l = \frac{1}{h}\int_a^b f(x)dx + \frac{f(a)+f(b)}{2}$$

$$+ \sum_{k=1}^{\infty} \frac{B_{2k} h^{2k-1}}{(2k)!}[f^{(2k-1)}(b) - f^{(2k-1)}(a)]$$

$$= \frac{1}{h}\int_a^b f(x)dx + \frac{f(a)+f(b)}{2}$$

$$+ \frac{h}{12}[f'(b) - f'(a)]$$

$$- \frac{h^3}{720}[f^{(3)}(b) - f^{(3)}(a)] + \cdots$$



Bernoulli numbers： $B_{2k} = \frac{1}{6}, \frac{-1}{30}, \frac{1}{42} \cdots$

单原子理想气体热容、能量均分原理

$$z=\sum_{n_x,n_y,n_z} e^{-\beta\varepsilon_{n_x n_y n_z}}=\sum_{n_x} e^{-\beta\varepsilon_{n_x}}\times\sum_{n_y} e^{-\beta\varepsilon_{n_y}}\times\sum_{n_z} e^{-\beta\varepsilon_{n_z}}$$

$$=z_x z_y z_z \qquad \Leftarrow \boxed{\text{互相不影响的自由度可以分别处理}}$$

$$z_x=\sum_{n_x=1}^{\infty} e^{-\beta\varepsilon_{n_x}}\simeq\int_0^{\infty} e^{-\frac{\beta\hbar^2\pi^2}{2mL_x^2}n_x^2}dn_x=\left(\frac{2mL_x^2}{\beta\hbar^2\pi^2}\right)^{1/2}\int_0^{\infty} e^{-x^2}dx \quad \boxed{x^2\to t}$$

$$=\left(\frac{2mL_x^2}{\beta\hbar^2\pi^2}\right)^{1/2}\int_0^{\infty}\frac{1}{2}e^{-t}t^{-1/2}dt$$

$$=\left(\frac{2mL_x^2}{\beta\hbar^2\pi^2}\right)^{1/2}\frac{1}{2}\Gamma(1/2)$$

$$=\left(\frac{2mL_x^2}{\beta\hbar^2\pi^2}\right)^{1/2}\frac{\sqrt{\pi}}{2}=L_x\left(\frac{2\pi mk_BT}{h^2}\right)^{1/2}=\frac{L_x}{\lambda_T}$$

$$z=L_xL_yL_z\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}=\frac{L_xL_yL_z}{\lambda_T^3}$$

$$=V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}=\frac{V}{\lambda_T^3} \qquad \lambda_T=\left(\frac{h^2}{2\pi mk_BT}\right)^{1/2}=\frac{h}{p_T}$$

第一类 Euler 积分

$$\int_0^{\infty} t^{\alpha-1}e^{-t}dt=\Gamma(\alpha)$$

$$\Gamma(\alpha+1)=\alpha\Gamma(\alpha)$$

$$\Gamma(n+1)=n!$$

$$\Gamma(1/2)=\sqrt{\pi}$$

单原子理想气体状态方程

$$U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V = Nk_BT^2\left(\frac{\partial \ln z}{\partial T}\right)_V = Nk_BT^2\frac{\partial}{\partial T}\ln\left[V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]_V$$

$$= \frac{3}{2}Nk_BT$$

内能只和温度有关，和体积无关

$$p = Nk_BT\left(\frac{\partial \ln z}{\partial V}\right)_T = \frac{Nk_BT}{V} = \frac{nN_Ak_BT}{V} = \frac{nRT}{V} \qquad \Rightarrow R = N_Ak_B$$

$$S = \frac{U}{T} + Nk_B\ln z = \frac{3Nk_B}{2} + Nk_B\ln\left[V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]$$

$$F = U - TS = -k_BT\ln Z = -Nk_BT\ln z = -Nk_BT\ln\left[V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3Nk_B}{2} = \frac{3nR}{2}$$

☞能量均分原理：$U = 3Nk_BT/2$，每个运动自由度对热力学性质平均贡献相同，能量都贡献 $k_BT/2$ 的能量，热容都贡献 $k_B/2$

边界条件：周期性边界条件

$$\hat{h}(\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} \qquad \hat{h}\psi(\boldsymbol{r}) = \varepsilon\psi(\boldsymbol{r})$$

$$\psi(\boldsymbol{r}) = \psi(\boldsymbol{r} + L_x\hat{e}_x) = \psi(\boldsymbol{r} + L_y\hat{e}_y) = \psi(\boldsymbol{r} + L_z\hat{e}_z)$$

$$\psi_{\boldsymbol{k}=(k_x,k_y,k_z)}(\boldsymbol{r}) = \frac{1}{\sqrt{V}}e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \qquad \varepsilon(\boldsymbol{k}) = \frac{\hbar^2\boldsymbol{k}^2}{2m} = \frac{\hbar^2k_x^2}{2m} + \frac{\hbar^2k_y^2}{2m} + \frac{\hbar^2k_z^2}{2m}$$

$$e^{ik_xL_x} = e^{ik_yL_y} = e^{ik_zL_z} = 1 \qquad \Rightarrow \qquad k_x = 2n_x\pi/L_x\cdots$$

$$\boldsymbol{k} = \frac{n_x2\pi}{L_x}\hat{e}_x + \frac{n_y2\pi}{L_y}\hat{e}_y + \frac{n_z2\pi}{L_z}\hat{e}_z \qquad n_x, n_y, n_z = \cdots, -2, -1, 0, 1, 2, \cdots$$

$$z_x = \sum_{n_x=-\infty}^{\infty} e^{-\beta\hbar^2n_x^2(2\pi)^2/(2mL_x^2)} = \int_{-\infty}^{\infty} e^{-n_x^2h^2/(2mk_BTL_x^2)}dn_x$$

$$= \sqrt{\frac{2mk_BTL_x^2}{h^2}} \times \int_{-\infty}^{\infty} e^{-x^2}dx = 2\int_0^{\infty} e^{-t}dt^{1/2} = \int_0^{\infty} e^{-t}t^{1/2-1}dt = \Gamma(\frac{1}{2})$$

$$= L_x\left(\frac{2\pi mk_BT}{h^2}\right)^{1/2} \Rightarrow z = z_xz_yz_z = V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}$$

与边界条件无关

周期性边界条件：直接对 k 求和

$$k_x = \frac{2n_x\pi}{L_x} \Rightarrow \Delta k_x = \frac{2\pi}{L_x} \qquad \varepsilon_x(k_x) = \frac{\hbar^2 k_x^2}{2m}$$

$$\begin{aligned}
z_x &= \sum_{k_x} e^{-\beta\varepsilon_x(k_x)} = \sum_{k_x} e^{-\beta\hbar^2 k_x^2/(2m)} \\
&= \int_{-\infty}^{\infty} \frac{dk_x}{2\pi/L_x} e^{-\hbar^2 k_x^2/(2mk_BT)} = L_x \int_{-\infty}^{\infty} \frac{dk_x}{2\pi} e^{-\hbar^2 k_x^2/(2mk_BT)} \\
&= \frac{L_x}{2\pi}\left(\frac{2mk_BT}{\hbar^2}\right)^{1/2} \int_{-\infty}^{\infty} e^{-x^2} dx \\
&= L_x\left(\frac{2\pi mk_BT}{h^2}\right)^{1/2} = L_x/\lambda_T
\end{aligned}$$

$$z = z_x z_y z_z = V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} = V/\lambda_T^3$$

- 在热力学极限下（$L \Rightarrow \infty$），不同边界条件得到的热力学量是相同的
- 选取计算最简便、物理图像最简单的边界条件，通常就是周期性边界条件
- 周期性边界条件下，动量 $\boldsymbol{p} = \hbar\boldsymbol{k}$ 是好量子数

周期性边界条件：直接对 k 求和

$$\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/(2m) = \hbar^2(k_x^2+k_y^2+k_z^2)/(2m)$$

$$z = \sum_{k_x k_y k_z} e^{-\beta\varepsilon(\boldsymbol{k})} = \int_{-\infty}^{\infty} \frac{dk_x}{2\pi/L_x}\frac{dk_y}{2\pi/L_y}\frac{dk_z}{2\pi/L_z} e^{-\beta\varepsilon(\boldsymbol{k})}$$

$$= L_xL_yL_z\int\frac{d^3\boldsymbol{k}}{(2\pi)^2}e^{-\beta\varepsilon(\boldsymbol{k})} = V\int\frac{d^3\boldsymbol{k}}{(2\pi)^3}e^{-\beta\varepsilon(\boldsymbol{k})}$$

$$= \frac{V}{(2\pi)^3}\int_0^\infty k^2dk\int_0^\pi \sin\theta d\theta\int_0^{2\pi} d\phi e^{-\beta\hbar^2k^2/(2m)}$$

$$= \frac{4\pi V}{(2\pi)^3}\int_0^\infty e^{-\hbar^2k^2/(2mk_BT)}k^2dk$$

$$= \frac{4\pi V}{(2\pi)^3}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\int_0^\infty e^{-x^2}x^2dx \quad \boxed{= \int_0^\infty e^{-t}t\frac{1}{2}t^{-1/2}dt = \frac{1}{2}\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{4}}$$

$$= V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} = \frac{V}{\lambda_T^3}$$

- 周期性边界条件写下 $\hbar\boldsymbol{k}$ 就是是动量，计算时可以不必求解本征方程，直接利用色散关系 $\varepsilon_{\boldsymbol{p}} = \boldsymbol{p}^2/(2m) = \hbar^2\boldsymbol{k}^2/(2m)$ 计算配分函数

边界条件比较

- 箱边界条件

$$
\begin{aligned}
z_x &= \sum_{n_x=1}^{\infty} e^{-\hbar^2 n_x^2 \pi^2/(2mL_x^2 k_B T)} = \sum_{n_x=0}^{\infty} e^{-\hbar^2 n_x^2 \pi^2/(2mL_x^2 k_B T)} - 1 \\
&= \int_0^{\infty} e^{-\hbar^2 n_x^2 \pi^2/(2mL_x^2 k_B T)} dn_x + \frac{e^0 - e^{-\infty}}{2} - 1 + \cdots \\
&= L_x/\lambda_T - 1/2 + \cdots
\end{aligned}
$$

$$
\begin{aligned}
z &= z_x z_y z_z = V/\lambda_T^3 - \frac{1}{2}(L_y L_z + L_z L_x + L_x L_y)/\lambda_T^2 + \cdots \\
&= \frac{V}{\lambda_T^3} - c_A \frac{A\,\boxed{\text{表面积}}}{\lambda_T^2} + c_L \frac{L\,\boxed{\text{周长}}}{\lambda_T} + \cdots
\end{aligned}
$$

- 周期性边界条件

$$
z = V/\lambda_T^3 - c'_A A/\lambda_T^2 + c'_L L/\lambda_T + \cdots
$$

- 不同边界条件 $c_A, c_L, \cdots$ 不同，在热力学极限下这些项没有贡献。

7.7 双原子热容

- 经典的 Boltzmann 统计用于单原子气体取得非常好的结果
- 但是用于双原子分子气体时，取得的结果差强人意
  - 每个双原子分子对能量有贡献的自由度为 7
    每个分子平动三个自由度，转动两个自由度，
    振动两个自由度：动能 + 相互作用势能
  - 从经典统计（能量均分原理），热容应该是 $7Nk_B/2$，与温度无关
  - 但是实验发现在室温下，大多数双原子分子气体的热容为 $5Nk_B/2$
  - 温度下降，热容随之减小，尤其是氢气在低温下热容显著减小。
- 更复杂的系统，例如固体系统，同样有类似问题。例如元素晶体在室温附近满足能量均分原理，摩尔比热为 $3R$。但是温度降低后，比热降低。

多原子系统的比热问题

- 多原子体系的热容问题困扰了物理学家很长一段时间。Kelvin 在 1900 年的一次演讲中提到当时的物理学中的两朵乌云，其中一朵乌云就是和热容相关的。
  Lord Kelvin, “Nineteenth Century Clouds over the Dynamical Theory of Heat and Light”, Phil. Mag., Series 6, **2**, 1–40 (1901).

  The beauty and clearness of the dynamical theory, which asserts heat and light to be modes of motion, is at present obscured by two clouds. I. The first came into existence with the undulatory theory of light, and was dealt with by Fresnel and Dr. Thomas Young; it involved the question, How could the earth move through an elastic solid, such as essentially is the luminiferous ether? II. The second is the Maxwell-Boltzmann doctrine regarding the partition of energy.
  …

多原子系统的比热问题

- Boltzmann 最初猜测转动和质心运动没有耦合，因此转动自由度和质心运动不能达到热力学平衡，对热容没有贡献，因此双原子热容为 $5Nk_B/2$ (三个质心平动 + 两个振动自由度)。
- Kelvin 模拟双原子分子和粗糙容器壁的碰撞，发现转动自由度和质心运动可以互相转化，二者有耦合。因此转动自由度应该对热容有影响。
- Kelvin 文章的结论

  I am afraid we must still regards Cloud No. I as very dense.

  "··· The two atoms, however related, remains two atoms, and the degrees of freedom remain six in number.

  What would appear to be wanted is some escape from the destructive simplicity of the general conclusion."

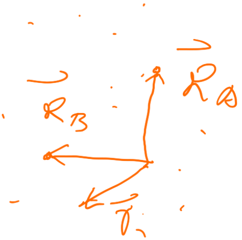
  The simplest way of arriving at this desired result is to deny the conclusion; and so, in the beginning of the twentieth century, to lose sight of a cloud which has obscured the brilliance of the molecular theory of heat and light during the last quater of the nineteenth century.

多原子系统的比热问题

☞ 解决热容问题需要考虑自由度冻结，即需要考虑量子效应

- 1905 年 Einstein, 1912 年 Debye 解决了固体热容问题
  能级量子化会冻结自由度 ⇒ 温度低于特征温度时，自由度冻结
- 1925 年 Einstein 推广 Bose 工作，发现即使能级量子化不重要，全同性波色子在低温下热容也会趋于零。
- 1927-28 年 Sommerfeld 利用 Fermi-Dirac 的结果，解决金属中电子热容问题，即由于量子全同性，也会发生强烈的自由度冻结。
- 1927 年 Dennison 理论上解决了 H_2 的热容问题，实验证实一直延续到 1930 年。

双原子分子单粒子问题



$$h = \frac{\mathbf{p}_A^2}{2M_A} + \frac{\mathbf{p}_B^2}{2M_B} + \frac{Z_A Z_B e^2}{\epsilon_0 |\mathbf{R}_A - \mathbf{R}_B|}$$

$$+ \sum_i \frac{\mathbf{p}_i^2}{2m_e} + \sum_{i<j} \frac{e^2}{\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,J} \frac{Z_J e^2}{\epsilon_0 |\mathbf{r}_i - \mathbf{R}_J|}$$

$$= \frac{\mathbf{p}_A^2}{2M_A} + \frac{\mathbf{p}_B^2}{2M_B} + \frac{Z_A Z_B e^2}{\epsilon_0 |\mathbf{R}_A - \mathbf{R}_B|} + h_e(\mathbf{R}_A, \mathbf{R}_B)$$

绝热近似：电子质量远比核质量小，运动速度快很多；可以把电子与核的运动分开来考虑

$$|\Psi_{N,e}(A, B, \{r_i, s_i\})\rangle = |\Psi_e(\{r_i, s_i\}|\mathbf{R}_A, \mathbf{R}_B)\rangle \otimes |\Psi_N(A, B)\rangle$$

$$\hat{O}_J |\Psi_{N,e}(A, B, \{r_i, s_i\})\rangle = |\Psi_e(\{r_i, s_i\}|\mathbf{R}_A, \mathbf{R}_B)\rangle \otimes \hat{O}_J |\Psi_N(A, B)\rangle$$

$$h_e(\mathbf{R}_A, \mathbf{R}_B)|\Psi_e^n(\{r_i, s_i\}|\mathbf{R}_A, \mathbf{R}_B)\rangle = E_e^n(|\mathbf{R}_A - \mathbf{R}_B|)|\Psi_e^n(\{r_i, s_i\}|\mathbf{R}_A, \mathbf{R}_B$$

$\Delta E_e^n \sim 1$ eV $\Rightarrow$ 自由度冻结，只要考虑电子基态即可

双原子分子单粒子问题

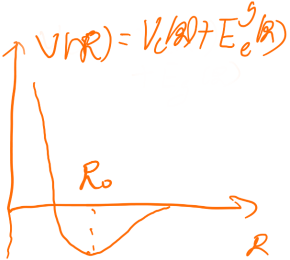
$$h|\Psi_N\rangle|\Psi_e\rangle = \left[\frac{\boldsymbol{p}_A^2}{2M_A} + \frac{\boldsymbol{p}_B^2}{2M_B} + \frac{Z_A Z_B e^2}{\epsilon_0|\boldsymbol{R}_A - \boldsymbol{R}_B|} + E_e^g(|\boldsymbol{R}_A - \boldsymbol{R}_B|)\right]|\Psi_N\rangle|\Psi_e\rangle$$

$$h|\Psi_N\rangle = \left[\frac{\boldsymbol{p}_A^2}{2M_A} + \frac{\boldsymbol{p}_B^2}{2M_B} + V(|\boldsymbol{R}_A - \boldsymbol{R}_B|)\right]|\Psi_N\rangle$$

$$V(|\mathbf{R}_A - \mathbf{R}_B|) = \frac{Z_A Z_B e^2}{\epsilon_0|\mathbf{R}_A - \mathbf{R}_B|} + E_e^g(|\mathbf{R}_A - \mathbf{R}_B|)$$

$$\mathbf{R}_c = \frac{m_A\mathbf{R}_A + m_B\mathbf{R}_B}{m_A + m_B}$$ 质心运动

$$\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B$$ 相对运动



$$h = \frac{\mathbf{P}_c^2}{2M} + \frac{\mathbf{p}^2}{2\mu} + V(R)$$

$$= \frac{\mathbf{P}_c^2}{2M} - \frac{\hbar^2}{2\mu}\left[\partial_R^2 + \frac{2}{R}\partial_R\right] + V(R) - \frac{\hbar^2}{2\mu R^2}\left[\left(\frac{1}{\sin\theta}\partial_\theta\right)^2 + \frac{1}{\sin^2\theta}\partial_\phi^2\right]$$

$= h_t$ 质心平动：和单原子体系相同 $+ h_{vr}$ 转动和振动

双原子分子的振动和转动

$$\Phi_{nlm} = \frac{Q_{nl}(R)}{R} Y_{lm}(\theta, \phi) \chi(s_A, s_B)$$

$$l = 0, 1, \cdots, m = -l, -l+1, \cdots, l-1, l$$

共有 2l+1 个

$$\hat{h}_{vr} \Phi_{nlm} = E_{nlm} \Phi_{nlm}$$

$$= \left\{ -\frac{\hbar^2}{2\mu} \left[\partial_R^2 + \frac{2}{R} \partial_R \right] + V(R) - \frac{\hbar^2}{2\mu R^2} \left[\left(\frac{1}{\sin\theta} \partial_\theta \right)^2 + \frac{1}{\sin^2\theta} \partial_\phi^2 \right] \right\} \Phi_{nlm}$$

$$= \left\{ -\frac{\hbar^2}{2\mu} \left[\partial_R^2 + \frac{2}{R} \partial_R \right] + V(R) + \frac{\hbar^2 l(l+1)}{2\mu R^2} \right\} \Phi_{nlm}$$

$$\ldots = \left[\partial_R^2 + \frac{2}{R} \partial_R \right] \frac{Q}{R} = \partial_R \left[\frac{Q'}{R} - \frac{Q}{R^2} \right] + \frac{2}{R} \left[\frac{Q'}{R} - \frac{Q}{R^2} \right]$$

$$= \frac{Q''}{R} - \frac{2Q'}{R^2} + \frac{2Q}{R^3} + \frac{2}{R} \left[\frac{Q'}{R} - \frac{Q}{R^2} \right] = \frac{Q''}{R}$$

$$\frac{E_{nl}}{R} Q_{nl}(R) = \frac{1}{R} \left\{ -\frac{\hbar^2}{2\mu} \partial_R^2 + V(R) + \frac{\hbar^2 l(l+1)}{2\mu R^2} \right\} Q_{nl}(R)$$

双原子分子的振动能谱和转动能谱

$\Theta_v = [E_{n+1,l} - E_{n,l}]/k_B \sim 1000\ K$

$\Theta_r = [E_{n,l+1} - E_{n,l}]/k_B \sim 1 - 10\ K$ 振动能级间隔和转动能级间隔相差很大，可以分开来考虑。$\Rightarrow$ Rigid rotor 近似

$$V(R) = V(R_0) + \frac{1}{2}\mu\omega^2(R - R_0)^2 + \cdots \qquad \boldsymbol{R} = \boldsymbol{R}_A - \boldsymbol{R}_B$$

$$h_{vr} \simeq -\frac{\hbar^2}{2\mu}\partial_R^2 + V(R_0) + \frac{1}{2}\mu\omega^2(R - R_0)^2 - \frac{\hbar^2}{2\mu R_0^2}\left[\left(\frac{1}{\sin\theta}\partial_\theta\right)^2 + \frac{1}{\sin^2\theta}\partial_\phi^2\right.$$

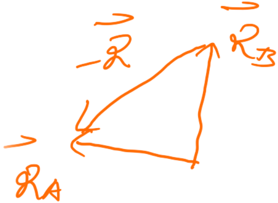
$$= h_v + h_r + \boxed{\Delta h_{vr} \simeq 0\ \text{混合转动和转动}}$$

$$h_v = -\frac{\hbar^2}{2\mu}\partial_x^2 + \frac{1}{2}\mu\omega^2 x^2 + V_0 \qquad (x = R - R_0)$$

$$h_r = -\frac{\hbar^2}{2I}\left[\left(\frac{1}{\sin\theta}\partial_\theta\right)^2 + \frac{1}{\sin^2\theta}\partial_\phi^2\right] \qquad (I = \mu R_0^2)$$

核的全同性对转动本征态的影响

A 和 B 核是否全同对分子的本征态有影响



$$\Phi_{nlm}(\mathbf{R}, s_A, s_B) = \frac{Q_n(R)}{R} Y_{lm}(\theta, \phi)\chi(s_A, s_B)$$

$$\xrightarrow{A \Leftrightarrow B} \Phi_{nlm}(-\mathbf{R}, s_B, s_A)$$

$$= \Phi_{nlm}(R, \pi - \theta, \pi + \phi, s_B, s_A)$$

$$= \frac{Q_n(R)}{R} Y_{lm}(\pi - \theta, \pi + \phi)\chi(s_B, s_A)$$

$$= (-1)^l \frac{Q_n(R)}{R} Y_{lm}(\theta, \phi)\chi(s_B, s_A)$$

- A、B 两个粒子不同时，没有对称性要求，所有态均可
- A、B 是全同的 Fermion 时，只有交换为负号时才允许
  $\Rightarrow \chi(s_A, s_B) = -(-)^l \chi(s_B, s_A) = (-)^{l+1} \chi(s_B, s_A)$
- A、B 是全同的 Boson 时，只有交换为正号时才允许
  $\Rightarrow \chi(s_A, s_B) = (-)^l \chi(s_B, s_A)$

☞ 振动自由度和全同交换无关

振动热容

$$
\begin{aligned}
h_v &= -\frac{\hbar^2}{2\mu}\partial_x^2 + \frac{1}{2}\mu\omega^2 x^2 + V_0 \\
h_v|Q_n\rangle &= \varepsilon_n|Q_n\rangle = [(n+1/2)\hbar\omega + V_0]|Q_n\rangle \qquad n = 0, 1, 2, \cdots, \omega_n = 1 \\
\Theta_v &= \hbar\omega/k_B \sim 100 - 1000\ K \\
z_v &= \sum_n e^{-\beta\varepsilon_n} = e^{-\beta(\hbar\omega/2+V_0)}\sum_{n=0}^{\infty} e^{-n\beta\omega_n} = \frac{e^{-\beta(\hbar\omega/2+V_0)}}{1-e^{-\beta\hbar\omega}} \\
U &= -N\left(\frac{\partial \ln z}{\partial\beta}\right) = N(V_0 + \hbar\omega/2) + \hbar\omega\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\
&= N\left(V_0 + \frac{\hbar\omega}{2}\right) + \frac{N\hbar\omega}{e^{\beta\hbar\omega}-1} = N\left(V_0 + \frac{\hbar\omega}{2}\right) + \frac{Nk_B\Theta_v}{e^{\Theta_v/T}-1} \\
C_v &= \left(\frac{\partial U}{\partial T}\right)_V = \frac{Nk_B\Theta_v^2}{T^2}\frac{e^{\Theta_v/T}}{(e^{\Theta_v/T}-1)^2} = \frac{Nk_B\Theta_v^2}{4T^2\sinh^2(\Theta_v/2T)}
\end{aligned}
$$

☞基态能量选择不影响热容

振动热容

$$C_v = \frac{Nk_B\Theta_v^2}{T^2}\frac{e^{\Theta_v/T}}{(e^{\Theta_v/T}-1)^2} = \frac{Nk_B\Theta_v^2}{4T^2\sinh^2(\Theta_v/2T)}$$

- 高温极限

$$T \gg \Theta_v \Rightarrow \Theta_v/T \ll 1 \Rightarrow \sinh x \simeq x$$

$$C_v = \frac{Nk_B\Theta_v^2}{4T^2\sinh^2(\Theta_v/2T)} = \frac{Nk_B\Theta_v^2}{4T^2(\Theta_v/2T)^2} = Nk_B$$

☞ 能量均分原理，$h_v = p^2/(2\mu) + \mu\omega^2x^2/2$

- 低温极限

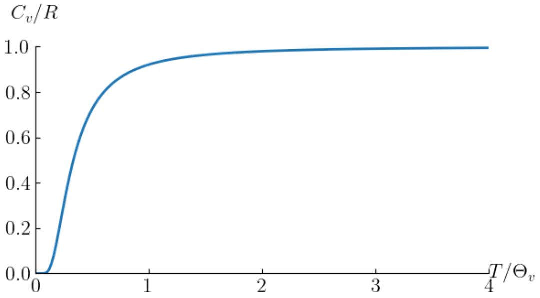
$$T \ll \Theta_v \Rightarrow \frac{\Theta_v}{T} \gg 1$$

$$C_v \simeq Nk_B\frac{\Theta_v^2}{T^2}e^{-\Theta_v/T}$$

和两能级系统结果相同

$$T \to 0 \Rightarrow C_v \to 0$$ 自由度冻结

振动热容



- 低温下：能级量子化重要，振动自由度冻结，$T \to 0$ 时，$C \to 0$，符合热力学第三定律
- 非常低温时和两能级系统结果相同
- 振动热容随温度升高单调上升
- 高温时恢复到经典结果，服从能量均分原理

A-B 式分子气体的转动热容

不考虑全同性，所有态都可能出现

$$h_r = \frac{\hat{L}^2}{2I} \qquad h_r|\psi_{lm}\chi(A,B)\rangle = \varepsilon_l|\psi_{lm}\rangle|S_A S_z^A\rangle|S_B S_z^B\rangle$$

$$\varepsilon_l = \frac{\hbar^2 l(l+1)}{2I} = l(l+1)k_B\Theta_r \qquad \Theta_r = \hbar^2/(2Ik_B)$$

$$\omega_l = (2l+1)(2S_A+1)(2S_B+1) \Leftarrow \begin{cases} m & = -l, -l+1, \cdots, l-1, l \\ S_z^A & = -S_A, -S_A+1, \cdots, S_A-1, S_A \\ S_z^B & = -S_B, -S_B+1, \cdots, S_B-1, S_B \end{cases}$$

$$= \omega_S(2l+1)$$

$$z_r = \sum_{l=0}^{\infty} \omega_l e^{-l(l+1)\Theta_r/T} = \omega_S \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T}$$

☞无解析解，只能先看高低温极限

A-B 式分子气体的转动热容

$$z_r = \sum_{l=0}^{\infty} \omega_l e^{-l(l+1)\Theta_r/T} = \omega_S \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T}$$

- 低温极限：$T \ll \Theta_r \Rightarrow \Theta_r/T \gg 1$

$$z_r = \omega_S \left[1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + 7e^{-12\Theta_r/T} + \cdots \right]$$

$$\ln z_r \simeq \ln \omega_S + 3e^{-2\Theta_r/T} + \cdots$$

$$U = Nk_B T^2 \left(\frac{\partial \ln z_r}{\partial T} \right) = 3Nk_B T^2 \times 2 \frac{\Theta_r}{T^2} e^{-2\Theta_r/T}$$

$$= 6Nk_B \Theta_r e^{-2\Theta_r/T}$$

$$C_r = \left(\frac{\partial U}{\partial T} \right)_V = 12Nk_B \frac{\Theta_r^2}{T^2} e^{-2\Theta_r/T} = 3Nk_B \left(\frac{2\Theta_r}{T} \right)^2 e^{-2\Theta_r/T}$$

$$C_v = Nk_B \left(\frac{\Theta_v}{T} \right)^2 e^{-\Theta_v/T}$$

和两能级系统或者振动热容类似，但第一激发态三重简并使转动热容变为三倍

A-B 式分子气体的转动热容

$$z_r = \sum_{l=0}^{\infty} \omega_l e^{-l(l+1)\Theta_r/T} = \omega_S \sum_{l=0}^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T}$$

- 高温极限：$T \gg \Theta_r \Rightarrow \Theta_r/T \ll 1$

$$\begin{aligned} z_r &= \omega_S \int_0^{\infty} (2l+1) e^{-l(l+1)\Theta_r/T} dl \simeq \omega_S \int_0^{\infty} e^{-l(l+1)\Theta_r/T} d[l(l+1)] \\ &= \omega_S T/\Theta_r \end{aligned}$$

$$\ln z_r \simeq \ln \omega_S + \ln T - \ln \Theta_r$$

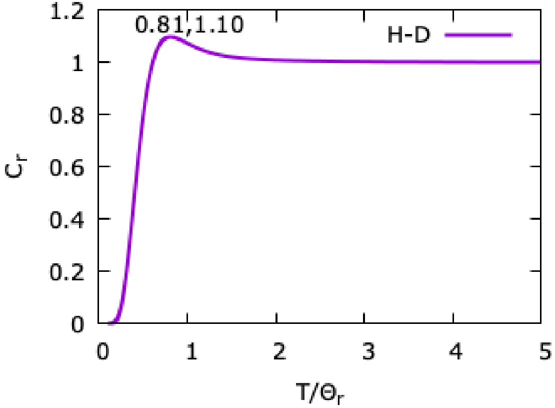
$$U = N k_B T^2 \left(\frac{\partial \ln z_r}{\partial T} \right) = N k_B T$$

$$C_r = \left(\frac{\partial U}{\partial T} \right)_V = N k_B$$

☞ 能量均分原理

A-B 式分子气体的转动热容

数值计算得到的转动热容，以 Nk_B 为单位



☞和振动热容不同，转动热容出现一个峰值

A-B 式分子气体的转动热容

$$f(x) = (2x+1)e^{-x(x+1)\Theta_r/T}$$

$$f(0) = 1 \qquad f'(0) = 2 - \Theta_r/T \qquad f^3(0) = -12\Theta_r/T + O(\Theta_r/T)^2$$

$$\frac{z_r}{\omega_S} = \sum_{l=0}^{\infty} f(l) \simeq \int_0^{\infty} f(x)dx + \frac{f(0)}{2} - \frac{1}{12}f'(0) + \frac{1}{720}f^{(3)}(0) + \cdots$$

$$= \frac{T}{\Theta_r} + \frac{1}{2} - \frac{1}{12}(2 - \Theta_r/T) + \frac{-12\Theta_r/T}{720} + \cdots$$

$$= \frac{T}{\Theta_r} + \frac{1}{3} + \frac{\Theta_r}{15T} + \cdots$$

$$\ln z_r = \ln\omega_s + \ln\frac{T}{\Theta_r} + \ln\left[1 + \frac{\Theta_r/T}{3} + \frac{(\Theta_r/T)^2}{15} + \cdots\right]$$

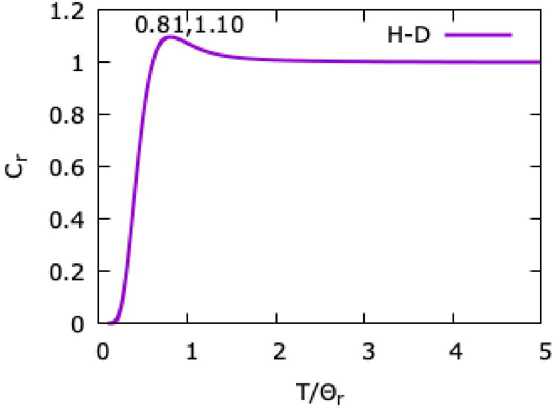
$$\simeq \ln\omega_s + \ln\frac{T}{\Theta_r} + \frac{\Theta_r}{3T} + \frac{\Theta_r^2}{90T^2} + \cdots$$

$$U = Nk_BT^2\left(\frac{\partial \ln z_r}{\partial T}\right) = Nk_B\left[T - \frac{\Theta_r}{3} - \frac{\Theta_r^2}{45T} + \cdots\right]$$

$$C_r = \left(\frac{\partial U}{\partial T}\right)_V = Nk_B + \frac{\Theta_r^2}{45T^2}Nk_B + \cdots > Nk_B$$

A-B 式分子气体的转动热容

数值计算得到的转动热容，以 Nk_B 为单位



☞和振动热容不同，转动热容出现一个峰值

☞第一激发态三重简并使转动热容随温度快速增长，冲过头了

H_2 转动热容

- H_2 是转动惯量最小的双原子分子
  $k_B\Theta_r = \hbar^2/(2I) \sim 100$ K$\gg$ 沸点 21 K
  是唯一一种能够在常压下观测到转动量子化效应的气体
- H_2 的热容问题困扰了物理学家几十年时间
  20 世纪初的几个大物理学家都曾经试图解决这个问题，但是都未获得成功，包括 Einstein, Bohr 等
- 量子化、全同性以及亚稳态等几个问题综合在一起造成了这一看似简单的体系难以得到解决

H_2 的转动能谱

$$h_r = \frac{\hat{L}^2}{2I} \qquad h_r|\psi_{lm}(\theta,\phi)\chi(A,B)\rangle = \varepsilon_l|\psi_{lm}(\theta,\phi)\rangle|\chi(A,B)\rangle$$

$$\varepsilon_l = \frac{\hbar^2 l(l+1)}{2I} = l(l+1)k_B\Theta_r \qquad \Theta_r = \hbar^2/(2I)$$

H 的核只有一个质子，自旋 1/2，是 Fermion，服从交换反对称

$$\begin{aligned}|\psi_{lm}(\theta,\phi)\rangle|\chi(A,B)\rangle \xrightarrow{A\Leftrightarrow B} & |\psi_{lm}(\pi-\theta,\pi+\phi)\rangle|\chi(B,A)\rangle \\ &= (-1)^l|\psi_{lm}(\theta,\phi)\rangle\chi(B,A)\rangle \\ &= -|\psi_{lm}(\theta,\phi)\rangle\chi(A,B)\rangle\end{aligned}$$

$$\Rightarrow \chi(A,B) = (-)^{l+1}\chi(B,A)$$

- ☞ 角动量量子数 l 奇偶不同的时候，角动量波函数的奇偶性不同，导致允许的自旋波函数奇偶性需要相应变化
- ☞ 核自旋虽然不影响能谱，但是影响允许的态，也就是简并度

H_2 的转动能谱

- 仲氢，parahydrogen：角动量波函数为偶，$l \in \{0, 2, 4, \cdots, \}$
  自旋波函数为奇

$$|\chi(A,B)\rangle = -|\chi(B,A)\rangle = \frac{1}{\sqrt{2}}\left[\left|\frac{1}{2}\right\rangle_A \left|\frac{-1}{2}\right\rangle_B - \left|\frac{-1}{2}\right\rangle_A \left|\frac{1}{2}\right\rangle_B\right]$$

$$= \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \qquad \boxed{S = 0, S_z = 0,\ \text{自旋单态}}$$

简并度：$\omega_l = 1 \times (2l + 1)$

- 正氢，orthohydrogen：角动量波函数为奇，$l \in \{1, 3, 5, \cdots, \}$
  自旋波函数为偶 $\boxed{\text{自旋三态}}$

$$|\chi(A,B)\rangle = |\chi(B,A)\rangle = \begin{cases} |\uparrow\uparrow\rangle & S = 1, S_z = 1 \\ \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle] & S = 1, S_z = 0 \\ |\downarrow\downarrow\rangle & S = 1, S_z = -1 \end{cases}$$

简并度：$\omega_l = 3 \times (2l + 1)$

平衡的 H_2 热容

$$z_r = \sum_l \omega_l e^{-\beta\varepsilon_l} = z_p + z_o$$

$$= \sum_{l=0,2,4,\cdots} 1 \times (2l+1) e^{-l(l+1)\Theta_r/T} + \sum_{l=1,3,5,\cdots} 3 \times (2l+1) e^{-l(l+1)\Theta_r/T}$$

- 高温极限

$$z_p = 1 \times \frac{1}{2}\int_0^\infty f(l)dl = \frac{1}{2}\frac{T}{\Theta_r}$$

$$z_o = 3 \times \frac{1}{2}\int_0^\infty f(l)dl = \frac{3}{2}\frac{T}{\Theta_r}$$

$$z_r = 2\frac{T}{\Theta_r}$$

A-B 分子 $z_r = 4T/\Theta_r$

$$U = Nk_BT \qquad C_r = Nk_B$$

能量均分原理

平衡的 H_2 热容

$$z_r = \sum_l \omega_l e^{-\beta\varepsilon_l} = z_p + z_o$$
$$= \sum_{l=0,2,4,\cdots} 1 \times (2l+1) e^{-l(l+1)\Theta_r/T} + \sum_{l=1,3,5,\cdots} 3 \times (2l+1) e^{-l(l+1)\Theta_r/T}$$

- 低温极限

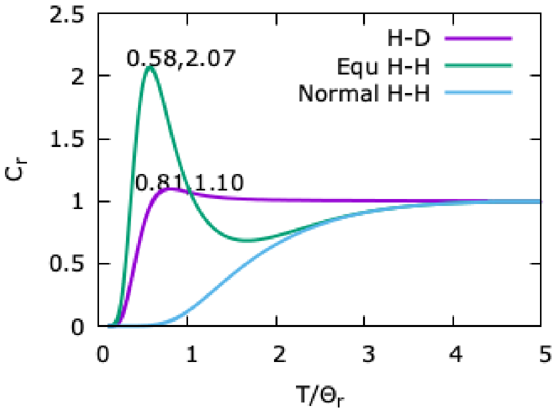
$$z_r = 1 + 9e^{-2\Theta_r/T} + \cdots$$

A-B 分子 $z_r = 4(1 + 3e^{-2\Theta_r/T} + \cdots)$

$$\ln z_r \simeq 9e^{-2\Theta_r/T}$$
$$U = 9Nk_B(2\Theta_r)e^{-2\Theta_r/T}$$
$$C_r = 9Nk_B\left(\frac{2\Theta_r}{T}\right)^2 e^{-2\Theta_r/T}$$

A-B 分子 $C_r = 3Nk_B\left(\frac{2\Theta_r}{T}\right)^2 e^{\frac{-2\Theta_r}{T}}$

平衡的 H_2 热容



- ☞ 第一激发态简并度是基态的 9 倍，峰的现象更加明显
- ☞ 实际上测量到的数据几乎看不到峰

正常氢和平衡氢

- 正氢之间可以互相转换、仲氢之间也可以互相转换
- 正氢和仲氢之间的转换速度非常慢
  低温下 $\sim 10^3$ 小时 ~ 1 个月
- 实验测 H_2 的热容时是基本上从室温降温后直接测量

☞ 实验测量的氢气实际上不是处于同一的平衡态，而是正氢系统和仲氢系统这两个子系统混合在一起的结果

平衡氢: 平衡态，正氢和仲氢比例按照当前温度的 Boltzmann 统计来确定

正常氢：从室温下降温得到的亚稳态，正氢和仲氢比例保持室温下的比例不变

正常氢和平衡氢

- 温度为 T 时，平衡氢中正氢和仲氢的比例

$$a_l = \frac{N}{z_r}\omega_l e^{-\beta\varepsilon_l}$$

$$n_{ortho} = \sum_{l\in ortho-hydrogen} a_l = \frac{N}{z_r}\sum_{l=1,3,\cdots} 3(2l+1)e^{-\beta\varepsilon_l} = N\frac{z_o}{z_r}$$

$$n_{para} = \sum_{l\in para-hydrogen} a_l = \frac{N}{z_r}\sum_{l=0,2,\cdots} 3(2l+1)e^{-\beta\varepsilon_l} = N\frac{z_p}{z_r}$$

$$\frac{n_{ortho}}{n_{para}} = \frac{z_o}{z_p}$$

- 室温下，正氢和仲氢的比例 = 正常氢的正氢和仲氢比例

$$z_p \simeq \frac{T}{2\Theta_r} \qquad z_o \simeq \frac{3T}{2\Theta_r} \qquad z_r = \frac{2T}{\Theta_r} \qquad T \gg \Theta_r$$

$$n_{para} = \frac{N}{4} \qquad n_{ortho} = \frac{3N}{4} \qquad n_{para} : n_{ortho} = 1:3$$

低温正常氢的热容

$$z_o = \sum_{l=1,3,\cdots} \omega_l e^{-\beta\varepsilon_l} = 3[3e^{-2\Theta_r/T} + 7e^{-12\Theta_r/T} + \cdots]$$

$$= 9e^{-2\Theta_r/T}[1 + 7/3e^{-10\Theta_r/T} + \cdots]$$

$$\ln z_o \simeq \ln 9 - 2\frac{\Theta_r}{T} + \frac{7}{3}e^{-10\Theta_r/T} + \cdots$$

$$U_o = Nk_BT^2\left(\frac{\partial \ln z_p}{\partial T}\right) = Nk_B\left[2\Theta_r + \frac{7}{3}\times 10\Theta_r e^{-10\Theta_r/T} + \cdots\right]$$

$$C_o = \left(\frac{\partial U_o}{\partial T}\right)_V = Nk_B \times \frac{7}{3}\times\left(\frac{10\Theta_r}{T}\right)^2 e^{-10\Theta_r/T}$$

$$z_p = \sum_{l=0,2,\cdots} \omega_l e^{-\beta\varepsilon_l} = 1 + 5e^{-6\Theta_r/T} + \cdots$$

$$\ln z_p = 5e^{-6\Theta_r/T} + \cdots$$

$$U_p = Nk_BT^2\left(\frac{\partial \ln z_p}{\partial T}\right) = Nk_B \times 5\times 6\Theta_r e^{-6\Theta_r/T}$$

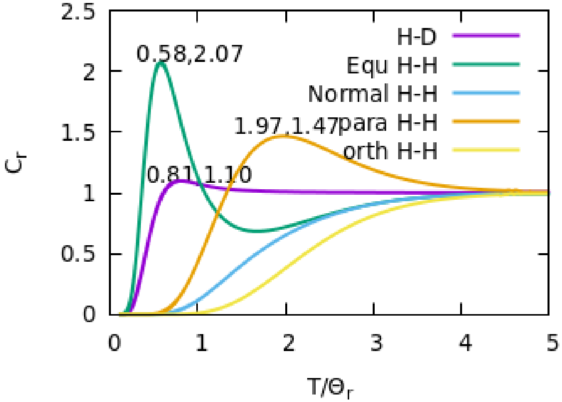
$$C_p = Nk_B \times 5\times\left(\frac{6\Theta_r}{T}\right)^2 e^{-6\Theta_r/T}$$

低温正常氢的热容

$$C_o = Nk_B \times \frac{7}{3} \times \left(\frac{10\Theta_r}{T}\right)^2 e^{-10\Theta_r/T}$$

$$C_p = Nk_B \times 5 \times \left(\frac{6\Theta_r}{T}\right)^2 e^{-6\Theta_r/T}$$

$$C_r = \frac{1}{4}C_p + \frac{3}{4}C_o$$



双原子分子气体热容

- 温度升高热容增加
  原来冻结的自由度“解冻”

$$C = \frac{3R}{2} \xrightarrow{T>\Theta_r \sim 10K} \frac{5R}{2} \xrightarrow{T>\Theta_v \sim 10^4 K} \frac{7R}{2}$$

$$\xrightarrow{T>\Theta_e \sim 10^{4-5} K} \frac{(N_e+7)}{2} R \xrightarrow{T>\Theta_M \sim 1MeV/k_B = 10^7 K} \frac{N_e + N_c + 7}{2} R$$

- 最大可能温度

$$C_v \simeq N k_B/2 \simeq \frac{U}{2Mc^2} k_B$$

$$\frac{dU}{dT} = C_v = \frac{U}{2Mc^2} k_B$$

$$T \simeq \frac{2Mc^2}{k_B} \ln \frac{U}{V} = \frac{2Mc^2}{k_B} \ln \rho c^2$$

$$T_{max} \sim \frac{2Mc^2}{k_B} \ln \rho_{Planck} c^2$$

7.8 准经典近似

- 单粒子量子力学描述：量子态
- 单粒子经典力学描述：相空间里的点 $\boldsymbol{r}, \boldsymbol{p}$
- 由测不准原理，量子力学里无法同时确定 $\boldsymbol{r}$ 和 $\boldsymbol{p}$
  ☞相空间中非常靠近的点在量子力学里无法区分
  ☞一个量子态占据相空间体积 $\Delta\boldsymbol{r}\Delta\boldsymbol{p} = h^d$

$$\sum_s f(s) \Rightarrow \sum_i f(\boldsymbol{r}_i, \boldsymbol{p}_i) = \int \frac{d\boldsymbol{r}d\boldsymbol{p}}{h^d} f(\boldsymbol{r}, \boldsymbol{p})$$

  ☞单粒子本征能量直接用单粒子 Hamitonian 取代

☞ Boltzmann 在计算微观状态数时，就是把相空间离散化，计算得到 $\Omega \Rightarrow z$。能量、热容等物理量和 ΔV 的选择无关，但是配分函数、熵的绝对数值和 ΔV 有关。

- 选取 $\Delta V = h^d$ 可以使得经典计算结果和量子计算结果完全一样，没有任何区别。

准经典近似

$$z = \sum_s e^{-\beta \varepsilon_s} \qquad \Rightarrow \qquad z_c = \int \frac{d\boldsymbol{r}\, d\boldsymbol{p}}{h^d} e^{-\beta h(\boldsymbol{r},\boldsymbol{p})}$$

$$a_l = \frac{N}{z} \omega_l e^{-\beta \varepsilon_l} \qquad f(\boldsymbol{r},\boldsymbol{p}) \Delta\boldsymbol{r} \Delta\boldsymbol{p} = \frac{N}{z_c} \frac{\Delta\boldsymbol{r} \Delta\boldsymbol{p}}{h^d} e^{-\beta h(\boldsymbol{r},\boldsymbol{p})}$$

$$f(\boldsymbol{r},\boldsymbol{p}) = \frac{N}{z_c h^d} e^{-\beta h(\boldsymbol{r},\boldsymbol{p})}$$

$$U = -N \left(\frac{\partial \ln z}{\partial \beta} \right)_V \qquad U = -N \left(\frac{\partial \ln z_c}{\partial \beta} \right)_V$$

$$= N k_B T^2 \left(\frac{\partial \ln z}{\partial T} \right)_V \qquad = N k_B T^2 \left(\frac{\partial \ln z_c}{\partial T} \right)_V$$

$$p = (N/\beta) \left(\frac{\partial \ln z}{\partial V} \right)_\beta \qquad p = (N/\beta) \left(\frac{\partial \ln z_c}{\partial V} \right)_\beta$$

$$= N k_B T \left(\frac{\partial \ln z}{\partial V} \right)_T \qquad = N k_B T \left(\frac{\partial \ln z_c}{\partial V} \right)_T$$

$$S = \frac{U}{T} + N k_B \ln z \qquad S = \frac{U}{T} + N k_B \ln z_c$$

$$F = -N k_B T \ln z \qquad F = -N k_B T \ln z_c$$

准经典近似：盒中理想气体

$$\hat{h} = \boldsymbol{p}^2/2m + V(\boldsymbol{r}) = \begin{cases} 0 & \boldsymbol{r} \in Box(L_x, L_y, L_z) \\ \infty & otherwise \end{cases}$$

$$z = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$z_c = \int \frac{d\boldsymbol{r}d\boldsymbol{p}}{h^3} e^{-\beta h(\boldsymbol{r},\boldsymbol{p})} = \frac{1}{h^3}\int_{Box} d\boldsymbol{r} \int d\boldsymbol{p}^3 e^{-\beta \boldsymbol{p}^2/(2m)}$$

$$= \frac{4\pi V}{h^3}\int_0^\infty dp\ p^2 e^{-p^2/(2mk_BT)} \qquad \boxed{u^2 = p^2/(2mk_BT) \to t = u^2}$$

$$= \frac{4\pi V}{h^3}(2mk_BT)^{3/2}\int_0^\infty e^{-u^2}u^2 du = \int_0^\infty e^{-t} t dt^{1/2} = \frac{1}{2}\int_0^\infty e^{-t} t^{1/2} dt$$

$$= 4\pi V\left(\frac{2mk_BT}{h^2}\right)^{3/2}\frac{1}{2}\boxed{\Gamma(3/2) = 1/2\Gamma(1/2) = \sqrt{\pi}/2}$$

$$= V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = z$$

Maxwell 速度分布

$$f_B(\boldsymbol{r},\boldsymbol{p}) = \frac{N}{z_c h^3} e^{-\beta h(\boldsymbol{r},\boldsymbol{p})}$$

$$f_B(\boldsymbol{r},\boldsymbol{p}) d\boldsymbol{r} d\boldsymbol{p} = f_B(\boldsymbol{r}, m\boldsymbol{v}) d\boldsymbol{r} d(m\boldsymbol{v}) = f_M(\boldsymbol{r},\boldsymbol{v}) d\boldsymbol{r} d\boldsymbol{v}$$

$$\begin{aligned} f_M(\boldsymbol{v}) = f_M(\boldsymbol{r},\boldsymbol{v}) &= m^3 f_B(\boldsymbol{r}, m\boldsymbol{v}) \\ &= m^3 \frac{N}{Vh^3}\left(\frac{2\pi m k_B T}{h^2}\right)^{-3/2} e^{-(m\boldsymbol{v})^2/(2mk_BT)} \\ &= \frac{N}{V}\left(\frac{2\pi k_B T}{m}\right)^{-3/2} e^{-m\boldsymbol{v}^2/(2k_BT)} \end{aligned}$$

$\overline{\boldsymbol{v}} = \boldsymbol{v}_m = 0$ ☞ 平均速度 = 最可几速度

高斯分布：满足大数定理

Maxwell 速度分布

$$f_M(v) = \int f_M(\boldsymbol{v})\delta(v - |\boldsymbol{v}|)d\boldsymbol{r} = 4\pi\frac{N}{V}\left(\frac{2\pi k_B T}{m}\right)^{-3/2} v^2 e^{-mv^2/(2k_BT)}$$

$$\overline{mv^2/2} = 3k_BT/2 \qquad \Rightarrow \overline{v^2} = 3k_BT/m$$

$$\overline{v} = \frac{\int v f_M(v)dv}{\int f_M(v)dv} = \sqrt{\frac{2k_BT}{m}}\frac{\int_0^\infty x^3 e^{-x^2}dx = 1/2\int_0^\infty te^{-t}dt}{\int_0^\infty x^2 e^{-x^2}dx = 1/2\int_0^\infty t^{1/2}e^{-t}dt}$$

$$= \sqrt{\frac{2k_BT}{m}}\frac{\Gamma(2)}{\Gamma(3/2)} = \sqrt{\frac{8k_BT}{\pi m}}$$

$$0 = f'_M(v_m) \propto [2v_m - mv_m^3/(k_BT)]$$

$$\Rightarrow v_m = \sqrt{2k_BT/m}$$

☞ 最可几速率 ≠ 平均速率

单粒子态密度

计算配分函数等物理量时，求和函数只依赖于能量，可以把对态的求和转化为对能量的积分，简化计算。

$$g(\varepsilon) = \sum_s \delta(\varepsilon - \varepsilon_s) = \sum_l \omega_l \delta(\varepsilon - \varepsilon_l)$$

$$g(\varepsilon)\Delta\varepsilon = \int_{\varepsilon}^{\varepsilon+\Delta\varepsilon} \sum_s \delta(\varepsilon - \varepsilon_s) d\varepsilon = \sum_{\{s|\varepsilon_s \in [\varepsilon, \varepsilon+\Delta\varepsilon]\}} 1$$

$$= \boxed{[\varepsilon, \varepsilon + \Delta\varepsilon]\ \text{之间的单粒子态数目}}$$

$$z = \sum_s e^{-\beta\varepsilon_s} = \int d\varepsilon \sum_s \delta(\varepsilon - \varepsilon_s) e^{-\beta\varepsilon_s}$$

$$= \int d\varepsilon\, e^{-\beta\varepsilon} \sum_s \delta(\varepsilon - \varepsilon_s) = \int d\varepsilon\, e^{-\beta\varepsilon} g(\varepsilon)$$

- ☞ 在能量量子化重要的情况下，写成态密度的形式并没有太大优势
- ☞ 在能量量子化不重要的时候，可以用准经典近似或者用求和化积分的方式得到 $g(\varepsilon)$，从而简化计算

单粒子态密度的计算

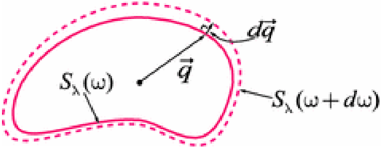
r 维空间，能谱为 $\varepsilon_s = \omega_\lambda(\boldsymbol{p},\boldsymbol{x})$，$\boldsymbol{p} = (p_1, p_2, \cdots, p_r)$，$\boldsymbol{x} = (x_1, x_2, \cdots, x_r)$，$\lambda$ 为离散量子数，例如自旋。

$$g(\varepsilon) = \sum_s \delta(\varepsilon - \varepsilon_s) = \sum_\lambda \int \frac{d^r p d^r x}{h^r} \delta[\varepsilon - \varepsilon_\lambda(\boldsymbol{p},\boldsymbol{x})]$$

$$= \sum_\lambda \int \frac{d^{2r} q}{h^r} \delta[\varepsilon - \omega_\lambda(\boldsymbol{q})] \qquad \boxed{\boldsymbol{q} = (\boldsymbol{p},\boldsymbol{x})}$$

$$= \sum_\lambda \oint_{S_\lambda(\omega)\text{ 为能量为 }\omega\text{ 的等能面}} \int \frac{dS_\lambda dq_\perp}{h^r} \delta[\varepsilon - \omega(\boldsymbol{q})]$$

$$= \sum_\lambda \oint_{S_\lambda(\omega)} \frac{dS_\lambda}{|\nabla_{\boldsymbol{q}} \omega(\boldsymbol{q})|}$$



单粒子态密度的计算

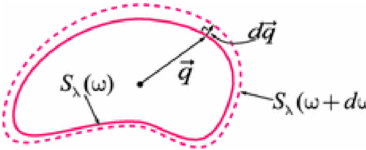
r 维空间，能谱为 $\varepsilon_s = \omega_\lambda(\boldsymbol{p},\boldsymbol{x})$，$\boldsymbol{p} = (p_1, p_2, \cdots, p_r)$，$\boldsymbol{x} = (x_1, x_2, \cdots, x_r)$，$\lambda$ 为离散量子数，例如自旋。

$$z(\varepsilon) = \sum_s \Theta(\varepsilon - \varepsilon_s) = \sum_{\{s|\varepsilon_s \le \varepsilon\}} 1$$

$$g(\varepsilon) = \frac{dz}{d\varepsilon} = \sum_s \delta(\varepsilon - \varepsilon_s)$$

$$z = \sum_\lambda \int_{\varepsilon_\lambda(\boldsymbol{p},\boldsymbol{x}) \le \varepsilon} \frac{d^r p d^r x}{h^r}$$

$$= \sum_\lambda \frac{1}{h^r} \int_{\omega \le \varepsilon} d\omega \oint \frac{dS_\lambda(\omega)}{|\nabla\omega(\boldsymbol{q})|}$$



- 不同的方法计算出来的结果是完全一样的。
- 使用哪种方法看具体问题。

一维谐振子的准经典近似

$$h(x,p) = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} \qquad \hat{h}|n\rangle = (n+1/2)\hbar\omega|n\rangle$$

$$z = \sum_n e^{-\beta(n+1/2)\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} \simeq \frac{k_B T}{\hbar\omega}$$

$$z_c = \int e^{-\beta h(x,p)} \frac{dxdp}{h} = \frac{1}{h}\int_{-\infty}^{\infty} e^{-\beta p^2/(2m)} dp \int_{-\infty}^{\infty} e^{-\beta m\omega^2 x^2/2} dx$$

$$= \frac{1}{h}\sqrt{\frac{2m}{\beta}}\sqrt{\frac{2}{\beta m\omega^2}} \times \left[2\int_0^{\infty} e^{-u^2} du = \int_0^{\infty} t^{-1/2} e^{-t} dt = \Gamma(1/2)\right]^2$$

$$= \frac{2\pi}{\beta h\omega} = \frac{k_B T}{\hbar\omega}$$

一维谐振子的准经典近似

$$g(\varepsilon) = \sum_{n=0}^{\infty} \delta[\varepsilon - (n+1/2)\hbar\omega] = \int_0^{\infty} \delta[\varepsilon - (n+1/2)\hbar\omega]\,dn \simeq \frac{1}{\hbar\omega}(\varepsilon > 0)$$

$$g(\varepsilon) = \int \delta(\varepsilon - p^2/2m - m\omega^2 x^2/2)\frac{dpdx}{h}$$

$$= \frac{1}{h}\int_{-\infty}^{\infty} \frac{dx}{|p/m|_{p=\pm\sqrt{2m\varepsilon - m^2\omega^2 x^2}}} = 2\frac{m}{h}\int_{-\sqrt{2\varepsilon/(m\omega^2)}}^{\sqrt{2\varepsilon/(m\omega^2)}} \frac{dx}{\sqrt{2m\varepsilon - m^2\omega^2 x^2}}$$

$$= \frac{2}{h\omega}\int_{-\sqrt{2m\varepsilon}}^{\sqrt{2m\varepsilon}} \frac{dx}{\sqrt{2m\varepsilon - x^2}} = \frac{2}{h\omega}\int_{-1}^{1} \frac{dx}{\sqrt{1-x^2}} \qquad \boxed{x \rightarrow \cos\theta}$$

$$= \frac{2\pi}{\hbar\omega} = \frac{1}{\hbar\omega}$$

$$z = \int d\varepsilon\, g(\varepsilon) e^{-\beta\varepsilon} = \int_0^{\infty} e^{-\beta\varepsilon}\frac{d\varepsilon}{\hbar\omega} = \frac{1}{\beta\hbar\omega} = \frac{k_B T}{\hbar\omega}$$

平动自由度的态密度

$$h(\boldsymbol{r},\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + V_{Box}(\boldsymbol{r})$$

$$g(\varepsilon) = \sum_s \delta(\varepsilon-\varepsilon_s) = \omega_S \boxed{\text{自旋自由度}} \int \delta[\varepsilon - h(\boldsymbol{r},\boldsymbol{p})] \frac{d\boldsymbol{r}d\boldsymbol{p}}{h^3}$$

$$= \frac{\omega_S V}{h^3}\int \delta(\varepsilon - p^2/2m)p^2 dp d\Omega$$

$$= \frac{4\pi V\omega_S}{h^3}\frac{p^2}{p/m}\bigg|_{p=\sqrt{2m\varepsilon}} = \frac{4m\pi V\omega_S}{h^3}\sqrt{2m\varepsilon}$$

$$= 2\pi V\omega_S\left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\varepsilon}$$

$$g_{2D}(\varepsilon) = \pi A\omega_S\frac{2m}{h^2} \qquad g_{1D}(\varepsilon) = \omega_S L\sqrt{\frac{m}{2h^2\varepsilon}}$$

一般情况：$\omega_S = (2S+1)$，例如电子 $S=1/2$，$\omega_S = 2$
光子：$S=1$，但是 $\omega_S = 2$

理想气体

利用态密度计算单粒子配分函数：$\omega_S = 1$

$$z = \sum_l \omega_l e^{-\beta\varepsilon_l} = \sum_s e^{-\beta\varepsilon_s}$$

$$= \int e^{-\beta\varepsilon(\boldsymbol{p})} \frac{d^3r d^3p}{h^3} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

$$= \int_0^\infty e^{-\varepsilon/(k_BT)} g(\varepsilon) d\varepsilon = \int_0^\infty e^{-\varepsilon/(k_BT)} 2\pi V\left(\frac{2m}{h^2}\right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

$$= 2\pi V\left(\frac{2mk_BT}{h^2}\right)^{3/2} \int_0^\infty e^{-x} x^{1/2} dx$$

$$= 2\pi V\left(\frac{2mk_BT}{h^2}\right)^{3/2} \Gamma\left(\frac{3}{2}\right) = \boxed{= \tfrac{1}{2}\Gamma(1/2) = \sqrt{\pi}/2}$$

$$= V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$$

☞不同方法计算结果都相同。