第七章　几率法
近独立子系组成系统的统计理论

7.9 Bose/Fermi 统计

- Fermi 和 Bose 统计的基本假设和步骤和 Boltzmann 统计完全相同
  - 确定单粒子的本征问题
  - 从单粒子态构造出系统的微观态
  - 利用等几率假设求出分布 $\{a_l\}$ 对应的系统微观态数目 $\Omega(\{a_l\})$
  - 利用等几率假设，找到最可几态 $\{\bar{a}_l\}$，此即热力学平衡态
- 不同的是，从单粒子态构造出系统微观态时需要考虑量子全同性
  - 经典粒子可以区分，不需要考虑全同性
  - Fermion/Boson 不能区分，需要考虑全同性
  - ☞ 由测不准原理，粒子的空间位置不是在某个确定的点上，而是有一定展宽 $\Rightarrow$ 波函数
  - ☞ 当两个粒子波函数有足够多的重叠时，无法区分二者
  - ☞ 全同粒子 $\Rightarrow$ 非定域系/nonlocalized；
    非全同粒子 $\Rightarrow$ 定域系/localized

Bose/Fermi 统计

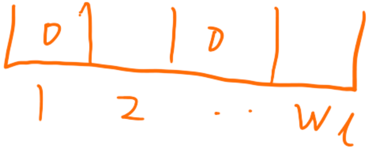
单粒子问题

$\hat{h}|\psi_s\rangle = \varepsilon_s(V)|\psi_s\rangle \qquad \hat{h}|\psi_{l\alpha}\rangle = \varepsilon_l(V)|\psi_{l\alpha}\rangle \qquad \alpha = 1, 2, \cdots, \omega_l$

分布函数 $\{a_l\} \Rightarrow \Omega(E, N, V, \{a_l\})$： $\sum_l a_l = N; \qquad \sum_l a_l \varepsilon_l = E$

- Fermion 粒子不可区分，但是不能有两个粒子处于相同的态：
  ☞每个能级中有 ω_l 个可能的态，选出 a_l 个态放置粒子
  $\Leftrightarrow$ ω_l 个格子放 a_l 个小球，每个格子最多只能放一个球

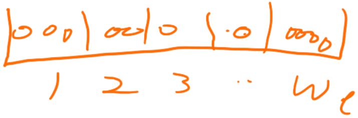
$$\Omega(E, N, V, \{a_l\}) = \prod_l \gamma(a_l, \omega_l) = \prod_l C_{\omega_l}^{a_l}$$



Bose/Fermi 统计

- Boson 粒子不可区分
  ☞每个能级中有 ω_l 个可能的态，安置 a_l 个粒子
  $\Leftrightarrow$ ω_l 个格子放 a_l 个小球，每个格子可以放任意个球 $\Rightarrow$
  $\omega_l - 1$ 个挡板和 a_l 个小球，挑出 $\omega_l - 1$ 个位置放置挡板

$$\Omega(E, N, V, \{a_l\}) = \prod_l \gamma(a_l, \omega_l) = \prod_l C_{\omega_l+a_l-1}^{\omega_l-1} = \prod_l C_{\omega_l+a_l-1}^{a_l}$$



Bose/Fermi 统计

- Boson 粒子不可区分

  ☞每个能级中有 ω_l 个可能的态，安置 a_l 个粒子

  $\Leftrightarrow$ ω_l 个格子放 a_l 个小球，每个格子可以放任意个球

  ☞递推法

$$\gamma(0,\omega_l)=1 \qquad \gamma(1,\omega_l)=\omega_l \qquad \gamma(a_l,1)=1$$

$$\gamma(a_l,\omega_l+1)=\gamma(a_l,\omega_l)+\gamma(a_l-1,\omega_l)+\cdots+\gamma(1,\omega_l)+\gamma(0,\omega_l)$$

$$\Rightarrow \gamma(a_l,\omega_l)=C_{\omega_l+a_l-1}^{\omega_l-1}$$

  ☞系数展开

$$(1+x+x^2+x^3+\cdots)\times\cdots\times(1+x+x^2+x^3+\cdots) \text{☞} \boxed{\omega_l \text{ 项}}$$

$$=\sum_{k=0}^{\infty}\gamma(k,\omega_l)x^k$$

$$(1-x)^{-\omega_l}=\sum_{k=0}^{\infty}\gamma(k,\omega_l)x^k \qquad \Rightarrow \qquad \gamma(a_l,\omega_l)=C_{\omega_l+a_l-1}^{\omega_l-1}$$

最可几态

- Fermion

$$\ln\Omega = \sum_l \ln\gamma(a_l,\omega_l) = \sum_l \ln\frac{\omega_l!}{a_l!(\omega_l-a_l)!}$$

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

$$-[(\omega_l-a_l)\ln(\omega_l-a_l)-(\omega_l-a_l)]\}$$

假设
$\omega_l, a_l, \omega_l - a_l \gg 1$
并非必要。从系综理论可以不需要这些假设。

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

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

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

$$= \sum_l \delta a_l[-\ln a_l+\ln(\omega_l-a_l)-\alpha-\beta\varepsilon_l]$$

$$\ln\frac{\omega_l-a_l}{a_l} = \alpha+\beta\varepsilon_l \qquad \Rightarrow \qquad a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}+1}$$

最可几态

- Boson

$$\ln \Omega = \sum_l \ln \gamma(a_l, \omega_l) = \sum_l \ln \frac{(\omega_l + a_l - 1)!}{(\omega_l - 1)! a_l!} \simeq \sum_l \ln \frac{(\omega_l + a_l)!}{\omega_l! a_l!}$$

$$\simeq \sum_l \{[(\omega_l + a_l)\ln(\omega_l + a_l) - (\omega_l + a_l)]$$

$$- (\omega_l \ln \omega_l - \omega_l) - (a_l \ln a_l - a_l)\}$$

假设 $\omega_l, a_l, \omega_l + a_l \gg 1$ 同样不是必要的。

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

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

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

$$= \sum_l \delta a_l [\ln(\omega_l + a_l) - \ln a_l - \alpha - \beta \varepsilon_l]$$

$$\ln \frac{\omega_l + a_l}{a_l} = \alpha + \beta \varepsilon_l \qquad \Rightarrow \qquad a_l = \frac{\omega_l}{e^{\alpha + \beta \varepsilon_l} - 1}$$

最可几态

☞ 最可几分布

$$a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} \pm 1} = \frac{\omega_l}{e^{\beta(\varepsilon_l-\mu)} + 1}$$

+1 Fermion； −1 Boson

$$\alpha = -\beta\mu$$

$$a_s = \frac{a_l}{\omega_l} = \frac{1}{e^{\alpha+\beta\varepsilon_s} \pm 1} = \frac{1}{e^{\beta(\varepsilon_s-\mu)} \pm 1}$$

态 s 上的平均粒子数

☞ 有两个未知参数 α, β
需要从粒子数和能量来确定 $\Rightarrow \alpha = \alpha(E, N, V), \beta = \beta(E, N, V)$
$\Rightarrow$ 数学上非常困难 $\Rightarrow$ 变换参量

巨配分函数

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

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

$$d \ln \overline{\Omega} = \alpha dN + \beta dE$$

$$\alpha = \alpha(E, N, V) = \left(\frac{\partial \ln \overline{\Omega}}{\partial N}\right)_{EV} \qquad \beta = \beta(E, N, V) = \left(\frac{\partial \ln \overline{\Omega}}{\partial E}\right)_{NV}$$

$$\ln \Xi = \ln \Xi(\beta, \alpha, V) = \ln \overline{\Omega} - \alpha N - \beta E$$

$$d \ln \Xi = -E d\beta - N d\alpha$$

巨配分函数

- Fermion

$$
\begin{aligned}
\ln \Xi = \ln \Xi(\beta, \alpha, V) &= \ln \overline{\Omega} - \alpha N - \beta E \\
&= \sum_l \{\omega_l \ln \omega_l - \omega_l - (a_l \ln a_l - a_l) \\
&\qquad - [(\omega_l - a_l) \ln(\omega_l - a_l) - (\omega_l - a_l)] - (\alpha + \beta\varepsilon) a_l\} \\
&= \sum_l \left\{\omega_l \ln \frac{\omega_l}{\omega_l - a_l} - a_l \ln \frac{a_l}{\omega_l - a_l} - (\alpha + \beta\varepsilon_l) a_l\right\}
\end{aligned}
$$

$$
a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} + 1} \qquad \omega_l - a_l = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l} + 1} = \frac{\omega_l}{1 + e^{-\alpha-\beta\varepsilon}}
$$

$$
\frac{\omega_l}{\omega_l - a_l} = 1 + e^{-\alpha-\beta\varepsilon_l} \qquad \frac{a_l}{\omega_l - a_l} = e^{-\alpha-\beta\varepsilon_l}
$$

$$
\begin{aligned}
\ln \Xi &= \sum_l \left[\omega_l \ln\left(1 + e^{-\alpha-\beta\varepsilon_l}\right) + a_l(\alpha + \beta\varepsilon_l) - a_l(\alpha + \beta\varepsilon_l)\right] \\
&= \sum_l \omega_l \ln\left(1 + e^{-\alpha-\beta\varepsilon_l}\right)
\end{aligned}
$$

巨配分函数

- Boson

$$
\begin{aligned}
\ln \Xi &= \ln \Xi(\beta, \alpha, V) = \ln \overline{\Omega} - \alpha N - \beta E \\
&= \sum_l \{[(\omega_l + a_l)\ln(\omega_l + a_l) - (\omega_l + a_l)] \\
&\qquad - (a_l \ln a_l - a_l) - (\omega_l \ln \omega_l - \omega_l) - (\alpha + \beta\varepsilon)a_l\} \\
&= \sum_l \left\{\omega_l \ln \frac{\omega_l + a_l}{\omega_l} + a_l \ln \frac{\omega_l + a_l}{a_l} - (\alpha + \beta\varepsilon_l)a_l\right\}
\end{aligned}
$$

$$
a_l = \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l} - 1} \qquad \omega_l + a_l = \frac{\omega_l e^{\alpha+\beta\varepsilon_l}}{e^{\alpha+\beta\varepsilon_l} - 1} = \frac{\omega}{1 - e^{-\alpha-\beta\varepsilon_l}}
$$

$$
\frac{\omega_l + a_l}{\omega_l} = [1 - e^{-\alpha-\beta\varepsilon_l}]^{-1} \qquad \frac{\omega_l + a_l}{a_l} = e^{\alpha+\beta\varepsilon_l}
$$

$$
\begin{aligned}
\ln \Xi &= \sum_l \left[\omega_l \ln\left(1 - e^{-\alpha-\beta\varepsilon_l}\right)^{-1} + a_l(\alpha + \beta\varepsilon_l) - a_l(\alpha + \beta\varepsilon_l)\right] \\
&= -\sum_l \omega_l \ln\left(1 - e^{-\alpha-\beta\varepsilon_l}\right)
\end{aligned}
$$

巨配分函数

- 巨配分函数

$$\ln \Xi = \pm \sum_l \omega_l \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_l}\right) \qquad \boxed{+:\ \text{Fermion};\quad -:\ \text{Boson}}$$

$$= \pm \sum_s \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_s}\right) = \pm \sum_s \ln\left[1 \pm e^{-\beta(\varepsilon_s-\mu)}\right]$$

$$\Xi = \prod_l \left(1 \pm e^{-\alpha-\beta\varepsilon_l}\right)^{\pm\omega_l} = \prod_l \left[1 \pm e^{-\beta(\varepsilon_l-\mu)}\right]^{\pm\omega_l}$$

$$= \prod_s \left(1 \pm e^{-\alpha-\beta\varepsilon_s}\right)^{\pm 1} = \prod_s \left[1 \pm e^{-\beta(\varepsilon_s-\mu)}\right]^{\pm 1}$$

- 通过 Legendre 变换，把自由参量从 (E, N, V) 变为了 $(\beta, \alpha, V) \Leftrightarrow (T, \mu, V)$
- 等价于是从孤立系统变成为开放系统
  系统和大热源和大粒子源接触，保持温度和化学势不变
- 在求平衡热力学量时候没有区别

7.10 物理量

$$d\ln\Xi = -Ed\beta - Nd\alpha \qquad U = E = -\left(\frac{\partial \ln\Xi}{\partial\beta}\right)_{\alpha V} \qquad N = -\left(\frac{\partial \ln\Xi}{\partial\alpha}\right)_{\beta V}$$

$$U = E = \sum_l a_l\varepsilon_l = \sum_l \frac{\omega_l\varepsilon_l}{e^{\beta\varepsilon_l+\alpha}\pm 1} = \sum_l \omega_l\varepsilon_l\frac{e^{-\alpha-\beta\varepsilon_l}}{1\pm e^{-\alpha-\beta\varepsilon_l}}$$

$$= \pm\sum_l \omega_l\left[(-)\frac{\partial}{\partial_\beta}\ln\left(1\pm e^{-\alpha-\beta\varepsilon_l}\right)\right]_{\alpha,V}$$

$$= -\frac{\partial}{\partial\beta}\left[(\pm)\sum_l \omega_l \ln\left(1\pm e^{-\alpha-\beta\varepsilon_l}\right)\right] = -\left(\frac{\partial\ln\Xi}{\partial\beta}\right)_{\alpha V}$$

$$N = \sum_l a_l = \sum_l \frac{\omega_l}{e^{\alpha+\beta\varepsilon_l}\pm 1} = \sum_l \frac{\omega_l e^{-\alpha-\beta\varepsilon_l}}{1\pm e^{-\alpha-\beta\varepsilon_l}}$$

$$= (\pm)\sum_l\left[\omega_l(-)\frac{\partial}{\partial\alpha}\left(\ln 1\pm e^{-\alpha-\beta\varepsilon_l}\right)_{\beta V}\right]$$

$$= -\frac{\partial}{\partial\alpha}\left[\pm\sum_l \omega_l\left(\ln 1\pm e^{-\alpha-\beta\varepsilon_l}\right)\right]_{\beta V} = -\left(\frac{\partial\ln\Xi}{\partial\alpha}\right)_{\beta V}$$

压强

$$
\begin{aligned}
U &= \sum_l a_l \varepsilon_l(V) \\
\delta U &= \sum_l \varepsilon_l \delta a_l + \sum_l a_l \delta \varepsilon_l \\
&= \sum_l (\varepsilon_l + \alpha/\beta)\delta a_l + \sum_l a_l \delta \varepsilon_l - (\alpha/\beta) \sum_l \delta a_l \\
&= \delta Q + \delta W + \mu \delta N \qquad \Rightarrow \qquad \alpha = -\beta\mu
\end{aligned}
$$

$$
\begin{aligned}
p &= \frac{\delta W}{\delta V} = -\sum_l a_l \left(\frac{\partial \varepsilon_l}{\partial V}\right) = -\sum_l \omega_l \left(\frac{\partial \varepsilon_l}{\partial V}\right) \frac{e^{-\alpha-\beta\varepsilon_l}}{1 \pm e^{-\alpha-\beta\varepsilon_l}} \\
&= \pm \sum_l \omega_l \left[\frac{\partial}{\beta \partial V} \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_l}\right)\right]_{\alpha,\beta} \\
&= \frac{\partial}{\beta\partial V}\left[(\pm)\sum_l \omega_l \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_l}\right)\right] = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\alpha\beta}
\end{aligned}
$$

熵和 Boltzmann 关系

$$\begin{aligned}
\beta\, \text{đ}Q &= \beta \sum_l (\varepsilon_l + \alpha/\beta) da_l = \sum_l (\beta\varepsilon_l + \alpha) da_l \\
&= \sum_l d[(\beta\varepsilon_l + \alpha)a_l] - \sum_l a_l d(\beta\varepsilon_l + \alpha) \\
&= d[\beta \sum_l a_l \varepsilon_l + \alpha \sum_l a_l] - \sum_l \frac{\omega_l}{e^{\beta\varepsilon_l + \alpha} \pm 1} d(\beta\varepsilon_l + \alpha) \\
&= d(\beta U + \alpha N) + \sum_l (\pm)\omega_l d \ln[1 \pm e^{-\beta\varepsilon_l - \alpha}] \\
&= d(\beta U + \alpha N) + d \ln \Xi = d(\beta U + \alpha N + \ln \Xi)
\end{aligned}$$

$\beta\, \text{đ}Q$ 是全微分 $\Rightarrow \beta$ 是积分因子 $\Rightarrow \beta = 1/(k_B T)$

$$S = k_B(\ln \Xi + \alpha N + \beta U) = k_B(\ln \Xi - \mu N/T + U/T) = k_B \ln \Xi - \frac{\mu N}{T} + \frac{U}{T}$$

$\ln \Xi = \ln \Omega - \alpha N - \beta U \Rightarrow$

$$S = k_B \ln \Omega$$

Boltzmann 关系，对 Boson/Fermion 也成立

巨势和巨配分函数

$$\ln \Xi = \ln \Omega - \alpha N - \beta U$$

$$k_B T \ln \Xi = T k_B \ln \Omega + \mu N - U = TS - U + \mu N = -(F - N\mu) = -J$$

$$J = -k_B T \ln \Xi = J(T, V, \mu)$$

巨势

$$J = F - N\mu = U - TS - N\mu \qquad \Rightarrow dJ = -SdT - pdV - Nd\mu$$

巨势和巨配分函数

$$\lambda = e^{-\alpha} = e^{\beta\mu}$$

$$\ln \Xi = \ln \Xi(\beta, \alpha, V) = \ln \Xi(\beta, \lambda, V) = \ln \Xi(T, \mu, V)$$

$$N = -\left(\frac{\partial \ln \Xi}{\partial \alpha}\right)_{\beta V} = \lambda\left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{\beta V} = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{\beta V} = k_B T\left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{TV}$$

$$U = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\alpha V} = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\lambda V} = -\frac{\partial(\ln \Xi, \alpha)}{\partial(\beta, \alpha)} = -\frac{\partial(\ln \Xi, \alpha)}{\partial(\beta, \mu)}\frac{\partial(\beta, \mu)}{\partial(\beta, \alpha)}$$

$$= -\left[\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\mu V}(-\beta) - \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{\beta V}\left(\frac{\partial \alpha}{\partial \beta}\right)_{\mu}\right]\frac{-1}{\beta}$$

$$= -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\mu V} + N\mu = k_B T^2\left(\frac{\partial \ln \Xi}{\partial T}\right)_{\mu V} + N\mu$$

$$p = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta \alpha} = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta \lambda}$$

$$= \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta, -\beta\mu} = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta, \mu} = k_B T\left(\frac{\partial \ln \Xi}{\partial V}\right)_{T, \mu}$$

7.11 弱简并理想气体

强简并和弱简并气体

单粒子基态能量 $\varepsilon_g = 0$,

$$a_s = \frac{1}{e^{\beta(\varepsilon_s-\mu)} \pm 1} = \frac{1}{e^{\beta\varepsilon_s+\alpha} \pm 1} = \frac{1}{e^{\beta\varepsilon_s}/\lambda \pm 1}$$

- If $\lambda = e^{-\alpha} = e^{\beta\mu} \ll 1$：弱简并，全同性不重要

$$a_s \simeq \lambda e^{-\beta\varepsilon_s} = e^{-\beta\varepsilon_s-\alpha}$$

Boltzmann 分布

- If $\lambda = e^{-\alpha} = e^{\beta\mu} \geq 1$：强简并，全同性重要

低能态上，Fermion

$$a_s = \frac{1}{e^{\varepsilon_s}/\lambda + 1} \simeq 1$$

低能态上，Boson $\lambda \leq 1$

$$a_s = \frac{1}{e^{\beta\varepsilon_s}/\lambda - 1} \simeq \begin{cases} \frac{\lambda}{1-\lambda} \simeq \frac{1}{1-\lambda} \to \infty & \varepsilon_s = 0 \\ \simeq \frac{1}{(1-\lambda)+\beta\epsilon_s} \simeq \frac{k_BT}{\varepsilon_s} & \varepsilon_s > 0 \end{cases}$$

强弱简并判据

$$\lambda = e^{-\alpha} = e^{\beta\mu}$$

- Fermion： $\lambda \geq 1 \Rightarrow \beta\mu \geq 0$
  强简并条件： $\mu/(k_B T) \gg 1$
- Boson： $\varepsilon_s - \mu \geq 0 \Rightarrow \mu \leq 0$
  强简并条件： $\mu \simeq 0$

$$\ln \Xi = \pm \sum_s \ln[1 \pm e^{-\beta(\varepsilon_s - \mu)}] = \pm \sum_s \ln[1 \pm \lambda e^{-\beta \varepsilon_s}]$$

$$= \pm \int_0^\infty g(\varepsilon) \ln[1 \pm \lambda e^{-\beta\varepsilon}] d\varepsilon$$

激发态贡献

$$\pm \omega_g \ln[1 \pm \lambda]$$

基态贡献，多数情况可以忽略不计。
强简并的 Bosonic 气体时需要考虑。

这里的简并指的是量子全同性是否重要，和量子力学中的简并（不同的态本征能量相同）没有关系。更准确的翻译应该是（自由度）强退化或者弱退化气体。

弱简并理想气体

$$g(\varepsilon) = \Omega_s \int \delta\left(\varepsilon - \frac{p^2}{2m}\right)\frac{d^3x d^3p}{h^3} = 2\pi V\Omega_s\left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\varepsilon}$$

$$\ln\Xi = \pm\sum_s \ln[1 \pm e^{-\beta(\varepsilon_s-\mu)}] = \pm\int_0^\infty g(\varepsilon)\ln[1 \pm e^{-\beta(\varepsilon-\mu)}]d\varepsilon$$

$\lambda = e^{\beta\mu}$

$$= \pm\int_0^\infty g(\varepsilon)\ln[1 \pm \lambda e^{-\beta\varepsilon}]d\varepsilon$$

上：Fermion；下 Boson

$$= \pm\int_0^\infty g(\varepsilon)\sum_{n=1}^\infty \frac{(-)^{n+1}(\pm\lambda e^{-\beta\varepsilon})^n}{n} = \sum_{n=1}^\infty \frac{(\mp)^{n+1}\lambda^n}{n}\int_0^\infty g(\varepsilon)e^{-n\beta\varepsilon}d\varepsilon$$

$$= 2\pi V\Omega_s\left(\frac{2m}{h^2}\right)^{3/2}\sum_{n=1}^\infty \frac{(\mp)^{n+1}\lambda^n}{n}\int_0^\infty \sqrt{\varepsilon}e^{-n\beta\varepsilon}d\varepsilon$$

$\lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}}$

$$= 2\pi V\Omega_s\left(\frac{2mk_BT}{h^2}\right)^{3/2}\sum_{n=1}^\infty \frac{(\mp)^{n+1}\lambda^n}{n^{5/2}}\int_0^\infty e^{-t}t^{1/2}dt$$

$= \Gamma(\tfrac{3}{2}) = \sqrt{\pi}/2$

$$= V\Omega_s\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}F_{5/2}^{(\mp)}(\lambda) = \frac{\Omega_S V}{\lambda_T^3}F_{5/2}^{(\mp)}(\lambda) = z(T,V)F_{5/2}^{(\mp)}(\lambda)$$

$$F_\nu^{(\mp)}(\lambda) = \sum_{n=1}^\infty \frac{(\mp)^{n+1}\lambda^n}{n^\nu}$$

z 是非全同粒子的单粒子配分函数

粒子数

$$\ln \Xi = V\Omega_s \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F_{5/2}^{(\mp)}(\lambda) \qquad = z(T,V) F_{5/2}^{(\mp)}(\lambda)$$

$$F_\nu^{(\mp)}(\lambda) = \sum_{n=1}^{\infty} \frac{(\mp)^{n+1}\lambda^n}{n^\nu} \qquad \lambda \left(\frac{\partial F_\nu^{(\mp)}}{\partial \lambda}\right)_{TV} = \sum_{n=1}^{\infty} \frac{(\mp)^{n+1}\lambda^n}{n^{\nu-1}} = F_{\nu-1}^{(\mp)}(\lambda)$$

$$N = \lambda \left(\frac{\partial \ln \Xi}{\partial \lambda}\right)_{TV} = z(T,V)\ F_{3/2}^{(\mp)}(\lambda) \xrightarrow{\lambda \ll 1} \lambda \simeq F_{3/2}^{(\mp)}(\lambda) = e^{-\alpha} = e^{\beta\mu} = \frac{N}{z}$$

- $\lambda \ll 1 \Rightarrow F_\nu^{\mp}(\lambda) \simeq \lambda$。
- 由此得到温度为 T，体积为 V，化学势为 μ 的粒子数 $N = N(T,\mu,V) = N(\beta,\lambda,V)$。
- 类似的，可以计算内能 $U = U(T,\mu,V)$，压强 $p = p(T,\mu,V)$ 等物理量。
- 但是在处理有静止质量的系统时，化学势 μ 不容易确定，而 N 容易确定。因此需要从上面的表达式中反解出 $\mu = \mu(T,N,V)$ 或者 $\lambda = \lambda(T,N,V)$，再进一步得到 $U = U(T,N,V)$。

非简并情况下从粒子数确定化学势

$$N = z(T,V)\ F^{(\mp)}_{3/2}(\lambda)$$

$$F^{(\mp)}_{3/2}(\lambda) = \frac{N}{z(T,V)} = \frac{N}{V\Omega_S}\left(\frac{2\pi m k_B T}{h^2}\right)^{-3/2} = \frac{N\lambda_T^3}{\Omega_S V} \ll 1$$

$$y(T, n = \frac{N}{V}) = \frac{N\lambda_T^3}{\Omega_S V} = \left(\frac{\lambda_T}{a}\right)^3 \ll 1 \Rightarrow \lambda_T \ll a$$

$a^3 = \frac{V}{N/\Omega_S}$， $a \sim$ 原子间

$$y = F^{(\mp)}_{3/2}(\lambda) = \lambda \mp \frac{\lambda^2}{2^{3/2}} + \frac{\lambda^3}{3^{3/2}} \mp \cdots$$

非全同： $\lambda = e^{-\alpha} = \frac{N}{z} = y$

需要反解出 $\lambda = \lambda(y)$，利用待定系数法

$$\lambda = a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \cdots$$

$$y = (a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \cdots) \mp \frac{(a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \cdots)^2}{2^{3/2}} + \frac{(a_0 + a_1 y + a_2 y^2 + a_3 y^3 + \cdots)^3}{3^{3/2}} \mp \cdots$$

$$0 = a_0 \mp \frac{a_0^2}{2^{3/2}} + \frac{a_0^3}{3^{3/2}} \mp \cdots = F^{(\mp)}_{3/2}(a_0) \Rightarrow a_0 = 0$$

从粒子数确定化学势

$$y = a_1 y + a_2 y^2 + a_3 y^3 + \cdots \mp \frac{y^2}{2^{3/2}}(a_1 + a_2 y + a_3 y^2 + \cdots)^2$$

$$+ \frac{y^3}{3^{3/2}}(a_1 + a_2 y + a_3 y^2 + \cdots)^3 \mp \cdots$$

$$= a_1 y + \left(a_2 \mp \frac{a_1^2}{2^{3/2}}\right) y^2 + \left(a_3 \mp \frac{2a_1 a_2}{2^{3/2}} + \frac{a_1^3}{3^{3/2}}\right) y^3 + \cdots$$

$$\Rightarrow a_1 = 1$$

$$0 = a_2 \mp \frac{a_1^2}{2^{3/2}} \qquad \Rightarrow a_2 = \frac{\pm 1}{2^{3/2}}$$

$$0 = a_3 \mp \frac{2a_1 a_2}{2^{3/2}} + \frac{a_1^3}{3^{3/2}} = a_3 - \frac{2}{2^3} + \frac{1}{3^{3/2}} \qquad \Rightarrow a_3 = \frac{1}{4} - \frac{1}{3^{3/2}}$$

$$\lambda = y \pm \frac{1}{2^{3/2}} y^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right) y^3 + \cdots$$

☞ 解析上可以利用 Lagrange inversion theorem 来计算高阶修正。现在多数情况下直接通过数值计算得到结果。

Lagrange inversion theorem

$$z = f(w)$$

$$w = g(z) = a + \sum_n g_n \frac{[z - f(a)]^n}{n!}$$

$$g_n = \lim_{w \to a} \frac{d^{n-1}}{dw^{n-1}} \left\{ \left[\frac{w - a}{f(w) - f(a)} \right]^n \right\}$$

Lagrange inversion theorem

Special case $a = 0$, $f(0) = 0$,

$$z = f(w) = \sum_{k=1}^{\infty} f_k \frac{w^k}{k!} \Rightarrow w = g(z) = \sum_{k=1}^{\infty} g_k \frac{z^k}{k!}$$

$$g_n = \frac{1}{f_1^n} \sum_{k=1}^{n-1} (-)^k n^{(k)} B_{n-1,k}(\hat{f}_1, \hat{f}_2, \cdots, \hat{f}_{n-k}), \qquad n \geq 2$$

$$\hat{f}_k = \frac{f_{k+1}}{(k+1) f_1} \qquad n^{(k)} = n(n+1)\cdots(n+k-1) = \frac{(n+k-1)!}{(n-1)!}$$

Bell 多项式

$$B_{n,k}(x_1, x_2, \cdots, x_{n-k+1}) = \sum_{\substack{j_1+j_2+\cdots+j_{n-k+1}=1 \\ j_1+2j_2+\cdots+(n-k+1)j_{n-k+1}=n}} \frac{n!}{j_1! j_2! \cdots j_{n-k+1}!}$$

$$\times \left(\frac{x_1}{1!}\right)^{j_1} \left(\frac{x_2}{2!}\right)^{j_2} \cdots \left(\frac{x_{n-k+1}}{(n-k+1)!}\right)^{j_{n-k+1}}$$

内能和热容

$$\ln \Xi = V\Omega_s \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F_{5/2}^{\mp}(\lambda) = z(T,V)F_{5/2}^{\mp}(\lambda)$$

$$U = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{\lambda V} = k_B T^2 \left(\frac{\partial \ln \Xi}{\partial T}\right)_{\lambda V} = k_B T^2 \left(\frac{\partial z}{\partial T}\right)_V F_{5/2}^{(\mp)}(\lambda)$$

$$= \frac{3k_B T}{2} z F_{5/2}^{(\mp)}(\lambda) = \frac{3k_B T}{2} z F_{3/2}^{(\mp)}(\lambda) \frac{F_{5/2}^{(\mp)}(\lambda)}{F_{3/2}^{(\mp)}(\lambda)}$$

$$= \frac{3Nk_B T}{2} \frac{F_{5/2}^{(\mp)}(\lambda)}{F_{3/2}^{(\mp)}(\lambda)} = \frac{3Nk_B T}{2y}\left(\lambda \mp \frac{1}{2^{5/2}}\lambda^2 + \frac{1}{3^{5/2}}\lambda^3 + \cdots\right)$$

$$= \frac{3Nk_B T}{2y}\left[y \pm \frac{y^2}{2^{3/2}} + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)y^3 + \cdots\right.$$

$$\left. \mp \frac{y^2}{2^{5/2}}\left(1 \pm \frac{y}{2^{3/2}} + \cdots\right)^2 + \frac{y^3}{3^{5/2}}(1 + \cdots)^3\right]$$

$$y = \frac{N}{V\Omega_s}\left(\frac{2\pi m k_B T}{h^2}\right)^{-\frac{3}{2}}$$

$$= \frac{3Nk_B T}{2}\left[1 \pm \left(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\right)y + \left(\frac{1}{4} - \frac{1}{3^{3/2}} - \frac{2}{2^{5/2}\cdot 2^{3/2}} + \frac{1}{3^{5/2}}\right)y^2 + \cdots\right]$$

$$U = \frac{3Nk_B T}{2}\left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)y^2 + \cdots\right]$$

$$= 3Nk_B T/2 \times (1 \pm 0.1768y - 0.0033y^2 + \cdots)$$

内能和热容

$$\ln \Xi = V\Omega_s \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F_{5/2}^{\mp}(\lambda) = z(T,V) F_{5/2}^{\mp}(\lambda)$$

$$U = \frac{3Nk_BT}{2}\left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)y^2 + \cdots\right]$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{NV} = \frac{3Nk_B}{2}\left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)y^2 + \cdots\right]$$

$$+ \frac{3Nk_BT}{2}\left[\pm\frac{1}{2^{5/2}}\left(\frac{\partial y}{\partial T}\right)_{NV} + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\left(\frac{\partial y^2}{\partial T}\right)_{NV} + \cdots\right]$$

$$= \frac{3Nk_B}{2}\left\{1 \pm \frac{1}{2^{5/2}}\left[y + T\left(\frac{\partial y}{\partial T}\right)_{NV}\right] + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\left[y^2 + T\left(\frac{\partial y^2}{\partial T}\right)_{NV}\right] + \cdot\right.$$

$$= \frac{3Nk_B}{2}\left\{1 \pm \frac{1}{2^{5/2}}(1-3/2)y + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)(1-3)y^2 + \cdots\right\}$$

$$= \frac{3Nk_B}{2}\left\{1 \mp \frac{y}{2^{7/2}} - \left(\frac{1}{4} - \frac{4}{3^{5/2}}\right)y^2 + \cdots\right\}$$

$$= 3Nk_B/2 \times (1 \mp 0.08839y + 0.0066y^2 + \cdots)$$

热容的另外一种表达式

$$U=\frac{3k_BTz(T,V)}{2}F_{5/2}^{(\mp)}(\lambda) \qquad N=z(T,V)F_{3/2}^{\pm}(\lambda)$$

$$C_V=\left(\frac{\partial U}{\partial T}\right)_{NV}=\frac{3k_B}{2}\left(\frac{\partial[Tz]}{\partial T}\right)_{NV}F_{5/2}^{\mp}(\lambda)+\frac{3k_BTz}{2}\left(\frac{\partial F_{5/2}^{\mp}}{\partial T}\right)_{NV}$$

$$\left(\frac{\partial X}{\partial T}\right)_N=\frac{\partial(X,N)}{\partial(T,N)}=\frac{\partial(X,N)}{\partial(T,\lambda)}\frac{\partial(T,\lambda)}{\partial(T,N)}=\left(\frac{\partial X}{\partial T}\right)_\lambda-\left(\frac{\partial X}{\partial \lambda}\right)_T\left(\frac{\partial N}{\partial T}\right)_\lambda\Big/\left(\frac{\partial N}{\partial \lambda}\right)_T$$

$$\left(\frac{\partial F_{5/2}^{\mp}}{\partial T}\right)_N=\left(\frac{\partial F_{5/2}^{\mp}}{\partial T}\right)_\lambda\boxed{=0}$$

$$-\left(\frac{\partial F_{5/2}^{\mp}}{\partial \lambda}\right)_T\boxed{=\frac{F_{3/2}^{\mp}}{\lambda}}\times\left(\frac{\partial N}{\partial T}\right)_\lambda\boxed{=\frac{3N}{2T}}\Big/\left(\frac{\partial N}{\partial \lambda}\right)_T\boxed{=\frac{zF_{1/2}^{\mp}}{\lambda}}$$

$$C_V=\frac{15k_Bz}{4}F_{5/2}^{\mp}-\frac{9Nk_B}{4}\frac{F_{3/2}^{\mp}}{F_{1/2}^{\mp}}=\frac{15Nk_B}{4}\frac{F_{5/2}^{\mp}(\lambda)}{F_{3/2}^{\mp}(\lambda)}-\frac{9Nk_B}{4}\frac{F_{3/2}^{\mp}(\lambda)}{F_{1/2}^{\mp}(\lambda)}$$

压强

$$p = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{T,V} = \frac{k_B T}{V}\ln \Xi = \frac{2U}{3V}$$

$$= N k_B T\left[1 \pm \frac{y}{2^{5/2}} + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)y^2 + \cdots\right]$$

- Fermionic 系统的能量和压强比经典系统大
  - 由于 Pauli 不相容原理，Fermion 更倾向于占据高能的单粒子态，导致能量和压强增大
  - 等价于有个统计上的排斥作用
- Bosonic 系统的能量和压强比经典系统小
  - Boson 更加抱团一点，都倾向于呆在低能的单粒子态上
  - 等价于有个统计上的吸引作用

经典极限

非定域系 $\lambda = e^{\beta\mu} \ll 1$

$$\ln \Xi = \pm \sum_s \ln[1 \pm \lambda e^{-\beta\varepsilon_s}]$$

$$= \lambda \sum_s e^{-\beta\varepsilon_s} = \lambda z$$

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

$$a_s = \frac{1}{\frac{1}{\lambda}e^{\beta\varepsilon_s} \pm 1} \simeq \lambda e^{-\beta\varepsilon_s}$$

$$U = k_B T^2\left(\frac{\partial \ln \Xi}{\partial T}\right)_{\lambda V} = k_B T^2\left(\frac{\partial [\lambda z]}{\partial T}\right)_{\lambda V}$$

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

$$P = k_B T\left(\frac{\partial \ln \Xi}{\partial V}\right)_{T\lambda} = N k_B T\left(\frac{\partial \ln z}{\partial V}\right)_T$$

定域系 $\lambda = e^{\beta\mu} = e^{-\alpha} = N/z$

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

$$N = e^{\beta\mu} z = \lambda z$$

$$a_s = \frac{N}{z} e^{-\beta\varepsilon_s} = \lambda e^{-\beta\varepsilon_s}$$

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

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

经典极限

非定域系 $\lambda = e^{\beta\mu} \ll 1$

$$\ln \Xi = \pm \sum_s \ln[1 \pm \lambda e^{-\beta\varepsilon_s}]$$

$$= \lambda \sum_s e^{-\beta\varepsilon_s} = \lambda z$$

$$\mu = k_B T \ln \lambda = k_B T \ln N/z$$

$$S = k_B \ln \Xi - N\mu/T + U/T$$

$$= k_B N - Nk_B \ln(N/z) + U/T$$

$$= Nk_B \ln z + U/T - k_B(N \ln N - N)$$

$$= Nk_B \ln z + U/T - k_B \ln N!$$

$$= k_B \ln \Omega_{nonlocal}$$

$$F = U - TS = -Nk_B T \ln z + k_B T \ln N!$$

定域系 $\lambda = e^{\beta\mu} = e^{-\alpha} = N/z$

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

$$\mu = k_B T \ln N/z$$

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

$$= k_B \ln \Omega_{local}$$

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

经典极限

非定域系 $\lambda = e^{\beta\mu} \ll 1$

$$S = Nk_B \ln z + U/T - k_B \ln N!$$
$$= k_B \ln \Omega_{nonlocal}$$

定域系 $\lambda = e^{\beta\mu} = e^{-\alpha} = N/z$

$$S = Nk_B \ln z + U/T$$
$$= k_B \ln \Omega_{local}$$

$$\Omega_{nonlocal} = \Omega_{local}/N!$$

- 弱简并条件

$$F^{\pm}_{3/2}(\lambda) = \sum_{l=1}^{\infty} \frac{(\mp)^{l-1}\lambda^l}{l^{3/2}} = y = \frac{1}{\Omega_S}\frac{N}{V}\left(\frac{h^2}{2\pi mk_BT}\right)^{3/2}$$

$$\lambda \simeq y = \frac{N}{\Omega_S V}\left(\frac{h}{\sqrt{2\pi mk_BT}}\right)^3 \sim \left(\frac{\lambda_T}{a}\right)^3$$

$$a = \left(\frac{V}{N}\right)^{1/3}$$ 粒子平均距离 $p_T^2/2m \sim k_BT$

$$\lambda_T = \frac{h}{p_T} = \frac{h}{\sqrt{2mk_BT}}$$ 热运动 de Broglie 波长

经典极限

$\Omega_{nonlocal} = \Omega_{local}/N!$

- 弱简并极限条件

$$\lambda \simeq y \sim (\lambda_T/a)^3 \ll 1$$

- ☞ 全同粒子不可区分
  测不准原理，粒子位置在空间有一定扩展，导致实验上无法精确跟踪每个粒子的运动。当两个全同粒子靠近时，扩展部分交叠，因此无法区分两个粒子。
  空间扩展范围 $\sim \lambda_T$
- ☞ 当粒子距离比较远时，粒子空间扩展导致的效果很小，其效果基本可以忽略不计
  $\Rightarrow$ 内能，压强等和 Boltzmann 统计的结果相同
- ☞ 但是全同性仍然有作用

$$a_s = \lambda e^{-\beta\varepsilon_s} \ll 1$$

平均每个态上粒子数很小，全同性只体现在粒子交换导致的系统态数目减少 $\Rightarrow \Omega_{nonlocal} = \Omega_{local}/N!$

弱简并极限

$a_s = e^{-\beta(\varepsilon_s-\mu)} \ll 1$，因此计算系统微观态数时基本不需要考虑有两个粒子占据相同的单粒子态，全同和非全同差别仅仅体现在粒子在占据态里的交换。

$\Omega_{nonlocal} = \Omega_{local}/N!$

- 不同统计的微观态数目
  - Boltzmann 统计

$$\Omega_{local} = \frac{N!}{\prod_l a_l!}\prod_l \omega_l^{a_l} = N!\prod_l \frac{\omega_l^{a_l}}{a_l!}$$

  - Fermi 统计

$$\Omega_{Fermion} = \prod_l \gamma(a_l,\omega_l) = \prod_l \frac{\omega_l!}{a_l!(\omega_l-a_l)!}$$

$$= \prod_l \frac{\omega_l(\omega_l-1)\cdots(\omega_l-a_l+1)}{a_l!} \simeq \prod_l \frac{\omega_l^{a_l}}{a_l!} \qquad \omega_l \gg a_l \gg 1$$

  - Bose 统计

$$\Omega_{Boson} = \prod_l \gamma(a_l,\omega_l) = \prod_l \frac{(\omega_l+a_l-1)}{a_l!(\omega_l-1)!}$$

$$= \prod_l \frac{(\omega_l+a_l-1)\cdots(\omega_l+1)\omega_l}{a_l!} \simeq \prod_l \frac{\omega_l^{a_l}}{a_l!} \qquad \omega_l \gg a_l \gg 1$$

Gibbs' paradox

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

$$S_{nonlocal}(T,V,N) = S_{local}(T,V,N) - k_B \ln N! = Nk_B \ln z + U/T - k_B \ln N$$

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

$$= Nk_B \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] + 5Nk_B/2$$

Sackur-Tetrode equation

$$S_{local}(T,2V,2N) = 2Nk_B \ln\left[2V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] + 3Nk_B$$

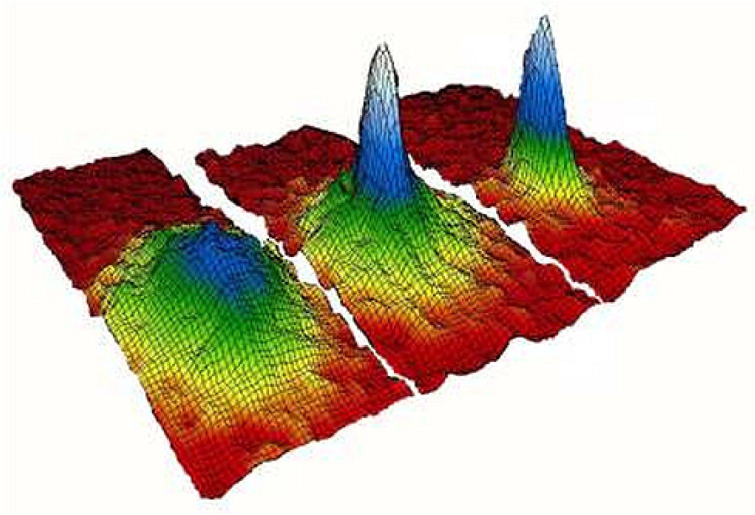
$$= 2S_{local}(T,V,N) + 2Nk_B \ln 2$$

☞ Gibbs' paradox

$$S_{nonlocal}(T,2V,2N) = 2Nk_B \ln\left[\frac{2V}{2N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] + 5Nk_B$$

$$= 2S_{nonlocal}(T,V,N)$$

7.12 Bose-Einstein 凝聚



☞有宏观多的粒子处在基态上，$a_g \sim N^1$

两能级体系的 BEC

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

- Boltzmann 分布

$$a_0 = \frac{N}{1+e^{-\beta\varepsilon}} \qquad a_1 = \frac{Ne^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} \qquad \frac{a_1}{a_0} = e^{-\beta\varepsilon}$$

  - 量子化极限，$\frac{\varepsilon}{k_B T} \gg 1$，$a_1 \simeq Ne^{-\beta\varepsilon} \ll a_0 \simeq N$
  - 经典极限（量子化不重要），$1 \ll \frac{k_B T}{\varepsilon}$，$a_1 \simeq a_0 \simeq N/2 \sim O(N)$

两能级体系的 BEC

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

- Bose 分布

$$a_0 = \frac{1}{e^{-\beta\mu} - 1} \qquad a_1 = \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} \qquad a_0 + a_1 = N \Rightarrow \mu = ?$$

  - 量子化极限，$\frac{\varepsilon}{k_B T} \gg 1$，$a_1 \simeq e^{-\beta(\varepsilon-\mu)} \ll a_0$
  - 经典极限（量子化不重要），$1 \ll \frac{k_B T}{\varepsilon} \sim 10^{12} \ll N \sim 10^{23}$

$$a_0 > 0 \Rightarrow \mu < 0 \Rightarrow a_1 < \frac{1}{e^{\beta\varepsilon} - 1} \simeq \frac{k_B T}{\varepsilon} \sim O(N^0) \ll N$$

$$a_0 \simeq \frac{k_B T}{-\mu} = N - a_1 \simeq N \gg a_1 \qquad \mu \simeq -\frac{k_B T}{N} \sim O(N^{-1})$$

☞ 即使在量子化不重要的时候，量子全同性也非常重要
$\Rightarrow$ 在所有温度下，两能级的宏观 Bose 系统处在激发态上的粒子数有上限 $\sim O(N^0)$，几乎所有粒子都在基态上，基态上粒子数 $\sim N$。

两能级体系的 BEC

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

- 从热力学角度理解两能级体系的 BEC
  - 经典粒子
    分布为 $\{a_0, a_1\}$ 时微观态数目为 $\Omega = C_N^{a_1} = N!/(a_0!a_1!)$

$$S = k_B \ln\Omega = N\ln N - (N-a_1)\ln(N-a_1) - a_1\ln a_1$$

$$U = a_1\varepsilon$$

$$F = U - TS = a_1\varepsilon - k_BT[N\ln N - (N-a_1)\ln(N-a_1) - a_1\ln a_1]$$

$$0 = \left(\frac{\partial F}{\partial a_1}\right) = \varepsilon + k_BT[-\ln(N-a_1) + \ln a_1] \Leftarrow \boxed{\text{自由能极小}}$$

$$\frac{a_1}{N-a_1} = \frac{a_1}{a_0} = e^{-\varepsilon/(k_BT)}$$

  - Boson
    粒子是全同的，分布为 $\{a_0, a_1\}$ 时微观态数目为 $\Omega = 1$

$$S = k_B\ln\Omega = 0 \qquad U = a_1\varepsilon \qquad F = U - TS = a_1\varepsilon$$

自由能极小 $\Rightarrow a_1 = 0$，$a_0 = N$ ☞ BEC

弱简并的三维 Bose 气体

- 分布

$$a_s = \frac{1}{e^{\beta(\varepsilon_s - \mu)} - 1}$$

- 弱简并时 $\lambda = e^{\beta\mu} = \frac{N}{z} = \frac{N\lambda_T^3}{V} \ll 1$

$$a_s = e^{\beta\mu - \beta\varepsilon_s} = \frac{N}{z} e^{-\beta\varepsilon_s} = \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} e^{-\beta\varepsilon_s} \qquad \sim O(N^0)$$

☞ 由于能级无穷多个，基态上的粒子数远比总粒子数少，$N_g = a_g \simeq \lambda e^{-\beta\varepsilon_g} = \lambda = \frac{N}{V}\lambda_T^3 \sim O(N^0) \ll N$，几乎所有粒子都处在激发态上，$N_{ex} = N - N_g \simeq N$。

- Einstein 注意到由于 Boson 的 $\mu \le 0$，$\lambda \le 1$，因此激发态上的粒子数有个上限，不能是无限增加。$\Rightarrow$ BEC

$$N_{ex} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(\lambda) \le V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(\lambda)$$

三维 Bose 气体的 BEC

$$N_g = \frac{1}{e^{-\beta\mu} - 1} = \frac{1}{1/\lambda - 1} = \frac{\lambda}{1-\lambda} \qquad \lambda < 1$$

$$N_{ex} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(\lambda) \le V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(1) = N_c(T,V)$$

- 处于激发态上的粒子数有上限：$N_c(T,V)$
- 保持温度和容积不变，往容器里逐个增加粒子，一开始 $\lambda \ll 1$，处于基态上的粒子数很少 $N_g \sim \lambda \sim O(1)$，粒子基本处于激发态上，$N_{ex} = N$
- 粒子数 N 增加时，λ 增加，但 $N_g \sim \lambda \sim O(1)$，粒子仍然基本上处于激发态上，$N_{ex} = N$
- N 增加到 N_c 时，N_{ex} 不能继续增加，新添加的粒子只能处于基态上 $\quad \Rightarrow$BEC

$$\lambda = 1 - O(1/N) \qquad \Rightarrow \qquad N_g = \frac{\lambda}{O(1/N)} = O(N)$$

$$N_{ex} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}[1 - O(1/N)] = N_c$$

$$n_c(T) = \frac{N_c}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(1)$$

相变温度

- 类似的，可以从温度改变角度来看 BEC，高温时，$\lambda \ll 1$，粒子主要在激发态上
- 温度降低时，λ 增加，直到 $N_{ex} = T_c$
- 相变温度 T_c

$$N = N_{ex} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(1)$$

$$T_c = \frac{h^2}{2\pi m k_B}[F^{+}_{3/2}(1)]^{-2/3} n^{2/3}$$

- $T < T_c$ 时，激发态上的粒子数

$$N_{ex} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(1) = \left(\frac{T}{T_c}\right)^{3/2} V\left(\frac{2\pi m k_B T_c}{h^2}\right)^{3/2} F^{+}_{3/2}(1)$$

$$= N\left(\frac{T}{T_c}\right)^{3/2}$$

$$N_g = N - N_{ex} = [1 - (T/T_c)^{3/2}]N$$

热容

$$T \geq T_c$$

$$U = U_{ex} + N_g \varepsilon_g = \frac{3k_B T}{2} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} F^+_{5/2}(\lambda)$$

$$C_V = \frac{15 N k_B}{4} \frac{F^+_{5/2}(\lambda)}{F^+_{3/2}(\lambda)} - \frac{9 N k_B}{4} \frac{F^+_{3/2}(\lambda)}{F^+_{1/2}(\lambda)}$$

$$F^+_{5/2}(1) = 1.34145$$
$$F^+_{3/2}(1) = 2.61139$$
$$F^+_{1/2}(1) = \infty$$

$$T \leq T_c$$

$$U = U_{ex} + N_g \varepsilon_g = U_{ex} = \frac{3k_B T}{2} V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} F^-_{5/2}(1)$$

$$= \frac{3k_B T}{2} \left(\frac{T}{T_c} \right)^{3/2} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)} V \left(\frac{2\pi m k_B T_c}{h^2} \right)^{5/2} F^+_{3/2}(1)$$

$$= \frac{3N k_B T}{2} \left(\frac{T}{T_c} \right)^{3/2} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)} = 0.770 N k_B T (T/T_c)^{3/2}$$

$$C_V = \frac{15 N k_B}{4} (T/T_c)^{3/2} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)} = 1.93 N k_B (T/T_c)^{3/2}$$

BEC 相变类型

- C_v 连续但其导数不连续，之前认为是三阶相变

$$C_V(T_c^+) = \frac{15Nk_B}{4}\frac{F_{5/2}^+(1)}{F_{3/2}^+(1)} - \frac{9Nk_B}{4}\frac{F_{3/2}^+(1)}{F_{1/2}^+(1)} = \frac{15Nk_B}{4}\frac{F_{5/2}^+(1)}{F_{3/2}^+(1)}$$
$$\simeq 1.93Nk_B$$
$$C_V(T_c^-) = \frac{15Nk_B}{4}(T/T_c)^{3/2}\frac{F_{5/2}^+(1)}{F_{3/2}^+(1)} \simeq 1.93Nk_B$$

- 目前一般认为是特殊的一阶相变
  - 凝聚相
    $U_g = N_g\varepsilon_g = 0$，$S = 0$，$\mu = 0$
  - 正常相
    $U_{ex} \neq 0$，$S_{ex} \neq 0$，$\mu = 0$
  - ☞ 这两相混合在一起，不象一般系统那样有界面把二者分开
    $p_g = 0$，$p_{ex} \neq 0$
- 保持粒子数和体积不变，降低温度，两相的比例改变，导致 C_V 仍然连续

等温情况下体积变动导致的 BEC

在保持温度和粒子数不变时，减小体积同样会导致粒子密度变大，从而发生 BEC

- 当体积大于 V_c 时，粒子主要占据激发态

$$N = V_c\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(1) = \frac{V_c}{\lambda_T^3} F^{+}_{3/2}(1)$$

$$V_c = N\lambda_T^3 \frac{1}{F^{+}_{3/2}(1)}$$

- 当体积小于 V_c 时，有宏观多的粒子占据单粒子基态，发生 BEC

$$N_{ex} = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^{+}_{3/2}(1) = N\frac{V}{V_c}$$

$$N_g = N - N_{ex} = N\left(1 - \frac{V}{V_c}\right)$$

BEC 状态方程

$$\lambda_T = \hbar/\sqrt{2\pi m k_B T}$$

$$\ln \Xi = -\ln(1-\lambda) + V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F_{5/2}^{+}(\lambda) = -\ln(1-\lambda) + \frac{V}{\lambda_T^3} F_{5/2}^{+}(\lambda)$$

正常相： $\lambda = e^{-\alpha} = e^{\beta\mu} < 1$

$$N = N_{ex} = V\left(\frac{2mk_B T}{h^2}\right)^{3/2} F_{3/2}^{+}(\lambda) = \frac{V}{\lambda_T^3} F_{3/2}^{+}(\lambda)$$

$$N_g = 0$$

$$p = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial V} = \frac{k_B T}{\lambda_T^3} F_{5/2}^{+}(\lambda) = \frac{N k_B T}{V}\frac{F_{5/2}^{+}(\lambda)}{F_{3/2}^{+}(\lambda)}$$

$$S = \frac{5 V k_B}{2\lambda_T^3} F_{5/2}^{+}(\lambda) - N k_B \ln \lambda = \frac{5 N k_B}{2}\frac{F_{5/2}^{+}(\lambda)}{F_{3/2}^{+}(\lambda)} - N k_B \ln \lambda$$

$$C_V = \frac{15 N k_B}{4}\frac{F_{5/2}^{+}(\lambda)}{F_{3/2}^{+}(\lambda)} - \frac{9 N k_B}{4}\frac{F_{3/2}^{+}(\lambda)}{F_{1/2}^{+}(\lambda)}$$

BEC 状态方程

$$\lambda_T = \hbar/\sqrt{2\pi m k_B T}$$

$$\ln\Xi = -\ln(1-\lambda) + V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} F^+_{5/2}(\lambda) = -\ln(1-\lambda) + \frac{V}{\lambda_T^3} F^+_{5/2}(\lambda)$$

BEC： $\lambda = e^{\beta\mu} = 1 \Rightarrow \mu = 0$

$$N = N_{ex} = \frac{V}{\lambda_T^3} F^+_{3/2}(1)$$

BEC 相变条件

$$N_{ex} = \frac{V}{\lambda_T^3} F^+_{3/2}(1) = N(T/T_c)^{3/2}$$

$$N_g = N - N_{ex} = N\left[1 - (T/T_c)^{3/2}\right]$$

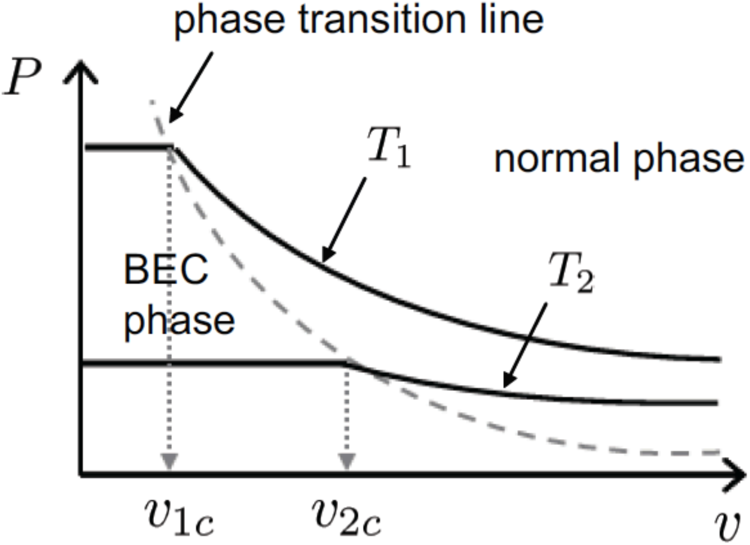
$$p = \frac{k_B T}{\lambda_D^3(T)} F^+_{5/2}(1)$$

☞ 与体积无关

$$S = \frac{5 k_B V}{2\lambda_T^3} F^+_{5/2}(1) = \frac{5 N_{ex} k_B}{2} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)} \propto N_{ex}$$

$$C_V = \frac{15 V k_B}{4\lambda_T^3} F^+_{5/2}(1) = \frac{15 N_{ex} k_B}{4} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)} \propto N_{ex}$$

BEC 的等温线



phase transition line
P
T1
normal phase
BEC
phase
T2
v1c
v2c
v

BEC 相变是一阶相变

- 等温线
  - 一阶相变（例如气液相变）等温过程在两相共存时压强不变
    $V = n_l v_l + n_g v_g$
  - 发生 BEC 后等温过程压强不变
    $V = N_{ex} v_{ex} + N_g v_g \Rightarrow v_{ex} = \frac{\lambda_T^3}{F^+_{3/2}(1)}$， $v_g = 0$
- 正常相每个粒子贡献熵 $\frac{5k_B}{2} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)}$ ， 凝聚相熵为零，有潜热。

$$L = T\Delta S = \frac{5k_B T}{2} \frac{F^+_{5/2}(1)}{F^+_{3/2}(1)}$$

- 满足 Clayperon-Clausius 方程 $\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$

$$p = \frac{k_B T}{\lambda_D^3(T)} F^+_{5/2}(1) \qquad \Rightarrow \qquad \frac{dp}{dT} = \frac{5p}{2T} = \frac{5k_B}{2\lambda_T^3} F^+_{5/2}(1)$$

$$\frac{\Delta S}{\Delta V} = \frac{5k_B F^+_{5/2}(1)/[2F^+_{3/2}(1)]}{\lambda_T^3 / F^+_{3/2}(1)} = \frac{5k_B}{2\lambda_T^3} F^+_{5/2}(1)$$

BEC 实验实现

- 1924 年 Einstein 证明存在 BEC
  在低温下，$C_V \propto (T/T_c)^{3/2}$，符合热力学第三定律。Einstein 揭示了即使在能级量子化不重要的时候，全同性也可以导致自由度退化。
- 一般气体达到 BEC 时，都已经液化，相互作用比较强，不能当成气体。因此实验实现很难。
- London 认为超流 ^{4}He 相变是 BEC，但由于相互作用太大，很多人反对。
- 1995 年 Cornell & Wieman 利用激光致冷和磁陷阱蒸发的方法，得到 170 nK 的低温，实现将近 2000 个 ^{87}Rb 的 BEC。Ketterle 随后实现了 10^5 个 ^{23}Na 的 BEC。
- 分子、自旋波、光子等 BEC
- 费米子对的 BEC
- 有相互作用系统的 BEC
  - 处于基态的粒子整体运动，形成宏观量子力学系统
  - 具有长程非对角关联

BEC 实验

在一个弱磁陷阱里约束粒子，$V(\boldsymbol{r}) = M\omega^2\boldsymbol{r}^2/2$。

- 不发生 BEC，近似为 Boltzmann 分布，那么粒子数密度随空间位置的变化为

$$
\begin{aligned}
n(\boldsymbol{r}) &= \int \frac{1}{e^{\beta[\boldsymbol{p}^2/2m+V(\boldsymbol{r})-\mu]} - 1} \frac{d^3p}{h^3} \\
&\simeq \int e^{-\beta[\boldsymbol{p}^2/2m+V(\boldsymbol{r})-\mu]} \frac{d^3p}{h^3} \propto Ne^{-\beta V(\boldsymbol{r})} \\
&\propto N \exp\left(-\frac{M\omega^2\boldsymbol{r}^2}{2k_BT}\right) \propto N \exp\left(-\boldsymbol{r}^2/2r_T^2\right) \\
n(\boldsymbol{p}, \boldsymbol{r}) &\propto Ne^{-(\boldsymbol{p}^2/(2p_T^2)-\boldsymbol{r}^2/(2r_T^2))} \\
r_T^2 &= \frac{k_BT}{M\omega^2} \\
p_T^2 &\sim Mk_BT
\end{aligned}
$$

BEC 实验

- 发生 BEC，并且所有粒子都在基态上，那么系统波函数为 $\Psi(\{\boldsymbol{r}_i\}) = \prod_{i=1}^{N} \varphi_0(\boldsymbol{r}_i)$，$\varphi_0$ 为单粒子基态波函数。那么粒子数密度随空间变化

$$n_0(\boldsymbol{r}) = N|\varphi_0(\boldsymbol{r})|^2 \propto N \exp\{-\boldsymbol{r}^2/(2r_c^2)\}$$

$$n_0(\boldsymbol{p}) = \int n_0(\boldsymbol{r}) e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar} d\boldsymbol{r} \propto N \exp -\boldsymbol{p}^2/(2p_c^2)$$

$$r_c^2 = \frac{\hbar}{M\omega} \qquad p_c^2 \sim \frac{\hbar^2}{r_c^2} = \hbar M\omega$$

测不准原理

$$\frac{r_T^2}{r_c^2} = \frac{k_B T/(M\omega^2)}{\hbar/(M\omega)} = \frac{k_B T}{\hbar\omega} \gg 1 \Leftarrow$$

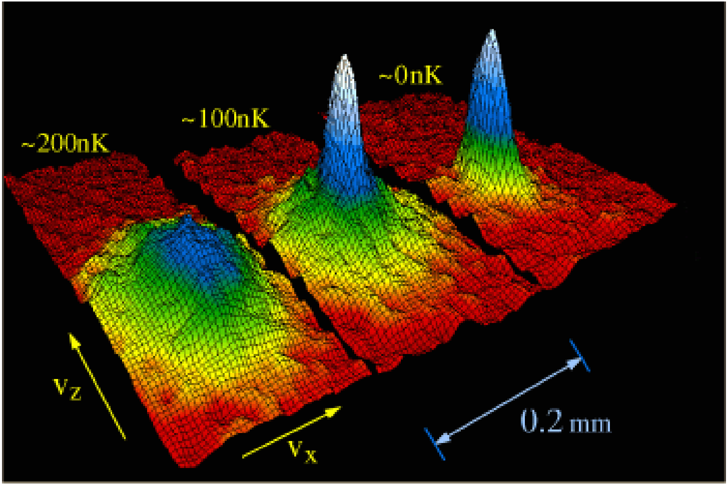
发生 BEC 时，能级量子化并不重要

$$\frac{p_T^2}{p_c^2} = \frac{M k_B T}{M\hbar\omega} = \frac{k_B T}{\hbar\omega} \gg 1$$

☞ 发生 BEC 后，粒子在实空间和动量（速度）空间上的扩展范围是单粒子基态波函数的扩展，远远小于由于热运动导致的扩展。

BEC 的实验结果

2 D velocity distributions



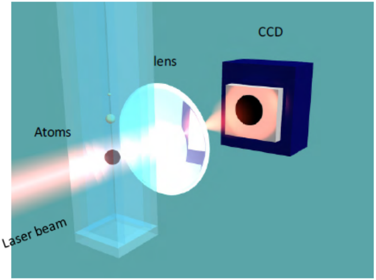
三个不同温度下粒子的速度分布。

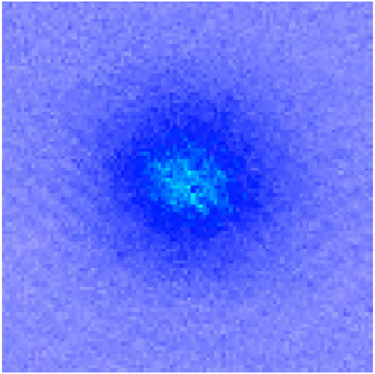
速度分布测量方法

- Time-of-flight 测量法：把磁陷阱去除 $\Rightarrow$ 原子自由运动
- 经过一段时间 t 之后，粒子位置 $\boldsymbol{r}_0 + \boldsymbol{v}t \simeq \boldsymbol{v}t$
- 测量 $n(\boldsymbol{r}, t) \Rightarrow n_0(\boldsymbol{v})$
- 无 BEC 时，速度分布基本对称。BEC 后，零能态中有明显不对称，这种不对称起源于量子效应：磁陷阱具有不对称性，约束越紧的方向扩展越大。

$$r_c^2 = \frac{\hbar}{2M\omega} \qquad p_c^2 = \hbar M\omega$$

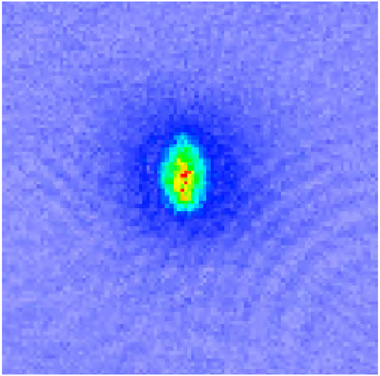
Absorption Imaging



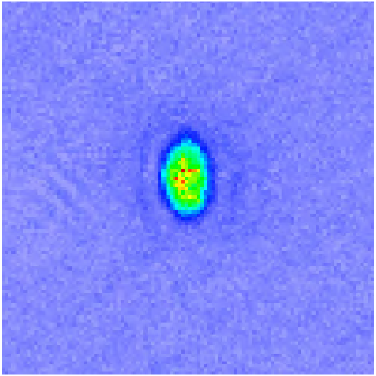


500 nK

Absorption Imaging



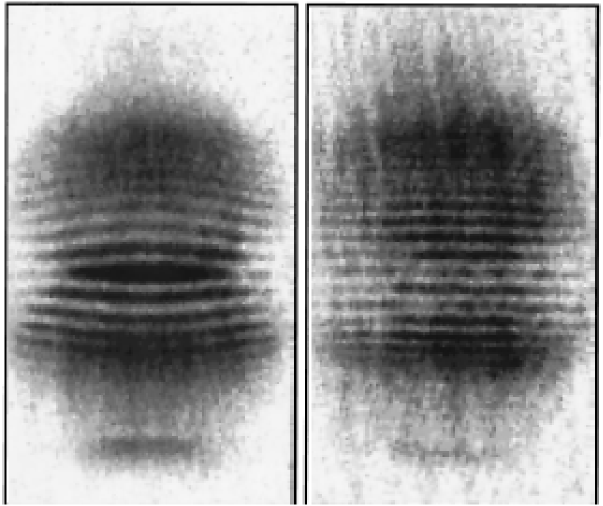
300 nK



100 nK

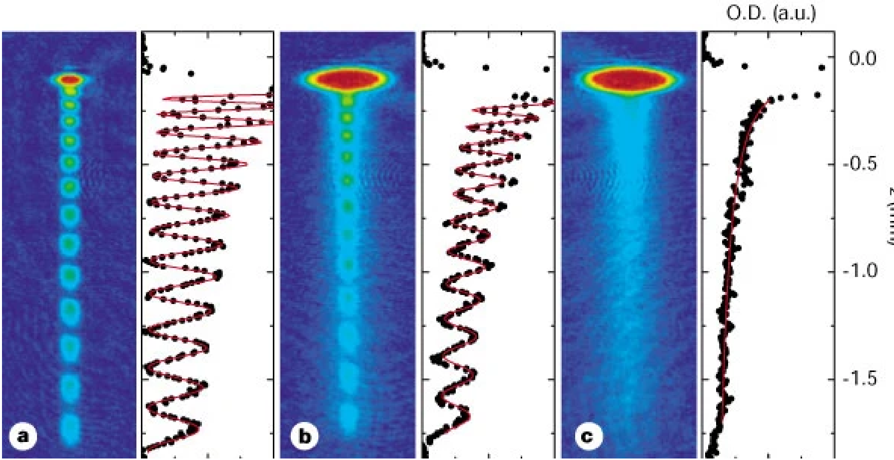
量子相干测量

"Observation of Interference Between Two Bose Condensates", Ketterle group, Science **275**, 637 (1995)



量子相干测量

“Measurement of the spatial coherence of a trapped Bose gas at the phase transition”, Bloch *et. al.*, Nature **403**, pp 166—170 (2000): $T \ll T_c$, $T \leq T_c$ 和 $T > T_c$ 三种不同情况



一团 BEC 气体“双缝”干涉条纹：利用激光在两个不同位置激发粒子，粒子在重力作用向下运动，造成类似于双缝干涉的效果。

非对角长程序

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$$\rho(s) = \rho(|\boldsymbol{r} - \boldsymbol{r}'|) = \sum_{\boldsymbol{k}} \bar{n}_{\boldsymbol{k}} \psi^*_{\boldsymbol{k}}(\boldsymbol{r}) \psi_{\boldsymbol{k}}(\boldsymbol{r}')$$

$$= \frac{N_0}{V} + \int \frac{d^3\boldsymbol{k}}{(2\pi)^3} \frac{e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}')}}{e^{[(\hbar^2 k^2/2m)-\mu]/k_B T} - 1}$$

$$\simeq \frac{N_0}{V} + \frac{m k_B T}{2h^2} \frac{e^{-s/r_0}}{s} \qquad r_0 = \frac{\hbar}{\sqrt{2m|\mu|}}$$

☞Eq. (3.51), p25, “Bose—Einstein Condensation and Superfluidity”, Pitaevskii and Stringari, Oxord (2016)。

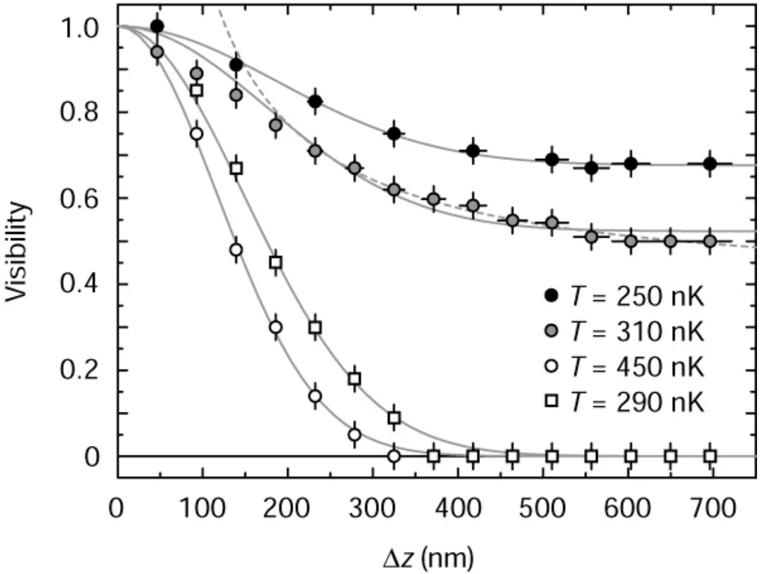
对角长程序:

$$\delta\hat{n}(\boldsymbol{r}) = \hat{n}(\boldsymbol{r}) - \bar{n}(\boldsymbol{r})$$

$$C(\boldsymbol{r}, \boldsymbol{r}') = \langle \delta n(\boldsymbol{r}) \delta n(\boldsymbol{r}') \rangle \xrightarrow{|\boldsymbol{r}-\boldsymbol{r}'|\Rightarrow\infty} C_0$$

非对角长程序的测量

Bloch *et. al.*, Nature **403**, pp 166—170 (2000)



不同温度下，干涉条纹的可见度随“双缝”间距 Δz 的关系。

7.13 光子/声子气体

- 有一类粒子，其粒子数不守恒
  - ☞ 最低能量为零，可以随意产生或者消灭粒子
- 满足化学势为零的 Bose 或者 Fermi 统计

$$a_s = n(\varepsilon_s) = \frac{1}{e^{\beta\varepsilon_s} \pm 1}$$

  - 求最可几分布时，不需要加上粒子数守恒的约束，只要一个 Lagrange 乘子 $\beta \Rightarrow \mu = 0$
  - Bosonic 粒子：光子、声子、magnon
    Fermionic 粒子：中微子 (?)
- 粒子数不守恒的系统中化学势为零的物理含义

$$dF = -SdT - pdV + \mu dN \qquad \Rightarrow \mu = \left(\frac{\partial F}{\partial N}\right)_{TV}$$

在粒子数不确定的体系中, $N = \bar{N}$, 满足 $F(T,V) = F(T,V,\bar{N})$。达到平衡时，$\bar{N}$ 取值使得自由能极小，因此 $\mu = \left(\frac{\partial F}{\partial N}\right)_{TV} = 0$。

- 化学势为零 $\Leftrightarrow$ 粒子数不守恒?

☞ BEC?

光子气体

$$\boldsymbol{p} = \hbar \boldsymbol{k} \qquad \omega = ck \qquad \varepsilon(\boldsymbol{p}) = \hbar\omega = cp$$

$$g(\varepsilon) = 2\boxed{\text{自旋 / 偏振自由度}} \times \int \delta(\varepsilon - cp)\frac{d^3p\,d^3r}{h^3}$$

$$= \frac{2V}{h^3}4\pi\int_0^\infty \delta(\varepsilon - cp)p^2dp = \frac{8\pi V}{h^3}\frac{p^2}{c}\bigg|_{p=\varepsilon/c}$$

$$= \frac{8\pi V}{h^3c^3}\varepsilon^2$$

$$g(\omega)d\omega \Rightarrow g(\varepsilon)d\varepsilon = g(\varepsilon = \hbar\omega)d(\hbar\omega) = \frac{8\pi V(\hbar\omega)^2}{h^3}\hbar d\omega$$

$$g(\omega) = \frac{V\omega^2}{\pi^2c^3}$$

$$n(\omega) = n(\varepsilon = \hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

- 按照能量均分原理，每个运动自由度对热容贡献 $k_B/2$
- 运动自由度：$g(\omega \Rightarrow \infty) \Rightarrow \infty$

☞ 紫外灾难

黑体辐射

$$\ln \Xi = -\sum_s \ln\left(-e^{-\beta \varepsilon_s}\right) = -\int_0^\infty g(\varepsilon)\ln\left(1-e^{-\beta\varepsilon}\right)d\varepsilon$$

$$= \int_0^\infty \frac{8\pi V}{h^3c^3}\varepsilon^2 \sum_{n=1}^\infty \frac{1}{n} e^{-n\beta\varepsilon} d\varepsilon$$

$$= \frac{8\pi V (k_B T)^3}{h^3 c^3} \sum_{n=1}^\infty \frac{1}{n^4} \boxed{= \zeta(4)} \int_0^\infty t^2 e^{-t} dt \boxed{= \Gamma(3) = 2}$$

$$\zeta(s) = \sum_{n=1}^\infty \frac{1}{n^s} \qquad \zeta(2) = \frac{\pi^2}{6} \qquad \zeta(4) = \frac{\pi^4}{90} \qquad \cdots$$

$$\ln \Xi = \frac{8\pi^5 (k_B T)^3 V}{45 h^3 c^3} = \frac{\pi^2 (k_B T)^3 V}{45 \hbar^3 c^3}$$

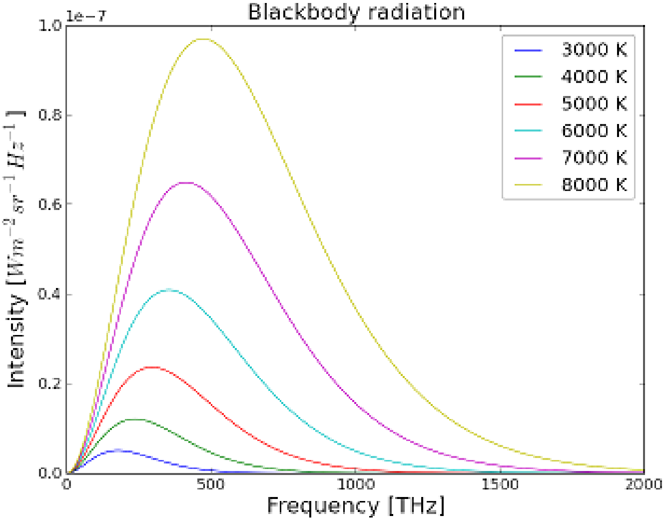
$$U(T,V) = k_B T^2 \left(\frac{\partial \ln \Xi}{\partial}\right)_V = \frac{\pi^2 (k_B T)^4}{15\hbar^3 c^3} V$$

$$u(T) = \frac{U(T,V)}{V} = \frac{\pi^2 (k_B T)^4}{15\hbar^3 c^3}$$

黑体辐射谱

$$u(\omega, T) = \frac{U(\omega)}{V} = \varepsilon n(\omega) g(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1}$$

Planck's law



黑体辐射谱

$$u(\omega,T)=\frac{U(\omega)}{V}=\varepsilon n(\omega)g(\omega)=\frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{e^{\beta\hbar\omega}-1}$$ Planck's law

$$=\begin{cases}\frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{\beta\hbar\omega}=\frac{k_BT\omega^2}{\pi^2c^3} & \hbar\omega\ll k_BT \\ \frac{\hbar\omega^3}{\pi^2c^3}e^{-\hbar\omega/k_BT} & \hbar\omega\gg k_BT\end{cases}$$

Rayleigh–Jeans law

Wien's law

$$u(T)=\int_0^\infty u(\omega,T)d\omega=\frac{\hbar}{\pi^2c^3}\int_0^\infty\frac{\omega^3}{e^{\beta\hbar\omega}-1}d\omega$$

$$=\frac{\hbar}{\pi^2c^3}(\beta\hbar)^{-4}\int_0^\infty\frac{x^3}{e^x-1}dx\boxed{=\sum_l\frac{3!}{l^4}=\frac{6\pi^4}{90}}=\frac{\pi^2k_B^4T^4}{15c^3\hbar^3}$$

$$J(\omega,T)=\frac{c}{4}u(\omega,T)\Rightarrow J(T)=\frac{c}{4}u(T)=\frac{\pi^2k_B^4T^4}{60c^3\hbar^3}=\sigma T^4$$

$$\sigma=\frac{\pi^2k_B^4}{60c^3\hbar^3}$$ Stephan-Boltzmann 常数

Don't feel bad if you don't know how to calculate

$$I = \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

On a Certain Integral Arising In Quantum Mechanics

By H. E. BUCHANAN
Tulane University

National Mathematics Magazine, April 1936, pp. 247–248.

1. In the consideration of a research problem in quantum mechanics, Professor J. C. Morris of Princeton University recently encountered the integral

$$I = \int_0^{\infty} \frac{x^3\, dx}{e^x - 1}. \tag{1}$$

Since the integral does not yield to any ordinary methods of attack, Professor Morris asked the author to evaluate it. The evaluation affords an interesting exercise in several phases of advanced calculus, and thus may be of interest to students and teachers of senior or first year graduate grade.

积分

$$I_n = \int_0^\infty \frac{x^n}{e^x - 1} dx = \int_0^\infty x^n \frac{e^{-x}}{1 - e^{-x}} dx$$

$$= \int_0^\infty x^n e^{-x} \sum_{p=0}^\infty e^{-px} dx = \sum_{p=1}^\infty \int_0^\infty x^n e^{-px} dx$$

$$= \sum_{p=1}^\infty \frac{1}{p^{n+1}} \int_0^\infty x^{n+1-1} e^{-x} dx \boxed{= \Gamma(n+1) = n!}$$

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

Riemann ζ 函数： $\zeta(n) = \sum_{p=1}^\infty p^{-n}$

$$\zeta(2) = 1 + \frac{1}{2^2} + \frac{1}{3^2} + \cdots = \frac{\pi^2}{6}$$

$$\zeta(4) = 1 + \frac{1}{2^4} + \frac{1}{3^4} + \cdots = \frac{\pi^4}{90}$$

$\cdots$

$$I_3 = 3!\zeta(4) = 6\frac{\pi^4}{90} = \frac{\pi^4}{15}$$

- Basel 问题: $\zeta(2) = \frac{1}{1^2} + \frac{1}{2^2} + \cdots =$?，1650 年提出，1735 年 Euler 解决。
- Euler 首先计算了 $\zeta(2) = 1.64493407$，发现这个结果和 $\pi^2/6$ 基本相同。然后他试图证明这个结果。
- 利用下面方法他计算出所有 $\zeta(2n)$。

Euler 公式

如果你被困在无人岛上，手机、平板和电脑都没电，闲极无聊想找点乐子

$$
\begin{aligned}
\frac{\sin z}{z} &= (1-\frac{z}{\pi})(1-\frac{z}{-\pi})(1-\frac{z}{2\pi})(1-\frac{z}{-2\pi})(1-\frac{z}{3\pi})(1-\frac{z}{-3\pi})\cdots \\
&= (1-\frac{z^2}{\pi^2})(1-\frac{z^2}{2^2\pi^2})(1-\frac{z^2}{3\pi^2})(1-\frac{z^2}{4^2\pi^2})\cdots \\
&= 1-\frac{z^2}{\pi^2}\left[\frac{1}{1^2}+\frac{1}{2^2}+\frac{1}{3^2}+\cdots\right] \\
&+\frac{z^4}{\pi^4}\left[\frac{1}{1^2\cdot 2^2}+\frac{1}{1^2\cdot 3^2}+\cdots+\frac{1}{2^2\cdot 3^2}+\frac{1}{2^2\cdot 4^2}+\cdots\right]+\cdots \\
&= 1+S_2 z^2+S_4 z^4+\cdots
\end{aligned}
$$

$$
\frac{\sin z}{z} = 1-\frac{z^2}{3!}+\frac{z^4}{5!}-\frac{z^6}{7!}+\cdots
$$

$$
S_2 = -\frac{1}{\pi^2}\sum_n \frac{1}{n^2} = -\frac{\zeta(2)}{\pi^2}
$$

$$
\frac{1}{3!} = -S_2 = \frac{1}{\pi^2}\zeta(2) \qquad \Rightarrow \qquad \zeta(2) = \frac{\pi^2}{6}
$$

Euler 公式

如果你被困在无人岛上，手机、平板和电脑都没电，闲极无聊想找点乐子

$$S_4 = \frac{1}{\pi^4}\sum_{i<j}\frac{1}{i^2\cdot j^2} = \frac{1}{2\pi^4}\sum_{i\neq j}\frac{1}{i^2\cdot j^2} = \frac{1}{2\pi^4}\left[\sum_{i,j}\frac{1}{i^2 j^2} - \sum_{i=j}\frac{1}{i^2 j^2}\right]$$

$$= \frac{1}{2\pi^4}\left[\left(\sum_i \frac{1}{i^2}\right)\cdot\left(\sum_j \frac{1}{j^2}\right) - \sum_i \frac{1}{i^4}\right]$$

$$= \frac{\zeta(2)^2 - \zeta(4)}{2\pi^4}$$

$$\frac{1}{5!} = S_4 = \frac{\zeta(2)^2}{2\pi^4} - \frac{1}{2\pi^4}\zeta(4) = \frac{1}{72} - \frac{\zeta(4)}{2\pi^4}$$

$$\Rightarrow \zeta(4) = 2\pi^4\left[\frac{1}{72} - \frac{1}{120}\right] = \frac{\pi^4}{90}$$

Wien's 位移定律

$$J(\omega_m) \Rightarrow 0 = \left(\frac{\partial J}{\partial \omega}\right)|_{\omega=\omega_m}$$

$$= C\frac{\partial}{\partial \omega}\frac{\omega^3}{e^{\beta\hbar\omega}-1} = C\left[\frac{3\omega^2}{e^{\beta\hbar\omega}-1} - \frac{\beta\hbar\omega^3 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\right]$$

$$0 = 3(e^{\beta\hbar\omega_m}-1) - \beta\hbar\omega_m e^{\beta\hbar\omega_m} \Rightarrow 0 = 3(1-e^{-x_m}) - x_m \Rightarrow x_m \simeq 2.82$$

$$\omega_m = x_m k_B T/\hbar \propto T$$

$$U = uV = \frac{V\pi^2 k_B^4}{15c^3\hbar^3}T^4 \Rightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{4V\pi^2 k_B^4}{15c^3\hbar^3}T^3$$

$$N = \int_0^\infty g(\omega)f(\hbar\omega)d\omega = \frac{V}{\pi^2c^3}\int_0^\infty \frac{\omega^2}{e^{\hbar\omega/k_BT}-1}d\omega$$

$$= \frac{Vk_B^3T^3}{\pi^2c^3\hbar^3}\int_0^\infty \frac{x^2}{e^x-1}dx = 2\zeta(3)\frac{Vk_B^3T^3}{\pi^2c^3\hbar^3} \propto T^3$$

☞ 每个光子对热容贡献大约为 $k_B \Rightarrow$ 能量均分原理

零点振动和 Casimir 效应

$$U = \int g(\omega)[n(\omega) + 1/2]\hbar\omega d\omega = \frac{4V\pi^2 k_B^4 T^4}{15c^3\hbar^3} + \boxed{\frac{V\hbar}{2\pi^2 c^3}\int_0^\infty \omega^3 d\omega \Rightarrow \infty}$$

考虑两个距离为 a、面积为 A 的平行金属板之间的辐射

$$\psi_n(k_x, k_y) = e^{-i\omega_n(k_x,k_y)t + k_x x + k_y y}\sin\frac{n\pi z}{a}$$

$$\omega_n(k_x, k_y) = c\sqrt{k_x^2 + k_y^2 + \frac{n^2\pi^2}{a^2}}$$

$$E_0 = \frac{1}{2}\sum_{nk_xk_y}\hbar\omega_n(k_x, k_y) = \frac{A\hbar c}{2}\sum_n\int\frac{dk_x dk_y}{(2\pi)^2}\omega_n(k_x, k_y)$$

$$= \lim_{s\to 0}\frac{A\hbar c}{2}\sum_n\int\frac{dk_x dk_y}{(2\pi)^2}\omega_n(k_x, k_y)\times|\omega_n(k_x, k_y)|^{-s}\ \boxed{\text{zeta regulation}}$$

$$= -\lim_{s\to 0}\frac{\hbar c^{1-s}\pi^{2-s}}{2a^{3-s}}\frac{1}{3-s}\sum_n|n|^{3-s} = -\lim_{s\to 0}\frac{\hbar c^{1-s}\pi^{2-s}}{2a^{3-s}(3-s)}\zeta(-3+s)$$

$$= -\frac{\hbar c\pi^2}{720a^3} \qquad \boxed{\zeta(-3) = \frac{1}{120}}$$

声子气体、固体热容

$$\boldsymbol{p} = \hbar \boldsymbol{k} \qquad \omega = v_s k$$

v_s： 声速

$$\varepsilon(\boldsymbol{p}) = \hbar\omega = v_s p$$

$$g(\varepsilon) = 3\,\boxed{\text{一支纵向、两只横向声学声子}} \times \int \delta(\varepsilon - v_s p)\frac{d^3p d^3r}{h^3}$$

$$= \frac{2V}{h^3}4\pi\int_0^\infty \delta(\varepsilon - v_s p)p^2 dp = \frac{12\pi V}{h^3}\frac{p^2}{v_s}\Big|_{p=\varepsilon/c}$$

$$= \frac{12\pi V \varepsilon^2}{h^3 v_s^3}$$

$$g(\omega)d\omega \Rightarrow g(\varepsilon)d\varepsilon = g(\varepsilon = \hbar\omega)d(\hbar\omega) = \frac{12\pi V(\hbar\omega)^2}{h^3}\hbar d\omega$$

$$g(\omega) = \frac{3V\omega^2}{2\pi^2 v_s^3}$$

$$n(\omega) = n(\varepsilon = \hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}$$

声子气体、固体热容

Debye 频率：原子总振动自由度 $3N$ ＝振动模式数目

$$3N = \int_0^{\omega_D} g(\omega)d\omega = \frac{V\omega_D^3}{2\pi^2 v_s^3} \Rightarrow \omega_D^3 = \frac{6N\pi^2 v_s^3}{V}$$

$$\Theta_D = \hbar\omega_D / k_B$$

Debye 温度 ~ 10-100 K

$$U = \int_0^{\omega_D} n(\omega) g(\omega) \hbar\omega d\omega = \frac{3V\hbar}{2\pi^2 v_s^3}\int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega}-1} d\omega$$

$$= \frac{3V\hbar}{2\pi^2 v_s^3 (\beta\hbar)^4}\int_0^{\beta\hbar\omega_D = \Theta_D/T} \frac{x^3}{e^x - 1} dx$$

$$= 9N \frac{V}{6N\pi^2 v_s^3}\left(= \frac{1}{\omega_D^3}\right)\frac{(k_B T)^4}{\hbar^3} D(T/\Theta_D) = 9Nk_B \frac{T^4}{\Theta_D^3} D(T/\Theta_D)$$

$$D(T/\Theta_D) = \int_0^{\Theta_D/T} \frac{x^3}{e^x - 1} dx = \begin{cases} \int_0^\infty \frac{x^3}{e^x - 1} = \frac{\pi^4}{15} & T \ll \Theta_D \\ \int_0^{\Theta_D/T} \frac{x^3}{x} dx = \frac{1}{3}(\Theta_D/T)^3 & T \gg \Theta_D \end{cases}$$

声子气体、固体热容

- 低温极限

$$U = Nk_B \frac{3\pi^4 T^4}{5\Theta_D}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{NV} = \frac{12\pi^4}{5} Nk_B T^3/\Theta_D^3 \propto T^3$$

低温下能够被激发起来的声子 $\hbar\omega \le k_B T = \hbar\omega_T \Rightarrow$ 可激发的声子模式 $N_{ex} = \int_0^{\omega_T} g(\omega)d\omega \propto \omega_T^3 \propto T^3$
能量均分原理：$C_V \propto N_{ex} k_B \propto T^3$

- 高温极限

$$U = 3Nk_B T \qquad \Rightarrow \qquad C_V = 3Nk_B$$

7.14 强简并 Fermi 气体

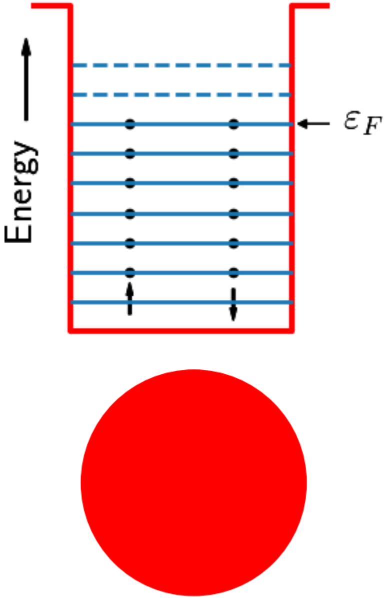
- 判据：
  $\lambda = e^{\beta\mu} \gg 1 \Rightarrow \mu/(k_B T) \gg 1 \Rightarrow \mu \gg k_B T$
- 强简并条件：
  弱简并条件：$\lambda \simeq y = \frac{1}{2}\left(\frac{\hbar^2}{2\pi m k_B T}\right)^{3/2}\frac{N}{V} \ll 1$
  $\Rightarrow$ 高温，低浓度

  强简并条件：低质量，低温，高浓度
  典型强简并 Fermion 体系：金属中的电子，白矮星中的电子，中子星，液体 ^{3}He，$\cdots$
- 简并度最大：$T = 0$，系统处于基态上

系统的基态

全同 Fermion，系统波函数是单粒子态的 Slater 行列式。因此一旦知道了每个单粒子态的占据情况，我们就可以写出这种情况下的体系波函数。

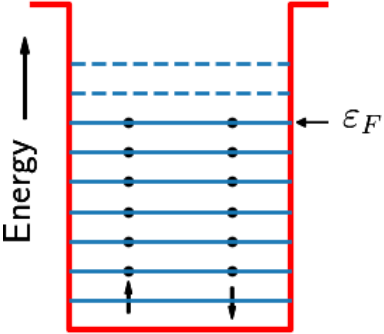
在一个系统中，不能有粒子占据相同的单粒子态，否则系统的波函数为零。这就是 Pauli 不相容原理。利用这个原理，我们可以把 Fermion 逐个地往单粒子态上填充，从而确定独立粒子（无相互作用）体系的基态。

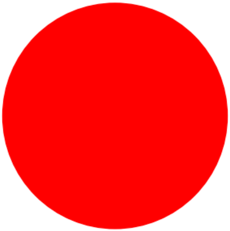


系统的基态

基态是能量最低的状态。所以最好粒子都填在能量最低的单粒子态上。但是由于 Pauli 不相容原理，这是不可能的。如能量低的单粒子态已经有填有粒子，其他粒子就必须填在能量较高的态上。所以，在动量空间中，系统处于基态时，粒子从能量最低点开始，由低能量到高能量逐层向外填充，一直到所有粒子都填完为止。由于等能面为球面，所以，在动量空间中，粒子填充的部分为球体，称为 Fermi 球（Fermi sphere）。

因此，体系的基态是一个 Fermi 球，其表面是一个等能面，称为 Fermi 面，对应的能量是 Fermi 能。Fermi 面是占据态和非占据态的边界。





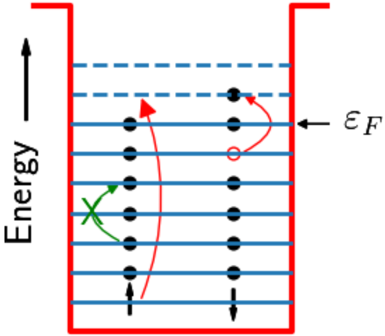
系统的低能激发态

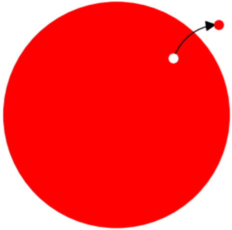
系统的低能激发态：Fermi 面下的占据态激发到 Fermi 面以上的空态。

因此我们可以看到，由于 Pauli 不相容原理，系统的基态和低能激发态并不反映单粒子的基态和低能激发态，而是反映 Fermi 面以及 Fermi 面附近的态的性质。

从动量空间看，这种激发相当于有一个粒子从 Fermi 球里跳到球外，在 Fermi 球里留下一个空洞。因此这种激发又被成为粒子—空穴激发（particle-hole exication）。

这里的“空穴”指的是 Fermi 球里缺少一个粒子，和能带论里的“空穴”概念稍有差别。





系统的低能激发态

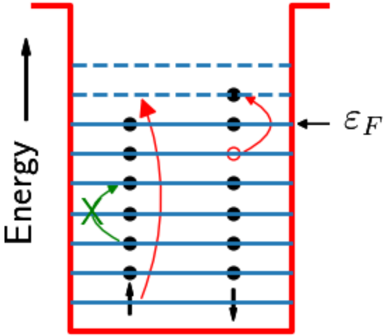
低能激发能量

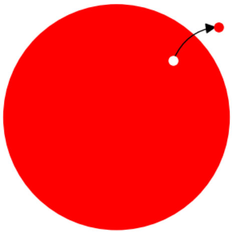
$$\Delta E_{ex} = E - E_g = \varepsilon_2 \boxed{> \varepsilon_F} - \varepsilon_1 \boxed{< \varepsilon_F}$$

$$= (\varepsilon_2 - \varepsilon_F) + (\varepsilon_F - \varepsilon_1)$$

$$= \varepsilon_p \boxed{\text{粒子型激发} \geq 0}$$

$$+ \varepsilon_h \boxed{\text{空穴型激发} \geq 0}$$





系统激发态能量可以表示为粒子型激发的能量和空穴型激发的能量之和。处于低能激发态时，ε_p 和 ε_h 都很小，也就是说 ε_1 和 ε_2 都很接近 ε_F。

在低温时，远离 Fermi 面的那些单粒子态，不管是高能还是低能态，其自由度都被冻结，不会被激发。低温下，只有能量在 Fermi 面附近的 $k_B T$ 范围内的态对热力学性质有贡献。

Fermi 面

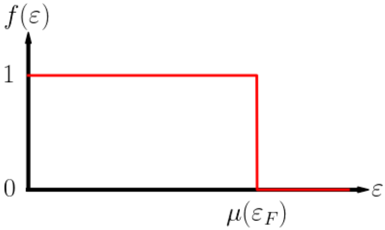
因此，Fermi 面在强简并的 Fermion 体系里中扮演了非常重要的角色。我们可以给出一系列的和 Fermi 面相关的物理量的定义：

- Fermi 能 ε_F
- Fermi 温度 T_F，$k_B T_F = \varepsilon_F$
- Fermi 动量 p_F，$\varepsilon_F = p_F^2/2m$，$p_F = \sqrt{2m\varepsilon_F}$
- Fermi 波矢 k_F：$k_F = p_F/\hbar = \sqrt{2m\varepsilon_F}/\hbar$
- Fermi 速度 v_F：$v_F = p_F/m = \hbar k_F/m$

金属中的电子气是一个典型的强简并 Fermion 体系，$T_F \sim 10^4 - 10^5$ K，$v_F \sim 10^6$m/s。

$T = 0$ K 时的 Fermi 分布

$$
\begin{aligned}
a_s &= \frac{1}{e^{\beta(\varepsilon_s-\mu)}+1} = \frac{1}{e^{(\varepsilon_s-\mu)/k_BT}+1} \\
&= f(\varepsilon_s, T=0) \\
&= \begin{cases} 1 & \varepsilon_s < \mu \\ 0 & \varepsilon_s > \mu \end{cases} \\
&= \Theta(\mu - \varepsilon_s)
\end{aligned}
$$



- 能量低于 μ 的单粒子态被完全占据，能量高于 μ 的单粒子态完全空，和我们前面讨论的系统基态（Fermi 球）相同。
- $T = 0$ K 时的化学势和 Fermi 能量相同：$\mu(T=0K) = \varepsilon_F$。

$$dU = TdS - pdV + \mu dN$$

$$\mu = \mu(T, V, N) = U(N+1) - U(N) = \varepsilon_F$$

- 在 Fermi 面处，分布函数不连续。

Fermi 面

Fermi 能的计算：

$$N\,\boxed{\text{总粒子数}} = 2\,\boxed{\text{自旋因子}} \int \Theta[\varepsilon_F - \varepsilon(p)] \frac{d^3p\,d^3r}{h^3}$$

$$= \int_0^{\infty} \Theta(\varepsilon_F - \varepsilon) g(\varepsilon)\, d\varepsilon = \int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon$$

$$g(\varepsilon) = 2\int \delta[\varepsilon - \varepsilon(p)] \frac{d^3r\,d^3p}{h^3} = \frac{8\pi V}{h^3}\int_0^{\infty} \delta(\varepsilon - p^2/2m) p^2 dp$$

$$= \frac{8\pi V}{h^3} \frac{p^2}{p/m}\bigg|_{p=\sqrt{2m\varepsilon}} = \frac{8\pi V}{h^3} m\sqrt{2m\varepsilon} = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\varepsilon}$$

$$N = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2} \times \frac{2}{3}\varepsilon_F{}^{3/2} \qquad N = \frac{2V}{h^3}\frac{4\pi p_F^3}{3} \Rightarrow p_F = h\left(\frac{3N}{8\pi V}\right)^{1/3}$$

$$\varepsilon_F = \frac{p_F^2}{2m} = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} \propto \left(\frac{N}{V}\right)^{2/3} \propto n^{2/3}$$

Fermi 面

系统的基态能量：

$$U = \int_0^{\varepsilon_F} \varepsilon g(\varepsilon)\, d\varepsilon = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon = \frac{8\pi V}{5}\left(\frac{2m}{h^2}\right)^{3/2} \varepsilon_F^{5/2}$$

$$u = \frac{U}{V} = \frac{3}{5} n\varepsilon_F \qquad ☞ \qquad u_0 = \frac{U}{N} = \frac{3}{5}\varepsilon_F$$

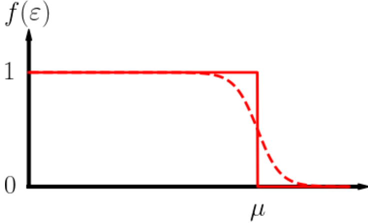
显然，即使在绝对零度，强简并的费米子仍有相当大的平均能量（平均动能），这与经典结果是截然不同的。根据经典理论，粒子的平均动能为：$3k_BT/2$，当温度 $T \to 0$ K 时，应为零。而根据量子理论，费米子分布必须服从泡利原理，即使在绝对零度也不可能所有粒子都处于最低能量状态。这对强简并费米子系统的性质具有很大影响。例如在金属中，即使是在 0K 下，参与热运动的电子具有很高的能量，典型的速度 $v \sim 10^6$m/s。

简并压

$$U = \frac{8\pi V}{5}\left(\frac{2m}{h^2}\right)^{3/2}\varepsilon_F^{5/2} = \frac{8\pi V}{5}\left(\frac{2m}{h^2}\right)^{3/2}\left[\frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3}\right]^{5/2}$$
$$= \frac{8\pi V}{5}\frac{\hbar^2}{2m}\left(\frac{3N}{8\pi V}\right)^{5/3} \propto \frac{N^{5/3}}{V^{2/3}}$$
$$P = -\left(\frac{\partial F}{\partial V}\right)_{TV}\Big|_{T=0} = -\left(\frac{\partial U}{\partial V}\right)_{TN}\Big|_{T=0} = \frac{2U}{3V} = \frac{2}{3}u \propto n^{5/3}$$

- 简并压：在 $T = 0$ 时，Fermi 气体对外仍然有很大的压强。
- 简并压对金属的压缩系数或者体模量有重要贡献。
- 某些条件下简并压对星体的稳定性有很重要的作用：
  - 白矮星：$\rho \sim 10^9\mathrm{kg/m^3}$，电子简并压阻止引力塌缩，$M < 1.44\ M_{sun}$（Chandrasekhar 极限）
  - 中子星：$\rho \sim 10^{17}\mathrm{kg/m^3}$，中子简并压阻止引力塌缩，$M < 2.1?M_{sun}$（Tolman–Oppenheimer–Volkoff 极限）

有限温度下的结果



分布函数

$$f(\varepsilon)=\frac{1}{e^{\beta(\varepsilon-\mu)}+1}=\frac{1}{e^{(\varepsilon-\mu)/(k_BT)}+1}$$

- $\varepsilon<\mu$， $f(\varepsilon)<1$， 有一部分粒子被激发出去，Fermi 面下粒子数减少 $\Leftrightarrow$ 空穴型激发数目：

$$f_h=1-f(\varepsilon)=\frac{e^{\beta(\varepsilon-\mu)}}{e^{\beta(\varepsilon-\mu)/k_BT}}=\frac{1}{e^{\beta(\mu-\varepsilon)}+1}=\frac{1}{e^{\beta\varepsilon_h}+1}$$

- $\varepsilon>\mu$， $f(\varepsilon)>0$ Fermi 面熵粒子数增加 $\Leftrightarrow$ 粒子型激发数目：

$$f_p=f(\varepsilon)=\frac{1}{e^{\beta(\varepsilon-\mu)}+1}=\frac{1}{e^{\beta\varepsilon_p}+1}$$

☞ 粒子、空穴型激发能量零点为 μ

☞ $T=0\,\mathrm{K}$， $\mu=\varepsilon_F$

有限温度下的结果

$$N = \int_0^\infty g(\varepsilon) f(\varepsilon)\, d\varepsilon \qquad\qquad U = \int_0^\infty \varepsilon\, g(\varepsilon) f(\varepsilon)\, d\varepsilon$$

$$N(\varepsilon) = \int_0^\varepsilon g(\varepsilon) d\varepsilon \Rightarrow N'(\varepsilon) = g(\varepsilon)$$

$$\begin{aligned}
\ln \Xi &= \int_0^\infty \ln[1 + e^{-\beta(\varepsilon-\mu)}]\, g(\varepsilon) d\varepsilon \\
&= \int_0^\infty \ln[1 + e^{-\beta(\varepsilon-\mu)}]\, dN(\varepsilon) = N(\varepsilon) \ln[1 + e^{-\beta(\varepsilon-\mu)}]\Big|_0^\infty \\
&\qquad - \int_0^\infty N(\varepsilon) d \ln[1 + e^{-\beta(\varepsilon-\mu)}] = \beta \int_0^\infty \frac{N(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}\, d\varepsilon \\
&= \beta \int_0^\infty N(\varepsilon) f(\varepsilon)\, d\varepsilon
\end{aligned}$$

从 $N = N(T, \mu, V)$ 求解出 μ，再由此得到 U，$\cdots$

需要计算积分 $\int_0^\infty f(\varepsilon) I(\varepsilon)\, d\varepsilon$ $\qquad \Rightarrow$ Sommerfeld 展开

Sommerfeld 展开

温度 $T > 0$ K 时的计算比较复杂，但在低温下可以利用 $f(\varepsilon)$ 和零温的 $f(\varepsilon) = \Theta(\mu-\varepsilon)$ 很接近这个特点，把结果按照温度展开。

$$I = \int_0^\infty I(\varepsilon)f(\varepsilon)d\varepsilon = \int_0^\infty I(\varepsilon)[f(\varepsilon) - \Theta(\mu-\varepsilon) + \Theta(\mu-\varepsilon)]d\varepsilon$$

$$= \int_0^\mu I(\varepsilon)d\varepsilon + \int_\mu^\infty I(\varepsilon)f(\varepsilon)d\varepsilon \boxed{\text{粒子型}} - \int_0^\mu I(\varepsilon)[1-f(\varepsilon)]d\varepsilon \boxed{\text{空穴型}}$$

三部分贡献： Fermi 球贡献 + 粒子型激发贡献 + 空穴型激发贡献

$$= I_0 + \int_\mu^\infty \frac{I(\varepsilon)}{e^{(\varepsilon-\mu)/k_BT}+1}d\varepsilon - \int_0^\mu \frac{I(\varepsilon)}{e^{(\mu-\varepsilon)/k_BT}+1}d\varepsilon$$

$$= I_0 + \int_0^\infty \frac{I(\mu+\varepsilon) - I(\mu-\varepsilon)}{e^{\varepsilon/k_BT}+1}d\varepsilon + \int_\mu^\infty \frac{I(\mu-\varepsilon)}{e^{\varepsilon/k_BT}+1} \boxed{\sim e^{-\mu/k_BT} \sim 0}$$

$$= I_0 + 2I'(\mu)\int_0^\infty \frac{\varepsilon}{e^{\varepsilon/k_BT}+1}d\varepsilon + 2\frac{I^{(3)}(\mu)}{3!}\int_0^\infty \frac{\varepsilon^3}{e^{\varepsilon/k_BT}+1}d\varepsilon + \cdots$$

$$= I_0 + 2I'(k_BT)^2\int_0^\infty \frac{x}{e^x+1}dx \boxed{= C_1} + 2\frac{I^{(3)}(k_BT)^4}{3!}\int_0^\infty \frac{x^3}{e^x+1} \boxed{= C_3} + \cdots$$

Sommerfeld 展开

$$C_n = \int_0^\infty \frac{x^n}{e^x+1}dx = \int_0^\infty \frac{x^n e^{-x}}{1+e^{-x}}dx = \int_0^\infty x^n e^{-x}\sum_{p=0}^\infty (-)^p e^{-px}dx$$

$$= \sum_{p=0}^\infty (-)^p \int_0^\infty x^n e^{-(p+1)x}dx = \sum_{p=0}^\infty \frac{(-)^p}{(p+1)^{n+1}} \int_0^\infty t^{n+1-1}e^{-t}dt$$

$$= n!\sum_{p=1}^\infty \frac{(-1)^{p-1}}{p^{n+1}} = n!\Big[\sum_{m=0}^\infty \frac{1}{(2m+1)^{n+1}} - \sum_{m=1}^\infty \frac{1}{(2m)^{n+1}}\Big]$$

$$\zeta(z) = \sum_{p=1}^\infty \frac{1}{p^z}$$

Riemann ζ 函数： $\zeta(z) = \frac{1}{\Gamma(z)}\int_0^\infty \frac{x^{z-1}}{e^x-1}dx$

$$= \sum_{m=0}^\infty \frac{1}{(2m+1)^z} + \sum_{m=1}^\infty \frac{1}{(2m)^z}$$

$$= \frac{1}{2^z}\sum_{m=1}^\infty \frac{1}{m^z} = \zeta(z)/2^z$$

$$\sum_{m=0}^\infty \frac{1}{(2m+1)^z} = \Big[1 - \frac{1}{2^z}\Big]\zeta(z)$$

Sommerfeld 展开

$$C_n = n!\left[\left(1-\frac{1}{2^{n+1}}\right)\zeta(n+1) - \frac{1}{2^{n+1}}\zeta(n+1)\right] = n!\left(1-\frac{1}{2^n}\right)\zeta(n+1)$$

$$I = \int_0^\infty I(\varepsilon)f(\varepsilon)d\varepsilon$$

$$= I_0 + 2\sum_{l=0}^{\infty}\frac{I^{(2l+1)}(k_BT)^{2l+2}}{(2l+1)!}C_{2l+1}$$

$$= (2l+1)!\left[1-\frac{1}{2^{2l+1}}\right]\zeta(2l+2)$$

$$= I_0(\mu) + 2\sum_{l=0}^{\infty} I^{(2l+1)}(\mu)\ (k_BT)^{2l+2}\left[1-\frac{1}{2^{2l+1}}\right]\zeta(2l+2)$$

$$= \int_0^\mu I(\varepsilon)d\varepsilon + \frac{\pi^2(k_BT)^2}{6}I'(\mu) + \frac{7\pi^4(k_BT)^4}{360}I^{(3)}(\mu) + \cdots$$

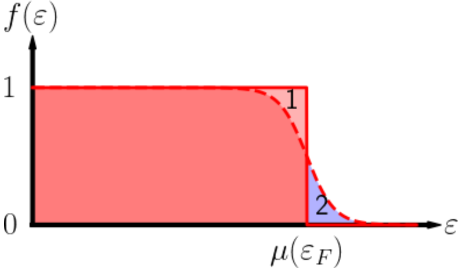
$$\zeta(2) = \sum_n \frac{1}{n^2} = \frac{\pi^2}{6} \qquad \zeta(4) = \sum_n \frac{1}{n^4} = \frac{\pi^4}{90} \qquad \cdots$$

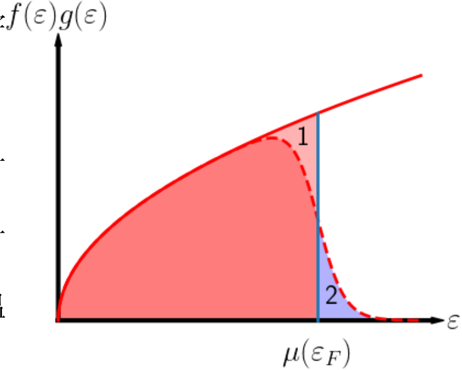
化学势随温度的变化

$$
\begin{aligned}
I &= \int_0^\infty I(\varepsilon) f(\varepsilon) d\varepsilon \\
&= \int_0^\mu I(\varepsilon) d\varepsilon + \frac{\pi^2 (k_B T)^2}{6} I'(\mu) + \frac{7\pi^4 (k_B T)^4}{360} I^{(3)}(\mu) + \cdots \\
N &= \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = \int_0^\mu g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + \cdots \\
&= \int_0^{\varepsilon_F} g(\varepsilon) + \int_{\varepsilon_F}^\mu g(\varepsilon) + \frac{\pi^2}{6} (k_B T)^2 g'(\mu) + \cdots \\
&\simeq N + g(\varepsilon_F)(\mu - \varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 g'(\varepsilon_F) \\
\Delta\mu &= \mu - \varepsilon_F \simeq -\frac{\pi^2}{6} (k_B T)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)} \\
&= -\frac{\pi^2}{6} (k_B T)^2 [\ln g(\varepsilon_F)]' = -\frac{\pi^2}{12} \frac{(k_B T)^2}{\varepsilon_F}
\end{aligned}
$$

化学势随温度的变化

- 热激发沿 μ 对称分布
  $f(\mu+\Delta\varepsilon) = 1 - f(\mu-\Delta\varepsilon)$
  ☞ 右上图中面积 1 = 面积 2
- 总粒子数
  $N = \int f(\varepsilon)g(\varepsilon)d\varepsilon$
  态密度不对称
  ☞ 右下图中面积 1 ≠ 面积 2
- 为了保持总粒子数不变，化学势必然随温度改变
  $$\Delta\mu \simeq -\frac{\pi^2}{6}\frac{g'(\varepsilon_F)}{g(\varepsilon_F)}(k_BT)^2$$
  ☞ $g'(\varepsilon) > 0$ 时，μ 随温度上升而下降
  ☞ $g'(\varepsilon) < 0$ 时，μ 随温度上升而上升
  ☞ $g'(\varepsilon) = 0$ 时，μ 基本不随温度改变





化学势随温度的变化

☞ $g'(\varepsilon) > 0$ 时，μ 随温度上升而下降
☞ $g'(\varepsilon) < 0$ 时，μ 随温度上升而上升

是否违反热力学规律？Gibbs-Duhem 方程：

$$d\mu = -s dT + v dp \qquad \Rightarrow \qquad \left(\frac{\partial \mu}{\partial T}\right)_p = -s < 0$$

化学势随温度的变化

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是否违反热力学规律？Gibbs-Duhem 方程：

$$d\mu = -sdT + vdp \qquad \Rightarrow \qquad \left(\frac{\partial \mu}{\partial T}\right)_p = -s < 0$$

$$\begin{aligned}
\left(\frac{\partial \mu}{\partial T}\right)_v &= \frac{\partial(\mu, v)}{\partial(T, v)} = \frac{\partial(\mu, v)}{\partial(T, p)}\frac{\partial(\mu, p)}{\partial(T, v)} \\
&= \left[\left(\frac{\partial \mu}{\partial T}\right)_p \left(\frac{\partial v}{\partial p}\right)_T - \left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial v}{\partial T}\right)_p\right]\left(\frac{\partial p}{\partial v}\right)_T \\
&= -s + v\frac{\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p}{-\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T} = -s + \frac{\alpha v}{\kappa_T}
\end{aligned}$$

Fermi 函数积分的 Polylogarithm （多重对数函数）表示

在做数值计算的时候，经常用 Polylogarithm 表示 Fermi 函数的积分。

$$Li_s(z) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{x^{s-1}}{e^x/z - 1} dx = \sum_{l=1}^{\infty} \frac{z^l}{l^s} \qquad (|z| < 1)$$

$$\begin{aligned} I_j &= \int_0^\infty \frac{\varepsilon^j}{e^{(\varepsilon-\mu)/k_B T} + 1} d\varepsilon \\ &= (k_B T)^{j+1} \int_0^\infty \frac{x^j}{e^x/z + 1} dx \qquad z = e^{\mu/k_B T} \\ &= -(k_B T)^{j+1} \Gamma(j+1) Li_{j+1}(-z) \end{aligned}$$

$$Li_s(-e^y) = y^s \sum_{k=0}^{\infty} (-1)^k [1 - 2^{1-2k}] (2\pi)^{2k} \frac{B_{2k}}{(2k)!} \frac{y^{-2k}}{\Gamma(s+1-2k)}$$

B_n 是 Bernoulli 数，$B_0 = 1$，$B_2 = \frac{1}{6}$, $B_4 = -\frac{1}{30}$，$\cdots$

电子热容

强简并时只有位于费米面附近 $k_B T$ 的少数电子才能受到热激发，对热容有贡献。其它大部分粒子是不能被激发，不参与热过程的，因此对热容等热力学性质没有贡献。

参与热容贡献的大体估计：

☞ 参与热过程的电子数

$N_t \simeq g(\varepsilon_F)$ [Fermi 面态密度] $\times k_B T$ [可以被激发的能量范围]

☞ 每个电子贡献的热激发能量 $\simeq 3k_B T/2$ [能量均分原理]

☞ 热激发能量 $\Delta U \simeq N_t \times 3k_B T/2 = 3g(\varepsilon_F)k_B T^2/2$

☞ 热容 $C_e \simeq \dfrac{\partial \Delta U}{\partial T} = 3g(\varepsilon_F)k_B^2 T = 3\dfrac{3N}{2\varepsilon_F}k_B^2 T = \dfrac{9Nk_B T}{2T_F} \propto \dfrac{T}{T_F}$。

电子热容

严格计算要用到 Sommerfeld 展开，

$$
\begin{aligned}
U_0 &= \int_0^{\varepsilon_F} g(\varepsilon)\varepsilon\, d\varepsilon \\
U &\simeq \int_0^{\mu} g(\varepsilon)\varepsilon\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 [g(\mu)\mu]' \\
&\simeq U_0 + [g(\varepsilon_F)\varepsilon_F]\Delta\mu + \frac{\pi^2}{6}(k_B T)^2 [g(\varepsilon_F)\varepsilon_F]' \\
\Delta U &= g(\varepsilon_F)\varepsilon_F \left[-\frac{\pi^2}{6}(k_B T)^2 \frac{g'(\varepsilon)}{g(\varepsilon_F)}\right] + \frac{\pi^2}{6}(k_B T)^2 [g'(\varepsilon_F)\varepsilon_F + g(\varepsilon_F)] \\
&= \frac{\pi^2}{6}(k_B T)^2 g(\varepsilon_F) \\
C_e &= \frac{\partial \Delta U}{\partial T} = \frac{\pi^2}{3} g(\varepsilon_F) k_B^2 T \\
&= \frac{\pi^2}{2} \frac{N}{\varepsilon_F} k_B^2 T = \frac{\pi^2}{2} N k_B \frac{T}{T_F}
\end{aligned}
$$

相互作用对电子气体的影响：排斥相互作用

- Wigner-Seitz 半径 r_s：粒子间距

$$\frac{4\pi}{3}r_s^3 = \frac{N}{V} \Rightarrow r_s = \left(\frac{3N}{4\pi V}\right)^{1/3} = \frac{h}{\sqrt[3]{2}\, p_F}$$

- Fermi 统计的特点

$$K \sim \varepsilon_F = \frac{p_F^2}{2m} \sim \frac{h^2}{2m}\frac{1}{r_s^2} \qquad\qquad U \sim \frac{e^2}{\varepsilon_0 r_s}$$

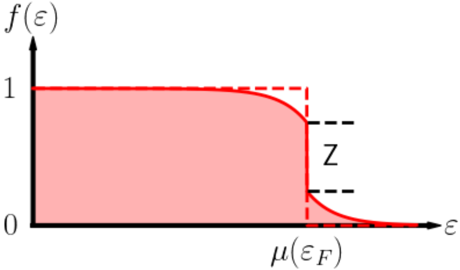
☞ 非常反直觉的结果：一般系统，密度越大，相互作用越重要，例如稀疏的原子动能远大于相互作用，因此形成气体；高密度的原子相互作用占主导，形成晶体。
但是对于电子气体，密度越大，r_s 越小，K 相对于 U 就越大，电子越接近独立电子的行为。
☞ 低密度电子系统可能形成 Wigner 晶体

- 电子屏蔽使得 Coulomb 作用减小
- Pauli 不相容原理保证电子基本不受散射

Landau Fermi 液体理论

如果相互作用不导致能隙，那么即使考虑相互作用：

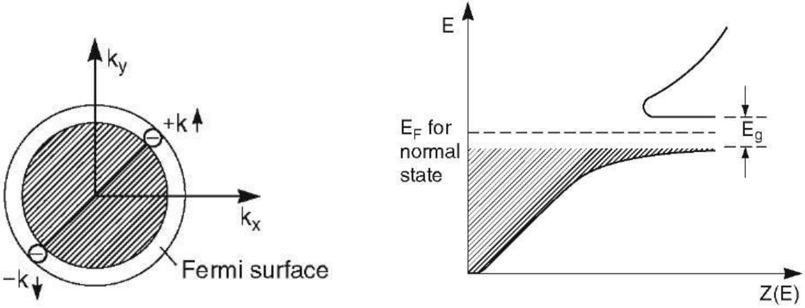
- 低能的元激发和独立粒子类似
- 零温下仍然存在 Fermi 面



☞ 有无相互作用不改变定性的物理图像

☞ 热容等物理量仍然是和温度成正比

吸引作用 ⇒ BCS 基态



- Fermi 面和吸引作用导致 Cooper 对，降低能量 ⇒ 基态不再是 Fermi 球，而是 BCS 基态
- 此时的低能激发态不再是无能隙的粒子 - 空穴对激发，而是存在能隙
- 例子：超导体、超流 ^{3}He、重原子核、超流中子星、···

分数统计

- 二维系统中存在介乎玻色和费米子之间的“粒子”: $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi(\boldsymbol{r}_2, \boldsymbol{r}_1)e^{i\theta}$
  - Fermion： $\theta = (2n+1)\pi$， $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = -\psi(\boldsymbol{r}_2, \boldsymbol{r}_1)$
  - Boson： $\theta = 2n\pi$， $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \psi(\boldsymbol{r}_2, \boldsymbol{r}_1)$
  - (Abelian) Anyon / 任意子： $\theta = \not{n}\pi$
- Anyon 满足所谓的分数统计
  - 即使没有相互作用，多粒子子 anyon 的系统波函数无法写成单粒子波函数的组合。
  - 一般情况下，即使没有相互作用，多粒子 anyon 的系统本征能量也不是单粒子能量之和。
  - 最简单的 anyon 系统的统计规律也是非常复杂的，不能用单粒子分布函数来描述。
- 参考资料

  - “Fractional Statistics and Quantum Theory”, 2nd ed, A. Khar, World Scientific (2005)
  - “Anyons: Quantum Mechanics of Particles with Fractional Statistics”, A. Lerda, Springer (1992)

复杂系统的统计

- 两相共存的系统

  I 相和二相，单粒子本征能级和简并度分别为 ε_l^σ 和 ω_l^σ，$\sigma = I, II$ 是相指标，l 是能级指标。分布函数为 $\{a_l^\sigma\}$，相应的微观状态数 $\Omega = \Omega(\{a_l^\sigma\})$。约束条件是

$$N \equiv N^I + N^{II} = \sum_{\sigma l} a_l^\sigma$$

$$E \equiv E^I + E^{II} = \sum_{\sigma l} a_l^\sigma \varepsilon_l^\sigma$$

  热平衡分布使得在这两个约束条件下 Ω 达到最大，引入两个 Lagrange 乘子 α，β

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

  求出 $a_l^\sigma = a_l^\sigma(\alpha, \beta)$。和单相时结果相比，$a_l^\sigma = a_l^\sigma(\alpha_\sigma, \beta_\sigma)$，

  $\beta_I = \beta_{II} = \beta \quad \Rightarrow \quad$ 两相共存时温度相等

  $\alpha_I = \alpha_{II} = \alpha = -\beta\mu \quad \Rightarrow \quad$ 两相共存时化学势相同

复杂系统的统计

- 化学反应：例如 $N_2 + 3H_2 = 2NH_3$
  单粒子本征能级和简并度分别为 ε_l^i 和 ω_l^i，$i = H_2, N_2, NH_3$ 是组分指标，l 是能级指标。分布函数为 $\{a_l^i\}$，相应的微观状态数 $\Omega = \Omega(\{a_l^i\})$。约束条件是

$$N_N \equiv 2N_{N_2} + N_{NH_3} = \sum_l [2a_l^{N_2} + a_l^{NH_3}] \qquad \boxed{\text{N 原子数目守恒}}$$

$$N_H \equiv 2N_{H_2} + 3N_{NH_3} = \sum_l [2a_l^{H_2} + 3a_l^{NH_3}] \qquad \boxed{\text{H 原子数目守恒}}$$

$$E \equiv E^{N_2} + E^{H_2} + E^{NH_3}$$

热平衡分布使得在这两个约束条件下 Ω 达到最大，引入三个 Lagrange 乘子 α_N，α_H，β

$$\begin{aligned} 0 &= \delta \ln \Omega - \alpha_N \delta N_N - \alpha_H \delta N_H - \beta \delta E \\ &= \delta \ln \Omega - \beta \delta E - \sum_l [2\alpha_H \delta a_l^{H_2} + 2\alpha_N \delta a_l^{N_2} + \alpha_N + 3\alpha_H \delta a_l^{NH_3}] \end{aligned}$$

复杂系统的统计

- 化学反应：例如 $N_2 + 3H_2 = 2NH_3$
  求出平衡分布

$$a_l^{H_2} = a_l^{H_2}(\alpha_H, \beta) = a_l^{H_2}(-\beta\mu_{H_2}, \beta) \qquad \Rightarrow \mu_{H_2} = -2\alpha_H/\beta$$

$$a_l^{N_2} = a_l^{N_2}(\alpha_N, \beta) = a_l^{N_2}(-\beta\mu_{N_2}, \beta) \qquad \Rightarrow \mu_{N_2} = -2\alpha_N/\beta$$

$$a_l^{NH_3} = a_l^{NH_3}(\alpha_N + 3\alpha_H, \beta) = a_l^{NH_3}(-\beta\mu_{NH_3}, \beta)$$

$$\Rightarrow \mu_{NH_3} = -\frac{\alpha_N + 3\alpha_N}{\beta} = \frac{\mu_{N_2} + 3\mu_{H_2}}{2}$$

$$\Rightarrow 0 = 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}$$

☞ 化学平衡条件

复杂系统的统计

- 相对论粒子

  例如：由于质能关系，电子数 N_e 和正电子数 N_p 并不守恒，但是由于规范不变，总电量守恒，即 $N_e - N_p \equiv -Q/e$。分布为 a_l^i，$i = e, p$，l 为能级指标。约束条件为

$$-Q/e \equiv N_e - N_p = \sum_l (a_l^e - a_l^p)$$

$$E \equiv \sum_l (a_l^e \varepsilon_l^e - a_l^p \varepsilon_l^p)$$

极值条件

$$0 = \delta \ln \Omega - \alpha\delta(-Q/e) - \beta\delta E = \delta \ln \Omega - \beta\delta E - \alpha \sum_l \delta a_l^e + \alpha \sum_l \delta a_l^p$$

分布

$$a_l^e = a_l^e(\alpha, \beta) = a_l^e(-\beta\mu_e, \beta)$$

$$a_l^p = a_l^p(-\alpha, \beta) = a_l^p(-\beta\mu_p, \beta)$$

$$\Rightarrow \mu_p = -\mu_e$$

复杂系统的统计

- 相对论粒子

$$\varepsilon(\boldsymbol{p}) = \sqrt{m_e c^2 + c^2 p^2} \simeq m_e c^2 + \boldsymbol{p}^2/(2m)$$

$$a^e(\boldsymbol{p}) = \frac{1}{e^{\beta(\varepsilon(\boldsymbol{p})-\mu)} + 1}$$

$$a^p(\boldsymbol{p}) = \frac{1}{e^{\beta(\varepsilon(\boldsymbol{p})+\mu)} + 1}$$

如果总电荷为负，低温下 $\mu \simeq m_e c^2$，$\Rightarrow$ 正电荷数目

$$N_p \simeq e^{-2m_e c^2/(k_B T)} \int e^{-\boldsymbol{p}^2/(2mk_B T)} \simeq 0$$