热力学与统计物理学复习

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> 桜井雪子的筆記只有他自己能看懂，只對他自己有用。
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区分：状态参量、态函数。

1 热力学基本方程

1.1 导论

三个重要参数：$\frac{\partial V}{\partial T}\Big|_p \frac{\partial T}{\partial p}\Big|_V \frac{\partial p}{\partial V}\Big|_T = -1 \Rightarrow \alpha = \beta\kappa_T p$

- 等压膨胀：$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p$
- 等容压缩：$\beta = \frac{1}{p}\frac{\partial p}{\partial T}\Big|_V$
- 等温压缩：$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T$

理想气体三个系数。

$$pV = \nu RT$$

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_p = \frac{1}{T},\ \beta = \frac{1}{p}\frac{\partial p}{\partial T}\bigg|_V = \frac{1}{T},\ \kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T = \frac{1}{p}$$

物态方程 $p(V_m - b) = RT\exp[-a/(V_m RT)]$ 的 α.

$$\alpha = \frac{1}{V_m}\frac{\partial V_m}{\partial T}\bigg|_p = \dots$$

$$\mathrm{d}V = \frac{\partial V}{\partial T}\bigg|_p \mathrm{d}T + \frac{\partial V}{\partial p}\bigg|_T \mathrm{d}p = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p \Rightarrow \frac{\mathrm{d}V}{V} = \alpha\,\mathrm{d}T - \kappa_T\,\mathrm{d}p$$

$\alpha = 1/T$, $\kappa_T = 1/p$ 推导状态方程。

$$\frac{\mathrm{d}V}{V} = \alpha\,\mathrm{d}T - \kappa_T\,\mathrm{d}p = \frac{\mathrm{d}T}{T} - \frac{\mathrm{d}p}{p} \Rightarrow \mathrm{d}(\frac{pV}{T}) = 0$$

$\alpha = \beta = 1/T$ 推导状态方程。

$$\mathrm{d}T = \left.\frac{\partial T}{\partial V}\right|_p \mathrm{d}V + \left.\frac{\partial T}{\partial p}\right|_V \mathrm{d}p = \frac{1}{\alpha V}\,\mathrm{d}V + \frac{1}{\beta p}\,\mathrm{d}p$$

$$\mathrm{d}T = \frac{T}{V}\,\mathrm{d}V + \frac{T}{p}\,\mathrm{d}p \Rightarrow \mathrm{d}(\frac{pV}{T}) = 0$$

$\alpha = \frac{R}{pV_m} + \frac{a}{V_m T^2}$, $\kappa_T = \frac{RT}{p^2 V_m}$ 推导物态方程。

$$\frac{\mathrm{d}V_m}{V_m} = \alpha\,\mathrm{d}T - \kappa_T\,\mathrm{d}p = (\frac{R}{pV_m} + \frac{a}{V_m T^2})\,\mathrm{d}T - \frac{RT}{p^2 V_m}\,\mathrm{d}p \Rightarrow \mathrm{d}\left[p\left(V_m + \frac{a}{T}\right) - RT\right] = 0$$

1.2 热力学第一定律

热容：稳定系统 $C_p > C_V$

- 热容：$C \equiv \frac{\mathrm{d}Q}{\mathrm{d}T}$
- 等容热容：$C_V = \left.\frac{\partial U}{\partial T}\right|_V$
- 等压热容：$C_p = \left.\frac{\partial H}{\partial T}\right|_p = \left.\frac{\partial (U+pV)}{\partial T}\right|_p$

多方过程 $pV^n = \mathrm{const}$。

$$pV^n = \mathrm{const} \Rightarrow \frac{\mathrm{d}p}{p} + n\frac{\mathrm{d}V}{V} = 0,\ pV = \nu RT \Rightarrow \frac{\mathrm{d}p}{p} + \frac{\mathrm{d}V}{V} = \frac{\mathrm{d}T}{T}$$

根据第一定律证明两条绝热线不可能相交。
若相交，可构造不吸放热、仅做功的循环。

1.3 热力学第二定律

根据第二定律证明两条绝热线不可能相交。

若相交，取一条等温线与它们交于此交点上方，则可构造不放热只做功的循环，违反开尔文表述。

热力学第二定律的数学表述：

- 卡诺定理：$1-\frac{Q_2}{Q_1}\leq 1-\frac{T_1}{T_2}$
- 克劳修斯不等式：$\oint\frac{\mathrm{d}Q}{T}\leq 0$
- 熵：$\mathrm{d}S=\mathrm{d}Q_{\mathrm{rev}}/T$，注意可逆过程
- 熵增加原理：孤立系统的熵永不减少。

求理想气体的熵。

$$\nu C_{Vm}\,\mathrm{d}T=T\,\mathrm{d}S-p\,\mathrm{d}V\Rightarrow \mathrm{d}S=\nu C_{Vm}\frac{\mathrm{d}T}{T}+\frac{p}{T}\,\mathrm{d}V=\nu C_{Vm}\frac{\mathrm{d}T}{T}+\nu R\frac{\mathrm{d}V}{V}$$

or:

$$\mathrm{d}S=\nu C_{Vm}\frac{\mathrm{d}T}{T}+\nu R\frac{\mathrm{d}V}{V}=\nu C_{Vm}\frac{\mathrm{d}T}{T}+\nu R(\frac{\mathrm{d}T}{T}-\frac{\mathrm{d}p}{p})=\nu C_{pm}\frac{\mathrm{d}T}{T}-\nu R\frac{\mathrm{d}p}{p}$$

求理想气体自由膨胀过程中的熵变。

只需注意到对于自由膨胀过程有 $\mathrm{d}T=0$.

已知 $U=bVT^4=3pV$, $S(T=0)=0$，求 $S(T)$.

$$\mathrm{d}U=bT^4\,\mathrm{d}V+4bVT^3\,\mathrm{d}T=T\,\mathrm{d}S-p\,\mathrm{d}V=T\,\mathrm{d}S-\frac{bT^4}{3}\,\mathrm{d}V$$

$$\mathrm{d}S=\frac{4}{3}bT^3\,\mathrm{d}V+4bT^2V\,\mathrm{d}T=\mathrm{d}\left[\frac{4}{3}bT^3V\right]$$

1.4 热力学基本方程

$$\begin{aligned}
\mathrm{d}U(S,V)&=+T\,\mathrm{d}S-p\,\mathrm{d}V\\
\mathrm{d}(U+pV)=\mathrm{d}H(S,p)&=+T\,\mathrm{d}S+V\,\mathrm{d}p\\
\mathrm{d}(U-TS)=\mathrm{d}F(T,V)&=-S\,\mathrm{d}T-p\,\mathrm{d}V\\
\mathrm{d}(U-TS+pV)=\mathrm{d}G(T,p)&=-S\,\mathrm{d}T+V\,\mathrm{d}p
\end{aligned}$$

- 通过全微分得到状态参量和态函数偏导数的关系；
- 通过交换偏导次序得到 Maxwell 关系。

2 均匀闭系的热力学性质

2.1 Maxwell 关系

$$\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x}$$

（有一个记忆法则来着，很管用）

$$\left.\frac{\partial T}{\partial V}\right|_S = -\left.\frac{\partial p}{\partial S}\right|_V, \left.\frac{\partial T}{\partial p}\right|_S = +\left.\frac{\partial V}{\partial S}\right|_p, \left.\frac{\partial S}{\partial V}\right|_T = +\left.\frac{\partial p}{\partial T}\right|_V, \left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p$$

还可以利用

$$\frac{\partial x \partial y}{\partial f(x,y)} = \frac{\partial y \partial x}{\partial f(x,y)}$$

得到四个倒过来的关系。

2.2 Maxwell 关系的典型应用

2.2.1 复合函数法

1. $U(T,V) = U[S(T,V),V]$
   - 定容热容：$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \left.\frac{\partial U}{\partial S}\right|_V \left.\frac{\partial S}{\partial T}\right|_V = T \left.\frac{\partial S}{\partial T}\right|_V$
   - $\left.\frac{\partial U}{\partial V}\right|_T = \left.\frac{\partial U(T,V)}{\partial V}\right|_T = \left.\frac{\partial U[S(T,V),V]}{\partial V}\right|_T = \left.\frac{\partial U}{\partial S}\right|_V \left.\frac{\partial S}{\partial V}\right|_T + \left.\frac{\partial U}{\partial V}\right|_S = T \left.\frac{\partial p}{\partial T}\right|_V - p$
2. $H(T,p) = H[S(T,p),p]$
   - 定压热容：$C_p = \left.\frac{\partial H}{\partial T}\right|_p = \left.\frac{\partial H}{\partial S}\right|_p \left.\frac{\partial S}{\partial T}\right|_p = T \left.\frac{\partial S}{\partial T}\right|_p$
   - $\left.\frac{\partial H}{\partial p}\right|_T = \left.\frac{\partial H(T,p)}{\partial p}\right|_T = \left.\frac{\partial H[S(T,p),p]}{\partial p}\right|_T = \left.\frac{\partial H}{\partial S}\right|_p \left.\frac{\partial S}{\partial p}\right|_T + \left.\frac{\partial H}{\partial p}\right|_S = -T \left.\frac{\partial V}{\partial T}\right|_p + V$
3. 迈耶公式
   - $S(T,p) = S[T,V(T,p)] \Rightarrow \left.\frac{\partial S}{\partial T}\right|_p = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_p$
   - $C_p - C_V = T\left[\left.\frac{\partial S}{\partial T}\right|_p - \left.\frac{\partial S}{\partial T}\right|_V\right] = T \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_p = T \left.\frac{\partial p}{\partial T}\right|_V \left.\frac{\partial V}{\partial T}\right|_p = \alpha\beta p V T = -T\frac{\left(\left.\frac{\partial p}{\partial T}\right|_V\right)^2}{\left.\frac{\partial p}{\partial V}\right|_T}$

2.2.2 Jacobi 行列式法

唯一需要特殊记忆的性质：$\frac{\partial(x,v)}{\partial(u,v)} = \left.\frac{\partial x}{\partial u}\right|_v$，其他的：反对称、倒数、链式法则

$$\frac{C_p}{C_V} = \frac{\left.\frac{\partial S}{\partial T}\right|_p}{\left.\frac{\partial S}{\partial T}\right|_V} = \frac{\frac{\partial(S,p)}{\partial(T,p)}}{\frac{\partial(S,V)}{\partial(T,V)}} = \frac{\frac{\partial(T,V)}{\partial(T,p)}}{\frac{\partial(S,V)}{\partial(S,p)}} = \frac{\left.\frac{\partial V}{\partial p}\right|_T}{\left.\frac{\partial V}{\partial p}\right|_S} = \frac{-\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T}{-\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_S} \equiv \frac{\kappa_T}{\kappa_S}$$

$p = f(V)T$，试证明其内能以 (V,T) 为参数时不显含体积。

$$\left.\frac{\partial U(V,T)}{\partial V}\right|_T = \left.\frac{\partial U[S(V,T),V]}{\partial V}\right|_T = \cdots = T\left.\frac{\partial p}{\partial T}\right|_T - p = Tf(V) - p = 0$$

证明：一个均匀物体在准静态等压过程中熵随体积的增减取决于等压条件下温度随体积的增减。

$$\left.\frac{\partial S(p,V)}{\partial V}\right|_p = \left.\frac{\partial S(T(p,V),V)}{\partial V}\right|_p = \left.\frac{\partial S}{\partial V}\right|_T + \left.\frac{\partial S}{\partial T}\right|_V \cdot \left.\frac{\partial T}{\partial V}\right|_p = \left.\frac{\partial p}{\partial T}\right|_V + \frac{C_V}{T} \cdot \left.\frac{\partial T}{\partial V}\right|_p$$
$$\left.\frac{\partial S(p,V)}{\partial V}\right|_p = \left.\frac{\partial S(T(p,V),p)}{\partial V}\right|_p = \left.\frac{\partial S}{\partial T}\right|_p \left.\frac{\partial T}{\partial V}\right|_p = \frac{C_p}{T} \left.\frac{\partial T}{\partial V}\right|_p$$

证明：$\mathrm{d}S = \frac{C_p}{T}\,\mathrm{d}T - \left.\frac{\partial V}{\partial T}\right|_p \mathrm{d}p$

$$\mathrm{d}S = \left.\frac{\partial S}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial S}{\partial p}\right|_T \mathrm{d}p = \frac{C_p}{T}\,\mathrm{d}T - \left.\frac{\partial V}{\partial T}\right|_p \mathrm{d}p$$

证明：$\left.\frac{\partial C_V}{\partial V}\right|_T = T\left.\frac{\partial^2 p}{\partial T^2}\right|_V$，$\left.\frac{\partial C_p}{\partial p}\right|_T = -T\left.\frac{\partial^2 V}{\partial T^2}\right|_p$

$$\left.\frac{\partial C_V}{\partial V}\right|_T = \left.\frac{\partial}{\partial V}\right|_T \left(T\left.\frac{\partial S}{\partial T}\right|_V\right) = T\left.\frac{\partial}{\partial T}\right|_V \left.\frac{\partial S}{\partial V}\right|_T = T\left.\frac{\partial}{\partial T}\right|_V \left.\frac{\partial p}{\partial T}\right|_V = T\left.\frac{\partial^2 p}{\partial T^2}\right|_V,\ \cdots$$

证明 van de Waals 气体的等容热容与体积无关。

$$\left.\frac{\partial C_V}{\partial V_m}\right|_T = T\left.\frac{\partial^2 p}{\partial T^2}\right|_{V_m} = T\left.\frac{\partial^2}{\partial T^2}\right|_{V_m}\left[\frac{RT}{V_m-b} - \frac{a}{V_m^2}\right] = 0$$

求范式气体的内能和熵。

$$\mathrm{d}U = C_V\,\mathrm{d}T + \frac{a}{V_m^2}\,\mathrm{d}V_m$$
$$\mathrm{d}S = \frac{C_V}{T}\,\mathrm{d}T + \frac{RT}{V_m-b}\,\mathrm{d}V_m$$

2.3 特性函数

实验测量得到的量（认为已知）：$f(p,V,T)=0$, $C_V = C_V(T,V)$, $C_p = C_p(T,p)$；
核心的两个态函数：U, S。

$$
\begin{aligned}
\mathrm{d}U(T,V) &= \left.\frac{\partial U}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial U}{\partial V}\right|_T \mathrm{d}V = C_V\,\mathrm{d}T + \left[T\left.\frac{\partial p}{\partial T}\right|_V - p\right]\mathrm{d}V \\
\mathrm{d}S(T,V) &= \left.\frac{\partial S}{\partial T}\right|_V \mathrm{d}T + \left.\frac{\partial S}{\partial V}\right|_T \mathrm{d}V = \frac{C_V}{T}\,\mathrm{d}T + \left.\frac{\partial p}{\partial T}\right|_V \mathrm{d}V \\
\mathrm{d}H(T,p) &= \left.\frac{\partial H}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial H}{\partial p}\right|_T \mathrm{d}p = C_p\,\mathrm{d}T + \left[-T\left.\frac{\partial V}{\partial T}\right|_p + V\right]\mathrm{d}p \\
\mathrm{d}S(T,p) &= \left.\frac{\partial S}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial S}{\partial p}\right|_T \mathrm{d}p = \frac{C_p}{T}\,\mathrm{d}T - \left.\frac{\partial V}{\partial T}\right|_p \mathrm{d}p
\end{aligned}
$$

求 van de Waals 气体的内能和熵。

$$
\mathrm{d}U(T,V_m) = C_{Vm}\,\mathrm{d}T + \left[T\left.\frac{\partial p}{\partial T}\right|_{V_m} - p\right]\mathrm{d}V_m = C_{Vm}\,\mathrm{d}T + \left[T\frac{R}{V_m-b} - p\right]\mathrm{d}V_m = C_{Vm}\,\mathrm{d}T + \frac{a}{V_m^2}\,\mathrm{d}V_m
$$

$$
\mathrm{d}S(T,V_m) = \frac{C_{Vm}}{T}\,\mathrm{d}T + \frac{R}{V_m-b}\,\mathrm{d}V_m
$$

已知某固体物态方程为: $V(T,p) = V(T_0,0)\left[1+\alpha(T-T_0)-\kappa_T p\right]$。证明其等压热容只与温度有关，与压强无关。设等压热容为 C_p，求焓和熵。

$$
\left.\frac{\partial C_p}{\partial p}\right|_T = -T\left.\frac{\partial^2 V}{\partial T^2}\right|_p = 0
$$

$$
\begin{aligned}
\mathrm{d}H(T,p) &= C_p\,\mathrm{d}T + \left[-TV(T_0,0)\alpha + V\right]\mathrm{d}p = C_p\,\mathrm{d}T + V(T_0,0)\left(1-\alpha T_0-\kappa_T p\right)\mathrm{d}p \\
\mathrm{d}S(T,p) &= \frac{C_p}{T}\,\mathrm{d}T - V(T_0,0)\alpha\,\mathrm{d}p
\end{aligned}
$$

已知某个态函数？那么它的偏导数，即两个状态参量也已知。现在你需要做的是把其他的热力学量表示成这些量的组合：已知态函数 + 这个态函数的两个自变量，亦即将两个已知的状态参量替换为偏导数形式。

特性函数是联系热力学和统计物理学的桥梁。

$F(T,V)$:

- $S(T,V) = -\frac{\partial F}{\partial T}$, $p(T,V) = -\frac{\partial F}{\partial V}$
- $U = F + TS = F - T\frac{\partial F}{\partial T} = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)$
- $H = U + pV = F - T\frac{\partial F}{\partial T} - V\frac{\partial F}{\partial V}$
- $G = F + pV = F - V\frac{\partial F}{\partial V}$

$G(T,p)$:

- $S(T,p) = -\frac{\partial G}{\partial T},\ V(T,p) = \frac{\partial G}{\partial p}$
- $H = G + TS = G - T\frac{\partial G}{\partial T} = -T^2\frac{\partial}{\partial T}\left(\frac{G}{T}\right)$
- $U = H - pV = G - T\frac{\partial G}{\partial T} - p\frac{\partial G}{\partial p}$
- $F = G - pV = G - p\frac{\partial G}{\partial p}$

2.4 绝热降温与节流降温

2.4.1 绝热降温：等熵过程

$$
\begin{aligned}
\left.\frac{\partial T}{\partial p}\right|_S &= \frac{\partial(T,S)}{\partial(p,S)} = \frac{\partial(T,S)}{\partial(T,p)}\frac{\partial(T,p)}{\partial(p,S)} = -\left.\frac{\partial S}{\partial p}\right|_T\frac{T}{C_p} = \frac{T}{C_p}\left.\frac{\partial V}{\partial T}\right|_p = \frac{VT\alpha}{C_p} \\
\left.\frac{\partial T}{\partial V}\right|_S &= \frac{\partial(T,S)}{\partial(V,S)} = \frac{\partial(T,S)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(V,S)} = -\left.\frac{\partial S}{\partial V}\right|_T\frac{T}{C_V} = -\frac{T}{C_V}\left.\frac{\partial p}{\partial T}\right|_V = -\frac{pT\beta}{C_V}
\end{aligned}
$$

2.4.2 节流降温：等焓过程

节流过程是绝热不可逆过程。

Joule-Thomson 系数：

$$\mu_{\mathrm{JT}} = \left.\frac{\partial T}{\partial p}\right|_H = \frac{\partial(T,H)}{\partial(p,H)} = \frac{\partial(T,H)}{\partial(T,p)}\frac{\partial(T,p)}{\partial(p,H)} = \left.\frac{\partial H}{\partial p}\right|_T\cdot\frac{1}{-C_p} = \frac{1}{C_p}\left[T\left.\frac{\partial V}{\partial T}\right|_p - V\right] = \frac{V}{C_p}(\alpha T - 1)$$

- 制冷区/节流降温：$\mu_{\mathrm{JT}} > 0$
- 制热区/节流升温：$\mu_{\mathrm{JT}} < 0$
- 反转曲线：$\mu_{\mathrm{JT}} = 0 \Rightarrow T\left.\frac{\partial V}{\partial T}\right|_p - V = 0$，即 (p,T) 图上的一条线。

证明：$\left.\frac{\partial T}{\partial p}\right|_S - \left.\frac{\partial T}{\partial p}\right|_H > 0$

$$\left.\frac{\partial T}{\partial p}\right|_S = \left.\frac{\partial V}{\partial S}\right|_p,\quad \left.\frac{\partial T}{\partial p}\right|_H = -\left.\frac{\partial T}{\partial H}\right|_p\left.\frac{\partial H}{\partial p}\right|_T = -\frac{1}{C_p}\left[-T\left.\frac{\partial V}{\partial T}\right|_p + V\right]$$

又 $C_p > 0$，即证：

$$0 < C_p\left.\frac{\partial V}{\partial S}\right|_p - \left[T\left.\frac{\partial V}{\partial T}\right|_p - V\right] = T\left.\frac{\partial S}{\partial T}\right|_p\left.\frac{\partial V}{\partial S}\right|_p - \left[T\left.\frac{\partial V}{\partial T}\right|_p - V\right] = V$$

3 单元复相系的热力学性质

3.1 开系的热力学基本方程

3.1.1 化学势

- 在四个态函数的全微分中加入一项 $+\mu\,\mathrm{d}N$

- 由上一步可得：$\mu \equiv \frac{\partial U}{\partial N}\big|_{S,V} \equiv \frac{\partial H}{\partial N}\big|_{S,p} \equiv \frac{\partial F}{\partial N}\big|_{T,V} \equiv \frac{\partial G}{\partial N}\big|_{T,p}$
- 再次根据交换偏导次序结果不变，可以得到一些 Maxwell 关系
- $G = \mu N$ 的来源/逻辑：由广延性证明 $U = TS - PV + \nu N$，再利用 $G = U + pV - TS$

3.1.2 热力学巨势

- $J \equiv F - \mu N = F - G = -pV$
- $\mathrm{d}J = -S\,\mathrm{d}T - p\,\mathrm{d}V - N\,\mathrm{d}\mu$
- 由此可以用 J 的偏导数表示一些状态参量

3.2 热动平衡

3.2.1 热动平衡判据

- （态函数）平衡和稳定判据：$\delta(\star) = 0, \delta^2(\star) \neq 0$，熵极大，其他极小。
- 虚变动：$\sum \delta(\text{广延量}) = 0, \delta(\text{强度量})_i = 0$

3.2.2 热动平衡条件

- 平衡：$T_\mathrm{A} = T_\mathrm{B}, p_\mathrm{A} = p_\mathrm{B}, \mu_\mathrm{A}(T,p) = \mu_\mathrm{B}(T,p)$
- 稳定：$C_p > C_V > 0, \kappa_T > \kappa_S > 0$

3.3 Clausius-Clapeyron 方程

$$-S_{0\mathrm{A}}\,\mathrm{d}T + V_{0\mathrm{A}}\,\mathrm{d}p = \mathrm{d}\mu_\mathrm{A} = \mathrm{d}\mu_\mathrm{B} = -S_{0\mathrm{B}}\,\mathrm{d}T + V_{0\mathrm{B}}\,\mathrm{d}p$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_{0\mathrm{B}} - S_{0\mathrm{A}}}{V_{0\mathrm{B}} - V_{0\mathrm{A}}} \equiv \frac{L_{0,\mathrm{A}\to\mathrm{B}}/T}{V_{0\mathrm{B}} - V_{0\mathrm{A}}} = \frac{L_{m,\mathrm{A}\to\mathrm{B}}}{T(V_{m\mathrm{B}} - V_{m\mathrm{A}})}$$

（上式通常为正；也可以用热机循环推导）

饱和蒸气压方程

- A 相固/液，B 相气，$V_{m\mathrm{A}} \ll V_{m\mathrm{B}}$，i.e. $V_{m\mathrm{B}} - V_{m\mathrm{A}} = V_{m\mathrm{B}}$
- 理想气体：$pV_{m\mathrm{B}} = RT$

$$\frac{\mathrm{d}p}{p} = \frac{L_m(T)}{RT^2}\,\mathrm{d}T \xrightarrow{pV_m = RT} \frac{1}{V_m}\frac{\mathrm{d}V_m}{\mathrm{d}T} = \frac{1}{T}(1 - \frac{L_m}{RT})$$

$$
\begin{aligned}
\frac{\mathrm{d}L_m}{\mathrm{d}T}=\frac{\mathrm{d}\left[T\left(\Delta S_m\right)\right]}{\mathrm{d}T}=\Delta S_m+T\Delta\left(\frac{\mathrm{d}S_m(T,p)}{\mathrm{d}T}\right)=&\Delta S_m+T\Delta\left(\left.\frac{\partial S_m}{\partial T}\right|_p+\left.\frac{\partial S_m}{\partial p}\right|_T\frac{\mathrm{d}p}{\mathrm{d}T}\right)\\
=&\Delta S_m+T\Delta\left(\frac{C_{pm}}{T}-\left.\frac{\partial V_m}{\partial T}\right|_p\cdot\frac{L_m}{T(V_{m\mathrm{B}}-V_{m\mathrm{A}})}\right)\\
=&\Delta S_m+\Delta C_{pm}-\left.\frac{\partial \Delta V_m}{\partial T}\right|_p\cdot\frac{L_m}{\Delta V_m}\\
\xlongequal{pV_m=RT}&\Delta C_{pm}
\end{aligned}
$$

3.4 气液相变理论

- van der Walls 方程：$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT$
- 临界点（指温度再高就没有气液共存了）：$\left.\frac{\partial p}{\partial V_m}\right|_T=0$，$\left.\frac{\partial^2 p}{\partial V_m^2}\right|_T=0$
- 看一下关于稳定性的分析

还有等面积法则什么的……

区分能级和（单粒子）态。

4 统计物理 Introduction

4.1 描述微观状态

4.1.1 单粒子：态密度

暂未考虑自旋自由度。

经典粒子的（半经典）态密度：（自由度 r）

$$\Sigma(E)=\int\cdots\int_{H\le E}\mathrm{d}q_1\ldots\mathrm{d}q_r\,\mathrm{d}p_1\ldots\mathrm{d}p_r\,,\ D(E)=\frac{1}{h^r}\frac{\mathrm{d}\Sigma(E)}{\mathrm{d}E}$$

- 三维经典自由粒子 $r=3$

$$H=\frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right)$$

$$\Sigma(E)=\iiint_V\mathrm{d}q_x\,\mathrm{d}q_y\,\mathrm{d}q_z\iiint_{H\le E}\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z\xlongequal{\text{后面那个事对有某个半径的三维球的积分}}\frac{4\pi V}{3}(2mE)^{3/2}$$

$$D(E)=\frac{1}{h^3}\frac{\mathrm{d}\Sigma(E)}{\mathrm{d}E}=\frac{2\pi V}{h^3}(2m)^{3/2}E^{1/2}$$

- 二维经典自由粒子 $r=2$： $D(E)=\frac{2\pi mS}{h^2}$
- 一维经典自由粒子 $r=1$： $D(E)=\frac{L}{h}\sqrt{2m}E^{-1/2}$
- 一维谐振子（$r=1$）

$$H=\frac{p^2}{2m}+\frac{m\omega^2x^2}{2}$$

$$\Sigma=\int\mathrm{d}q\int_{H\le E}\mathrm{d}p\xlongequal{\text{其实事二维相空间中的一个椭圆的面积}}\frac{2\pi E}{\omega}$$

$$D(E)=h^{-1}\frac{\mathrm{d}\Sigma(E)}{\mathrm{d}E}=\frac{1}{\hbar\omega}$$

- 三维相对论性自由粒子 $r=3$

$$H=+\sqrt{p^2c^2+m^2c^4}$$

$$\Sigma(E)=\iiint_V\mathrm{d}q_x\,\mathrm{d}q_y\,\mathrm{d}q_z\iiint_{H\le E}\mathrm{d}p_x\,\mathrm{d}p_y\,\mathrm{d}p_z=\frac{4\pi V}{3}\left(\frac{E^2-m^2c^2}{c^2}\right)^{3/2}$$

$$D(E)=h^{-3}\frac{\mathrm{d}\Sigma(E)}{\mathrm{d}E}=\frac{4\pi VE\sqrt{E^2-m^2c^4}}{h^3c^3}$$

- 二维相对论性自由粒子 $r=2$：$D(E)=\frac{2\pi S}{h^2c^2}E$
- 一维相对论性自由粒子 $r=1$：$D(E)=\frac{2L}{hc}\frac{E}{\sqrt{E^2-m^2c^4}}$

量子粒子的态密度：

$$g(\varepsilon)=\frac{\mathrm{d}n(\varepsilon)}{\mathrm{d}\varepsilon}$$

- （一维）谐振子

$$\varepsilon=\left(n+\frac{1}{2}\right)\hbar\omega$$

$$n(\varepsilon)=\frac{\varepsilon}{\hbar\omega}-\frac{1}{2},\ g(\varepsilon)=\frac{\mathrm{d}n(\varepsilon)}{\mathrm{d}\varepsilon}=\frac{1}{\hbar\omega}$$

- 高维谐振子注意简并度。对于 s 个谐振子，第 N 个能级的情况（$E=(N+s/2)\hbar\omega$），相当于把 N 分为 s 个非负整数的和，相当于把 $N+s$ 分为 s 个正整数的和，相当于在 $N+s-1$ 个小球直接插入 $s-1$ 个隔板，即 $C_{N+s-1}^{s-1}=C_{N+s-1}^{N}$。

- 二维谐振子

$$\varepsilon=\varepsilon_1+\varepsilon_2=(n_1+\frac{1}{2})\hbar\omega_1+(n_2+\frac{1}{2})\hbar\omega_2$$

$$n(\varepsilon)\underbrace{\left(=\sum_{n_1=0}^{n}\sum_{n_2=0}^{n-n_1}1\right)}_{\text{这个式子有点问题，但是有助于理解}}=\int_0^{\varepsilon}\frac{\mathrm{d}\varepsilon_1}{\hbar\omega_1}\int_0^{\varepsilon-\varepsilon_1}\frac{\mathrm{d}\varepsilon_2}{\hbar\omega_2}=\frac{\varepsilon^2}{2\omega_1\omega_2\hbar^2}$$

$$g(\varepsilon)=\frac{\mathrm{d}n(\varepsilon)}{\mathrm{d}\varepsilon}=\frac{\varepsilon}{\omega_1\omega_2\hbar^2}$$

4.1.2 独立粒子系统

- 能级：里面可能有一堆简并态

考虑某个能级 s 上的情况，M 个单粒子态，N 个粒子。

	全同粒子系统	可分辨粒子系统
量子态	$\|\Psi_{\text{s, IP}}\rangle=\|n_1,\ldots,n_\sigma,\ldots,n_m\rangle$	$\|\Psi_{\text{s, MB}}\rangle=\|\psi_1,\ldots,\psi_i,\ldots,\psi_N\rangle$
能量	$E_s=\sum_{\sigma=1}^{M}\varepsilon_\sigma n_\sigma,\ N_s=\sum_{\sigma=1}^{M}n_\sigma$	$E=\sum_{i=1}^{N}\varepsilon_i$
微观状态数	玻色子：$C_{N+M-1}^{N}=\frac{(N+M-1)!}{N!(M-1)!}$，费米子：$C_M^N=\frac{M!}{N!(M-N)!}$	M^N

表 1: 全同粒子系统关注单粒子态，可分辨粒子系统关注粒子。

另外，经典极限：$a_l\ll g_l$

现在考虑一大堆能级组成的系统的情况，对于能级 l，g_l 个单粒子态，a_l 个粒子（分布就事 $\{a_l\}$）。

	全同粒子系统	可分辨粒子系统
微观状态数	玻色子：$\prod_l C_{g_l+a_l-1}^{a_l}$，费米子：$\prod_l C_{g_l}^{a_l}$	$\frac{N!}{\prod_l a_l!}\prod_l g_l^{a_l}$

表 2: 把每个能级的微观状态数乘起来

说实话，这玩意儿我每次看见都得想一会儿，还不一定能想清楚。通过这个东西可以通过拉

格朗日乘子法导出三个统计分布，但是按照我们下面的、从系综出发的方式，则他们是不必要的。（但是我也不敢说老师考不考）

- 分布：告诉你每个能级上有几个粒子，但是不告诉你每个能级里面的每个态上有几个粒子。
- 占据: 告诉你每个态上有几个粒子, 但是, 你是否知道这些态的能量（以便由此得到“分布”）与我无关。

4.2 统计物理基本原理

4.2.1 基本观点与假设

孤立系统的等概率原理：处于热力学平衡状态的孤立系统，每个可能的微观状态出现的概率相等。

4.2.2 温度和熵的基本定义

Ω 不具有广延性（悲），但 $\ln\Omega$ 具有。

$$S = k\ln\Omega,\ \mathrm{d}S \equiv \frac{1}{T}(\mathrm{d}E + p\,\mathrm{d}V - \mu\,\mathrm{d}N) \Rightarrow \beta = \frac{1}{kT} = \frac{1}{k}\left(\frac{\partial S}{\partial E}\right)_{V,N} \equiv \left(\frac{\partial \ln\Omega}{\partial E}\right)_{V,N}$$

至于化学势，可以解释成“等温等压下增加一个粒子所需的能量”（大概）。

4.2.3 系综理论

事实是“系综”是一个在物理学中非常常见的概念，在量子物理的基本概念等地方出现了与它相同的事物。我觉得我们应该用一个统一的名称来命名，但似乎大家还不是很愿意这样做……

约束条件	系综	特性函数
(E,V,N)	微正则系综	$S(E,V,N)$
(T,V,N)	正则系综	$F(T,V,N)$
(T,V,μ)	巨正则系综	$J(T,V,\mu)$

- V 很害羞，它通常藏在对于单粒子的描述中；
- 必须指出，对于特殊的问题，有特殊的约束条件（例如做化学实验常有保持压强为大气压），可以构造特殊的系综理论。

5 正则系综

5.1 配分函数

$$\text{系统}(E_s) + \text{恒温热源}(E_r = E_0 - E_s, \Omega_r(E_0 - E_s)) = \text{孤立系统}(E_0, \Omega_0)$$
$$\ln\Omega_r(E_0 - E_s) = \ln\Omega_r(E_0) - \frac{\partial \ln\Omega_r}{\partial E}E_s = \ln\Omega_r(E_0) - \frac{E_s}{kT}$$

系统处于某个态 s，即热源处于某个态 r 的概率

$$\rho_s = \frac{\Omega_r(E_0 - E_s)}{\Omega_0} \propto \mathrm{e}^{-\beta E_s}$$

证明：$S = -k\sum_s \rho_s \ln \rho_s$

$$\begin{aligned} S = S_0 - S_r =& k\ln\Omega - \sum_s \rho_s \times k\ln\Omega = k\ln\Omega - \sum_s \rho_s \times k\ln\Omega_r = k\ln\Omega - \sum_s \rho_s \times k\ln\rho_s\Omega_0 \\ =& k\ln\Omega - k\ln\Omega\sum_s \rho_s - \sum_s \rho_s \times k\ln\rho_s = -k\sum_s \rho_s\ln\rho_s \end{aligned}$$

将此概率归一化，则有归一化因子，即配分函数：

$$Z = \sum_s \mathrm{e}^{-\beta E_s}$$

- 全同粒子系统：

$$E_s = \sum_{\text{所有态}\sigma=1}^{M} n_\sigma\varepsilon_\sigma,\ Z_{\mathrm{IP}} = \sum_{\text{所有分布情况}} \mathrm{e}^{-\beta\sum_{\sigma=1}^{M} n_\sigma\varepsilon_\sigma} \text{ with } N \equiv \sum_{\sigma=1}^{M} n_\sigma$$

  经典极限下，$Z_{\mathrm{IP}} = \frac{Z_{\mathrm{MB}}}{N!} = \frac{Z_1^N}{N!}$

- 可分辨粒子系统：

$$E_s = \sum_{i=1}^{N}\varepsilon_i, Z_{\mathrm{MB}} = \sum_{\text{所有情况}} \mathrm{e}^{-\beta\sum_{i=1}^{N}\varepsilon_i} = \sum_{\text{所有情况}}\prod_{i=1}^{N}\mathrm{e}^{-\beta\varepsilon_i} = \prod_{i=1}^{N}\sum_{\sigma=1}^{M}\mathrm{e}^{-\beta\varepsilon_\sigma} = \left[\sum_{\sigma=1}^{M}\mathrm{e}^{-\beta\varepsilon_\sigma}\right]^N \equiv Z_1^N$$

单粒子配分函数：

$$Z_1 = \sum_{\text{态}\sigma}\mathrm{e}^{-\beta\varepsilon_\sigma} = \sum_{\text{能级}l} g_l\mathrm{e}^{-\beta\varepsilon_l} = \int D(\varepsilon)\mathrm{e}^{-\beta\varepsilon}\,\mathrm{d}\varepsilon$$

求一些系统的单粒子配分函数

- 一维谐振子

$$Z_1 = \sum_{n=1}^{\infty}\mathrm{e}^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega} = \frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}}$$

- 双能级系统，能级 $(0,\Delta)$，简并度 (g_1, g_2)

$$Z_1 = \sum_{l=1}^{2} g_l\mathrm{e}^{-\beta\varepsilon_l} = g_1 + g_2\mathrm{e}^{-\beta\Delta}$$

- 三维经典自由粒子

$$D(\varepsilon) = \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2} \Rightarrow Z_1 = \frac{2\pi V(2m)^{3/2}}{h^3}\int_0^\infty \varepsilon^{1/2}\mathrm{e}^{-\beta\varepsilon}\,\mathrm{d}\varepsilon = \frac{V}{\lambda^3},\ \lambda \equiv \frac{h}{\sqrt{2\pi mkT}}$$

or

$$Z_1 = \sum_{\vec{k}}\mathrm{e}^{-\frac{\beta\hbar^2k^2}{2m}} = \int\frac{\mathrm{d}\vec{k}}{(2\pi)^3/V}\mathrm{e}^{-\frac{\beta\hbar^2k^2}{2m}} = \frac{V}{(2\pi)^3}\left[\int_{-\infty}^{\infty}\mathrm{d}k_x\,\mathrm{e}^{-\frac{\beta\hbar^2}{2m}k_x^2}\right]^3 = \dots$$

- 二维经典自由粒子

$$Z_1 = \frac{A}{\lambda^2}$$

- 一维经典自由粒子

$$Z_1 = \frac{L}{\lambda}$$

- 三维极端相对论性自由粒子

$$Z_1 = \frac{8\pi V}{h^3 c^3 \beta^3}$$

- 二维极端相对论性自由粒子

$$Z_1 = \frac{2\pi S}{h^2 c^2 \beta^2}$$

- 一维极端相对论性自由粒子

$$Z_1 = \frac{2L}{hc\beta}$$

5.2 热力学函数

$$U = \sum_s \rho_s E_s = -\frac{\partial}{\partial \beta} \ln Z$$

$$p = \sum_s \rho_s \left(-\frac{\partial E_s}{\partial V}\right) = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z$$

$$\mathrm{d}S = \frac{1}{T}(\mathrm{d}U + p\,\mathrm{d}V) \Rightarrow S = k\left(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z\right)$$

$$F = -kT \ln Z$$

5.3 二能级系统

这玩意儿可以用正则系综分析吗？如果是像顺磁性固体模型那样的系统，粒子事定域的，那肯定是可分辨系统。如果是位形空间中的两层楼，那么……

5.4 理想气体

$$Z_1 = \frac{V}{\lambda^3},\ \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

全同粒子的经典极限（注意到此时有 Gibbs 修正因子）

$$Z_N = \frac{Z_1^N}{N!} = \frac{V^N}{\lambda^{3N} N!}$$

$$F = -kT \ln Z_N \xlongequal{N \gg 1, \ln N! = N(\ln N - 1)} -NkT \ln \frac{V}{N\lambda^3} - NkT$$

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} NkT,\ p = -\frac{\partial F}{\partial V} = \frac{NkT}{V},\ S = -\frac{\partial F}{\partial T} = Nk\left[\frac{5}{2} + \ln \frac{V}{N\lambda^3}\right]$$

$$C_V=\frac{3}{2}Nk$$

可分辨粒子

$$Z_N=Z_1^N,\ S_{\mathrm{MB}}=Nk\left[\frac{3}{2}+\ln\frac{V}{\lambda^3}\right]$$

不满足广延性，即 Gibbs 佯谬。

> 以上相当于三维经典自由粒子组成的理想气体。
>
> - 二维经典自由粒子
>
> $$\ln Z_N=N\ln\left[\frac{2\pi mS}{Nh^2\beta}\right]+N,\ pS=NkT,\ E=NkT$$
>
> - 一维经典自由粒子
>
> $$\ln Z_N=N\ln\left[\frac{\sqrt{2\pi m}L}{Nh}\beta^{-1/2}\right]+N,\ pL=NkT,\ E=\frac{1}{2}NkT$$
>
> - 三维极端相对论性自由粒子
>
> $$\ln Z_N=N\ln\left[\frac{8\pi V}{Nh^3c^3\beta^3}\right]+N,\ pV=NkT,\ E=3NkT$$

5.5 局域系统/定域子系

5.5.1 顺磁性固体

电子的角动量和磁矩:

$$\vec{\mu}=-g\frac{e}{2m}\vec{J},\ g=\begin{cases}1,\ \text{orbit}\\ 2,\ \text{spin}\end{cases}$$

$$H=-\vec{\mu}\cdot\vec{B}=\pm\mu_B B$$

$$Z_1=\mathrm{e}^{+\beta\mu_B B}+\mathrm{e}^{-\beta\mu_B B}=2\cosh\left(\beta\mu_B B\right)\Rightarrow Z_N=Z_1^N=2^N\cosh^N\left(\beta\mu_B B\right)$$

$$\begin{aligned}
F=&-kT\ln Z_N=-NkT\ln\left[\cosh\left(\beta\mu_B B\right)\right]-NkT\ln 2\\
U=&-\frac{\partial}{\partial\beta}\ln Z_N=-N\mu_B B\tanh\left(\beta\mu_B B\right)\Rightarrow M=\frac{U}{-B}=\dots\\
\chi\equiv&\frac{\partial M}{\partial H}=\mu_0\frac{\partial M}{\partial B}=\frac{N\beta\mu\mu_B^2}{\cosh^2\left(\beta\mu_B B\right)}\xrightarrow[\text{Curie law}]{\beta\mu_B B\to 0}\frac{N\mu_0\mu_B^2}{kT}\\
S=&-\left(\frac{\partial F}{\partial T}\right)_{B,N}=Nk\ln\left[2\cosh\left(\frac{\mu_B B}{kT}\right)\right]-\frac{N\mu_B B}{T}\tanh\left(\frac{\mu_B B}{kT}\right)
\end{aligned}$$

> 自旋量子数为 $s=1$ 的顺磁性固体
>
> $$H=-2\mu_B B,\ 0,\ 2\mu_B B$$

$$Z_1=\mathrm{e}^{+2\beta\mu_B B}+1+\mathrm{e}^{-2\beta\mu_B B}=1+2\cosh\left(2\beta\mu_B B\right),\ Z_N=Z_1^N$$

$$\begin{aligned}
F=&-NkT\ln\left[1+2\cosh\left(2\beta\mu_B B\right)\right]\\
U=&-4N\mu_B B\frac{\sinh(2\beta\mu_B B)}{2\cosh(2\beta\mu_B B)+1}\\
S=&-\frac{\partial F}{\partial T}=kN\ln\left[2\cosh\left(\frac{2\mu_B B}{kT}\right)+1\right]-\frac{4N\mu_B B}{T}\frac{\sinh\left(\frac{2\mu_B B}{kT}\right)}{2\cosh\left(\frac{2\mu_B B}{kT}\right)+1}
\end{aligned}$$

5.5.2 固体振动：Einstein 模型

一维谐振子：

$$\varepsilon_n=\left(n+\frac{1}{2}\right)\hbar\omega$$

$$E=\sum_{i=1}^{3N}\left(n_i+\frac{1}{2}\right)\hbar\omega$$

$$Z_1=\frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}}\Rightarrow Z_N=Z_1^{3N}=\left[\frac{\mathrm{e}^{-\beta\hbar\omega/2}}{1-\mathrm{e}^{-\beta\hbar\omega}}\right]^{3N}$$

$$U=-\frac{\partial}{\partial\beta}\ln Z=\frac{3}{2}N\hbar\omega+\frac{3N\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1}=\begin{cases}\frac{3}{2}N\hbar\omega, & T\to 0\\ \frac{3}{2}N\hbar\omega+3NkT=3NkT, & T\to\infty\end{cases}$$

$$C_V=\left(\frac{\partial U}{\partial T}\right)_V=3Nk\left(\frac{\Theta_T}{T}\right)^2\frac{\mathrm{e}^{\Theta_T/T}}{\left(\mathrm{e}^{\Theta_T/T}-1\right)^2}=\begin{cases}3Nk\left(\frac{\Theta_T}{T}\right)^2\mathrm{e}^{-\frac{\Theta_T}{T}}, & T\to 0\\ 3Nk, & T\to\infty\end{cases},\ \Theta_T\equiv\frac{\hbar\omega}{k}$$

5.5.3 固体振动：Debye 模型

固体内的波可以视作声子的运动，声子是一个奇怪的东西，它的自旋可以理解为 1，并且不同自旋态的速度不同。在频率空间中，可以仿照三维极端相对论性气体来计算得到态密度

$$D(\varepsilon)=\frac{\partial\Sigma}{\partial\varepsilon}=\frac{4\pi V}{h^3c^3}\varepsilon^2\Rightarrow D(\omega)=\frac{\partial\Sigma}{\partial\omega}=\frac{V}{2\pi^2c^3}\omega^2$$

似乎应该有 $g(\omega)=(2s+1)D(\omega)$，但是由于不同自旋的速度不同，所以实际上是

$$g(\omega)=V\left(\frac{\omega^2}{2\pi^2c_{\mathrm{l}}^3}+\frac{\omega^2}{\pi^2c_{\mathrm{t}}^3}\right)$$

粒子数（注意我们在计算态密度时区分了声子的不同自旋态, 所以这里总粒子数事 $3N$ 而不是 N）

$$3N=\int_0^{\omega_{\mathrm{D}}}g(\omega)\,\mathrm{d}\omega\Rightarrow\omega_{\mathrm{D}}^3=18\pi^2\frac{N}{V}\left(\frac{1}{c_{\mathrm{l}}^3}+\frac{2}{c_{\mathrm{t}}^3}\right)^{-1}$$

$$g(\omega)=9N\frac{\omega^2}{\omega_{\mathrm{D}}^3},\ \omega<\omega_{\mathrm{D}}$$

$$
\begin{aligned}
E &= \int_0^{\omega_{\mathrm{D}}} \langle\varepsilon\rangle(\omega) g(\omega)\,\mathrm{d}\omega \\
C_V &= \frac{\partial E}{\partial T} = 3Nk \times \frac{3}{x_0^3} \int_0^{x_0} \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2}\,\mathrm{d}x\,,\ x_0 = \frac{\hbar\omega_{\mathrm{D}}}{kT} \\
C_V &\xlongequal{x_0 \to 0} 3Nk \times \left(1 - \frac{x_0^2}{20}\right) \\
C_V &\xlongequal{x_0 \to \infty} 3Nk \times \frac{4\pi^4}{5x_0^3} \propto T^3
\end{aligned}
$$

6 巨正则系综

这一章处理具体系统显然有两个思路，一个是和正则系综处理经典系统一样先求出一个无敌的函数然后疯狂求导，另一个是利用巨正则系综推出的费米狄拉克分布和玻色爱因斯坦分布从统计的角度积分。现在我有个想法是先介绍巨正则系综方法，再介绍统计分布方法，之后开始分两条路处理几个具体的系统。这应该会使得两种思路更加清晰，尽管有的系统实在无法用另一种方法处理。应该提及，正则系综方法也有对应的统计分布方法即麦克斯韦玻尔兹曼方法。巨正则系综方法面对一些问题力不从心，因为存在大量数学上的困难以及我们对化学势认识的肤浅。

6.1 巨正则系综方法：理论

6.1.1 巨配分函数

系统(E_s, N_s)+恒温热源、恒化学势粒子源$(E_r = E_0 - E_s, N_r = N_0 - N_s, \Omega(E_r, N_r))$ = 孤立系统(E_0, N_0, Ω_0)

$$
\ln\Omega_r(E_0 - E_s, N_0 - N_s) = \ln\Omega_r(E_0, N_0) - \frac{\partial \ln\Omega_r}{\partial E} E_s - \frac{\partial \ln\Omega_r}{\partial N} N_s = \ln\Omega_r(E_0, N_0) - \frac{E_s}{kT} + \frac{\mu N}{kT}
$$

系统处于某个态 s，即热源处于某个态 r 的概率

$$
\rho_s = \frac{\Omega_r(E_0 - E_s, N_0 - N_s)}{\Omega_0} \propto \mathrm{e}^{-\beta(E_s - \mu N_s)}
$$

将此概率归一化，则有归一化因子，即巨配分函数：

$$
Z_{\mathrm{GC}} = \sum_s \mathrm{e}^{-\beta(E_s - \mu N_s)} = \sum_{\text{所有占据的情况}\sigma} \mathrm{e}^{-\sum_\sigma \beta(\varepsilon_\sigma - \mu) n_\sigma} = \prod_\sigma \sum_{n_\sigma} \mathrm{e}^{-\beta(\varepsilon_\sigma - \mu) n_\sigma} \equiv \prod_\sigma Z_\sigma
$$

单粒子态配分函数

$$
Z_\sigma = \left[1 - g_\pm \mathrm{e}^{-\beta(\varepsilon_\sigma - \mu)}\right]^{-g_\pm},\quad \begin{cases} g_+ \equiv +1,\ \text{玻色子} \\ g_- \equiv -1,\ \text{费米子} \end{cases}
$$

$$
\Rightarrow \ln Z_{\mathrm{GC}} = -g_\pm \sum_\sigma \ln\left[1 - g_\pm \mathrm{e}^{-\beta(\varepsilon_\sigma - \mu)}\right] = -g_\pm \sum_\sigma \ln\left[1 - g_\pm \mathrm{e}^{\alpha - \beta\varepsilon_\sigma}\right],\ \alpha \equiv \beta\mu
$$

通常我们不用真的做出这个求和。另外，巨正则系综和正则系综的关系、巨配分函数和配分函数的关系

$$
Z_{\mathrm{GC}} = \sum_{\text{所有态}s} \mathrm{e}^{-\beta(E_s - \mu N_s)} = \sum_{N=0}^{\infty} \sum_{s_N} \mathrm{e}^{-\beta(E_{s_N} - \mu N)} = \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \left(\sum_{s_N} \mathrm{e}^{-\beta E_{s_N}}\right) = \sum_{N=0}^{\infty} z^N Z_N
$$

6.1.2 热力学函数

从现在开始明确，在巨正则系综里我们不使用变量 (β, V, μ)，而使用 (α, β, V)。

$$Z_{\mathrm{GC}}(\alpha, \beta, V) = \sum_s \mathrm{e}^{\alpha N_s - \beta E_s},\ \alpha \equiv \beta\mu$$

$$J = -kT \ln Z_{\mathrm{GC}} = -\frac{g_\pm}{\beta} \sum_\sigma \ln\left[1 - g_\pm \mathrm{e}^{\alpha - \beta\varepsilon_\sigma}\right]$$

$$S = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu},\ p = -\left(\frac{\partial J}{\partial V}\right)_{\mu,T},\ N = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V},\ U = J + TS + \mu N$$

$$N \equiv \sum_s \rho_s N_s = \frac{\partial}{\partial \alpha} \ln Z_{\mathrm{GC}}(\alpha, \beta, V)$$

$$U \equiv \sum_s \rho_s E_s = -\frac{\partial}{\partial \beta} \ln Z_{\mathrm{GC}}(\alpha, \beta, V)$$

$$p \equiv \sum_s \rho_s \left(-\frac{\partial E_s}{\partial V}\right)_{S,N} = \frac{1}{\beta}\frac{\partial}{\partial V} \ln Z_{\mathrm{GC}}(\alpha, \beta, V)$$

$$\text{单粒子态的平均占据数}\bar{n} \equiv \sum_s \rho_s n_s = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_s} \ln Z_{\mathrm{GC}}$$

$Z_{\mathrm{GC}} = Z_{\mathrm{GC}}(\alpha, \beta, V)$，求熵 $S = k\left[\ln Z_{\mathrm{GC}} - \alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} - \beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right]$

$$\begin{aligned}
\mathrm{d}S =& \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N \\
=& -\frac{1}{T}\,\mathrm{d}\left[\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] + \frac{1}{T}\left[\frac{1}{\beta}\frac{\partial}{\partial V}\ln Z_{\mathrm{GC}}\right]\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}\left[\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}}\right] \\
\frac{\mathrm{d}S}{k} =& -\beta\,\mathrm{d}\left[\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] + \frac{\partial}{\partial V}\ln Z_{\mathrm{GC}}\,\mathrm{d}V - \alpha\,\mathrm{d}\left[\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}}\right] \\
=& \frac{\partial}{\partial V}\ln Z_{\mathrm{GC}}\,\mathrm{d}V + \frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}}\,\mathrm{d}\alpha + \frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\,\mathrm{d}\beta - \mathrm{d}\left[\beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] - \mathrm{d}\left[\alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}}\right] \\
=& \,\mathrm{d}\left[\ln Z_{\mathrm{GC}} - \alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} - \beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right]
\end{aligned}$$

6.2 统计分布方法：理论

推导出 BS 和 FD 分布。

$$\ln Z_{\mathrm{GC}} = -g_\pm \sum_\sigma \ln\left[1 - g_\pm \mathrm{e}^{\alpha - \beta\varepsilon_\sigma}\right]$$

$$\begin{aligned}
N =& \frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} = -g_\pm \sum_\sigma \frac{-g_\pm \mathrm{e}^{\alpha-\beta\varepsilon_\sigma}}{1 - g_\pm \mathrm{e}^{\alpha-\beta\varepsilon_\sigma}} = \sum_\sigma f_{\sigma,\pm} \\
E =& -\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} = g_\pm \sum_\sigma \frac{g_\pm \varepsilon_\sigma \mathrm{e}^{\alpha-\beta\varepsilon_\sigma}}{1 - g_\pm \mathrm{e}^{\alpha-\beta\varepsilon_\sigma}} = \sum_\sigma \varepsilon_\sigma f_{\sigma,\pm}
\end{aligned}$$

其中

$$f_{\sigma,\pm} = \frac{1}{\mathrm{e}^{\beta\varepsilon_\sigma - \alpha} - g_\pm}$$

统计分布与熵

- 量子情况

$$f_{\sigma,\pm} = \frac{1}{\mathrm{e}^{\beta\varepsilon_\sigma - \alpha} - g_\pm} \Rightarrow \mathrm{e}^{\alpha - \beta\varepsilon_\sigma} = \frac{f_{\sigma,\pm}}{1 + g_\pm f_{\sigma,\pm}}$$

$$\ln Z_{\mathrm{GC}} = -\, g_\pm \sum_\sigma \ln\left[1 - g_\pm \mathrm{e}^{\alpha - \beta\varepsilon_\sigma}\right] = g_\pm \sum_\sigma \ln\left[1 + g_\pm f_{\sigma,\pm}\right]$$

$$\begin{aligned}
-\beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} &= \sum_\sigma \beta\varepsilon_\sigma f_{\sigma,\pm} \\
-\alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} &= \sum_\sigma -\alpha f_{\sigma,\pm}
\end{aligned}$$

$$\begin{aligned}
\frac{S}{k} &= \mathrm{d}\left[\ln Z_{\mathrm{GC}} - \alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} - \beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] \\
&= \sum_\sigma g_\pm \ln\left[1 + g_\pm f_{\sigma,\pm}\right] + (\beta\varepsilon_\sigma - \alpha) f_{\sigma,\pm} \\
&= \sum_\sigma -f_{\sigma,\pm}\ln f_{\sigma,\pm} + (g_\pm + f_{\sigma,\pm})\ln\left[1 + g_\pm f_{\sigma,\pm}\right]
\end{aligned}$$

- 经典情况

$$f_\sigma = \mathrm{e}^{\alpha - \beta\varepsilon_\sigma}$$

$$\begin{aligned}
\ln Z_{\mathrm{GC}} &= \sum_\sigma f_\sigma \\
-\beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} &= \sum_\sigma \beta\varepsilon_\sigma f_\sigma \\
-\alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} &= \sum_\sigma -\alpha f_\sigma
\end{aligned}$$

$$\begin{aligned}
\frac{S}{k} &= \mathrm{d}\left[\ln Z_{\mathrm{GC}} - \alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} - \beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] \\
&= \sum_\sigma f_\sigma + (\beta\varepsilon_\sigma - \alpha) f_\sigma \\
&= \sum_\sigma f_\sigma - f_\sigma \ln f_\sigma
\end{aligned}$$

统计分布方法的两个核心公式:

$$
\begin{aligned}
N &= \int g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon \\
E &= \int \varepsilon g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon
\end{aligned}
$$

6.3 巨正则系综方法：应用

6.3.1 二能级系统

通过能量零点的选择使得两个能级为 $(+\varepsilon, -\varepsilon)$，而它们的简并度为 (g_1, g_2)。

$$
\begin{aligned}
\ln Z_{\mathrm{GC}} =& -g_\pm g_1 \ln\left[1 - g_\pm \mathrm{e}^{\alpha-\beta\varepsilon}\right] - g_\pm g_2 \ln\left[1 - g_\pm \mathrm{e}^{\alpha+\beta\varepsilon}\right] \\
N =& \frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} = \frac{g_1}{\mathrm{e}^{+\beta\varepsilon-\alpha} - g_\pm} + \frac{g_2}{\mathrm{e}^{-\beta\varepsilon-\alpha} - g_\pm} \\
E =& -\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} = \frac{g_1\varepsilon}{\mathrm{e}^{+\beta\varepsilon-\alpha} - g_\pm} - \frac{g_2\varepsilon}{\mathrm{e}^{-\beta\varepsilon-\alpha} - g_\pm}
\end{aligned}
$$

这个结果显然和统计分布方法所得到的一样。

6.3.2 三维经典自由气体

$$
\begin{aligned}
D(\varepsilon) =& \frac{2\pi V}{h^3}(2m)^{3/2}\varepsilon^{1/2} \\
Z_1 =& \int_0^\infty D(\varepsilon)\mathrm{e}^{-\beta\varepsilon}\,\mathrm{d}\varepsilon = \frac{V}{\lambda^3},\ \lambda = \frac{h}{\sqrt{2\pi mkT}} \\
Z_N =& \frac{Z_1^N}{N!} \\
Z_{\mathrm{GC}} =& \sum_{N=0}^{\infty} z^N Z_N = \exp\left[zZ_1\right], \\
\ln Z_{\mathrm{GC}} =& zZ_1 = \mathrm{e}^\alpha \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \\
N =& \frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} = \ln Z_{\mathrm{GC}} \\
E =& -\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} = \frac{3}{2}\frac{\ln Z_{\mathrm{GC}}}{\beta} = \frac{3}{2}NkT \\
C_V =& \frac{\partial E}{\partial T} = \frac{3}{2}Nk \\
p =& \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z_{\mathrm{GC}} = \frac{\ln Z_{\mathrm{GC}}}{\beta V} \Rightarrow pV = NkT \\
S =& k\left[\ln Z_{\mathrm{GC}} - \alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} - \beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] \\
=& k\left[\ln Z_{\mathrm{GC}} - \alpha\ln Z_{\mathrm{GC}} + \beta\frac{3}{2}\frac{1}{\beta}\ln Z_{\mathrm{GC}}\right] \\
=& k\left[N - \alpha N + \frac{3}{2}N\right] = Nk\left[\frac{5}{2} - \alpha\right]
\end{aligned}
$$

6.3.3 三维极端相对论性自由气体

$$
\begin{aligned}
D(\varepsilon) =& \frac{4\pi\varepsilon^2}{h^3c^3} \\
Z_1 =& \frac{8\pi V}{h^3c^3\beta^3} \\
\ln Z_{\mathrm{GC}} =& \mathrm{e}^{\alpha}\frac{8\pi V}{h^3c^3\beta^3} \\
N =& \frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} = \ln Z_{\mathrm{GC}} \\
E =& -\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}} = 3\frac{\ln Z_{\mathrm{GC}}}{\beta} = 3NkT \\
C_V =& \frac{\partial E}{\partial T} = 3Nk \\
p =& \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z_{\mathrm{GC}} = \frac{\ln Z_{\mathrm{GC}}}{\beta V} \Rightarrow pV = NkT \\
S =& k\left[\ln Z_{\mathrm{GC}} - \alpha\frac{\partial}{\partial\alpha}\ln Z_{\mathrm{GC}} - \beta\frac{\partial}{\partial\beta}\ln Z_{\mathrm{GC}}\right] \\
=& k\left[\ln Z_{\mathrm{GC}} - \alpha\ln Z_{\mathrm{GC}} + \beta\frac{3}{\beta}\ln Z_{\mathrm{GC}}\right] \\
=& k[N - \alpha N + 3N] = Nk[4-\alpha]
\end{aligned}
$$

6.3.4 弱简并气体

弱简并近似:

$$
\begin{aligned}
\ln Z_{\mathrm{GC}} =& -g_{\pm}\sum_{\sigma}\ln\left[1 - g_{\pm}z\mathrm{e}^{-\beta\varepsilon_\sigma}\right] \\
\xlongequal{z\ll 1}& -g_{\pm}\sum_{\sigma}\left[-g_{\pm}z\mathrm{e}^{-\beta\varepsilon_\sigma} - \frac{1}{2}z^2\mathrm{e}^{-2\beta\varepsilon_\sigma}\right] \\
=& \sum_{\sigma}\left[z\mathrm{e}^{-\beta\varepsilon_\sigma} + \frac{1}{2}g_{\pm}z^2\mathrm{e}^{-2\beta\varepsilon_\sigma}\right] \\
=& \frac{Vz}{\lambda^3}\left(1 + \frac{g_{\pm}}{4\sqrt{2}}z\right) = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\mathrm{e}^{\alpha}\left(1 + \frac{g_{\pm}}{4\sqrt{2}}\mathrm{e}^{\alpha}\right)
\end{aligned}
$$

$$
\begin{aligned}
Z_1 \equiv \sum_{\sigma}\mathrm{e}^{-\beta\varepsilon_\sigma} =& \int\frac{\mathrm{d}^3k}{(2\pi)^3/V}\mathrm{e}^{-\beta\varepsilon_k} = \frac{V}{\lambda^3} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} \\
\sum_{\sigma}\mathrm{e}^{-2\beta\varepsilon_\sigma} =& V\left(\frac{\sqrt{2\pi m}}{h\sqrt{2\beta}}\right)^3 = \frac{V}{2\sqrt{2}\lambda^3}
\end{aligned}
$$

热力学量:

$$
\begin{aligned}
N =& \frac{\partial}{\partial \alpha}\ln Z_{\mathrm{GC}} = \ln Z_{\mathrm{GC}}\frac{1+\frac{g_\pm}{2\sqrt{2}}\mathrm{e}^{\alpha}}{1+\frac{g_\pm}{4\sqrt{2}}\mathrm{e}^{\alpha}} \approx \ln Z_{\mathrm{GC}}\left[1+\frac{g_\pm}{4\sqrt{2}}\mathrm{e}^{\alpha}\right] \\
E =& -\frac{\partial}{\partial \beta}\ln Z_{\mathrm{GC}} = \frac{3}{2}\frac{\ln Z_{\mathrm{GC}}}{\beta} \approx \frac{3}{2}NkT\left[1-\frac{g_\pm}{4\sqrt{2}}\mathrm{e}^{\alpha}\right] \\
C_V =& \left(\frac{\partial E}{\partial T}\right)_{V,N} \approx \frac{3}{2}Nk\left(1+\frac{g_\pm}{8\sqrt{2}}n\lambda^3\right) \\
p =& \frac{1}{\beta}\frac{\partial}{\partial V}\ln Z_{\mathrm{GC}} = \frac{\ln Z_{\mathrm{GC}}}{\beta V} \approx nkT\left[1-\frac{g_\pm}{4\sqrt{2}}\mathrm{e}^{\alpha}\right] \\
S =& Nk\left[\frac{5}{2}\frac{1+\frac{g_\pm}{4\sqrt{2}}\mathrm{e}^{\alpha}}{1+\frac{g_\pm}{2\sqrt{2}}\mathrm{e}^{\alpha}}-\alpha\right] \approx Nk\left[\frac{5}{2}\left(1-\frac{g_\pm}{4\sqrt{2}}\mathrm{e}^{\alpha}\right)-\alpha\right]
\end{aligned}
$$

6.4 统计分布方法：应用

6.4.1 强简并费米气体：零温

“费米子在零温下从相空间的零点开始向外堆积”那种做法显然更物理，但是直接用统计分布的做法更加清晰直接。

$$
f(\varepsilon) = \frac{1}{\mathrm{e}^{\beta(\varepsilon-\mu)}+1} \xrightarrow{T\to 0,\beta\to\infty} \begin{cases} 1,\ \varepsilon<\mu_0 \\ 0,\ \varepsilon>\mu_0 \end{cases},\ \mu_0 \equiv \mu(T=0)
$$

区分考虑了自旋和不考虑自旋的态密度

$$
g(\varepsilon) = (2s+1)D(\varepsilon) = (2s+1)\frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\varepsilon^{1/2}
$$

$$
\begin{aligned}
N = N_0 = \int_0^\infty g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon = (2s+1)\frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^{\mu_0}\varepsilon^{1/2}\,\mathrm{d}\varepsilon = \frac{(2s+1)V}{6\pi^2\hbar^3}(2m)^{3/2}\mu_0^{3/2} \\
E_0 = \int_0^\infty \varepsilon g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon = (2s+1)\frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^{\mu_0}\varepsilon^{3/2}\,\mathrm{d}\varepsilon = \frac{(2s+1)V}{10\pi^2\hbar^3}(2m)^{3/2}\mu_0^{5/2}
\end{aligned}
$$

$$
\frac{\hbar^2 k_{\mathrm{F}}^2}{2m} \equiv \varepsilon_{\mathrm{F}} \equiv \mu_0 = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{2s+1}\right)^{2/3},\ E = \frac{3}{5}N\varepsilon_{\mathrm{F}}
$$

$$
p_0 = -\left(\frac{\partial E_0}{\partial V}\right)_{S,N} = \frac{2}{3}\frac{E_0}{V}
$$

6.4.2 强简并费米气体：有限低温

索末菲展开（推导见维基百科“索末菲展开”页面）:

$$
\int_{-\infty}^{\infty}\frac{H(\varepsilon)}{\mathrm{e}^{\beta(\varepsilon-\mu)}+1}\,\mathrm{d}\varepsilon \xlongequal{\beta\gg 1} \int_{-\infty}^{\mu}H(\varepsilon)\,\mathrm{d}\varepsilon + \frac{\pi^2}{6}(\frac{1}{\beta})^2 H'(\mu) + \mathcal{O}\left(\frac{1}{\beta\mu}\right)^4
$$

注意这个积分是从 $-\infty$ 开始的，因此我们需要一个拓展的态密度

$$
g(\varepsilon) = (2s+1)D(\varepsilon) = \begin{cases} (2s+1)\frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\varepsilon^{1/2}, & \varepsilon \geq 0 \\ 0, & \varepsilon < 0 \end{cases}
$$

$$
\begin{aligned}
N=&\int_{-\infty}^{\infty} g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon=\frac{(2s+1)V}{4\pi^2\hbar^3}(2m)^{3/2}\int_{-\infty}^{\infty}\varepsilon^{1/2}f(\varepsilon)\,\mathrm{d}\varepsilon\\
=&\frac{(2s+1)V}{4\pi^2\hbar^3}(2m)^{3/2}\left[\int_0^\mu \varepsilon^{1/2}\,\mathrm{d}\varepsilon+\frac{\pi^2}{6\beta^2}\left.\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\varepsilon^{1/2}\right|_\mu\right]\\
=&\frac{(2s+1)V}{4\pi^2\hbar^3}(2m)^{3/2}\left[\frac{2}{3}\mu^{3/2}+\frac{\pi^2}{6\beta^2}\frac{1}{2}\mu^{-1/2}\right]\\
\Rightarrow \varepsilon_{\mathrm{F}}^{3/2}=&\mu^{3/2}+\frac{\pi^2}{8\beta^2}\mu^{-1/2}\\
\Rightarrow \mu^{3/2}\approx&\varepsilon_{\mathrm{F}}^{3/2}-\frac{\pi^2}{8\beta^2}\varepsilon_{\mathrm{F}}^{-1/2}=\varepsilon_{\mathrm{F}}^{3/2}\left[1-\frac{\pi^2}{8\beta^2}\varepsilon_{\mathrm{F}}^{-2}\right]\\
\Rightarrow \mu=&\varepsilon_{\mathrm{F}}\left[1-\frac{\pi^2}{8\beta^2}\varepsilon_{\mathrm{F}}^{-2}\right]^{2/3}\approx\varepsilon_{\mathrm{F}}\left[1-\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_{\mathrm{F}}}\right)^2\right]\\
E=&\int_{-\infty}^{\infty}\varepsilon g(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon=\frac{(2s+1)V}{4\pi^2\hbar^3}(2m)^{3/2}\int_{-\infty}^{\infty}\varepsilon^{3/2}f(\varepsilon)\,\mathrm{d}\varepsilon\\
=&\frac{(2s+1)V}{4\pi^2\hbar^3}(2m)^{3/2}\left[\int_0^\mu \varepsilon^{3/2}\,\mathrm{d}\varepsilon+\frac{\pi^2}{6\beta^2}\left.\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\varepsilon^{3/2}\right|_\mu\right]\\
=&\frac{(2s+1)V}{4\pi^2\hbar^3}(2m)^{3/2}\left[\frac{2}{5}\mu^{5/2}+\frac{\pi^2}{6\beta^2}\frac{3}{2}\mu^{1/2}\right]\\
=&\frac{3}{5}N\varepsilon_{\mathrm{F}}\times\left(\frac{\mu}{\varepsilon_{\mathrm{F}}}\right)^{5/2}\left[1+\frac{5\pi^2}{8}\left(\frac{kT}{\mu}\right)^2\right]\\
\approx&\frac{3}{5}N\varepsilon_{\mathrm{F}}\times\left[1+\frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_{\mathrm{F}}}\right)^2\right]\\
C_V=&\frac{\partial E}{\partial T}\approx Nk\frac{\pi^2}{2}\frac{kT}{\varepsilon_{\mathrm{F}}}
\end{aligned}
$$

6.4.3 强简并玻色气体：BEC

将系统的基态能量记作 ε_0, 观察玻色爱因斯坦分布及其粒子数

$$
f(\varepsilon)=\frac{1}{\mathrm{e}^{\beta(\varepsilon-\mu)}-1},\ N=\int_{\varepsilon_0}^{\infty}\frac{g(\varepsilon)}{\mathrm{e}^{\beta(\varepsilon-\mu)}-1}\,\mathrm{d}\varepsilon
$$

欲保持粒子数不变，则 $T\downarrow\Rightarrow\mu\uparrow$，可能 $\exists\, T_c$ s.t. $\mu(T_c)=\varepsilon_0$，我们要求

$$
\mu(T)=\begin{cases}\text{某函数}, & T>T_c\\ \varepsilon_0, & T<T_c\end{cases}
$$

$T<T_c$ 时有

$$
N=N(T)=N_0(T)+\int_{\varepsilon_0+0}^{\infty}\frac{g(\varepsilon)}{\mathrm{e}^{\beta(\varepsilon-\varepsilon_0)}-1}\,\mathrm{d}\varepsilon\xlongequal{\text{假设}g(\varepsilon=\varepsilon_0)=0}N_0(T)+\int_{\varepsilon_0}^{\infty}\frac{g(\varepsilon)}{\mathrm{e}^{\beta(\varepsilon-\varepsilon_0)}-1}\,\mathrm{d}\varepsilon
$$

而

$$
N=N(T_c)=\int_{\varepsilon_0}^{\infty}\frac{g(\varepsilon)}{\mathrm{e}^{\beta_c(\varepsilon-\varepsilon_0)}-1}\,\mathrm{d}\varepsilon
$$

你会发现老师的讲义中用的是分离的能级，而我写的是连续的能级。这实际上在概率论中有专门的介绍：如何处理一个既有离散取值又有连续取值的随机变量。然而，在物理中追究这种数学细节是得不偿失的。

桜井雪子：请问有没有更直接的引入 BEC 的讲法?
夏宁：可以从非对角长程序的角度引入
oy：他说的确实是对的（）
TDLI-xiao：他说的确实没错，当年是这么学的

$$
\begin{aligned}
E =& N_0(T)\varepsilon_0 + \int_{\varepsilon_0+0}^{\infty} \frac{\varepsilon g(\varepsilon)}{\mathrm{e}^{\beta(\varepsilon-\varepsilon_0)}-1}\,\mathrm{d}\varepsilon \\
C_V =& \left(\frac{\partial E}{\partial T}\right)_{V,N} \\
p =& -\left(\frac{\partial E}{\partial V}\right)_{N,S}
\end{aligned}
$$

$g(\varepsilon) = A\varepsilon^{\alpha}$, $\varepsilon_0 = 0$，实际上要求 $\alpha > 0$

$$N = \int_0^{\infty} \frac{A\varepsilon^{\alpha}}{\mathrm{e}^{\beta_c\varepsilon}-1}\,\mathrm{d}\varepsilon = N_0(T) + \int_0^{\infty} \frac{A\varepsilon^{\alpha}}{\mathrm{e}^{\beta\varepsilon}-1}\,\mathrm{d}\varepsilon$$

$$N = A\beta_c^{-\alpha-1}\Gamma(\alpha+1)\mathrm{Li}_{\alpha+1}(1) = N_0(T) + A\beta^{-\alpha-1}\Gamma(\alpha+1)\mathrm{Li}_{\alpha+1}(1)$$

$$T_c = \frac{1}{k}\left[\frac{N}{A\Gamma(\alpha+1)\mathrm{Li}_{\alpha+1}(1)}\right]^{\frac{1}{1+\alpha}}$$

$$\frac{N_0(T)}{N} = 1 - \left(\frac{T}{T_c}\right)^{1+\alpha}$$

$$
\begin{aligned}
E =& \int_0^{\infty} \frac{\varepsilon \times A\varepsilon^{\alpha}}{\mathrm{e}^{\beta\varepsilon}-1}\,\mathrm{d}\varepsilon = A\Gamma(\alpha+2)\mathrm{Li}_{\alpha+2}(1)\beta^{-\alpha-2} \\
C_V =& \frac{\partial E}{\partial T} = A\Gamma(\alpha+2)\mathrm{Li}_{\alpha+2}(1)k(kT)^{\alpha+1}
\end{aligned}
$$

对于理想气体还可以算压强。

α	$\frac{1}{2}$	1	2
T_c	$\frac{1}{k}\left[\frac{N}{A}\frac{2}{\sqrt{\pi}\zeta(\frac{3}{2})}\right]^{2/3}$	$\frac{1}{k}\left[\frac{N}{A}\frac{6}{\pi^2}\right]^{1/2}$	$\frac{1}{k}\left[\frac{N}{A}\frac{1}{2\zeta(3)}\right]^{1/3}$

一维谐振子：$g(\varepsilon) = 1/\hbar\omega, \varepsilon_0 = \hbar\omega/2$

$$N = \sum_{n=0}^{\infty} \frac{1}{\mathrm{e}^{\beta_c(\varepsilon_n - \frac{\hbar\omega}{2})}-1} = N_0(T) + \sum_{n=1}^{\infty} \frac{1}{\mathrm{e}^{\beta(\varepsilon_n - \frac{\hbar\omega}{2})}-1}$$

$$N = \frac{1}{\hbar\omega}\int_{\hbar\omega/2}^{\infty} \frac{\mathrm{d}\varepsilon}{\exp\left[\beta_c\left(\varepsilon - \frac{\hbar\omega}{2}\right)\right]-1} = N_0(T) + \frac{1}{\hbar\omega}\int_{\hbar\omega/2}^{\infty} \frac{\mathrm{d}\varepsilon}{\exp\left[\beta\left(\varepsilon - \frac{\hbar\omega}{2}\right)\right]-1}$$

这一积分发散，因此一维谐振子系统不存在 BEC。

7 番外篇

7.1 热力学涨落

某个热力学量的热力学涨落就事它的标准差:

$$\sigma_O = \sqrt{\overline{\left(O-\bar{O}\right)^2}} = \sqrt{\overline{O^2}-\bar{O}^2}$$

粒子数

$$\bar{N} = \sum_s \rho_s N_s = \frac{1}{Z_{\mathrm{GC}}}\frac{\partial Z_{\mathrm{GC}}}{\partial \alpha},\ \overline{N^2} = \sum_s \rho_s N_s^2 = \frac{1}{Z_{\mathrm{GC}}}\frac{\partial^2 Z_{\mathrm{GC}}}{\partial \alpha^2} = \frac{1}{Z_{\mathrm{GC}}}\frac{\partial\left(Z_{\mathrm{GC}}\bar{N}\right)}{\partial \alpha} = \bar{N}^2 + \frac{\partial \bar{N}}{\partial \alpha} \Rightarrow \sigma_N = \sqrt{\frac{\partial \bar{N}}{\partial \alpha}}$$

能量

$$\sigma_E = \sqrt{-\frac{\partial \bar{E}}{\partial \beta}}$$

对于三维经典理想气体

$$\sigma_N = \sqrt{\frac{\partial \bar{N}}{\partial \alpha}} = \sqrt{\bar{N}},\ \sigma_E = \sqrt{-\frac{\partial \bar{E}}{\partial \beta}} = \frac{\sqrt{6}}{2}\sqrt{\bar{N}}kT$$

即

$$\frac{\sigma_N}{\bar{N}} = \frac{1}{\sqrt{\bar{N}}} \to 0,\ \frac{\sigma_E}{\bar{E}} = \frac{\sqrt{6}}{3\sqrt{\bar{N}}} \to 0$$

7.2 Ising 模型

这一段完全事抄的林宗涵先生的书……

$$H = -J\sum_{\langle ij\rangle} s_i s_j - \mu\mathcal{H}\sum_{i=1}^{N} s_i = -\sum_i \mu s_i\left[\mathcal{H} + \frac{J}{\mu}\sum_j{}' s_j\right]$$

$$H_{\mathrm{MF}} = -\sum_i \mu s_i\left[\mathcal{H}+\bar{h}\right],\ \bar{h} \equiv \frac{zJ}{\mu}\bar{s}$$

现在系统又变成了和顺磁性固体类似的系统

$$Z_N = \left[2\cosh\left(\frac{\mu\mathcal{H}}{kT} + \frac{zJ}{kT}\bar{s}\right)\right]^N$$

$$F = -kT\ln Z_N,\ \bar{\mathcal{M}} = N\mu\bar{s} = -\frac{\partial F}{\partial \mathcal{H}} \Rightarrow \bar{s} = \tanh\left(\frac{\mu\mathcal{H}}{kT} + \frac{zJ}{kT}\bar{s}\right)$$

接下来的讨论大概是这样:

- $\mathcal{H} = 0$（自发磁化）
  - 低温下三个解，两个是自发磁化，不同温度下解的情况
  - 高温下一个解，不物理
  - 从低温向临界温度趋近时物理量的行为

- $\mathcal{H} \neq 0$
  - 直接取零级近似得到一个解
  - 讨论临界温度附近时物理量的行为

我真没想到这东西竟然这么长……