1.8 ① 棒稳态 $T(x)$ 与 t 无关；均匀棒

$$T(x) = T_2 + \frac{x}{L}(T_1 - T_2)$$

x 处的微元 $dx\rho \cdot A = dm$

$$dQ = dm\, C_p\, (T_0 - T(x))$$

绝热，$\int dQ = \int_0^L \rho A C_p dx\, (T_0 - T(x)) = 0$

$$\Rightarrow \quad T_0 = \frac{1}{2}(T_1 + T_2)$$

熵变：$\Delta S = \int_0^L dx \int_{T(x)}^{T_0} \frac{\rho A C_p dT}{T}$

$$= \rho A L C_p \left[\log\left(\frac{T_1+T_2}{2}\right) + 1 + \frac{T_2 \log T_2 - T_1 \log T_1}{T_1 - T_2}\right]$$

1.9. (1) $S = A(NVU)^{\frac{1}{3}} \iff U = \frac{S^3}{A^3 NV}$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{A(NV)^{\frac{1}{3}}}{3U^{\frac{2}{3}}}$$

$$U(N,V,T) = \frac{A^{3/2}}{3\sqrt{3}}(NVT^3)^{\frac{1}{2}}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N} \Rightarrow P = \frac{3}{A}\left(\frac{P^2 V}{N}\right)^{\frac{1}{3}}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{A^{3/2}}{2\sqrt{3}}(NVT)^{\frac{1}{2}}$$

(2) 令 $C_V = \lambda\sqrt{T}$ 过程中热源 N, V 不变

最低温：效率最大 $\frac{dQ_2}{-dQ_1} = \frac{T_2}{T_1}$

$$\Rightarrow \quad T_f = \frac{1}{4}(\sqrt{T_1} + \sqrt{T_2})^{\frac{1}{2}}$$

最高温：不做功

$$dQ_2 = -dQ_1$$

$$\Rightarrow \quad T_2^{\frac{1}{2}} dT_2 = T_1^{\frac{1}{2}} dT_1$$

$$\Rightarrow \quad T_f = \left(\frac{T_1^{3/2} + T_2^{3/2}}{2} \right)^{\frac{2}{3}}$$

1.12 微分形式： $ds = \frac{p}{T} dV + \frac{1}{T} dU$

$$d \circ ds = 0 = \frac{1}{T} dp \wedge dV - \frac{p}{T^2} dT \wedge dV - \frac{1}{T^2} dT \wedge dU$$

$$\frac{1}{T} dp \wedge dV - \frac{p}{T^2} dT \wedge dV - \frac{1}{T^2} dT \wedge \left(\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \right) = 0$$

$$T \, dp \wedge dV = \left(p + \left(\frac{\partial U}{\partial V}\right)_T \right) dT \wedge dV \qquad \square$$

1.14 $\quad dF = -S dT - p dV + \mu dN \qquad F = U - ST$

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

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

$$= F + ST$$

$$= U$$

1.15 $\quad J = F - \mu N = U - ST - \mu N$

$$q = -\frac{J}{T} = S + \frac{\mu N}{T} - \frac{U}{T}$$

$$dq = dS + N d\left(\frac{\mu}{T}\right) + \frac{\mu}{T} dN - U d\frac{1}{T} - \frac{1}{T} dU$$

$$= dS + \frac{\mu}{T} dN - \frac{1}{T} (T dS - p dV + \mu dN) + \frac{\mu}{T} dN - U d\frac{1}{T}$$

$$dq = -U\,d\left(\frac{1}{T}\right) + \frac{p}{T}\,dV + N\,d\left(\frac{\mu}{T}\right)$$

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

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

1.16. 求导即可 $\quad J = -S\,dT - p\,dV - N\,d\mu$

$$p = -\left(\frac{\partial J}{\partial V}\right)_{T,\mu} = \frac{8\pi}{12c^3h^3}\left(\mu^4 + 2\pi^2\mu^2\frac{1}{\beta^2} + \frac{7\pi^4}{15}\frac{1}{\beta^4}\right)$$

$$N_I = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V} = \frac{8\pi}{3h^3c^3}\left(\mu^3 + \pi^2\mu\frac{1}{\beta^2}\right)V$$

$$S = \frac{1}{T}\left(\frac{\partial J}{\partial \log\beta}\right)_{V,\mu} = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu} = \frac{8\pi V}{3h^3c^3T}\left(\pi^2\mu^2\frac{1}{\beta^2} + \frac{7\pi^4}{15}\frac{1}{\beta^4}\right)$$

$$U = J + TS + \mu N = \frac{2\pi}{h^3c^3}\left(\mu^4 + 2\pi^2\mu^2\frac{1}{\beta^2} + \frac{7\pi^4}{15}\frac{1}{\beta^4}\right)V$$

$$N_I = 0 \quad \Rightarrow \quad \mu = 0$$

第三次作业：

$$\frac{t+r+2v}{2}$$

2.1 单原子气体. $C_V = \frac{3}{2}Nk_B$ $\qquad pV = Nk_BT$

$$dU = TdS - pdV \quad \Rightarrow dS = \frac{1}{T}dU + \frac{1}{T}pdV$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dS = \frac{1}{T}\left(C_V dT + 0\, dV\right) + \frac{1}{T}pdV$$

$$S(T,V,N) = \int_{T_0}^{T}\frac{1}{T}C_V dT + \int_{V_0}^{V}\frac{Nk_B}{V}dV$$

$$= Nk_B\left(\frac{3}{2}\log\frac{T}{T_0} + \log\frac{V}{V_0}\right) + \underset{\text{全同}}{\text{修正项}}$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad U = \int dU$$

对 ideal gas：单原子：$C_V = \frac{3}{2}Nk_B$

$$U(T) = \frac{3}{2}Nk_BT$$

$$\Rightarrow S(U,V,N) = Nk_B\left(\frac{3}{2}\log\frac{2U}{3Nk_BT_0} + \log\frac{V}{V_0}\right) + \cdots$$

2.2 $\qquad dU = \underset{\substack{\downarrow \\ 0 \text{ for adiabatic}}}{\underline{TdS}} - pdV \qquad pV = Nk_BT$

$$C_V dT + pdV = 0 \quad \Rightarrow \quad C_V dT + p\left(\frac{Nk_B dT}{p} - Nk_BT\frac{1}{p^2}dp\right) = 0$$

$$\Rightarrow \left(C_V + Nk_B\right)dT - \frac{Nk_BT}{p}dp = 0$$

$$C_p\frac{1}{T}dT = \frac{Nk_B}{p}dp$$

$$\Rightarrow C_p\frac{dT}{T} = \left(C_p - C_V\right)\frac{p}{p} \quad \Rightarrow \quad \frac{\gamma}{\gamma - 1}\frac{dT}{T} = \frac{dp}{p}$$

$$\Rightarrow \left(1 + \frac{1}{\gamma-1}\right)\frac{dT}{T} = \frac{dp}{p} \quad \Rightarrow \quad \log T + \log F(T) = \log p + C$$

2.3 $\left(\frac{\partial T}{\partial p}\right)_H = 0 \Rightarrow \frac{\partial(T,H)}{\partial(p,H)} = 0$ $H(T) = U + pV$

$$\frac{\partial(T,H)}{\partial(T,p)} \frac{\partial(T,p)}{\partial(p,H)} = -\left(\frac{\partial H}{\partial p}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_p = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{\partial(H,T)}{\partial(p,S)} \frac{\partial(p,S)}{\partial(p,T)}$$

$$= V - T\left(\frac{\partial V}{\partial T}\right)_p$$ 代入 $pV = Nk_BT$

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \Rightarrow \left(\frac{\partial T}{\partial p}\right)_H = 0$$

2.4 $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V = c$

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial U}{\partial T}\right)_p = \frac{\partial(U,p)}{\partial(T,V)} \frac{\partial(T,V)}{\partial(T,p)} = c + \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \underbrace{-p + T\left(\frac{\partial p}{\partial T}\right)_V = \frac{a}{V^2}}$$ 解出 $p(V,T)$

$$p(V,T) = \frac{Nk_BT}{V} - \frac{a}{V^2}$$ EOS

$$\Rightarrow C_p = c + Nk_B\frac{pV^2+a}{pV^2-a}$$

2.5 $p = \frac{Nk_BT}{V-Nb} - a\frac{N^2}{V^2}$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk_B}{p - \frac{N^2a}{V^2} + \frac{2abN^3}{V^3}} \Rightarrow \alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk_B}{pV - \frac{N^2a}{V} + \frac{2abN^3}{V^2}}$$

(b) $C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = C_V + p\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$

$$C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p = Nk_B\frac{p + \frac{aN^2}{V^2}}{p - \frac{N^2a}{V^2} + \frac{2abN^3}{V^3}}$$

2.5. (c) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

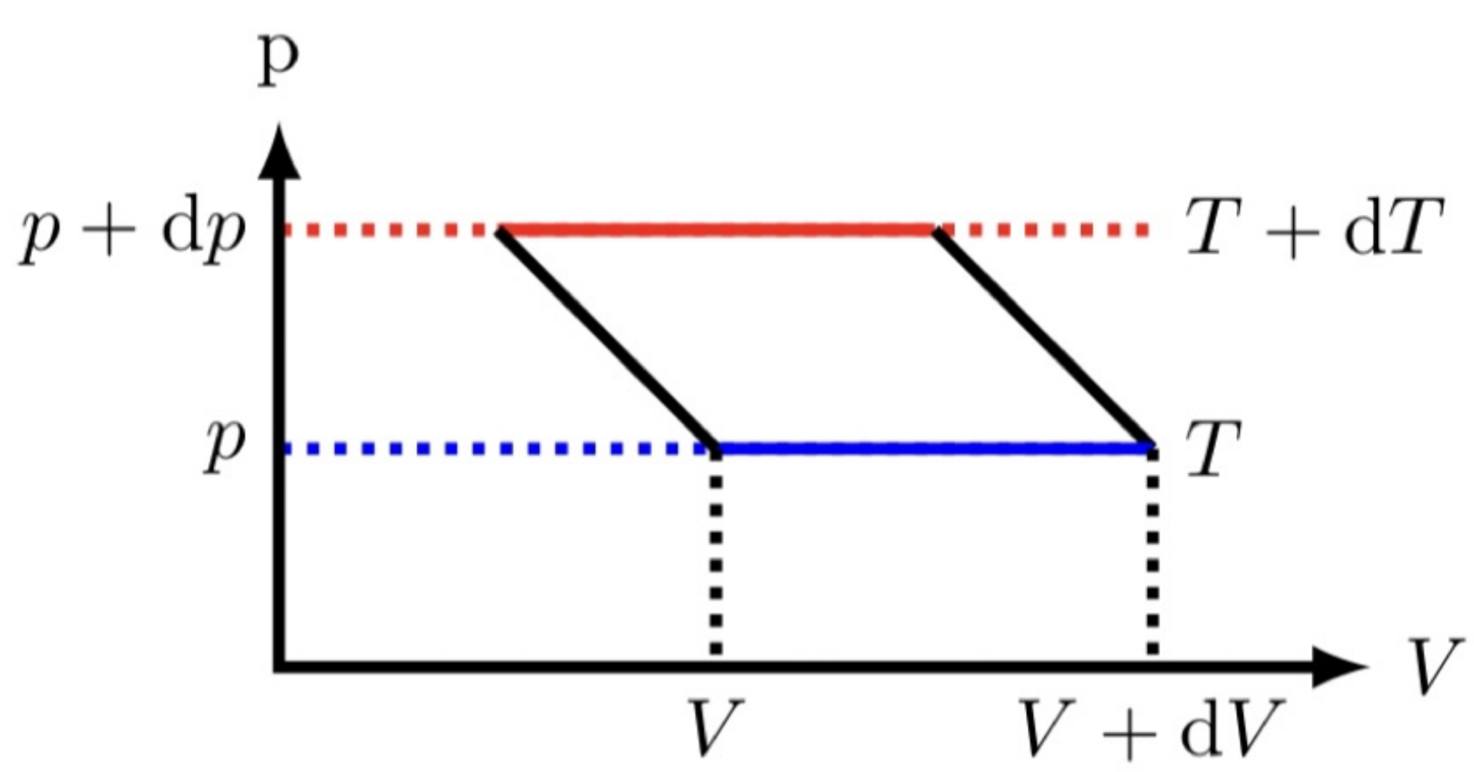
$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV = \int_{V_1}^{V_2} \frac{Nk_B}{V-Nb} dV = Nk_B \log\frac{V_2-Nb}{V_1-Nb}$$

第四次作业

2.6 考察与周围环境绝热的处于均匀磁场 B 中的顺磁系统。系统的磁化强度为：$M = CB/T$，热容量为：$C_H = b/T^2$，其中 C 和 b 是常数。当 B 准静态降为零时，系统温度会发生怎样的变化？为了使最终温度比初始温度变化 2 倍，初始 B 的强度应该是多少？

$\mathcal{H} = \frac{1}{\mu_0}B - M \qquad \mathcal{H} = \frac{B}{\mu}$

2.7 假设采用光子气体作为卡诺热机的工作物质，已知光子气体的状态方程为：$p = u(T)/3$，其中 $u(T)$ 为单位体积的光子气体的内能。设计如下的无穷小的卡诺循环：



(a) 试计算 $đW$，用 $\mathrm{d}p, \mathrm{d}V$ 表示；

(b) 在等温膨胀（也就是等压膨胀）过程中，试计算光子气体从温度为 T 的热源吸收的热量 Q，用 $p, \mathrm{d}V$ 表示；

(c) 用卡诺循环的效率，得到 W, Q 与 $T, \mathrm{d}T$ 之间的关系，进一步证明：$u(T) \propto T^4$；

(d) 试计算光子气体的绝热指数，即在 pV 图上，绝热曲线方程是什么？

2.6 $\quad dU = TdS + BdM \qquad d \cdot dU = 0$

$$dT \wedge dS = - dB \wedge dM \qquad \frac{\partial(T,S)}{\partial(B,M)} = -1$$

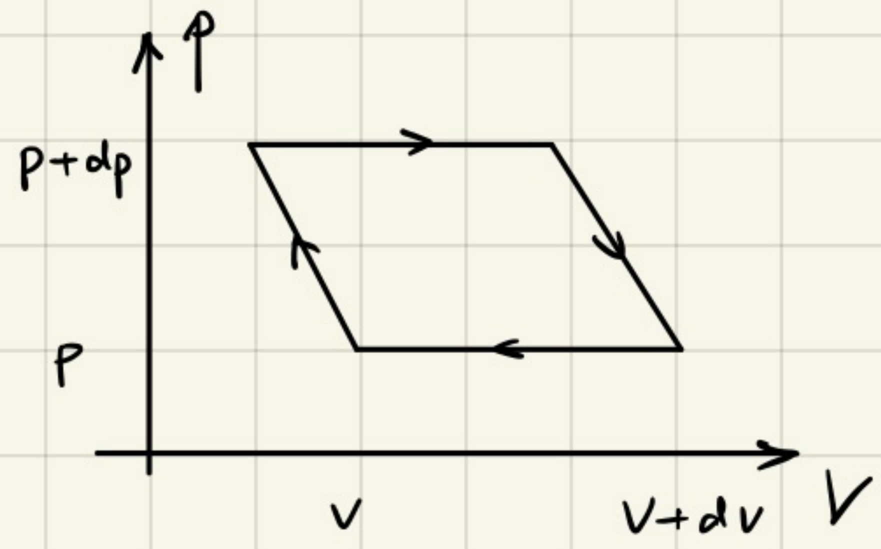
$$\left(\frac{\partial T}{\partial M}\right)_S = -\mu^{-1}\left(\frac{\partial B}{\partial S}\right)_M$$

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{\partial(T,S)}{\partial(B,S)} = \frac{\partial(T,S)}{\partial(B,M)} \frac{\partial(B,M)}{\partial(B,T)} \frac{\partial(B,T)}{\partial(B,S)}$$

$$= -\frac{T}{C_H} \cdot \left(\frac{\partial M}{\partial T}\right)_B = \frac{CB}{TC_H} > 0$$

$$T_f = T_i \exp\left(-\frac{C}{2b} B_i^2\right) \qquad \log\frac{T_f}{T_i} = \frac{1}{2} \Rightarrow B = \sqrt{\frac{2b}{c}\log 2}$$

2.7 (a)



与工质是否是光子无关，无穷小 Carnot 循环对外做功为平四面积

$dW = dp \cdot dV$

(b) T 温度下等温膨胀，内能 $\Delta U = \Delta V \cdot u(T) > 0$

$$Q = u(T) \cdot \Delta V + p \Delta V = 4 p \Delta V$$

(c) $$\frac{W}{W + Q} = 1 - \frac{T}{T + dT} = \frac{dT}{T + dT}$$

$W \sim p dV$

$Q \sim dV$

dT

$$\Rightarrow T W = Q \, dT$$

$$p T dV = 4 p \, dV dT$$

$$4 \frac{dT}{T} = \frac{dp}{p} \Rightarrow p \propto C T^4$$

(d) $dU = \cancel{TdS} - p dV$ 绝热过程

$$-4 \frac{dV}{V} = 3 \frac{dp}{p} \Rightarrow p V^{\frac{4}{3}} = \text{const}.$$

2.8 总能量守恒 $u(T) = a T^4 \Rightarrow a T_1^4 V_1 = a T_2^4 V_2$

$$\Rightarrow T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\frac{1}{4}}$$

$$S = \frac{4}{3} a T^3 V \Rightarrow \Delta S = \frac{4}{3} a \left(T_2^3 V_2 - T_1^3 V_1 \right) = \frac{4}{3} a V_1 T_1^3 \left(\left(\frac{V_1}{V_2} \right)^{\frac{1}{4}} - 1 \right)$$

2.10 $\left(\frac{\partial T}{\partial B} \right)_M = \frac{T}{B}$ $\left(\frac{\partial T}{\partial M} \right)_B = - \frac{T^2}{cB}$

$$dT = \left(\frac{\partial T}{\partial B} \right)_M dB + \left(\frac{\partial T}{\partial M} \right) dM = \frac{T}{B} dB - \frac{T^2}{cB} dM$$

$ddT = 0$ 成立，现求 $T(B, M)$

$$T = f(M) \cdot B$$

$$f'(M) B = - \frac{f^2(M) B^2}{c B}$$

$$\Rightarrow f(M) = \frac{c}{M - M_0}$$

$$\Rightarrow M = M_0 + \frac{cB}{T}$$

3.1 系统处于稳定平衡态

(c) 若F, V 不变，T取最大还是最小？

考虑① 由热力学第二定律: $đQ \le TdS \Rightarrow \delta U \le T\delta S + đW$

$$\delta F = \delta(U - ST) \le T\delta S + đW - \delta S T - S\delta T$$

$$\Rightarrow \quad S\delta T \le đW - \delta F$$

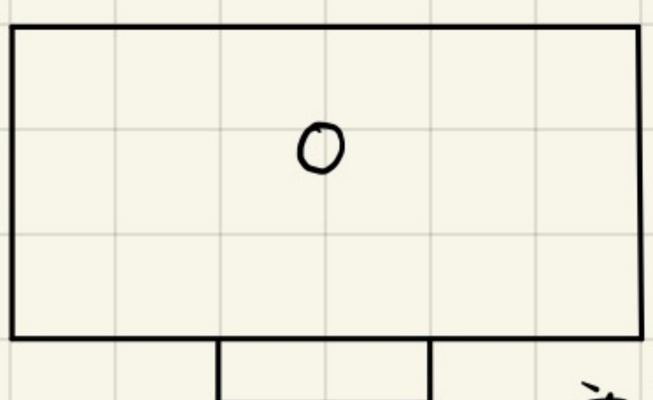
$\delta F = 0$; $\delta V = 0 \Leftrightarrow đW = 0$

则 $\delta T \le 0$

; 若 δF 与 $\delta V = 0$，热二允许的所有变动都有 $\delta T \le 0$，即温度降低

即对稳定平衡状态的系统，$\delta T \le 0$ 的过程不存在，即T处在最小值点（或局域最小值点）

考虑②：系统与另一大系统（下标0）接触 二者构成孤立系统，因此孤立系统稳定平衡时有熵判据.



对稳定平衡状态的孤立系统，若有虚变动发生必然导致熵减：$\delta S + \delta S_0 \le 0$

约束1：$\delta T - \delta T_0 = 0$ 虚变动前后系统仍处于平衡态

为了保证所给约束、必然有能量交换 $\delta U + \delta U_0 = 0$ $U = F + TS$

当 $\delta F = \delta F_0 = 0 \Rightarrow \delta U = T\delta S + S\delta T$

$$T\delta S + S\delta T + T_0\delta S_0 + S_0\delta T_0 = 0$$

$$T(\delta S + \delta S_0) + (S + S_0)\delta T = 0$$

$$(S + S_0)\delta T \ge 0 \Rightarrow \delta T \ge 0$$

这说明对这个系统在满足约束下任何对旧平衡的偏离，会导致温度上升，因此稳定平衡点，T最小

3.2 $dF = dU + d(Vp) - d(TS)$

$$dF = \sum_i \mu_i dn_i + \underbrace{Vdp - SdT}_{\text{vanished}}$$

$p + e^- \rightleftharpoons H + \gamma$

$$dF = (\mu_e + \mu_p - \mu_H) dn_e = 0$$ 自由能判据.

若给定T, p. 则用 Gibbs 判据. 不影响结论.

3.3. $\frac{dp}{dT} = \frac{L}{T\Delta V}$

$$\Delta U_m = \Delta Q_m + \Delta W_m$$
$$= L - p\Delta V_m$$
$$= L - \frac{pL}{T}\left.\frac{dT}{dp}\right|_\gamma$$

若其中一相为凝聚相, 另一相为气相.

则 $V_{cond,m} \ll V_{gas,m}$ $\Delta V \simeq V_{g,m}$ $\frac{dp}{dT} \simeq \frac{L}{T V_g} \underset{\text{EoS}}{\simeq}$

$$\Rightarrow \Delta U_m = L - RT$$

3.4. $\Delta U = mL - p\Delta V$

$$= 4.0\times10^{-3}\,kg \times 8.63\times10^{5}\,J\cdot kg^{-1} - 1.013\times10^{5}\,N\cdot m^{-2} \times 4.0\times10^{-3}\,kg \cdot 0.607\,m^3\cdot kg^{-1}$$
$$= 3.206\times10^{3}\,J$$

3.5. $\frac{dp}{dT} = \frac{L_{,m}}{T V_g} \simeq \frac{pL_{,m}}{RT^2}$

$$\Rightarrow \log\frac{P}{P_0} = -\frac{L_m}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

$$\Rightarrow L = 5.65\times10^{4}\,J\cdot mol^{-1}$$

3.6 C_V, C_p, α_p, κ_T 由定义出发即可

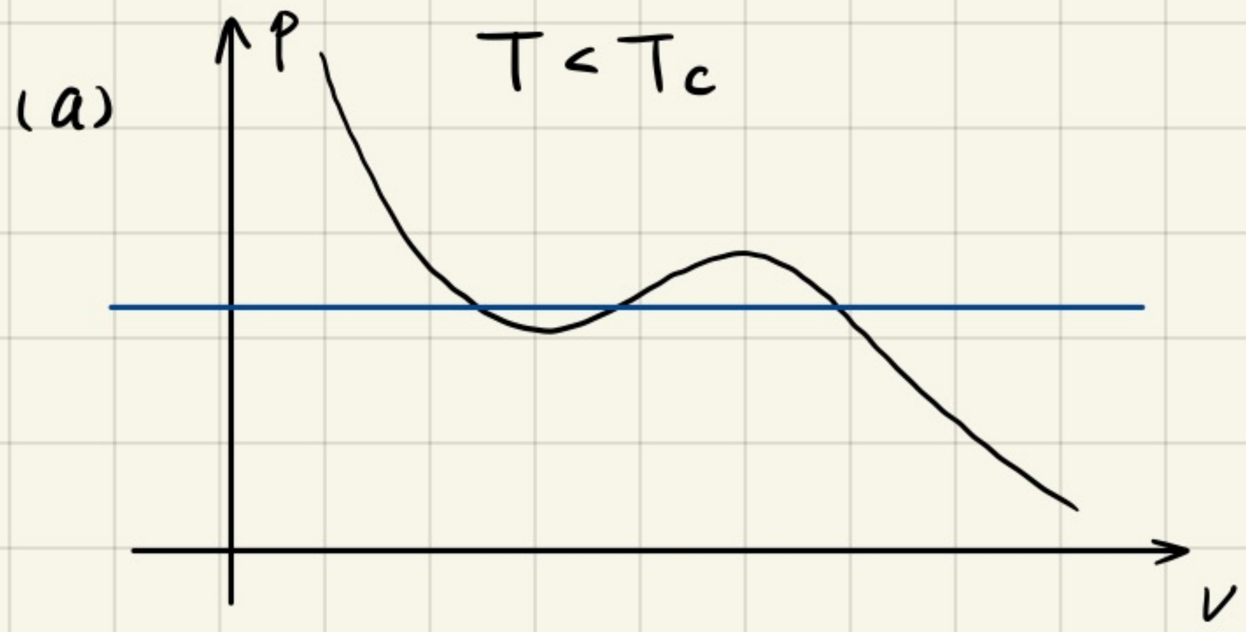
3.7 $p = \frac{RT}{V-b} - \frac{a}{V^2}$ $\Rightarrow \frac{dp}{dV} = 0$

$$\Rightarrow \frac{2a}{V^3} = \frac{RT}{(V-b)^2} = \left(p + \frac{a}{V^2}\right)\left(\frac{1}{V-b}\right)$$

$$\Rightarrow pV^3 = a(V-2b)$$

3.8 范德瓦尔斯气体 $\left(p+\frac{a}{v^2}\right)(v-b)=RT$

(a)

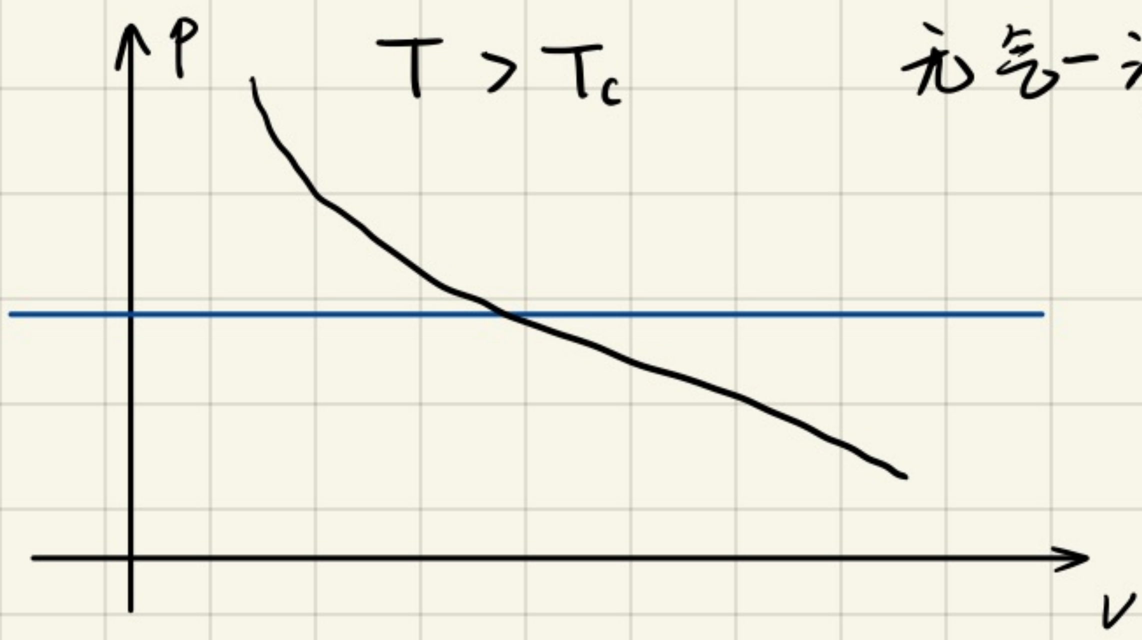


临界点处发生了什么? 讲义 3.4.1

$$pv^3-(pb+RT)v^2+av-ab=0$$

$T=T_c$ 时:

$$p_c(v-v_c)^3=0$$



无气-液相变

$$\Longrightarrow \begin{cases} -p_c v_c^3=-ab \\ 3p_c v_c^2=a \\ 3p_c v_c=p_c b+RT_c \end{cases}$$

$$\Longrightarrow \quad v_c=3b \qquad p_c=\frac{a}{27b^2} \qquad T_c=\frac{8a}{27b}$$

(c) 对应态原理:

$$\tilde{v}=\frac{v}{v_c} \qquad \tilde{p}=\frac{p}{p_c} \qquad \tilde{T}=\frac{T}{T_c}$$

$$\tilde{p}=\frac{8\tilde{T}}{3\tilde{v}-1}-\frac{3}{\tilde{v}^2}$$

3.9

EoS: $$p=\frac{k_BT}{v-b}\exp\left(-\frac{a}{k_BTv}\right)$$

$$\left(\frac{\partial p}{\partial v}\right)_T=\frac{1}{v^2(v-b)^2}\left(-k_BTv^2+av-ab\right)\exp\left(-\frac{a}{k_BTv}\right)$$

$-k_BT\,v^2+av-ab=0$ 只有一个实根

$$a^2-4abk_BT=0 \Longrightarrow T_c=\frac{+a}{4bk_B}$$

$$v_c=2b$$

$$p_c=\frac{a}{4e^2b^2} \quad \Longrightarrow \quad \frac{p_cv_c}{k_BT_c}=\frac{2}{e^2}$$

临界指数

$$p - p_c \sim (v - v_c)^{\delta}$$

在临界点附近：

$$p - p_c = \left(\frac{\partial p}{\partial v}\right)_T\bigg|_c (v-v_c) + \frac{1}{2!}\left(\frac{\partial^2 p}{\partial v^2}\right)_T\bigg|_c (v-v_c)^2 + \frac{1}{3!}\left(\frac{\partial^3 p}{\partial v^3}\right)_T\bigg|_c (v-v_c)^3 + \cdots$$

在 (p_c, V_c, T_c) 处. $\left(\frac{\partial p}{\partial v}\right)_T = 0$ $\quad \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$

显然, $\left(\frac{\partial^3 p}{\partial v^3}\right)_T \neq 0$ 则 $\delta = 3$

$$K_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \sim (T - T_c)^{-\gamma}$$

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial p}{\partial v}\right)\bigg|_c + \left(\frac{\partial^2 p}{\partial T \partial v}\right)\bigg|_c (T - T_c) + \cdots$$

$$\frac{\partial^2 p}{\partial T \partial v} = -\frac{k_B}{e^2 b^2} \neq 0 \qquad \Rightarrow \left(\frac{\partial p}{\partial v}\right) \sim (T - T_c)^1$$

$$K_T \sim (T - T_c)^{-1}$$

$v_{I} - v_{II} \sim (T - T_c)^{\beta}$ 对 EoS 作无量纲化： $v = \frac{v}{v_c}$ $\quad p = \frac{p}{p_c}$ $\quad T = \frac{T}{T_c}$

$$\hat{p} = e^2 \frac{\hat{T}}{2\hat{v} - 1} e^{-\frac{2}{\hat{T}\hat{v}}}$$

$$\frac{\hat{T}}{2\hat{v}_{I} - 1} e^{-\frac{2}{\hat{T}\hat{v}_{I}}} = \frac{\hat{T}}{2\hat{v}_{II} - 1} e^{-\frac{2}{\hat{T}\hat{v}_{II}}}$$

$$\Rightarrow \quad \hat{T} = 2\left(\frac{\hat{v}_{II} - \hat{v}_{I}}{\hat{v}_{I}\hat{v}_{II}}\right) \Big/ \log\left(1 + \frac{2(\hat{v}_{II} - \hat{v}_{I})}{2\hat{v}_{I} - 1}\right)$$

$$\simeq 1 + (\hat{v}_{II} - \hat{v}_{I})^1 + \cdots$$

$$\beta = 1$$

$$f(x) = f(x_0) + (x - x_0) f'(x_0) + \frac{1}{2} f''(x_0)(x - x_0)^2 + \cdots$$

若 $f(x) = (x - x_0)^{\pi}$?

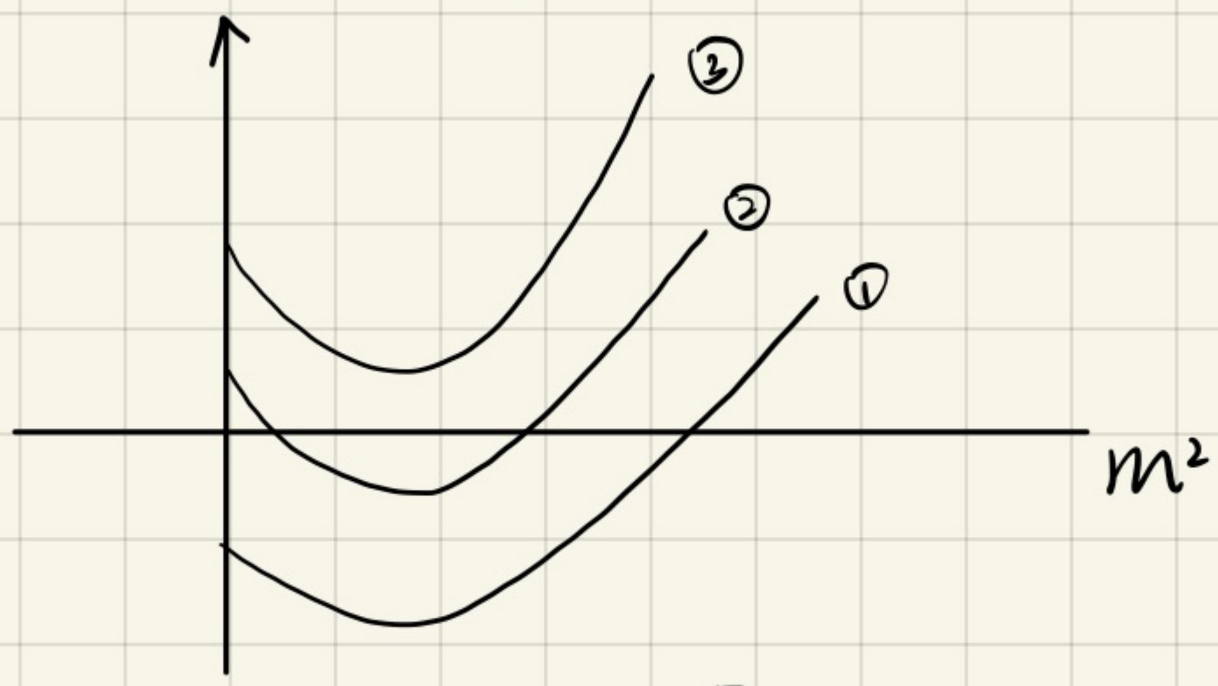
$$\log f(x) = \pi \log(x - x_0)$$

3.10

$$F(T,m) = a(T)m^2 + b(T)m^4 + c(T)m^6$$

$$\frac{\partial F}{\partial m} = 2a(T)m + 4b(T)m^3 + 6c(T)m^5 = 2m(a + 2bm^2 + 3cm^4)$$

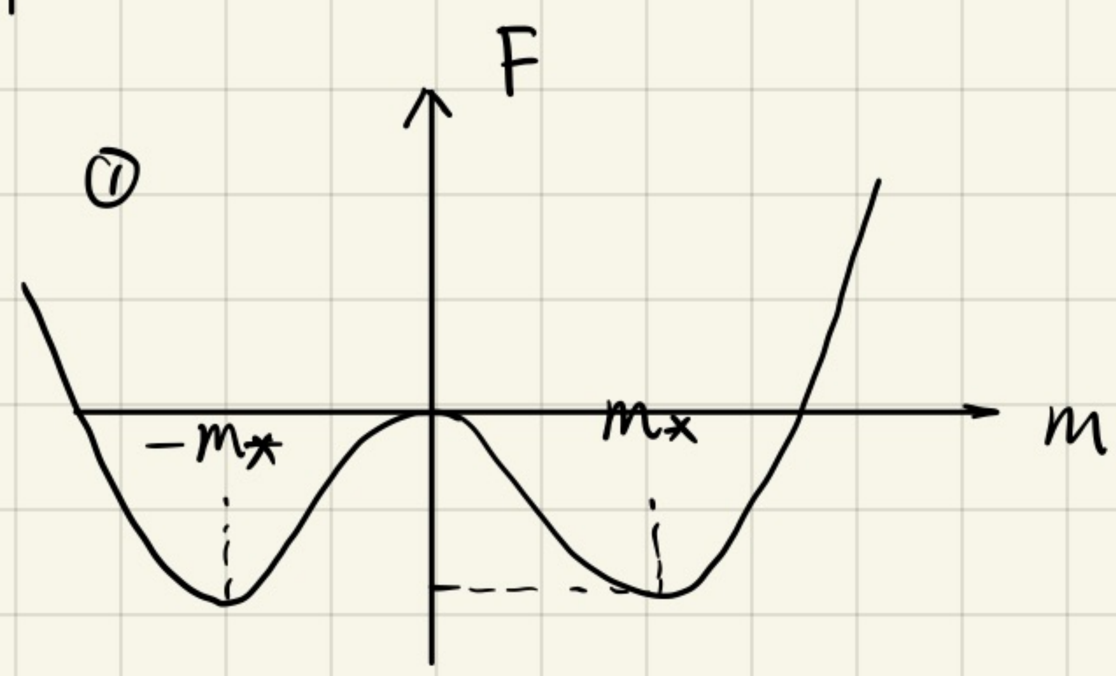
令 $g(T,m) = 3cm^4 + 2bm^2 + a$ g关于m^2是2次函数，对称轴 $-\frac{b}{3c} > 0$



$g=0 \Rightarrow \Delta = 4b^2 - 4a\times 3c$

$\Rightarrow a = \frac{b^2}{3c}$ 则 g只有一个根

①



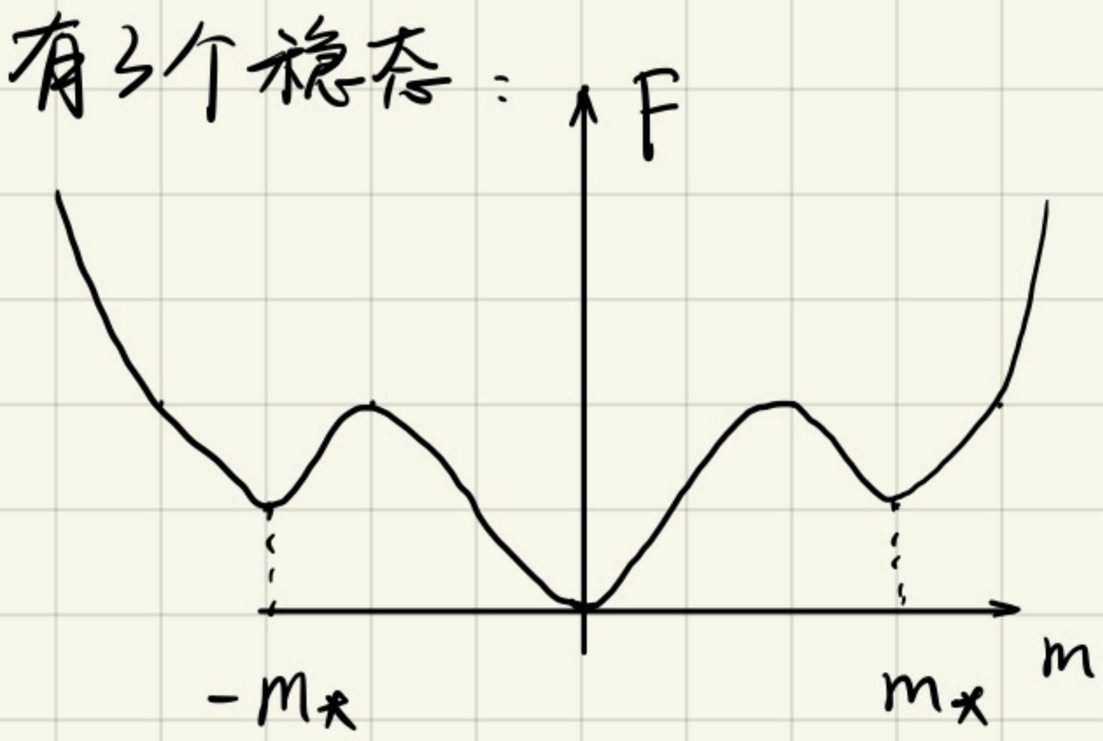
有2个稳态 $g(T,m)=0$

$$m_*^2 = \frac{-b+\sqrt{b^2-3ac}}{3c}, \quad m_* > 0$$

$$\Rightarrow m_* = \sqrt{\frac{-b+\sqrt{b^2-3ac}}{3c}}$$

$$F(T,\pm m_*) = -\frac{ab}{9c} + \frac{-b+\sqrt{b^2-3ac}}{3c}\left(\frac{2}{3}a - \frac{2b^2}{9c}\right) < 0$$

② 有3个稳态：



$0 < a < \frac{b^2}{3c}$

比较 $F(T,m_*)$ 的符号 判断亚稳与稳

$$a < \frac{b^2}{4c} \Longleftrightarrow F_0 < 0$$

③ $a \geqslant \frac{b^2}{3c}$ F只有一个极小值.

当系统发生一级相变时、系统$F(m,T)$有新的极小值出现、且F的一阶导数在极值处不等.

$$a(T_c) = \frac{b(T_c)^2}{4C(T_c)} \quad 则 \quad m_* = \sqrt{\frac{-b+\sqrt{b^2-3ac}}{3c}}$$

同时 $\left.\frac{\partial F}{\partial T}\right|_{m=0} \neq \left.\frac{\partial F}{\partial T}\right|_{m_*}$ 即一级相变

3.11.

(a) $B=0 \quad dS = \frac{C}{T}dT$

① $C_s = \alpha V T^3$

$$S_s(T) = \int_0^T \alpha V T^2 = \frac{1}{3}\alpha V T^3$$

② $C_n = V(\gamma\alpha T + \beta T^3)$

$$S_n(T) = \int_0^T (\alpha\gamma V + \beta V T^2)\, dT = \frac{1}{3}\beta V T^3 + \alpha\gamma V T$$

(b) $L=0 \Rightarrow S_s(T_c) = S_n(T_c)$

$$\Rightarrow T_c = \sqrt{\frac{3\gamma\alpha}{\alpha-\beta}}$$

(c) $U_s(T) = U_s(T=0) + \int_0^T T dS_s$

$$= U_s(T=0) + \frac{1}{4}\alpha V T^4 = U_0 - \Delta V + \frac{1}{4}\alpha V T^4$$

$$U_n(T) = U_n(T=0) + \int_0^T T dS_n = \qquad U_0 + \frac{1}{4}V\beta T^4 + \frac{1}{2}\alpha\gamma V T^2$$

(d) 同上，通过 Legendre 变换 $G = U + pV - TS$ 同化学势

$$G_n(T_c) = G_s(T_c) \Rightarrow \Delta = \frac{3\gamma^2\alpha^2}{4(\alpha-\beta)}$$

(e) $dU = TdS \cancel{- pdV} + BdM \cancel{+ \mu dN}$

$$U_n(T,B) = U_n(T=0,B=0) + \frac{1}{4}V\beta T^4 + \frac{1}{2}\alpha\gamma V T^2$$

$$U_s(T,B) = U_0 - \Delta V + \frac{1}{4}\alpha V T^4 + \int_0^B -B\frac{V}{4\pi}dB$$

$$= U_0 - \Delta V + \frac{1}{4}\alpha V T^4 - \frac{V}{8\pi}B^2 \qquad dG \supseteq -MdB$$

$$G_n(B_c, T) = G_s(B_c, T) \qquad G = U + pV - BM - TS$$

$$U_0 + \frac{1}{4}\beta V T^4 + \frac{1}{2}\alpha\gamma V T^2 - T_c S_n(T) = U_0 + \frac{1}{4}\alpha V T^4 + \frac{V}{8\pi}B_c^2 + T S_s(T) - \Delta V$$

$$\Delta V = \frac{1}{4}\alpha\gamma T_c^2 V$$

$$\Rightarrow -\frac{1}{12}(\alpha-\beta)T^4 + \frac{1}{2}\alpha\gamma V T^2 - \frac{1}{4}\alpha\gamma V T_c^2 = -\frac{V}{8\pi}B_c^2$$

且又有 $(\alpha-\beta) = \frac{3\alpha\gamma}{T_c^2} \Rightarrow \frac{1}{8\pi}B_c^2 = +\frac{1}{4}\alpha\gamma T_c^2\left[1 - \left(\frac{T}{T_c}\right)^2\right]^2$

$$\Rightarrow B_c = B_0\left(1 - \frac{T^2}{T_c^2}\right)$$

4.11 什么是光的多普勒效应？

观测者系：设光源的4-速度 $U^\mu = (\gamma c, \gamma v_x, \gamma v_y, \gamma v_z)$，发出的朝观测者（z方向）的光子4动量为：

$$p^\mu = \left(\frac{h\nu}{c}, 0, 0, \frac{h\nu}{c}\right) \quad ; \text{注意 } p^\mu p_\mu = \left(\frac{h\nu}{c}\right)^2 - \left(\frac{h\nu}{c}\right)^2 = 0$$

$\eta_{\mu\nu} p^\mu U^\nu$ 是 Lorentz scalar，因此 Lorentz 变换下不变

在光源随动静止系中 $\eta_{\mu\nu} p^\mu U^\nu = h\nu_0$

因此 $h\nu_0 = h\nu\gamma - \frac{v_z}{c} h\nu$ $\qquad \gamma = \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}$

$$\Longrightarrow \nu_0 = \left(\gamma - \gamma\frac{v_z}{c}\right)\nu \quad \text{即} \quad \boxed{\lambda = \lambda_0 \gamma \left(1 - \frac{v_z}{c}\right)}$$

设θ为光源运动速度 $\vec{v}$ 与 z（视线方向）的夹角、 $v_z = v\cos\theta$

且仅考虑热运动非相对论的情形，将上述结果展开至线性阶。

$$\lambda = \lambda_0\left(1 - \frac{v\cos\theta}{c}\right) = \lambda_0\left(1 - \frac{v_z}{c}\right)$$

光强 ∝ 能量 ∝ 相同波长光子数

$$I(v_z) \propto \exp\left(-\frac{m}{2k_BT} v_z^2\right)$$

$$I(\lambda) \propto \exp\left[\underbrace{-\frac{mc^2}{2k_BT}\left(1 - \frac{\lambda}{\lambda_0}\right)^2}_{\frac{(\lambda-\lambda_0)^2}{\lambda_0^2}\cdot\frac{mc^2}{2k_BT}}\right]$$

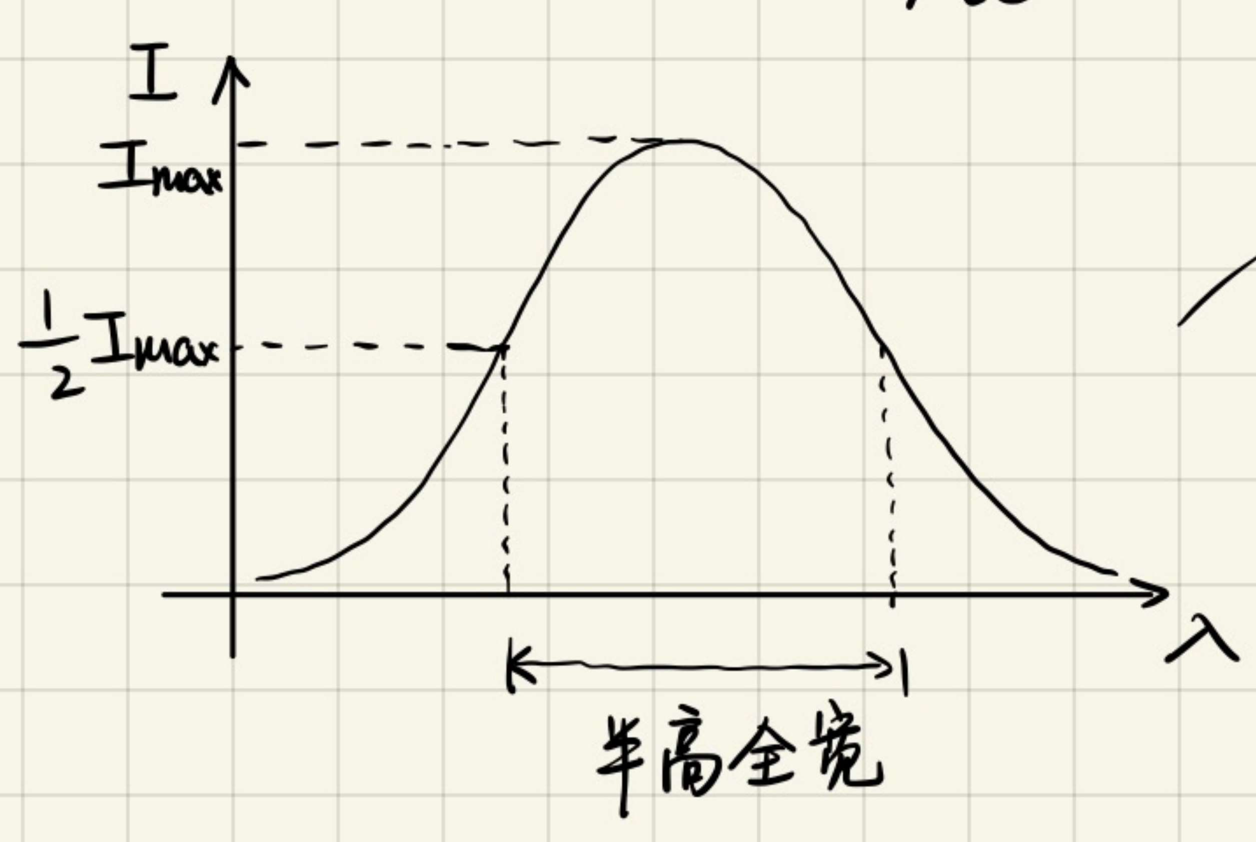
$$\Rightarrow \langle\lambda\rangle = \lambda_0$$

高斯分布

$$P(x) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

$$\sigma^2 = \langle(\lambda - \langle\lambda\rangle)^2\rangle = \langle\lambda^2\rangle - \langle\lambda\rangle^2$$

$$= \frac{\lambda_0^2 k_BT}{mc^2}$$



若该分布是高斯分布

半高全宽 $= 2\sqrt{2\log 2}\,\sigma$

5.20. 费米子压强：

$$P = g\frac{1}{h^3}\int d^3p\, f(\epsilon,\mu)\frac{p^2c^2}{3\epsilon} \qquad \text{(讲义 5.65)}$$

对本题，我们将 ε 中的 m_0c^2 项吸收到化学势中，且在非相对论极限下计算：

$$P = \frac{g}{(2\pi\hbar)^3}\int_0^{+\infty} 4\pi p^2 dp \frac{1}{\exp[\beta(\frac{p^2}{2m}-\mu)]+1}\cdot\frac{p^2}{3m}$$

$$= \frac{4\pi g}{(2\pi\hbar)^3}\cdot\frac{1}{6m}\int_0^{+\infty}\frac{(p^2)^{3/2}\,d(p^2)}{\exp[\beta(\frac{p^2}{2m}-\mu)]+1}$$，令 $\frac{p^2}{2m}=\hat{\epsilon}\cdot\mu$，$\frac{1}{\mu\beta}=\hat{T}$

则有：

$$P = \frac{4\pi g}{6m}\cdot\frac{(2m\mu)^{5/2}}{(2\pi\hbar)^3}\int_0^{\infty}\frac{\hat{\epsilon}^{3/2}}{\exp[(\hat{\epsilon}-1)/\hat{T}]+1}d\hat{\epsilon}$$

接下来处理该积分：令 $\frac{\hat{\epsilon}-1}{\hat{T}}=x$.

考察 $\int_{-\frac{1}{\hat{T}}}^{+\infty}\frac{(1+\hat{T}x)^{3/2}}{e^x+1}\hat{T}\,dx$.

$$= \hat{T}\int_{-\frac{1}{\hat{T}}}^{0}\frac{(1+\hat{T}x)^{3/2}}{e^x+1}dx + \hat{T}\int_0^{+\infty}\frac{(1+\hat{T}x)^{3/2}}{e^x+1}dx$$

$$= \hat{T}\int_0^{\frac{1}{\hat{T}}}\frac{e^x(1-\hat{T}x)^{3/2}}{e^x+1}dx + \hat{T}\int_0^{+\infty}\frac{(1+\hat{T}x)^{3/2}}{e^x+1}dx$$

$$= \hat{T}\int_0^{\frac{1}{\hat{T}}}(1-\hat{T}x)^{\frac{3}{2}}dx + \hat{T}\left[\int_0^{+\infty}\frac{(1+\hat{T}x)^{\frac{3}{2}}}{e^x+1}dx - \int_0^{\frac{1}{\hat{T}}}\frac{(1-\hat{T}x)^{\frac{3}{2}}}{e^x+1}dx\right]$$

$$= \frac{2}{5} + \hat{T}\left[\int_0^{+\infty}\frac{(1+\hat{T}x)^{\frac{3}{2}}}{e^x+1} + (-1)\int_0^{\frac{1}{\hat{T}}}\frac{(1-\hat{T}x)^{\frac{3}{2}}}{e^x+1}dx\right]$$

强简并：$\beta\mu \gg 1 \Longleftrightarrow z = e^{\mu\beta} \gg 1 \Rightarrow \frac{1}{\hat{T}} \gg 1$

即 $\hat{T}\int_{-\frac{1}{\hat{T}}}^{+\infty}\frac{(1+\hat{T}x)^{\frac{3}{2}}}{e^x+1}dx \simeq \frac{2}{5} + \hat{T}\int_0^{+\infty}\frac{(1+\hat{T}x)^{\frac{3}{2}}-(1-\hat{T}x)^{\frac{3}{2}}}{e^x+1}dx$

$\simeq$

即：$\hat{T}\int_{-\frac{1}{\hat{T}}}^{+\infty}\frac{(1+\hat{T}x)^{\frac{3}{2}}}{e^x+1}dx \simeq \frac{2}{5}+3\hat{T}^2\int_0^{+\infty}\frac{x^1}{e^x+1}dx$

$$+\left(-\frac{\hat{T}^4}{8}\right)\int_0^{+\infty}\frac{x^3}{e^x+1}dx$$

$$=\frac{2}{5}+3\hat{T}^2\,\Gamma(2)\zeta(2)\left(1-\frac{1}{2}\right)-\frac{1}{8}\hat{T}^4\,\Gamma(4)\zeta(4)\left(1-\frac{1}{2^3}\right)$$

$$=\frac{2}{5}+\frac{\pi^2}{4}\hat{T}^2-\frac{7\pi^4}{960}\hat{T}^4$$

$$\Rightarrow p=\frac{a}{V}\left[\frac{4}{15}\mu^{\frac{5}{2}}+\frac{\pi^2}{4\beta^2}\mu^{\frac{1}{2}}-\frac{7\pi^4}{1440\beta^4}\mu^{-\frac{3}{2}}\right]$$

$$\Rightarrow J=-pV \qquad S=-\left(\frac{\partial J}{\partial T}\right)_{\mu,V}$$

$$Z=\exp(-\beta J)$$

5.21. $\mathcal{N}=2$（维） 0温时Fermion数密度

$$\Sigma=\frac{2\times 2\pi}{(2\pi\hbar)^2}\int_0^{p_F}p\,dp \Rightarrow p_F=\left(\frac{\Sigma h^2}{2\pi}\right)^{\frac{1}{2}}$$

$$=\sqrt{2\pi\hbar^2\Sigma}$$

化学势：$\mu=\frac{p_F^2}{2m}=\frac{\pi\hbar^2\Sigma}{m}$

内能密度：$UA=\frac{2A}{(2\pi\hbar)^2}\cdot 2\pi\int_0^{p_F}p_E\frac{p_E}{2m}=\frac{(2\pi\hbar)^2}{8\pi m}A\Sigma^2$

$$\Rightarrow u=\frac{(2\pi\hbar)^2}{8\pi m}\Sigma^2$$

压强：$p_{0K}=\frac{2}{3}u=\frac{2\cdot 2\pi}{(2\pi\hbar)^2}\int_0^{p_F}p\,dp\,\frac{p^2}{3m}=\frac{(2\pi\hbar)^2}{12\pi m}\Sigma^2$

(b) $T\neq 0K$. 但低温极限.

$$\Sigma=\frac{2}{(2\pi\hbar)^2}\cdot 2\pi\int_0^{+\infty}p\,f(p,\epsilon)\,dp=\frac{4\pi m}{(2\pi\hbar)^2}\int_0^{+\infty}\frac{d\epsilon}{\exp[\beta(\epsilon-\mu)]+1}$$

令 $\beta(\epsilon-\mu)=x \Rightarrow d\varepsilon=k_BT\,dx$

$$\Sigma=\frac{4\pi m}{(2\pi\hbar)^2}k_BT\int_{-\mu\beta}^{+\infty}\frac{dx}{e^x+1}\qquad e^x=t.\quad dx=\frac{1}{t}dt.$$

$$=\frac{4\pi m}{(2\pi\hbar)^2}k_BT\log\left(1+e^{\mu\beta}\right)$$

即: $\mu=k_BT\log\left[\exp\left(\frac{(2\pi\hbar)^2\Sigma}{4\pi mk_BT}\right)-1\right]$

在低温极限 $T\to 0$ 时回到之前的结果

内能.

$$u=\frac{4\pi m}{(2\pi\hbar)^2}\int_0^{+\infty}\epsilon f(\epsilon,\mu)\,d\epsilon$$; 与前述技巧雷同.

$$=\frac{4\pi m}{(2\pi\hbar)^2}(k_BT)\int_{-\mu\beta}^{+\infty}\frac{\mu+k_BTx}{e^x+1}dx\qquad x=\frac{\epsilon-\mu}{k_BT}$$

这个积分大家一定要熟悉.

$$=\frac{4\pi m}{(2\pi\hbar)^2}k_BT\left[\mu\log(1+z)-\frac{\mu^2}{2k_BT}+\frac{\pi^2}{6}k_BT\right]$$

在 $T\to 0K$ 时. 该结果同样有 $\frac{h^2\Sigma^2}{8\pi m}$.

而 $p=\frac{2}{3}u$. 毋需重复计算。

5.23. $D(\epsilon)d\epsilon = A\sqrt{\epsilon}\, d\epsilon$

$$n_c = \int_0^{+\infty} D(\epsilon) f(\epsilon,\mu)\, d\epsilon = \int_0^{+\infty} \frac{D(\epsilon)\, d\epsilon}{e^{\beta(-\mu+\epsilon)}+1}$$

$$\Rightarrow n_c = \frac{N}{e^{(\mu+\Delta)\beta}} = \int_0^{+\infty} \frac{D(\epsilon)\, d\epsilon}{e^{\beta(\epsilon-\mu)}+1}$$

$$= e^{\mu\beta} \int_0^{+\infty} \frac{A\sqrt{\epsilon}\, d\epsilon}{e^{\beta\epsilon}+e^{\mu\beta}}$$

$z = e^{\mu\beta} \ll 1 < e^{\beta\epsilon}$

$$\simeq e^{\mu\beta} \int_0^{+\infty} A\sqrt{\epsilon}\, e^{-\beta\epsilon}\, d\epsilon$$

$$= A e^{\mu\beta} \sqrt{\frac{\pi (k_B T)^3}{4}}$$

$$\Rightarrow N e^{-\beta(\mu+\Delta)} = e^{+\mu\beta} \frac{A}{2} \sqrt{\pi (k_B T)^3}$$

$$2\mu = -\Delta + k_B T \log\left(\frac{2N}{A\sqrt{\pi (k_B T)^3}}\right)$$

5.24 (a) $\bar{\rho} = \frac{M}{V} = \frac{M}{\frac{4}{3}\pi R^3} \simeq 4.77 \times 10^8 \,kg\cdot m^{-3}$

电子完全电离，若为C whited dwarf. $\mu_e \simeq 2$ 若为F-WD $\mu_e \simeq 2.15$

$$P_F = \left(3\pi^2 \frac{\rho}{\mu_e m}\right)^{\frac{1}{3}} \hbar \simeq 1.74 \times 10^{-22} \,kg\cdot m\cdot s^{-1}$$

$\epsilon_F = \frac{1}{2m_e} P_F^2 = 1.595 \times 10^{-14} J$, $T_F = \frac{\epsilon_F}{k_B} = 1.15 \times 10^9 K \gg 10^7 K$

强简并.

$$T_F(\text{neuclon}) \propto \frac{1}{m_p} \sim 10^{-3}\, T_F(\text{electron})$$

$\Rightarrow$ 核子弱简并.

(b) $\rho \propto \frac{1}{R^3} \Rightarrow \rho_N = 4.77\times 10^{17}\ kg\cdot m^{-3}$.

$P_{F,N} \propto \rho_N \simeq 10^3 P_{F,WD}$; $\epsilon_{F,N} = 10^3 \epsilon_{F,WD}$ $> m_e c^2$ 极端相对论 可工作的范围

$T_{F,N}(\text{electron}) \sim 10^{12}K. \gg T_N$ 强简并电子.

$T_{F,N}(\text{neucleon}) \gg T_N$，强简并核子.

(c) $n \to p - e^- + \nu_e$ 忽略电子中微子的能量与化学势.

参照讲义中的计算.

$\mu_n = \mu_p + \mu_e$ 电中性: $n_e = n_p$.

$E_n = E_p + E_e$ $E_{pF} = E_{eF}$

极端相对论时

$E \sim p$ $\quad p_{nF} \simeq 2p_{pF}$ 课堂讲过

$$\Rightarrow \frac{n_n}{n_p} \sim \left(\frac{p_{nF}}{p_{pF}}\right)^3 \simeq 8.$$

5-25. 白矮星也为电中性,而质子 $m_p \gg m_e$

$$N_p \sim \frac{M_\otimes}{m_p} \simeq N_e = N_p$$

电子自由程λ $\sim \frac{R}{N^{\frac{1}{3}}} \sim \rho^{-\frac{1}{3}}$

$$P_e \sim \frac{\hbar}{\lambda} \sim \hbar\frac{N^{1/3}}{R} \qquad U_p \sim \frac{U_e}{(m_p/m_e)} \ll U_e$$

$$U_e \sim N_e \frac{P_e^2}{2m_e} \sim \frac{\hbar^2}{m_e R^2}\left(\frac{M}{m_p}\right)^{\frac{2}{3}}$$

(b) $E = E_g + U_e + U_p \sim -\gamma\frac{GM^2}{R} + \frac{\hbar^2}{m_e R^2}\left(\frac{M}{m_p}\right)^{\frac{2}{3}}$

$$\frac{\delta E}{\delta R} = 0 \Rightarrow C_1\frac{M^2}{R^2} - C_2\frac{M^{\frac{5}{3}}}{R^3} = 0 \Rightarrow R \sim M^{-\frac{1}{3}}$$

6.1.

(a) $$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\Gamma(E)} \int_{E<H<E+\Delta E} d q^{3N} d p^{3N} \, x_i \frac{\partial H}{\partial x_j}$$

其中 $\Gamma(E) \equiv \int_{E<H<E+\Delta E} d q^{3N} d p^{3N}$

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\Delta E}{\Gamma(E)} \frac{\partial}{\partial E} \int_{H<E} d^{3N}q \, d^{3N}p \, x_i \frac{\partial}{\partial x_j}(H-E)$$

See §6.4. Statistical Mechanics by Kerson Huang

Noting: $\frac{\partial E}{\partial x_j} = 0$; 注意到.

$$\int_{H<E} dp^{3N} dq^{3N} \, x_i \frac{\partial H}{\partial x_j} = \underbrace{\int_{H<E} dp^{3N} dq^{3N} \frac{\partial}{\partial x_j}\Big(x_i (H-E) \Big)}_{\text{surface term.}} - \delta_{ij} \int_{H<E} d^{3N}p \, d^{3N}q \, (H-E)$$

$$\Rightarrow \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\Delta E}{\Gamma(E)} \delta_{ij} \frac{\partial}{\partial E} \int_{H<E} d^{3N}q \, d^{3N}p \, (E-H)$$

$$= \frac{\delta_{ij}}{\omega(E)} \int_{H<E} dp^{3N} d^{3N}q = \frac{\delta_{ij}}{\omega(E)} \Sigma(E)$$

其中: $\omega(E)\Delta E = \Gamma(E)$

$$= \delta_{ij} \frac{\Sigma(E)}{\partial \Sigma / \partial E} = \delta_{ij} \left(\frac{\partial}{\partial E} \log \Sigma(E) \right)^{-1}$$

$$= \delta_{ij} k_B T$$

(b) 根据 (a) 的结果: 取 $x_i = x_j = q_\alpha$ $\quad \frac{\partial H}{\partial q_\alpha} = -\dot{p}_\alpha$

$$-\langle q_\alpha \dot{p}_\alpha \rangle = k_B T$$

$$\sum_{\alpha=1}^{3N} \langle q_\alpha \dot{p}_\alpha \rangle = -3N k_B T$$

6.2. 将系统分为有2个有热接触的子系统，热平衡时 $\beta_1=\beta_2$.
能量分别为 $E_{s_1}^{(1)}$ $E_{s_2}^{(2)}$

$$Z_{12}=\sum_{s_1 s_2} e^{-\beta(E_s^{(12)})}=\sum_{s_1 s_2} e^{-\beta(E_{s_1}^{(1)}+E_{s_2}^{(2)})}$$

$$=\sum_{s_1} e^{-\beta E_{s_1}^{(1)}} \sum_{s_2} e^{-\beta E_{s_2}^{(2)}}$$

$$= Z_1 \cdot Z_2$$

$$E=-\frac{\partial}{\partial\beta}\log Z \Rightarrow E \text{ 具有可加性.}$$

6.3. 略，方法与期中考题解答类同.

6.4. $\rho_s \equiv \frac{1}{Z} e^{-\beta E_s}$ $\quad Z \equiv \sum_s e^{-\beta E_s}$

$$S=-\left(\frac{\partial F}{\partial T}\right)_{V,N}= k_B \log Z+\frac{1}{\beta}\frac{1}{Z}\frac{\partial Z}{\partial T}$$

$$\Rightarrow S = k_B \log Z+\frac{1}{T}\sum_s E_s e^{-\beta E_s}\frac{1}{Z}$$

$$= k_B \sum_s \rho_s (\log Z+\beta E_s)$$

$$= -k_B \sum_s \rho_s \log \rho_s$$

注意这并非一个"证明"
这只是说明在一定情形下
这个定义与用状态数的定义
等价.

6.7. & 6.8. 计算 Z

6.10 相对论性单原子分子的统计

$$H = \sum_{i=1}^{N} |p_i| c \qquad Z = \frac{1}{N!(2\pi\hbar)^{3N}} \int d\Pi \ e^{-\beta H} \qquad d\Pi \equiv d^{3N}p \, d^{3N}q$$

$$Z = \frac{V^N}{N!(2\pi\hbar)^{3N}} \left(\int_0^{+\infty} 4\pi p^2 e^{-\beta pc} dp \right)^N$$

$$= \frac{V^N}{N!(2\pi\hbar)^{3N}} \times \left(4\pi \left(\frac{1}{\beta c}\right)^3 \Gamma(3) \right)^N$$

$$= \frac{1}{(2\pi)^{3N} N!} \left(\frac{k_B T V}{\hbar c} \right)^{3N}$$

$$\Rightarrow \quad F = -k_B T \log Z = -N k_B T \left(1 - 2\log\pi + 3\log\frac{k_B T}{\hbar c} + \log\frac{V}{N} \right)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{N k_B T}{V}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = N k_B \left\{ 4 - 2\log\pi - \log\left[\frac{V}{N}\left(\frac{k_B T}{\hbar c}\right)^3\right] \right\}$$

$$U = F + TS = 3 N k_B T \qquad \left(即 \ \frac{U}{V} = 3p \right)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_B T \left[2\log\pi - \log\left[\frac{V}{N}\left(\frac{k_B T}{\hbar c}\right)^3\right] \right]$$

6.11

(a) $$\mathcal{Z} = \prod_{j=1}^{\infty} \sum_{N=0}^{\infty} e^{-Nj\beta\hbar\omega} \qquad 玻色子的巨配分函数$$

$$= \prod_{j=1}^{\infty} \frac{1}{1 - e^{-j\beta\hbar\omega}}$$

小于1

$$\log \mathcal{Z} = -\sum_{j=1}^{\infty} \log\left(1 - e^{-\beta j\hbar\omega}\right)$$

$$= \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} \frac{1}{k} e^{-\beta k j\hbar\omega} \qquad \Rightarrow \langle E \rangle = -\frac{\partial}{\partial\beta} \log \mathcal{Z}$$

$$= \sum_{k=1}^{\infty} \frac{1}{k} \frac{1}{e^{\beta\hbar\omega k} - 1} \qquad = \frac{1}{2}\hbar\omega \sum_{k=1}^{\infty} \frac{1}{\cosh(\beta k\hbar\omega) - 1}$$

高温近似： $\beta\hbar\omega \ll 1$

$$\log Z \cong \sum_{k=1}^{\infty} \frac{1}{\beta\hbar\omega}\frac{1}{k^2} = \frac{\pi^2}{6}\frac{1}{\beta\hbar\omega}$$

$$F = -k_B T \log Z \simeq -\frac{\pi^2}{6}\frac{1}{\beta^2\hbar\omega}$$

(b) 在大N极限下

$$Z = \sum_{N=0}^{+\infty} \frac{1}{4\sqrt{3}N} \exp\left(\sqrt{\frac{2N}{3}}\pi - \sqrt{N}\beta\hbar\omega\right)$$

该级数要收敛，至少要有 $\left(\frac{2N}{3}\right)^{\frac{1}{2}}\pi < \beta\hbar\omega\sqrt{N}$

$$\Rightarrow k_B T < \frac{\sqrt{6}}{2\pi}\hbar\omega$$

6.12. 正则配分函数

$E = E_{固有} + E_{弹性}$ (张力)

$L \times F$

这个体系的 Hamiltonian，当有 i个子链的 $l=a$，$N-i$个子链 $l=b$ 时

$$H_{i,\{n_j\},\{l_j\}} = \left\{ \sum_{j=1}^{N} \left(\frac{1}{2}+n_j\right)\hbar\omega_{l_j} + \left[ai + b(N-i)\right]F \right\}$$

$$Z = \sum_{l_j\in\{a,b\}} \sum_{n_j=0}^{\infty} \sum_{i=0}^{N} \binom{N}{i} e^{-\beta H_{i,n_j,l_j}}$$

$$= \sum_{i=0}^{N} \binom{N}{i} e^{-\beta aFi}\left(\frac{e^{-\frac{1}{2}\hbar\omega_a\beta}}{1-e^{-\beta\hbar\omega_a}}\right)^{i} e^{-\beta bF(N-i)}\left(\frac{e^{-\frac{1}{2}\hbar\omega_a\beta}}{1-e^{-\beta\hbar\omega_a}}\right)^{N-i}$$

$$= \left[e^{-a\beta F}\frac{e^{-\frac{1}{2}\hbar\omega_a\beta}}{1-e^{-\beta\hbar\omega_a}} + e^{-b\beta F}\frac{e^{-\frac{1}{2}\hbar\omega_a\beta}}{1-e^{-\beta\hbar\omega_a}} \right]^{N}$$

$$Z = \left(\frac{e^{-\beta aF}}{2\sinh\left(\frac{1}{2}\hbar\omega_a\beta\right)} + \frac{e^{-\beta bF}}{2\sinh\left(\frac{1}{2}\hbar\omega_b\beta\right)} \right)^{N}$$

换个角度理解这个结果
是各链元相互作用，因此
可以用单节配分函数连乘

$$\mathcal{F} = -k_BT\log Z = -Nk_BT\log\left(\frac{e^{-\beta aF}}{2\sinh\left(\frac{1}{2}\hbar\omega_a\beta\right)} + \frac{e^{-\beta bF}}{2\sinh\left(\frac{1}{2}\hbar\omega_b\beta\right)} \right)$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\log Z \qquad 令\ \frac{1}{2}\hbar\omega_{a,b}\beta = \Lambda_{a,b}$$

$$= -\frac{N}{2}\,\frac{(2aF+\hbar\omega_a\coth\Lambda_a)e^{\beta bF}\sinh\Lambda_b + (2bF+\hbar\omega_b\coth\Lambda_b)e^{\beta aF}\sinh\Lambda_b}{e^{\beta bF}\sinh\Lambda_b + e^{\beta aF}\sinh\Lambda_a}$$

$$\langle L\rangle = \frac{\partial}{\partial F}\left(-\frac{1}{\beta}\log Z\right)$$

$$= \frac{a e^{bF\beta}\sinh\Lambda_b + b e^{aF\beta}\sinh\Lambda_a}{e^{\beta bF}\sinh\Lambda_b + e^{\beta aF}\sinh\Lambda_a} N$$

高温极限： $\Lambda \ll 1$ $\qquad \sinh\Lambda \sim \Lambda$

$$e^{\beta aF} \sim (1+\beta aF) \qquad e^{\beta bF} \sim (1+\beta bF)$$

$$\coth\Lambda \sim \Lambda^{-1}$$

$$\langle E\rangle = Nk_BT\,\frac{(\omega_a+\omega_b)e^{\beta F(a+b)}}{\omega_a e^{\beta aF} + \omega_b e^{\beta bF}}$$

$$\langle L\rangle = \frac{a e^{\beta bF}\omega_b + b e^{\beta aF}\omega_a}{\omega_a e^{\beta aF} + \omega_b e^{\beta bF}} N$$

低温极限： $\Lambda \gg 1$ $\qquad \sinh\Lambda \sim \frac{1}{2}e^{\Lambda}$

$$\coth\Lambda \sim 1$$

$$\langle E\rangle = \frac{(Fa+\Lambda_a)e^{\beta bF+\Lambda_b} + (Fb+\Lambda_b)e^{\beta aF+\Lambda_a}}{e^{\beta aF+\Lambda_a} + e^{\beta bF+\Lambda_b}} N$$

若 $a=b$ ，$\beta\to\infty$（零温极限），$\langle E\rangle = N(Fa+\Lambda_a)$ 零点能＋张力能

$$\langle L\rangle = \frac{b e^{\beta aF+\Lambda_a} + a e^{\beta bF+\Lambda_b}}{e^{\beta aF+\Lambda_a} + e^{\beta bF+\Lambda_b}}$$

6.16

色散关系：$\omega = c_s k$　　类似光子

$$D(\omega)d\omega = \frac{L^2}{\pi c_s^2}\,\omega\, d\omega$$

$$3N \quad 2N = \int_0^{\omega_D} D(\omega)d\omega = \frac{\omega_D^2 L^2}{2\pi c_s^2} \Rightarrow \omega_D = c_s\left(\frac{4\pi N}{L^2}\right)^{\frac{1}{2}}$$

$$= c_s\,(4\pi\sigma)^{\frac{1}{2}}$$

此处有误

$$Z_\omega = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} = \frac{1}{1-e^{-\beta\hbar\omega}}$$

经讨论在正常的二维体系如石墨烯中晶格总自由度仍可为3N

$$\log Z_{phonon} = \int_0^{\omega_D} \log Z_\omega\, D(\omega)d\omega$$

内能：$U = \int_0^{\omega_D} D(\omega)d\omega\left(\frac{1}{2}\hbar\omega + \frac{1}{e^{\hbar\beta\omega}-1}\hbar\omega\right)$

$$= \frac{2}{3}N\hbar\omega_D + \underbrace{2N}_{3N}k_BT\,\frac{2}{x^2}\int_0^x \frac{t^2dt}{e^t-1} \qquad t \equiv \frac{\hbar\omega_D}{k_BT}$$

高温极限：$t \ll 1$

$$U \simeq \frac{2}{3}N\hbar\omega_0 + \underbrace{2N}_{3N}k_BT$$

$$C \simeq \underbrace{2N}_{3N}k_B$$

低温：

$$U \simeq \frac{2}{3}N\hbar\omega_D + \underbrace{2N}_{3N}k_BT\cdot t^2 \times 2\,\zeta(3)$$

$$\Rightarrow C \simeq \frac{24\,\zeta(3)}{\left(\frac{\hbar^2\omega_D^2}{k_B^2}\right)}Nk_B T^2 \simeq 24Nk_B\zeta(3)\left(\frac{T}{T_D}\right)^2$$

6.18

$$Z = \frac{1}{N!}\frac{1}{\lambda^{3N}}\int \prod d^{3N} r_i\, e^{-\beta\sum_{j<k} V_{jk}}$$ 其中 $\lambda \equiv \left(\frac{2\pi\hbar^2}{mk_BT}\right)^{\frac{1}{2}}$

定义 Mayer function： $f_{ij} \equiv e^{-\beta V(r_{ij})} - 1$

$$Z = \frac{1}{N!}\frac{1}{\lambda^{3N}}\int \prod_i d^{3N} r_i \prod_{j>k}(1+f_{jk})$$

$$= \frac{1}{N!}\frac{1}{\lambda^{3N}}\int \prod_i^N d^{3N} r_i \left(1 + \sum_{j>k} f_{jk} + \sum_{j>k,l>m} f_{jk} f_{lm} + \cdots\right)$$

其中一阶项： $\int \prod_i^N d^{3N} r_i\, f_{12} = V^{N-2}\int d^3r_1 d^3r_2\, f(r_{12}) = V^{N-1}\int d^3r\, f(r)$

$$Z(N,V,T) \simeq Z_{ideal}\left(1 + \frac{N}{2V}\int d^3r\, f(r) + \cdots\right)^N$$

$$\int d^3r\, f(r) = \int_0^{+\infty} 4\pi r^2 f(r)\, dr$$

$$= -4\pi\left(\int_0^{\sigma} r^2 dr + \int_{\sigma}^{r_0} r^2(1-e^{\beta V_0})\, dr\right)$$

$$= -\frac{4}{3}\pi\left[\sigma^3 + (1-e^{\beta V_0})(r_0^3-\sigma^3)\right]$$

EoS： $pV = Nk_BT\left(1 + a_2(T)\frac{N}{V} + \cdots\right)$

$$a_2(T) = \frac{2\pi}{3}\left(r_0^3 - e^{\frac{V_0}{k_BT}}(r_0^3-\sigma^3)\right)$$

6月10日作业

6.14.

6.9. (a) $J>0$. 系统中自旋都取为同向时整体能量最低.

由于 σ_i 有 q 种取值 $\Rightarrow$ 系统应该具有 q 种基态.

(b) 假定一个格点周围最近邻格点数为 γ. 在 N 个格点中有 N_1 个格点自旋为 S_1, 有 N_2 个格点自旋为 S_2. 有 N_3 个格点自旋为 S_3. 显然有

$$N = N_1 + N_2 + N_3.$$

如果每个格点都向最近似伸出一条线. 那~~相邻~~共伸出 γN 条线. 那最近邻格点间有两条线 $\Rightarrow$ 最近似对数为 $\frac{1}{2}\gamma N$.

近邻格点间自旋共有6种可能性. 11, 12, 13, 22, 23, 33.

数量分别记为 N_{11}, N_{12}, N_{13}, N_{22}, N_{23}, N_{33}.

我们现在让所有自旋为1的格点向最近邻伸出一条线. 线总数为 γN_1.

那11自旋对间有两条线, 12, 13 对间有一条线.

$$\Rightarrow \gamma N_1 = 2N_{11} + N_{12} + N_{13}.$$

同理有 $\gamma N_2 = 2N_{22} + N_{12} + N_{23}$. $\gamma N_3 = 2N_{33} + N_{13} + N_{23}$.

记 $\frac{N_1}{N} = \frac{1}{3}(1+L_1)$ $\frac{N_2}{N} = \frac{1}{3}(1+L_2) \Rightarrow \frac{N_3}{N} = \frac{1}{3}(1-L_1-L_2)$.

取平均场近似: 在 $\frac{1}{2}\gamma N$ 中取一对, 其自旋出现几率对两格点近似独立

$$\Rightarrow \frac{N_{ij}}{\frac{1}{2}\gamma N} = \left(\frac{N_i}{N}\right)\cdot\left(\frac{N_j}{N}\right)\cdot(2-\delta_{ij})$$

$$\Rightarrow \frac{N_{11}}{\frac{1}{2}\gamma N} = \left(\frac{N_1}{N}\right)^2 \qquad \frac{N_{22}}{\frac{1}{2}\gamma N} = \left(\frac{N_2}{N}\right)^2 \qquad \frac{N_{33}}{\frac{1}{2}\gamma N} = \left(\frac{N_3}{N}\right)^2.$$

$$\frac{N_{12}}{\frac{1}{2}\gamma N} = 2\cdot\frac{N_1}{N}\cdot\frac{N_2}{N} \qquad \frac{N_{13}}{\frac{1}{2}\gamma N} = 2\cdot\frac{N_1}{N}\cdot\frac{N_3}{N} \qquad \frac{N_{23}}{\frac{1}{2}\gamma N} = 2\cdot\frac{N_2}{N}\cdot\frac{N_3}{N}$$

和 $S_1 = \begin{pmatrix}1\\0\end{pmatrix}$ $S_2 = \begin{pmatrix}-1/2\\ \sqrt{3}/2\end{pmatrix}$ $S_3 = \begin{pmatrix}-1/2\\ -\sqrt{3}/2\end{pmatrix}$.

$$\Rightarrow S_i\cdot S_j = \begin{cases} 1, & i=j \\ -\frac{1}{2}, & i\neq j \end{cases}$$

$$\Rightarrow E = -\frac{2}{3}J\left[N_{11} + N_{22} + N_{33} - \frac{1}{2}(N_{12} + N_{13} + N_{23})\right].$$

$$= -\frac{2}{3}J\left[N_{11} + N_{22} + N_{33} - \frac{1}{2}\left(\frac{1}{2}\gamma N - N_{11} - N_{22} - N_{33}\right)\right]$$

$$= -J(N_{11} + N_{22} + N_{33}) + \frac{1}{6}\gamma N J.$$

将平均场近似结果代入得到

$$E = -\frac{1}{2}\gamma N J\left[\left(\frac{N_1}{N}\right)^2 + \left(\frac{N_2}{N}\right)^2 + \left(\frac{N_3}{N}\right)^2\right] + \frac{1}{6}\gamma N J.$$

$$= -\frac{1}{18}\gamma N J\left[(1+L_1)^2 + (1+L_2)^2 + (1-L_1-L_2)^2 - 3\right]$$

$$= -\frac{1}{9}\gamma N J(L_1^2 + L_2^2 + L_1 L_2).$$

序参量为 L_1, L_2 时系统简并度为

$$g(L_1, L_2) = \frac{N!}{N_1!\,N_2!\,N_3!} = C_N^{N_1} \cdot C_{N-N_1}^{N_2} \cdot C_{N-N_1-N_2}^{N_3}$$

正则系综配分函数为

$$Z = \sum_{L_1, L_2} g(L_1, L_2)\, e^{-\beta E(L_1, L_2)}$$ 用最概然时 $\bar{L}_1, \bar{L}_2$ 替代

$$\Rightarrow \cancel{\ln Z =} \ln g(L_1, L_2)\, e^{-\beta E(L_1, L_2)} = \ln Z_0.$$

$$= \ln g(L_1, L_2) + \frac{1}{9}\gamma\beta N J(L_1^2 + L_2^2 + L_1 L_2)$$

$$\approx N\left[\ln N - \frac{1+L_1}{3}\ln\frac{1+L_1}{3} - \frac{1+L_2}{3}\ln\frac{1+L_2}{3} - \frac{1-L_1-L_2}{3}\ln\frac{1-L_1-L_2}{3} + \frac{1}{9}\gamma\beta J(L_1^2 + L_2^2 + L_1 L_2)\right].$$

$$\Rightarrow \frac{\partial}{\partial L_1}\ln Z_0 = N\cdot\left[\frac{1}{3}\ln\frac{1-L_1-L_2}{L_1+1} + \frac{1}{9}\gamma\beta J(2L_1 + L_2)\right]$$

$$\frac{\partial}{\partial L_2}\ln Z_0 = N\cdot\left[\frac{1}{3}\ln\frac{1-L_1-L_2}{1+L_2} + \frac{1}{9}\gamma\beta J(2L_2 + L_1)\right].$$

最概然时 $\bar{L}_1, \bar{L}_2$ 满足方程

$$\gamma\beta J(2\bar{L}_1 + \bar{L}_2) = 3\ln\frac{1+\bar{L}_1}{1-\bar{L}_1-\bar{L}_2} \quad ①$$

$$\gamma\beta J(2\bar{L}_2 + \bar{L}_1) = 3\ln\frac{1+\bar{L}_2}{1-\bar{L}_1-\bar{L}_2} \quad ②$$

上述方程必然有 $\bar{L}_1 = \bar{L}_2 = 0$ 的解. 相变对应上述方程有非平零解.

① 计算磁矩. $\vec{m} = \langle S_i \rangle = \frac{N_1}{N}\vec{S}_1 + \frac{N_2}{N}\vec{S}_2 + \frac{N_3}{N}\vec{S}_3$

$$= \begin{pmatrix} \frac{N_1}{N} - \frac{N_2}{2N} - \frac{N_3}{2N} \\ \frac{\sqrt{3}N_2}{2N} - \frac{\sqrt{3}N_3}{2N} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}\bar{L}_1 \\ \frac{\sqrt{3}}{6}(\bar{L}_1 + 2\bar{L}_2) \end{pmatrix}.$$

在平凡解 $\bar{L}_1=\bar{L}_2=0$ 下，可以发现 $\vec{m}=\vec{0}$ 即系统不呈现磁性。

在非平凡解处，可知 $\vec{m}\neq\vec{0}$，即系统体现磁性。

② 用配分函数中最概然部分来近似它

$$\Rightarrow F=-kT\ln Z_0$$

$$=-NkT\ln N+NkT\left(\frac{1+\bar{L}_1}{3}\ln\frac{1+\bar{L}_1}{3}+\frac{1+\bar{L}_2}{3}\ln\frac{1+\bar{L}_2}{3}+\frac{1-\bar{L}_1-\bar{L}_2}{3}\ln\frac{1-\bar{L}_1-\bar{L}_2}{3}\right)-\frac{1}{9}\gamma NJ(\bar{L}_1^2+\bar{L}_2^2+\bar{L}_1\bar{L}_2).$$

③ 讨论相变

先求解平均场下系统的临界温度 T_c，对方程①②两侧关于 $\bar{L}_1,\bar{L}_2$ 做微分

$$\Rightarrow \frac{\gamma J}{kT}(2d\bar{L}_1+d\bar{L}_2)=3\cdot(2d\bar{L}_1+d\bar{L}_2)$$

$$\frac{\gamma J}{kT}(2d\bar{L}_2+d\bar{L}_1)=3\cdot(2d\bar{L}_2+d\bar{L}_1).$$

$$\Rightarrow \left(\frac{\gamma J}{kT}-3\right)(2d\bar{L}_1+d\bar{L}_2)=0$$

$$\left(\frac{\gamma J}{kT}-3\right)(2d\bar{L}_1+d\bar{L}_2)=0.$$

可见对于方程①等式左右两曲面在 $\bar{L}_1=\bar{L}_2=0$ 处~~切平~~相切条件为 $\frac{\gamma J}{kT}-3=0$。

而方程②相切条件与①相同，由此可得临界温度

$$T_c=\frac{\gamma J}{3k}$$

在 $T>T_c$ 时①②方程仅有平凡解 $\bar{L}_1=\bar{L}_2=0$。

在 $T<T_c$ 时①②方程有非平凡解 $\bar{L}_1',\bar{L}_2'$

$$\Rightarrow U=E=\begin{cases}0 & T>T_c\\ -\frac{1}{9}\gamma NJ(\bar{L}_1^2+\bar{L}_2^2+\bar{L}_1\bar{L}_2) & T<T_c.\end{cases}$$

随温度连续改变，$\bar{L}_1,\bar{L}_2$ 连续地从非零变为零 $\Rightarrow$ E 随温度连续改变。

$$\Rightarrow C(T)=\frac{\partial E}{\partial T}=\begin{cases}0 & T>T_c\\ -\frac{1}{9}\gamma NJ\frac{d}{dT}(\bar{L}_1^2+\bar{L}_2^2+\bar{L}_1\bar{L}_2) & T<T_c.\end{cases}$$

C(T) 不连续变化，故系统在平均场近似后为存在一个二级相变。

6.13 相对论性单原子分子

$$\mathcal{Z} = \sum_{N=0}^{\infty} \int \frac{1}{N!} \frac{d^{3N}q\, d^{3N}p}{(2\pi\hbar)^{3N}} \exp(-\beta H(q_\alpha, p_\alpha) + \mu\beta N)$$

$$\beta \equiv \frac{1}{k_B T}$$

$$= \sum_{N=\infty}^{\infty} \frac{V^N}{N!(2\pi\hbar)^3} e^{\mu\beta N} \left(4\pi \int_0^\infty p^2 dp\, e^{-\beta pc}\right)^N$$

$$= \sum_{N=\infty}^{\infty} \frac{V^N}{N!(2\pi\hbar)^3} e^{\mu\beta N} \left(4\pi \frac{1}{\beta^3 c^3} \Gamma(3)\right)^N$$

$$= \exp\left(\frac{V e^{\mu\beta}}{\pi^2 \hbar^3 \beta^3 c^3}\right)$$

$$J = -\frac{1}{\beta} \log \mathcal{Z} = -\frac{1}{\beta} e^{\mu\beta} \frac{V}{\pi^2 \hbar^3 \beta^3 c^3}$$

$$p = -\left(\frac{\partial J}{\partial V}\right)_{\mu,T} = e^{\mu\beta} \frac{1}{\beta^4 c^3 \pi^2 \hbar^3}$$

$$\langle N \rangle = -\left(\frac{\partial J}{\partial \mu}\right)_{V,T} = \frac{V e^{\mu\beta}}{\beta^3 c^3 \pi^2 \hbar^3}$$

$$\langle S \rangle = -\left(\frac{\partial J}{\partial T}\right)_{V,\mu} = (4 - \mu\beta) k_B \frac{V e^{\mu\beta}}{\beta^3 c^3 \pi^2 \hbar^3}$$

状态方程： $pV = \langle N \rangle k_B T$

化学势、 $\mu = k_B T \log\left(\frac{\langle N \rangle}{V} \pi^2 \hbar^3 c^3 \beta^3\right)$

6.20

$$\mathcal{Z} = -\sum_{N=0}^{\infty} \frac{1}{N!} \int \frac{d^{3N}q\, d^{3N}p}{(2\pi\hbar)^{3N}} \exp(-\beta H(q_\alpha, p_\alpha) + \mu\beta N)$$

忽略相互作用项 H_{int}

$$\Rightarrow H_{system} = N H_{single\text{-}particle}$$

$$\Rightarrow \mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\mu\beta} \Lambda}{(2\pi\hbar)^3}\right)^N$$

其中 Λ 为单粒子动量积分

$$\Lambda \equiv \int d^3p\, e^{-\beta H_{single\ particle}}$$

在体积V中找到n个粒子的概率为

$$p_n = \frac{1}{Z} \frac{1}{n!} \left(\frac{e^{\mu\beta}\Lambda}{(2\pi\hbar)^3}\right)^n \qquad 令 \lambda = \frac{e^{\mu\beta}\Lambda}{(2\pi\hbar)^3}$$

$$\sum_{n=0}^{\infty} p_n = 1 = \sum_{n=0}^{\infty} \frac{1}{Z} \frac{1}{n!} \lambda^n = \frac{1}{Z} e^{\lambda} \Rightarrow Z = e^{\lambda}$$

$$\langle n \rangle = \frac{1}{V} \frac{\partial}{\partial \mu}\left(\frac{1}{\beta} \lambda\right) = \lambda$$

$$\Rightarrow \quad p_n = \frac{1}{n!} \langle n \rangle^n e^{-\langle n \rangle}$$

6.21 标准过程，可参考 Lee 的统计力学 §1.4

系统总能量： $E = \sum_\alpha n_\alpha \varepsilon_\alpha$ 　　 α 为 α 能级指标

$$\begin{aligned} Z &\equiv \sum_{\{n_\alpha\}} e^{\beta\mu\sum_\alpha n_\alpha} \exp\left(-\beta \sum_\alpha n_\alpha \varepsilon_\alpha\right) \\ &= \prod_\alpha \sum_{\{n_\alpha\}} e^{n_\alpha\mu\beta} \exp\left(-\beta n_\alpha \varepsilon_\alpha\right) \\ &= \prod_\alpha \left(1 + e^{-\beta\varepsilon_\alpha + \mu\beta}\right) \end{aligned}$$

6.24

$$\langle EN \rangle = -\frac{\partial^2}{\partial\alpha\partial\beta} \log Z \qquad \alpha \equiv -\mu\beta, \quad \beta \equiv \frac{1}{k_B T}$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \log Z$$

$$\langle N \rangle = \frac{\partial}{\partial\alpha} \log Z$$

$\langle E \rangle$ 依赖 $\langle N \rangle$

一般不相等，举一例即可.

6月14日作业

6.5. (a) $$Z = \sum_{N=0}^{\infty} e^{-\beta E_N} = \sum_{N=0}^{\infty} e^{-\beta \Delta \epsilon N}$$

$$= \frac{1}{1 - e^{-\beta\Delta\varepsilon}}$$

(b) $$\langle L \rangle = \frac{1}{Z}\sum_{N=0}^{\infty} (l_0 + Nl)\, e^{-\beta\Delta\epsilon N}$$

$$= l_0 + \frac{l}{\Delta\varepsilon}\frac{1}{Z}\frac{\partial}{\partial\beta}Z$$

$$= l_0 + \frac{l}{\Delta\varepsilon}\frac{\partial}{\partial\beta}\log Z$$

$$= l_0 + l\,\frac{1}{e^{\beta\Delta\varepsilon}-1}$$

高温极限：$\langle L \rangle = l_0 + l\,\frac{k_B T}{\Delta\varepsilon}$

6.6. 正则配分函数

$$\mathcal{Z} = \sum_{j=0}^{2N_0} z^j Z_s(j)$$

$z \equiv e^{\mu\beta}$

N_0个格点中 n_A个格点，只有A被占据

n_B个格点，只有B被占据

n_e个未占据.

n_{AB}个 A，B都被占据.

$$Z_s(j) = \binom{N_0}{n_e \;\; n_A \;\; n_B \;\; n_{AB}} \exp\left[-\beta\left(-n_A\epsilon_A - n_B\epsilon_B - 2n_{AB}\left(\frac{\epsilon_A+\epsilon_B}{2} - \mu_{AB}\right)\right)\right]$$

其中有. $\begin{cases} n_A + n_B + 2n_{AB} = j \\ n_e + n_A + n_B + n_{AB} = N_0 \end{cases}$

$$\Rightarrow n_e = N_0 - j + n_{AB}$$

$\mathcal{Z} = \sum_{j=0}^{2N_0} z^j Z_s(j)$ 的计算有技术上的困难，但我们发现题目

只需要我们计算吸附率，而对于格点吸附的粒子数不关心，因此我们换一个思路

将每个格点视为一个粒子，可以有4种状态：空、A占据、B占据、AB都占据

用正则系综来处理.

$$Z = Z_s^{N_0} = \left(1 + e^{+\beta\epsilon_A} + e^{+\beta\epsilon_B} + e^{+\beta(\varepsilon_A+\varepsilon_B-\mu_{AB})}\right)^{N_0}$$

$$F = -N_0 k_B T Z_s$$

占据率即这样的格点粒子具有能量(被激发)的比率.

未吸附的格点数：$N_0 \dfrac{1}{Z}$

$$\text{占据数} = N_0\left(1 - \frac{1}{Z}\right)$$

$$\text{占据率} = \left(1 - \frac{1}{Z}\right)$$

$$z \equiv e^{\mu\beta}$$

6.15 (a)

$$\mathcal{Z}_F = 1 + z + z e^{-\beta\epsilon} + z e^{-3\beta\epsilon} + z^2 e^{-\beta\epsilon} + z^2 e^{-3\beta\epsilon} + z^2 e^{-4\beta\epsilon}$$

$$\langle N \rangle = \frac{\partial}{\partial \log z} \log \mathcal{Z}_F = \frac{z(1+e^{-\beta\epsilon}+e^{-3\beta\epsilon}) + 2z^2(e^{-\beta\epsilon}+e^{-3\beta\epsilon}+e^{-4\beta\epsilon})}{1+z(1+e^{-\beta\epsilon}+e^{-3\beta\epsilon})+z^2(e^{-\beta\epsilon}+e^{-3\beta\epsilon}+e^{-4\beta\epsilon})}$$

(b)

$$\mathcal{Z}_B = \mathcal{Z}_F + z^2(1+e^{-2\beta\epsilon}+e^{-6\beta\epsilon})$$

$$\langle N \rangle = \frac{\partial}{\partial \log z} \log \mathcal{Z}_B$$

6.17 $H = H_{free} + H_{int}$

$$H_{int} = \sum_{i<j} V_{ij}(|\vec{r}_i - \vec{r}_j|) \qquad H_{free} = \sum_{i=1}^{n} \frac{\vec{p}_i^{\,2}}{2m}$$

$$Z = \frac{1}{N!}\frac{1}{(2\pi\hbar)^2}\int d^{2N}q\, d^{2N}p\; e^{-\beta H}$$

$$= \frac{1}{N!}\left(\frac{m k_B T}{2\pi\hbar^2}\right)^N \left(\int d^{2N}q\; e^{-\beta\sum_{i<j}V_{ij}}\right)$$

Mayer function : $f_{ij} = e^{-\beta V_{ij}} - 1$

保留至一阶

$$Z \simeq \frac{1}{N!}\left(\frac{m k_B T}{2\pi\hbar^2}\right)^N \left[\binom{N}{2} A^{N-2}\int d^2r_1\, d^2r_2\, f_{12} + A^N\right]$$

$$\int d^2r_1\, d^2r_2\, f_{12} = A\int_0^{+\infty} 2\pi r\, dr\left(e^{-\frac{\phi(r)}{k_B T}} - 1\right) \overset{\text{def}}{=} -\frac{2}{N} A B_2$$

$$\Rightarrow Z = \frac{1}{N!}\left(\frac{m k_B T}{2\pi\hbar^2}\right)^N A^N\left(1 - \frac{N}{A}B_2\right)$$

$$= \frac{A^N}{N!\,\lambda_T^{2N}}\left(1-\frac{N}{A}B_2\right) \Rightarrow F = -k_B T \log Z$$

$$P = -\left(\frac{\partial F}{\partial A}\right)_{T,N}$$

$$F = -Nk_BT\left[\log\left(\frac{A}{N\lambda_T^2}\right)+1\right] - k_BT\log\left(1-\frac{N}{A}B_2\right)$$

$$p = \frac{Nk_BT}{A}\left(1 + \frac{AB_2}{A-NB_2}\right)$$

$$\Rightarrow \quad p \simeq \frac{Nk_BT}{A}\left(1+\frac{B_2}{A}\right)$$