

热统习题的部分答案 (野生版)

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1 第一章

1.1 习题 1.6

$$\begin{aligned}
 \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{\nu R}{pV} &\Rightarrow \left(\frac{\partial V}{\partial T} \right)_p = \frac{\nu R}{p} \\
 &\Rightarrow V = \frac{\nu RT}{p} + g(p) \quad \text{代入 } \kappa = \frac{1}{p} + \frac{a}{V} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \\
 &\Rightarrow d(pg(p)) = -\frac{a}{2} dp^2 \\
 &\Rightarrow pg(p) = -\frac{a}{2} p^2 + \text{const} \quad \text{代入第二行式子并整理} \\
 &\Rightarrow pV = \nu RT - \frac{a}{2} p^2 + \text{const}.
 \end{aligned}$$

1.2 习题 1.8

1) 利用广延量假设,

$$\begin{aligned}
 S = Ns, V = Nv, U = Nu &\Rightarrow s = A(vu)^{1/3} \\
 &\Rightarrow Tds = TA \frac{vdu + u dv}{3(vu)^{2/3}} = du + p dv \\
 du, dv \text{ 前的系数对应相等并恢复广延量} &\Rightarrow \begin{cases} T = \frac{3u^{2/3}}{Av^{1/3}} = \frac{3U^{2/3}}{A(NV)^{1/3}} \quad \text{易得: } U \sim T^{3/2} \\ p = \left(\frac{N}{V} \right)^{1/2} \left(\frac{AT}{3} \right)^{3/2} \end{cases}
 \end{aligned}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{1}{2} \sqrt{\frac{A^3 NV T}{3}} \quad \text{利用了前面的温度表达式.}$$

2) 对于每个热源而言, 我们有:

$$dQ = dU \sim T^{1/2} dT,$$

由于高温热源放出热量 ($\Delta Q_h < 0$) 必定大于等于低温热源吸热 ($\Delta Q_c > 0$), 不失一般性, 我们假设 $T_1 > T_2$,

$$\begin{aligned}
 \Delta Q_h + \Delta Q_c \leq 0 &\Rightarrow \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f} \right) T^{1/2} dT \leq 0 \\
 &\Rightarrow T_f \leq \left(\frac{T_1^{3/2} + T_2^{3/2}}{2} \right)^{2/3};
 \end{aligned}$$

另一方面, 由热力学第二定律: $\Delta S \geq 0$,

$$\begin{aligned}
 \Delta S = \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f} \right) \frac{dQ}{T} &\sim \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f} \right) \frac{1}{T^{1/2}} dT \geq 0 \\
 &\Rightarrow T_f \geq \left(\frac{T_1^{1/2} + T_2^{1/2}}{2} \right)^2.
 \end{aligned}$$

由第一题的温度表达式, 我们得到:

$$U = \left(\frac{AT(NV)^{1/3}}{3} \right)^{3/2} = CT^{3/2}.$$

对于整个系统而言,

$$W = -\Delta U_{\text{总}} = C \left(T_1^{3/2} + T_2^{3/2} - 2T_f^{3/2} \right) \leq \sqrt{\frac{A^3 NV}{27}} \left[T_1^{3/2} + T_2^{3/2} - 2 \left(\frac{T_1^{1/2} + T_2^{1/2}}{2} \right)^3 \right].$$

1.3 习题 1.11

首先, 我们需要求出范氏气体的内能表达式,

$$\begin{aligned}
 \text{由范氏气体的状态方程} &\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V-b} \\
 \text{代入书上式子 (1.9.16)} &\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = -p + T \left(\frac{\partial p}{\partial T}\right)_V = \frac{a}{V^2} \\
 &\Rightarrow dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \frac{a}{V^2} dV \\
 &\Rightarrow U = C_V T - \frac{a}{V} + U_0.
 \end{aligned}$$

1) 对于等温过程,

$$\begin{aligned}
 \Delta U &= -\frac{a}{V_f} + \frac{a}{V_i} \\
 W &= \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \left(\frac{RT_i}{V-b} - \frac{a}{V^2} \right) dV = RT_i \ln \left(\frac{V_f-b}{V_i-b} \right) + \frac{a}{V_f} - \frac{a}{V_i} \\
 \Delta S &= \frac{\Delta U + W}{T_i} = R \ln \frac{V_f-b}{V_i-b};
 \end{aligned}$$

2) 对于等压过程,

$$\begin{aligned}
 W &= p_i(V_f - V_i) = \left(\frac{RT_i}{V_i-b} - \frac{a}{V_i^2} \right) (V_f - V_i) \\
 \text{利用状态方程} &\Rightarrow T_f = \left(p_i + \frac{a}{V_f^2} \right) (V_f - b)/R = \left(\frac{RT_i}{V_i-b} - \frac{a}{V_i^2} + \frac{a}{V_f^2} \right) (V_f - b)/R \\
 &\Rightarrow \Delta U = C_V(T_f - T_i) - \frac{a}{V_f} + \frac{a}{V_i} = C_V \left[\left(\frac{RT_i}{V_i-b} - \frac{a}{V_i^2} + \frac{a}{V_f^2} \right) (V_f - b)/R - T_i \right] - \frac{a}{V_f} + \frac{a}{V_i} \\
 \text{由等压条件} &\Rightarrow T dS = dQ = C_p dT \\
 &\Rightarrow dS = C_p d(\ln T) \\
 &\Rightarrow \Delta S = C_p \ln \frac{T_f}{T_i} = C_p \ln \left[\frac{V_f-b}{V_i-b} - a \left(\frac{1}{V_i^2} - \frac{1}{V_f^2} \right) \frac{V_f-b}{RT_i} \right];
 \end{aligned}$$

3) 对于绝热过程,

$$\begin{aligned}
 dQ = dU + p dV &= \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV = C_V dT + \left(\frac{a}{V^2} + p \right) dV = 0, \\
 \text{结合状态方程} &\Rightarrow C_V dT + \frac{RT}{V-b} dV = 0 \\
 &\Rightarrow C_V \ln T + R \ln(V-b) = 0 \\
 &\Rightarrow T^{C_V} (V-b)^R = \text{const} \\
 &\Rightarrow T_f = T_i \left(\frac{V_i-b}{V_f-b} \right)^{R/C_V}
 \end{aligned}$$

因此, 我们容易得到:

$$\begin{aligned}
 \Delta U &= C_V T_i \left[\left(\frac{V_i-b}{V_f-b} \right)^{R/C_V} - 1 \right] - \frac{a}{V_f} + \frac{a}{V_i} \\
 W &= -\Delta U \\
 \Delta S &= 0.
 \end{aligned}$$

1.4 习题 1.13

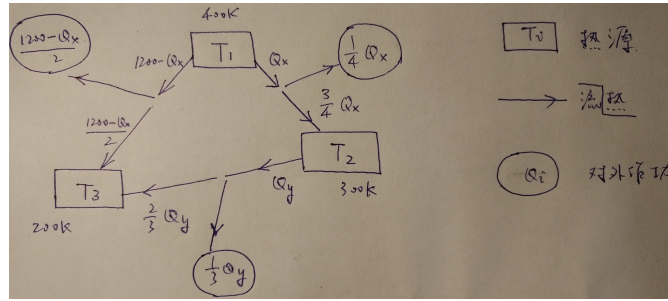
其中一个物体降温 (放热): $T_1 \rightarrow T_2$, 另一个物体升温 (吸热): $T_1 \rightarrow T_x$. 考虑整个体系, 由热力学第二定律,

$$\Delta S = \left(\int_{T_1}^{T_2} + \int_{T_1}^{T_x} \right) \frac{C_p dT}{T} \geq 0 \Rightarrow T_x \geq \frac{T_1^2}{T_2}.$$

因此,

$$W \geq \Delta Q = C_p(T_x + T_2 - 2T_1) \geq C_p \left(\frac{T_1^2}{T_2} + T_2 - 2T_1 \right) = C_p \frac{(T_1 - T_2)^2}{T_2}.$$

1.5 习题 1.22



由图, 我们有以下关系:

$$\begin{aligned} \frac{1200 - Q_x}{2} + \frac{Q_y}{3} + \frac{Q_x}{4} &= 200 \Rightarrow \frac{3}{4}Q_x - Q_y = 1200 \\ &\Rightarrow \begin{cases} Q_2 = \frac{3}{4}Q_x - Q_y = 1200\text{J} \\ Q_3 = \frac{1200 - Q_x}{2} + \frac{2Q_y}{3} = -200\text{J} \end{cases} \\ &\Rightarrow \begin{cases} \Delta S_1 = \frac{Q_1}{T_1} = \frac{-1200}{400} = -3\text{J/K} \\ \Delta S_2 = \frac{Q_2}{T_2} = \frac{1200}{300} = 4\text{J/K} \\ \Delta S_3 = \frac{Q_3}{T_3} = \frac{-200}{200} = -1\text{J/K} \\ \Delta S_{\text{总}} = \sum_{i=1}^3 \Delta S_i = 0\text{J/K}. \end{cases} \end{aligned}$$

1.6 习题 1.23

考虑等熵过程 ($S = S_0$),

$$\begin{aligned} W_{S_0} &= \int_{V_0}^V p(S_0, V') dV' = RS_0 \ln \frac{V}{V_0} \Rightarrow p(S_0, V) = \frac{dW_{S_0}}{dV} = \frac{RS_0}{V} \\ U(S_0, V) - U(S_0, V_0) &= -W_{S_0} \Rightarrow U(S_0, V) = U_0 - RS_0 \ln \frac{V}{V_0}. \end{aligned}$$

现在考虑一个等体过程 ($V, S_0 \rightarrow V, S$),

$$\begin{aligned} U(S, V) - U(S_0, V) &= \int_{T(S_0, V)}^{T(S, V)} T(S', V) dS' \\ &= \int_{S_0}^S \frac{RV_0}{V} \left(\frac{S'}{S_0} \right)^a dS' \\ &= \frac{RV_0 S_0}{(a+1)V} \left[\left(\frac{S}{S_0} \right)^{a+1} - 1 \right] \end{aligned}$$

因此,

$$U(S, V) = \frac{RV_0 S_0}{(a+1)V} \left[\left(\frac{S}{S_0} \right)^{a+1} - 1 \right] - RS_0 \ln \frac{V}{V_0} + U_0$$

又由:

$$\begin{aligned} \left(\frac{\partial p}{\partial S} \right)_V &= - \left(\frac{\partial T}{\partial V} \right)_S = \frac{RV_0}{V^2} \left(\frac{S}{S_0} \right)^a \\ \Rightarrow \quad p(S, V) &= \frac{RV_0 S_0}{(a+1)V^2} \left[\left(\frac{S}{S_0} \right)^{a+1} - 1 \right] + \frac{RS_0}{V} \\ W(S, V_0 \rightarrow V) &= \int_{V_0}^V p(S, V') dV' = \frac{RV_0 S_0}{a+1} \left[\left(\frac{S}{S_0} \right)^{a+1} - 1 \right] \left(\frac{1}{V_0} - \frac{1}{V} \right) + RS_0 \ln \frac{V}{V_0}. \end{aligned}$$

2 第二章

2.1 习题 2.2

$$\begin{aligned}\overline{v^n} &= \frac{\int_0^{+\infty} v^{n+2} e^{-mv^2/2k_B T} dv}{\int_0^{+\infty} v^2 e^{-mv^2/2k_B T} dv} \\&= \frac{\int_0^{+\infty} \left(\frac{2k_B T}{m}\right)^{\frac{n+3}{2}} s^{\frac{n+1}{2}} e^{-s} ds}{\int_0^{+\infty} \left(\frac{2k_B T}{m}\right)^{\frac{3}{2}} s^{\frac{1}{2}} e^{-s} ds} \quad \text{变量代换: } s = \frac{mv^2}{2k_B T} \\&= \left(\frac{2k_B T}{m}\right)^{\frac{n}{2}} \frac{\Gamma(\frac{n+3}{2})}{\Gamma(\frac{3}{2})} \quad \text{利用 } \Gamma \text{ 函数的定义} \\&= \frac{2}{\sqrt{\pi}} \left(\frac{2k_B T}{m}\right)^{\frac{n}{2}} \Gamma\left(\frac{n+3}{2}\right).\end{aligned}$$

2.2 习题 2.12

直接利用书上例 1 的结果,

$$\begin{aligned}F &= -Nk_B T \ln Z = -Nk_B T \left(\ln V_1 + \frac{3}{2} \ln(2\pi m k_B T) \right), \\S_{\text{混前总}} &= Nk_B [\ln V_1 V_2 + 3 \ln(2\pi m k_B T) + 3] + 2S_0 \\&= 2Nk_B [\ln \sqrt{V_1 V_2} + \frac{3}{2} \ln(2\pi m k_B T) + \frac{3}{2}] + 2S_0, \\S_{\text{混后总}} &= 2Nk_B [\ln(V_1 + V_2) + \frac{3}{2} \ln(2\pi m k_B T) + \frac{3}{2}] + 2S_0, \\ \Delta S &= S_{\text{混后总}} - S_{\text{混前总}} \\&= 2Nk_B \ln \left(\frac{V_1 + V_2}{\sqrt{V_1 V_2}} \right) \\&= 2Nk_B \ln \left(\frac{p_1 + p_2}{\sqrt{p_1 p_2}} \right) \quad \text{利用理想气体的状态方程.}\end{aligned}$$

2.3 习题 2.15

利用书上式子 2.5.16 及 2.5.22:

$$\begin{cases} \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T = \frac{R}{v-b} \\ T\left(\frac{\partial p}{\partial T}\right)_v - p = \left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2} \end{cases} \Rightarrow \left(p + \frac{a}{v^2}\right)(v-b) = RT.$$

2.4 习题 2.16

a,b)

$$\begin{aligned}dU &= TdS - pdV = T\left(\frac{\partial S}{\partial p}\right)_V dp + \left[T\left(\frac{\partial S}{\partial V}\right)_p - p\right]dV \\&\Rightarrow \begin{cases} \left(\frac{\partial U}{\partial p}\right)_V = T\left(\frac{\partial S}{\partial p}\right)_V = -T\left(\frac{\partial V}{\partial T}\right)_S; \\ \left(\frac{\partial U}{\partial V}\right)_p = T\left(\frac{\partial S}{\partial V}\right)_p - p = T\left(\frac{\partial p}{\partial T}\right)_S - p. \end{cases}\end{aligned}$$

c)

$$\begin{aligned}
dU &= TdS - pdV = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]dV \\
&\Rightarrow T\left(\frac{\partial S}{\partial V}\right)_T - p = \left(\frac{\partial U}{\partial V}\right)_T = \frac{-1}{\left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V} \quad \text{and} \quad \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \\
&\Rightarrow \left(\frac{\partial T}{\partial V}\right)_U = p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial T}{\partial U}\right)_V \\
&= p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial S}{\partial V}\right)_T \frac{1}{T} \left(\frac{\partial T}{\partial S}\right)_V \\
&= p\left(\frac{\partial T}{\partial U}\right)_V + \left(\frac{\partial T}{\partial V}\right)_S \\
&= p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial p}{\partial U}\right)_V \quad \text{利用 a) 结论.}
\end{aligned}$$

d)

$$\begin{aligned}
dH &= TdS + Vdp = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp \\
&\Rightarrow T\left(\frac{\partial S}{\partial p}\right)_T + V = \left(\frac{\partial H}{\partial p}\right)_T \quad \text{and} \quad \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p \\
&\text{与 c) 类似的程序} \Rightarrow \left(\frac{\partial T}{\partial p}\right)_H = \left(\frac{\partial T}{\partial p}\right)_S - V\left(\frac{\partial T}{\partial H}\right)_p; \\
dH &= TdS + Vdp = T\left(\frac{\partial S}{\partial V}\right)_p dV + \left[T\left(\frac{\partial S}{\partial p}\right)_V + V\right]dp \\
&\Rightarrow \left(\frac{\partial H}{\partial V}\right)_p = T\left(\frac{\partial S}{\partial V}\right)_p = T\left(\frac{\partial p}{\partial T}\right)_S; \\
&\text{综上} \Rightarrow \left(\frac{\partial T}{\partial p}\right)_H = T\left(\frac{\partial V}{\partial H}\right)_p - V\left(\frac{\partial T}{\partial H}\right)_p.
\end{aligned}$$

e)

$$\begin{aligned}
dH &= TdS + Vdp = V\left(\frac{\partial p}{\partial T}\right)_S dT + \left[V\left(\frac{\partial p}{\partial S}\right)_T + T\right]dS \\
&\Rightarrow V\left(\frac{\partial p}{\partial S}\right)_T + T = \left(\frac{\partial H}{\partial S}\right)_T \quad \text{and} \quad \left(\frac{\partial H}{\partial T}\right)_S = V\left(\frac{\partial p}{\partial T}\right)_S \\
&\Rightarrow \left(\frac{\partial T}{\partial S}\right)_H = -\frac{\left(\frac{\partial H}{\partial S}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_S} \\
&= -\frac{T}{V}\left(\frac{\partial T}{\partial p}\right)_S - \frac{\left(\frac{\partial p}{\partial S}\right)_T}{\left(\frac{\partial p}{\partial T}\right)_S} \\
&= -\frac{T}{V}\left(\frac{\partial T}{\partial p}\right)_S + \frac{T}{T\left(\frac{\partial S}{\partial T}\right)_p} \\
&= -\frac{T^2}{V}\left(\frac{\partial V}{\partial H}\right)_p + \frac{T}{C_p} \quad \text{利用了 d) 第 5 行.}
\end{aligned}$$

2.5 习题 2.17

a)

$$\begin{aligned} dU &= TdS - pdV = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV \\ &= C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV; \\ dH &= TdS + Vdp = T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right] dp \\ &= C_p dT + \left[-T\left(\frac{\partial V}{\partial T}\right)_p + V\right] dp. \end{aligned}$$

由全微分条件

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \left(\frac{\partial \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]}{\partial T}\right)_V = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V; \\ \left(\frac{\partial C_p}{\partial p}\right)_T &= \left(\frac{\partial \left[-T\left(\frac{\partial V}{\partial T}\right)_p + V\right]}{\partial T}\right)_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p. \end{aligned}$$

对于理想气体而言:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial C_p}{\partial p}\right)_T = 0,$$

因此, 其 C_V, C_p 均仅为温度的函数. 对于范氏气体而言:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0,$$

因此, 其 C_V 仅为温度的函数.

b) 由前半小题, 我们有

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V = \int \frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T dT; \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p = \int \frac{1}{T} \left(\frac{\partial C_p}{\partial p}\right)_T dT. \end{aligned}$$

易得,

$$\begin{aligned} S &= \int_V dV \int_T \frac{1}{T} \left(\frac{\partial C_V}{\partial V}\right)_T dT = \int_T \frac{1}{T} dT \int_V dV \left(\frac{\partial C_V}{\partial V}\right)_T = \int_T \frac{C_{V_0}}{T} dT; \\ S &= \int_p dp \int_T \frac{1}{T} \left(\frac{\partial C_p}{\partial p}\right)_T dT = \int_T \frac{1}{T} dT \int_p dp \left(\frac{\partial C_p}{\partial p}\right)_T = \int_T \frac{C_{p_0}}{T} dT \end{aligned}$$

因此,

$$\begin{aligned} F &= - \int p dV - \int S dT = - \int p dV - \int dT \int \frac{C_{V_0}}{T} dT; \\ G &= \int V dp - \int S dT = \int V dp - \int dT \int \frac{C_{p_0}}{T} dT. \end{aligned}$$

2.6 习题 2.19

能量由两部分组成, 分别是平动动能 ϵ^t 与转动动能 ϵ^r . 注意到我们的目标是求状态方程, 因此我们只需要关心配分函数对 V 的依赖,

$$Z = Z^t \cdot Z^r = \int e^{-\beta \frac{p^2}{2m}} dx dy dz dp_x dp_y dp_z \times \int e^{-\frac{\beta}{2I} \left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2 \theta} \right)} d\theta d\varphi dp_\theta dp_\varphi = V \times g(\text{不涉及 } V).$$

因此, 状态方程为:

$$p = \frac{N}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{N}{\beta V},$$

即为理想气体的状态方程.

3 第三章

3.1 习题 3.1

先计算体系的配分函数

$$P = Z^N = V^N \left[\frac{2\pi m}{\beta} \right]^{\frac{3N}{2}},$$

a) 由此可得体系的平均能量

$$\bar{E} = -\frac{\partial \ln P}{\partial \beta} = \frac{3}{2} N k_B T;$$

b) 求最概然能量 E_p 需写出能量的概率分布

$$f(E) dE = e^{-\Psi - \beta E} d\Omega(E) = e^{-\Psi - \beta E} \Omega'(E) dE \propto e^{-\beta E} E^{\frac{3N}{2}-1} dE \Rightarrow f(E) \propto e^{-\beta E} E^{\frac{3N}{2}-1},$$

因此

$$\left. \frac{\partial f(E)}{\partial E} \right|_{E=E_p} = 0 \Rightarrow E_p = \left(\frac{3}{2} N - 1 \right) k_B T.$$

3.2 习题 3.3

考虑到每个自旋有两种状态, 记为: $+1, -1$, 且分别对应了两个能量的取值: $-\mu H, +\mu H$. 体系的所有自旋的状态的选取确定了体系的一个构型 (configuration), 例: $\{s_i\} = \{+1, -1, -1, -1, +1, \dots\}$, 表示体系第 1 个自旋处于 $+1$ 的状态, 第 2 个自旋处于 -1 的状态, 等等. 为了求体系的配分函数, 我们需要对体系的所有构型求和

$$\begin{aligned} P &= \sum_{\{s_i\}} e^{-\beta \sum_{i=1}^N (-1)^{(s_i+1)/2} \mu H} = \sum_{\{s_i\}} \prod_{i=1}^N e^{-\beta (-1)^{(s_i+1)/2} \mu H} \\ &= \prod_{i=1}^N \sum_{s_i=\pm 1} e^{-\beta (-1)^{(s_i+1)/2} \mu H} = \prod_{i=1}^N (e^{-\beta \mu H} + e^{\beta \mu H}) \\ &= (2 \cosh(\beta \mu H))^N, \end{aligned}$$

因此可得体系的内能, 熵, 热容和总磁矩分别为

$$\begin{cases} U = -\frac{\partial}{\partial \beta} \ln P = -N \mu H \tanh(\beta \mu H); \\ S = S_0 + k_B (\ln P - \beta \frac{\partial}{\partial \beta} \ln P) = S_0 + N k_B (\ln(2 \cosh \beta \mu H) - \beta \mu H \tanh \beta \mu H); \\ C_H = \left(\frac{\partial U}{\partial T} \right)_H = -k_B \beta^2 \left(\frac{\partial U}{\partial \beta} \right)_H = N k_B \frac{(\beta \mu H)^2}{\cosh^2(\beta \mu H)}; \\ M = \frac{1}{\beta} \frac{\partial \ln P}{\partial H} = N \mu \tanh(\beta \mu H). \end{cases}$$

3.3 习题 3.7

先求体系的配分函数

$$P = V^N \left[4\pi \int_0^{+\infty} e^{-\beta c p} p^2 dp \right]^N = \left[\frac{8\pi V}{(c\beta)^3} \right]^N,$$

由此可得体系的状态方程与内能

$$\begin{cases} p = \frac{1}{\beta} \frac{\partial \ln P}{\partial V} = \frac{N}{\beta V} \Rightarrow pV = N k_B T; \\ U = -\frac{\partial \ln P}{\partial \beta} = 3 N k_B T. \end{cases}$$

3.4 习题 3.11

由能均分定理

$$\overline{\frac{1}{2}mv_i^2} = \frac{1}{2}k_B T \Rightarrow \overline{v_i^2} = \frac{k_B T}{m},$$

a)

$$\overline{v_x^3} \propto \int_{-\infty}^{+\infty} e^{-\beta mv_x^2/2} v_x^3 dv_x = 0;$$

b)

$$\overline{v_x^3 v_y} \propto \int_{-\infty}^{+\infty} e^{-\beta mv_x^2/2} v_x^3 dv_x \times \int_{-\infty}^{+\infty} e^{-\beta mv_y^2/2} v_y dv_y = 0;$$

c)

$$\overline{v_x^2 v_y^2} = \overline{v_x^2} \times \overline{v_y^2} = \left(\frac{k_B T}{m}\right)^2;$$

d)

$$\overline{(v_x + av_y)^2} = \overline{v_x^2 + 2av_x v_y + a^2 v_y^2} = \overline{v_x^2} + 0 + a^2 \overline{v_y^2} = (a^2 + 1) \frac{k_B T}{m};$$

e)

$$\overline{v^2 v_x} = \overline{v_x^3} + \overline{v_y^2 v_x} + \overline{v_z^2 v_x} = 0.$$

3.5 习题 3.12

a)

$$\text{由能均分定理} \Rightarrow \bar{\epsilon} = \frac{5}{2} k_B T;$$

b)

$$\overline{\frac{1}{2}m(v_y - v_0)^2} = \overline{\frac{1}{2}mv_y^2 + \frac{1}{2}mv_0^2 - mv_y v_0} = \frac{1}{2}mv_y^2 - \frac{1}{2}mv_0^2 = \frac{1}{2}k_B T,$$

因此, 我们有

$$\overline{\frac{1}{2}mv_y^2} = \frac{1}{2}k_B T + \frac{1}{2}mv_0^2.$$

3.6 习题 3.15

a)

$$\begin{aligned} \left\langle \frac{\Omega(E)}{\Omega'(E)} \right\rangle_{\text{c.e.}} &= \int_{\Omega} e^{-\Psi - \beta E} \frac{\Omega(E)}{\Omega'(E)} d\Omega(E) \\ &= \int_0^{+\infty} e^{-\Psi - \beta E} \Omega(E) dE \\ &= -\frac{1}{\beta} \int e^{-\Psi} \Omega(E) d e^{-\beta E} \\ &= -\frac{1}{\beta} e^{-\Psi - \beta E} \Omega(E) \Big|_{E=0}^{E=+\infty} + \frac{1}{\beta} \int_{\Omega} e^{-\Psi - \beta E} d\Omega(E) \\ &= \frac{1}{\beta}; \end{aligned}$$

b) 由能量的概率分布

$$f(E)dE = e^{-\Psi-\beta E}d\Omega(E) = e^{-\Psi-\beta E}\Omega'(E)dE \Rightarrow f(E) = e^{-\Psi-\beta E}\Omega'(E),$$

我们有

$$\left. \frac{\partial f(E)}{\partial E} \right|_{E=E_p} = 0 \Rightarrow \frac{\Omega''(E_p)}{\Omega'(E_p)} = \beta.$$

3.7 补充 S1

先求体系的配分函数

$$P = Z^N = V^N \left[\frac{2\pi m}{\beta} \right]^{\frac{3N}{2}},$$

由此得到系统的状态方程, 内能, 熵和热容量为

$$\begin{cases} p = \frac{1}{\beta} \frac{\partial \ln P}{\partial V} \Rightarrow pV = Nk_B T; \\ U = -\frac{\partial \ln P}{\partial \beta} = \frac{3}{2} Nk_B T; \\ S = S_0 + Nk_B \left[\ln V + \frac{3}{2} \ln(2\pi m k_B T) + \frac{3}{2} \right]; \\ C_v = \frac{\partial U}{\partial T} = \frac{3}{2} Nk_B. \end{cases}$$

最后, 我们来算体系的能量涨落:

$$\begin{aligned} \bar{E}^2 &= \int E^2 e^{-\Psi-\beta E} d\Omega = e^{-\Psi} \frac{\partial^2 e^{\Psi}}{\partial \beta^2} = \frac{\partial^2 \Psi}{\partial \beta^2} + \left(\frac{\partial \Psi}{\partial \beta} \right)^2 \\ &\Downarrow \\ (E - \bar{E})^2 &= \bar{E}^2 - \bar{E}^2 = \frac{\partial^2 \Psi}{\partial \beta^2} = \frac{3}{2} Nk_B^2 T^2. \end{aligned}$$

3.8 补充 S2

先求体系的配分函数

$$Z_{g.c.} = e^{\zeta} = \sum_N \frac{e^{-N\alpha}}{N!} \int e^{-\beta E} d\Omega = \sum_N \frac{(e^{-\alpha})^N}{N!} V^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} = \exp \left[e^{-\alpha} V \left(\frac{2\pi m}{\beta} \right)^{3/2} \right],$$

因此

$$\zeta = e^{-\alpha} V \left(\frac{2\pi m}{\beta} \right)^{3/2}.$$

由此我们能得到体系的状态方程, 内能, 熵, 化学势和分子数的相对涨落

$$\begin{cases} \bar{N} = -\frac{\partial \zeta}{\partial \alpha} = \zeta; \\ p = \frac{1}{\beta} \frac{\partial \zeta}{\partial V} = \frac{\zeta}{\beta V} \Rightarrow pV = \bar{N}k_B T; \\ U = -\frac{\partial \zeta}{\partial \beta} = \frac{3}{2} \bar{N}k_B T; \\ S = S_0 + k_B \left(\zeta - \beta \frac{\partial \zeta}{\partial \beta} - \alpha \frac{\partial \zeta}{\partial \alpha} \right) = S_0 + \left(\frac{5}{2} + \alpha \right) \bar{N}k_B; \\ \mu = -\alpha k_B T; \\ \overline{N^2} = \sum_N \frac{e^{-\zeta-N\alpha} N^2}{N!} \int \dots = e^{-\zeta} \frac{\partial^2 \zeta}{\partial \alpha^2} Z_{g.c.} = e^{-\zeta} \frac{\partial^2}{\partial \alpha^2} e^{\zeta} = \zeta + \zeta^2; \\ (\Delta N)^2 / \bar{N}^2 = \frac{\overline{N^2} - \bar{N}^2}{\bar{N}^2} = \frac{1}{\zeta} = \frac{1}{\bar{N}}. \end{cases}$$

4 第四章

4.1 习题 4.4

a) 由书 P216 的 (4.14.3): $p_F \propto n^{1/3}$, 可知三个铜块的费米球半径相同.

b)

$$\begin{aligned}\bar{\epsilon} &= \frac{3}{5}\mu_0; \\ \overline{\epsilon^2} &= \frac{8\pi V}{h^3 N} \int_{|p| \leq \sqrt{2m\mu_0}} \epsilon^2 p^2 dp = \frac{8\pi V}{h^3 N} \sqrt{2} m^{3/2} \int_0^{\mu_0} \epsilon^{5/2} d\epsilon = \frac{8\pi V}{h^3 N} \sqrt{2} m^{3/2} \frac{2}{7} \mu_0^{7/2} = \frac{3}{7} \mu_0^2; \\ &\Downarrow \\ \overline{(\epsilon - \bar{\epsilon})^2} &= \overline{\epsilon^2} - \bar{\epsilon}^2 = \frac{12}{175} \mu_0^2.\end{aligned}$$

4.2 习题 4.14

$$f(v)dv = \frac{4\pi gV}{h^3} \frac{p^2 dp}{e^{(\epsilon - \mu)/k_B T} - 1} = \frac{4\pi g m^3 V}{h^3} \frac{v^2 dv}{\exp[(mv^2/2 - \mu)/k_B T] - 1};$$

$$\text{易得最概然速率 } v_p \text{ 满足的方程} \quad \left. \frac{d}{dv} \left(\frac{v^2}{\exp[(mv^2/2 - \mu)/k_B T] - 1} \right) \right|_{v=v_p} = 0;$$

$$\Rightarrow \quad v_p^2 = \frac{2k_B T}{m} \frac{\exp[(mv_p^2/2 - \mu)/k_B T] - 1}{\exp[(mv_p^2/2 - \mu)/k_B T]};$$

在 $T > T_c$ 时, 有 $\exp[(mv_p^2/2 - \mu)/k_B T] \gg 1$

$$\Rightarrow \quad v_p = \sqrt{\frac{2k_B T}{m}}.$$

4.3 习题 4.17

考虑到膨胀前后的粒子数不变, $N_1 = N_2 = N$

$$\begin{aligned}N_1 &= \frac{8\pi V_1}{3h^3} (2m)^{3/2} \mu_0^{3/2}; \\ N_2 &= \frac{8\pi V_2}{3h^3} (2m)^{3/2} \mu^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right], \\ &\Rightarrow \quad \mu^{3/2} \approx \frac{V_1}{V_2} \mu_0^{3/2} \left[1 - \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 \right], \\ &\Rightarrow \quad \mu^{5/2} \approx \left(\frac{V_1}{V_2} \right)^{5/3} \mu_0^{5/2} \left[1 - \frac{5\pi^2}{24} \left(\frac{k_B T}{\mu} \right)^2 \right]\end{aligned}$$

显然, 膨胀前后内能也不发生改变, $E_1 = E_2 = E$

$$\begin{aligned}
E_1 &= \frac{8\pi V_1}{h^3} \sqrt{2} m^{3/2} \frac{2}{5} \mu_0^{5/2}; \\
E_2 &= \frac{8\pi V_2}{h^3} \sqrt{2} m^{3/2} \frac{2}{5} \mu^{5/2} \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \\
&\approx \frac{8\pi V_2}{h^3} \sqrt{2} m^{3/2} \frac{2}{5} \left(\frac{V_1}{V_2} \right)^{5/3} \mu_0^{5/2} \left[1 - \frac{5\pi^2}{24} \left(\frac{k_B T}{\mu} \right)^2 \right] \left[1 + \frac{5\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \\
&\approx \frac{8\pi V_2}{h^3} \sqrt{2} m^{3/2} \frac{2}{5} \left(\frac{V_1}{V_2} \right)^{5/3} \mu_0^{5/2} \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\mu} \right)^2 \right], \\
&\Rightarrow V_1 \mu_0^{5/2} = V_2 \left(\frac{V_1}{V_2} \right)^{5/3} \mu^{5/2} \left[1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\mu} \right)^2 \right], \\
&\Rightarrow \frac{k_B T}{\mu} = \sqrt{\frac{12}{5\pi^2} \left[\left(\frac{V_2}{V_1} \right)^{2/3} - 1 \right]}.
\end{aligned}$$

最后再利用一下 μ 粗的近似

$$\begin{aligned}
\mu &\approx \left(\frac{3}{8\pi} \right)^{2/3} \frac{h^2}{2m} \left(\frac{N}{V_2} \right)^{2/3}, \\
\Rightarrow T &= \left(\frac{3}{8\pi} \right)^{2/3} \frac{h^2}{2mk_B} \left(\frac{N}{V_2} \right)^{2/3} \sqrt{\frac{12}{5\pi^2} \left[\left(\frac{V_2}{V_1} \right)^{2/3} - 1 \right]}.
\end{aligned}$$

4.4 习题 4.19

利用可逆绝热条件及黑体辐射的相关结论

$$\begin{aligned}
0 &= TdS = dU + pdV; \\
p &= \frac{1}{3}u = \frac{1}{3}aT^4; \\
U &= uV = aT^4V,
\end{aligned}$$

将 p 与 U 代入热一公式后整理得到

$$d(3 \log T + \log V) = 0 \quad \Rightarrow \quad VT^3 = \text{const} \quad \Rightarrow \quad T_f = 500\text{K}.$$

4.5 习题 4.20

由苏书 (4.14.9) 及 (4.14.4)

$$\begin{aligned}
\left(\frac{\partial p}{\partial V} \right)_{T=0} &= -\frac{h^2}{3mV} \left(\frac{3}{8\pi} \right)^{2/3} \left(\frac{N}{V} \right)^{5/3} = -\frac{2}{3V} \epsilon_F n, \\
\Rightarrow \kappa|_{T=0} &= -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T=0} = \frac{3}{2} \frac{1}{n \epsilon_F}.
\end{aligned}$$

4.6 习题 4.25

a) $\phi_{\vec{p}} \propto \exp(i\vec{p} \cdot \vec{r}/\hbar)$ 由边界条件 $\Rightarrow p_{\alpha} L = 2\pi\hbar n_{\alpha} \quad (\alpha = x, y, z)$

$$\Rightarrow \epsilon = c|\vec{p}| = \frac{2\pi c\hbar}{V^{1/3}} \sqrt{n_x^2 + n_y^2 + n_z^2}.$$

b) $p = \frac{U}{3V}, p_s = \frac{U}{3NV}$, U 用玻色-爱因斯坦分布算出后再代入...

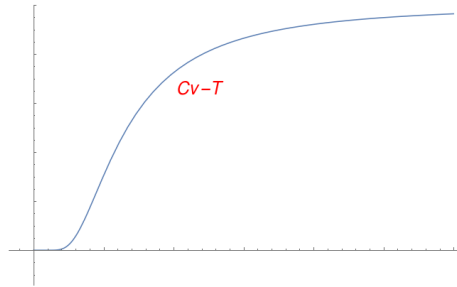
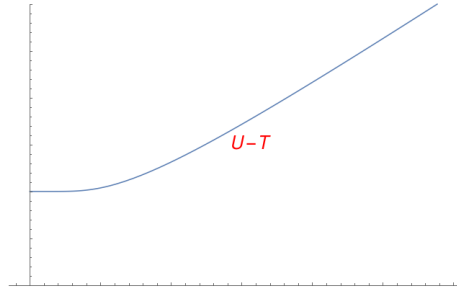
4.7 习题 4.26

a) 由各向同性, $\bar{v}_x = 0$.

b) $\overline{v_x^2} = \frac{1}{3} \overline{v^2} = \frac{1}{3} \frac{2}{m} \bar{\epsilon} = \frac{2}{3m} \frac{3}{5} \mu_0 = \frac{2\epsilon_F}{5m}$.

4.8 习题 4.30

$$\begin{aligned} \mathcal{Z} &= \sum_{n=0}^{+\infty} e^{-\beta(n+1/2)\gamma V^{-1}} = \frac{\exp(-\beta\gamma/(2V))}{1 - \exp(-\beta\gamma/V)}; \\ \Rightarrow \log \mathcal{Z} &= -\frac{1}{2}\beta\gamma V^{-1} - \log(1 - e^{-\beta\gamma V^{-1}}); \\ \Rightarrow U &= -N \frac{\partial \log \mathcal{Z}}{\partial \beta} = \frac{N\gamma}{2V} \frac{1 + e^{-\beta\gamma V^{-1}}}{1 - e^{-\beta\gamma V^{-1}}} = \frac{N\gamma}{2V} \coth(\beta\gamma/(2V)); \\ \Rightarrow C_V &= \left(\frac{\partial U}{\partial T} \right)_V = -\frac{1}{k_B T^2} \left(\frac{\partial U}{\partial \beta} \right)_V = \frac{N\gamma^2}{4k_B T^2 V^2 \sinh^2(\beta\gamma/(2V))}; \\ \Rightarrow p &= \frac{N}{\beta} \frac{\partial \log \mathcal{Z}}{\partial V} = \frac{N\gamma}{2V^2} \coth(\beta\gamma/(2V)); \\ \Rightarrow \bar{N}_n &= N \frac{e^{-\beta(n+1/2)\gamma V^{-1}}}{\sum_{n'=0}^{+\infty} e^{-\beta(n'+1/2)\gamma V^{-1}}} = N e^{-n\beta\gamma V^{-1}} (1 - e^{-\beta\gamma V^{-1}}) = 2N e^{-(n+1/2)\beta\gamma V^{-1}} \sinh(\beta\gamma/(2V)). \end{aligned}$$



5 第五章

5.1 习题 5.3

$$\begin{aligned}\frac{dp}{dT} = \frac{L}{T\Delta v} \quad \Rightarrow \quad \frac{d^2p}{dT^2} &= \frac{dL}{dT} \frac{1}{T\Delta v} - \frac{L}{(T\Delta v)^2} \frac{d(T\Delta v)}{dT} \\ &= \left[\left(\frac{\partial L}{\partial T} \right)_p + \left(\frac{\partial L}{\partial p} \right)_T \frac{dp}{dT} \right] \frac{1}{T\Delta v} - \frac{L}{(T\Delta v)^2} \left[\Delta v + T \left\{ \left(\frac{\partial \Delta v}{\partial T} \right)_p + \left(\frac{\partial \Delta v}{\partial p} \right)_T \frac{dp}{dT} \right\} \right]\end{aligned}$$

利用

$$L = T\Delta s \quad \Rightarrow \quad \left(\frac{\partial L}{\partial T} \right)_p = \Delta s + \Delta c_p \quad \text{and} \quad \left(\frac{\partial L}{\partial p} \right)_T = T \left(\frac{\partial \Delta s}{\partial p} \right)_T = -T \left(\frac{\partial \Delta v}{\partial T} \right)_p \quad \text{maxwell rel.},$$

以及近似条件

- a) 气相体积大于液相 $\Delta v \approx v_2$;
- b) 气相定压膨胀 (等温压缩) 比液相大 $(\partial \Delta v / \partial T)_p \approx (\partial v_2 / \partial T)_p$ and $(\partial \Delta v / \partial p)_T \approx (\partial v_2 / \partial p)_T$;
- c) 气相近似为理想气体.

由此得

$$\begin{aligned}\frac{d^2p}{dT^2} &= \left[\Delta s + \Delta c_p - T \left(\frac{\partial \Delta v}{\partial T} \right)_p \frac{L}{T\Delta v} \right] \frac{1}{T\Delta v} - \frac{L}{(T\Delta v)^2} \left[\Delta v + T \left(\frac{\partial \Delta v}{\partial T} \right)_p + T \left(\frac{\partial \Delta v}{\partial p} \right)_T \frac{L}{T\Delta v} \right] \\ &\approx \left[\Delta s + \Delta c_p - T \left(\frac{\partial v_2}{\partial T} \right)_p \frac{L}{Tv_2} \right] \frac{1}{Tv_2} - \frac{L}{(Tv_2)^2} \left[v_2 + T \left(\frac{\partial v_2}{\partial T} \right)_p + T \left(\frac{\partial v_2}{\partial p} \right)_T \frac{L}{Tv_2} \right] \\ &\approx \left[\Delta s + \Delta c_p - \frac{L}{T} \right] \frac{1}{Tv_2} - \frac{L}{(Tv_2)^2} \left[v_2 + v_2 - \frac{L}{p} \right] \\ &= \frac{\Delta c_p}{Tv_2} - \frac{2L}{T^2v_2} + \frac{L^2}{T^2v_2^2p} \\ &\approx \frac{\Delta c_p}{Tv_2} - \frac{2L}{T^2v_2} + \frac{L^2}{RT^3v_2}.\end{aligned}$$

最后, 代入具体的数值计算.

5.2 习题 5.8

$$\begin{aligned}pv = RT \quad \Rightarrow \quad p dv + v dp &= R dT \quad \Rightarrow \quad p \frac{dv}{dT} + v \frac{dp}{dT} = R \\ \Rightarrow \quad \frac{RT}{v} \frac{dv}{dT} + v \frac{L}{Tv} &= R \quad \Rightarrow \quad d(\ln v) = \frac{dT}{T} - \frac{L dT}{RT^2} \\ \Rightarrow \quad v &= v_0 T e^{L/RT}.\end{aligned}$$

5.3 习题 5.9

$$\begin{aligned}
\frac{dL}{dT} &= c_{p2} - c_{p1} + \frac{L}{T} - \left(\frac{\partial \Delta v}{\partial T} \right)_p \frac{L}{\Delta v} \approx c_{p2} - c_{p1} + \frac{L}{T} - \left(\frac{\partial v_2}{\partial T} \right)_p \frac{L}{v_2} \\
&= c_{p2} - c_{p1} + \frac{L}{T} - \frac{L}{v_2} \left[\frac{v_2}{T} + \frac{RT}{p} \left(\frac{dB}{dT} p + \frac{dC}{dT} p^2 + \dots \right) \right] \quad \text{用了物态方程} \\
&\approx c_{p2} - c_{p1} - T v_2 \frac{dp}{dT} \frac{RT}{p v_2} \left(\frac{dB}{dT} p + \frac{dC}{dT} p^2 + \dots \right) \\
&= c_{p2} - c_{p1} - RT^2 \left(\frac{dB}{dT} \frac{dp}{dT} + \frac{1}{2} \frac{dC}{dT} \frac{dp^2}{dT} + \dots \right) \\
\Rightarrow L &= L_0 + \int_0^T (c_p^0 - c_p^l) dT - RT^2 \left(\frac{dB}{dT} p + \frac{1}{2} \frac{dC}{dT} p^2 + \dots \right).
\end{aligned}$$

5.4 习题 5.13

定义跃迁矩阵 [见苏书 (5.6.6)]

$$\mathcal{T} = \begin{pmatrix} e^{\beta(\epsilon+H)} & e^{-\beta\epsilon} \\ e^{-\beta\epsilon} & e^{\beta(\epsilon-H)} \end{pmatrix},$$

记其本征值为 $\lambda_+ > \lambda_-$, 对应的本征态分别为 $|+\rangle, |-\rangle$, 即 $\mathcal{T} = \lambda_+ |+\rangle\langle+| + \lambda_- |-\rangle\langle-|$.

由系综平均的定义式 (考虑周期边界条件, \mathcal{P} 是配分函数)

$$\begin{aligned}
\mathcal{P}\langle S_i S_{i+j} \rangle_{\text{Ising}} &= \sum_{S_1} \dots \sum_{S_N} \langle S_1 | \mathcal{T} | S_2 \rangle \dots \langle S_{i-1} | \mathcal{T} | S_i \rangle S_i \langle S_i | \mathcal{T} | S_{i+1} \rangle \dots \langle S_{i+j-1} | \mathcal{T} | S_{i+j} \rangle S_{i+j} \langle S_{i+j} | \mathcal{T} | S_{i+j+1} \rangle \dots \langle S_N | \mathcal{T} | S_1 \rangle \\
&= \sum_{S_i} \sum_{S_{i+j}} S_{i+j} \langle S_{i+j} | \mathcal{T}^{N-j} | S_i \rangle S_i \langle S_i | \mathcal{T}^j | S_{i+j} \rangle \\
&= \text{Tr} [\sigma_z \mathcal{T}^{N-j} \sigma_z \mathcal{T}^j] \\
&= \text{Tr} \left[\sigma_z \left(\lambda_+^{N-j} |+\rangle\langle+| + \lambda_-^{N-j} |-\rangle\langle-| \right) \sigma_z \left(\lambda_+^j |+\rangle\langle+| + \lambda_-^j |-\rangle\langle-| \right) \right] \\
&= \lambda_+^N |\langle+|\sigma_z|+\rangle|^2 + \lambda_+^{N-j} \lambda_-^j |\langle+|\sigma_z|-\rangle|^2 + \lambda_+^j \lambda_-^{N-j} |\langle-|\sigma_z|+\rangle|^2 + \lambda_-^N |\langle-|\sigma_z|-\rangle|^2 \\
\Rightarrow \langle S_i S_{i+j} \rangle_{\text{Ising}} &= |\langle+|\sigma_z|+\rangle|^2 + \left(\frac{\lambda_-}{\lambda_+} \right)^j |\langle+|\sigma_z|-\rangle|^2 \quad \text{考虑热力学极限 } N \rightarrow \infty.
\end{aligned}$$

当 $H = 0$ 时, 我们有

$$\lambda_+ = 2 \cosh(\beta\epsilon) \quad |+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \lambda_- = 2 \sinh(\beta\epsilon) \quad |-\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix},$$

因此

$$\lim_{N \rightarrow \infty} \langle S_i S_{i+j} \rangle_{\text{Ising}} = [\tanh(\beta\epsilon)]^j.$$

5.5 习题 5.14

$$\begin{aligned}
\left(\frac{\partial p}{\partial V} \right)_T &= -\frac{RT}{(V-b)^2} e^{-a/RTV} + \frac{RT}{V-b} e^{-a/RTV} \frac{a}{RTV^2} = -\frac{p}{V-b} + \frac{ap}{RTV^2} \Rightarrow \left. \frac{a(V-b)}{RTV^2} \right|_c = 1 \\
\left(\frac{\partial^2 p}{\partial V^2} \right)_T &= -\left(\frac{\partial p}{\partial V} \right)_T \frac{1}{V-b} + \frac{p}{(V-b)^2} + \left(\frac{\partial p}{\partial V} \right)_T \frac{a}{RTV^2} - \frac{2ap}{RTV^3} \Rightarrow \left. \frac{2a(V-b)^2}{RTV^3} \right|_c = 1.
\end{aligned}$$

因此

$$\left. \frac{pV}{RT} \right|_c = \frac{2p(V-b)}{RT} \frac{RTV^3}{2a(V-b)^2} \frac{a(V-b)}{RTV^2} \Big|_c = 2e^{-a/RTV} = 2e^{-2} \approx 0.27.$$