热统习题的部分答案 (野生版)

2023 年 2 月 7 日

目录

1 第一章

1.1 习题 1.6

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

1.2 习题 1.8

1) 利用广延量假设,

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

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

2) 对于每个热源而言, 我们有:

$$
\text{đ}Q = \mathrm{d}U \sim T^{1/2}\mathrm{d}T,
$$

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 $T_1 > T_2$,

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

另一方面, 由热力学第二定律: $\Delta S \ge 0$,

$$
\begin{aligned}
\Delta S = \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f}\right)\frac{\text{đ}Q}{T} \sim & \left(\int_{T_1}^{T_f} + \int_{T_2}^{T_f}\right)\frac{1}{T^{1/2}}\mathrm{d}T \ge 0 \\
& \Rightarrow \quad T_f \ge \left(\frac{T_1^{1/2} + T_2^{1/2}}{2}\right)^2.
\end{aligned}
$$

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,

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

1.3 习题 1.11

首先，我们需要求出范氏气体的内能表达式,

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

1) 对于等温过程,

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

2) 对于等压过程,

$$
W = p_i(V_f - V_i) = \left(\frac{RT_i}{V_i - b} - \frac{a}{V_i^2}\right)(V_f - V_i)
$$

$$
\begin{aligned}
\text{利用状态方程} \quad &\Rightarrow \quad T_f = \left(p_i + \frac{a}{V_f^2}\right)(V_f - b)/R = \left(\frac{RT_i}{V_i - b} - \frac{a}{V_i^2} + \frac{a}{V_f^2}\right)(V_f - b)/R \\
&\Rightarrow \quad \Delta U = C_V(T_f - T_i) - \frac{a}{V_f} + \frac{a}{V_i} = C_V\left[\left(\frac{RT_i}{V_i - b} - \frac{a}{V_i^2} + \frac{a}{V_f^2}\right)(V_f - b)/R - T_i\right] - \frac{a}{V_f} + \frac{a}{V_i}
\end{aligned}
$$

$$
\begin{aligned}
\text{由等压条件} \quad &\Rightarrow \quad T\mathrm{d}S = \text{đ}Q = C_p\mathrm{d}T \\
&\Rightarrow \quad \mathrm{d}S = C_p \mathrm{d}(\ln T) \\
&\Rightarrow \quad \Delta S = C_p \ln\frac{T_f}{T_i} = C_p \ln\left[\frac{V_f - b}{V_i - b} - a\left(\frac{1}{V_i^2} - \frac{1}{V_f^2}\right)\frac{V_f - b}{RT_i}\right]\,;
\end{aligned}
$$

3) 对于绝热过程,

$$
\text{đ}Q = \mathrm{d}U + p\mathrm{d}V = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\mathrm{d}V = C_V\mathrm{d}T + \left(\frac{a}{V^2} + p\right)\mathrm{d}V = 0\,,
$$

$$
\begin{aligned}
\text{结合状态方程} \quad &\Rightarrow \quad C_V\mathrm{d}T + \frac{RT}{V-b}\mathrm{d}V = 0 \\
&\Rightarrow \quad C_V \ln T + R\ln(V-b) = 0 \\
&\Rightarrow \quad T^{C_V}(V-b)^R = \mathrm{const} \\
&\Rightarrow \quad T_f = T_i\left(\frac{V_i - b}{V_f - b}\right)^{R/C_V}
\end{aligned}
$$

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

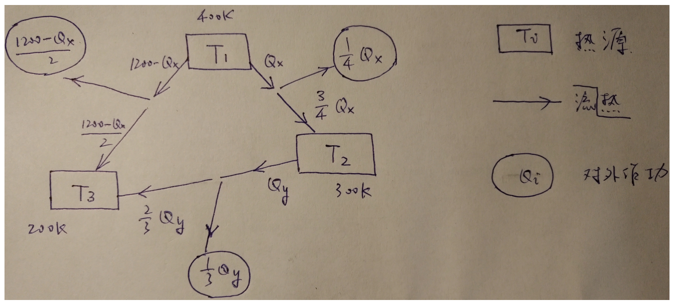
其中一个物体降温 (放热): $T_1 \to T_2$, 另一个物体升温 (吸热): $T_1 \to T_x$. 考虑整个体系, 由热力学第二定律,

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

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:

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

1.6 习题 1.23

考虑等熵过程 ($S = S_0$),

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

现在考虑一个等体过程 ($V, S_0 \to V, S$) ,

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

因此,

$$U(S,V)=\frac{RV_0S_0}{(a+1)V}\left[\left(\frac{S}{S_0}\right)^{a+1}-1\right]-RS_0\ln\frac{V}{V_0}+U_0$$

又由:

$$\left(\frac{\partial p}{\partial S}\right)_V=-\left(\frac{\partial T}{\partial V}\right)_S=\frac{RV_0}{V^2}\left(\frac{S}{S_0}\right)^a$$

$$\Rightarrow\quad p(S,V)=\frac{RV_0S_0}{(a+1)V^2}\left[\left(\frac{S}{S_0}\right)^{a+1}-1\right]+\frac{RS_0}{V}$$

$$W(S,V_0\to V)=\int_{V_0}^{V}p(S,V')\mathrm{d}V'=\frac{RV_0S_0}{a+1}\left[\left(\frac{S}{S_0}\right)^{a+1}-1\right]\left(\frac{1}{V_0}-\frac{1}{V}\right)+RS_0\ln\frac{V}{V_0}\,.$$

2 第二章

2.1 习题 2.2

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

2.2 习题 2.12

直接利用书上例 1 的结果,

$$
\begin{aligned}
F &= -Nk_BT \ln Z = -Nk_BT\big(\ln V_1 + \frac{3}{2}\ln(2\pi m k_BT)\big), \\
S_{\text{混前总}} &= Nk_B[\ln V_1V_2 + 3\ln(2\pi m k_BT) + 3] + 2S_0 \\
&= 2Nk_B[\ln\sqrt{V_1V_2} + \frac{3}{2}\ln(2\pi m k_BT) + \frac{3}{2}] + 2S_0, \\
S_{\text{混后总}} &= 2Nk_B[\ln(V_1+V_2) + \frac{3}{2}\ln(2\pi m k_BT) + \frac{3}{2}] + 2S_0, \\
\Delta S &= S_{\text{混后总}} - S_{\text{混前总}} \\
&= 2Nk_B \ln\left(\frac{V_1+V_2}{\sqrt{V_1V_2}}\right) \\
&= 2Nk_B \ln\left(\frac{p_1+p_2}{\sqrt{p_1p_2}}\right) \quad \text{利用理想气体的状态方程.}
\end{aligned}
$$

2.3 习题 2.15

利用书上式子 2.5.16 及 2.5.22:

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

2.4 习题 2.16

a,b)

$$
\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V = T\left(\frac{\partial S}{\partial p}\right)_V \mathrm{d}p + \left[T\left(\frac{\partial S}{\partial V}\right)_p - p\right]\mathrm{d}V
$$

$$
\Rightarrow \quad
\begin{cases}
\left(\frac{\partial U}{\partial p}\right)_V = T\left(\frac{\partial S}{\partial p}\right)_V = -T\left(\frac{\partial V}{\partial T}\right)_S; \\
\left(\frac{\partial U}{\partial V}\right)_p = T\left(\frac{\partial S}{\partial V}\right)_p - p = T\left(\frac{\partial p}{\partial T}\right)_S - p.
\end{cases}
$$

c)

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

d)

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

e)

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

2.5 习题 2.17

a)

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

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

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

易得,

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

因此,

$$\begin{aligned}F &= -\int p\mathrm{d}V - \int S\mathrm{d}T = -\int p\mathrm{d}V - \int \mathrm{d}T \int \frac{C_{V_0}}{T}\mathrm{d}T\,; \\ G &= \int V\mathrm{d}p - \int S\mathrm{d}T = \int V\mathrm{d}p - \int \mathrm{d}T \int \frac{C_{p_0}}{T}\mathrm{d}T\,.\end{aligned}$$

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,

$$Z = Z^t \cdot Z^r = \int e^{-\beta \frac{p^2}{2m}} \mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \times \int e^{-\frac{\beta}{2I}\left(p_\theta^2 + \frac{p_\varphi^2}{\sin^2\theta}\right)} \mathrm{d}\theta\mathrm{d}\varphi\mathrm{d}p_\theta\mathrm{d}p_\varphi = V \times g(\text{不涉及 } V).$$

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

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

b) 求最概然能量 E_p 需写出能量的概率分布

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

因此

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

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: $\{s_i\} = \{+1,-1,-1,-1,+1,\cdots\}$, 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

$$\begin{aligned}
P &= \sum_{\{s_i\}} e^{-\beta\sum_{i=1}^{N}(-1)^{(s_i+1)/2}\mu H} = \sum_{\{s_i\}}\prod_{i=1}^{N} e^{-\beta(-1)^{(s_i+1)/2}\mu H} \\
&= \prod_{i=1}^{N}\sum_{s_i=\pm1} e^{-\beta(-1)^{(s_i+1)/2}\mu H} = \prod_{i=1}^{N}\left(e^{-\beta\mu H}+e^{\beta\mu H}\right) \\
&= \big(2\cosh(\beta\mu H)\big)^N,
\end{aligned}$$

因此可得体系的内能, 熵, 热容和总磁矩分别为

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

3.3 习题 3.7

先求体系的配分函数

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

由此可得体系的状态方程与内能

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

3.4 习题 3.11

由能均分定理

$$\overline{\frac{1}{2}mv_i^2}=\frac{1}{2}k_BT \quad \Rightarrow \quad \overline{v_i^2}=\frac{k_BT}{m},$$

a)

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

b)

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

c)

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

d)

$$\overline{(v_x+av_y)^2}=\overline{v_x^2+2av_xv_y+a^2v_y^2}=\overline{v_x^2}+0+a^2\overline{v_y^2}=(a^2+1)\frac{k_BT}{m}\,;$$

e)

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

3.5 习题 3.12

a)

$$\text{由能均分定理} \quad \Rightarrow \quad \bar{\epsilon}=\frac{5}{2}k_BT\,;$$

b)

$$\overline{\frac{1}{2}m(v_y-v_0)^2}=\overline{\frac{1}{2}mv_y^2+\frac{1}{2}mv_0^2-mv_yv_0}=\overline{\frac{1}{2}mv_y^2}-\frac{1}{2}mv_0^2=\frac{1}{2}k_BT\,,$$

因此, 我们有

$$\overline{\frac{1}{2}mv_y^2}=\frac{1}{2}k_BT+\frac{1}{2}mv_0^2\,.$$

3.6 习题 3.15

a)

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

b) 由能量的概率分布

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

我们有

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

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

$$\begin{cases} p = \frac{1}{\beta}\frac{\partial \ln P}{\partial V} \quad \Rightarrow \quad pV = Nk_BT\,; \\ U = -\frac{\partial \ln P}{\partial \beta} = \frac{3}{2}Nk_BT\,; \\ S = S_0 + Nk_B\big[\ln V + \frac{3}{2}\ln(2\pi m k_B T) + \frac{3}{2}\big]\,; \\ C_{\mathrm{v}} = \frac{\partial U}{\partial T} = \frac{3}{2}Nk_B\,. \end{cases}$$

最后, 我们来算体系的能量涨落:

$$\bar{E^2} = \int E^2 e^{-\Psi-\beta E}\mathrm{d}\Omega = e^{-\Psi}\frac{\partial^2 e^{\Psi}}{\partial\beta^2} = \frac{\partial^2\Psi}{\partial\beta^2} + \left(\frac{\partial\Psi}{\partial\beta}\right)^2$$

$$\Downarrow$$

$$(E-\bar{E})^2 = \bar{E^2} - \bar{E}^2 = \frac{\partial^2\Psi}{\partial\beta^2} = \frac{3}{2}Nk_B^2T^2\,.$$

3.8 补充 S2

先求体系的配分函数

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

因此

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

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

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

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)

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

4.2 习题 4.14

$$f(v)\mathrm{d}v = \frac{4\pi g V}{h^3}\frac{p^2\mathrm{d}p}{e^{(\epsilon-\mu)/k_BT}-1} = \frac{4\pi g m^3 V}{h^3}\frac{v^2\mathrm{d}v}{\exp[(mv^2/2-\mu)/k_BT]-1}\,;$$

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

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

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

$$\Rightarrow \quad v_p = \sqrt{\frac{2k_BT}{m}}\,.$$

4.3 习题 4.17

考虑到膨胀前后的粒子数不变, $N_1 = N_2 = N$

$$\begin{aligned}
N_1 &= \frac{8\pi V_1}{3h^3}(2m)^{3/2}\mu_0^{3/2}\,; \\
N_2 &= \frac{8\pi V_2}{3h^3}(2m)^{3/2}\mu^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\cdots\right],
\end{aligned}$$

$$\Rightarrow \quad \mu^{3/2} \approx \frac{V_1}{V_2}\mu_0^{3/2}\left[1-\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2\right],$$

$$\Rightarrow \quad \mu^{5/2} \approx \left(\frac{V_1}{V_2}\right)^{5/3}\mu_0^{5/2}\left[1-\frac{5\pi^2}{24}\left(\frac{k_BT}{\mu}\right)^2\right]$$

显然, 膨胀前后内能也不发生改变, $E_1 = E_2 = E$

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

$$
\Rightarrow \quad V_1\mu_0^{5/2} = V_2\left(\frac{V_1}{V_2}\right)^{5/3}\mu_0^{5/2}\left[1+\frac{5\pi^2}{12}\left(\frac{k_BT}{\mu}\right)^2\right],
$$

$$
\Rightarrow \quad \frac{k_BT}{\mu} = \sqrt{\frac{12}{5\pi^2}\left[\left(\frac{V_2}{V_1}\right)^{2/3}-1\right]}\,.
$$

最后再利用一下 μ 粗的近似

$$
\mu \approx \left(\frac{3}{8\pi}\right)^{2/3}\frac{h^2}{2m}\left(\frac{N}{V_2}\right)^{2/3},
$$

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

4.4 习题 4.19

利用可逆绝热条件及黑体辐射的相关结论

$$
\begin{aligned}
0 &= T\mathrm{d}S = \mathrm{d}U + p\mathrm{d}V\,; \\
p &= \frac{1}{3}u = \frac{1}{3}aT^4\,; \\
U &= uV = aT^4V\,,
\end{aligned}
$$

将 p 与 U 代入热一公式后整理得到

$$
\mathrm{d}\left(3\log T + \log V\right) = 0 \quad \Rightarrow \quad VT^3 = \mathrm{const} \quad \Rightarrow \quad T_{\mathrm{f}} = 500\mathrm{K}\,.
$$

4.5 习题 4.20

由苏书 (4.14.9) 及 (4.14.4)

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

4.6 习题 4.25

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

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

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

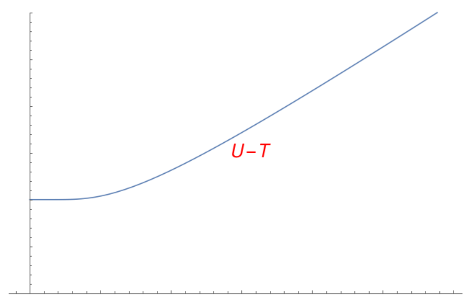
4.7 习题 4.26

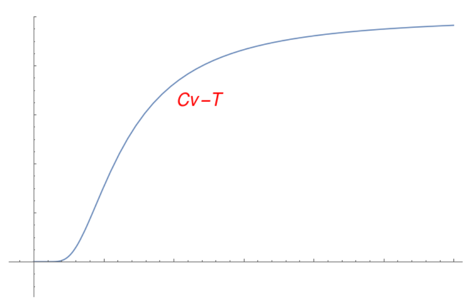
a) 由各向同性, $\bar{v}_x = 0$.

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

4.8 习题 4.30

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





5 第五章

5.1 习题 5.3

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T\Delta v} \quad \Rightarrow \quad \frac{\mathrm{d}^2p}{\mathrm{d}T^2} = \frac{\mathrm{d}L}{\mathrm{d}T}\frac{1}{T\Delta v} - \frac{L}{(T\Delta v)^2}\frac{\mathrm{d}(T\Delta v)}{\mathrm{d}T}$$
$$= \left[\left(\frac{\partial L}{\partial T}\right)_p + \left(\frac{\partial L}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T}\right]\frac{1}{T\Delta v} - \frac{L}{(T\Delta v)^2}\left[\Delta v + T\left\{\left(\frac{\partial \Delta v}{\partial T}\right)_p + \left(\frac{\partial \Delta v}{\partial p}\right)_T \frac{\mathrm{d}p}{\mathrm{d}T}\right\}\right]$$

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

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

最后, 代入具体的数值计算.

5.2 习题 5.8

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

5.3 习题 5.9

$$
\begin{aligned}
\frac{\mathrm{d}L}{\mathrm{d}T} &= c_{p_2} - c_{p_1} + \frac{L}{T} - \left(\frac{\partial \Delta v}{\partial T}\right)_p \frac{L}{\Delta v} \approx c_{p_2} - c_{p_1} + \frac{L}{T} - \left(\frac{\partial v_2}{\partial T}\right)_p \frac{L}{v_2} \\
&= c_{p_2} - c_{p_1} + \frac{L}{T} - \frac{L}{v_2}\left[\frac{v_2}{T} + \frac{RT}{p}\left(\frac{\mathrm{d}B}{\mathrm{d}T}p + \frac{\mathrm{d}C}{\mathrm{d}T}p^2 + \cdots\right)\right] \quad \text{用了物态方程} \\
&\approx c_{p_2} - c_{p_1} - Tv_2\frac{\mathrm{d}p}{\mathrm{d}T}\frac{RT}{pv_2}\left(\frac{\mathrm{d}B}{\mathrm{d}T}p + \frac{\mathrm{d}C}{\mathrm{d}T}p^2 + \cdots\right) \\
&= c_{p_2} - c_{p_1} - RT^2\left(\frac{\mathrm{d}B}{\mathrm{d}T}\frac{\mathrm{d}p}{\mathrm{d}T} + \frac{1}{2}\frac{\mathrm{d}C}{\mathrm{d}T}\frac{\mathrm{d}p^2}{\mathrm{d}T} + \cdots\right) \\
\Rightarrow \quad L &= L_0 + \int_0^T (c_p^0 - c_p^l)\mathrm{d}T - RT^2\left(\frac{\mathrm{d}B}{\mathrm{d}T}p + \frac{1}{2}\frac{\mathrm{d}C}{\mathrm{d}T}p^2 + \cdots\right).
\end{aligned}
$$

5.4 习题 5.10

a)

$$
\begin{aligned}
\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad \Rightarrow \quad \mathrm{d}c_p &= \left(\frac{\partial c_p}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial c_p}{\partial p}\right)_T \mathrm{d}p = \left(\frac{\partial c_p}{\partial T}\right)_p \mathrm{d}T + T\left[\frac{\partial}{\partial p}\left(\frac{\partial s}{\partial T}\right)_p\right]_T \mathrm{d}p \\
&= \left(\frac{\partial c_p}{\partial T}\right)_p \mathrm{d}T + T\left[\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right)_T\right]_p \mathrm{d}p = \left(\frac{\partial c_p}{\partial T}\right)_p \mathrm{d}T - T\left[\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial T}\right)_p\right]_p \mathrm{d}p \\
&= \left(\frac{\partial c_p}{\partial T}\right)_p \mathrm{d}T - T\left[\alpha\left(\frac{\partial v}{\partial T}\right)_p + v\left(\frac{\partial \alpha}{\partial T}\right)_p\right]\mathrm{d}p \quad \text{making use of } (\partial v/\partial T)_p = \alpha v
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{d}c_{p1} = \mathrm{d}c_{p2} \quad &\Rightarrow \quad \left(\frac{\partial c_{p1}}{\partial T}\right)_p \mathrm{d}T - T\left[\alpha_1\left(\frac{\partial v_1}{\partial T}\right)_p + v_1\left(\frac{\partial \alpha_1}{\partial T}\right)_p\right]\mathrm{d}p = \left(\frac{\partial c_{p2}}{\partial T}\right)_p \mathrm{d}T - T\left[\alpha_2\left(\frac{\partial v_2}{\partial T}\right)_p + v_2\left(\frac{\partial \alpha_2}{\partial T}\right)_p\right]\mathrm{d}p \\
&\Rightarrow \quad \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta\left(\partial c_p/\partial T\right)_p}{Tv\Delta\left(\partial \alpha/\partial T\right)_p} \quad \text{making use of } \alpha_1 = \alpha_2,\ v_1 = v_2 \equiv v, \text{ and } (\partial v_1/\partial T)_p = (\partial v_2/\partial T)_p.
\end{aligned}
$$

b)

$$
\begin{aligned}
\mathrm{d}\alpha &= \left(\frac{\partial \alpha}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial \alpha}{\partial p}\right)_T \mathrm{d}p = \left(\frac{\partial \alpha}{\partial T}\right)_p \mathrm{d}T + \left[\frac{\partial}{\partial p}\left\{\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p\right\}\right]_T \mathrm{d}p \\
&\sim \left(\frac{\partial \alpha}{\partial T}\right)_p \mathrm{d}T + \frac{1}{v}\left[\frac{\partial}{\partial p}\left(\frac{\partial v}{\partial T}\right)_p\right]_T \mathrm{d}p \quad \text{inspired by the last step in a), we have omitted one term here} \\
&= \left(\frac{\partial \alpha}{\partial T}\right)_p \mathrm{d}T + \frac{1}{v}\left[\frac{\partial}{\partial T}\left(\frac{\partial v}{\partial p}\right)_T\right]_p \mathrm{d}p = \left(\frac{\partial \alpha}{\partial T}\right)_p \mathrm{d}T - \frac{1}{v}\left(\frac{\partial[\kappa v]}{\partial T}\right)_p \mathrm{d}p \\
&\sim \left(\frac{\partial \alpha}{\partial T}\right)_p \mathrm{d}T - \left(\frac{\partial \kappa}{\partial T}\right)_p \mathrm{d}p \quad \text{similarly, we have omitted one term here}
\end{aligned}
$$

$$
\begin{aligned}
\mathrm{d}\alpha_1 = \mathrm{d}\alpha_2 \quad &\Rightarrow \quad \left(\frac{\partial \alpha_1}{\partial T}\right)_p \mathrm{d}T - \left(\frac{\partial \kappa_1}{\partial T}\right)_p \mathrm{d}p = \left(\frac{\partial \alpha_2}{\partial T}\right)_p \mathrm{d}T - \left(\frac{\partial \kappa_2}{\partial T}\right)_p \mathrm{d}p \\
&\Rightarrow \quad \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta(\partial \alpha/\partial T)_p}{\Delta(\partial \kappa/\partial T)_p}.
\end{aligned}
$$

c)

$$\mathrm{d}\kappa = \left(\frac{\partial \kappa}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial \kappa}{\partial p}\right)_T \mathrm{d}p = -\left(\frac{\partial \alpha}{\partial p}\right)_T \mathrm{d}T + \left(\frac{\partial \kappa}{\partial p}\right)_T \mathrm{d}p \quad \text{the derivation is similar to b)}$$

$$\mathrm{d}\kappa_1 = \mathrm{d}\kappa_2 \quad \Rightarrow \quad \frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta(\partial\alpha/\partial p)_T}{\Delta(\partial\kappa/\partial p)_T}\,.$$

5.5 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)

$$\begin{aligned}
\mathcal{P}\langle S_i S_{i+j}\rangle_{\text{Ising}} &= \sum_{S_1}\cdots\sum_{S_N}\langle S_1|\mathcal{T}|S_2\rangle\cdots\langle S_{i-1}|\mathcal{T}|S_i\rangle S_i\langle S_i|\mathcal{T}|S_{i+1}\rangle\cdots\langle S_{i+j-1}|\mathcal{T}|S_{i+j}\rangle S_{i+j}\langle S_{i+j}|\mathcal{T}|S_{i+j+1}\rangle\cdots\langle S_N|\mathcal{T}|S_1\rangle \\
&= \sum_{S_i}\sum_{S_{i+j}} S_{i+j}\langle S_{i+j}|\mathcal{T}^{N-j}|S_i\rangle S_i\langle S_i|\mathcal{T}^j|S_{i+j}\rangle \\
&= \mathrm{Tr}\left[\sigma_z\mathcal{T}^{N-j}\sigma_z\mathcal{T}^j\right] \\
&= \mathrm{Tr}\left[\sigma_z\left(\lambda_+^{N-j}|+\rangle\langle+| + \lambda_-^{N-j}|-\rangle\langle-|\right)\sigma_z\left(\lambda_+^j|+\rangle\langle+| + \lambda_-^j|-\rangle\langle-|\right)\right] \\
&= \lambda_+^N|\langle+|\sigma_z|+\rangle|^2 + \lambda_+^{N-j}\lambda_-^j|\langle+|\sigma_z|-\rangle|^2 + \lambda_+^j\lambda_-^{N-j}|\langle+|\sigma_z|-\rangle|^2 + \lambda_-^N|\langle-|\sigma_z|-\rangle|^2
\end{aligned}$$

$$\Rightarrow \quad \langle S_i S_{i+j}\rangle_{\text{Ising}} = |\langle+|\sigma_z|+\rangle|^2 + \left(\frac{\lambda_-}{\lambda_+}\right)^j|\langle+|\sigma_z|-\rangle|^2 \quad \text{考虑热力学极限 } N\to\infty\,.$$

当 $H=0$ 时, 我们有

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

因此

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

5.6 习题 5.14

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

因此

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

5.7 习题 5.15

$$K_p = \frac{x_{\mathrm{CO_2}}x_{\mathrm{H_2}}}{x_{\mathrm{CO}}x_{\mathrm{H_2O}}} = \frac{0.7\times 80.38}{9.46\times 9.46} \approx 0.6287\,.$$