热统习题的部分答案 (野生版)

2020 年 11 月 22 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,

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

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

2) 对于每个热源而言, 我们有:

$$
đQ = \mathrm{d}U \sim T^{1/2}\mathrm{d}T,
$$

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: $\Delta S \ge 0$,

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

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,

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

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

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

3) 对于绝热过程,

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

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

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

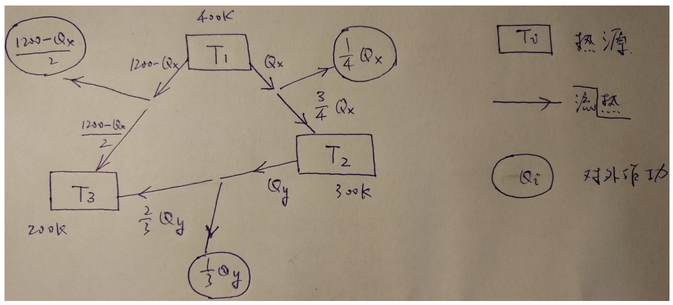
其中一个物体降温 (放热): $T_1 \to T_2$, 另一个物体升温 (吸热): $T_1 \to T_x$. 考虑整个体系, 由热力学第二定律,

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

因此,

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

1.5 习题 1.22



由图, 我们有以下关系:

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

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,

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

2.3 习题 2.15

利用书上式子 2.5.16 及 2.5.22:

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

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

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

b) 求最概然能量 E_p 需写出能量的概率分布

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

因此

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

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

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

因此可得体系的内能, 熵, 热容和总磁矩分别为

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

3.3 习题 3.7

先求体系的配分函数

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

由此可得体系的状态方程与内能

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

3.4 习题 3.11

由能均分定理

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

a)

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

b)

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

c)

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

d)

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

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)

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

b)

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

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

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

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, 内能和熵为

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

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

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