

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

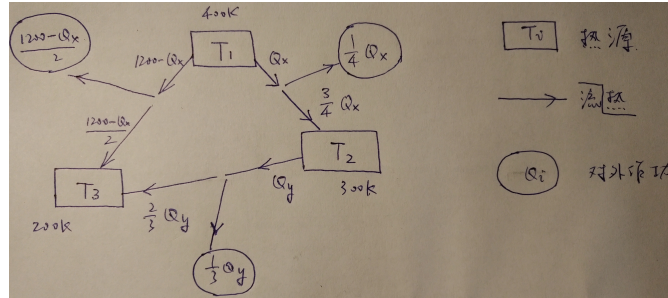
其中一个物体降温 (放热): $T_1 \rightarrow T_2$, 另一个物体升温 (吸热): $T_1 \rightarrow T_x$. 考虑整个体系, 由热力学第二定律,

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

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:

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

1.6 习题 1.23

考虑等熵过程 ($S = S_0$),

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

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)

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

b)

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

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)

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

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, 内能和熵为

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

3.8 补充 S2

先求体系的配分函数

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

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

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