Solutions to Pathria's Statistical Mechanics
Chapter 1

SM-at-THU

March 9, 2016

Problem 1.1

$$\ln \Omega^{(0)}(E^{(0)}, E_1) = \ln \Omega(E_1) = \ln(\Omega_1(E_1)\Omega_2(E_2)) \tag{1}$$

We can expand $\ln \Omega_1(E_1)$ and $\ln \Omega_2(E_1)$ into series near $\bar{E}_1$, and the leading terms are

$$\ln \Omega_1(E_1) = \ln \Omega_1(\bar{E}_1) + \left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} (E_1 - \bar{E}_1) + \frac{1}{2} \left.\frac{\partial^2 \Omega_1(E_1)}{\partial E_1^2}\right|_{E_1=\bar{E}_1} (E_1 - \bar{E}_1)^2 + \cdots \tag{2}$$

$$\ln \Omega_2(E_1) = \ln \Omega_2(\bar{E}_1) + \left.\frac{\partial \Omega_2(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} (E_1 - \bar{E}_1) + \frac{1}{2} \left.\frac{\partial^2 \Omega_2(E_1)}{\partial E_1^2}\right|_{E_1=\bar{E}_1} (E_1 - \bar{E}_1)^2 + \cdots \tag{3}$$

We can set the complicated derivatives to simple symbols

$$\left.\frac{\partial \Omega_1(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} = a_1 \tag{4}$$

$$\left.\frac{\partial \Omega_2(E_1)}{\partial E_1}\right|_{E_1=\bar{E}_1} = a_2 \tag{5}$$

$$\left.\frac{\partial^2 \Omega_1(E_1)}{\partial E_1^2}\right|_{E_1=\bar{E}_1} = b_1 \tag{6}$$

$$\left.\frac{\partial^2 \Omega_2(E_1)}{\partial E_1^2}\right|_{E_1=\bar{E}_1} = b_2 \tag{7}$$

$$\ln \Omega(E_1) = \ln(\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_1)) + (a_1 + a_2)(E_1 - \bar{E}_1) + \frac{b_1 + b_2}{2}(E_1 - \bar{E}_1)^2 + \cdots \tag{8}$$

This fuction reach its maximum under thermodynamic equilibrium condition at $E_1 = \bar{E}_1$. Thus the linear term must vanish.

$$\ln \Omega(E_1) = \ln(\Omega_1(\bar{E}_1)\Omega_2(\bar{E}_1)) + \frac{b_1 + b_2}{2}(E_1 - \bar{E}_1)^2 + \cdots \tag{9}$$

$$\approx \frac{b_1 + b_2}{2}(E_1 - \bar{E}_1)^2 + \ln(\Omega(\bar{E}_1)) \tag{10}$$

$$\Omega(E_1) = e^{(b_1+b_2)(E_1-\bar{E}_1)^2+\ln(\Omega(\bar{E}_1))} = Ae^{\frac{b_1+b_2}{2}(E_1-\bar{E}_1)^2} \tag{11}$$

$$A = e^{\ln(\Omega(\bar{E}_1))} \tag{12}$$

Which is obviously a gaussian function.
Gaussian RMS can be easily determined to be

$$\frac{1}{2(b_1+b_2)} = \frac{1}{2}\frac{1}{(\frac{\partial\beta_1}{\partial E_1}+\frac{\partial\beta_2}{\partial E_2})} = \frac{1}{2}\frac{1}{\frac{1}{kT_1{}^2C_{v1}}+\frac{1}{kT_2{}^2C_{v2}}} \tag{13}$$

For the example of ideal classical gases, we can subtitute $C_vi = \frac{3}{2}N_ik$ and obtain $\frac{3}{2}k^2T^2\frac{N_1N_2}{N_1+N_2}$

Problem 1.2

Utilizing the additive characteristic of $S = f(\Omega)$ and get

$$S = S_1 + S_2 = f(\Omega_1) + f(\Omega_2) \tag{14}$$

$$(\frac{dS}{d\Omega_1})_{\Omega_2} = f'(\Omega_1) \tag{15}$$

$$(\frac{dS}{d\Omega_2})_{\Omega_1} = f'(\Omega_2) \tag{16}$$

Inspect a small pertubation near the equilibrium state using the fact that $S = f(\Omega) = f(\Omega_1\Omega_2)$

$$(\frac{dS}{d\Omega_1})_{\Omega_2} = \lim_{\Delta\to 0}\frac{f((\Omega_1+\Delta)\Omega_2) - f(\Omega_1\Omega_2)}{\Delta} \tag{17}$$

Assume that $\delta = \Delta\Omega_2$

$$(\frac{dS}{d\Omega_1})_{\Omega_2} = \lim_{\Delta\to 0}\Omega_2\frac{f(\Omega_1\Omega_2+\Delta\Omega_2) - f(\Omega_1\Omega_2)}{\Delta\Omega_2} = \lim_{\delta\to 0}\Omega_2\frac{f(\Omega+\delta)-f(\Omega)}{\delta} = \Omega_2 f'(\Omega) \tag{18}$$

Apply to $(\frac{dS}{d\Omega_2})_{\Omega_1}$, we can get similar result.

$$(\frac{dS}{d\Omega_2})_{\Omega_1} = \Omega_1 f'(\Omega) \tag{19}$$

Finally,

$$f'(\Omega_1) = \Omega_2 f'(\Omega) = \frac{\Omega_2}{\Omega_1}f'(\Omega_2) \tag{20}$$

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) \tag{21}$$

It is obvious that this equation holds for all Ω. Set the value of the equation constant k.

$$\Omega\frac{df(\Omega)}{d\Omega} = k \tag{22}$$

$$f(\Omega) = kln\Omega + C \tag{23}$$

Using a special value $\Omega = 1$

$$f(\Omega * 1) = f(\Omega) + f(1) \tag{24}$$

$$C = f(1) = 0 \tag{25}$$

And get the result

$$S = f(\Omega) = k\ln\Omega \tag{26}$$

Problem 1.3

When the two systems are brought together, they can form an isolated system. Energy and particle number are constant while entropy will not not decreasing in such a system.

$$E_A + E_B = E_0 \tag{27}$$
$$N_A + N_B = N_0 \tag{28}$$
$$dS_A + dS_B \geq 0 \tag{29}$$

Apply derivation and get

$$dE_A + dE_B = 0 \tag{30}$$
$$dN_A + dN_B = 0 \tag{31}$$
$$dS_A + dS_B \geq 0 \tag{32}$$

Subtitute these relations into equation

$$dE_A = T_A dS_A - p_A dV_A + \mu_A dN_A \tag{33}$$
$$dE_B = T_B dS_B - p_B dV_B + \mu_B dN_B \tag{34}$$
$$dV_A = 0 \tag{35}$$
$$dV_B = 0 \tag{36}$$

and get

$$\frac{dE_A}{dN_A} \geq \frac{\mu_A T_B - \mu_B T_A}{T_B - T_A} \tag{37}$$

Problem 1.4

Suppose N is the number of particles, v_0 is the volume occupied by one particle and therefore the total number of microstates Ω is

$$\Omega = \frac{1}{N!}(\frac{V}{v_0})\dots(\frac{V}{v_0} - N + 1) \tag{38}$$

Following (1.4.2), we have

$$\frac{P}{T} = k\left(\frac{\partial \ln \Omega}{\partial V}\right)_{N,E} \tag{39}$$
$$= k\frac{\partial \Omega}{\Omega \partial V} \tag{40}$$
$$= k\frac{N}{V}\left(1 + \frac{(N-1)v_0}{2V} + \dots\right) \tag{41}$$

Considering only the first two terms, it corresponds to $P(V-b) = NkT$ with $b = Nv_0/2$.
Notes: I don't know why the problem says $b = 4Nv_0$ since this gas is hard sphere gas. Anyone has an idea?

Problem 1.5

Using equation $(A.11)$, and setting $K = \pi\sqrt{\varepsilon}/L$, it is straight forward to achieve

$$\Sigma_1(\varepsilon) = \frac{\pi}{6}\varepsilon^{3/2} \pm \frac{3\pi}{8}\varepsilon \tag{42}$$

where the first term is the volume term ($V = L^3$) and the next one is the surface correction ($S = 6L^2$).

Problem 1.6

Use the formula for ideal gas $PV = NkT$.

$$Nk \times 300 = 10^5 \times \frac{\pi}{10} \tag{43}$$

Thus $\Delta T = 10^4/Nk \sim 955K$.

Problem 1.10

Just use equation (1.4.21) and (1.4.23), we have:

$$S(N, V, E) = Nk \ln \left[V \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{3}{2} Nk \tag{44}$$

Since He and Ar have the same N,V. We can get the T that He and Ar have the same entropy:

$$T = 0K(?)$$

Problem 1.11

As N_2 and O_2 are mixed together at the same pressure and temperature, we can know that the volume of mixed gas is: $V = V_1 + V_2$. And we can get the entropy of mixing by utilizing equation (1.5.3):

$$\Delta S = k \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] \tag{45}$$

for per mole of the air formed:

$$\begin{aligned} \Delta S_n &= k \left[N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \right] / (n_1 + n_2) \\ &= R \left[n_1 \ln \frac{V}{V_1} + n_2 \ln \frac{V}{V_2} \right] / (n_1 + n_2) \\ &= 4.16 \ J \cdot mol^{-1} \cdot K^{-1} \end{aligned} \tag{46}$$

Problem 1.12

(a) Equation (1.5.3a) can be written as:

$$\begin{aligned} (\Delta S)_{1 \equiv 2} &= N_1 \ln \frac{(V_1 + V_2)N_1}{V_1(N_1 + N_2)} + N_2 \ln \frac{(V_1 + V_2)N_2}{V_2(N_1 + N_2)} \\ &= (N_1 + N_2) \left[y \ln \frac{y}{x} + (1 - y) \ln \frac{1 - y}{1 - x} \right] \end{aligned} \tag{47}$$

Here $x = V_1/(V_1 + V_2), y = N_1/(N_1 + N_2)$.

Consider the function $f(x, y) = y \ln \frac{y}{x}$, we can get the second derivatives:

$$D^2 f(x, y) = \begin{bmatrix} y/x^2 & -1/x \\ -1/x & 1/y \end{bmatrix} \tag{48}$$

Since $D^2 f(x,y)$ is a positive-semidefinite, $f(x,y)$ is a convex function. Then we can know that:

$$\frac{1}{2}f(x,y) + \frac{1}{2}f(1-x,1-y) \geq f(1/2,1/2) = 0 \tag{49}$$

This means $(\Delta S)_{1\equiv 2} \geq 0$ and the equality holding only when $N_1/V_1 = N_2/V_2$

(b) Suppose that $N = N_1 + N_2$. And we have $(\Delta S)^*$ by utilizing equation (1.5.4) :

$$\begin{aligned}(\Delta S)^* &= k\left[N_1 \ln\frac{N}{N_1} + N_2 \ln\frac{N}{N_2}\right] \\ &= k\left[N\ln N - N_1 \ln N_1 - N_2 \ln N_2\right]\end{aligned} \tag{50}$$

Then we have the derivative of $(\Delta S)^*$ with respect to N_1:

$$\begin{aligned}\frac{d\,(\Delta S)^*}{dN_1} &= -\ln N_1 - \frac{\partial N_2}{\partial N_1}\ln N_2 \\ &= -\left(\ln N_1 - \ln N_2\right)\end{aligned} \tag{51}$$

It shows that $\frac{d(\Delta S)^*}{dN_1}$ satisfies:

$$\frac{d\,(\Delta S)^*}{dN_1}\begin{cases} <0 & N_1 > N_2 \\ =0 & N_1 = N_2 \\ >0 & N_1 < N_2 \end{cases} \tag{52}$$

So we can know that $(\Delta S)^*$ have the only maximum value at $N_1 = N_2$:

$$\max\,(\Delta S)^* = (N_1 + N_2 \ln 2) \tag{53}$$

Then we get:

$$\max\,(\Delta S)^* \leq (N_1 + N_2 \ln 2) \tag{54}$$

The equality holding when and only when $N_2 = N_2$

Problem 1.16

Theorem:
If $f(x,y,z) = 0$,then we have

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial z}\right)_y = -1$$

(a)

$$\frac{S}{N} = -\left(\frac{\partial \mu}{\partial T}\right)_P$$

$$\frac{V}{N} = \left(\frac{\partial \mu}{\partial P}\right)_T$$

$$\frac{S}{V} = -\frac{\left(\frac{\partial \mu}{\partial T}\right)_P}{\left(\frac{\partial \mu}{\partial P}\right)_T} = -\frac{1}{\left(\frac{\partial T}{\partial \mu}\right)_P \left(\frac{\partial \mu}{\partial P}\right)_T} = \left(\frac{\partial P}{\partial T}\right)_\mu$$

(b)

$$\frac{V}{N} = \left(\frac{\partial \mu}{\partial P}\right)_T$$

$$V\left(\frac{\partial P}{\partial \mu}\right)_T = N$$