Variance in Energy

(1) $$Z = \sum_n e^{-\beta E_n}, \quad \text{so}$$

(2) $$-\frac{\partial Z}{\partial \beta} = \sum_n -\frac{\partial}{\partial \beta}\left(e^{-\beta E_n}\right) = \sum_n e^{-\beta E_n} E_n \quad \text{and so}$$

$$\left(-\frac{\partial}{\partial \beta}\right)\left(-\frac{\partial Z}{\partial \beta}\right) = \sum_n -\frac{\partial}{\partial \beta}\left(e^{-\beta E_n}\right) E_n$$

(3) $$\left(-\frac{\partial}{\partial \beta}\right)^2 Z = \sum_n e^{-\beta E_n} E_n^2$$

So

$$\boxed{\langle E^2 \rangle = \frac{\sum_n e^{-\beta E_n} E_n^2}{\sum_n e^{-\beta E_n}} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}}$$

Similarly

$$\boxed{\langle E^m \rangle = \left[\left(-\frac{\partial}{\partial \beta}\right)^m Z\right] \Big/ Z}$$

Since

$$\left(-\frac{\partial}{\partial \beta}\right)^m \sum_n e^{-\beta E_n} = \sum_n e^{-\beta E_n} E_n^m$$

(b) Then

$$\langle \delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2$$

Now last week we showed

- $\langle E \rangle = \frac{-1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-\partial}{\partial \beta}\ln Z$

So

$$-\frac{\partial}{\partial \beta}\left(\frac{1}{Z}\,\partial_\beta Z\right) = -\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 + \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

$$-\frac{\partial}{\partial \beta}\langle E \rangle = -\langle E \rangle^2 + \langle E^2 \rangle = \sigma_E^2$$

Note then that

$$\boxed{\frac{\partial^2}{\partial \beta^2}\ln Z = \frac{-\partial \langle E \rangle}{\partial \beta} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) = \sigma_E^2}$$

c) For the two state system

$$Z = 1 + e^{-\beta\Delta}$$

- $$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{e^{-\beta\Delta}}{(1+e^{-\beta\Delta})}\Delta$$

And

- $$\sigma_E^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = \frac{e^{-\beta\Delta}}{(1+e^{-\beta\Delta})}\Delta^2 + \frac{-e^{-\beta\Delta}}{(1+e^{-\beta\Delta})^2} e^{-\beta\Delta}\Delta^2$$

$$= \frac{e^{-\beta\Delta}}{(1+e^{-\beta\Delta})^2}\Delta^2 \left[1 + e^{-\beta\Delta} - e^{-\beta\Delta} \right]$$

$$\boxed{\sigma_E^2 = \Delta^2 \frac{e^{-\beta\Delta}}{(1+e^{-\beta\Delta})^2}}$$ Same as before

d) We use

$$\langle E \rangle = \frac{\hbar\omega_0}{(e^{\beta\hbar\omega_0}-1)}$$

Then

$$\sigma_E^2 = -\frac{\partial}{\partial \beta}\langle E \rangle = \frac{-\hbar\omega_0}{(e^{\beta\hbar\omega_0}-1)^2} e^{\beta\hbar\omega_0}(-\hbar\omega_0)$$

$$\boxed{\sigma_E^2 = (\hbar\omega_0)^2 \, e^{\beta\hbar\omega_0}/(e^{\beta\hbar\omega_0}-1)^2}$$

e) At low thermal temperature

$$e^{\beta\hbar\omega_0} \gg 1 \quad \text{and} \quad e^{-\beta\hbar\omega_0} \ll 1$$

- So

$$\sigma_E^2 = (\hbar\omega_0)^2 \frac{e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega_0})^2}$$

Since $e^{-\beta\hbar\omega_0} \ll 1$ we can drop it in comparison to one, $(1 - e^{-\beta\hbar\omega_0}) \simeq 1$ yieding

$$\boxed{\sigma_E = (\hbar\omega_0)^2 \, e^{-\beta\hbar\omega_0}}$$

f) The probability is

$$P_n = e^{-n\beta\hbar\omega_0}(1 - e^{-\beta\hbar\omega_0})$$

- Then $e^{-\beta\hbar\omega_0} \ll 1$ since the temperature is low. Call it $\underline{u \equiv e^{-\beta\hbar\omega_0} \ll 1}$

P_N: $\quad P_n = u^n(1-u)$

P_0: $\quad P_0 = 1 - u$

P_1: $\quad P_1 = u(1-u) \simeq u + O(u^2)$

P_2: $\quad P_2 = u^2(1-u) \simeq O(u)$ etc.

So similary $P_n \simeq O(u^n)$. Working to first order in u

$$\boxed{\begin{aligned} P_0 &= 1 - e^{-\beta\hbar\omega} \\ P_1 &\simeq e^{-\beta\hbar\omega_0} \end{aligned}}$$

So

$$\langle \delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$\langle E \rangle = E_0 P_0 + E_1 P_1 = 0 + \hbar\omega_0 e^{-\beta\hbar\omega_0}$$

$$\langle E^2 \rangle = E_0^2 P_0 + E_1^2 P_1 = 0 + (\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}$$

So

(small)^2

$$\langle \delta E^2 \rangle = (\hbar\omega_0)^2 e^{-\beta\hbar\omega_0} - \cancel{(\hbar\omega_0 e^{-\beta\hbar\omega_0})^2}$$

but this is of order $u^2 = e^{-2\beta\hbar\omega_0}$

Leading to

$$\boxed{\langle \delta E^2 \rangle = (\hbar\omega_0)^2 e^{-\beta\hbar\omega_0}}$$

this agrees with part e)

g) Then

$$\langle \delta E^2 \rangle = (\hbar\omega_0)^2 \frac{e^{\beta\hbar\omega_0}}{(e^{\beta\hbar\omega_0}-1)^2}$$

For high temperature $\beta\hbar\omega_0 \equiv x \ll 1$ so we expand

$$\langle \delta E^2 \rangle = (\hbar\omega_0)^2 \frac{e^x}{(e^x-1)^2}$$

$e^x \simeq 1 + O(x)$

$e^x - 1 \simeq x$

$$\langle \delta E^2 \rangle \simeq (\hbar\omega_0)^2 \frac{1}{x^2}$$

$$\boxed{\langle \delta E^2 \rangle = (\hbar\omega_0)^2 \left(\frac{kT}{\hbar\omega_0}\right)^2 = (kT)^2}$$

Estimates of Entropy

$$S = Nk_B \left[\log\left(\frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{E}{N} \right)^{3/2} \right) + \frac{5}{2} \right]$$

$\boxed{a}$ Then

$$S = Nk_B \log V + \frac{3}{2} Nk_B \log E + \text{const}$$

Similarly

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3}{2}\frac{Nk}{E} = \frac{1}{T}$$

$$\frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E = \frac{Nk_B}{V}$$

$\boxed{c}$ So

$$pV = NkT$$

Then

$$\frac{V}{N} = \frac{kT}{p} = \frac{N_A k \; T}{N_A p} = \frac{R\,T}{N_A p}$$

$$l_0 = \left(\frac{V}{N}\right)^{1/3} = \left(\frac{RT}{N_A p}\right)^{1/3} = \left(\frac{8.32\,J/K \cdot 300K}{6\times10^{23} \cdot 10^5\,N/m^2}\right)^{1/3} =$$

$$\boxed{l_0 = 3.5\,nm}$$

d) Then

$$\boxed{\lambda_{th} = \frac{hc}{(2\pi(m_{He}c^2)(k_B T))^{1/2}} = 0.052 \text{ nm}}$$

So

e) $$\frac{S}{Nk_B} = \log\left(\left(\frac{V}{\lambda_{th}^3}\right)\right) + \frac{5}{2}$$

$$= 3\log\left(\frac{l_0}{\lambda_{th}}\right) + \frac{5}{2} = \boxed{15.15 = \frac{S}{Nk_B}}$$

f) So

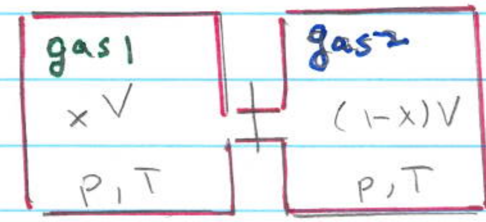
$$\boxed{S = \underbrace{N_A k_B}_{=R} \cdot 15.15 = 15.15\, R = 126 \frac{J}{{}^\circ K}}$$

$$\Omega = e^{S/k_B} = e^{15.15 \times 6 \times 10^{23}} = e^{9. \times 10^{24}} = 10^{\overbrace{\log_{10} e}^{0.43} \cdot 9. \times 10^{24}}$$

$$\boxed{\Omega = 10^{3.9 \times 10^{24}}}$$

Entropy of Mixing

- Consider two gasses separated by a partition as shown below (see slide)



- The two gasses intermingle, when the valve is opened and entropy increases. Since the ΔS does not depend on the path we can replace the non-equilibrium process with an equilibrium one. We will connect the state A (gas with volume xV) to the final state B (gas with volume V) via an isothermal expansion

$$dS = \cancel{\frac{1}{T}\, dU}^{\,0} + \frac{p}{T}\, dV$$

- dU is zero since for an ideal gas, U is only a function of temperature

$$\Delta S_1 = \int_{xV_f}^{V_f} \underbrace{\left(\frac{N_1 k T}{V\, T}\right)}_{\text{this is } \frac{p}{T}} dV = N_1 k \log\left(\frac{V_f}{x V_f}\right) = -N_1 k \log x$$

Entropy of Mixing

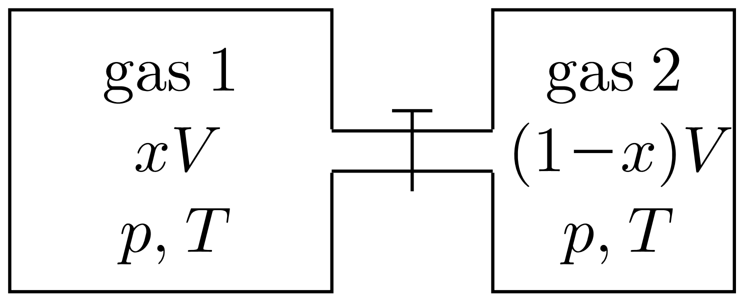
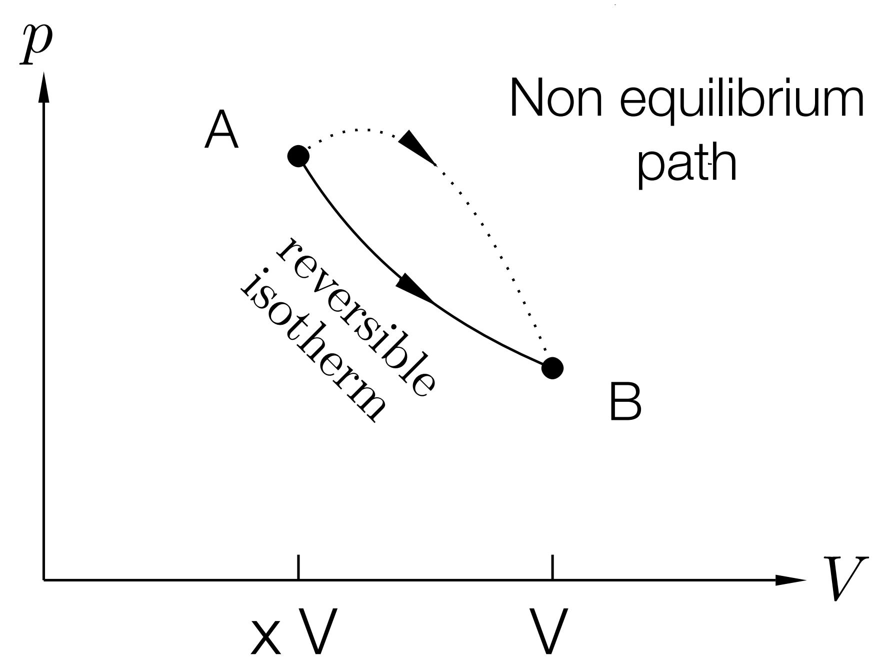


Fig. 14.6 Gas 1 is confined in a vessel of volume xV, while gas 2 is confined in a vessel of volume $(1-x)V$. Both gases are at pressure p and temperature T. Mixing occurs once the tap on the pipe connecting the two vessels is opened.

Computational strategy for finding the entropy change: replace the non-equilibrium process with an equilibrium one



Similarly for gas 2

$$\Delta S_2 = \int_{(1-x)V_f}^{V_f} \frac{NkT}{VT}\, dV$$

$$= -N_2 k \ln(1-x)$$

So, finally since the initial temperatures and pressures are equal

$$p = \frac{NkT}{V}, \quad \text{so}, \quad N \propto V$$

And So

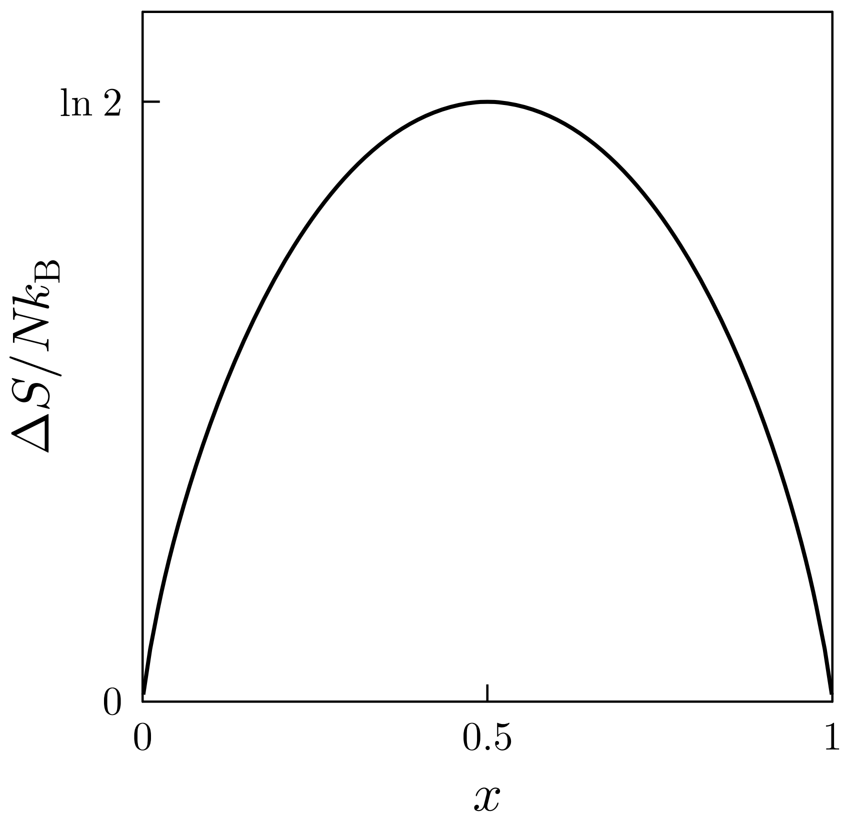
$$N_1 = x \cdot N \quad \text{and} \quad N_2 = (1-x) N$$

So $\frac{N_1}{N_2} = \frac{xV}{(1-x)V}$ and $N_1 + N_2 = N$

So finally

$$\boxed{\Delta S_{tot} = Nk\left(-x\ln x - (1-x)\ln(1-x)\right)}$$

A plot of this formula is shown below.



$$\frac{S}{Nk_B} = -x\log(x) - (1-x)\log(1-x)$$

Problem 4

$$S = Nk_B \log V + \frac{3Nk_B}{2} \log E + \text{const}$$

- $$dS = \frac{Nk_B}{V} dV + \frac{3Nk_B}{2} \frac{dE}{E}$$

- Now in an adiabatic expansion of a MAIG:

$$\underline{TV^{\gamma-1} = \text{const}} \qquad \text{and } \gamma = \frac{C_V + Nk}{C_V} = 1 + \frac{Nk}{\frac{3}{2}Nk}$$

$$\underline{\gamma - 1 = \frac{2}{3}}$$

- So we have

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \qquad \text{So we have} \qquad E = \frac{3Nk_B}{2} T$$

$$dE = \frac{3}{2} Nk_B \, dT$$

$$dS = \frac{Nk_B}{V} dV + \frac{1}{T} dE$$

$$dS = \frac{Nk_B}{V} dV + \frac{3}{2} \frac{Nk_B}{T} dT$$

Now for an ddiabatic expansion

$$T V^{2/3} = \text{const}$$

$$dT\, V^{2/3} + T \frac{2}{3} \frac{dV}{V^{1/3}} = 0$$

- So

$$\boxed{\frac{dT}{T} + \frac{2}{3}\frac{dV}{V} = 0}$$ from $T V^{\gamma - 1} = \text{const}$

- So we have from dS

$$dS = \frac{N k_B}{V} dV + \frac{3}{2} N k_B \left(-\frac{2}{3} \frac{dV}{V} \right) = 0 \checkmark$$

☆ What is going on is that the volume in space is inceasing, while the volume in momentum space is decreasing (gas is getting colder), leaving the total phase space volume fixed.