

A chain of H-atoms

$$a) \quad Z = \sum_{\text{states}} e^{-\beta \epsilon_s} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_0 n} = \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega_0})^n$$

↑ $\epsilon_n = n \hbar \omega_0$ for a harmonic oscillator

$$Z = \frac{1}{1 - e^{-\beta \hbar \omega_0}}$$

↑ we used the geometric series

$$\frac{1}{1-x} = 1 + x + x^2 + \dots$$

$$b) \quad \text{So } \ln Z = -\ln(1 - e^{-\beta \hbar \omega_0}) \text{ and}$$

$$\langle \epsilon \rangle = - \frac{\partial \ln Z}{\partial \beta} = + \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta \hbar \omega_0})$$

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

$$\langle \epsilon \rangle = \frac{\hbar \omega_0 e^{-\beta \hbar \omega_0}}{1 - e^{-\beta \hbar \omega_0}} = \frac{\hbar \omega_0}{e^{\beta \hbar \omega_0} - 1}$$

Then

$$\langle (\delta \epsilon)^2 \rangle = - \frac{\partial \langle \epsilon \rangle}{\partial \beta} = + \frac{\partial^2 \ln Z}{\partial \beta^2}$$

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

We have derived here the partition function and energy for a single atom. For N atoms

$$Z_N = Z_1^N \quad \leftarrow \text{the atoms are distinguishable}$$

$$\ln Z_N = N \ln Z_1 \quad \text{Each atom is at one site on the chain,}$$

So we have that

$$\langle E \rangle = - \frac{\partial \ln Z_N}{\partial \beta} = N \langle E \rangle$$

$$\langle E^2 \rangle = + \frac{\partial^2 \ln Z_N}{\partial \beta^2} = N \langle E^2 \rangle$$

c) At high temperature $\beta \hbar \omega \ll 1$

$$\langle E \rangle \approx \frac{\hbar \omega}{\beta (1 + \frac{\hbar \omega \beta}{2})}$$

$$e^{\beta \hbar \omega} = 1 + \hbar \omega \beta + \frac{(\hbar \omega \beta)^2}{2} + \dots$$

$$\langle E \rangle \approx \frac{1}{\beta} \left(1 - \frac{\hbar \omega \beta}{2} \right)$$

$$\langle E \rangle \approx kT - \frac{\hbar \omega}{2}$$

So if we replace Hydrogen with deuterium

$$\Delta E = N \left(kT - \frac{\hbar \omega_D}{2} \right) - N \left(kT - \frac{\hbar \omega_H}{2} \right)$$

$$\Delta E = \frac{N\hbar(\omega_H - \omega_D)}{2}$$

where

$$\omega_D = \sqrt{\frac{k_0}{m_D}}$$
$$\omega_H = \sqrt{\frac{k_0}{m_H}}$$

Entropy change in the mixing of Hot & Cold Gasses

(a) Energy is conserved and the gasses ultimately have the same temperature.

$$E_1 + E_2 = E$$

$$\frac{3}{2} N_1 k T_1 + \frac{3}{2} N_2 k T_2 = \frac{3}{2} (N_1 + N_2) k T$$

$$\frac{N_1 T_1 + N_2 T_2}{(N_1 + N_2)} = T$$

(b) The entropy of Each Gas is

$$S = Nk \ln V + \frac{3}{2} Nk \ln E + \text{const}$$

$$S = Nk \ln V + \frac{3}{2} Nk \ln T + \text{const}$$

$E \propto T$
← a different constant

So

$$\Delta S = Nk \ln \frac{V_f}{V_i} + \frac{3}{2} Nk \ln \frac{T_f}{T_i}$$

Here we have two gasses:

$$\frac{V_f}{V_i} = \frac{V}{V/2} = 2$$

$$\frac{T_f}{T_i} = \frac{T}{T_1} \quad \text{for gas \#1}$$

$$\frac{T_f}{T_i} = \frac{T}{T_2} \quad \text{for gas \#2}$$

S_0

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$\Delta S = (N_1 + N_2) k \ln 2 + \frac{3}{2} N_1 k \ln \frac{T}{T_1} + \frac{3}{2} N_2 k \ln \frac{T}{T_2}$$

Ideal Gas in 1D

a) $Z = \frac{1}{N!} Z_1^N$ $Z_1 = \int \frac{dx dp}{h} e^{-p^2/2mT}$

we assumed here that N is large $1/N! \simeq (e/N)^N$

$$Z = \left(\frac{e Z_1}{N} \right)^N = L \int_{-\infty}^{\infty} \frac{dp}{h} e^{-p^2/2mT}$$

So $= \frac{L \sqrt{2\pi m k T}}{h} \equiv \frac{L}{\lambda_{th}}$

$$F = -kT \ln Z$$

$$F^{gas} = -kT N \left[\ln \left(\frac{e Z_1}{N} \right) \right]$$

$$f_1 \equiv -kT \ln \left(\frac{e Z_1}{N} \right)$$

$$F^{gas} = N f_1$$

$$F^{gas} = -kT N \left[\ln \left(\frac{L}{N \lambda_{th}} \right) + 1 \right]$$

b) $du = \delta Q + \delta W$ $\delta Q = T ds$

$$dU = T ds - p dV$$

$$\delta W = -p dV$$

Now $T ds = d(Ts) - S dT$ so

$$dU = d(Ts) - S dT - p dV$$

So defining $F = U - TS$ we find

$$\underline{dF = -SdT - p dV}$$

So

$$(c) \quad S = - \left(\frac{\partial F}{\partial T} \right)_V$$

with

$$\frac{F}{N} = -kT \left[\ln \left(\frac{L}{N \lambda_{th}} \right) + 1 \right] \quad \updownarrow \quad \text{use } \lambda_{th} \propto T^{-1/2}$$

So:

$$\frac{S}{N} = k \left[\ln \left(\frac{L}{N \lambda_{th}} \right) + 1 \right] + kT \frac{\partial}{\partial T} \left[\ln T^{1/2} + \text{const} \right]$$

$$\frac{S}{N} = k \left[\ln \left(\frac{L}{N \lambda_{th}} \right) + 1 \right] + \frac{k}{2}$$

$$\boxed{\frac{S}{N} = k \left[\ln \left(\frac{L}{N \lambda_{th}} \right) + \frac{3}{2} \right]}$$

(d) The partition fn is similar

$$Z_{\text{tot}} = \frac{1}{N!} Z_1^N$$

$$\begin{aligned} Z_1 &= \sum_s \int \frac{d\mathbf{x} d\mathbf{p}}{h} e^{-\beta(p^2/2m + \epsilon_s)} \\ &= Z_1^{\text{trans}} Z_1^{\text{internal}} \end{aligned}$$

where $Z_1^{\text{internal}} = \sum_i e^{-\beta \epsilon_i} = (1 + e^{-\beta \Delta})$

and $Z_1^{\text{trans}} = \int \frac{d\mathbf{x} d\mathbf{p}}{h} e^{-p^2/2mkT} = L/\lambda_{th}$ as in part (a)

S₀

$$Z_{\text{tot}} = \left(\frac{e z_1^{\text{trans}}}{N} z_1^{\text{internal}} \right)^N$$

• S₀

$$F = -kT \ln Z_{\text{tot}}$$

$$F = \underbrace{-kTN \ln \left(\frac{e z_1^{\text{trans}}}{N} \right)}_{\text{Same as (c)}} - \underbrace{kT \ln (z_1^{\text{internal}})^N}_{\text{new part} = N(-kT \ln z_1^{\text{internal}})}$$

Same as (c)

new part = $N(-kT \ln z_1^{\text{internal}})$

$$\frac{F}{N} = \left(\frac{F}{N} \right)_{\text{gas}} + -kT \ln z_1^{\text{internal}}$$

This is the free energy per particle from the internal partition function

$$\frac{F}{N} = \frac{F^{\text{gas}}}{N} + -kT \ln(1 + e^{-\beta \Delta})$$

• S₀

$$S = -\partial F / \partial T$$

$$\frac{S}{N} = \frac{S^{\text{gas}}}{N} + -k \ln(1 + e^{-\beta \Delta}) + kT \frac{\partial}{\partial T} \ln(1 + e^{-\beta \Delta})$$

Now use: $T \frac{\partial}{\partial T} = -\beta \frac{\partial}{\partial \beta}$ and $-\beta \frac{\partial}{\partial \beta} \ln(1 + e^{-\beta \Delta}) = \frac{\beta \Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}$

Assembling the ingredients from part (c)

$$\frac{S}{Nk} = \ln \left(\frac{L}{N\lambda_{th}} \right) + \frac{3}{2} + \ln(1 + e^{-\beta\Delta}) + \frac{\beta\Delta e^{-\beta\Delta}}{(1 + e^{-\beta\Delta})}$$

• In the low temperature limit, $e^{-\beta\Delta} \rightarrow 0$, and

$$\ln(1 + e^{-\beta\Delta}) + \frac{\beta\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \rightarrow \ln(1) + 0 = 0$$

And thus, the entropy per particle is unchanged. This makes sense: there are no extra states.

• In the high temperature limit $\beta\Delta \rightarrow 0$, and $e^{-\beta\Delta} \rightarrow 1$

$$\frac{S}{Nk} = \ln \left(\frac{L}{N\lambda_{th}} \right) + \frac{3}{2} + \ln(1+1) + 0$$

part (c)

$\ln 2$

So in the high temperature limits the entropy per particle increases by $\ln 2$. This makes sense there are twice as many states per particle due to the internal structure of the molecule