

SHO

a)

$$d^2P = C e^{-H/k_B T} dx dp$$

$$= C e^{-p^2/2mk_B T} e^{-\frac{1}{2}m\omega_0^2 x^2/k_B T} dx dp$$

Let  $\sigma_x^2 = \frac{k_B T}{m\omega_0^2}$  and  $\sigma_p^2 = m k_B T$

So

this is a product:  $f_{cn}(x) = f_{cn}(p)$

$$d^2P = C e^{-x^2/2\sigma_x^2} e^{-p^2/2\sigma_p^2} dx dp$$

We know the normalization of a gaussian:

$$\int du e^{-u^2/2\sigma^2} = (2\pi\sigma^2)^{1/2}$$

Leading to  $\int dx dp f_{cn}(x) f_{cn}(p) = \int dx f_{cn}(x) \cdot \int dp f_{cn}(p)$ , or

$$d^2P = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dx dp \quad (\text{see below})$$

$$d^2P = P(x) dx P(p) dp$$

Integrating over  $p$ , determines  $P(x) = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}}$

- In greater detail:

$$\int d\mathcal{P} = C \int e^{-x^2/2\sigma_x^2} dx \int e^{-p^2/2\sigma_p^2} = 1$$

$$= C (2\pi\sigma_x^2)^{1/2} (2\pi\sigma_p^2)^{1/2} = 1$$

$$C = \frac{1}{(2\pi\sigma_x^2)^{1/2}} \frac{1}{(2\pi\sigma_p^2)^{1/2}}$$

- Since the probability density factorizes, it is helpful to note that the probability to find  $x$ , without regard to  $p$ , is found by summing all possible values of  $p$  (leaving  $x$ -fixed)

$$d\mathcal{P}_x = \int_p d\mathcal{P}_{x,p} = \int_p \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dx dp$$

$$= \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} dx \underbrace{\int_{-\infty}^{\infty} dp \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}}}_{=1}$$

$$d\mathcal{P}_x = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} dx \equiv P(x) dx$$

- Similarly a small calculation shows that:

$$d\mathcal{P}_p = \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} dp = P(p) dp$$

So

$$\underline{b)} \quad \langle x^2 \rangle = \int_{-\infty}^{\infty} dx \, x^2 P(x)$$

Here  $dP_x = P(x) dx = \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}} dx$

So

$$\boxed{\langle x^2 \rangle} = \int_{-\infty}^{\infty} dx \, x^2 \frac{e^{-x^2/2\sigma_x^2}}{(2\pi\sigma_x^2)^{1/2}}$$

$$= \sigma_x^2 \int_{-\infty}^{\infty} du \, \frac{u^2 e^{-u^2/2}}{\sqrt{2\pi}} = \boxed{\sigma_x^2 = \frac{k_B T}{m\omega_0^2}}$$

Similarly

$$\boxed{\langle p^2 \rangle} = \int_{-\infty}^{\infty} dp \, p^2 \frac{e^{-p^2/2\sigma_p^2}}{(2\pi\sigma_p^2)^{1/2}} = \sigma_p^2 = \boxed{m k_B T}$$

the integral is the same as the x-case

c) Note

$$\langle K \rangle = \left\langle \frac{p^2}{2m} \right\rangle = \frac{1}{2m} \langle p^2 \rangle = \frac{1}{2m} m k T = \frac{1}{2} k T \quad \checkmark$$

Similarly

$$\langle U \rangle = \frac{1}{2} m \omega_0^2 \langle x^2 \rangle = \frac{1}{2} m \omega_0^2 \left( \frac{kT}{m \omega_0^2} \right) = \frac{1}{2} kT$$

The h

$$\langle E \rangle = \langle U \rangle + \langle K \rangle = kT$$

Thus each oscillator consists of two dof.

$$2 \times \frac{1}{2} kT = kT$$

d) The energy is

$$U = N \left( \underset{\substack{\uparrow \\ \text{translations}}}{3 \times \frac{1}{2} k_B T} + 2 \underset{\substack{\uparrow \\ \text{rotations}}}{\frac{1}{2} k_B T} + 2 \times \underset{\substack{\uparrow \\ \text{vibrations}}}{\frac{1}{2} k_B T} \right)$$

$$= N \frac{7}{2} k_B T$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{7}{2} N k_B$$

$$C_P = C_V + N k_B = \frac{9}{2} N k_B$$

So for one mole

$$C_p^{\text{int}} = N_A \frac{9}{2} k_B = \frac{9}{2} R$$

So at the highest temperature it agrees.



## Two State

Then

$$Z = \sum_n e^{-\beta E_n}$$

$$-\frac{\partial Z}{\partial \beta} = \sum_n E_n e^{-\beta E_n}$$

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

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

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

### Problem 5

(b)  $V = \frac{NkT}{p}$

$$\beta_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{Nk}{pV} = \frac{1}{T}$$

(c)  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = +\frac{1}{V} \left( \frac{NkT}{p^2} \right) = \frac{1}{p}$

(d)  $dQ = 0 \quad du = -p dV$

Then  $C_v dT = -p dV$

So

$$dV = \frac{1}{\beta_p} dT - V \kappa_T dp$$

$$= -\frac{V \beta_p p}{C_v} dV - V \kappa_T dp$$

$$\left( 1 + \frac{V NkT}{C_v} \right) dV = -V \kappa_T dp$$

$$\frac{C_p}{C_v} dV = -V \kappa_T dp$$

So

$$K_s = -\frac{1}{V} \left( \frac{dV}{dP} \right)_{\text{adiab}} = \frac{\gamma}{\gamma}$$

e)

So

$$C_s = \left( \frac{\gamma}{\rho K_T} \right)^{1/2} = \left( \frac{\gamma n k T}{\rho} \right)^{1/2} = \left( \gamma \frac{k T}{m} \right)^{1/2}$$



$$K_T = \frac{1}{P} = \frac{1}{n k T}$$

So inserting avagadros number

$$C_s = \left( \gamma \frac{N_A k T}{N_A m} \right)^{1/2} = \left( \gamma \frac{R T}{m_{\text{mol}}} \right)^{1/2} = \left( \frac{1.4 \times 8.325 \times 300}{28 \text{ g}} \right)^{1/2}$$



$$\text{molar mass} = 353 \text{ m/s}$$

$\gamma = \frac{7}{5}$  for diatomic molecules

of  $N_2$  28g

f)

The frequency of 440 Hz corresponds to a period of  $\sim 2 \text{ ms}$  this is way too short for heat conduction in the gas.



## Otto Cycle

- Between  $1 \rightarrow 2$  we have

$$\Delta u = \cancel{Q} + W_{12}$$

So

see next item

$$W_{12} = C_v \Delta T_{12} = C_v T_2 \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

- Now  $1 \rightarrow 2$  is adiabatic

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{So } \Delta T_{12} = T_1 (r^{\gamma-1} - 1)$$

$$\left(\frac{T_2}{T_1}\right) = r^{\gamma-1} \quad \text{so}$$

- Then for  $2 \rightarrow 3$

$$C_v \Delta T_{23} = Q + \cancel{W}$$

$$\Delta T_{12} = T_2 \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

$$\Delta T_{23} = \frac{Q_{in}}{C_v}$$

- Then similarly for  $3 \rightarrow 4$

$$\Delta u = W$$

$$T_4 = T_3 \left(\frac{V_3}{V_4}\right)^{\gamma-1} = T_3 \frac{1}{r^{\gamma-1}}$$

$$\Delta u = C_v (T_4 - T_3)$$

$$\Delta W = -C_v T_3 \left(1 - \frac{1}{r^{\gamma-1}}\right) = W_{34}$$

So

$$= Q_{in}$$

$$W_{net} = W_{34} + W_{12} = -C_V (T_3 - T_2) \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

Finally

$$\eta = -\frac{W_{net}}{Q_{in}} = + \frac{Q_{in}}{Q_{in}} \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

$$\boxed{\eta = 1 - \frac{1}{r^{\gamma-1}}}$$

b) For 1 mol

$$pV = Nk_B T$$

$$V = \frac{N k_B T}{p} = \frac{RT}{p} = \frac{8.32 \frac{J}{mol \cdot K} \cdot 300 K}{10^5 N/m^2} = 25.2$$

Now the volume of the cylinder is 2.5L  
So

$$\frac{2.5L}{25L} = \frac{n_{ml}}{1 \text{ mol}} \Rightarrow \boxed{n_{ml} = 0.1}$$

c) We use

$$\boxed{1 \rightarrow 2} \quad T_f = T_i \left( \frac{V_i}{V_f} \right)^{\gamma-1} \quad P_f = P_i \left( \frac{V_i}{V_f} \right)^{\gamma}$$

$$T_2 = T_1 r^{\gamma-1}$$

$$P_2 = P_1 r^{\gamma}$$

$$V_2 = V_1 / r$$

$$\underline{T_2 = 689 \text{ } ^\circ\text{K}}$$

$$\underline{P_2 = 18.4 \text{ b}}$$

$$\underline{V_2 = 0.3 \text{ L}}$$

$$\Delta U_{12} = W_{1 \rightarrow 2} = C_v (T_f - T_i) = C_v T_i (r^{\gamma-1} - 1)$$

Now  $C_v T_i = U_i$ , for 1 mol we have

$$C_v^{1\text{mol}} = \frac{5R}{2}$$

$$C_v^{0.1\text{mol}} = 0.1 \times \frac{5R}{2} = 0.832 \frac{\text{J}}{^\circ\text{K}} \times \frac{5}{2} = 2.08 \frac{\text{J}}{^\circ\text{K}}$$

$$\underline{\Delta U_{12} = \Delta W_{12} = 810 \text{ J}, \quad Q = 0}$$

$\boxed{2 \rightarrow 3}$

Now

$$\underline{\Delta U_{23} = Q_{in} + \overset{0}{W} = 2,200 \text{ J} \quad W = 0}$$

$$C_v (T_3 - T_2) = Q_{in}$$

$$Q_{in} = 0.1 \text{ mol} \times \frac{22,000 \text{ J}}{\text{mol}} = 2,200 \text{ J}$$

$$\underline{T_3 = T_2 + \frac{Q_{in}}{C_v} = 1747 \text{ } ^\circ\text{K}}$$

$$P_3 = \frac{Nk_B T}{V}$$

$$\frac{P_3}{P_2} = \frac{T_3}{T_2}$$

$$\underline{P_3} = P_2 \frac{T_3}{T_2} = \underline{46,5 \text{ b}}$$

$$\underline{V_3 = 0,3 \text{ L}}$$

3 → 4

$$\Delta U = \cancel{Q} + W$$

$$\Delta U = C_v (T_f - T_i)$$

$$= -C_v T_i \left(1 - \frac{1}{r^{\gamma-1}}\right)$$

$$\underline{W_{34} = \Delta U = -2052 \text{ J}}$$

4 → 1

$$\Delta U = Q + \cancel{W}$$

$$C_v (T_1 - T_4) = Q$$

$$\underline{\Delta U = Q = -958 \text{ J}}$$

$$W = 0$$

Adiabatic

$$T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$$

$$T_4 = T_3 \frac{1}{r^{\gamma-1}}$$

$$\underline{T_4 = 760^\circ \text{ K}}$$

$$\underline{\frac{P_4}{P_1} = \frac{T_4}{T_1} = 6,33 \text{ b}}$$

$$\underline{V_4 = 2,5 \text{ L}}$$

As a quick check we note

$$W_{\text{net}} = W_{12} + W_{34} = -1242.5$$

$$Q_{\text{in}} = 2200.5$$

So

$$\eta = \frac{|W|_{\text{net}}}{Q} = 0.56$$

which should be compared  
with  $1 - \frac{1}{r^{x-1}} = 1 - \frac{1}{8^{x-1}} \approx 0.56$