

8/31

Last time:

Classical ideal gas (monoatomic)

- High  $T$
- Low  $n$
- $N$  non-interacting particles (point-like) in volume  $V$ .
- No spatial correlation between molecules.
- No overlap of wave packets for each particle.

How to find  $\Omega(N, E, V)$ ?

$$\Omega(N, E, V) \propto V^N = \underbrace{\Omega(N, E)}_A V^N = A V^N$$

Since each particle can be anywhere in  $V$   
the number of microstates has to be proportional  
to  $V$ .

We saw last time that  $dS = \frac{dE}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$

$$\begin{aligned} \therefore \frac{P}{T} &= \left. \frac{\partial S}{\partial V} \right|_{E, N} = k \left. \frac{\partial \ln \Omega}{\partial V} \right|_{N, E} = k \left. \frac{\partial \ln A V^N}{\partial V} \right|_{N, E} \\ &= k A \frac{N V^{N-1}}{A V^N} = \frac{k N}{V} = k n \quad \rightarrow \text{density.} \end{aligned}$$

$$\therefore \frac{P}{T} = \frac{Nk}{V} \Rightarrow \boxed{PV = NkT}$$

ideal gas  
equation of  
state.

- obtained empirically at the lab.
- obtained from kinetic theory
- Now obtained from statistics.

$$PV = NkT = \underbrace{V}_{\substack{\downarrow \\ \gamma N_A}} \underbrace{N_A}_{\substack{\downarrow \\ \# \text{ of moles}}} \underbrace{k}_{\substack{\downarrow \\ R}} T = \gamma R T$$

To obtain other properties of the gas we need to find  $\Omega(E, N)$ :

We need to find out in how many ways we can satisfy the following equations:

$$E = \sum_i n_i \epsilon_i \quad \text{and} \quad N = \sum_i n_i$$

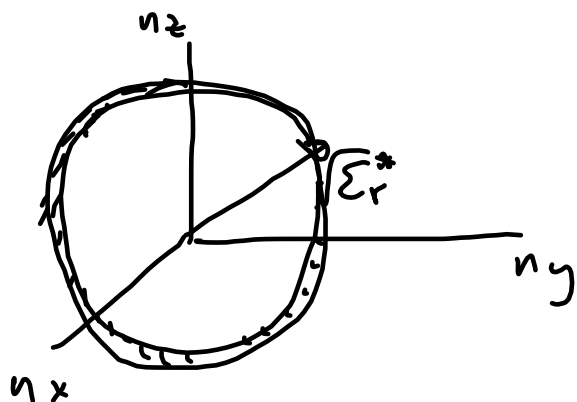
$\epsilon_i$  come naturally from quantum mechanics and arbitrarily in classical mechanics.

Consider a non-relativistic particle of mass  $m$  in a box of volume  $V = L^3$ . If  $\psi = 0$  at the walls:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = \epsilon_r \psi$$

$$\epsilon_r \equiv \epsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad n_i = 1, 2, 3, \dots$$

The # of states for one single particle with energy  $\epsilon_r$  are in a shell of a sphere of radius  $\sqrt{\epsilon_r}$  in  $(n_x, n_y, n_z)$ -space



$$n_x^2 + n_y^2 + n_z^2 = \frac{8mL^2 \epsilon_r}{h^2} = \frac{8mV^{2/3} \epsilon_r}{h^2} = \epsilon_r^*$$

For  $N$  independent particles

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}}{h^2} E = E^*$$

We see that the # of microstates will depend on the combination  $V^{2/3} \bar{E}$  then

$$S(N, V, E) \equiv S(N, V^{2/3} E)$$

if  $S$  and  $N$  are constant

(adiabatic process)  
reversible

$$V^{2/3} \bar{E} = \text{constant} = C$$

no heat exchanged.

$$\therefore \bar{E} = C V^{-2/3}$$

$$\begin{aligned} \therefore P &= - \left. \frac{\partial \bar{E}}{\partial V} \right|_{N, S} = + C \frac{2}{3} V^{-5/3} = C \frac{2}{3} V^{-4/3} V^{-1} = \\ &= \frac{2}{3} \frac{\bar{E}}{V} \end{aligned}$$

Since  $PV = NkT \Rightarrow P = \frac{NkT}{V}$

and  $\frac{NkT}{V} = \frac{2}{3} \frac{E}{V} \therefore \boxed{E = \frac{3}{2} NkT}$  Theorem of energy equipartition.

Since  $E \propto T \Rightarrow V^{2/3} E \propto V^{2/3} T = \text{constant}$  adiabatic condition for the ideal gas.

$V^{\gamma-1} T = \text{constant}$  in an adiabatic process  
 $\gamma$  depends on the system

For ideal gas  $\gamma = 5/3$ .

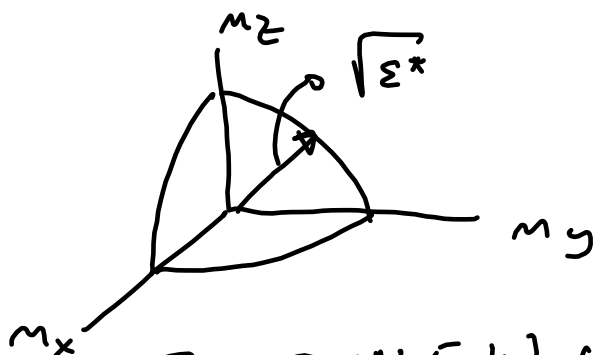
Also  $P = \frac{2}{3} \frac{E}{V} = \frac{2}{3} \frac{\overbrace{E V^{2/3}}^C}{V V^{2/3}} = \frac{2C}{3V^{5/3}} \therefore PV^{5/3} = \text{constant}$   
 in adiabatic process.

Evaluation of  $\Omega$ :

Classical gas: Distinguishable particles.  
(we can identify each individual molecule).

$\circ_i \quad \bullet_j \neq \bullet_i \quad \circ_j$

Quantum mechanical:  $\Omega(N, \epsilon, V)$



$$\epsilon^* = \frac{8mV^{2/3}\epsilon}{h^2} = u_x^2 + u_y^2 + u_z^2$$

The points on the surface of the sector give us  $\Omega(N, \epsilon, V)$

For  $\Omega(N, \epsilon, V)$  we need the points on the surface of the hypersector of radius  $\sqrt{\epsilon^*}$ .



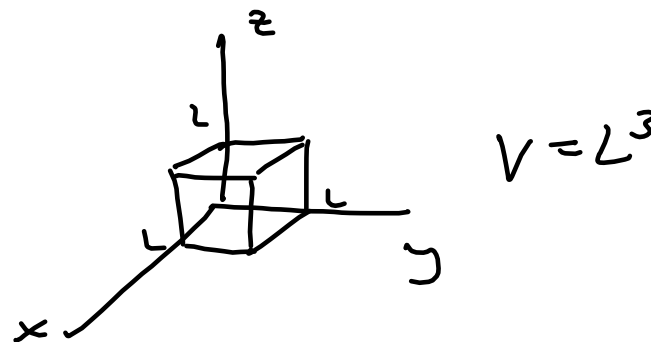
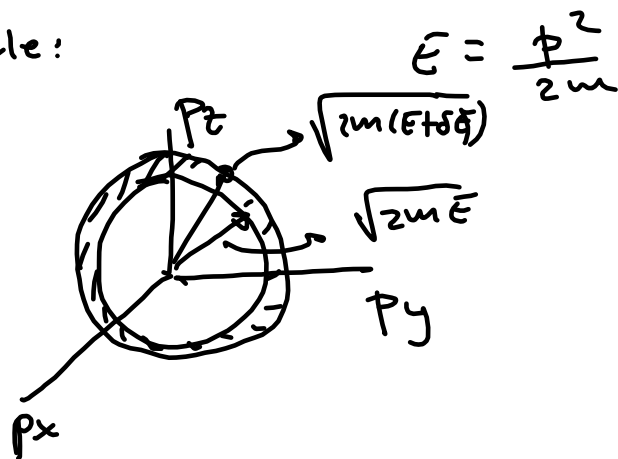
See section 1.4 in Pathria for details.

We will now consider a classical approach.

$$K = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad E = K \quad \text{only kinetic energy.}$$

How many states are possible within energy  $\bar{E}$  and  $\bar{E} + \delta\bar{E}$ .

1 particle:



$$\Omega(N, E, V) \propto (2mE)^{3/2} V \delta E$$

For  $N$  particles

$$\Omega(N, E, V) \propto (2mE)^{\frac{3N}{2}} V^N \delta E$$

$$\therefore \ln \Omega \approx N \ln V + \frac{3N}{2} \ln E + \text{constant}$$

$$S = k \ln \Omega = k N \ln V + \frac{3Nk}{2} \ln E + \text{constant}$$

Compare with

$$S = Nk \ln V + \frac{3Nk}{2} \ln E + \frac{3}{2} Nk \left( 1 + \ln \frac{4\pi m}{3Nh^2} \right)$$

From 1.4 Pathria.

Now we can obtain:

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N,V} = \frac{3Nk}{2E} \Rightarrow E = \frac{3}{2} NkT$$

$$C_V = \left. \frac{dE}{dT} \right|_V = \frac{3}{2} Nk$$

Also from  $S$  we can get  $E = E(S, V, N)$ :

$$\ln E = (S - kN \ln V - C) \frac{2}{3Nk}$$

$$E = C' e^{\frac{2S}{3Nk}} V^{-2/3}$$

This is how  $E$  can be obtained from  $S$ .

then:

$$P = - \left. \frac{\partial E}{\partial V} \right|_{N,S} = \frac{2}{3} \frac{E}{V} = \frac{2}{3} \frac{3}{2} \frac{NkT}{V} = \frac{NkT}{V} \quad \text{eq. of state.}$$

$$C_p = \left. \frac{\partial H}{\partial T} \right|_{N,P} = \left. \frac{\partial (E + PV)}{\partial T} \right|_{N,T} = \frac{\partial}{\partial T} \left( \frac{3}{2} NkT + NkT \right) =$$

$$= \frac{5}{2} Nk$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2} Nk}{\frac{3}{2} Nk} = \frac{5}{3}$$

Gibbs paradox:

We found that

$$S(N, V, E) = Nk \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3Nk}{2} \quad (1)$$

(from Patricia)

If  $N \rightarrow \alpha N$ ,  $V \rightarrow \alpha V$ ,  $E \rightarrow \alpha E$   
 we expect  $S \rightarrow \alpha S$  as an extensive property should  
 do:

$$S(\alpha N, \alpha V, \alpha E) = \alpha Nk \ln \left[ \frac{\alpha V}{h^3} \left( \frac{4\pi m \alpha E}{3\alpha N} \right)^{3/2} \right] + \frac{3\alpha Nk}{2} \neq \alpha S$$

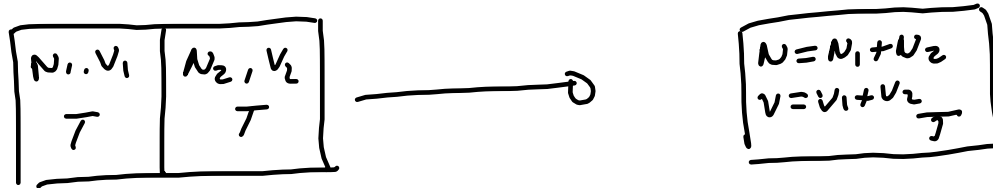
problem

We see that

$$S_T \neq \sum_i S_i$$

entropy of the whole is not  
 equal to the sum of the  
 entropy of the parts.

Another way of seeing the problem is by looking at the entropy of mixing:



Before:

$$S_i = N_i k \ln V_i + \frac{3}{2} N_i k \left\{ 1 + \ln \left( \frac{2\pi m_i k T}{h^2} \right) \right\}$$

$$S_0 = \sum_{i=1}^2 S_i \quad i=1,2$$

After

$$S_T = \sum_{i=1}^2 \left[ N_i k \ln V + \frac{3}{2} N_i k \left\{ 1 + \ln \left( \frac{2\pi m_i k T}{h^2} \right) \right\} \right]$$

$$V = V_1 + V_2$$

$$\Delta S = S_T - \sum_{i=1}^2 S_i = k \left[ N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right]$$

$> 0.$

irreversible process.  
disorder increases.

Notice that if  $\frac{N_1}{V_1} = \frac{N_2}{V_2}$  (equal densities)

$$\frac{V_1 + V_2}{V_1} = \frac{V_1 \frac{N_1}{V_1} + V_2 \frac{N_2}{V_2}}{V_1 \frac{N_1}{V_1}} = \frac{N_1 + N_2}{N_1}$$

and

$$\frac{V_1 + V_2}{V_2} = \frac{N_1 + N_2}{N_2}$$

$$\therefore (\Delta S)^* = k \left[ N_1 \ln \left( \frac{N_1 + N_2}{N_1} \right) + N_2 \ln \left( \frac{N_1 + N_2}{N_2} \right) \right] > 0$$

fixed density

But what happens if both gases are the same?

$(\Delta S)^* > 0$  but it should be zero!

Gibbs paradox!!!