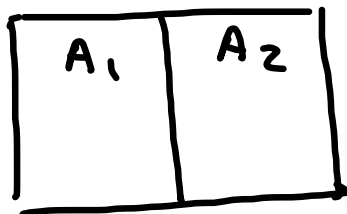


Last time:

8/23



in equilibrium

$$\beta_1 = \beta_2 \longrightarrow$$

it wall allows  $E$  exchange

$$\mu_1 = \mu_2 \longrightarrow$$

movable wall

$$\xi_1 = \xi_2 \longrightarrow$$

porous wall

$$\beta = \frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E} \Big|_{N, V}$$

$$\xi = \frac{\partial \ln \Omega}{\partial N} \Big|_{E, V}$$

$$\mu = \frac{\partial \ln \Omega}{\partial V} \Big|_{N, E}$$

What are  $\xi$  and  $\mu$  related to?

From thermodynamics we know that

$$\bar{E} = E(S, N, V)$$

$$d\bar{E} = \underbrace{\frac{\partial \bar{E}}{\partial S}}_{\frac{1}{T}} \bigg|_{N, V} dS + \underbrace{\frac{\partial \bar{E}}{\partial N}}_{\mu} \bigg|_{S, V} dN + \underbrace{\frac{\partial \bar{E}}{\partial V}}_{-P} \bigg|_{S, N} dV \quad (1)$$

From statistics we found  $S = k \ln \Omega$

$$\text{From (1) } dS = \frac{d\bar{E}}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

Then

$$\boxed{\mu} = \frac{\partial \ln \Omega}{\partial V} \bigg|_{N, \bar{E}} = \frac{1}{k} \frac{\partial S}{\partial V} \bigg|_{N, \bar{E}} = \boxed{\frac{1}{k} \frac{P}{T}}$$

And

$$\boxed{\xi = \frac{\partial \ln \Omega}{\partial N} \Big|_{E, V} = \frac{1}{k} \frac{\partial S}{\partial N} \Big|_{E, V} = - \frac{\mu}{kT}}$$

Then we see that the statistical equilibrium conditions are equivalent to thermodynamic equilibrium conditions:

$$\begin{array}{l} \beta_1 = \beta_2 \longrightarrow T_1 = T_2 \\ \eta_1 = \eta_2 \longrightarrow P_1 = P_2 \\ \xi_1 = \xi_2 \longrightarrow \mu_1 = \mu_2 \end{array}$$

Recipe to obtain thermodynamics from statistics:

- 1) For a macrostate  $(N, V, E)$  find  $\Omega(N, V, E)$  (# of compatible microstates).
- 2) Find  $S = k \ln \Omega \Rightarrow S(N, V, E)$
- 3) Obtain  $T$ ,  $P$  and  $\mu$  from derivatives of  $S$  with respect to  $E$ ,  $V$  and  $N$ :

$$\textcircled{1} \frac{1}{T} = \frac{\partial S}{\partial E} \Big|_{N, V} \quad \textcircled{2} \frac{P}{T} = \frac{\partial S}{\partial V} \Big|_{N, E} \quad \textcircled{3} -\frac{\mu}{T} = \frac{\partial S}{\partial N} \Big|_{V, E}$$

4) Alternatively you can obtain  $T$ ,  $P$ , and  $\mu$  from  $\bar{E}(S, N, V)$  obtained by inverting  $S(E, N, V)$

$$T = \frac{\partial \bar{E}}{\partial S} \Big|_{N, V}$$

$$P = \frac{\partial S}{\partial V} \Big|_{N, \bar{E}} = - \frac{\partial \bar{E}}{\partial V} \Big|_{S, N}$$

$$\mu = \frac{-\frac{\partial S}{\partial N} \Big|_{V, \bar{E}}}{\frac{\partial S}{\partial \bar{E}} \Big|_{N, V}} = \frac{\partial \bar{E}}{\partial N} \Big|_{S, V}$$

since  $\frac{\partial x}{\partial y} \Big|_z = \frac{-\frac{\partial z}{\partial x} \Big|_y}{\frac{\partial z}{\partial y} \Big|_x}$

$$= \frac{\partial z}{\partial x} \Big|_y$$

Other useful thermodynamic functions.

From  $\Omega \rightarrow S \rightarrow \bar{E} = \bar{E}(N, V, S)$

but it is hard to measure  $S$ .

We usually measure  $T$ , but if we know  $\bar{E}(T, V, N)$  we cannot find  $S$ !

However, we can use pairs of **conjugate** variables  $TS, PV, \mu N$ , etc. to define useful functions.

Helmoltz free energy  $F$  (book uses  $A$ )

$$F = E - TS$$

$$dF = dE - TdS - SdT = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT = -SdT - pdV + \mu dN$$

$$F = F(T, V, N) \quad \text{Now } S = -\left. \frac{\partial F}{\partial T} \right|_{V, N}$$

$V$  and  $T$  are easy to measure.

Gibbs free energy  $G$ :

$$G = F + PV = E - TS + PV = \cancel{TS} - \cancel{PV} + \mu N -$$

$$+ \cancel{TS} + \cancel{PV} = \mu N$$

$$dG = dF + PdV + VdP = -SdT + VdP + \mu dN$$

$$G = G(T, P, N)$$

Useful for processes  
in which  $V$  does not  
matter such as  
phase coexistence.



Enthalpy  $H$  (heat function)

$$H = E + PV$$

$$dH = dE + PdV + VdP = \underbrace{TdS}_{\delta Q} + VdP + \mu dN$$

$$H = H(S, P, N)$$

If  $dP = dN = 0$

$$dH = \delta Q$$

amount of transferred  
heat at constant  
pressure.

Specific heat:

$$Q = C \Delta T$$

↳ process dependent.

$$C_V = T \frac{\partial S}{\partial T} \Big|_{V, N} = \frac{\partial \bar{E}}{\partial T} \Big|_{V, N}$$

$$C_P = T \frac{\partial S}{\partial T} \Big|_{P, N} = \frac{\partial \bar{H}}{\partial T} \Big|_{P, N}$$

The classical ideal gas (monoatomic)

$\Omega(N, V, E)$  can be evaluated.

- High  $T$  and low  $N$  ( $\frac{N}{V}$  density) limit of real gases.
- $N$  non-interacting particles confined to a volume  $V$ .
- No spatial correlations between the molecules. (The probability of a molecule to be at  $\vec{r}$  not affected by position of other molecules).

- Negligible interactions.
- No overlap of wave packets for each particle  
(this allows classical instead of quantum treatment).

Then:

$$\Omega(N, \bar{E}, V) \propto V^N$$
$$\Omega(N, \bar{E}) V^N = A V^N \quad \textcircled{1}$$

We found before that

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

Then

$$\frac{P}{T} = \frac{k N}{V} \text{ or}$$

$$\boxed{PV = NkT}$$

equation  
of  
state.

$$PV = NkT$$

$$N = n N_A$$

$$PV = n \underbrace{N_A k}_R T$$

↪ # of moles

$$\boxed{PV = nRT} \text{ eq. of state.}$$

For other properties of the gas we need to evaluate  $\Omega(E, N)$ .

We need to find out in how many ways

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

In quantum mechanics

$$E = \sum_{r=1}^{3N} \epsilon_r$$

↓  
 $n_x, n_y, n_z$

3N # of degrees  
of freedom for  
N free particles  
in 3D (3 components  
of  $\vec{p}$ ).  
All kinetic  
energy.

The  $V$  dependence of  $\Omega$   
arises from the  $V$  dependence  
of  $\epsilon_r$ .

Non-relativistic particles of mass  $m$  in a  
box of volume  $V = L^3$  with  $\psi = 0$  on the walls.

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

If  $\epsilon_r$  is very large so is the # of combinations of  $n_i$ 's compatible with it.

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

$\Omega(1, \epsilon, V)$  is the # of  $\{n_i\}$  that leads to energy  $\epsilon$  for one particle.



Then for  $N$  particles

$$\sum_{r=1}^{3N} m_r^2 = \frac{8 m V^{2/3} \bar{E}}{h^2} = E^*$$

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

↪ because the # of states increases according to this combination.

If  $dS = dN = 0$  (adiabatic process)

$$\text{then } V^{2/3} \bar{E} = \text{constant.} \Rightarrow \bar{E} = C V^{-2/3}$$

$$\therefore P = -\left. \frac{\partial \bar{E}}{\partial V} \right|_{N, S} = C \frac{2}{3} V^{-5/3} = \frac{2}{3} \frac{\bar{E}}{V}$$

$$P = \frac{2}{3} \frac{E}{V} \quad \text{and since} \quad PV = NkT \Rightarrow P = \frac{NkT}{V}$$

$$\frac{NkT}{V} = \frac{2}{3} \frac{E}{V} \quad \text{or} \quad \boxed{E = \frac{3}{2} NkT}$$

equipartition of energy ( $\frac{1}{2} kT$  per degree of freedom)

$$\text{Since } E \propto T \Rightarrow V^{2/3} E \propto V^{2/3} T = \text{constant}$$

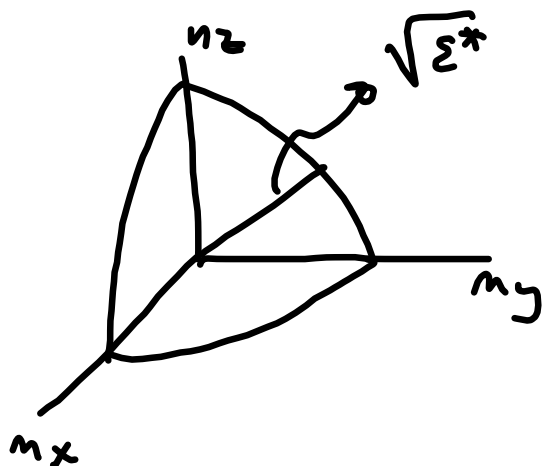
3N d.o.f. for ideal gas.  
(for  $dS=0$ )

$$V^{\gamma-1} T = \text{constant (adiabatic condition)}$$

$$\text{Then } \gamma - 1 = \frac{2}{3} \Rightarrow \gamma = \frac{5}{3}$$

Evaluation of  $\Omega$ :

Classical approach: Distinguishable particles.



$$\begin{array}{ccccc} \bigcirc & \bullet & \neq & \bullet & \bigcirc \\ i & j & & i & j \end{array}$$

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

The points on the surface of the sector of radius  $\sqrt{\epsilon^*}$  gives us  $\Omega(1, \epsilon, V)$ .

For  $\Omega(N, \epsilon, V)$  we need the points in a shell of radius  $\sqrt{\epsilon}$  in  $3N$  space.

See section 1.4 in Pathria for details of the calculation.

He finds that

$$\ln \Omega(N, E, V) \approx N \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N$$

then

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

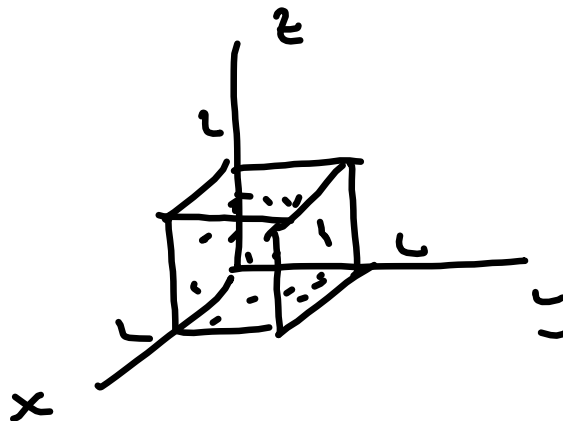
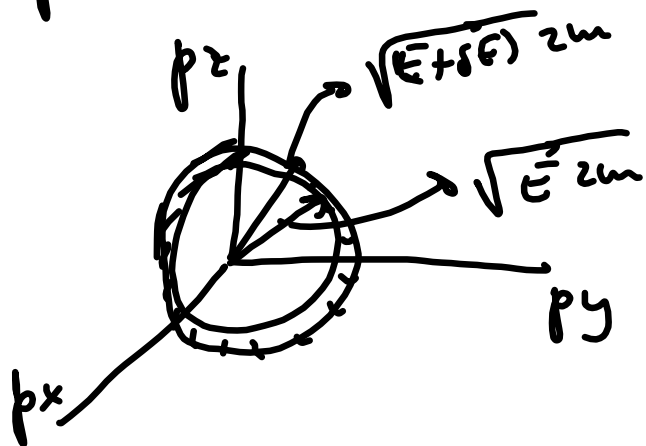
You see that  $\Omega \propto V^N$  and  $V^{2/3} E$  is the  $VE$  dependence.

Classical gas:

$$K = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad V = L^3$$

If  $E$  is in the interval  $E, E + \delta E$  how many states are compatible with that?

1 particle: 6D space



$$\Omega(1, E, V) \propto (2mE)^{3/2} V \delta E$$

For  $N$  particles

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

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

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

Compare with S quantum:

$$S_q = Nk \ln V + \frac{3Nk}{2} \ln E + \frac{3}{2} Nk \left[ 1 + \ln \frac{4\pi m}{3Nh^2} \right]$$