

Lecture 9

Recall idea of stat mech:

Macrostate = thermodynamic state
defined by thermo variables
say (E, N, V)

Microstate = complete (up to QM limits)
description of state of each particle

Many microstates correspond to each macrostate
number = $\Omega(E, N, V)$

Basic postulate:

$$\text{Entropy } S = k_B \ln \Omega$$

Get all thermo from this

Today: see how this works by calculating Ω
for monatomic ideal gas, mass m atoms

Assume box, side L , volume $V = L^3$

From QM, know allowed energies for each particle

$$E = \{j_x j_y j_z\} = \frac{h^2}{8mL^2} (j_x^2 + j_y^2 + j_z^2)$$

$$j\text{'s} = 1, 2, 3, \dots$$

For N particles, have total energy

$$E = \sum_{i=1}^N \frac{h^2}{8mL^2} (j_{ix}^2 + j_{iy}^2 + j_{iz}^2)$$

$$\equiv \frac{h^2}{8mL^2} \sum_{r=1}^{3N} j_r^2 \quad \text{reliable subscripts}$$

$$E = \frac{h^2}{8mV^{2/3}} \sum j_r^2$$

So given E, V, N , $\Omega = \#$ of ways we can choose set $\{j_r\}$ to satisfy eqn

Or in dimensionless form, need

$$\sum j_r^2 = \frac{8mEV^{2/3}}{h^2} \equiv E^*$$

Assume for now that particles are distinguishable

Then each possible set $\{j_r\}$ is a distinct microstate

If particles were identical, would need to worry about over-counting, since exchanging j 's for any pair of particles would not change state.

Deal with that later.

Now, $\sum j_r^2 = E^*$ defines $3N$ -dimensional sphere
radius = $\sqrt{E^*}$

Then $\Omega = \#$ of positive integer points lying on sphere

Immediately run into trouble

expect few points to lie on sphere

many points arbitrarily close

Since E is never perfectly well-defined,
should really allow range of energies Δ :

$$E^* - \frac{\Delta}{2} \leq \sum_j j_r^2 \leq E^* + \frac{\Delta}{2}$$

Define $\Gamma(E^*; \Delta) = \#$ of points in this shell

$$\text{So } \Omega = \lim_{\Delta \rightarrow 0} \Gamma$$

Hope that answers don't depend on Δ
(they won't)

Easiest to get Γ by defining

$$\Sigma(E^*) = \# \text{ of points with } \sum_j j_r^2 \leq E^*$$

$$\text{Then } \Gamma(\Delta) = \Sigma(E^* + \frac{\Delta}{2}) - \Sigma(E^* - \frac{\Delta}{2})$$

Remember, only allow $j_r > 0$:

$$\text{So } \Sigma(E^*) \approx \left(\frac{1}{2}\right)^{3N} \times (\text{volume of } 3N\text{-sphere})$$

How to calculate volume of n -sphere:

$$\text{Start with } \int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

$$\text{so } \int \dots \int e^{-\sum_{i=1}^n x_i^2} dx_1 \dots dx_n = \pi^{n/2}$$

$$\text{But } dx_1, \dots, dx_n = S_n R^{n-1} dR$$

$$\text{for } R^2 = \sum x_i^2$$

$$\text{and } S_n R^{n-1} = \text{surface area of } n\text{-sphere}$$

$$\text{So, } \int_0^\infty e^{-R^2} S_n R^{n-1} dR = \pi^{n/2}$$

$$\text{Consider } \int_0^\infty e^{-R^2} R^{n-1} dR$$

$$u = R^2$$

$$du = 2R dR$$

$$\rightarrow \frac{1}{2} \int_0^\infty e^{-u} u^{n/2} du$$

$$\equiv \frac{1}{2} \Gamma\left(\frac{n}{2}\right)$$

$$\text{Let's take } n \text{ even ... } \Gamma\left(\frac{n}{2}\right) = \left(\frac{n}{2} - 1\right)!$$

$$\text{So, get } S_n \frac{1}{2} \left(\frac{n}{2} - 1\right)! = \pi^{n/2}$$

$$\begin{aligned} \text{But also know volume } V_n &= \int_0^R S_n r^{n-1} dr \\ &= \frac{1}{n} S_n R^n \end{aligned}$$

$$\text{Gives } V_n = R^n \cdot \frac{1}{n} \frac{\pi^{n/2}}{\frac{1}{2} \cdot \left(\frac{n}{2} - 1\right)!} = \boxed{R^n \frac{\pi^{n/2}}{\left(\frac{n}{2}\right)!}}$$

Applying to our problem, see

$$\Sigma(E^*) = \left(\frac{1}{2}\right)^{3N} (E^*)^{3N/2} \frac{\pi^{3N/2}}{(3N/2)!}$$

$$E^* = \frac{8mEV^{2/3}}{h^2}$$

So

$$\begin{aligned} \Sigma(E, N, V) &= \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} \left(\frac{4V^{2/3}}{h^2}\right)^{3N/2} (2mE)^{3N/2} \\ &= \boxed{\left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}} \end{aligned}$$

OK, we want

$$\begin{aligned} S &= k_B \ln \Omega \approx k_B \ln \Gamma \\ &= k_B \ln \left[\Sigma(E + \frac{\Delta}{2}) - \Sigma(E - \frac{\Delta}{2}) \right] \\ &\approx k_B \ln \left[\Delta \frac{\partial \Sigma}{\partial E} \right] \end{aligned}$$

Since $\Sigma = \left(\frac{1}{2}\right)^{3N} E^{3N/2}$

$$\begin{aligned} \text{have } \frac{\partial \Sigma}{\partial E} &= \frac{3N}{2} \left(\frac{1}{2}\right)^{3N} E^{\frac{3N}{2} - 1} \\ &= \frac{3N}{2} \frac{\Sigma}{E} \end{aligned}$$

$$\begin{aligned} \text{and } S &= k_B \ln \left[\frac{3N}{2} \Sigma \frac{\Delta}{E} \right] \\ &= k_B \left[\ln \Sigma + \ln \frac{3N}{2} + \ln \frac{\Delta}{E} \right] \end{aligned}$$

See problem as $\Delta \rightarrow 0$

But as long as Δ not too small, OK

For instance, take $\Delta \sim \frac{E}{N}$

For large N , even this would be impossible
for current measurements

Then have $\ln \frac{\Delta}{E} \sim -\ln N$

and $S = k_B [\ln \Sigma + O(\ln N)]$

But $\ln \Sigma = N \ln \frac{V}{h^3} + \frac{3N}{2} \ln(2\pi m E) - \ln \left(\frac{3N}{2}\right)!$

Use Stirling approx: $\ln n! \approx n \ln n - n$

Then $\ln \Sigma \approx N \left\{ \ln \left[\frac{V}{h^3} (2\pi m E)^{3/2} \right] - \frac{3}{2} \ln \frac{3N}{2} + \frac{3}{2} \right\}$
 \sim order N

Much larger than $\ln N$ terms

So, neglect extra terms

Leaves

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

Indep of Δ (as long as Δ not too small)

In fact, could have just said $S = k_B \ln \Sigma$

count all microstates with energy $\leq E$

Why?

of microstates grows very fast w/ E
 \Rightarrow # of states w/energy near E dominates
 # w/energy $\leq E$

So does our S make sense?

Expect $\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V, N}$

$$= N k_B \cdot \frac{3}{2} \cdot \frac{1}{E}$$

or $E = \frac{3}{2} N k_B T$ as expected

Plus in to get $S(T, V, N)$:

$$= N k_B \left\{ \ln \left[\frac{V}{h^3} \left(\frac{2\pi m k_B T}{N} \right)^{3/2} \right] + \frac{3}{2} \right\}$$

$$\sim N k_B \ln V T^{3/2} + \text{const}$$

as we got from thermo ✓

However!

In reality, particles aren't distinguishable
 Need to account for this

Really should count microstates differently

Say $n_j = \#$ of particles with energy ϵ_j

(really $n_{j_1 j_2 j_3}$ since $\epsilon = \epsilon_{j_1 j_2 j_3}$)

Don't try to say which atom in which state

Then microstate defined by $\{n_i\}$

vs $\{j_r\}$ before

Clear that each $\{n_i\}$ state corresponds to
many $\{j_r\}$ states
= # of permutations of the j_r 's

From combinatorics, # of permutations of N
objects over states $\{n_i\}$ is

$$P(\{n_i\}) = \frac{N!}{n_1! n_2! \dots}$$

Dealing with this correctly is job of quantum SM.
We'll do later,

For now, suppose gas hot & low density
 \Rightarrow many more states available than particles

Then chance of $n_i > 1$ is small

Since $0! = 1! = 1$, take $P(\{n_i\}) \rightarrow N!$

So to account for this, we can just reduce
 Ω (or Σ) by $N!$

$$S \rightarrow N k_B \left\{ \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} + \frac{3}{2} \right] - k_B (N \ln N - N) \right\}$$

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

Still have $E = \frac{3}{2} NkT$

So

$$S(T, V, N) = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

Sackur-Tetrode eqn

Remember as

$$S = Nk \left\{ \frac{5}{2} - \ln \rho/\rho_Q \right\}$$

$$\rho = \frac{N}{V}$$

$$\rho_Q = \frac{1}{\Lambda^3} \quad \text{for} \quad \Lambda = \sqrt{\frac{h^2}{2\pi m kT}}$$

"Thermal de Broglie wavelength"

\approx de Broglie wavelength of particle with $\epsilon = kT$

So $\rho/\rho_Q = \#$ of particles w/in a de Broglie λ of each other

Our counting method valid for $\rho/\rho_Q \ll 1$

"Classical" gas, quantum effects not important.

Note $S \rightarrow A$ const as $T \rightarrow 0$

Violates 3rd law

But classical appx isn't valid as $T \rightarrow 0$,
will be fixed in quantum derivation