2.5 Ideal Gas

The multiplicity of an ideal gas can be found from the eigen energies of particle in box.

Remember for 1-dimension $E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} = \frac{h^2 n^2}{8mL^2}$

For 3-dimension $E_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$

Unlike Harmonic oscillator, transferring quanta from 1 particle to another does <u>not</u> conserve energy.

However the quantum numbers are really big $\frac{hn}{2L} = P$
$\Rightarrow n = 2LP/h$ for N_2 at 300 m/s with $L = 1$ m gives
$n = 2 \times 1\,m \; 300\,m/s \; 4.7 \times 10^{-26}\,kg / 6.626 \times 10^{-34}\,Js = 4 \times 10^{10}$

Changing n by 1 is only $\sim 10^{-10}$ change in E for this example

1 particle — Start by looking at multiplicity for 1 atom/molecule

Let $\Omega(n)$ be number of states with $n_x^2 + n_y^2 + n_z^2$ between n^2 and $(n+1)^2$

To do this take advantage of $n \gg 1$, this is like doing integral for $\frac{1}{8}$ of spherical shell $\frac{1}{8} 4\pi r^2 \Delta r = \frac{\pi}{2} n^2$

$\Rightarrow \Omega_1(n) = \frac{\pi}{2} n^2 = \frac{\pi}{2} \frac{8mL^2}{h^2} E_n = \frac{\pi}{2}\left(\frac{2L}{h} P_n\right)^2$

2 particles — $E = \frac{h^2}{8mL^2}(n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2)$

~~$\Omega_2(n)$ is number of states with E between $\frac{h^2 n^2}{8mL^2}$ and $\frac{h^2 (n+1)^2}{8mL^2}$~~

To figure out number of states between n and $n+1$, figure out total total number of states $< n$ and take derivative $\frac{d}{dn}$

This trick will work in higher dimensions as well.
So detour to calculate volume of hypersphere

Volume of hypersphere d-dimension

$$V_d(R) \equiv \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty} \cdots \ \Theta\left(R - \sqrt{x_1^2 + x_2^2 + x_3^2 + \cdots}\right) dx_d\right] dx_{d-1} \cdots dx_1$$

$\Theta(x) = 1$ if $x > 0$ and 0 if $x < 0$

You should know $V_1(R) = 2R$, $V_2(R) = \pi R^2$, $V_3(R) = \frac{4\pi}{3} R^3$

How to go higher

$$V_4(R) = 2\pi \int_0^R V_2\left(\sqrt{R^2 - r^2}\right) r\,dr = 2\pi^2 \int_0^R (R^2 - r^2)\, r\,dr = 2\pi^2 \left(\frac{(R^2 - r^2)^2}{-4}\right)\Bigg|_0^R = \frac{\pi^2 R^4}{2}$$

$$V_6(R) = 2\pi \int_0^R V_4\left(\sqrt{R^2 - r^2}\right) r\,dr = \pi^3 \int_0^R (R^2 - r^2)^2\, r\,dr = \pi^3 \left(\frac{(R^2 - r^2)^3}{-6}\right)\Bigg|_0^R = \frac{\pi^3}{6} R^6$$

$$V_8(R) = 2\pi \int_0^R V_6\left(\sqrt{R^2 - r^2}\right) r\,dr = 2\pi^4 \frac{1}{6} \int_0^R (R^2 - r^2)^3\, r\,dr = 2\pi^4 \frac{1}{6} \left(\frac{(R^2 - r^2)^4}{-8}\right)\Bigg|_0^R = \frac{\pi^4}{24} R^8$$

If d is even $V_d(R) = \frac{\pi^{d/2}}{(d/2)!} R^d$

If you also restrict $x_1 > 0$, $x_2 > 0$, $x_3 > 0 \ldots$ $V_d(R) = \left(\frac{\pi}{4}\right)^{d/2} \frac{R^d}{(d/2)!}$

Back to ideal gas

If you have N particles $d = 3N$. The number of states with $E < \frac{h^2 n^2}{8mL^2}$ $\quad \beta(n) = \left(\frac{\pi}{4}\right)^{3N/2} \frac{n^{3N}}{(3N/2)!} \frac{1}{N!}$ ← for double counting

$$\Rightarrow \Omega_N(n) = \frac{d\beta(n)}{dn} = 3\left(\frac{\pi}{4}\right)^{3N/2} \frac{n^{3N-1}}{\left(\frac{3N}{2}\right)!} \frac{1}{(N-1)!}$$

This is the number of states between $E = \frac{h^2 n^2}{8mL^2}$ and $\frac{h^2 (n+1)^2}{8mL^2}$

Note $n \sim N \times$ (average n for 1 particle)

only for monatomic gas

In terms of thermodynamics variables E is internal/thermal energy U (in general $E = \frac{3}{f} U$)

$$\text{Use } n^2 = \frac{8mL^2}{h^2} U \Rightarrow \Omega_N(n) = 3\left(\frac{\pi}{4}\right)^{\frac{3N}{2}} \left(\frac{4L^2}{h^2}\right)^{\frac{3N-1}{2}} \frac{1}{\left(\frac{3N}{2}\right)!} \frac{1}{(N-1)!} (2mU)^{\frac{3N-1}{2}}$$

$$\Rightarrow \Omega_N(n) = \frac{3}{2} \frac{h}{L} \frac{V^N \pi^{\frac{3N}{2}}}{h^{3N}} \frac{(2mU)^{\frac{3N-1}{2}}}{\left(\frac{3N}{2}\right)!\,(N-1)!} \approx \frac{(2M\pi)^{3N/2}}{N!\left(\frac{3N}{2}\right)!\, h^{3N}} V^N U^{3N/2} = \Omega(U, V, N)$$

$n! = \sqrt{2\pi n}\; n^n e^{-n}$

Let's get an expression for Ω using Stirling's Approx.

$$\Omega \approx \left[\frac{(2m\pi U)^{3/2} V}{h^3}\right]^N \frac{1}{N!\left(\frac{3N}{2}\right)!} \approx \left[\frac{(2m\pi U)^{3/2} V}{h^3}\right]^N \frac{1}{\sqrt{2\pi N}} \left(\frac{e}{N}\right)^N \frac{1}{\sqrt{2\pi \frac{3N}{2}}} \left(\frac{2e}{3N}\right)^{3N/2}$$

$$\approx \frac{1}{N} \left[\frac{(2m\pi)^{3/2} (U/N)^{3/2} (V/N)\, e^{5/2}}{h^3} \left(\frac{2}{3}\right)^{3/2}\right]^N$$

Note that the main part of Ω depends on average single particle properties raised to the N^{th} power

monatomic gas

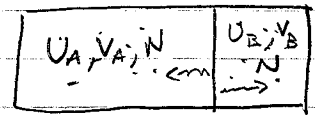
$\bar{E}_1 = U/N$ is average KE of 1 particle

$\bar{V}_1 = V/N$ is " volume occupied by 1 particle

$$\Omega = \frac{1}{N} \left[\left(\frac{4m\pi}{3}\right)^{3/2} \frac{\bar{E}_1^{3/2} V_1 e^{5/2}}{h^3}\right]^N$$

For non-monatomic gas $\bar{E}_1 = \frac{3}{f} \frac{U}{N}$

Suppose you have two interacting ideal gases



$N_A = N_B = N$ what $U_A = U - U_B$ gives largest Ω_{TOT}? wat $V_A = V - V_B$ gives largest Ω_{TOT}?

$$\Omega_{TOT} = (f(N))^2 \, [V_A V_B]^N \, (U_A U_B)^{3N/2} = [f(N)]^2 \, [V_A (V - V_A)]^N \, [U_A (U - U_A)]^{\frac{3N}{2}}$$

In general, for any variable $[s_A(s - s_A)]^{\gamma} \equiv y(s)$ (γ large)
has max at $s_A = s/2$

$s_A = \frac{s}{2} + x$ $\quad y = \left[\left(\frac{s}{2}\right)^2 - x^2\right]^{\gamma} = e^{\gamma \ln\left[\left(\frac{s}{2}\right)^2 - x^2\right]}$

$$y = e^{\gamma\left[\ln\left(\frac{s}{2}\right)^2 + \ln\left(1 - \left(\frac{x2}{s}\right)^2\right)\right]} \approx e^{\gamma \ln\left(\frac{s}{2}\right)^2} e^{-4\gamma x^2/s^2} = \left(\frac{s}{2}\right)^{\gamma} e^{-\frac{4\gamma}{s^2}x^2}$$

width $= \frac{s}{2}\frac{1}{\sqrt{\gamma}}$

For ideal gas Ω_{TOT} has max at $U_A = \frac{U}{2}$ with width $\frac{U}{2}\sqrt{\frac{2}{3}}\frac{1}{\sqrt{N}}$
" " " " $V_A = V/2$ " " $\frac{V}{2}\frac{1}{\sqrt{N}}$

A different question: Suppose you have N particles, what is the probability for finding all in the leftmost fraction, f

$$\text{Prob} = \frac{(fV)^N}{V^N} = f^N$$

Prob 2.27 Suppose $f = 0.99$ and $N = 100$ Prob $\stackrel{?}{=} 0.37$
$N = 1000$ Prob $= 4.3 \times 10^{-5}$
$N = 10000$ Prob $= 2 \times 10^{-44}$