Concluding Discussion on a Perfect Classical Gas

We found $\bar{E}^{int}$, S, and the ideal gas law

$$PV = NkT$$

T is absolute temperature. Actually, the equation proves $\Theta = T$ and another proof is with Carnot Energy.

$$E = \tfrac{3}{2}NkT + N\bar{\varepsilon}_{int} \qquad \bar{\varepsilon}_{int} = -\frac{\partial}{\partial\beta}\ln Z^{int} \qquad Z_1^{int} = \sum_\alpha e^{-\varepsilon_\alpha^{int}/kT}$$

Sum is over all internal states
ex. Diatomic Molecules
$\sum(\alpha_1 = \text{rot} \quad \alpha_2 = \text{rot} \quad \alpha_3 = \text{vib})$

What about electronic quantum states?
Not excited at room temperature $kT \sim 1/40\,eV$
whereas electron excitations $\sim 1eV$

When $\bar{n}_i \ll 1$ we saw that it doesn't matter if it is a fermion or a boson.

$$\bar{n}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \pm 1} \sim e^{-\beta(\varepsilon_i-\mu)} = e^{\beta\mu}\underbrace{e^{-\beta\varepsilon_i}} \quad \therefore \quad e^{\beta\mu} \ll 1$$

Classical limit damped exponential

$$\varepsilon_i = \varepsilon_s^{tr} + \varepsilon_\alpha^{int}$$

$$N = \sum \bar{n}_i = e^{\beta\mu}\sum_i e^{-\beta\varepsilon_i} = e^{\beta\mu}\underbrace{\sum_\alpha e^{-\beta\varepsilon_\alpha^{int}}}_{Z_1^{int}}\underbrace{\sum e^{-\beta\varepsilon_s^{tr}}}_{Z_1^{tr} = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}(2s+1)}$$

Convert this sum into an integral
Have to know the number of translational states between p and p+dp
and spin multiplicity

Memorize: $\boxed{N = e^{\beta\mu} Z_1^{int} V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}(2s+1)}$

Solve for $e^{\beta\mu} = \frac{N}{V}\underbrace{\frac{1}{Z_1^{int}}}_{<1}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\underbrace{\left(\frac{1}{2s+1}\right)}_{<1} \quad \therefore \ll 1$

$$\left(\frac{N}{V}\right)\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \ll 1 \text{ is classical gas}$$

dilute gas high Temp

Maxwell Distribution of Velocity of Molecules

Consider He gas at Room T and STP. The greater the mass, the easier to satisfy the condition. When you consider the conduction e-s in a gas, m is small. A quantum perfect gas is not a perfect classical gas.

Maxwell Distribution of Velocity

In a perfect classical gas: $\bar{n}(p) = e^{\beta\mu} - e^{-\beta(\varepsilon_s^{tr} + \varepsilon_\alpha^{int})}$

Write as the product of two things: $\bar{n}(p) = e^{\beta\mu} e^{-\beta\varepsilon_\alpha^{int}} \underbrace{\sum_\alpha e^{-\beta\varepsilon_\alpha^{int}}}_{Z_1^{int}} = e^{\beta\mu} Z_1^{int} e^{-\beta p^2/2m}$

This is the number of molecules per state.

$$dN = \bar{n}(p) \frac{V 4\pi p^2 dp}{h^3}(2s+1)$$

6-D phase space

1 per

$$dN = e^{\beta\mu} Z_1^{int} e^{-\beta p^2/2m} \frac{V 4\pi p^2 dp}{h^3}(2s+1)$$

Probability of getting a particle between p and p+dp

$$P(p)\,dp = \frac{dN}{N} = \frac{e^{\beta\mu} Z_1^{int} e^{-\beta p^2/2m} \left(\frac{V 4\pi p^2 dp}{h^3}\right)(2s+1)}{e^{\beta\mu} Z_1^{int} V \left(\frac{2\pi m k T}{h^2}\right)^{3/2}}$$

$$P(p)\,dp = \frac{4\pi}{(2\pi m k T)^{3/2}} e^{-p^2/2mkT} p^2 dp$$

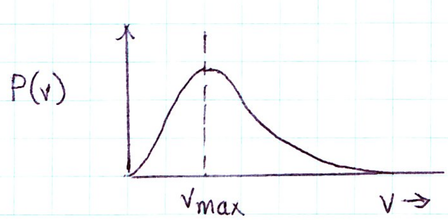
$$P(p)\,dp = \sqrt{\frac{2}{\pi}} \frac{1}{(mkT)^{3/2}} e^{-p^2/2mkT} p^2 dp$$

$p = mv$

$$P(v)\,dv = \sqrt{\frac{2}{\pi}} \frac{1}{(mkT)^{3/2}} e^{-\frac{1}{2}mv^2/kT} m^2 v^2 m\,dv$$

$$\boxed{P(v)\,dv = \sqrt{\frac{2}{\pi}} \left(\frac{m}{kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^2 dv}$$

when v is large e^{-v^2} dominates
v is small v^2 dominates



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Lecture 23 continued… Maxwell Distribution: $P(v)dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} e^{-\frac{1}{2}mv^2/kT} v^2 dv$

To find V_{max}:

$$\frac{dP}{dv} = 0$$

$$e^{-\frac{1}{2}mv_m^2/kT}(2v_m) + v_m^2 e^{-\frac{1}{2}mv_m^2/kT}(-mv_m/kT) = 0$$

$$V_m^2 = \frac{2kT}{m}$$

$$V_{max} = \sqrt{\frac{2kT}{m}} \quad \text{most probable speed}$$

$$\lim_{T\to\infty} V_{max} = \infty$$

To find average velocity:

$$\bar{v} = \int_0^\infty v P(v) dv \qquad \text{can show } \bar{v} = \sqrt{\frac{8kT}{\pi m}} = \frac{2}{\sqrt{\pi}} V_{max}$$

To find root mean square velocity:

$$\overline{v^2} = \int_0^\infty v^2 P(v) dv = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2}\int_0^\infty e^{-\frac{1}{2}mv^2/kT} v^4 dv \qquad \text{gaussian function}$$

make the integral dimensionless; $x = \frac{1}{2}mv^2/kT$

$$v^2 = \left(\frac{2kT}{m}\right)x$$

$$v = \sqrt{\frac{2kT}{m}}\, x^{1/2}$$

$$dv = \sqrt{\frac{2kT}{m}}\, \frac{1}{2} x^{-1/2} dx$$

$$\overline{v^2} = \sqrt{\frac{2}{\pi}}\left(\frac{m}{kT}\right)^{3/2} \frac{1}{2}\sqrt{\frac{2k}{m}}\left(\frac{2kT}{m}\right)^2 \int_0^\infty e^{-x} x^{3/2} dx$$

$$\overline{v^2} = \frac{4}{\sqrt{\pi}}\frac{kT}{m}\int_0^\infty e^{-x} x^{3/2} dx$$

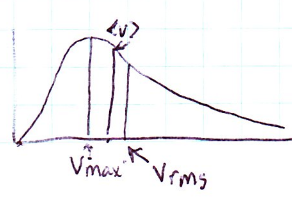
Memorize

$$\boxed{\text{Recall: } \Gamma(n) = \int_0^\infty e^{-x} x^{n-1} dx \qquad \Gamma(n+1) = n\Gamma(n) \qquad \Gamma(\tfrac{1}{2}) = \sqrt{\pi}}$$

$$\therefore \int_0^\infty e^{-x} x^{3/2} = \frac{3}{4}\sqrt{\pi}$$

$$\overline{v^2} = \frac{3kT}{m}$$

$$V_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3}{2}}\, V_{max}$$



Equipartition Theorem

<u>To get the average kinetic energy:</u>

$\langle K.E. \rangle = \langle \frac{1}{2} m v^2 \rangle = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m \left(\frac{3kT}{m} \right) = \frac{3}{2} kT$

<u>Equipartition theorem</u>

There are 3 translational degrees of freedom. The average K.E. $= \frac{3}{2} kT$
There is a theorem in statistical mechanics, the Equipartition Theorem, anything quadratic in v is $\frac{1}{2} kT$

$$\mathcal{E}_{tr} = \frac{p^2}{2m} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

The average of each contribution is $\frac{1}{2} kT$.

Recall the Simple Harmonic Oscillator of Classical Mechanics $E = \underbrace{\frac{p_x^2}{2m}}_{\frac{1}{2}kT} + \underbrace{\frac{1}{2} m \omega^2 x^2}_{\frac{1}{2}kT} = kT$

The exact result from quantum mechanics

$$\overline{\mathcal{E}}_{osc.} = \left(\frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \right)$$

classical limit $\lim_{\hbar \to 0} \overline{\mathcal{E}}_{osc} \approx \frac{\hbar\omega}{1 + \hbar\omega/kT - 1} = kT$

The equipartition theorem explains the simple harmonic oscillator energy.

Whatever the molecule, regardless of spin or internal structure, has some distribution of velocities in the classical limit.

At low temperatures gases exhibit other behavior: Bose-Einstein, etc.

Bose Gas	$\overline{n}_i$ = anything
Fermi Gas	$\overline{n}_i = 1$
Classical Gas	$\overline{n}_i = \frac{N}{V} \left(\frac{h^2}{2m\pi kT} \right)^{3/2} \ll 1$

It is difficult to satisfy the $\overline{n}_i \ll 1$ condition in a metal. Consider a metal with one electron per atom and (N/V) atoms per unit volume. It is much larger in that solid than in a gas. So, electrons in a metal are a Fermi gas.

Note: $m_e 1800 \sim m_p$

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Fermion Gas

$$\bar{\eta}_i = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$$

$$N = \sum_i \bar{\eta}_i = \sum_i \left(\frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}\right)$$

$$E = \sum_i \varepsilon_i \bar{\eta}_i = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i - \mu)} + 1}$$

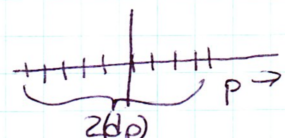
Density of States

To convert the sum to an integral we need to know the number of quantum states in the interval p and $p+dp$

Number per Volume for 3-D $\quad \dfrac{V(4\pi p^2 dp)}{h^3}(2s+1)$

Number per Area for 2-D $\quad \dfrac{A(2\pi p\, dp)}{h^2}(2s+1)$

Number per Line for 1-D $\quad \dfrac{L(2dp)}{h}(2s+1)$



for linear array consider both positive + negative

Consider a 3-D Volume

$$\varepsilon = \frac{p^2}{2m} \qquad p^2 = 2m\varepsilon \qquad dp = \sqrt{2m}\,\varepsilon^{-1/2} d\varepsilon$$

for electron $(2s+1) = 2$ because spin $s = 1/2$

from the solution to Schrodinger's equation for a particle-in-a-box:

$$f(\varepsilon)\,d\varepsilon = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

Electron Gas is a Fermi Gas

$$N = \int_0^\infty \eta_i f(\varepsilon)\,d\varepsilon = \int_0^\infty \frac{f(\varepsilon)\,d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1}$$

$$E = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1}$$

Fermi Gas NeutronStar Metal Electron Gas Fermi Level

Consider the temperature extremes

<u>Neutron Star</u>

$\lim_{T\to 0} n_i = 1$ everyone is at the lowest state but it is a Pauli state - only one particle per state

Neutron Star! Ideal Fermi gas at absolute zero not everything can go to ground state

$$\beta = \frac{1}{kT}$$

$\lim_{T\to\infty}$, $\beta \to 0$ let $x = \beta\varepsilon = \frac{\varepsilon}{kT} \Rightarrow 0$ $\varepsilon = kTx$ $d\varepsilon = kTx$

$$N = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\infty \frac{(kT)^{1/2}\,x^{1/2}\,dx\,(kT)}{e^{-\beta\mu}e^{x}+1}$$

$$N = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}(kT)^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{e^{-\beta\mu}e^{x}+1}$$

<u>Fermi Energy</u>

$\lim_{T\to 0}$ What happens when $T\to 0$? The chemical potential at $T=0$ is the Fermi Energy.

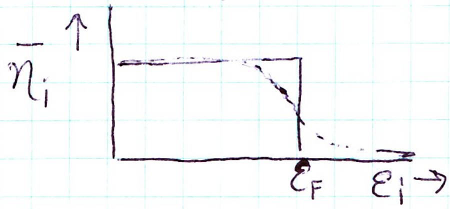
$$\mu \equiv \mu(T,V,N) \qquad \varepsilon_F = \mu(0,V,N)$$

Note: If $\varepsilon_F < 0$ $e^{-\beta\mu} \to \infty$ so $N \to 0$
That is a contradiction $\therefore$ $\varepsilon_F > 0$ by necessity

At $T=0$ $\bar{n}_i = \left(\frac{1}{e^{\beta(\varepsilon_i - \varepsilon_F)}+1}\right)$ for $\varepsilon_i < \varepsilon_F$ $\bar{n}_i = 1$, $\varepsilon_i > \varepsilon_F$ $\bar{n}_i = 0$ by inspection

Every quantum state up to ε_F are occupied by 1 entity.

ε_F is the energy of the highest occupied orbital. There is a very simple physical interpretation.



The total number of conduction electrons.

$$N = \int 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\varepsilon^{1/2}\,d\varepsilon\,(1) = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^{\varepsilon_F}\varepsilon^{1/2}\,d\varepsilon = \left(\frac{8\pi V}{3}\right)\left(\frac{2m\varepsilon_F}{h^2}\right)^{3/2}$$

$$\varepsilon_F = \frac{h^2}{2m}\left(\frac{3}{8\pi}\right)^{2/3}\left(\frac{N}{V}\right)^{2/3}$$

usually one conduction electron per atom. ε_F is different for different atoms. from periodic table $\frac{N}{V} = \frac{N_0\rho}{A} = ?$

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A = atomic weight is grams per N_A