

$$\bar{n}_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} \quad \begin{array}{l} - \text{ boson} \\ + \text{ fermion} \end{array}$$

The Classical Condition:  $\bar{n}_i \ll 1$

Implies that there are an infinite number of quantum states and many particles, but on average less than one particle per quantum state.

$$\bar{n}_i \sim e^{\beta\mu} e^{-\beta\epsilon_i} \quad \bar{n}_i \ll 1 \quad \text{perfect classical gas}$$

Can see that for low temperatures, you can have many particles

Deriving Thermodynamics from The Classical Condition

$$N = \sum_i \bar{n}_i = e^{\beta\mu} \sum_i e^{-\beta\epsilon_i} \quad (\text{all particles identical})$$

$\epsilon_i = \langle \epsilon \text{ of center-of-mass motion} \rangle + \langle \text{internal energy of atom interaction} \rangle$

$$\epsilon_i = \epsilon_s^{\text{translational}} + \epsilon_\alpha^{\text{internal}} = \epsilon_s^{\text{tr}} + \epsilon_\alpha^{\text{int}}$$

$$\sum_i = \sum_i s_i \alpha$$

$$\sum_i e^{-\beta\epsilon_i} = \sum_i e^{-\beta(\epsilon_s^{\text{tr}} + \epsilon_\alpha^{\text{int}})} = \underbrace{\sum_s e^{-\beta\epsilon_s^{\text{tr}}}}_{Z_1^{\text{tr}}} \underbrace{\sum_\alpha e^{-\beta\epsilon_\alpha^{\text{int}}}}_{\text{only on internal states of molecule } Z_1^{\text{int}}} = Z_1^{\text{tr}} Z_1^{\text{int}} \quad \text{for one molecule}$$

$$Z_1^{\text{tr}} = \sum_s e^{-\beta\epsilon_s^{\text{tr}}} \quad s = \text{translational state of molecule}$$

Find the number of quantum states of a single particle between  $p$  and  $dp$  in phase space

Start with quantum mechanics particle in a box  
The time independent Schrodinger equation is exactly like the time independent wave equation  
Standing elastic wave solution subject to boundary conditions of cubical volume.

$$(\nabla^2 + k^2)\Psi = 0 \quad k^2 = \frac{2mE}{\hbar^2}$$

$$\Psi(x, y, z) = C \sin(k_1 x) \sin(k_2 y) \sin(k_3 z) \quad k_i = \frac{n_i \pi}{L} \quad \begin{array}{l} n_i \neq 0 \text{ (no wavefn, no soln)} \\ n_i = 1, 2, 3, \dots \end{array}$$

# Density of States In Momentum Space

$$n_i = \frac{L}{\pi} k_i \quad n_i \neq 0 \quad n_i = 1, 2, 3, \dots$$

$$p_i = \hbar k_i \quad \text{mostly large } n$$

$$dn_i = \frac{L}{\pi} dk_i \quad \text{the number of quantum states in a small interval around } n_1, n_2, n_3$$

$$\underbrace{dn_1 dn_2 dn_3}_{\text{position}} = \left(\frac{L}{\pi}\right)^3 dk_1 dk_2 dk_3 = \left(\frac{L}{\pi}\right)^3 \frac{d^3 p}{\hbar^3} = \left(\frac{L}{\hbar\pi}\right)^3 d^3 p$$

$$d^3 n = \frac{V}{(\pi\hbar)^3} p^2 dp \sin\theta d\theta d\varphi = \frac{V}{(\pi\hbar)^3} p^2 dp d\Omega$$

$f(p)dp$  = the number of quantum states whose magnitude of the momentum lies between  $p$  and  $p+dp$  irrespective of the direction

We're only interested in direction - integrate over all to get  $4\pi = \int d\Omega$  and then take  $1/8$  of the spherical volume - just one quadrant

$$f(p)dp = \frac{V}{(\pi\hbar)^3} p^2 dp \left(\frac{4\pi}{8}\right) = \frac{\pi V}{2(\pi\hbar)^3} p^2 dp$$

We're only representing one quantum state for  $n_1, n_2,$  and  $n_3$ . The spin state can be up or down for every translational state there are  $(2s+1)$  spin states

$$f(p)dp = \frac{V}{(\pi\hbar)^3} \frac{\pi}{2} p^2 dp (2s+1) = \frac{V}{\pi^3 \hbar^3} \frac{(2\pi)^3 \pi}{2} p^2 dp (2s+1)$$

$$= \frac{V 4\pi p^2 dp (2s+1)}{\hbar^3} = \text{phase space of particle}$$

6 dimensional  
 3 ordinary components  
 3 components of momentum

$\nwarrow$   $\hbar$  not  $\hbar$   
 $\hbar = \frac{h}{2\pi}$

The volume of phase space  $V = 4\pi p^2 dp$

## Very Useful Result

the number of quantum states of a particle between  $p$  and  $p+dp$

$$f(p) dp = \frac{V 4\pi p^2 dp (2s+1)}{\hbar^3}$$

if dealing with electrons  $s=1/2$  so the multiplicity is 2

## Lecture 22 continued... Derive Thermodynamic Properties From Perfect Classical Gas

Use density of states to find  $N$ , the number of particles:  $E_i = p_i^2/2m$

$$N = \sum_i \bar{n}_i = e^{\beta\mu} \sum_i e^{-\beta E_i} = e^{\beta\mu} \int_0^{\infty} e^{-\beta p^2/2m} f(p) dp$$

\* - ok to make this approximation

$$N = Z_1^{int} e^{\beta\mu} \int_0^{\infty} e^{-\beta p^2/2m} \underbrace{\frac{4\pi p^2 dp (2s+1)}{h^3}}_{\text{density of quantum states}}$$

In order to do this integral take all the constants outside

$$N = Z_1^{int} e^{\beta\mu} \frac{4\pi V (2s+1)}{h^3} \int_0^{\infty} e^{-p^2/2mKT} p^2 dp$$

we want to express the integral in terms of dimensionless parameters

$$p^2 = 2mE \quad p = \sqrt{2m} E^{1/2} \quad E = \frac{p^2}{2m}$$

$$2p dp = 2m dE$$

$$dp = \frac{2m dE}{2\sqrt{2m} E^{1/2}} = \frac{\sqrt{2m}}{2} E^{-1/2} dE$$

first express the integral in terms of energy

$$N = e^{\beta\mu} Z_1^{int} \frac{4\pi V (2s+1)}{h^3} \int_0^{\infty} e^{-E/KT} (2mE) \frac{\sqrt{2m}}{2} E^{-1/2} dE$$

$$N = e^{\beta\mu} Z_1^{int} (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\infty} E^{1/2} e^{-E/KT} dE$$

this integral is in terms of kinetic energy or total translational energy of the molecule in the gas

Dimensionless variable  $x = E/KT$   $dE = KT dx$   $E = (KT)x$

$$N = e^{\beta\mu} Z_1^{int} (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (KT)^{3/2} \int_0^{\infty} e^{-x} x^{1/2} dx$$

now the integral is in terms of dimensionless quantity

Need to solve  $\int_0^{\infty} x^{1/2} e^{-x} dx$

Math

Gamma function  $\Gamma(n) = \int_0^{\infty} x^{n-1} e^{-x} dx$

$$\Gamma\left(\frac{3}{2}\right) = \int_0^{\infty} e^{-x} x^{1/2} dx$$

Properties of gamma function

$\Gamma(n+1) = n\Gamma(n)$  can prove with integration by parts.

$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$  good result to memorize

$$\therefore \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2}$$

$$N = e^{\beta\mu} Z_1^{\text{int}} (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{3/2} \int_0^{\infty} e^{-x} x^{1/2} dx$$

$$N = e^{\beta\mu} Z_1^{\text{int}} (2s+1) 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{3/2} \Gamma\left(\frac{3}{2}\right)$$

$$N = e^{\beta\mu} Z_1^{\text{int}} (2s+1) \left(\frac{2\pi m kT}{h^2}\right)^{3/2}$$

spin  
multiplicity  
factor

$$= Z_1^{\text{tr}}$$

easy interpretation like a volume  $\frac{1}{\lambda_{\text{DeBrogue}}^3}$   
some kind of a density

$$\frac{h}{p} = \lambda_{\text{DeBrogue}}$$

$$\frac{\overline{p^2}}{2m} \sim \frac{3}{2} kT \Rightarrow \overline{p^2} = 3mkT$$

$$p_{\text{rms}} = \sqrt{\overline{p^2}} = \sqrt{3mkT} \quad \overline{\lambda}_{\text{DB}} = \frac{h}{\sqrt{\overline{p^2}}} = \frac{h}{\sqrt{3mkT}}$$

$$\therefore \overline{\lambda}_{\text{DB}} \sim \frac{h}{\sqrt{2\pi mkT}}$$

$$\text{and } \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \sim \frac{1}{\overline{\lambda}_{\text{DB}}^3}$$

## Lecture 22 Continued... Thermodynamic Properties of Perfect Classical Gas

Now that we have  $N$  in terms of chemical potential and all that  
The best way to proceed is to solve for  $\mu$  to get helmholtz free energy  $F$

Solve for  $e^{\beta\mu}$

$$e^{\beta\mu} = \left(\frac{N}{V}\right) \left(\frac{h^2}{2\pi m kT}\right)^{3/2} \frac{1}{Z_1^{\text{int}}} \frac{1}{(2s+1)}$$

$$\beta\mu = \ln\left(\frac{N}{V}\right) + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m kT}\right) - \ln Z_1^{\text{int}} - \ln(2s+1)$$

$$\mu = kT \left[ \ln N - \ln V + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m kT}\right) - \ln Z_1^{\text{int}}(T) - \ln(2s+1) \right]$$

$\uparrow$   $N$        $\uparrow$   $V$

$\leftarrow$   $T$        $\uparrow$   $Z_1^{\text{int}}$  is a function of  $T$  only

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$\therefore F = \int \mu dN + \text{integration constant that depends on } T, V$$

$\nwarrow$  only the terms with integration variable are non-trivial

$$F = NkT \left[ \ln N - 1 - \ln V + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m kT}\right) - \ln Z_1^{\text{int}} - \ln(2s+1) \right] + C(T,V)$$

physical intuition used to get  $C$

if  $N \rightarrow 0$   $F \rightarrow 0$   $\therefore C(T,V) \rightarrow 0$  so by physical consideration  $C(T,V) = 0$

Now that we have Helmholtz free energy, can get pressure and entropy immediately, and then energy

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \quad E = F + TS \quad \text{or} \quad \bar{E} = \sum_i \epsilon_i \bar{n}_i$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{NkT}{V} \quad \text{only } \ln V \text{ depends on } V!$$

$PV = NkT$  perfect classical gas, essentially derived from statistical mechanics. - only get when  $\bar{n}_i \ll 1$  otherwise the condition is not satisfied.

So, when  $\bar{n}_i \ll 1$  we have a perfect classical gas and from statistical mechanics derive the ideal gas law:

$$PV = NkT$$

Entropy is more complicated

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = -NkT \left[ \frac{3}{2} \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \left( \frac{h^2}{2mk} \right)^{\frac{3}{2}} \left( \frac{1}{T^2} \right) - \frac{\partial \ln Z^{\text{int}}}{\partial T} \right]$$

$$- Nk \left[ \ln \left( \frac{N}{V} \right) - 1 - \ln(2\pi h) + \frac{3}{2} \ln \left( \frac{h^2}{2\pi mkT} \right) - \ln Z_1^{\text{int}} \right]$$

Sackur-Tetrode Equation

$$S = NkT \frac{\partial (\ln Z^{\text{int}})}{\partial T} + Nk \left[ \frac{5}{2} + \ln(2\pi h) - \frac{3}{2} \ln \left( \frac{h^2}{2\pi mkT} \right) + \ln Z_1^{\text{int}} - \ln \left( \frac{N}{V} \right) \right]$$

Note: For a monatomic gas  $S = \frac{5}{2} Nk$

$$E = F + TS$$

$$E = \underbrace{\frac{3}{2} NkT}_{\text{w/o internal energy it is the translational}} + NkT^2 \frac{\partial \ln Z_1^{\text{int}}}{\partial T}$$

w/o internal energy it is the translational

we can show  $kT^2 \frac{\partial \ln Z_1^{\text{int}}}{\partial T}$  is the average

internal energy of the molecule

3 translational DOF  
 $\frac{1}{2} kT$  per DOF

$$\bar{E}_{\text{int}} = - \frac{\partial \ln Z_1^{\text{int}}}{\partial \beta} = - \frac{\partial \ln Z_1^{\text{int}}}{\partial T} \frac{\partial T}{\partial \beta} = kT^2 \frac{\partial \ln Z_1^{\text{int}}}{\partial T}$$

$$\beta = \frac{1}{kT}, \quad T = \frac{1}{k\beta}, \quad \frac{\partial T}{\partial \beta} = \frac{1}{k} \left( \frac{-1}{\beta^2} \right) = -\frac{1}{k} k^2 T^2 = -kT^2$$

$$E = \frac{3}{2} NkT + N \bar{E}_{\text{int}} \quad \text{this makes sense}$$

$$E = \sum_i \bar{n}_i \epsilon_i \quad \text{just the Maxwellian distribution of velocity}$$