

PHYS 425 - W9L3

Last Time: Grand Canonical Ensemble

Grand partition func  $\Xi = \sum_j e^{-(U_j - \mu N_j)/k_B T}$

Grand potential  $\Phi_g = -k_B T \ln \Xi$

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

Consider a single energy level of energy  $\varepsilon$  that can be occupied by either zero or one particles.



occupied

$$N_1 = 1$$

$$\text{energy } U_1 = \varepsilon$$



empty

$$N_0 = 0$$

$$\text{energy } U_0 = 0$$

$$\Xi = \sum_j e^{-(\mu_j - \mu N_j)/k_B T} \\ = 1 + e^{-(\varepsilon - \mu)/k_B T}$$

$$\therefore \Phi_G = -k_B T \ln \left( 1 + e^{-(\varepsilon - \mu)/k_B T} \right)$$

$$\begin{aligned} \frac{\partial \Phi_G}{\partial \mu} &= \frac{-k_B T}{1 + e^{-(\varepsilon - \mu)/k_B T}} \cdot \frac{1}{k_B T} e^{-(\varepsilon - \mu)/k_B T} \\ &= -\frac{e^{-(\varepsilon - \mu)/k_B T}}{1 + e^{-(\varepsilon - \mu)/k_B T}} \cdot \frac{e^{(\varepsilon - \mu)/k_B T}}{e^{(\varepsilon - \mu)/k_B T}} \\ &= -\frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1} \end{aligned}$$

$$\boxed{N_{FD} = -\left(\frac{\partial \Phi_G}{\partial \mu}\right) = \frac{1}{1 + e^{(\varepsilon - \mu)/k_B T}}}$$

Fermi-Dirac dist'n. Avg. no. of identical Fermions in a state of energy  $\varepsilon$  at temp.  $T$ .

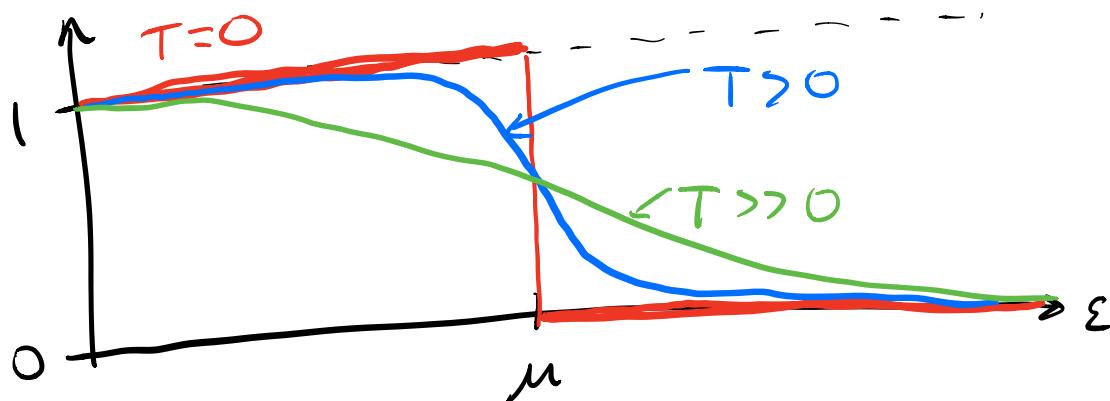
Plot  $\bar{N}_{FD}$  vs  $\varepsilon$  for  $T \rightarrow 0$ .

$$\varepsilon - \mu > 0 \quad e^{(\varepsilon - \mu)/k_B T} \rightarrow \infty$$

$$\bar{N}_{FD} = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1} \rightarrow 0$$

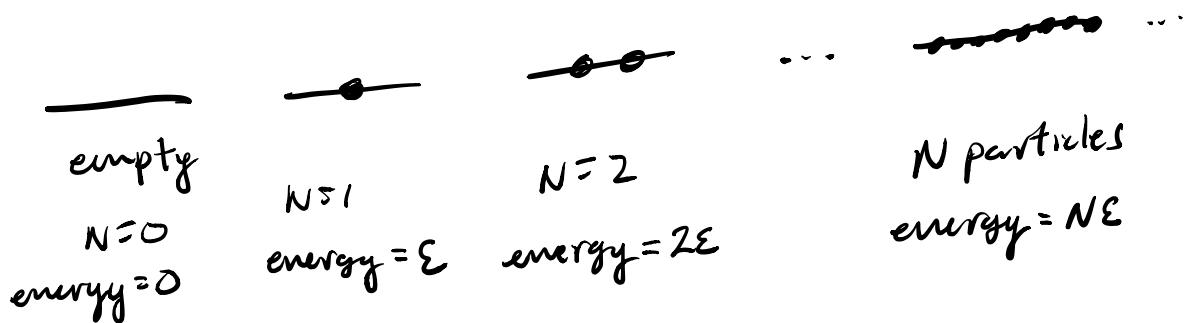
$$\varepsilon - \mu < 0 \quad e^{(\varepsilon - \mu)/k_B T} \rightarrow 0$$

$$\bar{N}_{FD} = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + 1} \rightarrow 1$$



What if could have any no. of particles (identical) in a quantum state of energy  $\epsilon$ ?

$$\Xi = \sum_{j=0}^{\infty} e^{-(\epsilon_j - \mu N_j)/k_B T}$$



$$\Xi = 1 + e^{-(\epsilon - \mu)/k_B T} + e^{-2(\epsilon - \mu)/k_B T} + \dots$$

$$+ e^{-N(\epsilon - \mu)/k_B T} + \dots$$

$$= 1 + e^{-(\epsilon - \mu)/k_B T} + \left( e^{-(\epsilon - \mu)/k_B T} \right)^2$$

$$+ \dots + \left( e^{-(\epsilon - \mu)/k_B T} \right)^N + \dots$$

geometric series

$$\sum_{q=0}^{\infty} r^q = \frac{1}{1-r} \text{ for } |r| < 1$$

$\Xi$  is a geometric series w/  $r = e^{-(\varepsilon-\mu)/k_B T}$

If  $\varepsilon - \mu > 0$ , then

$$\Xi = \frac{1}{1 - e^{-(\varepsilon-\mu)/k_B T}}$$

$$\Phi_G = -k_B T \ln \Xi = k_B T \ln \left( \frac{1}{\Xi} \right)$$

$$= k_B T \ln \left( 1 - e^{-(\varepsilon-\mu)/k_B T} \right)$$

$$\bar{N}_{BE} = -\left( \frac{\partial \Phi_G}{\partial \mu} \right) = \frac{+k_B T}{1 - e^{-(\varepsilon-\mu)/k_B T}} \left( \frac{+e^{-(\varepsilon-\mu)/k_B T}}{\cancel{k_B T}} \right)$$

$$\therefore \bar{N}_{BE} = \frac{e^{-(\varepsilon-\mu)/k_B T}}{1 - e^{-(\varepsilon-\mu)/k_B T}} \quad \frac{e^{(\varepsilon-\mu)/k_B T}}{e^{(\varepsilon-\mu)/k_B T}}$$

$$\boxed{\bar{N}_{BE} = \frac{1}{e^{(\varepsilon-\mu)/k_B T} - 1}}$$

Avg. no. of Bosons  
in a state of energy  
 $\varepsilon$  at temp.  $T$ .  
Bose-Einstein dist'n.

Ideal Monatomic gas entropy given by  
Sakur-Tetrode Eq'n.

$$S = Nk_B \left\{ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{mU}{3\pi h^2 N} \right) + \frac{5}{2} \right\}$$

$\underbrace{\hspace{10em}}$

$$\frac{mk_B T}{2\pi h^2} = \frac{1}{\lambda_B^2} *$$

Determine chemical pot. of this classical ideal gas from

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

$$\left( \frac{\partial S}{\partial N} \right)_{U,V} = k_B \left\{ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{mU}{3\pi h^2 N} \right) + \cancel{\frac{5}{2}} \right\}$$

$$+ Nk_B \left\{ -\frac{1}{N} - \frac{3}{2} \frac{1}{N} \right\}$$

$\underbrace{\hspace{4em}}$

$$- \frac{5}{2} k_B$$

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V} = -k_B T \left\{ \ln \left( \frac{V}{N} \right) + \underbrace{\frac{3}{2} \ln \left( \frac{m U}{3\pi \hbar^3 N} \right)}_{\frac{1}{\lambda_D^2}} \right\}$$

$$n = \frac{N}{V} \quad \frac{1}{\lambda_D^2}$$

$$\mu = -k_B T \left\{ -\ln n + \frac{3}{2} \ln \left( \frac{1}{\lambda_D^2} \right) \right\}$$

$$= k_B T \left\{ \ln n - \ln \left( \frac{1}{\lambda_D^3} \right) \right\}$$

$\lambda_D^3$  quantum volume of particle  
(small in classical limit)

$$n_Q = \frac{1}{\lambda_D^3} \quad (\text{large in classical limit})$$

$n = \frac{N}{V}$  small for a classical (non-interacting / dilute) gas.

$$\mu = k_B T \left( \ln n - \ln n_Q \right)$$

$$\boxed{\therefore \mu = k_B T \ln \left( \frac{n}{n_Q} \right)}$$

chemical pot. of  
monatomic ideal  
gas.

$$\therefore \frac{\mu}{k_B T} = \ln \left( \frac{n}{n_Q} \right) \quad \begin{array}{l} \text{For classical gas} \\ n \ll n_Q \end{array}$$

$$\therefore -\frac{\mu}{k_B T} = -\ln \left( \frac{n}{n_Q} \right) = \ln \left( \frac{n_Q}{n} \right) \gg 1$$

$$\bar{N}_{FD} = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} \quad \bar{N}_{BE} = \frac{1}{e^{(\varepsilon-\mu)/k_B T} - 1}$$

In classical limit

$$e^{(\varepsilon-\mu)/k_B T} \pm 1 = e^{\varepsilon/k_B T} \underbrace{e^{-\mu/k_B T}}_{\frac{n_Q}{n} \gg 1} \pm 1$$

$$= e^{\varepsilon/k_B T} \left( \frac{n_Q}{n} \right) \pm 1 \approx e^{\varepsilon/k_B T} \underbrace{\frac{n_Q}{n}}$$

$\therefore$  In classical limit

$$\bar{N}_{FD} \approx \bar{N}_{BE} \approx \frac{n}{n_Q} e^{-\varepsilon/k_B T}$$

In the high-temp, dilute limit the Fermi-Dirac and Bose-Einstein dist'n's become identical.

∴ Behaviour of classical gas does not depend on whether gas of particles is identical Fermions or Bosons.

Why?  $\bar{N}_{\text{classical}} \approx \frac{n}{n_p} e^{-\varepsilon/k_b T} \ll 1$



avg. no. of particles in state w/ energy  $\varepsilon$   
at temp.  $T$ .

∴ Regardless of if one has Bosons or Fermions, average occupation of quantum states always much less than one. → Whether or not particles need to obey Pauli Exclusion principle becomes irrelevant.