PHY 341/641 Thermodynamics and Statistical Mechanics
MWF: Online at 12 PM & FTF at 2 PM

Record!!!

Discussion for Lecture 28:

Quantum effects in statistical mechanics

Reading: Chapter 7 (mostly 7.3&4)

1. **Summary of results concerning statistical mechanics of Fermi and Bose particles**
2. **Examples of Fermi systems**
3. **Examples of Bose systems**

21	Mon: 03/22/2021	Chap. 6.1 & 6.5	Microcanonical and canonical ensembles		
22	Wed: 03/24/2021	Chap. 6.1-6.2	Canonical distributions	#18	03/26/2021
23	Fri: 03/26/2021	Chap. 6.1-6.7	Canonical distributions	6.49	03/29/2021
24	Mon: 03/29/2021	Chap. 6.1-6.7	Canonical distributions	#20	03/31/2021
25	Wed: 03/31/2021	App. A & Chap. 7.1	Quantum mechanical effects	#21	04/02/2021
26	Fri: 04/02/2021	Chap. 7.1-7.2	Quantum mechanical effects		
27	Mon: 04/05/2021	Chap. 7.3	Bose and Fermi statistics	#22	04/09/2021
	Wed: 04/07/2021	No class	*Holiday*		
28	Fri: 04/09/2021	Chap. 7.3 & 7.4	Bose and Fermi statistics	#23	04/12/2021

PHY 341/641 -- Assignment #23

April 9, 2021

Continue reading Chapter 7 in **Schroeder** .

1. In class, we evaluated the Grand potential for an ideal Fermi gas in the limit that T is approximately 0 K. From this result, we can estimate the internal energy U and the pressume P at very low temperature. Show that this estimate is consistent with the results presented in Section 7.3 of Schroeder.

Accumulated questions –

From Skye -- So when we are doing the taylor expansion, would the term inside the block have a negative sign? Since the derivative f'(x) = -5b(n)^4

Comment – You are correct. There is a minus sign error in the Lecture notes:

Original: Hint: Make a Taylor expansion of the argument of the delta function

$$\text{about } a-bx^5=0 \qquad a-bx^5 \approx 0+\left(x-\left(\frac{a}{b}\right)^{1/5}\right)5b\left(\frac{a}{b}\right)^{4/5}+\ldots$$

Corrected: Hint: Make a Taylor expansion of the argument of the delta function

$$\text{about } a-bx^5=0 \qquad a-bx^5 \approx 0-\left(x-\left(\frac{a}{b}\right)^{1/5}\right)5b\left(\frac{a}{b}\right)^{4/5}+\ldots$$

From Kristen -- 1. I don't quite understand the purpose of the triplet of positive integers (n) if you could elaborate on that I would appreciate it.
2. How is it that we can simply approximate the temperature T, to be zero?
3. Could you elaborate on what the Sommerfield expansion actually does?

Some results from last time

The Grand Partition Function for indistinguishable particles can be written in terms of the chemical potential μ:

$$Z_{Grand}(T) = \sum_{n_1 n_2 n_3 \ldots\ldots} \exp(-\beta(n_1(\epsilon_1 - \mu) + n_2(\epsilon_2 - \mu) + n_3(\epsilon_3 - \mu)\ldots))$$

Here we sum over all occupation numbers n_s and energies ϵ_s.

For N particles, the occupation numbers have the condition

$$N = \sum_s n_s.$$

For Fermi particles $n_s=0$ or $n_s=1$ only

$$\ln\left(Z_{GrandFermi}(T)\right) = \sum_s \ln\left(1 + e^{-\beta(\epsilon_s - \mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1} = N$$

For Bose particles, the summation over n_s is a geometric sum resulting the analytic form:

$$\ln\left(Z_{GrandBose}(T,\mu)\right) = -\sum_s \ln\left(1 - e^{-\beta(\epsilon_s-\mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}-1} = N$$

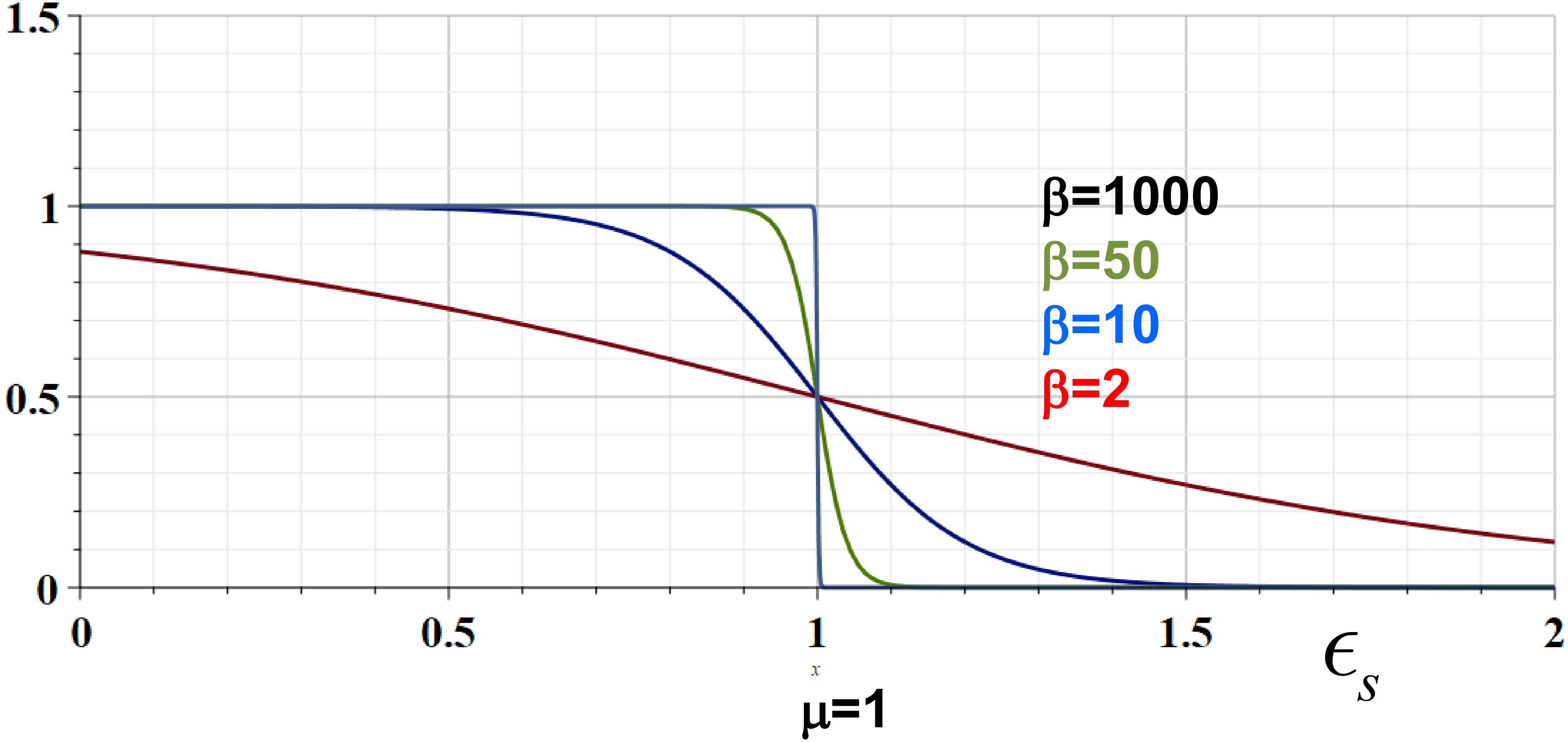
Summary of results for Fermi particles

$$\ln\left(Z_{GrandFermi}(T)\right) = \sum_s \ln\left(1 + e^{-\beta(\epsilon_s-\mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} = N$$

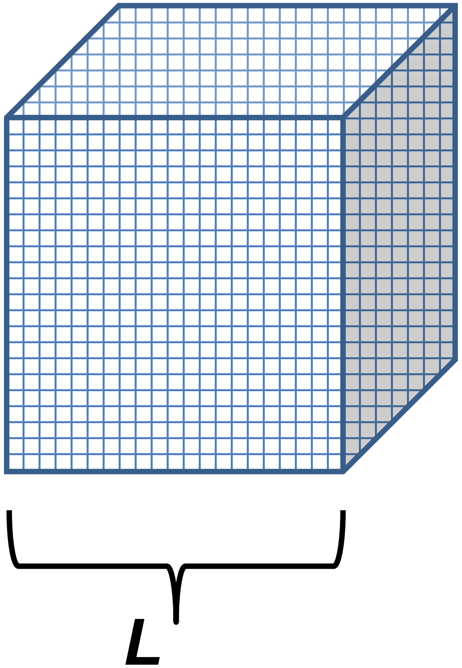
Fermi distribution function

$$\mathcal{F}(\epsilon_s) = \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1}$$



Evaluation for an ideal gas of Fermi particles

Recall that Fermi particles have intrinsic half integer spin. For example, electrons have spin s=1/2, so that each spatial state can be occupied by 0 or 1 spin up electrons and by 0 or 1 spin down electrons. Generally, the spin degeneracy factor is given by (2s+1). To evaluate the spatial states, for an ideal quantum gas, we can use the cube of length L similar to the photon analysis.



$L^3 = V$

Note that this a bit different from your textbook; $-\infty \le n_{x,y,z} \le \infty$

Spatial energy for electron: $$\epsilon_{n_x n_y n_z} = \frac{h^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Summing over all modes $(n_x.n_y, n_z)$ in continuum limit:

Let $q \equiv \sqrt{n_x^2 + n_y^2 + n_z^2}$ $$\int dn_x \int dn_y \int dn_z = 4\pi \int q^2 dq$$

$$g(\epsilon) = 2\, 4\pi \int q^2 dq\ \delta\left(\epsilon - \frac{h^2 q^2}{2mL^2}\right)$$

Spin degeneracy

Note that $$\int dx\, f(x)\ \delta(a-x) = f(a)$$

Let $x = \frac{h^2 q^2}{2mL^2}$ $$g(\epsilon) = 2\ 4\pi \left(\frac{2mL^2}{h^2}\right)^{3/2} \frac{1}{2} \int \sqrt{x} dx\ \delta(\epsilon - x)$$

$$g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \sqrt{\epsilon} \qquad V \equiv L^3$$

Evaluation of integrals --

$$\ln\left(Z_{GrandFermi}(T)\right) = \sum_s \ln\left(1 + e^{-\beta(\epsilon_s - \mu)}\right)$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} = N$$

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} \rightarrow \int d\epsilon\; g(\epsilon)\frac{1}{e^{\beta(\epsilon-\mu)}+1}$$

For $T = 0$:

$$\approx \int_0^{\mu} d\epsilon\; g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu} d\epsilon\; \sqrt{\epsilon}$$

$$\Rightarrow\; 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{3}\mu^{3/2} = \mathrm{N}$$

Determination of chemical potential for T=0:

$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} = N \rightarrow \int d\epsilon\; g(\epsilon)\frac{1}{e^{\beta(\epsilon-\mu)}+1} = N$$

$$\text{For } T=0: \qquad \approx \int_0^\mu d\epsilon\; g(\epsilon) = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\mu d\epsilon\; \sqrt{\epsilon}$$

$$\Rightarrow\; 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{3}\mu^{3/2} = N$$

$$\Rightarrow \mu(T=0) \equiv \epsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

What can we do with the Grand Partition function?

Summary of thermodynamic energies that we have studied so far:

Internal: $U(S,V,N)$ $\quad dU = TdS - PdV + \mu dN$

Enthalpy: $H(S,P,N) = U + PV$ $\quad dH = TdS + VdP + \mu dN$

Helmholtz: $F(T,V,N) = U - ST$ $\quad dF = -SdT - PdV + \mu dN$

Gibbs: $G(T,P,N) = F + PV$ $\quad dG = -SdT + VdP + \mu dN$

Using the Legendre transformation, we can define a thermodynamic energy measure that is a function of the chemical potential instead of the particle number.

Such a energy is called by some texts as the "Grand potential"

$$\Omega(T,V,\mu) = F - \mu N \qquad d\Omega = -SdT - PdV - Nd\mu$$

Properties of the "Grand potential"

$$\Omega(T,V,\mu) = F - \mu N \qquad d\Omega = -SdT - PdV - Nd\mu$$

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

The canonical partition function $Z(T,V,N)$
is directly connected to the Helmholtz free energy
according to $\quad F(T,V,N) = -kT\ln\left(Z(T,V,N)\right)$

$\Rightarrow$ The grand canonical partition function $Z_{Grand}(T,V,\mu)$
is directly connected to the Grand potential
according to $\quad \Omega(T,V,N) = -kT\ln\left(Z_{Grand}(T,V,\mu)\right)$

Evaluation of the Grand potential:

$$\Omega(T,V,\mu) = -kT\ln\left(Z_{GrandFermi}(T)\right) = -kT\sum_s \ln\left(1+e^{-\beta(\epsilon_s-\mu)}\right)$$

$$= -kT\int d\epsilon\; g(\epsilon)\ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

For $T\to 0,\ \beta\to\infty$: $\quad \ln\left(1+e^{-\beta(\epsilon_s-\mu)}\right) \approx \begin{cases} \beta(\mu-\epsilon) & \text{for } \epsilon<\mu \\ 0 & \text{for } \epsilon>\mu \end{cases}$

$$\Omega(T\to 0,V,\mu) = -\int_0^{\mu} d\epsilon\; g(\epsilon)(\mu-\epsilon)$$

$$= -4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^{\mu} d\epsilon\;\sqrt{\epsilon}\;(\mu-\epsilon)$$

$$= -4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\frac{4}{15}\;\mu^{5/2}$$

Summary of results for an ideal Fermi gas of s=1/2 particles in three dimensions evaluated in the limit that T→0 K

Evaluation of the Grand potential:

$$\Omega(T \to 0, V, \mu) = -\int_0^{\mu} d\epsilon\; g(\epsilon)(\mu - \epsilon)$$

$$= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu} d\epsilon\; \sqrt{\epsilon}\; (\mu - \epsilon)$$

$$= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{4}{15}\; \mu^{5/2}$$

$$\int d\epsilon\; g(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = N$$

$$\mu(T=0) \equiv \epsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

Properties of the "Grand potential"

$$\Omega(T, V, \mu) = F - \mu N = U - ST - \mu N \qquad d\Omega = -SdT - PdV - Nd\mu$$

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

Evaluating these functions for *T>0*

Evaluation of the Grand potential:

$$\Omega(T,V,\mu) = -kT\ln\left(Z_{GrandFermi}(T)\right)$$

$$= -kT\int d\epsilon\ g(\epsilon)\ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

$$= -4\pi V\left(\frac{2m}{h^2}\right)^{3/2} kT\int d\epsilon\ \sqrt{\epsilon}\ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

Convenient trick -- the following series of integrals are useful

$$f_{5/2}(z) \equiv \frac{4}{\sqrt{\pi}}\int_0^\infty dx\ x^2\ln\left(1+ze^{-x^2}\right) = \sum_{m=1}^{\infty}(-1)^{m+1}\frac{z^m}{m^{5/2}}$$

$$f_{3/2}(z) \equiv z\frac{d}{dz}f_{5/2}(z) = \frac{4}{\sqrt{\pi}}\int_0^\infty dx\ x^2\frac{z}{e^{x^2}+z} = \sum_{m=1}^{\infty}(-1)^{m+1}\frac{z^m}{m^{3/2}}$$

$$\Omega(T,V,\mu) = -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} kT \int d\epsilon\, \sqrt{\epsilon}\, \ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

$$f_{5/2}(z) \equiv \frac{4}{\sqrt{\pi}} \int_0^\infty dx\, x^2 \ln\left(1+ze^{-x^2}\right) = \sum_{m=1}^{\infty} (-1)^{m+1} \frac{z^m}{m^{5/2}}$$

Let $z \equiv e^{\beta\mu}$ $\qquad x^2 = \beta\epsilon$

$$\Omega(T,V,\mu) = -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} kT \int d\epsilon\, \sqrt{\epsilon}\, \ln\left(1+e^{-\beta(\epsilon-\mu)}\right)$$

$$= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} kT\; 2\left(kT\right)^{3/2} \frac{\sqrt{\pi}}{4} f_{5/2}(e^{\beta\mu})$$

This approach is useful at high temperatures; for low temperatures, further considerations are needed.