# PHY 341/641 Thermodynamics and Statistical Mechanics

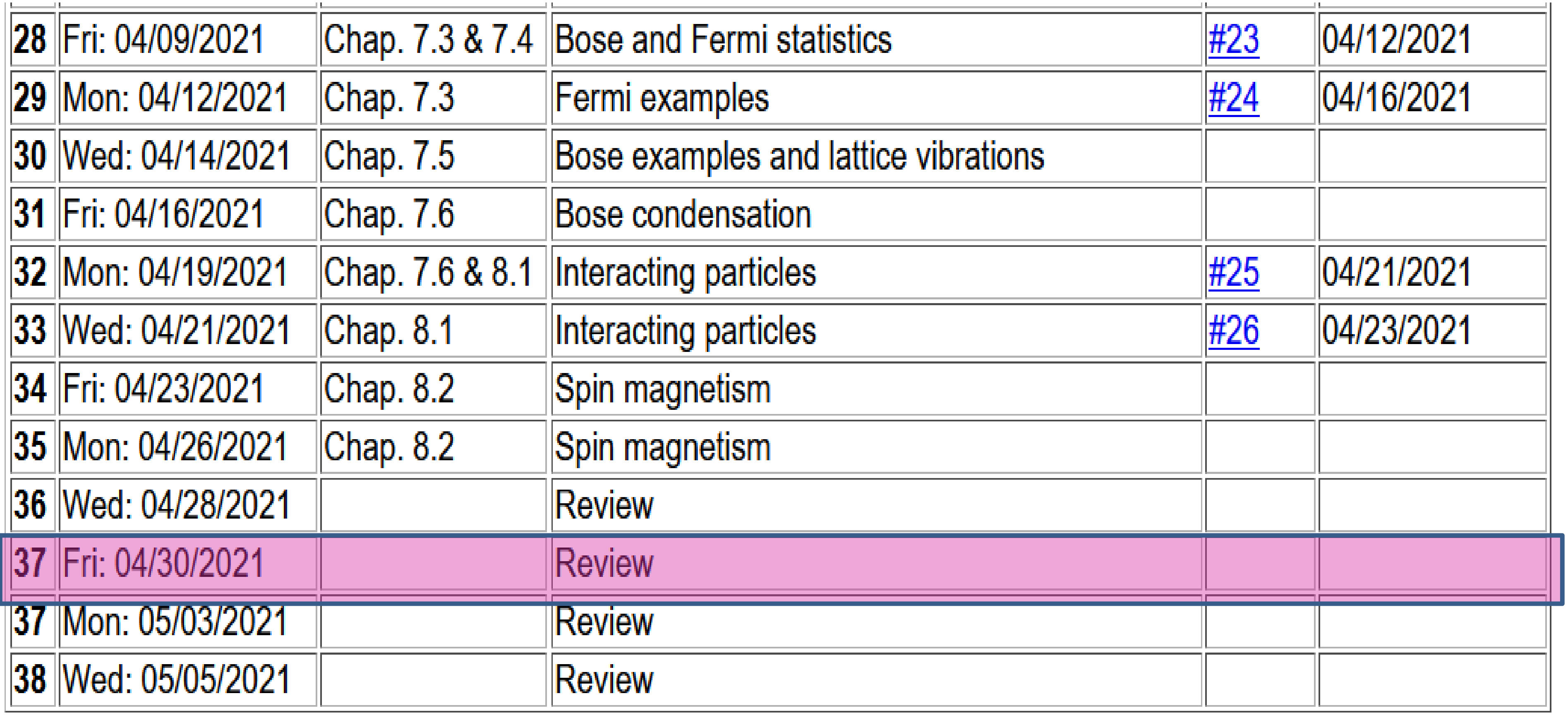
# MWF: Online at 12 PM & FTF at 2 PM

Record!!!

# Discussion for Lecture 37:

## Review Part 2

1. Canonical ensemble of ideal gas, including with internal degrees of freedom
2. Bose and Fermi ideal gases



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|---|---|---|---|---|---|
| 28 | Fri: 04/09/2021 | Chap. 7.3 & 7.4 | Bose and Fermi statistics | #23 | 04/12/2021 |
| 29 | Mon: 04/12/2021 | Chap. 7.3 | Fermi examples | #24 | 04/16/2021 |
| 30 | Wed: 04/14/2021 | Chap. 7.5 | Bose examples and lattice vibrations | | |
| 31 | Fri: 04/16/2021 | Chap. 7.6 | Bose condensation | | |
| 32 | Mon: 04/19/2021 | Chap. 7.6 & 8.1 | Interacting particles | #25 | 04/21/2021 |
| 33 | Wed: 04/21/2021 | Chap. 8.1 | Interacting particles | #26 | 04/23/2021 |
| 34 | Fri: 04/23/2021 | Chap. 8.2 | Spin magnetism | | |
| 35 | Mon: 04/26/2021 | Chap. 8.2 | Spin magnetism | | |
| 36 | Wed: 04/28/2021 | | Review | | |
| 37 | Fri: 04/30/2021 | | Review | | |
| 37 | Mon: 05/03/2021 | | Review | | |
| 38 | Wed: 05/05/2021 | | Review | | |

Important dates: Final exams available < May 6; due May 14
Outstanding work due May 14

Review 1 & 2 Summary of concepts/equations

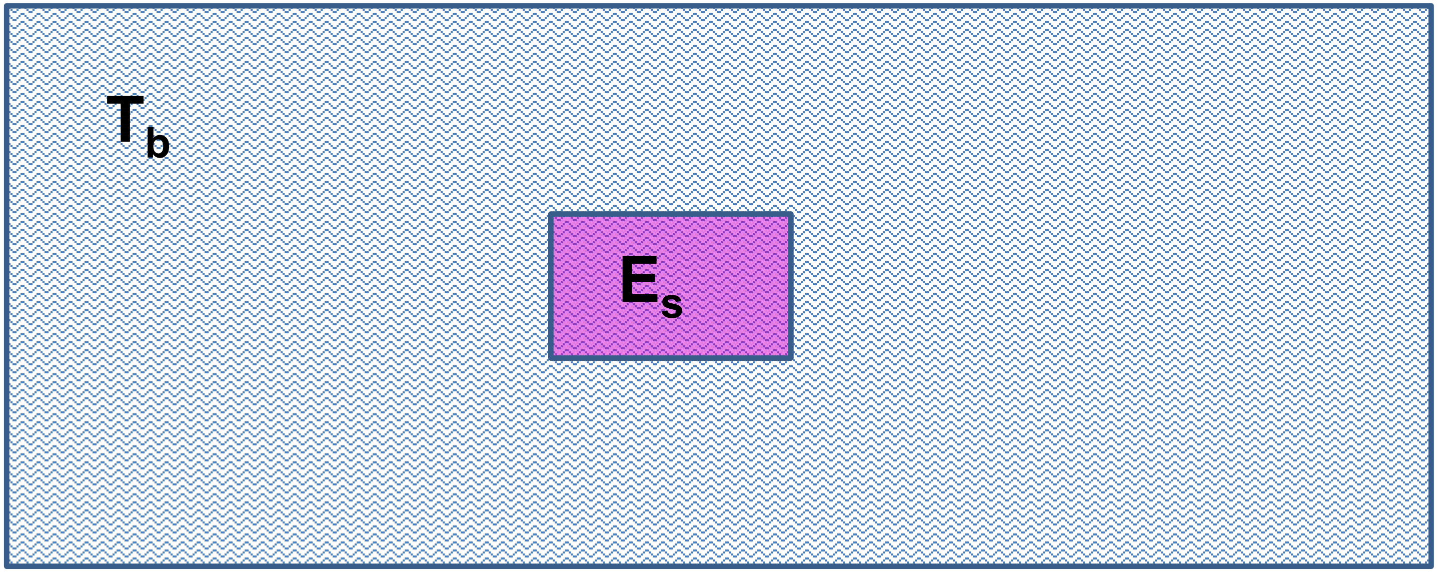
Review 3 & 4 Examples

Timelines –

- May 5 – Review 4 & take home exam available
- May 14 – all course materials due; outstanding homework, and completed exams

Please note that the complete lecture slides are posted on the course webpage and the zoom recordings are available on the shared google drive.

# Canonical ensemble --



In this case, we argue that the probability $\mathscr{P}_s$ of our system being in state $s$ depends on the internal energy $U_s$ and the bath temperature $T_b$ :

$$\mathscr{P}_s = \frac{1}{Z(T_b)} e^{-U_s/k_B T_b} \qquad \text{where the "partition" function is } Z(T_b) = \sum_s e^{-U_s/k_B T_b}$$

This enables us to determine the "canonical" average of system properties. For example, the average internal energy of our system is given by

$$\langle U \rangle = \sum_s U_s \mathscr{P}_s = \frac{1}{Z(T_b)} \sum_s U_s e^{-U_s/k_B T_b}$$

In the following $T_b \to T$

$k_B \to k$

Evaluating the canonical partition function for the $N$ particle

mono atomic ideal gas $U_s \to \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m}$

$$Z(T) = \sum_s e^{-U_s/kT} = \frac{1}{h^{3N} N!} \int d^3r_1 d^3r_2 \ldots d^3r_N \int d^3p_1 d^3p_2 \ldots d^3p_N \; e^{-\sum_i p_i^2/(2mkT)}$$

$$= \frac{V^N}{h^{3N} N!} \left( \int_{-\infty}^{\infty} dp_x e^{-p_x^2/(2mkT)} \right)^{3N} = \frac{V^N}{h^{3N} N!} (2\pi mkT)^{3N/2}$$

# Digression on notions of probability

While we will most often use the partition function to normalize our probability function: $\mathcal{P}_s = \frac{1}{Z(T)} e^{-U_s/kT}$, it is sometimes convenient to use other normalizations. For example, in section 6.4 of your textbook, we discussed the Maxwell speed distribution. In this case, since the particles are independent, we can consider the average for a single particle. From Boltzmann's idea, we know that the probability is proportional to $e^{-|\mathbf{p}|^2/2mkT} = e^{-m|\mathbf{v}|^2/2kT}$. In order to study the speed distribution for three dimensional motion, it is convenient to use spherical polar coordinates, and the normalized probability for the speed is $\mathcal{P}(v) = \frac{v^2 e^{-mv^2/2kT}}{\int_0^\infty dv\ v^2 e^{-mv^2/2kT}} = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-mv^2/2kT}$.

Various averages: $\langle v \rangle = \int_0^\infty dv\ v\mathcal{P}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty dv\ v^3 e^{-mv^2/2kT}$

Various averages:

$$\langle v \rangle = \int_0^\infty dv\, v\mathcal{P}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty dv\, v^3 e^{-mv^2/2kT} = \sqrt{\frac{8kT}{\pi m}}$$

$$\langle v^2 \rangle = \int_0^\infty dv\, v^2\mathcal{P}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \int_0^\infty dv\, v^4 e^{-mv^2/2kT} = \frac{3kT}{m}$$

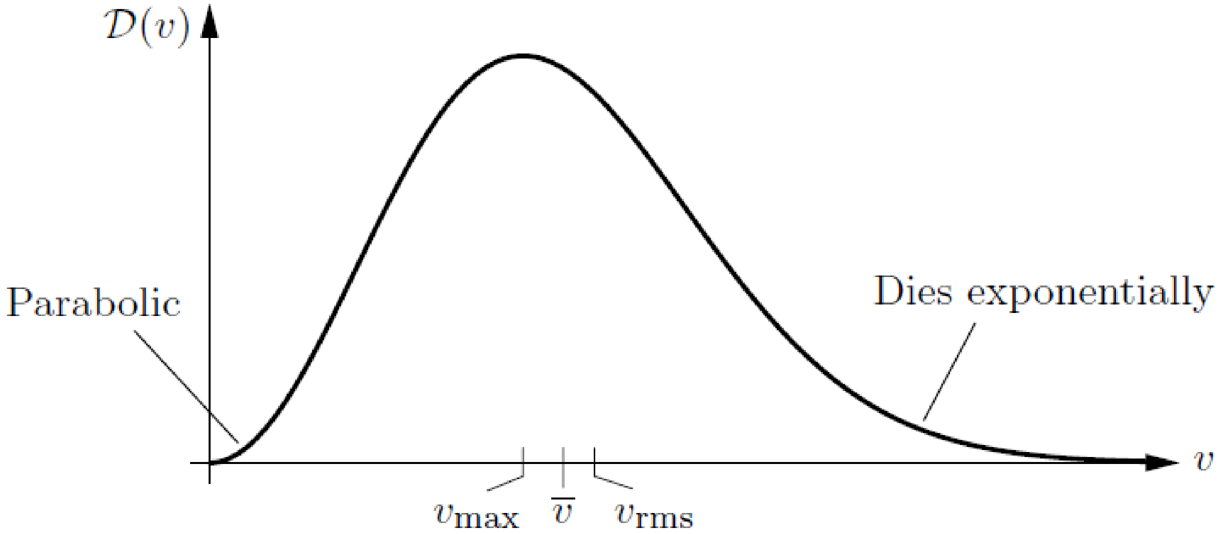


**Figure 6.13.** The Maxwell speed distribution falls off as $v \to 0$ and as $v \to \infty$. The average speed is slightly larger than the most likely speed, while the rms speed is a bit larger still. Copyright ©2000, Addison-Wesley.

# Back to the canonical distribution and the ideal gas

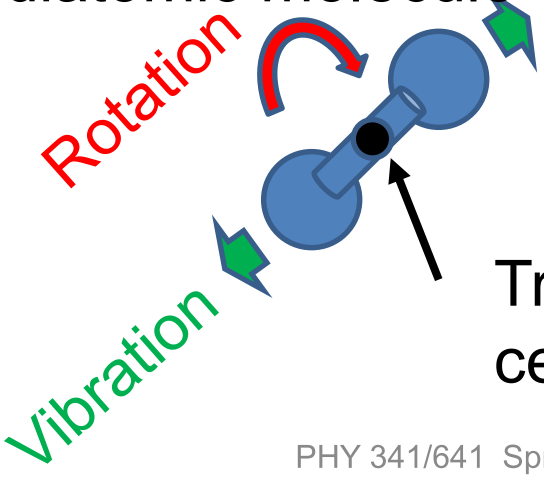
Evaluating the canonical partition function for the $N$ particle

mono atomic ideal gas $\quad U_s \rightarrow \sum_{i=1}^{N} \frac{\left|\mathbf{p}_i\right|^2}{2m}$

$$Z(T) = \sum_s e^{-U_s/kT} = \frac{1}{h^{3N} N!} \int d^3r_1 d^3r_2 \ldots d^3r_N \int d^3p_1 d^3p_2 \ldots d^3p_N \; e^{-\sum_i p_i^2/(2mkT)}$$

$$= \frac{V^N}{h^{3N} N!} \left( \int_{-\infty}^{\infty} dp_x e^{-p_x^2/(2mkT)} \right)^{3N} = \frac{V^N}{h^{3N} N!} \left(2\pi mkT\right)^{3N/2}$$

Now consider the motions of a more complicated system such as a diatomic molecule



$$U_s = U_{trans}(\mathbf{p}) + U_{rot}(j) + U_{vib}(\nu)$$

$$= U_{trans}(\mathbf{p}) + U_{\text{int}}(j, \nu, \ldots)$$

The translational and internal motions are independent and the partition functions can be taken as a product, $Z(T,V,N)=Z_{trans}(T,V,N)Z_{\text{int}}(T,N)$

The translational part is exactly the same as for the mono atomic ideal gas

$$Z_{trans}(T,V,N)=\frac{1}{h^{3N}N!}\int d^3r_1 d^3r_2...d^3r_N\int d^3p_1 d^3p_2...d^3p_N e^{-\sum_i p_i^2/(2mkT)}$$

$$=\frac{V^N}{h^{3N}N!}\left(2\pi mkT\right)^{3N/2}$$

$$Z(T,V,N)=\frac{V^N}{h^{3N}N!}\left(2\pi mkT\right)^{3N/2}Z_{\text{int}}(T,N)$$

In general, $Z_{\text{int}}(T,N)=\left(Z_{\text{int}}(T,1)\right)^N$

Helmholz free energy: $F(T,V,N)=-kT\ln\left(Z(T,V,N)\right)$

$$=-kT\left(\ln\left(Z_{trans}(T,V,N)\right)+\ln\left(Z_{\text{int}}(T,V,N)\right)\right)$$

# Analysis of a canonical ensemble for a molecular ideal gas

$$F(T,V,N) = -kTN\left( \ln\left( \frac{V}{N}\left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right) + 1 \right) - kTN \ln\left( Z_{\mathrm{int}}(T,1) \right)$$

$$S = -\left( \frac{\partial F}{\partial T} \right)_{V,N} \qquad \mathrm{C}_V = T\left( \frac{\partial S}{\partial T} \right)_{V,N} = -\ T\left( \frac{\partial^2 F}{\partial T^2} \right)_{V,N}$$

Approximate treatment for internal motion in terms of diatomic rotations

$$Z_{\mathrm{int}}(T,1) \approx \frac{kT}{\varepsilon}$$

Considering rotations only, limit of “high” temperature

$$F(T,V,N) = -kTN\left( \ln\left( \frac{V}{N}\left( \frac{2\pi mkT}{h^2} \right)^{3/2} \right) + 1 \right) - kTN \ln\left( \frac{kT}{\varepsilon} \right)$$

$$C_V = kN\left( \frac{3}{2} + 1 \right) = \frac{5}{2}kN$$

$$U = F + ST = \frac{5}{2}kNT$$

For our macroscopic treatment of the ideal gas, we have used the empirical parameter

$$\gamma \equiv \frac{C_P}{C_V} \text{ determined from experiment.}$$

In these terms the internal energy can be written:

$$U = \frac{NkT}{\gamma - 1}$$

# Treatment of Bose and Fermi particles

Quantum mechanics introduces additional physics for particles of integer (Bose) and half integer (Fermi) intrinsic spin. Their treatment motivate the introduction of the grand canonical partition function.

$$Z_{Grand}(T,\mu) \equiv \sum_{N'} Z(T,N')\, e^{\beta\mu N'}$$

The grand canonical partition function $Z_{Grand}(T,V,\mu)$

is directly connected to the Grand potential

according to $\Omega(T,V,N) = -kT\ln\left(Z_{Grand}(T,V,\mu)\right)$

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

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

Here we sum over all occupation numbers $n_s$ and energies $\epsilon_s$.

For $N$ particles, the occupation numbers have the condition

$$N = \sum_s n_s.$$

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"

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

Properties of the "Grand potential"

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

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

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

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

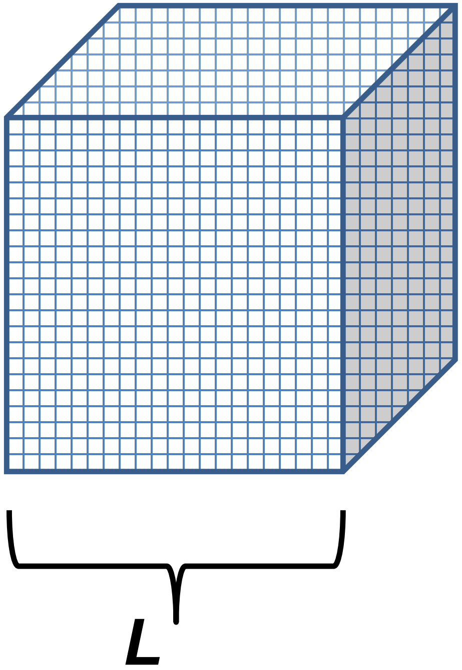
$$\sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)} - 1} = N$$

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

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

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

The summation over s depends on the system. For a three dimensional Fermi or Bose ideal gas it is convenient to calculation the density of states



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

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

Spin degeneracy for spin ½ case

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

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

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

# More general treatment for density of states for particle within a 3-dimensional box with volume *V=L³*

Spatial energy for particle in a given spatial state: $\epsilon_{n_x n_y n_z} = \frac{h^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

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

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

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

where $d_s = 2s+1$ denotes the spin degeneracy

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

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

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

# Evaluation for Fermi particles --

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

For $T=0$:

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

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

# Fermi case --

Determination of chemical potential for T=0:

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

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

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

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

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:

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

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

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

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

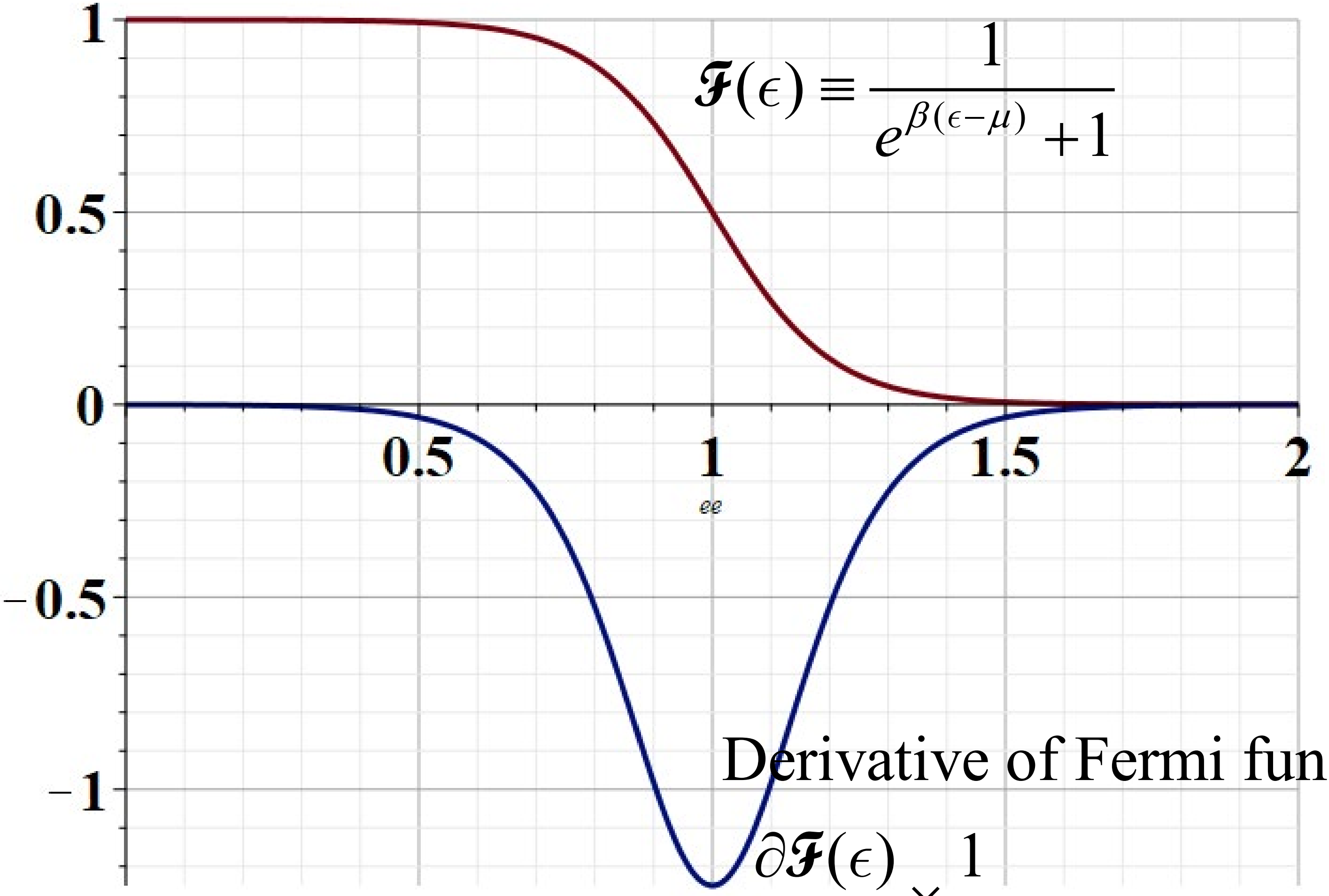
$$\mu(T=0)\equiv \epsilon_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\frac{N}{V}\right)^{2/3}$$

Properties of the "Grand potential"

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

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

# Evaluation of functions for T>0 --



Fermi function:

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

Derivative of Fermi function:

$$\frac{\partial \mathcal{F}(\epsilon)}{\partial \epsilon} \times \frac{1}{2}$$

Evaluation of $\int d\epsilon\ g(\epsilon)\mathcal{F}(\epsilon) = N$

Let $G(\epsilon) \equiv \int_0^\epsilon g(x)dx$

$$\int d\epsilon\ g(\epsilon)\mathcal{F}(\epsilon) = \int d\epsilon\ \frac{dG(\epsilon)}{d\epsilon}\mathcal{F}(\epsilon) = -\int d\epsilon\ G(\epsilon)\frac{d\mathcal{F}(\epsilon)}{d\epsilon}$$

$$\approx -\sum_{m=0}^{\infty}\frac{1}{m!}\frac{d^m G(\mu)}{d\epsilon^m}\int_0^\infty d\epsilon(\epsilon-\mu)^m\frac{d\mathcal{F}(\epsilon)}{d\epsilon}$$