

# **PHY 341/641 Thermodynamics and Statistical Mechanics**

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

**Record!!!**

## **Discussion for Lecture 29:**

**Quantum effects in statistical mechanics**

**Reading: Chapter 7 (mostly 7.3)**

- 1. Summary of results concerning statistical mechanics of Fermi particles**
- 2. Ideal Fermi gas of spin  $\frac{1}{2}$  particles; results at  $T=0$  K and at  $T>0$  K.**
- 3. Other examples of Fermi particle 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           | <i>Holiday</i>                         |      |            |
| 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. 8.1          | Interacting particles                  |      |            |
| 33 | Wed: 04/21/2021 | Chap. 8.2          | Spin magnetism                         |      |            |
| 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                                 |      |            |

# PHY 341/641 -- Assignment #24

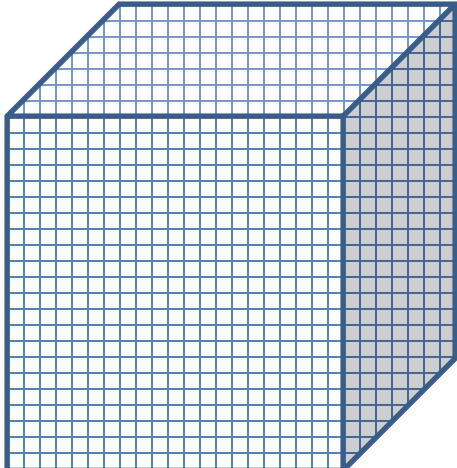
April 12, 2021

Continue reading Chapter 7 in **Schroeder**.

Consider an ideal Fermi gas of spin 1/2 particles confined in a two dimensional plane of length  $L$  and area  $A$ . Each particle has mass  $m$  and there are  $N$  particles. The spatial quantum states of the particles can be enumerated with the integers  $n_x$  and  $n_y$  for  $-\infty \leq n_{x,y} \leq \infty$  according to

$$\varepsilon = \hbar^2/(2mL^2) (n_x^2 + n_y^2).$$

1. Find the density of states  $g(\varepsilon)$  for this system. Do not be surprised to find that it does not depend on  $\varepsilon$ .
2. Evaluate the chemical potential  $\mu$  at  $T=0K$ .
3. Evaluate the Grand potential  $\Omega$  at  $T=0K$ .
4. Evaluate the internal energy  $U$  at  $T=0K$ .



$L$

Comment on evaluating  
density of states  $g(\epsilon)$  in  
3 dimensions --

$$L^3 = V \quad \text{For: } -\infty \leq n_{x,y,z} \leq \infty$$

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

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

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

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

Spin degeneracy

$$\text{Note that } \int dx f(x) \delta(a-x) = f(a)$$

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

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

# Important results from last time

## Properties of the "Grand potential"

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

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

## Relationship of Grand potentials to other thermodynamic potentials

Internal:  $U(S, V, N)$   $\Omega = U - ST - \mu N$

Enthalpy:  $H(S, P, N) = U + PV$   $\Omega = H - PV - ST - \mu N$

Helmholtz:  $F(T, V, N) = U - ST$   $\Omega = F - \mu N$

Gibbs:  $G(T, P, N) = F + PV$   $\Omega = G - PV - \mu N = -PV$

## Important results from last time

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

is directly connected to the Grand potential

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

**True for all indistinguishable quantum particles  
(Fermi or Bose).**

For the case of Fermi particles --

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

$$\sum_s \frac{1}{e^{\beta(\epsilon_s - \mu)} + 1} = N \quad \text{Constraint which defines } \mu.$$

**True for all indistinguishable and non-interacting Fermi quantum particles.**

## Examples of (approximately) non-interacting Fermi particles

1. 3 dimensional spin  $\frac{1}{2}$  Fermi gas (approximated by ideal 3-dimensional metals.)
2. 2 dimensional spin  $\frac{1}{2}$  Fermi gas (your homework problem)
3. Graphene (real 2 dimensional spin  $\frac{1}{2}$  Fermi gas; has a different density of states than your homework)
4. Semi-conductors and insulating materials
5. Electronic states of atoms and molecules

## Evaluation of integrals --

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

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

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

For 3 dimensional ideal Fermi gas

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

## Evaluation of integrals for T=0 --

$$\int d\epsilon g(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \approx \int_0^\mu d\epsilon g(\epsilon) = 4\pi V \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\mu d\epsilon \sqrt{\epsilon}$$

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

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

Evaluation of the Grand potential:

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

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

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

$$\begin{aligned} \Omega(T \rightarrow 0, V, \mu) &= - \int_0^\mu d\epsilon g(\epsilon)(\mu - \epsilon) \\ &= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\mu d\epsilon \sqrt{\epsilon} (\mu - \epsilon) \\ &= -4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{4}{15} \mu^{5/2} \end{aligned}$$

# 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:

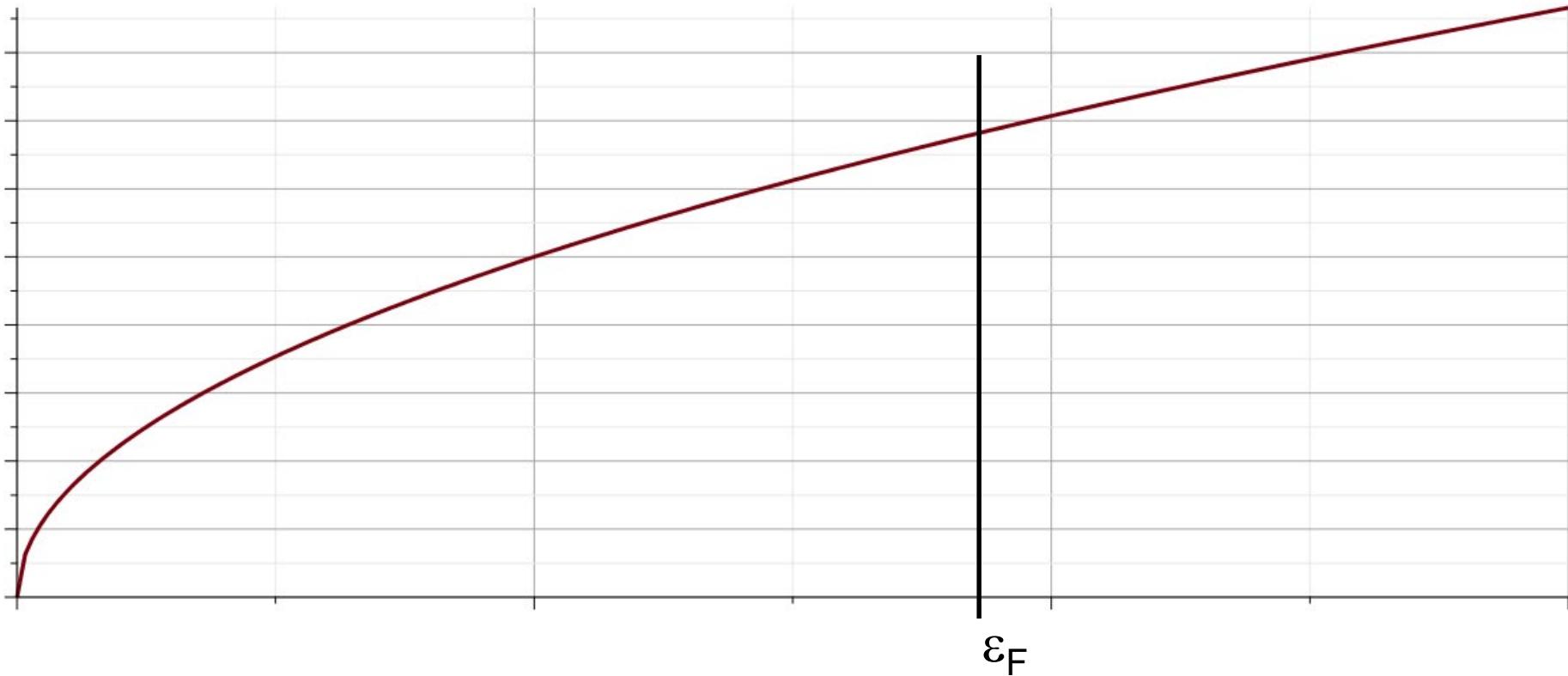
$$\begin{aligned}\Omega(T \rightarrow 0, V, \mu) &= -\int_0^\mu d\epsilon g(\epsilon)(\mu - \epsilon) \\ &= -4\pi V \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\mu d\epsilon \sqrt{\epsilon} (\mu - \epsilon) \\ &= -4\pi V \left( \frac{2m}{h^2} \right)^{3/2} \frac{4}{15} \mu^{5/2}\end{aligned}$$

$$\begin{aligned}\int d\epsilon g(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} &= N \\ \mu(T = 0) \equiv \epsilon_F &= \frac{h^2}{8m} \left( \frac{3}{\pi} \frac{N}{V} \right)^{2/3}\end{aligned}$$

# Some approximate Fermi energies for metals (from Ashcroft and Mermin, Solid State Physics)

| Metal | $\mu(T=0 \text{ K}) \text{ (eV)}$ |
|-------|-----------------------------------|
| Na    | 3.24                              |
| Mg    | 7.08                              |
| Al    | 11.70                             |
| Cu    | 7.00                              |
| Ag    | 5.49                              |
| Au    | 5.53                              |

# Visualization of density of states for ideal 3-dimensional Fermi gas



# Calculated density of states for Cu metal

G. Burdick, Phys. Rev. 129, 138 (1963)

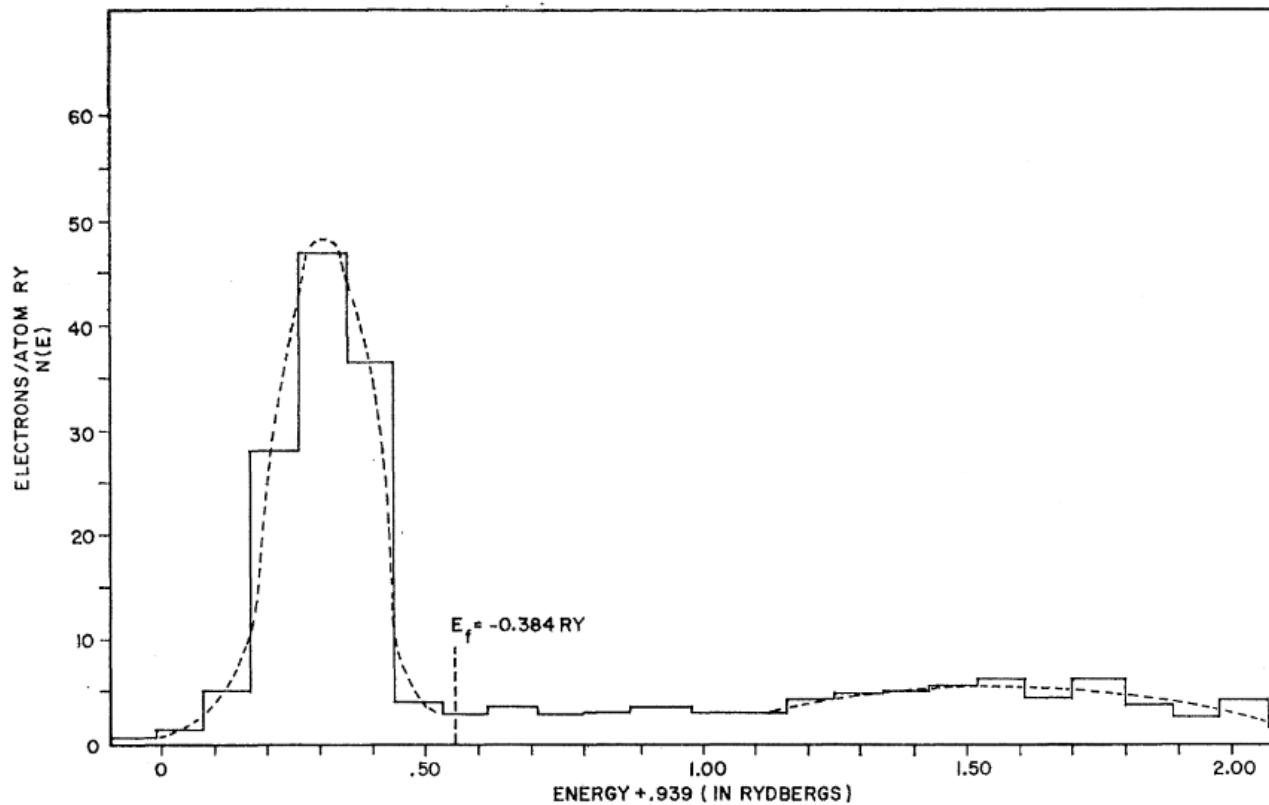


FIG. 5. Histogram for the density of states.

→ More modern theory takes into account modification to density of states due to more realistic quantum treatment

What about effects of  $T>0$ ?

Evaluation of  $\mu$ :

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

Evaluation of the Grand potential:

$$\Omega(T, V, \mu) = -kT \int d\epsilon g(\epsilon) \ln(1 + e^{-\beta(\epsilon-\mu)})$$

For 3 dimensional ideal Fermi gas

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

Evaluation of the Grand potential:

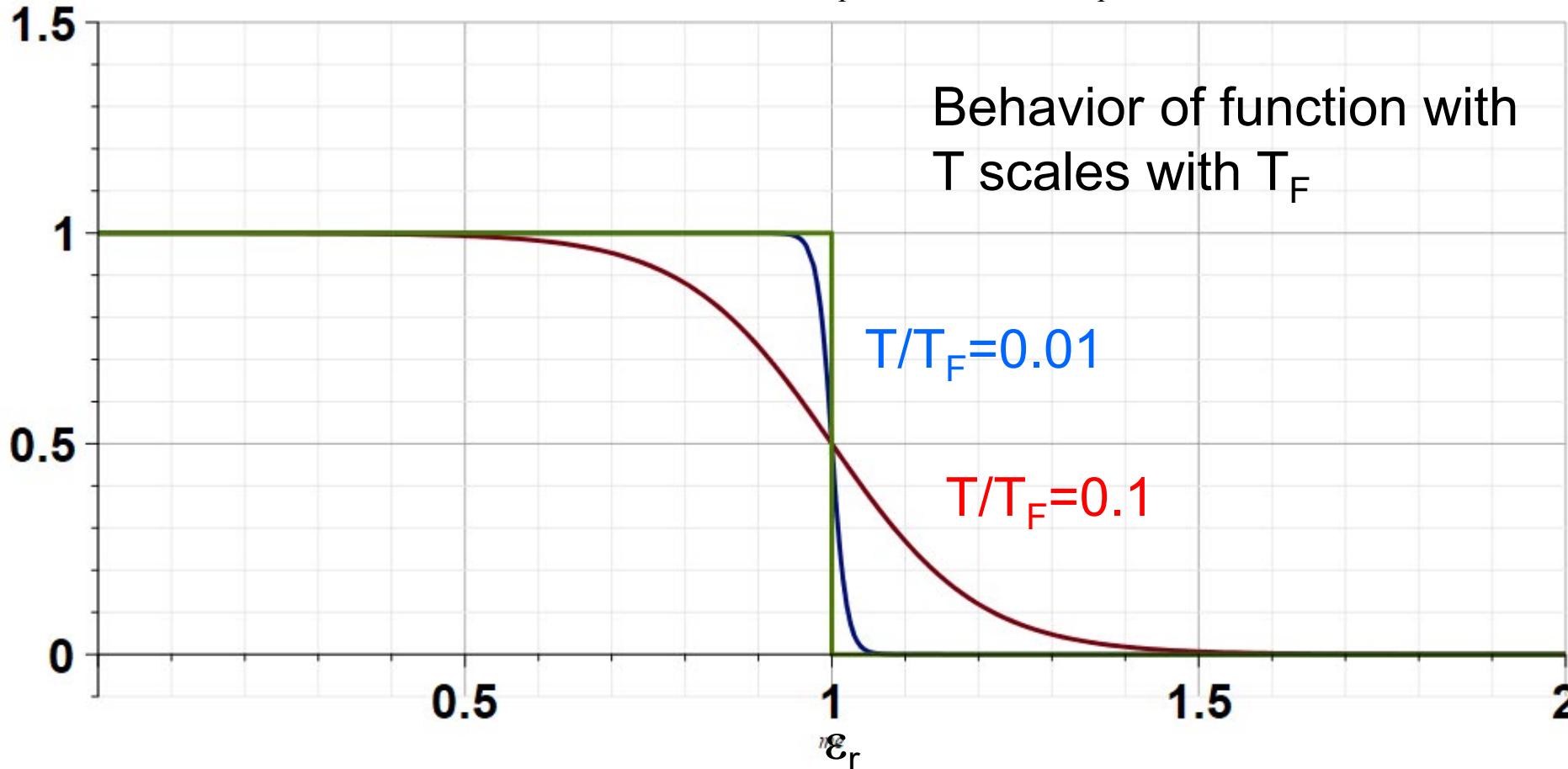
$$\Omega(T, V, \mu) = -kT \int d\epsilon g(\epsilon) \ln \left( 1 + e^{-\beta(\epsilon - \mu)} \right)$$

For  $g(\epsilon) = 4\pi V \left( \frac{2m}{h^2} \right)^{3/2} \sqrt{\epsilon}$  and integrating by parts --

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

Fermi function       $\mathcal{F}(\epsilon, T, \mu) \equiv \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \frac{1}{e^{\frac{T_F}{T}(\epsilon_r - \mu_r)} + 1}$

where       $T_F \equiv \frac{\mu(T=0)}{k} = \frac{\epsilon_F}{k}$        $\epsilon_r \equiv \frac{\epsilon}{\epsilon_F}$        $\mu_r \equiv \frac{\mu}{\epsilon_F}$



# Some approximate Fermi energies for metals (from Ashcroft and Mermin, Solid State Physics)

| Metal | $\mu(T=0 \text{ K}) \text{ (eV)}$ | $T_F \text{ (K)}$ |
|-------|-----------------------------------|-------------------|
| Na    | 3.24                              | 37700             |
| Mg    | 7.08                              | 82300             |
| Al    | 11.70                             | 136000            |
| Cu    | 7.00                              | 81600             |
| Ag    | 5.49                              | 63800             |
| Au    | 5.53                              | 64200             |

## Evaluating integrals for T>0K --

Note that all integrals we need to evaluate have the form

$$\int d\epsilon \mathcal{F}(\epsilon) H(\epsilon).$$

Suppose that  $H(\epsilon) \equiv \int_0^\epsilon d\epsilon h(\epsilon)$

Then:  $\int d\epsilon \mathcal{F}(\epsilon) H(\epsilon) = \int d\epsilon \mathcal{F}(\epsilon) \frac{dh(\epsilon)}{d\epsilon}.$

Some details --

$$\int_0^\infty d\epsilon \mathcal{F}(\epsilon) \frac{dh(\epsilon)}{d\epsilon} \approx (\mathcal{F}(\epsilon)h(\epsilon)) \Big|_0^\infty - \int_0^\infty d\epsilon \frac{d\mathcal{F}(\epsilon)}{d\epsilon} h(\epsilon)$$



Highly peaked function for

$$\epsilon \approx \mu$$

Results given in Sec. 7.3 of your textbook --

$$\mu = \epsilon_F \left( 1 - \frac{\pi^2}{12} \left( \frac{kT}{\epsilon_F} \right)^2 + \dots \right)$$

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F} \dots$$

# What about Fermi systems with different densities of states?

An example of an insulating material where the available electrons fill up the core and valence states of the material.

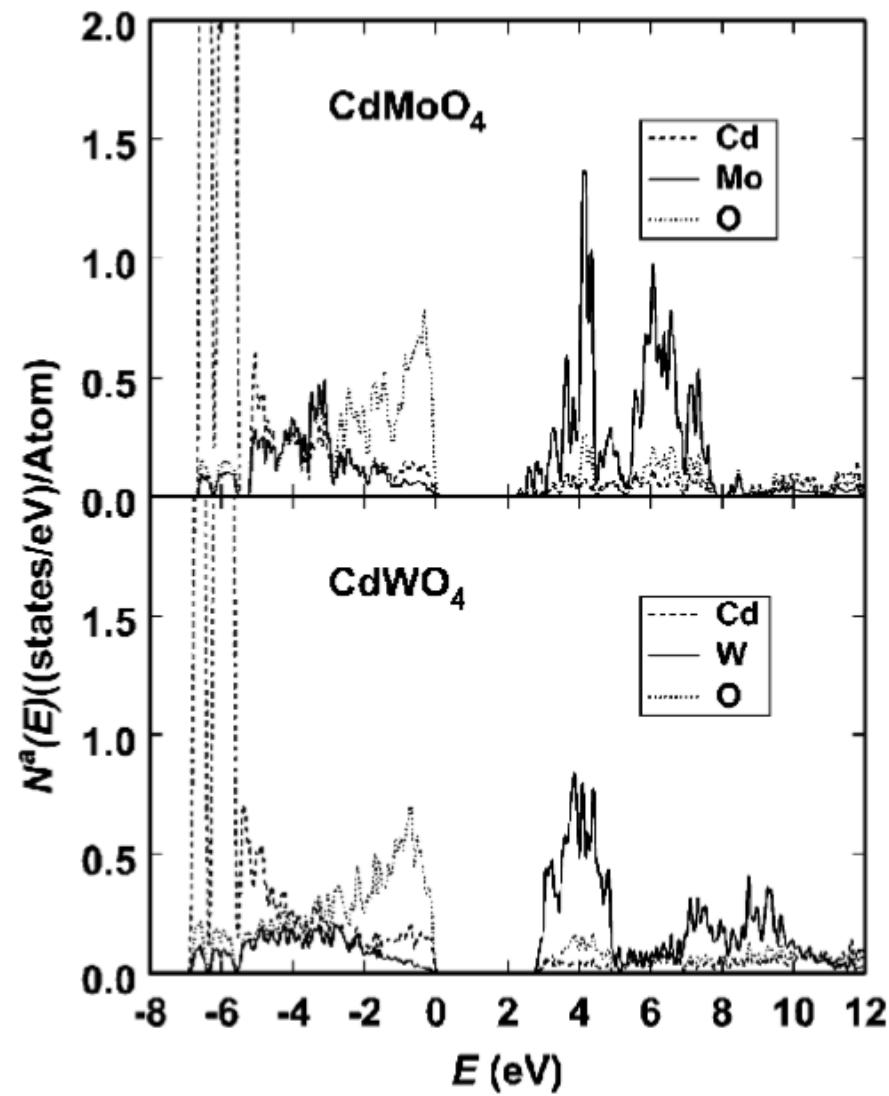
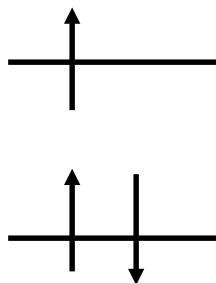


FIG. 2. Partial density-of-states for valence and conduction bands of  $\text{CdMoO}_4$  and  $\text{CdWO}_4$ , indicating Cd, Mo or W, and O contributions with dashed, solid, and dotted lines, respectively.

# Electronic structure of atoms and molecules

Each spatial state can accommodate up to 1 spin up state and 1 spin down state

Li atom



**PERIODIC TABLE**  
**Atomic Properties of the Elements**

NIST National Institute of Standards and Technology  
U.S. Department of Commerce

FREQUENTLY USED FUNDAMENTAL PHYSICAL CONSTANTS<sup>5</sup>

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of  $^{87}\text{Rb}$

| speed of light in vacuum                  | $c$              | 299 792 458 m s <sup>-1</sup>  |
|---|------------------|--|
| Planck constant                           | $h$              | 6.626 070 15 x 10 <sup>-34</sup> J Hz <sup>-1</sup>                    |
| elementary charge                         | $e$              | 1.602 176 034 x 10 <sup>-19</sup> C                                    |
| Avogadro constant                         | $N_A$            | 6.022 140 76 x 10 <sup>23</sup> mol <sup>-1</sup>                      |
| Boltzmann constant                        | $k$              | 1.380 649 x 10 <sup>-23</sup> J K <sup>-1</sup>                        |
| electron volt                             | $eV$             | 1.602 176 034 x 10 <sup>-19</sup> J                                    |
| electron mass                             | $m_e$            | 9.109 383 70 x 10 <sup>-31</sup> kg                                    |
| energy equivalent proton mass             | $m_p c^2$        | 0.510 998 950 MeV  |
| energy equivalent fine-structure constant | $\alpha$         | 1.672 621 924 x 10 <sup>-21</sup> kg                                   |
| Rydberg energy                            | $R_{\infty} h c$ | 938.272 088 MeV  |
| Newtonian constant of gravitation         | $G$              | 1/137.035 999  |
|   |                  | $R_{\infty} h c$   |
|   |                  | 13.605 693 1230 eV   |
|   |                  | $G = 6.674 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2}$ |

<sup>5</sup>For the most accurate values of these and other constants, visit [physics.nist.gov/cuu/Constants/](http://physics.nist.gov/cuu/Constants/).

Legend:

- Solids
- Liquids
- Gases
- Artificially Prepared

| Period | 1    | 2     | 3      | 4     | 5    | 6     | 7      | 8      | 9  | 10 | 11    | 12     | 13      | 14     | 15    | 16     | 17      | 18       |
|--------|------|-------|--------|-------|------|-------|--------|--------|----|----|-------|--------|---------|--------|-------|--------|---------|----------|
| 1      | 1 IA | 2 IIA | 3 IIIB | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 VIII | 9  | 10 | 11 IB | 12 IIB | 13 IIIA | 14 IVA | 15 VA | 16 VIA | 17 VIIA | 18 VIIIA |
| 2      | H    | Be    | Na     | Mg    |      |       |        |        |    |    |       |        | He      |        | O     | F      | Ne      |          |
| 3      | Li   | B     | Sc     | Ti    | V    | Cr    | Mn     | Fe     | Co | Ni | Cu    | Zn     | Al      | Si     | P     | S      | Cl      | Ar       |
| 4      | Ca   | Sc    | Ti     | V     | Cr   | Mn    | Fe     | Co     | Ni | Cu | Zn    | Ga     | Ge      | As     | Se    | Br     | Kr      |          |
| 5      | K    | Sc    | Ti     | V     | Cr   | Mn    | Fe     | Co     | Ni | Cu | Zn    | Ge     | As      | Se     | Br    | I      | Xe      |          |