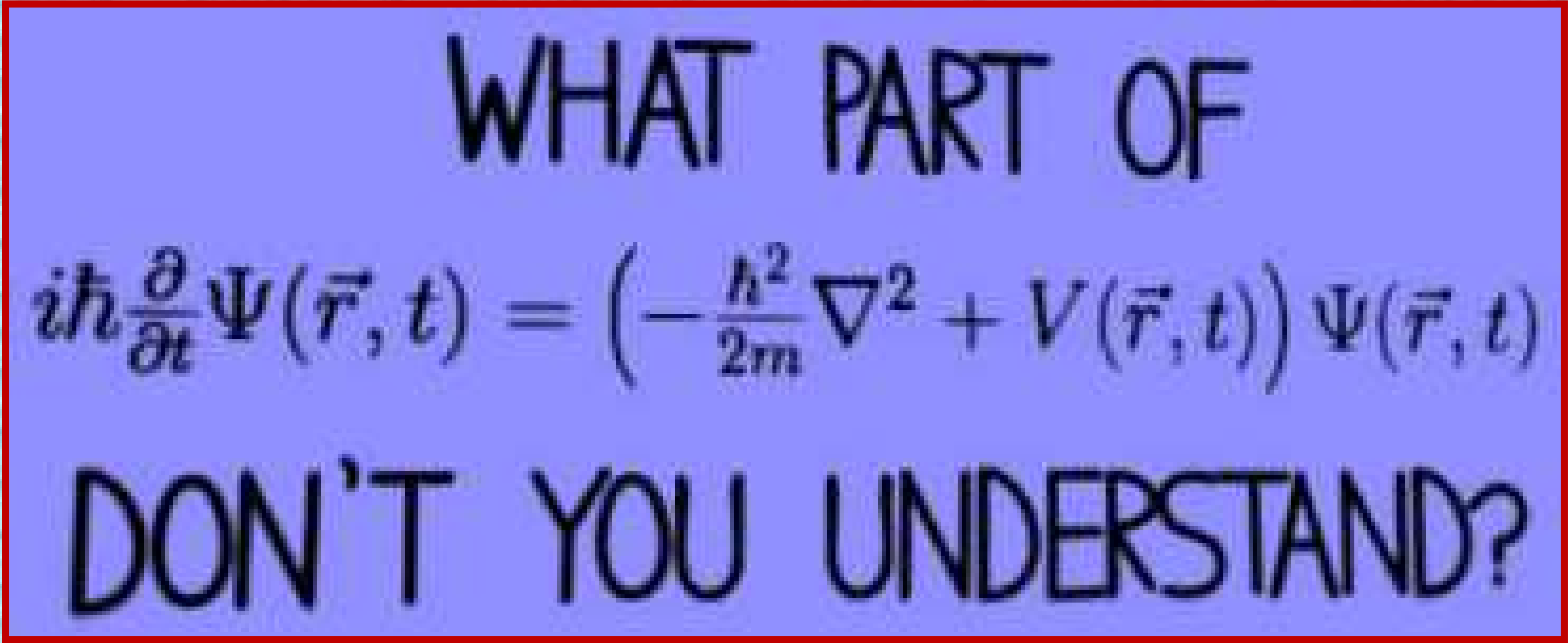
Chapter 6:
Free Electron Fermi Gas



WHAT PART OF

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r},t)\right)\Psi(\vec{r},t)$$

DON'T YOU UNDERSTAND?

Free Electron Theory

- **Conductors** fall into **2** ***main classes***; ***metals*** **& semiconductors.**
- Here, we focus on ***metals.***
- ***A metal*** is loosely ***defined*** as a solid with valence electrons that are not tightly bound to the atoms but are relatively easily able to move through the whole crystal.

- The **room temperature resistivity *of metals*** is in the range:

$$\boxed{\rho(RT)_{metals};10^{-6}-10^{-8}\Omega-m}$$

- ***Experiments show that*** ρ increases with the addition of small amounts of impurities. The resistivity normally decreases monotonically with decreasing temperature & it can be reduced by the addition of small amounts of impurity.

Question!

- **Why do mobile (conducting) electrons occur in some solids & not in others?**
- When the interactions between electrons are considered, this becomes a

Very Difficult Question to Answer.

Some Common Properties of Metals:

1. **Great Physical Strength**
2. **High Density**
3. **Good Electrical Conductivity**
4. **Good Thermal Conductivity**
5. **…….etc.**

- In this chapter, we outline a surprisingly ***simple theory*** which does ***a very good job*** of explaining many of these common properties of metals.
- In fact, the theory is so simple (***too simple to be realistic!***) that we may wonder why it works so well!

"The Free Electron Model"

- We begin with the assumption ***that conduction electrons exist*** & that they consist of the ***valence electrons*** **from the metal atoms.**
- Thus, metallic **Na, Mg & Al** are assumed to have **1, 2 & 3** mobile electrons per atom, respectively.
- This model seems at first as if it is

Way Too Simple!

- But, this simple model works ***remarkably well*** for many metals & it can be used to help to explain many properties of metals.

- According to this

  Free Electron Model **(FEM)**,

  the valence electrons are responsible for the conduction of electricity, & for this reason these electrons are called

  "Conduction Electrons".

- As an example, consider **Sodium (Na).** The **electron configuration** of the **Free Na Atom** is:

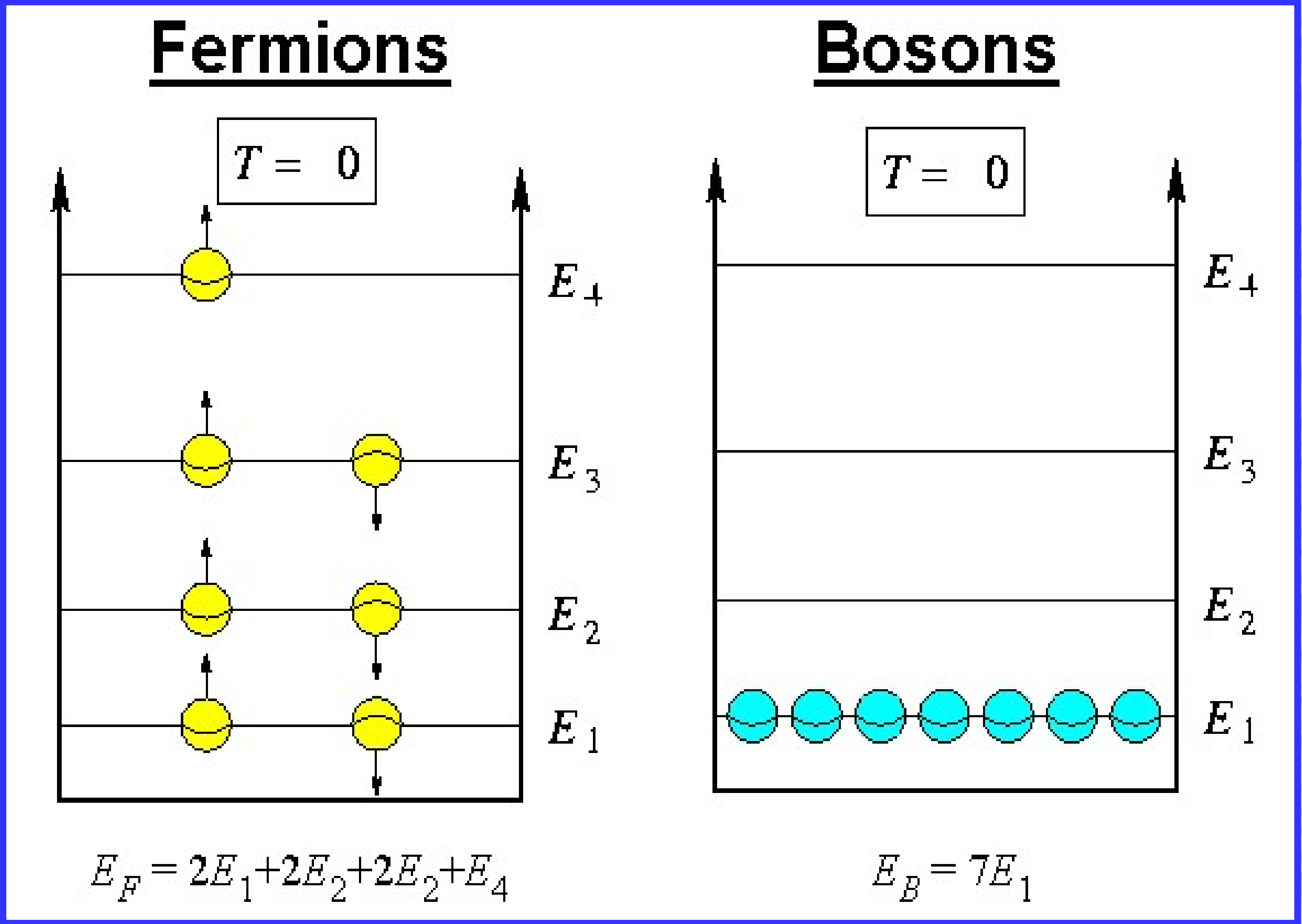
Core Electrons
(tightly bound)

$$\underbrace{1s^2\ 2s^2\ 2p^6}\ 3s^1$$

Valence Electrons
(loosely bound)

- The **outer electron in the third atomic shell** **(n = 3, ℓ = 0)** ***is the electron which is responsible for the physical & chemical properties of Na.***

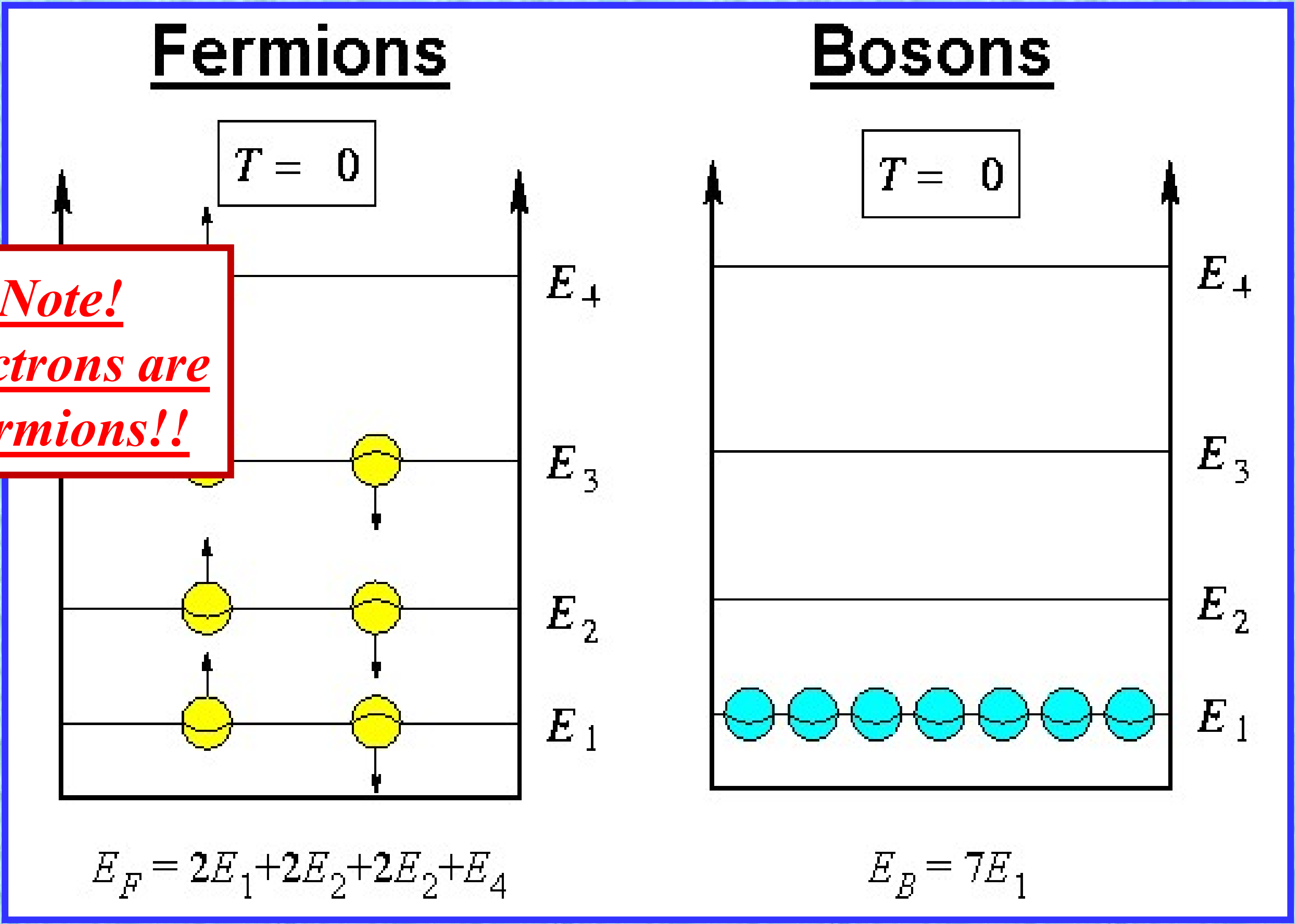
Consider Fermions & Bosons
in a 1-D Potential Well



$E_F = 2E_1 + 2E_2 + 2E_2 + E_4$

$E_B = 7E_1$

Consider Fermions & Bosons in a 1-D Potential Well



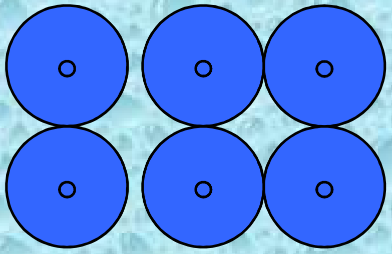
$E_F = 2E_1+2E_2+2E_2+E_4$

$E_B = 7E_1$

Note!

Electrons are Fermions!!

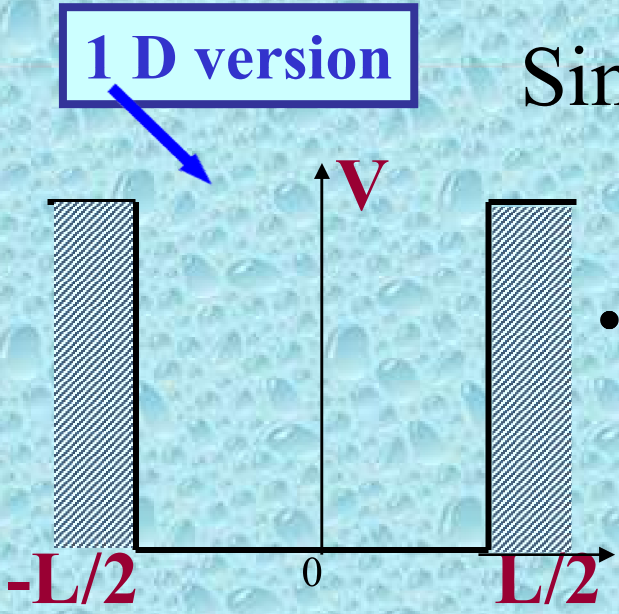
- When **Na atoms** are put together to form a **Na metal:**



Na metal

- **Na** has a BCC structure & the distance between nearest neighbours is **3.7 A°**
- The radius of the third shell in **Na** is **1.9 A°**
- In the solid, the electron wavefunctions of the **Na atoms** overlap slightly. From this observation it follows that a valence electron is no longer attached to a particular ion, but belongs to both neighbouring ions at the same time.

- Therefore, these conduction electrons can be considered as **moving independently** in a square well of finite depth & the edges of the well correspond to the edges of the sample.
- Consider a metal with a cubic shape with edge length **L**: **Ψ** & **E** can be found by solving the Schrödinger equation:



Since $\boxed{V = 0}$ $$\boxed{-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi}$$

- Use periodic boundary conditions & get **Ψ's** as travelling plane waves.

$$\boxed{\psi(x+L, y+L, z+L) = \psi(x, y, z)}$$

- The solutions to the Schrödinger equation are plane waves,

$$\boxed{\psi(x,y,z) = \underbrace{\frac{1}{\sqrt{V}}}_{\text{Normalization constant}} e^{i\vec{k}\vec{r}} = \frac{1}{\sqrt{V}} e^{i(k_x x + k_y y + k_z z)}}$$

$$\boxed{Na = p\lambda} \Longrightarrow \boxed{Na = p\frac{2\pi}{k}} \boxed{\left(where, k = \frac{2\pi}{\lambda} \right)} \Longrightarrow \boxed{k = \frac{2\pi}{Na} p = \frac{2\pi}{L} p}$$

V = volume of the cube, **V=L³**

- So the wave vector must be of the form:

$$\boxed{k_x = \frac{2\pi}{L} p} \qquad \boxed{k_y = \frac{2\pi}{L} q} \qquad \boxed{k_z = \frac{2\pi}{L} r}$$

where p, q, r take any + or - integer values or zero.

- The wave function **ψ(x,y,z)** corresponds to the energy

$$\boxed{E = \frac{\hbar^2 k^2}{2m}} \qquad \boxed{E = \frac{\hbar^2}{2m}\left(k_x{}^2 + k_y{}^2 + k_z{}^2\right)}$$

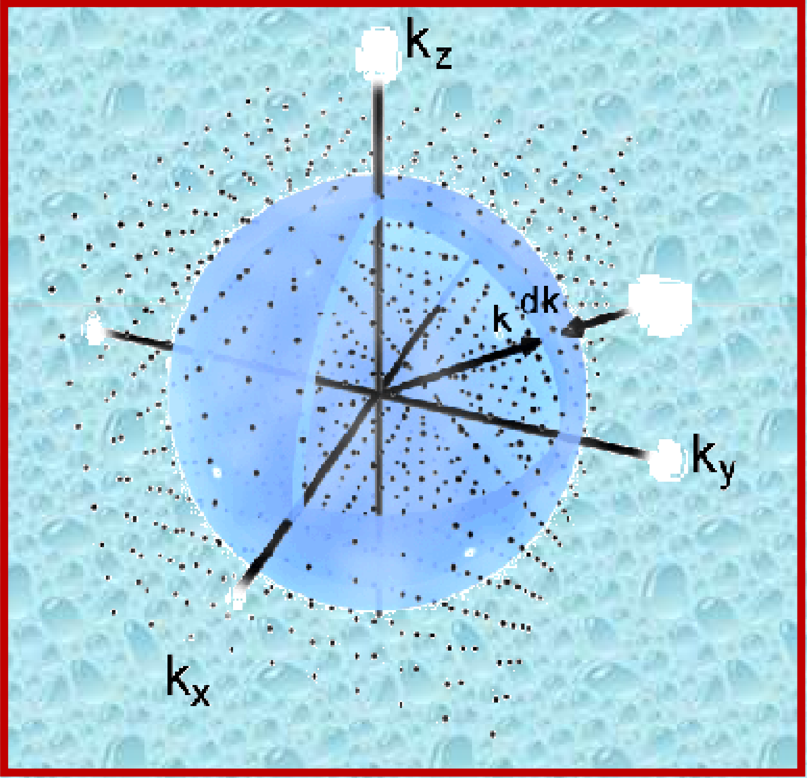
- The corresponding momentum is:

$$\boxed{p = \hbar(k_x, k_y, k_z)}$$

- The energy is completely kinetic:

$$\boxed{\frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m}} \Longrightarrow \boxed{m^2 v^2 = \hbar^2 k^2} \Longrightarrow \boxed{p = \hbar k}$$

- We know that number of allowed **k** values in a spherical shell of **k-space** of radius **k** is:



$$g(k)dk = \frac{Vk^2}{2\pi^2}dk,$$

- **g(k)** is called the density of states per unit magnitude of **k**.

Number of Allowed States per Unit Energy Range?

- **Each k state represents two possible electron states**, one for spin up, the other for spin down.

$$\boxed{g(E)dE = 2g(k)dk} \rightarrow \boxed{g(E) = 2g(k)\frac{dk}{dE}}$$

$$\boxed{E = \frac{\hbar^2 k^2}{2m}} \qquad \boxed{\frac{dE}{dk} = \frac{\hbar^2 k}{m}} \qquad \boxed{k = \sqrt{\frac{2mE}{\hbar^2}}}$$

$$g(E) = 2g(k)\frac{dk}{dE} \rightarrow g(E) = 2\frac{V}{2\pi^2}\frac{m}{\hbar^2 k}\,k\quad k$$

$$\boxed{g(E) = \frac{V}{2\pi^2\hbar^3}(2m)^{3/2}E^{1/2}}$$

Ground State of the Free Electron Gas (T = 0)

- Electrons are **Fermions (s = ± ½)** & obey the ***Pauli exclusion principle***; each state can accommodate only one electron.
- The lowest-energy state of **N** free electrons is therefore obtained by filling the **N** states of lowest energy.

- Thus all states are filled up to an energy E_F, ***known as The Fermi energy***, obtained by integrating the density of states between **0** and E_F, The result should equal **N.** Remember that

$$\boxed{g(E)=\frac{V}{2\pi^2\hbar^3}(2m)^{3/2}E^{1/2}}$$

$$\boxed{N=\int_0^{E_F}g(E)dE=\int_0^{E_F}\frac{V}{2\pi^2\hbar^3}(2m)^{3/2}E^{1/2}dE=\frac{V}{3\pi^2\hbar^3}(2mE_F)^{3/2}}$$

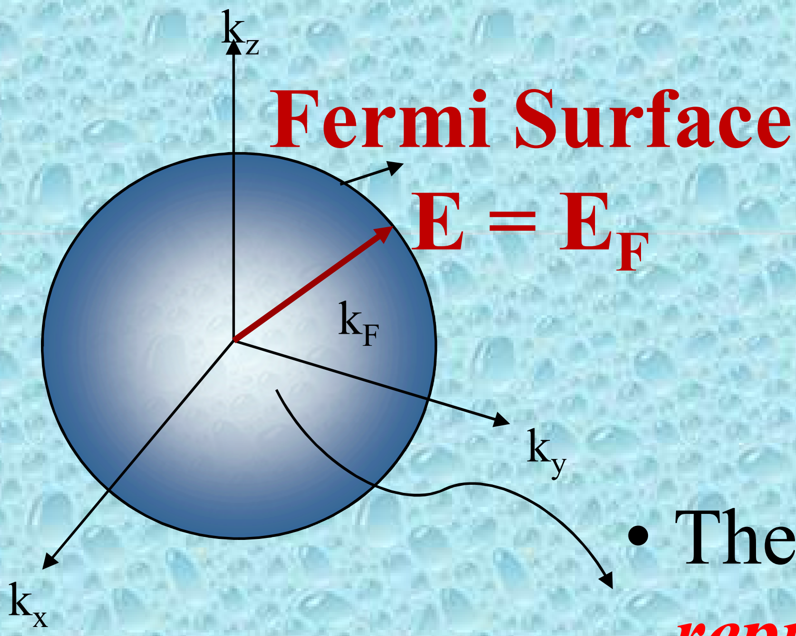
- Solving for E_F (***Fermi energy***);

$$\boxed{E_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2N}{V}\right)^{2/3}}$$

- The occupied states are inside the **Fermi sphere in k-space** as shown below; the radius is Fermi wave number $\mathbf{k_F}$.

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

$$E_F = \frac{\hbar^2 k_F^{\ 2}}{2m_e}$$



From these two equations, $\mathbf{k_F}$ can be found as,

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

- The ***surface of the Fermi sphere represents the boundary between occupied & unoccupied k states*** at **T = 0** for the free electron gas.

- Typical values may be obtained by using monovalant **potassium metal** (**K**) as an example; for potassium, the atomic density & hence **the valence electron density n = N/V = 1.402x10^{28} m^{-3}** so that

$$\boxed{E_F = 3.40\times10^{-19}J = 2.12eV}$$

$$\boxed{k_F = 0.746 A^{\circ -1}}$$

- The ***Fermi (degeneracy) Temperature*** **T$_F$** is given by

$$\boxed{E_F = k_B T_F} \qquad \boxed{T_F = \frac{E_F}{k_B} = 2.46\times10^4 K}$$

It is only at a temperature of this order that the particles in a classical gas can attain (gain) kinetic energies as high as **E_F .**

- Only at temperatures above **T_F** will the free electron gas behave like a classical gas.
- Fermi momentum $P_F = \hbar k_F \qquad P_F = m_e V_F$

$$\boxed{V_F = \frac{P_F}{m_e} = 0.86 \times 10^6 \, ms^{-1}}$$

- These are the momentum & velocity values of the electrons at the states on the Fermi surface of the Fermi sphere. So, the Fermi Sphere plays an important role in the behaviour of metals.

The Fermi wave vector: $k_F = (3\pi^2 n)^{1/3}$ ~1 Å^{-1}

The Fermi momentum: $p_{\mathrm{F}} = \hbar k_{\mathrm{F}}$ ~10^{-23} kg-m/s

The Fermi energy: $\varepsilon_F = \dfrac{\hbar^2 k_F^2}{2m}$ ~5 eV

The Fermi velocity: $v_{\mathrm{F}} = \dfrac{p_{\mathrm{F}}}{m} = \dfrac{\hbar}{m} k_{\mathrm{F}}$ ~10^6 m/s

The Fermi temperature: $T_F = \dfrac{\varepsilon_F}{k_B}$ ~10^4 K

Free Electron Gas at Non-Zero Temperature

- From Statistical Mechanics, at a temperature **T,** the probability of occupation of an electron state of energy **E** is given by the Fermi distribution function

$$\boxed{f_{FD} = \frac{1}{1 + e^{(E - E_F)/k_B T}}}$$

- The Fermi distribution function **$f_{FD}(E)$** ddetermines, at temperature **T**, the probability of finding an electron at energy **E.**

Fermi-Dirac Distribution & *The Fermi-Level*:
Main Application: Electrons in a Conductor

- **The Density of States g(E)** specifies *how many states exist at a given energy* E.
- **The Fermi Function f(E)** specifies *how many of the existing states at energy* E *will be filled* with electrons.

$$\boxed{f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}}$$

E_F = Fermi Energy or Fermi Level

k = Boltzmann Constant

T = Absolute Temperature in K

- **The Fermi Function f(E)** specifies, ***under equilibrium conditions,*** the ***probability*** that an available state at an energy E will be occupied by an electron. It is a ***probability distribution function.***

Fermi-Dirac Statistics

- The **Fermi Energy** $\mathbf{E_F}$ is essentially the same as the **Chemical Potential μ.**

$$F_{\mathrm{FD}} = \frac{1}{\exp(\beta(E - E_{\mathrm{F}})) + 1}$$

β ≡ (1/kT)

$\mathbf{E_F}$ is called ***The Fermi Energy***.

Note the following:

- When $\mathbf{E = E_F}$, the exponential term = **1** & $\mathbf{F_{FD} = (½)}$.
- In the limit as **T → 0:**

$$F_{\mathrm{FD}} = \begin{cases} 1 & \text{for } E < E_{\mathrm{F}} \\ 0 & \text{for } E > E_{\mathrm{F}} \end{cases}$$

- At **T = 0**, Fermions occupy the lowest energy levels.
- Near **T = 0**, there is little chance that thermal agitation will kick a **Fermion** to an energy greater than $\mathbf{E_F}$.

Fermi-Dirac Distribution

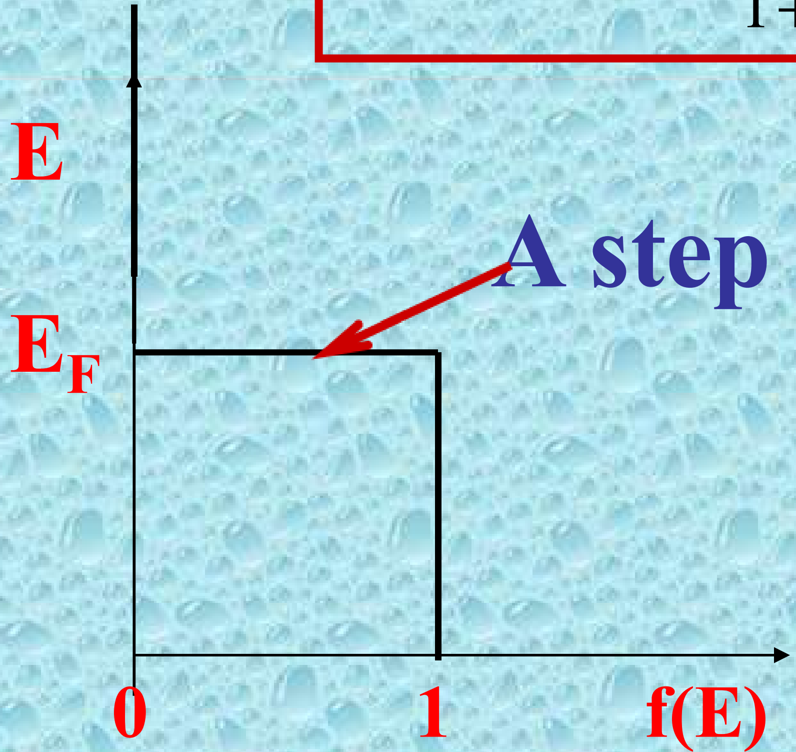
Consider $T \to 0$ K

For $E > E_F$:

$$f(E > E_F) = \frac{1}{1+\exp(+\infty)} = 0$$

For $E < E_F$:

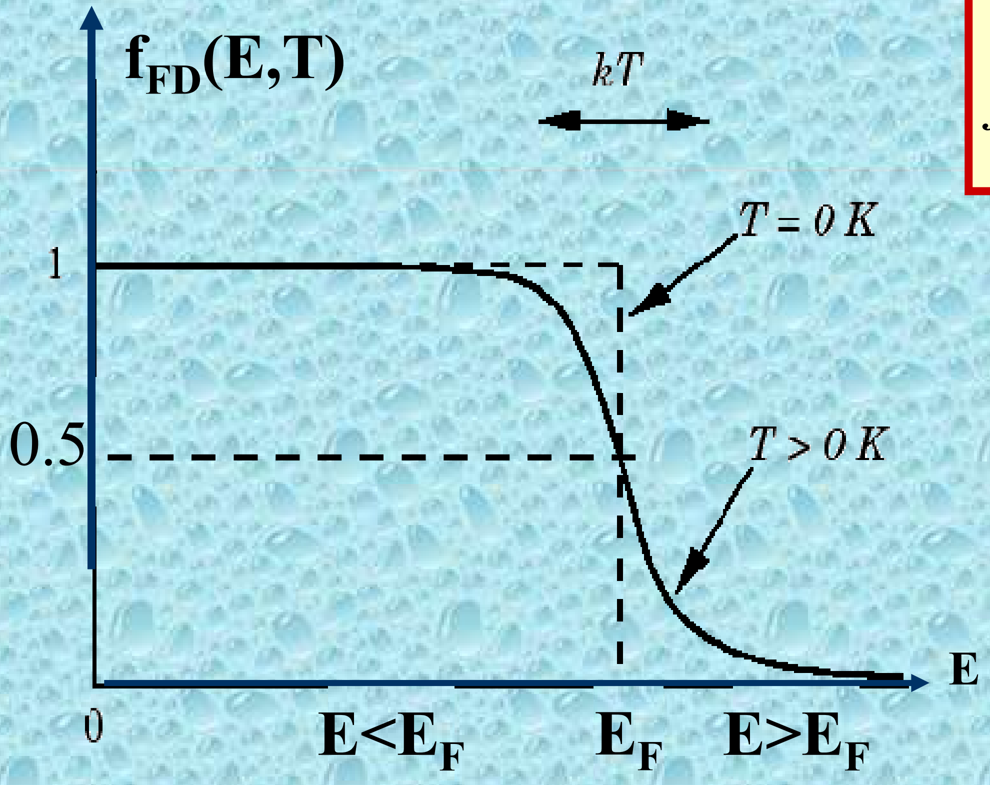
$$f(E < E_F) = \frac{1}{1+\exp(-\infty)} = 1$$



A step function!

Fermi Function at T = 0 & at a Finite Temperature

$$f_{FD} = \frac{1}{1+e^{(E-E_F)/k_BT}}$$



f_{FD}=? At 0°K

For $E < E_F$

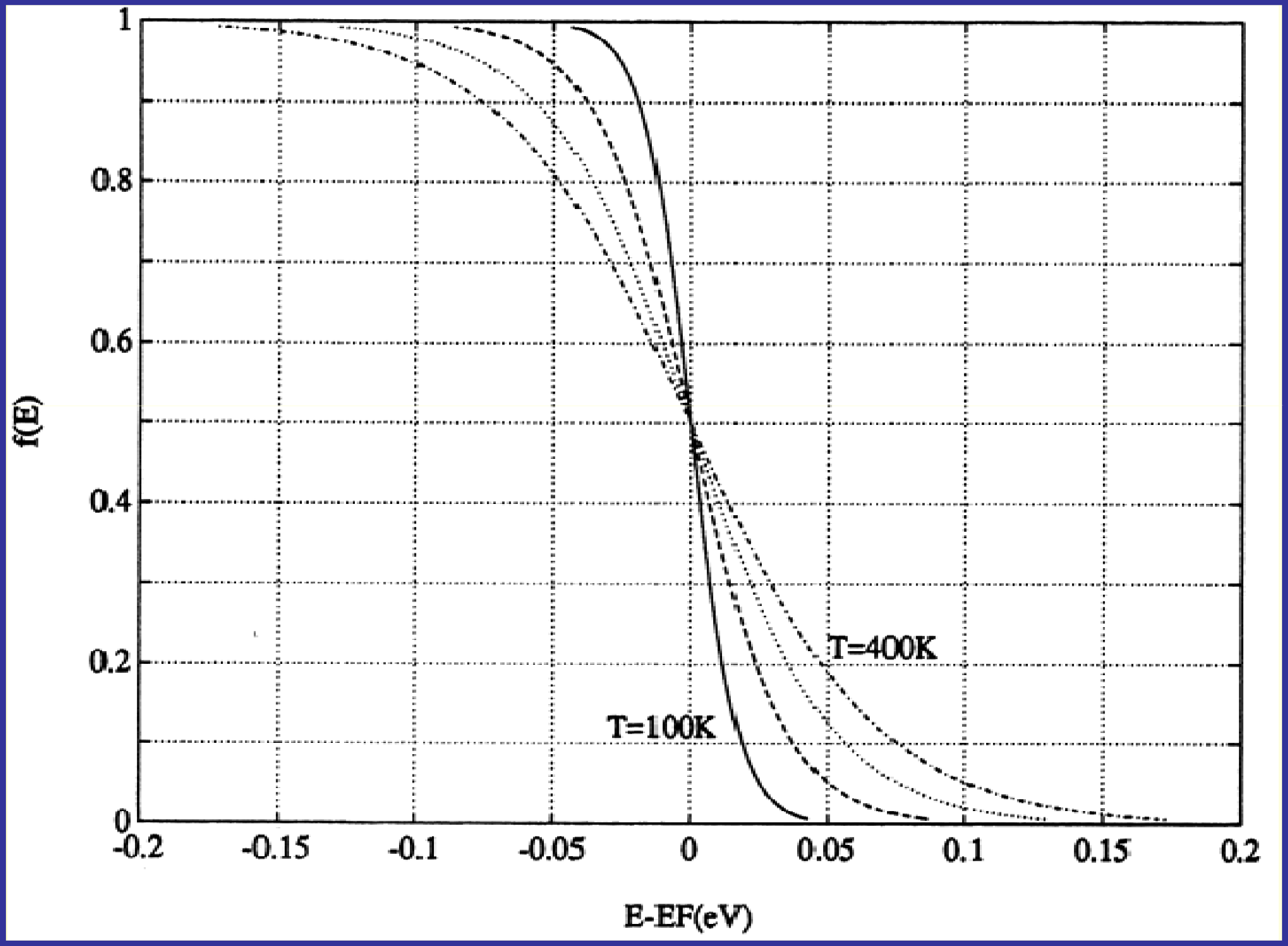
$$f_{FD} = \frac{1}{1+e^{(E-E_F)/k_BT}} = 1$$

For $E > E_F$

$$f_{FD} = \frac{1}{1+e^{(E-E_F)/k_BT}} = 0$$

Fermi-Dirac Distribution

Temperature Dependence



Fermi-Dirac Distribution: $T > 0$ K

FD Distribution

$$\boxed{f_{FD} = \frac{1}{1 + e^{(E - E_F)/k_B T}}}$$

1

- If **E = E$_F$** then **f(E$_F$) = ½ .**
- If $\boxed{E \le E_{\mathrm{F}} - 3kT}$ then: $\boxed{\exp\left(\frac{E - E_{\mathrm{F}}}{kT}\right) << 1}$
- So, the following approximation is valid:

T

$$\boxed{f(E) = \exp\left(\frac{-(E - E_{\mathrm{F}})}{kT}\right)}$$

- That is, most states at energies **3kT** above **E$_F$** ***are empty.***

Fermi-Dirac Distribution: $T > 0$ K

FD Distribution

$$\boxed{f_{FD} = \frac{1}{1 + e^{(E - E_F)/k_B T}}}$$

l

- If $\boxed{E \leq E_F - 3kT}$ then $\boxed{\exp\left(\frac{E - E_F}{kT}\right) >> 1}$
- So, the following approximation is valid:

L

$$\boxed{f(E) = 1 - \exp\left(\frac{E - E_F}{kT}\right)}$$

- That is, most states at energies **3kT** below **E$_F$** ***are occupied.***

Fermi-Dirac Distribution: Summary for $T > 0$ K

FD Distribution

$$\boxed{f_{FD} = \frac{1}{1 + e^{(E - E_F)/k_B T}}}$$

1

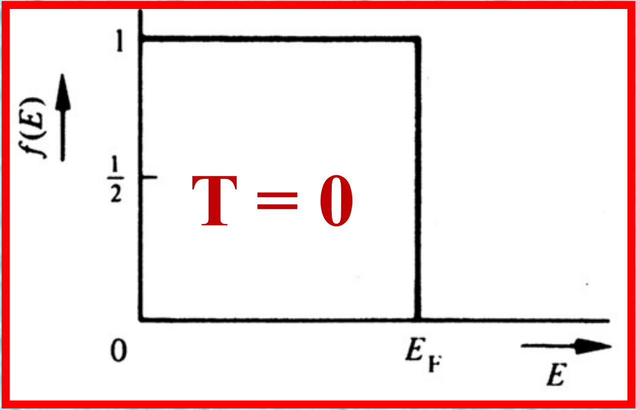
- ***So, the following is always true at room temperature***: Only states within ± **3kT** of $\mathbf{E_F}$ **will contribute** to temperature dependent properties of the conduction electrons.

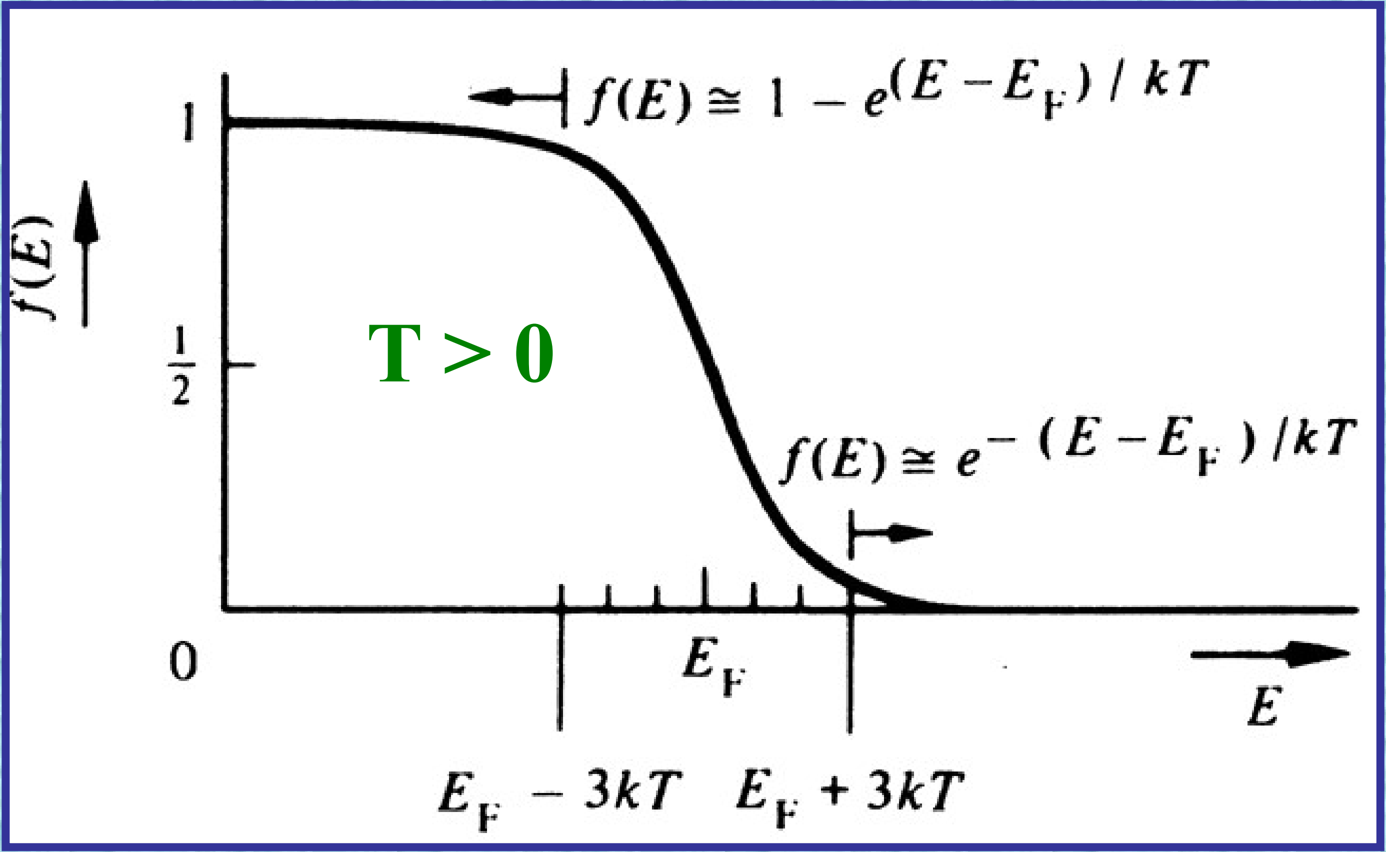
kT (at 300 K) = 0.025eV,

$\mathbf{E_g}$(Si) = 1.1eV,

- ***So 3kT is very small in comparison to other energies relelevant to the electrons.***

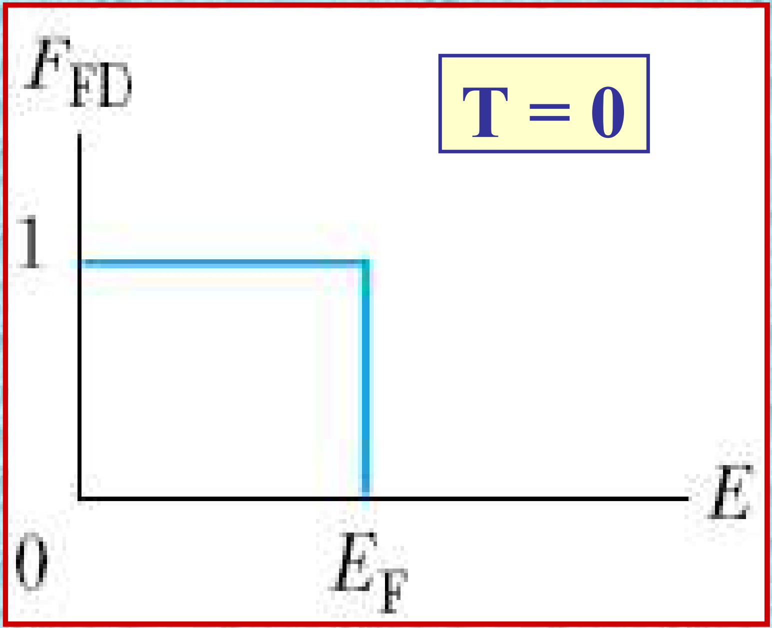
Fermi-Dirac Distribution
Temperature Dependence

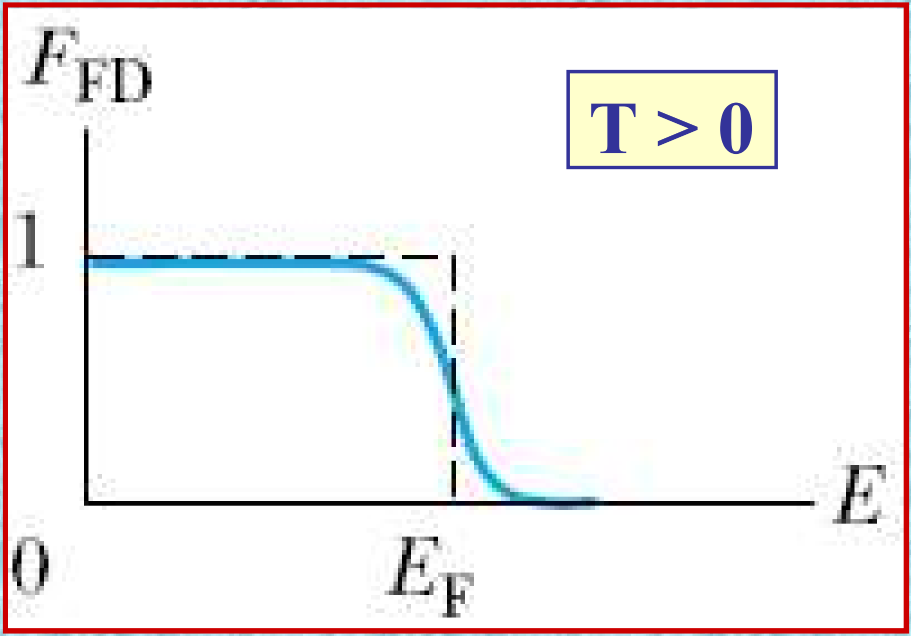




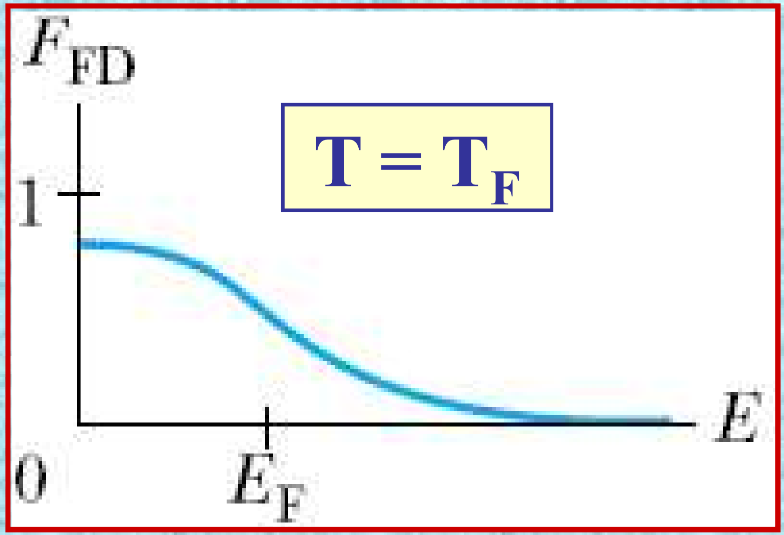
The Fermi **"Temperature"** is defined as

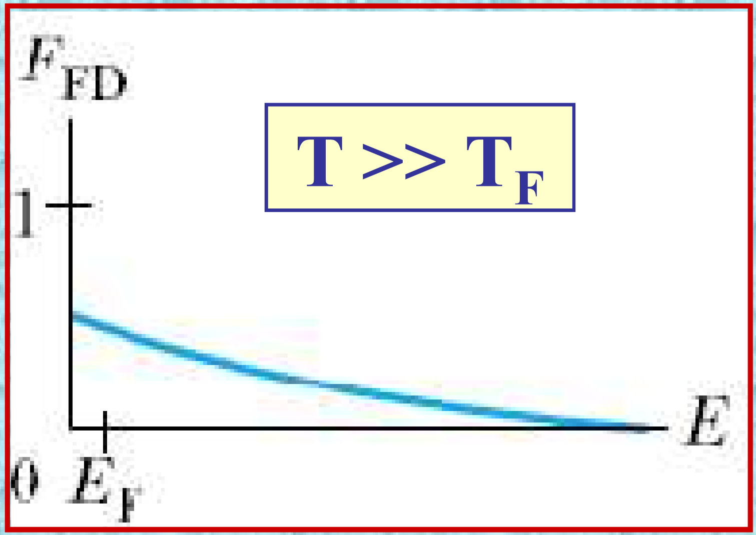
$$T_F \equiv (E_F)/(k_B).$$





As the temperature increases from **T = 0,** **The Fermi-Dirac Distribution** "smears out".





- As the temperature increases from **$T = 0$,** **The Fermi-Dirac Distribution** “smears out”.
- When **$T >> T_F$, F_{FD}** approaches a decaying exponential.

At T = 0 the Fermi Energy E_F *is the energy of the highest occupied energy level*.

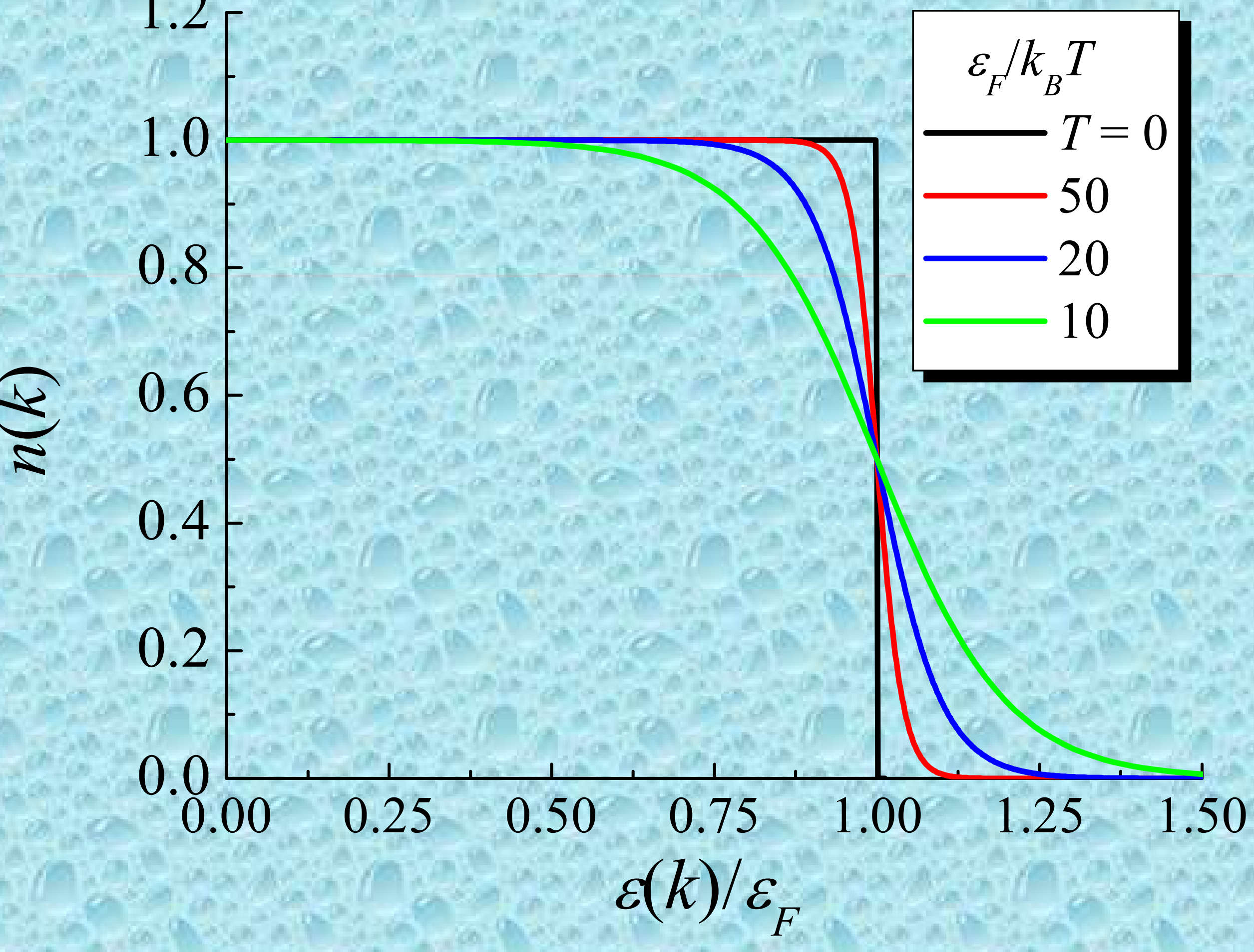
- If there are a total of **N electrons**, then is easy to show that $\mathbf{E_F}$ has the form:

$$N = \frac{1}{3}\pi\left(\frac{E_F}{E_1}\right)^{3/2}$$

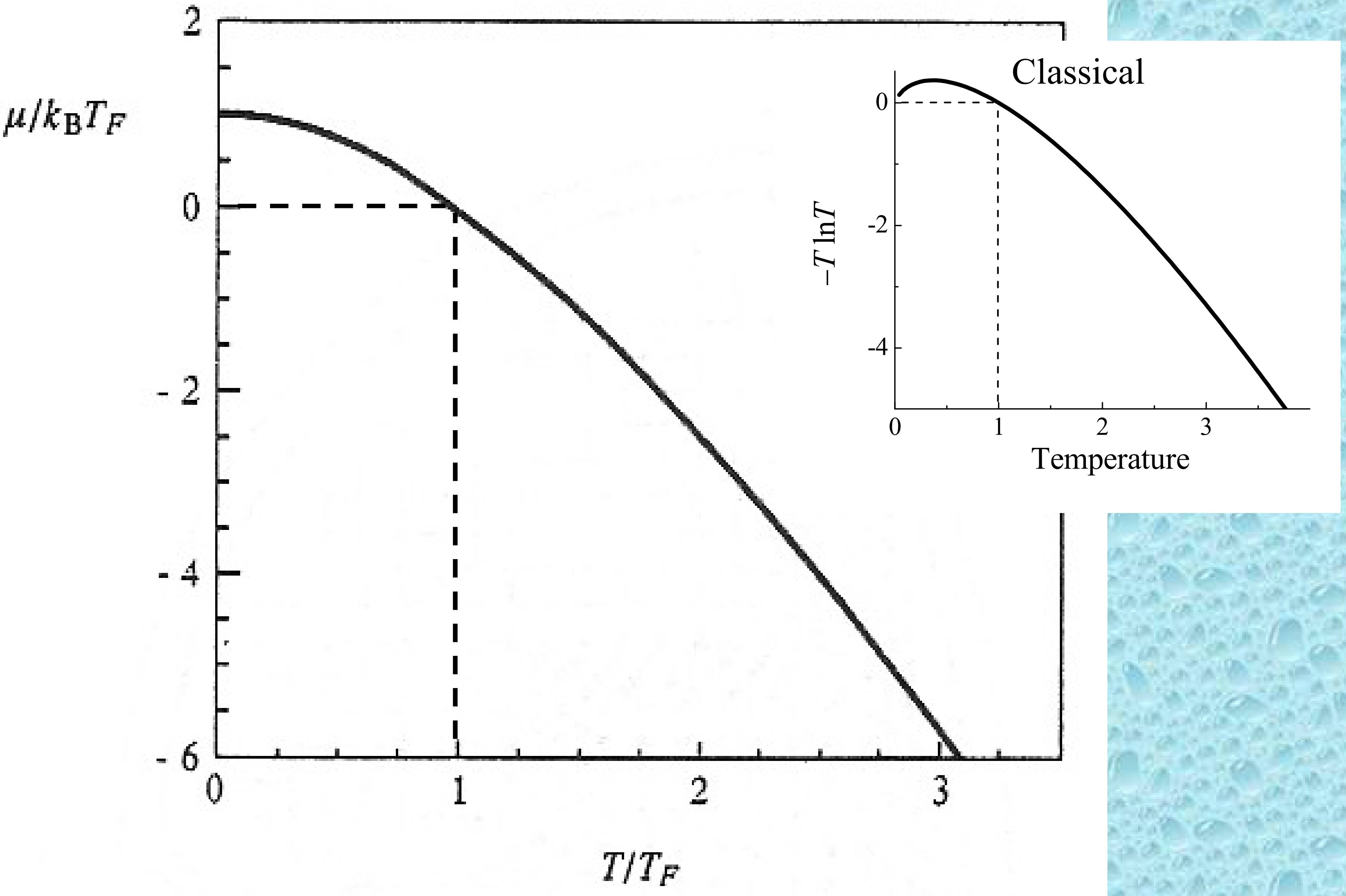
$$E_F = E_1\left(\frac{3N}{\pi}\right)^{2/3} = \frac{h^2}{8m}\left(\frac{3N}{\pi L^3}\right)^{2/3}$$

Fermi-Dirac Distribution Function

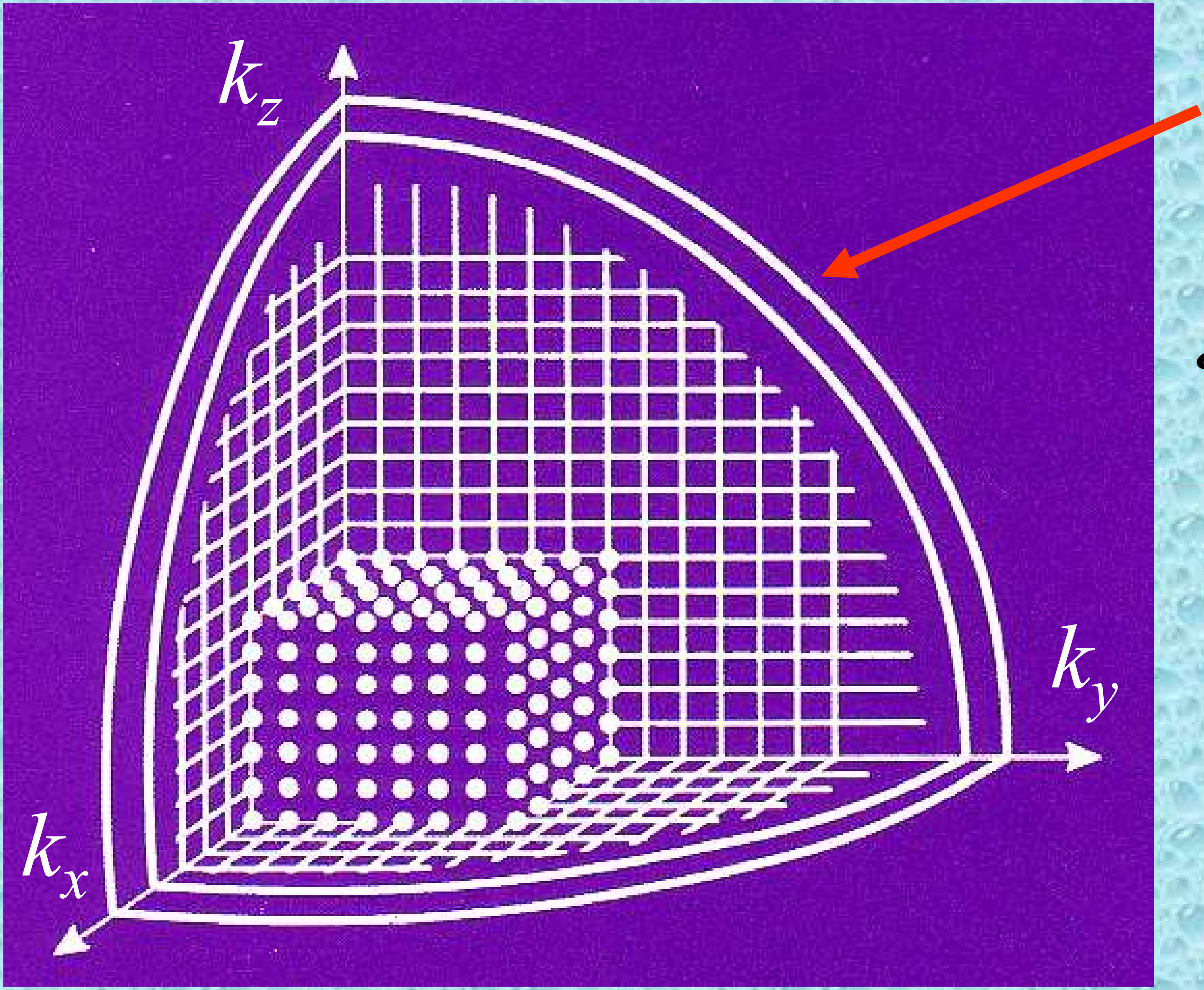
$$\boxed{n(k) = \frac{1}{e^{(\varepsilon(k)-\mu)/k_B T}+1}}$$



T-Dependence of the Chemical Potential



Fermi Surface



$$k_F = \left(3\pi^2 n\right)^{1/3}$$

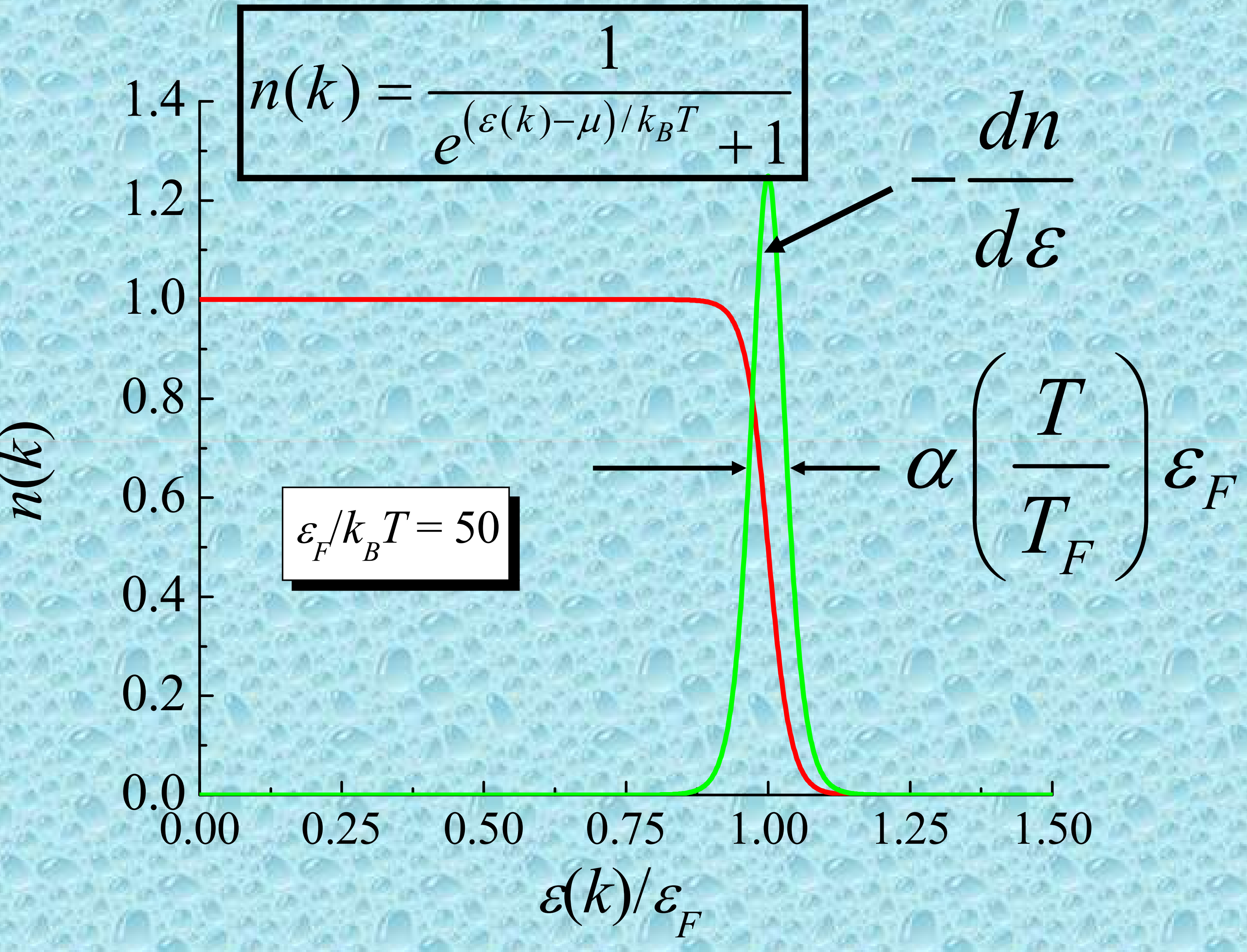
$$\varepsilon_F = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3}$$

$$T_F = \varepsilon_F / k_B$$

$$\bar{U} = \frac{3N\varepsilon_F}{5}$$

$$\bar{u} = \frac{3\varepsilon_F}{5}$$

Fermi-Dirac Distribution Function



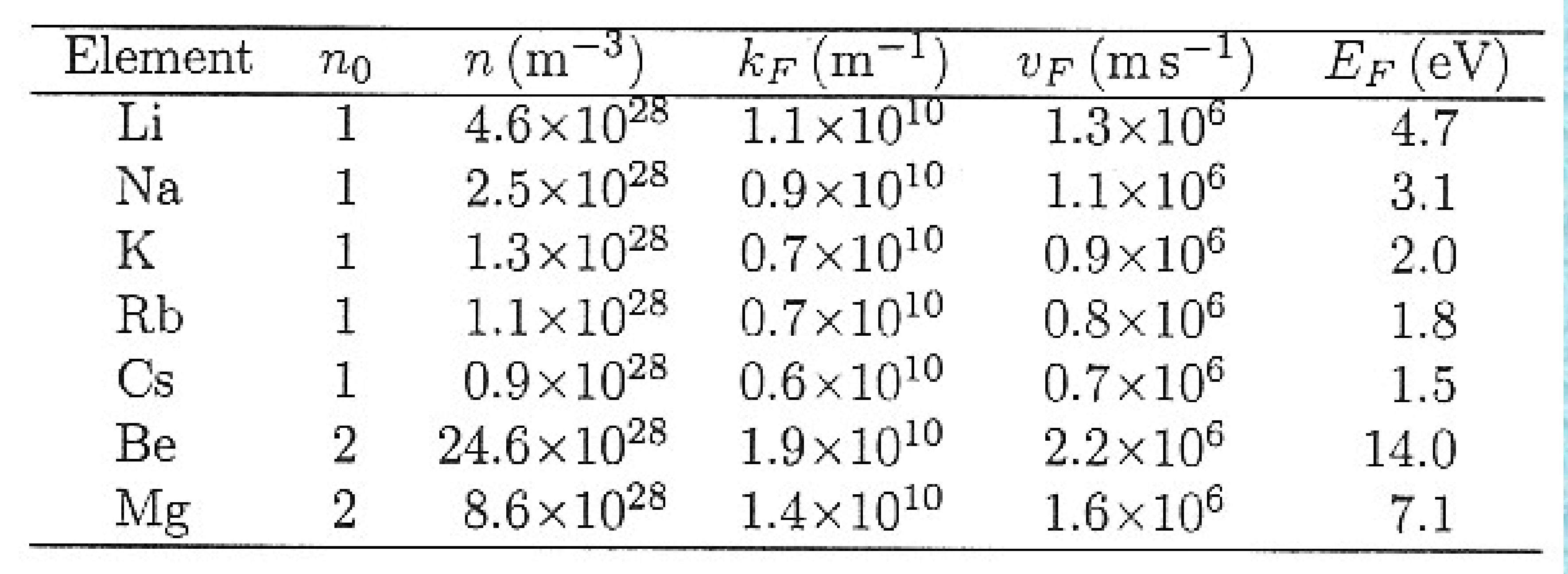
$$n(k) = \frac{1}{e^{(\varepsilon(k)-\mu)/k_B T}+1}$$

$$-\frac{dn}{d\varepsilon}$$

$$\alpha\left(\frac{T}{T_F}\right)\varepsilon_F$$

$\varepsilon_F/k_B T = 50$

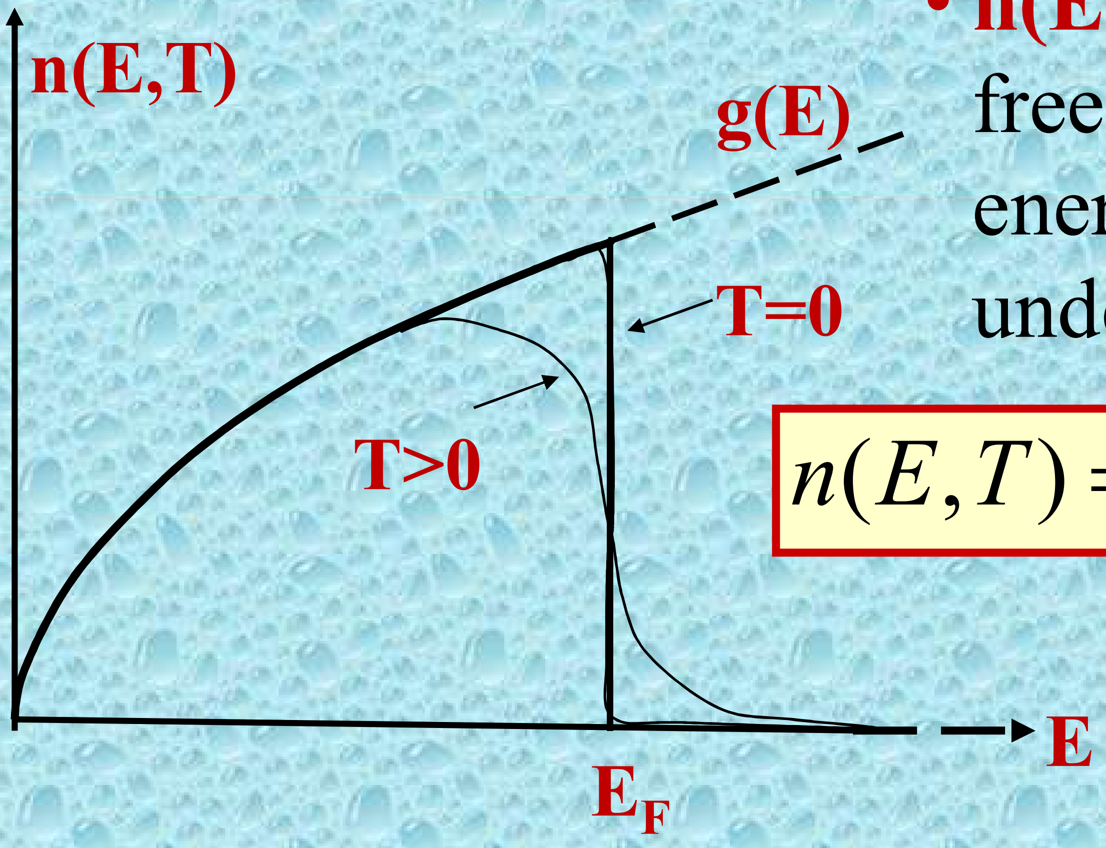
Examples of Fermi Systems



Element	n_0	$n\,(\mathrm{m}^{-3})$	$k_F\,(\mathrm{m}^{-1})$	$v_F\,(\mathrm{m\,s}^{-1})$	$E_F\,(\mathrm{eV})$
Li	1	4.6×10^{28}	1.1×10^{10}	1.3×10^{6}	4.7
Na	1	2.5×10^{28}	0.9×10^{10}	1.1×10^{6}	3.1
K	1	1.3×10^{28}	0.7×10^{10}	0.9×10^{6}	2.0
Rb	1	1.1×10^{28}	0.7×10^{10}	0.8×10^{6}	1.8
Cs	1	0.9×10^{28}	0.6×10^{10}	0.7×10^{6}	1.5
Be	2	24.6×10^{28}	1.9×10^{10}	2.2×10^{6}	14.0
Mg	2	8.6×10^{28}	1.4×10^{10}	1.6×10^{6}	7.1

Electrons in metals (dense system)

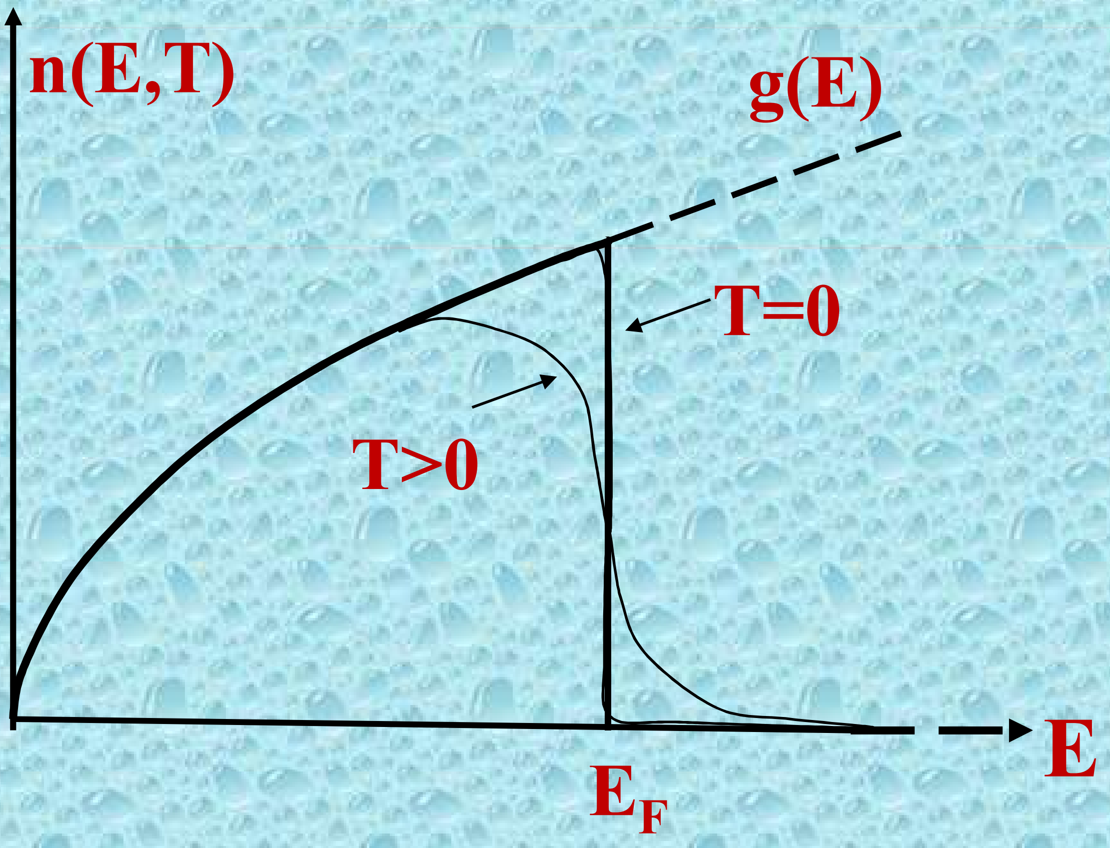
- What is ***the number of electrons per unit energy*** range according to the free electron model?
- This shows the change in distribution between absolute zero and a finite temperature.



- **n(E,T) =** number of free electrons per unit energy range = area under **n(E,T)** graph.

$$\boxed{n(E,T) = g(E)\, f_{FD}(E,T)}$$

- The **FD distribution function** is a symmetric function; at finite temperatures, the same number of levels below **E_F** are emptied and same number of levels above **E_F** are filled by electrons.



Equilibrium Distribution of Electrons

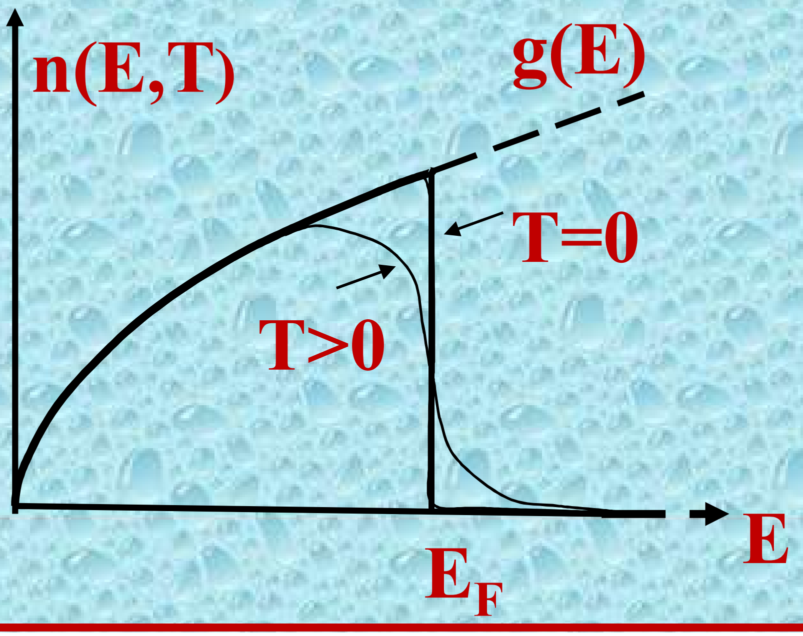
- **Distribution of Electrons at energy E =**
- **Density of States × Probability of**
- **Occupancy**

$$\equiv g(E)f(E)$$

- Total **number of conduction electrons at energy E** & temperature **T:**

$$N = \int_0^E g(E)\, f(E) dE$$

Total Energy of a Gas of N Electrons



Note:
E →ε
Sorry!

$$U = \int_0^\infty \varepsilon N(\varepsilon)\,d\varepsilon = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon)\,d\varepsilon = 4\pi V\left(\frac{2m}{h^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{3/2}\,d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1}.$$

$$U \approx \frac{3}{5}N\varepsilon_F\left[1+\frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2-\frac{\pi^4}{16}\left(\frac{T}{T_F}\right)^4+\ldots\right]$$

- At **$T = 0$, $U = (3/5)N\varepsilon_F$** , this energy is large because all the electrons must occupy the lowest energy states up to the Fermi level.

<ε> for a free electron in silver at T = 0:

$$\bar{\varepsilon}(0) = \frac{U(0)}{N} = \frac{3}{5}\varepsilon_F = \frac{3}{5}(5.6\ \mathrm{eV}) = 3.4\ \mathrm{eV}.$$

- The **mean kinetic energy of an electron**, even at **T = 0**, is **2 orders of magnitude greater** than the mean kinetic energy of an ordinary gas molecule at room temperature.

Heat Capacity at Low T

- The **Total Energy at Temperature T**:

$$\boxed{U \approx \frac{3}{5}N\varepsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 - \frac{\pi^4}{16}\left(\frac{T}{T_F}\right)^4 + \ldots\right]}$$

- The **electronic heat capacity C_e** can be found by taking the temperature derivative of **U**:

$$\boxed{C_e = \frac{dU}{dT} = \frac{\pi^2}{2}Nk\left[\left(\frac{T}{T_F}\right) - \frac{3\pi^2}{10}\left(\frac{T}{T_F}\right)^3 + \ldots\right].}$$

- For temperatures **T** small compared with T_F (true for any metal at room temperature), neglect the 2nd term in the expansion & get

$$\boxed{C_e \approx \frac{\pi^2}{2}Nk\left(\frac{T}{T_F}\right) = \frac{\pi^2}{2}Nk\left(\frac{kT}{\varepsilon_F}\right).}$$

- For silver at room temperature:

$$\boxed{C_e = \frac{\pi^2}{2} Nk\left(\frac{0.025 \text{ eV}}{5.6 \text{ eV}}\right) = 2.2 \times 10^{-2} Nk.}$$

- So, the electronic specific heat **= 2.2 x 10^{-2} R**. This small value explains why metals have a specific heat capacity of about 3R, the same as for other solids.
- It was originally believed that their free electrons should contribute an additional **(3/2) R** associated with their three translational degrees of freedom. The calculation shows that this contribution is negligible.
- The energy of the electrons changes only slightly with temperature (**dU/dT is small**) because only those electrons near the Fermi level can increase their energies as the temperature is raised, & there are very few of them.

$$S = \int_0^T \frac{C_e\,dT'}{T'} = \frac{\pi^2}{2} Nk\left[\left(\frac{T}{T_F}\right) - \frac{\pi^2}{10}\left(\frac{T}{T_F}\right)^3 + \dots\right]$$

- **S = 0 at T = 0, as it must be.**
- The Helmholtz function **F = U -TS is**

$$F = NkT_F\left[\frac{3}{5} - \frac{\pi^2}{4}\left(\frac{T}{T_F}\right)^2 + \frac{\pi^4}{80}\left(\frac{T}{T_F}\right)^4 + \dots\right]$$

- The **Fermion equation of state** is:

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

$$P = \frac{2}{5}\frac{NkT_F}{V}\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \dots\right]$$

- Silver: **$N/V = 5.9 \times 10^{28}\ m^{-3}$** so **$T_F = 65{,}000K$.**
- So,

$$\boxed{P = \frac{2}{5}\frac{NkT_F}{V}\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \dots\right]}$$

$$\mathbf{P = (2/5)\,(5.9\times10^{28})(1.38\times10^{-23})\,(6.5\times10^{4})}$$

$$\mathbf{= 2.1\times10^{10}\ Pa = 2.1\times10^{5}\ atm}$$

= *Pressure inside the electron gas!*

- Given this tremendous pressure, it is clear that the surface potential barrier needs to be huge in order to keep the electrons from evaporating from the metal.

Fermi energy for Aluminum assuming three electrons per Aluminum atom:

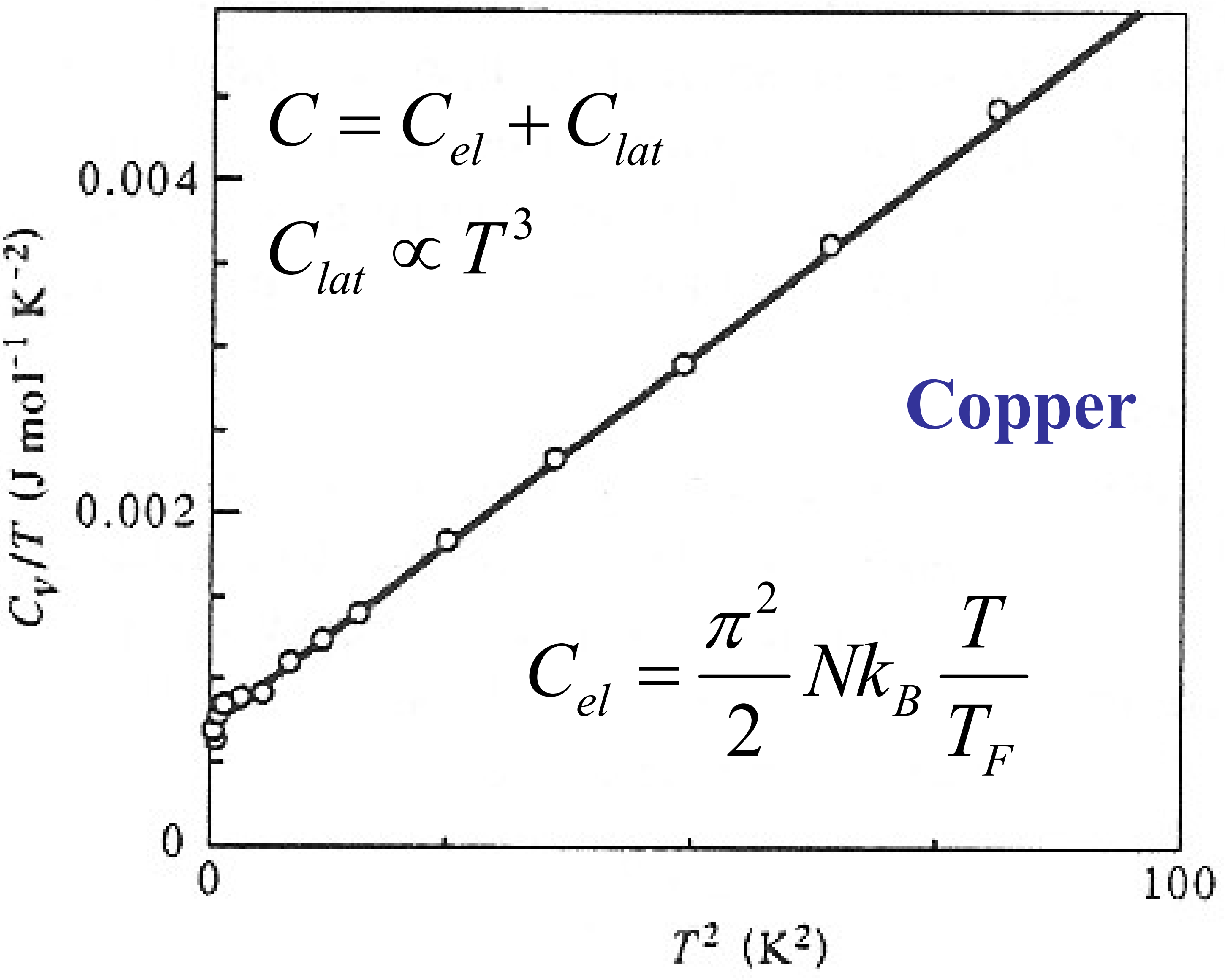
$$\frac{N}{V}=\frac{2.69\times10^{3}\,{}^{Kg}\!/_{m^3}}{27\,{}^{Kg}\!/_{kilomole}}\times6.02\times10^{26}\frac{atoms}{kilomole}=5.99\times10^{28}$$

$$\#\,\text{Density of electrons}=3\frac{N}{V}$$

$$\approx1.8\times10^{29}$$

$$\varepsilon_F=\frac{\left(6.63\times10^{-34}\right)^2}{2\times9.11\times10^{-31}}\left(\frac{3\times1.8\times10^{29}}{8\pi}\right)^{2/3}\approx5.6\times2.1=11.8\,eV$$

Low-Temperature Heat Capacity



$$C = C_{el} + C_{lat}$$

$$C_{lat} \propto T^3$$

Copper

$$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$