ChemE 2200 – Applied Quantum Chemistry Lecture 9

Today:

The Free-Electron Model for Solids

Defining Questions:

What defines the Fermi Level?

Reading for Today's Lecture:

Electrons in Solids, pp. 1-10.

Reading for Quantum Lecture 10:

Electrons in Solids, pp. 11-18.

Electrons in Solids

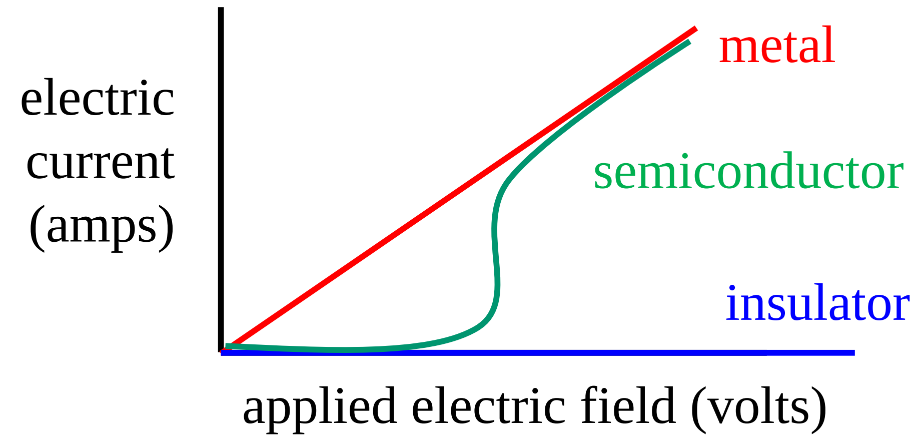
Goals: to predict …

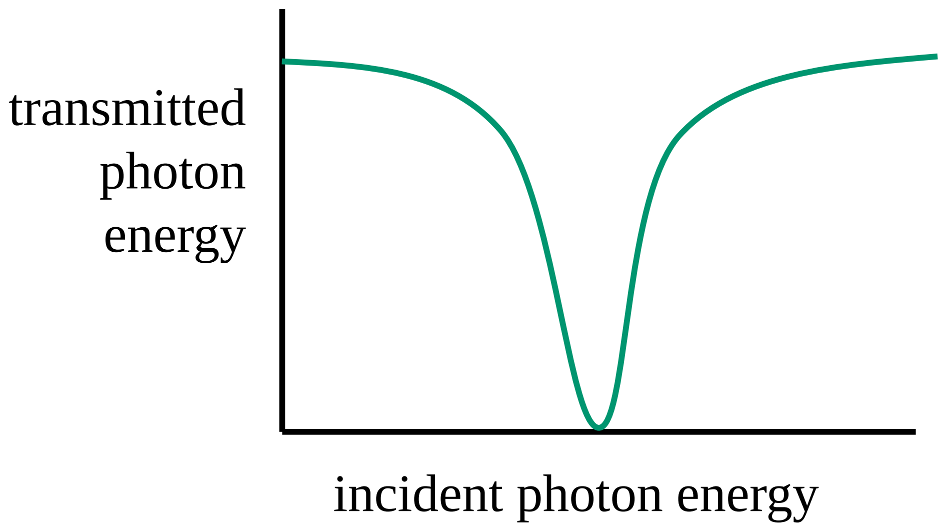
Electrical Conductivity

Thermal Conductivity

Heat Capacity

Absorption and emission of photons





All these properties are determined by the electron energy levels.

Why do metals absorb microwaves?

How to design the color of a light-emitting diode (LED)?

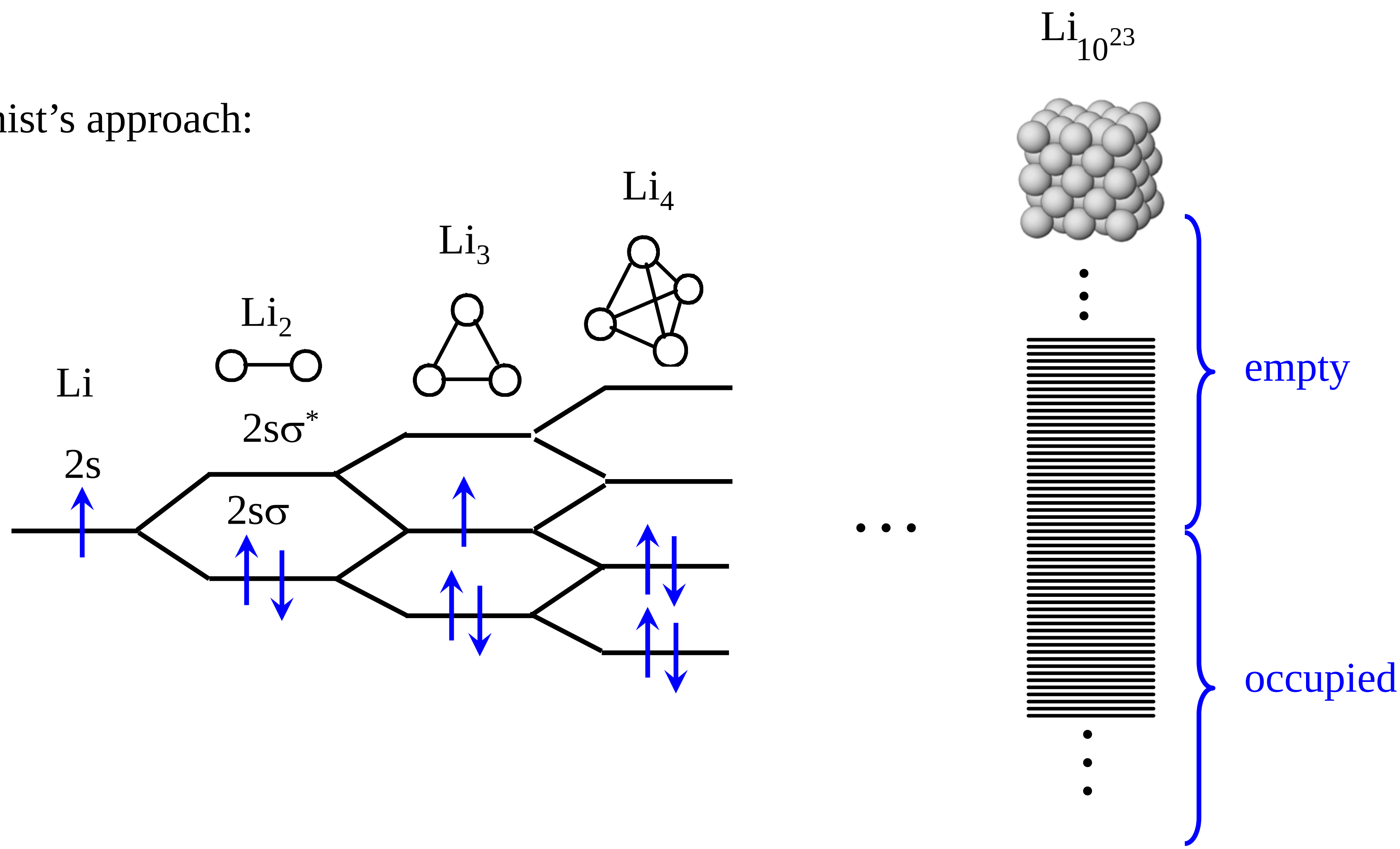
How to design night-vision goggles?

Models for Electrons in Solids

We will consider condensed matter. One 'molecule' has ~10^{23} atoms.

condensed matter:	molecular solids:
diamond	ice
silicon	sugar
iron	poly(ethylene)

Chemist's approach:



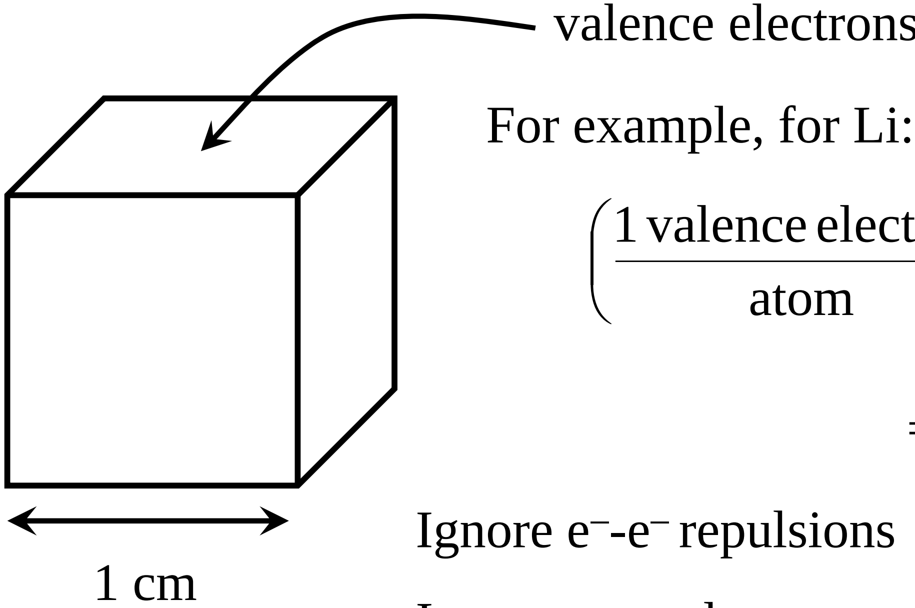
Models for Electrons in Solids

Physicist's approach:

The Free-Electron Model	Band Theory
$Li_{10^{23}}$	$Li_{10^{23}}$
10^{23} electrons uniform positive electric field	10^{23} electrons positive charges at fixed lattice sites
Ignore e^-–e^- repulsions. An electron gas.	electron energies confined to 'bands'.
Explains metals and superconductors.	Explains metals, superconductors, insulators, and semiconductors.

The Free-Electron Model

the box:



For example, for Li:

$$\left(\frac{1\text{ valence electron}}{\text{atom}}\right)\left(\frac{0.53\text{ g}}{\text{cm}^3}\right)\left(\frac{6\times10^{23}\text{ atoms}}{6.9\text{ g Li}}\right)$$

$= 4.6 \times 10^{22}$ electrons in the box.

Ignore e^--e^- repulsions

Ignore e^--nucleus attractions

} Partially cancels.

Quantum mechanical description of this system?

$$\hat{H}\Psi = E\Psi \Rightarrow \text{particles in a box}$$

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \qquad n_x = 1, 2, 3, \ldots \quad n_y = 1, 2, 3, \ldots \quad n_z = 1, 2, 3, \ldots$$

$= 3.7 \times 10^{-15}$ eV   characteristic spacing between energy levels

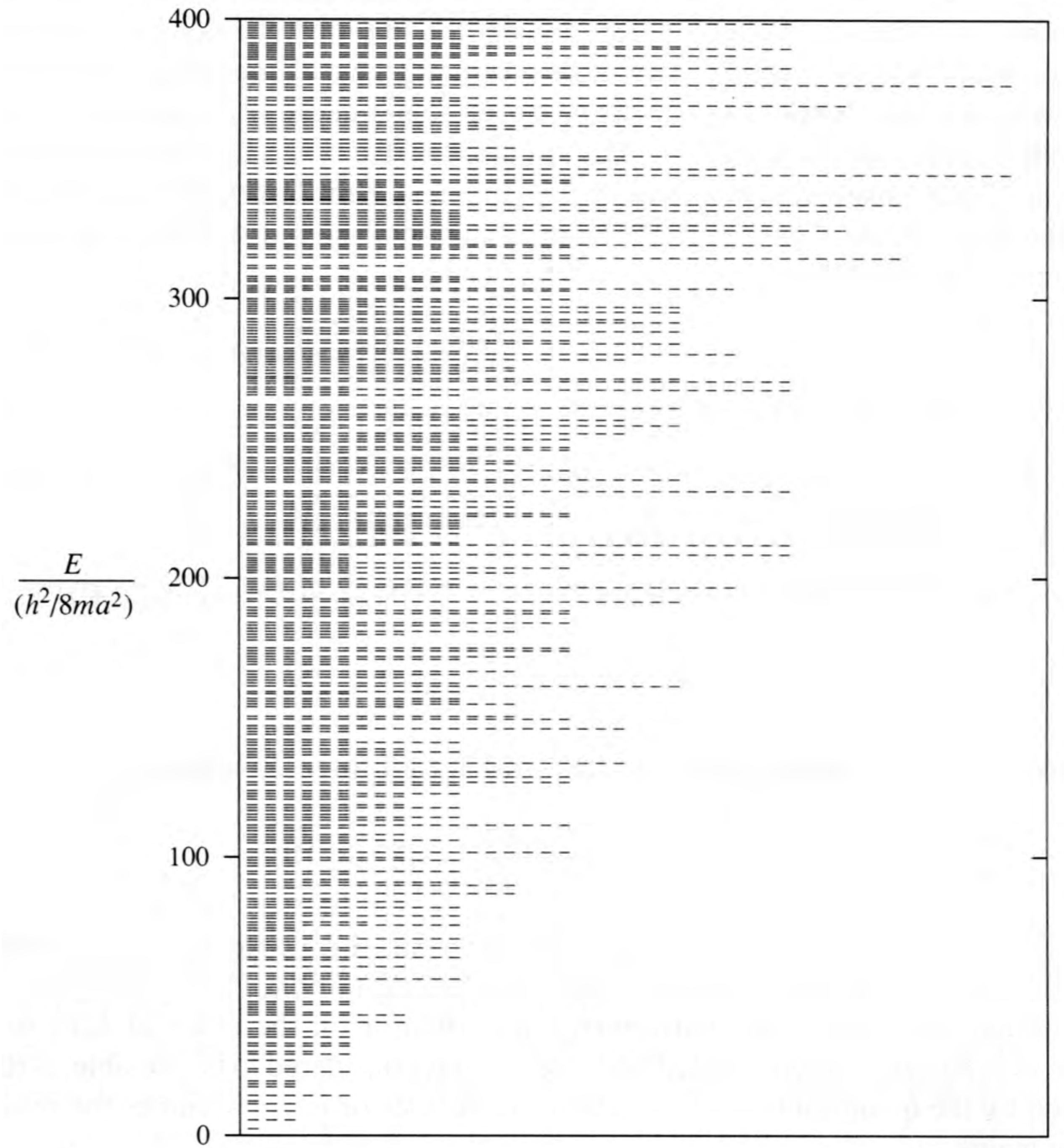
Compare to 10.2 eV for the 1s-2p spacing in a hydrogen atom.

Energy Levels for the Free-Electron Model

Add electrons to the 1 cm^3 box. Fill the lowest energy levels first.

electron	n_x	n_y	n_z	m_s
1,2	1	1	1	±½
3,4	2	1	1	±½
5,6	1	2	1	±½
7,8	1	1	2	±½
⋮				
9,030,675, 9,030,676	1735	1735	1735	±½
9,030,677, 9,030,678	3005	1	1	±½
9,030,679, 9,030,680	2125	2125	1	±½

Energy Levels for the Free-Electron Model



energy spacing
$\approx 4 \times 10^{-15}$ eV

flip vertically,
& rotate 90°
to plot
number of states
vs. energy

Figure 11.9 from *Physical Chemistry*, J. H. Noggle, 1996

Energy Levels for the Free-Electron Model

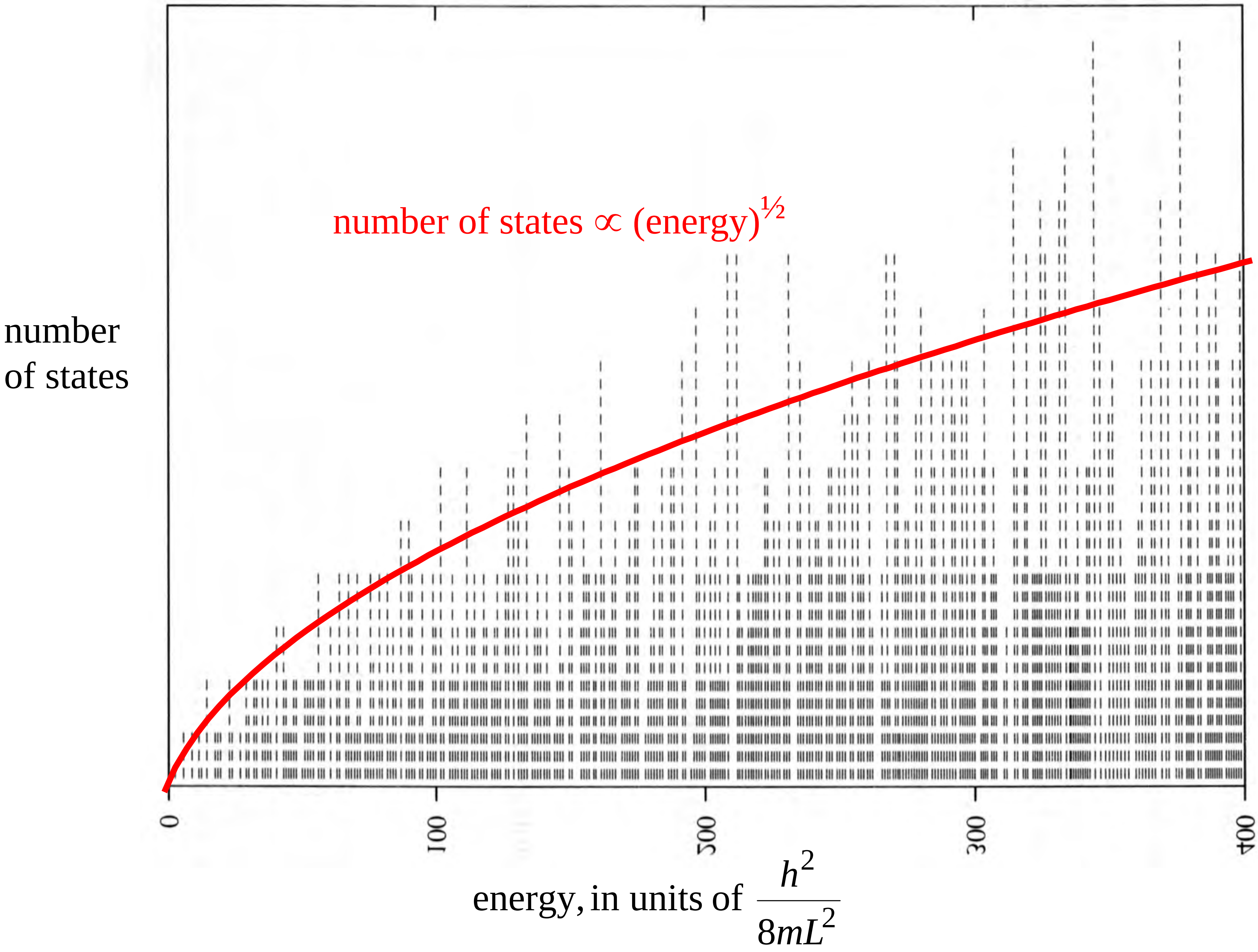


Figure 11.9 from *Physical Chemistry*, J. H. Noggle, 1996

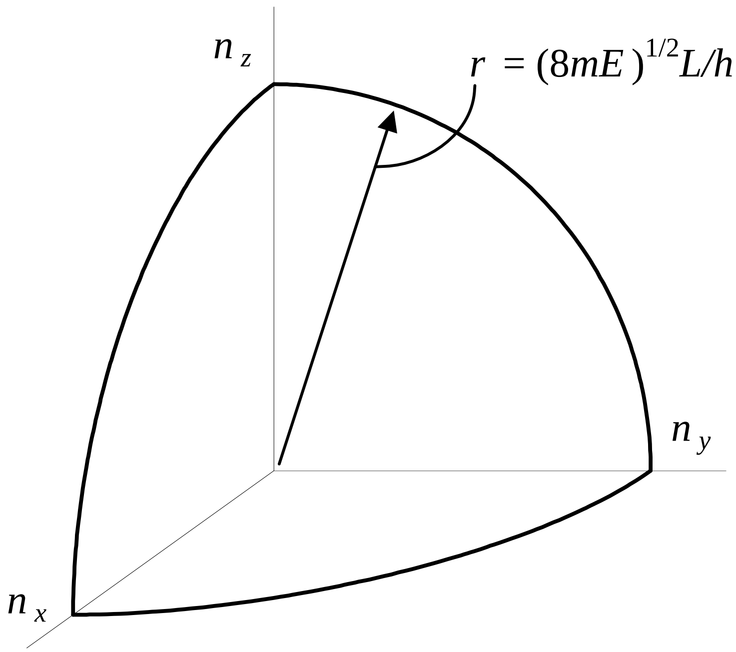
Filling Energy Levels for the Free-Electron Model

Filling electron energy levels sequentially is impractical, especially for 10^{23} electrons.

Instead, calculate the energy of the highest filled level.

$$E_{n_x n_y n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$$

Rearrange to $n_x^2 + n_y^2 + n_z^2 = \left[\frac{(8mE)^{1/2} L}{h}\right]^2$ This is the equation for a sphere, $x^2 + y^2 + z^2 = r^2$, with $r = \frac{(8mE)^{1/2} L}{h}$



Each energy state corresponds to a point in the positive octant.

What is the radius of an octant that contains N electron states ($= ½N_{\text{electrons}}$)?

$$N_{\text{states}} = \text{volume of octant} = \frac{1}{8}(\text{volume of sphere})$$

$$½N_{\text{electrons}} = \frac{1}{8}\left(\frac{4}{3}\pi r^3\right) = \frac{\pi}{6}\left[\frac{(8mE_{\text{max}})^{1/2} L}{h}\right]^3$$

Solve for E_{max}.

$$E_{\text{max}} = \frac{h^2}{8mL^2}\left(\frac{3}{\pi} N_{\text{electrons}}\right)^{2/3}$$

The Fermi Level

$$E_{max} = \frac{h^2}{8mL^2}\left(\frac{3}{\pi}N_{electrons}\right)^{2/3}$$

solid	$N_{electrons}$/cm^3	E_{max} calculated	E_{max} measured
Li	4.6×10^{22}	4.7 eV	2.5 eV
Na	2.5×10^{22}	3.1 eV	2.3 eV
K	1.3×10^{22}	2.0 eV	2.2 eV
Ag	5.9×10^{22}	5.5 eV	4.7 eV

The energy of the highest occupied electron state is the Fermi Level ≡ E_F.

More precisely, the energy between the highest *occupied* electron state and the lowest *unoccupied* electron state is the Fermi Level.

Density of Electron Energy States

Properties of solids: electrical conductivity, heat capacity, thermal conductivity } determined by electron energies.

What energy states are occupied?

What energy states are available?

How many energy states at a given *E*?

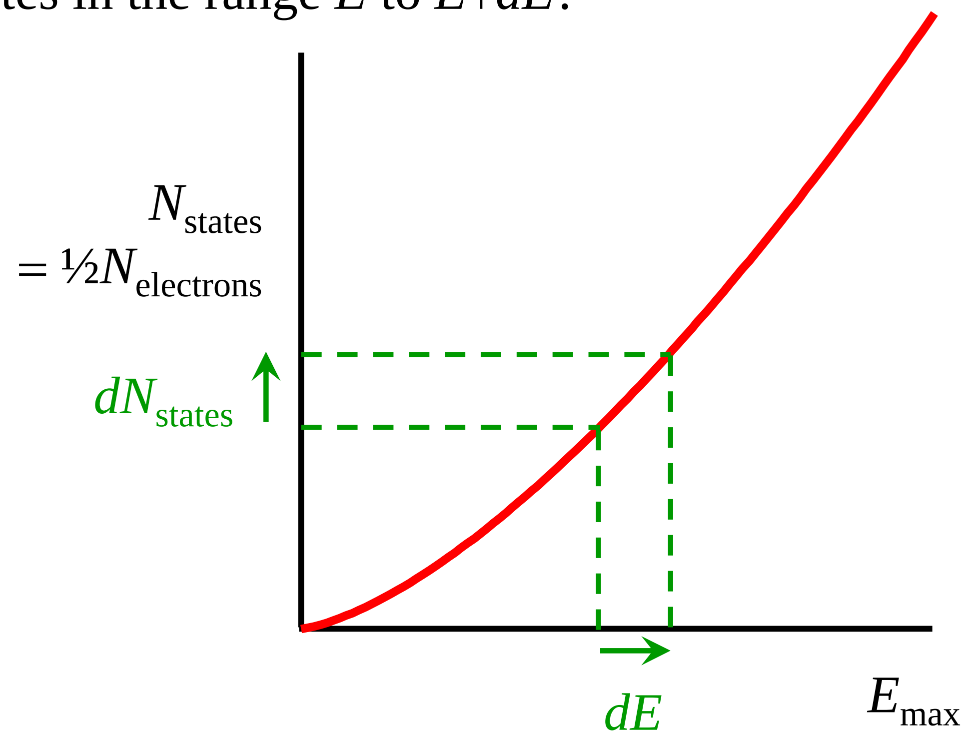
Better: How many energy states in the range *E* to *E*+*dE*?

What is the *density* of energy states in the range *E* to *E*+*dE*?

$$N_{\text{states}} = \frac{4}{3}\pi\left[\frac{(2m_{\text{electron}})^{1/2}L}{h}\right]^3 E_{\max}^{3/2}$$

$$dN_{\text{states}} = \left(\frac{dN_{\text{states}}}{dE_{\max}}\right)dE_{\max}$$

$$\boxed{\frac{dN_{\text{states}}}{dE_{\max}} = \frac{2\pi L^3(2m_{\text{electron}})^{3/2}}{h^3}E_{\max}^{1/2}}$$



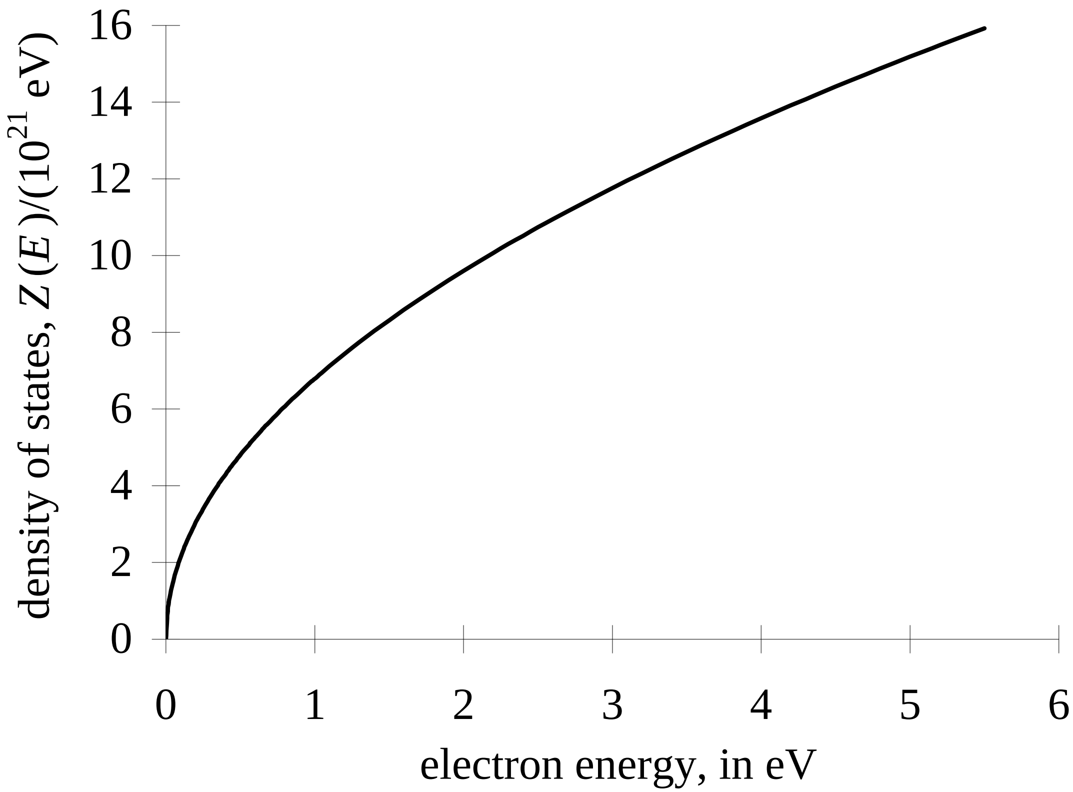
Density of Electron Energy States

Number of electrons with energies between E and $E+dE$ =

(density of available states) × (probability that the state is occupied)

$$N(E) = Z(E) \times F(E)$$

$$Z(E) = \frac{dN_{\text{states}}}{dE_{\text{max}}} = \frac{2\pi L^3 (2m_{\text{electron}})^{3/2}}{h^3} E_{\text{max}}^{1/2}$$

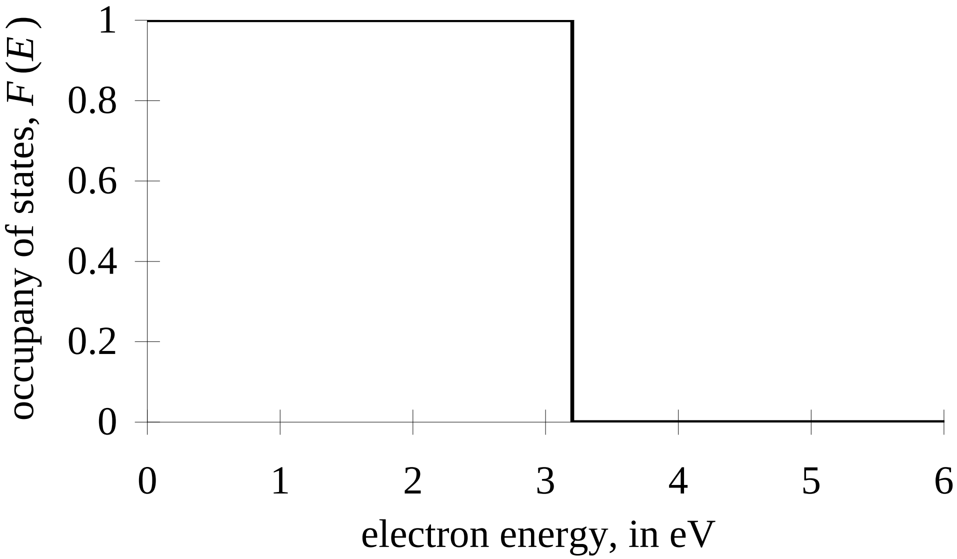


Compare to qualitative density of states on previous slide.

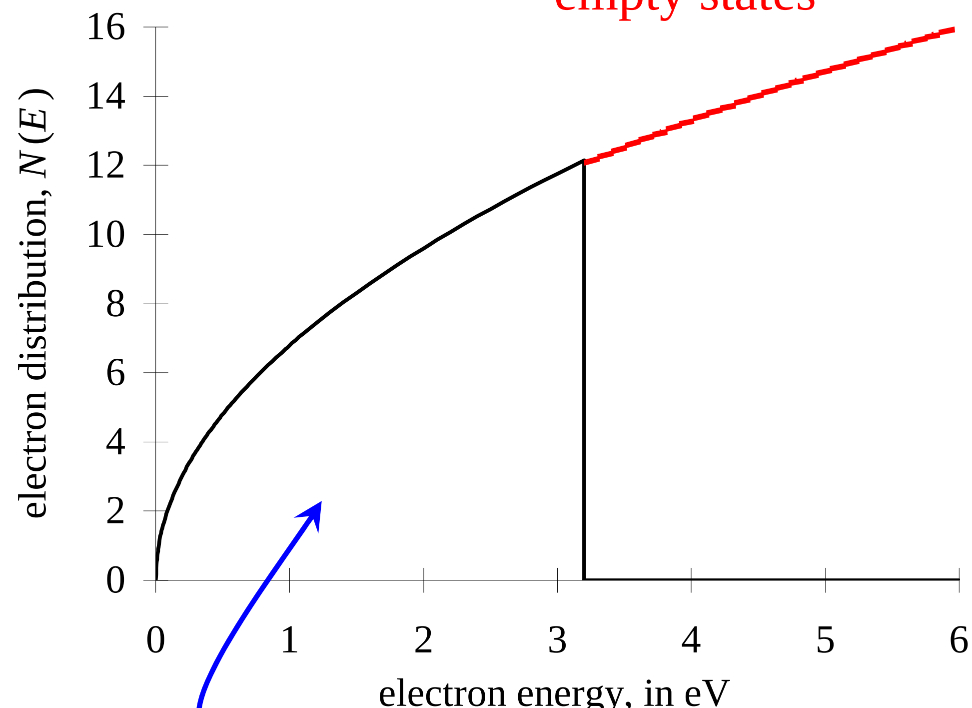
Probability that an Energy State is Occupied

Occupancy: all energy states below the Fermi Level are occupied;
all energy states above the Fermi Level are empty.

$$F(E) = 1 \text{ for } E < E_{\text{Fermi}}$$
$$= 0 \text{ for } E > E_{\text{Fermi}}$$



$Z(E)$: available, empty states



Electrons with energy E = availability × occupancy

$$N(E) = Z(E) \times F(E)$$

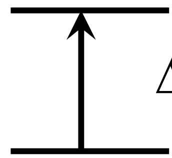
$$\text{area} = N_{\text{states}} = \int_0^E Z(E)\,dE$$

= number of filled states with energy $\leq E_F \propto E^{3/2}$

Probability that an Energy State is Occupied

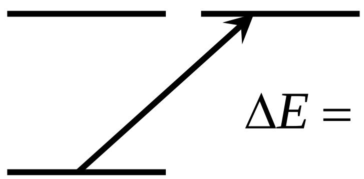
What is the probability that an electron
near the Fermi Level is thermally excited to a higher level?

Boltzmann statistics: state 2, state 1, ΔE



$$\left(\frac{\text{population of state 2}}{\text{population of state 1}}\right)_{\text{equilibrium}} = \exp\left[\frac{-\Delta E}{kT}\right]$$

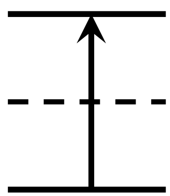
hydrogen atom: 2s, 2p, 1s



$\Delta E = 10.2$ eV

$$\frac{N(2\text{p})}{N(1\text{s})} = \exp\left[\frac{-10.2\ \text{eV}}{0.025\ \text{eV}}\right] = 10^{-178}$$

box of electrons: unoccupied, E_{Fermi}, occupied



$\Delta E \sim 1.1 \times 10^{-7}$ eV

see *Electrons in Solids*, p. 6

$$\frac{N(\text{above Fermi level})}{N(\text{below Fermi level})} = \exp\left[\frac{-1.1\times 10^{-7}\ \text{eV}}{0.025\ \text{eV}}\right] = 0.999996$$

Useful fact: $kT = 0.025$ eV at 298 K

Probability that an Energy State is Occupied

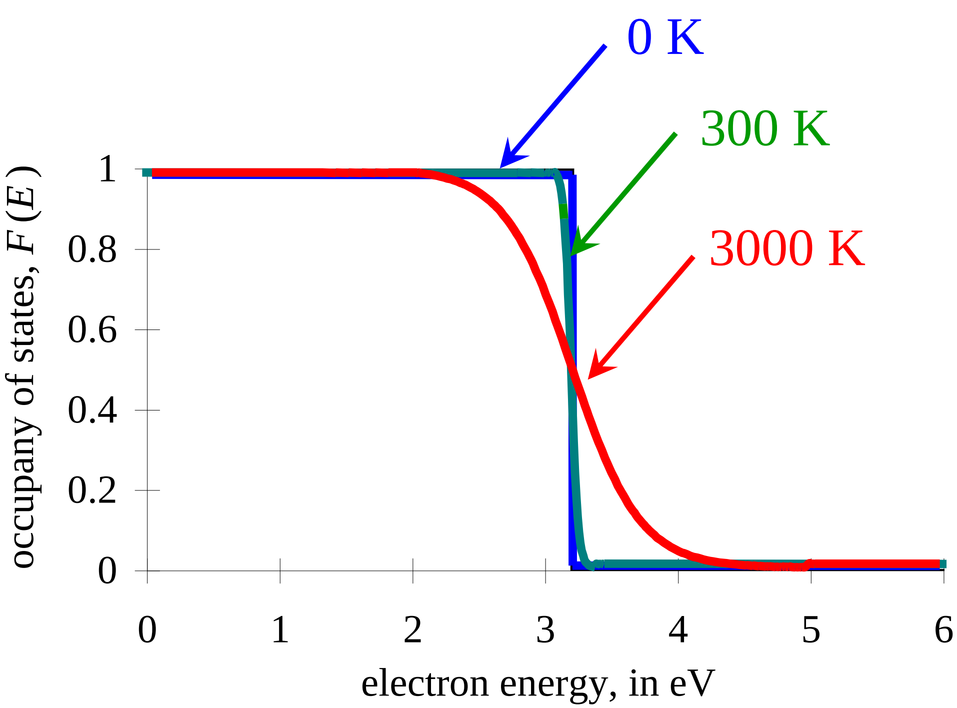
Electrons are fermions (not bosons) which obey Fermi-Dirac statistics:

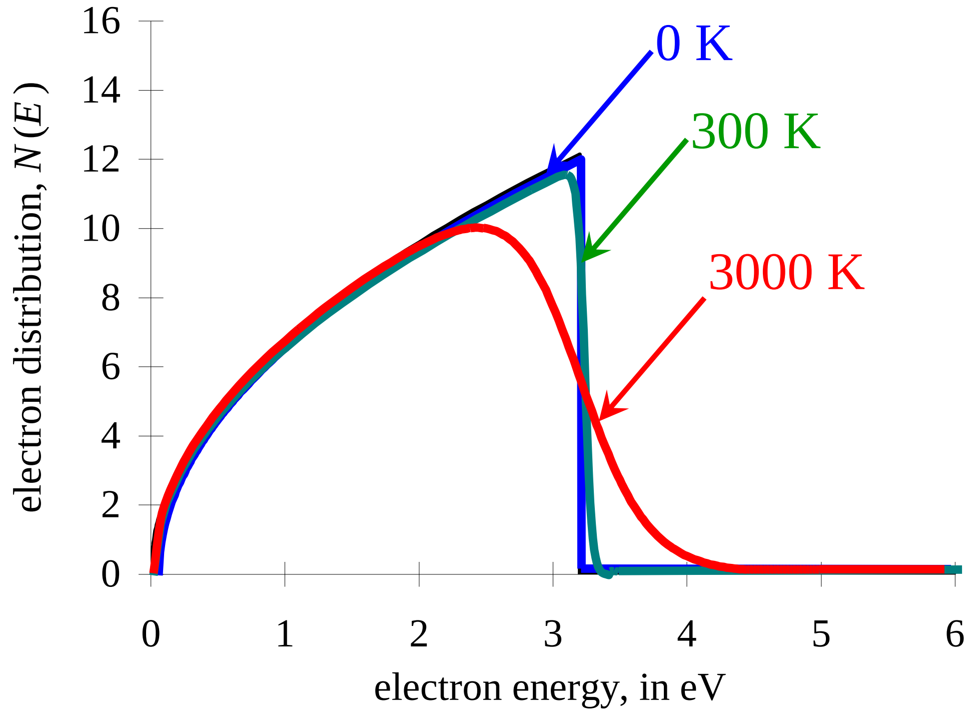
$$F(E) = \frac{1}{\exp\left[(E - E_{\text{Fermi}})/kT\right] + 1}$$

at $E = 0$: $F(E) = 1$

at $E >> E_{\text{Fermi}}$: $F(E) = 0$

at $E = E_{\text{Fermi}}$: $F(E) = ½$





Electrons with energy E = availability × occupancy

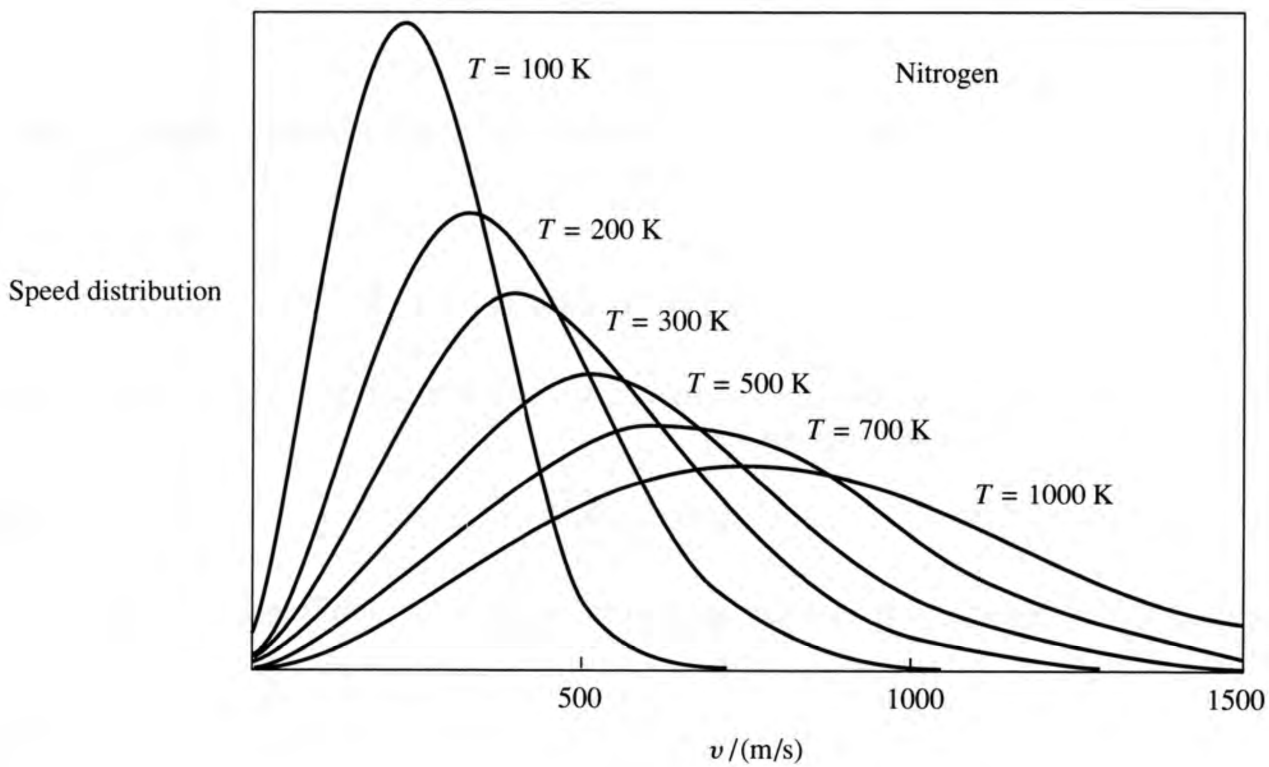
$$N(E) = Z(E) \times F(E)$$

Heat Capacity of an Ideal Gas

Are electrons in a box similar to ideal gas molecules in a box?

Electrons in the free-electron model and ideal gas molecules are both non-interacting. ✓

Electrons obey Fermi-Dirac statistics
and ideal gas molecules obey Maxwell-Boltzmann statistics. ✗



Gas molecules are bosons.

Every gas molecule has a nearby empty energy state.

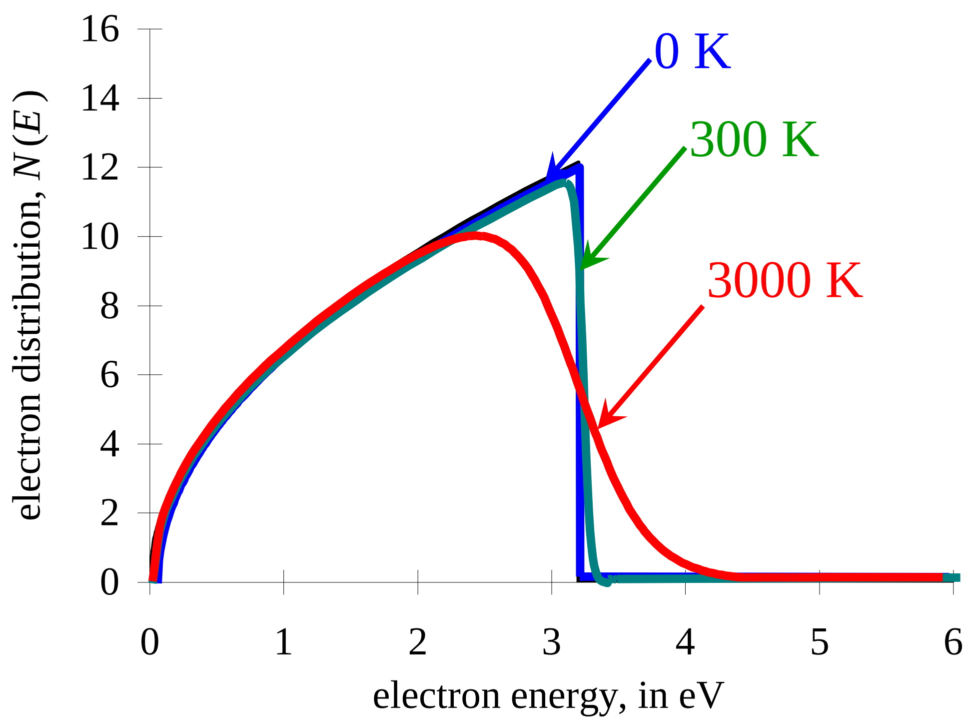
Every gas molecule can absorb thermal energy.

$$C_V = \frac{d\langle E\rangle}{dT} = \frac{d\left\langle N\frac{3}{2}kT\right\rangle}{dT}$$

$$= \frac{3}{2}Nk = \frac{3}{2}R$$

Figure 1.16 from *Physical Chemistry*, J. H. Noggle, 1996

Heat Capacity of an Electron Gas



To absorb thermal energy, an electron must have an empty state within a typical thermal excitation, $\sim kT = 0.025$ eV at 298 K.

Roughly 1/30 of the electrons have an empty state within 0.025 eV at 298 K.

$$C_V \approx \frac{1}{30}\left(\frac{3}{2}R\right)$$

An exact calculation yields $C_V = \left(\frac{\pi^2}{2}\frac{kT}{E_{Fermi}}\right)R$