ChemE 220 - Physical Chemistry II for Engineers – Spring 2025
Solution to Homework Assignment 4

1. The atomic radii of C, Si, and Ge decrease as Ge > Si > C. Thus a Ge-Ge interatomic distance is longer than Si-Si, which in turn is longer than C-C. Thus the number density of electrons is C > Si > Ge. Therefore a chunk of crystalline carbon (diamond) has the most atoms in a unit volume, and the most valence electrons in a unit volume. Given the same number of valence electrons on Ge, Si and C, the following equation,

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

says the Fermi energy is inversely proportional to the length squared, so the trend is $E_\mathrm{F}(\mathrm{C}) > E_\mathrm{F}(\mathrm{Si}) > E_\mathrm{F}(\mathrm{Ge})$.

2.(A) The free electron model applied to a raft of aluminum atoms is equivalent to particles in a two-dimensional box. Set $V = 0$ inside the box, so $E_\mathrm{total} = E_\mathrm{KE}$ and thus

$$E_\mathrm{total} = \frac{1}{2m}p^2 = \frac{h^2k^2}{2m}$$

Consequently a plot of E_total as a function of k is a paraboloid, as shown in figure 10.53 (p. 834) of Thomas and Finney, *Calculus* 9th edition. A cross section is a parabola, like figure 8 of the *Electrons in Solids* handout. For electrons to have a net flow, we need $\sum k \neq 0$. To determine if an applied electric field will shift the state occupancy and cause $\sum k \neq 0$, we need to calculate two quantities:

- the energy spacing at the Fermi level, and
- the probability of having "conduction" electrons at 300 K.

The Al raft has 100 Al atoms and each Al contributes 3 valence electrons. Thus there are 300 electrons in the delocalized bond. We can use the two-dimensional analysis on pp. 2-3 of the *Electrons in Solids* handout.

We need to know the radius of a quarter-circle that contains 150 coordinates. Each coordinate is a (n_x, n_y) pair, which corresponds to a state. Each state can hold two electrons. Solve for the radius of the circle.

$$150 = \frac{1}{4}\pi r^2$$

$$r = \sqrt{\frac{150\times 4}{\pi}} = 13.8$$

Thus the radius of the circle is about 14. A typical coordinate near the outer edge would be $(14/\sqrt{2}, 14/\sqrt{2}) = (10,10)$. Thus the state ($n_x$ =10, n_y =10) is at the Fermi level. Compute the energy splitting from an occupied state at (10, 10) to an unoccupied state at (11, 10). The "box" length is 10 × 2.5 Å = 25 Å.

$$\Delta E = E_{11,10} - E_{10,10} = \frac{h^2}{8m_eL^2}(11^2+10^2)-(10^2+10^2)$$

$$= \frac{(6.63\times 10^{-34}\,\mathrm{J\cdot sec})^2}{8\times(9.1\times 10^{-31}\,\mathrm{kg})(25\times 10^{-10}\,\mathrm{m})^2}(21) = 2\times 10^{-19}\,\mathrm{J}$$

$$\Delta E = 2\times 10^{-19}\,\mathrm{J}\,\frac{1\,\mathrm{eV}}{1.60\times 10^{-19}\,\mathrm{J}} = 1.3\,\mathrm{eV}$$

At 300 K, $kT = 0.025$ eV. The Boltzmann population of conduction electrons (electrons with $n = 11$) is proportional to $e^{-1.3/0.025} = 2\times 10^{-23}$. There are no conduction electrons.

Thus, a 10 × 10 raft of aluminum atoms is a semiconductor (or insulator).

(B) A 10,000 × 10,000 raft of aluminum atoms contains 10^8 aluminum atoms and thus 3×10^8 valence electrons. Using the same method as in part (a), the state (n_x =10,000, n_y =10,000) is at the Fermi level. The "box" length is 10,000 × 2.5 Å. Calculate the spacing between energy levels at the Fermi level.

$$\Delta E \;=\; E_{10{,}001,10{,}000} - E_{10{,}000,10{,}000} \;=\; \frac{h^2}{8m_e L^2}(10001^2 + 10000^2) - (10000^2 + 10000^2)$$

$$= \frac{(6.63\times10^{-34}\,\mathrm{J\cdot sec})^2}{8\times(9.1\times10^{-31}\,\mathrm{kg})(25\times10^{-7}\,\mathrm{m})^2}(20001) \;=\; 2\times10^{-22}\,\mathrm{J}$$

$$\Delta E \;=\; 2\times10^{-22}\,\mathrm{J}\,\frac{1\,\mathrm{eV}}{1.60\times10^{-19}\,\mathrm{J}} \;=\; 1.3\times10^{-3}\ \mathrm{eV}$$

Thus the Boltzmann population above the Fermi level is proportional to $e^{-0.0013/0.025} = 0.95$.

Thus, a 10,000 × 10,000 raft of aluminum atoms is a metal.

(C) Band theory will yield a generic plot of E versus k similar to figure 15 of *Electrons in Solids*. There are three electrons per potential well, so the Fermi level is halfway to the second band gap. Thus the calculation in part (B) applies and the molecule is a metal.

3. The free electron model applied to polyacetylene is equivalent to particles in a one-dimensional box. Set $V = 0$ inside the box, so $E_{\text{total}} = E_{\text{KE}}$ and thus

$$E_{\text{total}} \;=\; \frac{1}{2m}p^2 \;=\; \frac{h^2 k^2}{2m}$$

Consequently a plot of E_{total} as a function of k is a parabola, as in figure 8 of the *Electrons in Solids* handout. For electrons to have a net flow, we need $\sum k \neq 0$. To determine if an applied electric field will shift the state occupancy and cause $\sum k \neq 0$, we need to calculate 2 quantities:

- the energy spacing at the Fermi level, and
- the probability of having "conduction" electrons at 300 K.

(A) For $x = 10$, there are 20 carbon atoms and thus 20 electrons in the delocalized bond. Thus $n = 10$ at the Fermi level. The "box" length is 20 × 1.45Å, assuming the box ends midway along a C–CH_3 bond.

$$L \;=\; 2\times10\times1.45\times10^{-10}\,\mathrm{m} \;=\; 2.9\times10^{-9}\,\mathrm{m}$$

$$\Delta E \;=\; E_{11} - E_{10} \;=\; \frac{(2n+1)h^2}{8m_e L^2} \;=\; \frac{(2(10)+1)(6.63\times10^{-34}\,\mathrm{J\cdot sec})^2}{8\times(9.1\times10^{-31}\,\mathrm{kg})(2.9\times10^{-9}\,\mathrm{m})^2} \;=\; 1.5\times10^{-19}\,\mathrm{J}$$

$$\Delta E \;=\; 1.5\times10^{-19}\,\mathrm{J}\,\frac{1\mathrm{eV}}{1.60\times10^{-19}\,\mathrm{J}} \;=\; 0.9\mathrm{eV}$$

At 300 K, $kT = 0.025$ eV. The Boltzmann population of conduction electrons (electrons with $n = 11$) is proportional to $e^{-0.9/0.025} = 2 \times 10^{-16}$.

Thus, for $n = 10$, the molecule is a semiconductor (or insulator).

(B) For $x = 10{,}000$, there are 20,000 carbon atoms and thus 20,000 electrons in the delocalized bond. Thus $n = 10{,}000$ at the Fermi level. The "box" length is 20,000 × 1.45Å, assuming the box ends midway along a C–CH_3 bond.

$$L \;=\; 20{,}000\times1.45\times10^{-10}\,\mathrm{m} \;=\; 2.9\times10^{-6}\,\mathrm{m}$$

Calculate the spacing between energy levels at the Fermi level.

$$\Delta E \;=\; E_{10,001} - E_{10,000} \;=\; \frac{(2(10{,}000)+1)(6.63\times10^{-34}\,\mathrm{J\cdot sec})^2}{8\times(9.1\times10^{31}\,\mathrm{kg})(2.9\times10^{-6}\,\mathrm{m})^2} \;=\; 1.5\times10^{-22}\,\mathrm{J} \;=\; 0.0009\mathrm{eV}$$

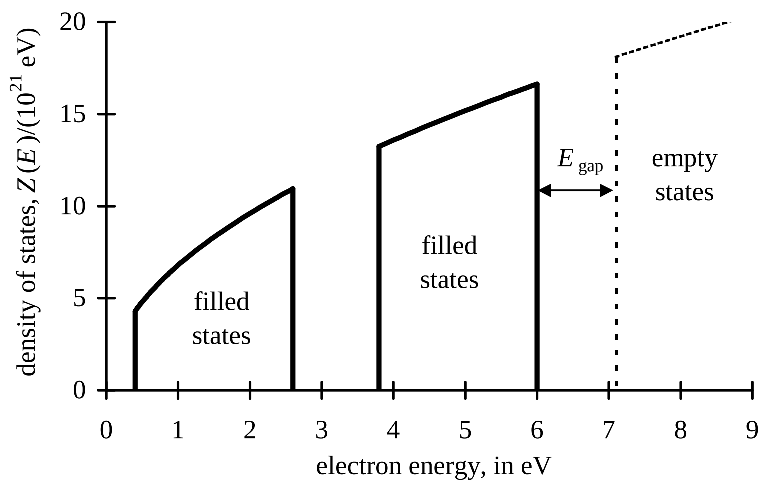
Thus the Boltzmann population above the Fermi level is proportional to $e^{-0.0009/0.025} = 0.96$.

Thus, for n = 10,000, the molecule is a metal.

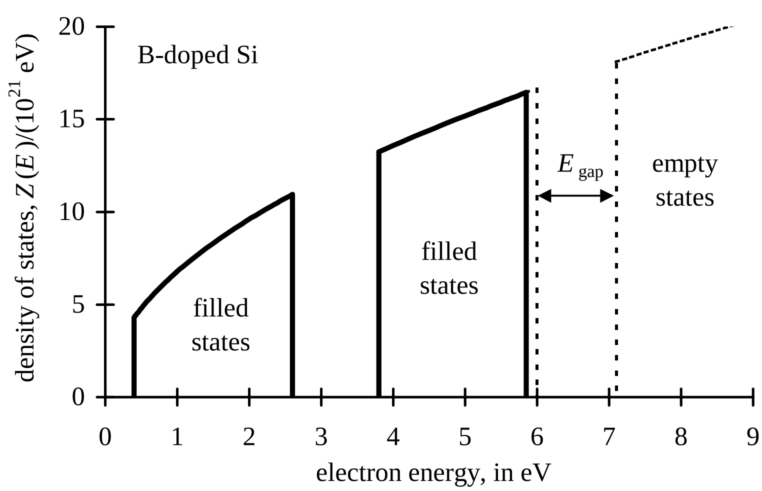
(C) Band theory will yield a generic plot of E versus k similar to figure 15 of *Electrons in Solids*. There is one electron per potential well, so the Fermi level is halfway to the first band gap. Thus the calculation in part (B) applies and the molecule is a metal.

(D) This molecule has two electrons per potential well and thus the Fermi level lies *in* the first band gap. Energy levels below the gap are filled and energy levels above the gap are empty. This molecule is a semiconductor, or an insulator.

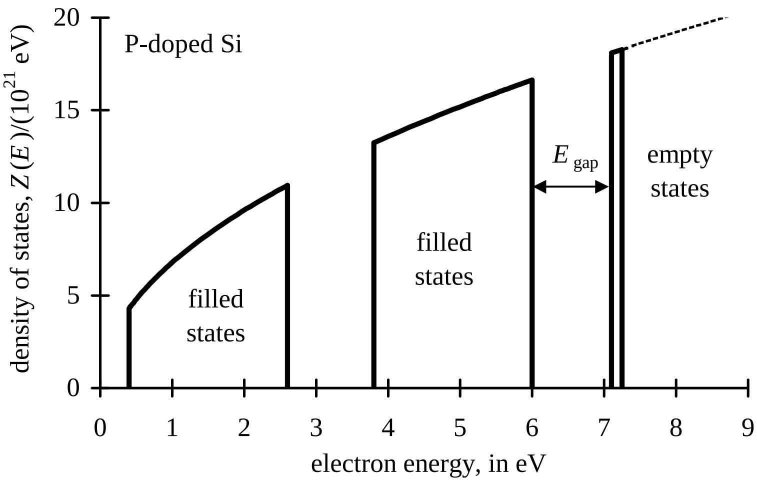
4. Silicon has four valence electrons. Thus the first two bands are filled and the states above the band gap are empty. The occupancy of states for silicon are shown in the figure below.



Boron has three valance electrons. Every silicon atom replaced by a boron atom creates a vacancy in the valence band below the band gap. Boron-doped silicon is a metallic conductor, as shown in the figure below.



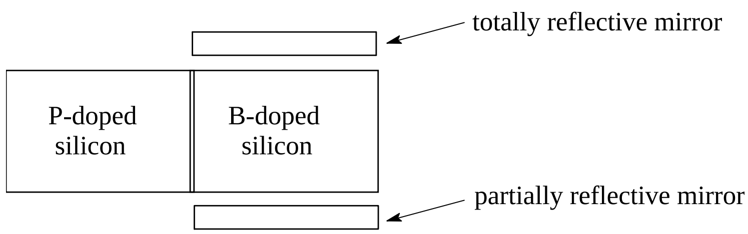
Phosphorus has five valance electrons. Phosphorus-doped silicon has electrons in the conduction band and thus is also a metallic conductor, as shown in the figure below.



Electrons flow through the P-doped Si by traveling in the conduction band. These electrons have energies above the band gap. When one of these electrons flows into the B-doped Si, the electron still has energy above the band gap. But B-doped Si has vacancies in the valence band. The electron falls to a state below the band gap. Thus the photon energy is 7.1 – 6.0 = 1.1 eV.

Optional problem - how to make a solid-state laser?

One might consider making a solid state laser by placing two mirrors around the B-doped Si, as shown below.



Photons reflect back and forth between the mirrors, stimulating transitions of exactly the same energy. A portion of the coherent photons pass through the partially reflective mirror and create a coherent beam. In practice, solid state lasers are a bit more tricky than this simple device.