11.9: Problems

1. Consider a spherical gold nanoparticle that contains 500 atoms. If the diameter of an atom is approximately 3 Å, what fraction of the gold atoms in the particle are on the surface?

2. Now consider small droplets of mercury that contains 500 atoms. Mercury atoms are also about 3 Å in diameter. The heat of vaporization of bulk mercury is 64.0 kJ/mol, and the vapor pressure of mercury is 0.00185 torr = 2.43 x 10^{-6} atm. The surface tension of mercury (γ_{Hg}) is 0.518 N/m, and the surface excess energy can be calculated as $\gamma_{Hg}A$, where A is the surface area. Using this information and the Clausius-Clapyron equation (P = const•exp($-\Delta H_{vap}/RT$)), calculate the vapor pressure of these small droplets of mercury.

3. James Heath and coworkers (Phys. Rev. Lett. 1995, 75, 3466) have observed Ostwald ripening in thin films of gold nanoparticles at room temperature. Starting with an uneven distribution of particle sizes, they find that the large particles grow at the expense of smaller ones. Can you explain this observation, based on your answers to problems (1) and (2)?

4. The bandgap of bulk germanium is 0.67 eV. What bandgap would you expect for a 4 nm diameter Ge nanocrystal? Use the Brus formula,

$$\Delta E_{gap} \approx \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \dots \tag{11.9.1}$$

where R is the particle radius, ε_{Ge} = 16.2, h = 6.6 10^{-34} J s, 1 eV = 1.6 10^{-19} J, 1 J = 1 kg m^2/s^2. and $e^2/4\pi\varepsilon_0$ = 1.44 10^{-9} eV m. Assume that the electron-hole reduced mass μ is approximately 40% of the free electron mass, m_e = 9.1 10^{-31} kg.

5. Grecian Formula (a hair coloring product) until recently contained lead acetate, which reacts with the cysteine in hair to make PbS. In bulk form, PbS is a semiconductor with a band gap of 0.3 eV (1 eV = 1240 nm). The particles are initially very small but grow as more Grecian Formula is applied and reacts with cysteine. As the particles grow, they change progressively from colorless to yellow to black. Explain why the particles are initially colorless and why their color changes. (Grecian formula now uses Bi, which is less toxic than Pb, and works by the same mechanism)