Solution:

Problem 1:

When octadecanethiol forms a SAM on a gold (111) surface, the molecules adopt a $\sqrt{3} \times \sqrt{3}R30°$ arrangement. This means the following:

- The molecular adsorption lattice is expanded by $\sqrt{3}$ relative to the atomic lattice of gold (111), which has a nearest-neighbor spacing of 0.288 nm
- The resulting center-to-center distance of the molecules is $a = \sqrt{3} \times 0.288\, nm$

Based on this information, please calculate the following:

a) Derive the center-to-center distance a of the SAM based on $\sqrt{3} \times \sqrt{3}R30°$ arrangement.

$$a = \sqrt{3} \cdot 0.288\,\mathrm{nm} = 0.5\,\mathrm{nm}$$

b) Calculate the area per molecule in the SAM assuming a hexagonal lattice.

$$A = \frac{\sqrt{3}}{2}a^2 = \frac{\sqrt{3}}{2}(0.5)^2 = 0.2165\,\mathrm{nm}^2$$

c) Calculate the SAM packing density in molecules per square nanometer.

$$\rho = \frac{1}{A} = \frac{1}{0.2165} \approx 4.62\,\mathrm{molecules/nm}^2$$

d) Calculate the total number of molecules in the SAM on a 1 cm^2 gold surface assuming a 90% coverage due to defect sites.

$$\text{Total molecules} = \rho \cdot \text{Total area} \cdot \text{Coverage fraction}$$

$$1\,\mathrm{cm}^2 = (10^7\,\mathrm{nm})^2 = 10^{14}\,\mathrm{nm}^2$$

$$\text{Total molecules} = \rho \cdot 10^{14} \cdot 0.9 = 4.158 \cdot 10^{14}\,\text{molecules}$$

Comparing with literature data: For octadecanethiol SAMs on gold surfaces, experimental studies typically report packing densities of 4.5–5.0 molecules/nm² under ideal conditions. Thus, the calculated result of **4.62 molecules/nm²** is consistent with these experimental values and is indeed accurate for the given assumptions.

Further reading if you'd like:

Alves *et al.,* Atomic Scale Imaging of Alkanethiolate Monolayers at Gold Surfaces with Atomic Force Microscopy, *J. Am. Chem. Soc., 111*, 4, **1992**.

Problem 2:

2. Gold nanoparticles (AuNPs) are widely used in biological and material science applications. When aggregated, their optical properties, such as plasmon resonance, and their interaction with light change significantly, which is useful in biosensing, imaging, and diagnostics. Let's work on a few problems that help us to understand AuNPs and plasmon resonance better.

a) Gold nanoparticles typically have a work function (Φ) that can vary with size. For small gold nanoparticles of approximately 10 nm, the work function is typically found to be around **5.1 eV**. Calculate the energy required to remove an electron from a gold nanoparticle (using the work function) and express this in Joules.
* 1 eV = 1.602×10^{-19} J

$$E = \Phi_{\text{AuNP}} \times \left(1.602 \times 10^{-19}\,\text{J/eV}\right)$$

Where the work function Φ is in eV

$$E = 5.1\,\text{eV} \times \left(1.602 \times 10^{-19}\,\text{J/eV}\right)$$

$$E = 8.17 \times 10^{-19}\,\text{J}$$

b) The work function (Φ) of bulk gold is approximately **5.47 eV**. How does the energy required to remove an electron from a gold nanoparticle compare to that of bulk gold, and what accounts for this difference?

It is easier to remove an electron from a gold nanoparticle compared to bulk gold, which we can see by comparing the work function – gold nanoparticles typically have a lower work function (around 5.1 eV) compared to bulk gold (5.47 eV). In nanoparticles with a larger surface-to-volume ratio, surface atoms are less tightly bound, which leads to more loosely held electrons, contributing to a lower work function. In bulk gold, atoms are more stable with a uniform electron distribution, making electron removal harder.

Problem 3:

3. The surface plasmon resonance (SPR) wavelength of gold nanoparticles depends on the size of the nanoparticle and the dielectric properties of the surrounding medium. Assume that the plasmon resonance wavelength (λ_{SPR}) for a spherical gold nanoparticle with a diameter of **20 nm** is **530 nm** in water.

a) Calculate the frequency of light corresponding to this plasmon resonance wavelength (λ_{SPR}=530 nm)

$$\lambda_{\text{SPR}} = 530\,\text{nm} = 530 \times 10^{-9}\,\text{m} \qquad f = \frac{c}{\lambda}$$

$$f = \frac{3.0 \times 10^{8}\,\text{m/s}}{530 \times 10^{-9}\,\text{m}} = 5.66 \times 10^{14}\,\text{Hz}$$

b) Using the frequency calculated in part (a), determine the energy of the photon at this frequency. Recall the equation for energy of a photon:

$$E_{\text{photon}} = h \text{ x } f$$

where h is Planck's constant = 6.626×10^{-34} J s
and f is the frequency of light

$$E_{\text{photon}} = (6.626 \times 10^{-34}\,\text{J s}) \times (5.66 \times 10^{14}\,\text{Hz}) = 3.75 \times 10^{-19}\,\text{J}$$

c) The plasmon resonance of gold nanoparticles shifts when they aggregate. This shift depends on the degree of aggregation, and the change in the plasmon resonance wavelength can be observed as a color change. Given that for isolated gold nanoparticles the plasmon resonance is at 530 nm, and when aggregated, it shifts to **600 nm**, calculate the fractional change in the plasmon resonance wavelength ($\Delta\lambda/\lambda_{\text{initial}}$). What is the relevance of this value (*i.e.,* what could it be useful for?).

$$\frac{\Delta\lambda}{\lambda_{\text{initial}}} = \frac{\lambda_{\text{final}} - \lambda_{\text{initial}}}{\lambda_{\text{initial}}} \qquad \lambda_{\text{initial}} = 530\,\text{nm}$$

$$\lambda_{\text{final}} = 600\,\text{nm}$$

$$\frac{\Delta\lambda}{\lambda_{\text{initial}}} = \frac{600\,\text{nm} - 530\,\text{nm}}{530\,\text{nm}} = \frac{70\,\text{nm}}{530\,\text{nm}} = 0.132$$

So, the fractional change in the plasmon resonance wavelength is approximately **0.132** or **13.2%**. This value demonstrates the sensitivity of the gold nanoparticles' optical properties to aggregation in this specific environment. This value can be used as a foundation in biosensing where analytes are detected by aggregation of nanoparticles.

d) What is the shift in the photon energy (in eV) corresponding to this change in plasmon resonance wavelength (from 530 nm to 600 nm)? Use the energy-wavelength relation:

$$E = \frac{h \cdot c}{\lambda}$$

where h is Planck's constant = 6.626×10^{-34} J s
and c = $3.0 \text{ x } 10^{8}$ m/s

$\lambda_{\text{initial}} = 530\,\text{nm}$:

$$E_{\text{initial}} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \cdot (3.0 \times 10^{8}\,\text{m/s})}{530 \times 10^{-9}\,\text{m}} = 3.75 \times 10^{-19}\,\text{J}$$

$\lambda_{\text{final}} = 600\,\text{nm}$:

$$E_{\text{final}} = \frac{(6.626 \times 10^{-34}\,\text{J s}) \cdot (3.0 \times 10^{8}\,\text{m/s})}{600 \times 10^{-9}\,\text{m}} = 3.31 \times 10^{-19}\,\text{J}$$

This shift in photon energy is:

$$\Delta E = E_{\text{initial}} - E_{\text{final}} = (3.75 \times 10^{-19}\,\mathrm{J}) - (3.31 \times 10^{-19}\,\mathrm{J}) = 0.44 \times 10^{-19}\,\mathrm{J}$$

$$\Delta E = \frac{0.44 \times 10^{-19}\,\mathrm{J}}{1.602 \times 10^{-19}\,\mathrm{J/eV}} \approx 0.27\,\mathrm{eV}$$

A shift in photon energy of 0.27 eV reflects the change in the energy required to excite surface plasmons in gold nanoparticles when they undergo aggregation. It is about 5% of the work function of bulk gold, which is a notable shift. Another comparison would be to the thermal energy at room temperature (298 K) where $k_BT \approx 0.025$ eV. So, 0.27 eV is about 20 times the thermal energy at room temperature, meaning it is large enough to overcome random thermal fluctuations that may influence the signal. Such shifts are important for real-world applications such as plasmonic sensing.