Physics 243A—Surface Physics-Spectroscopy
Suggested answers to Problem Assignment 1
---------------------------------------------
All of PS 1
[1.1] 1" = 2.54 cm

Area = 6.45 cm²

\[ \begin{align*}
100 \text{ Gbits} & = 10^{11} \text{ bits} \\
1" & = 2.54 \text{ cm} \\
10 \text{ nm} & = 10^{-7} \text{ cm}
\end{align*} \]

8. Bit Volume = \( 5 \times (6.45 \times 10^{-12}) \times 10^{-6} = 3.22 \times 10^{-17} \text{ cm}^3 \)

AND NO. ATOMS/BIT = \( \frac{3.22 \times 10^{-17}}{9.0 \times 10^{22}} = 2.90 \times 10^6 \)
[4.2](a) A general expression for the monolayer coverage time can be derived using the Maxwell-Boltzmann (M-B) distribution of kinetic energy, as described in any textbook on statistical mechanics.

The M-B distribution tells us the fraction of molecules with speeds $v_x$ to $v_x + dv_x$, $v_y$ to $v_y + dv_y$, and $v_z$ to $v_z + dv_z$ is given by

$$\frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m}{2kT} (v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z, \quad (1)$$

We now assume a test surface that is perpendicular to the $x$ axis, so that only $v_x$ determines the rapidity of approach. If the concentration of molecules with speeds in $v_x$ to $v_x + dv_x$ is $dn$, the number of collisions caused by them per cm$^2$ of area is:

$$d\Sigma = dn \cdot V_x \quad (2)$$

If the total number of molecules/cm$^3$ is $n$, then

$$dn = n \cdot dN/N$$

(as given by (1)). Substituting in (2) then gives
\[ dZ = n \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-\frac{m}{2kT}(u_x^2 + u_y^2 + u_z^2)} \ u_x \, du_x \, du_y \, du_z \]

Integrating now over \(-\infty \rightarrow +\infty\) in \(u_y\) and \(u_z\) and over \(0 \rightarrow +\infty\) in \(u_x\) to insure collision counting only on one side of the surface gives

\[ \text{(Total collision rate)} = Z = n \left( \frac{kT}{2\pi m} \right)^{1/2} \]

We are interested in the time to form a monolayer coverage with unit sticking probability \(P_s\). Let the molecular diameter be \(d\) and assume that an area \(d^2\) is occupied on the surface by each molecule that has sticks. Then

\[ \text{(Number of collisions required per monolayer per cm}^2\text{)} = \frac{1}{d^2} \]

\[ \therefore \text{(Time for monolayer formation)} = \frac{1}{P_s \cdot n \cdot d^2 \left( \frac{2\pi m}{kT} \right)^{1/2}} \]

As expected, as \(P_s\) decreases from its maximum value of 1, the time increases.

Or, noting that the pressure \(P\) is given by \(P = nkT\), \(n = \frac{P}{kT}\), and the time becomes finally

\[ \text{(Time for monolayer formation)} = \frac{(2\pi m k^2 T)^{1/2}}{P_s \cdot P \cdot d^2} \]
(b) \( P_s(t) = 1.0 \) (open area) + 0.0 (covered area) 
so average over surface values with time as:

\[ P_s(t) = 1.0 \left[ 1.0 - \int_0^t Z d^2 F_s(t) \, dt \right] \]

\[
= \frac{dP_s(t)}{dt} = -Z d^2 P_s(t)
\]

\[
\frac{dP_s(t)}{P_s(t)} = -Z d^2 dt
\]

\[ e^{-Z d^2 t} = e^{-\frac{P_d^2}{(2\pi m k_b T)^{1/2}} t} = e^{-t/\tau} \]

WHERE: \( \tau = \text{MONOLAYER TIME IF} \ P_s = 1.0 \)
FROM EQ. (6)

(c) (i) For the particular case of CO gas (a typical residual gas) at \( 10^{-9} \) torr, we thus have in cgs units:

\( T = 298^\circ K, \ P = 10^{-9} \) torr \( \left( \frac{1 \text{ atm}}{760 \text{ torr}} \right) \left( \frac{10^{6} \text{ dynes/cm}^2}{1 \text{ atm}} \right) = 1.32 \times 10^{-6} \text{ dynes/cm}^2 \)

\( m = 28/(6.02 \times 10^{23}) = 4.65 \times 10^{-23} \) gm, and \( d \approx 3.2 \) \( \AA \) (the effective dim. of CO as found in tables). Thus,

\[
\text{Time for monolayer formation} = \frac{[2\pi (4.65 \times 10^{-23}) (1.32 \times 10^{-6}) (298)]^{1/2}}{1.0 (1.32 \times 10^{-6}) (3.2 \times 10^{-8})^2} \approx 2.57 \times 10^{3} \text{ sec} \]

\( \approx 43 \text{ min} \) (consistent with values given in lecture)

(ii) If \( P_s(t) \) follows (7), then the coverage is given by

\[
\int_0^t Z d^2 P_s(t) \, dt = \frac{1}{\tau} \int_0^t e^{-t/\tau} \, dt = -e^{-t/\tau} \bigg|_0^t = 1 - e^{-t'/\tau}
\]

\( \tau \) takes an infinite time to form first monolayer.

As another relevant number, \( 1/2 \) monolayers would be reached at \( t' = 0.693 \tau \approx 29.8 \) min.

Or, 0.99 monolayers at \( t' = 4.60 \tau \approx 198.0 \) min.
(a) MIN. ENERGY = \( \Delta (\gamma A) = \gamma (A_{\text{nanoparticles}} - A_{1 \text{ cm cube}}) \)

with: \( \gamma = 1800 \text{ erg/cm}^2 \) for Pt

\[ A_{1 \text{ cm cube}} = 6 \text{ cm}^2 \]

\[ A_{\text{nanoparticles}} = 6 \left(10^{-9} \text{ cm}^3\right) \times \text{no. particles} = 6 \times 10^{-12} \times 10^{15} = 6 \times 10^2 \text{ cm}^2 \]

\[
\text{no. particles} = (10^6)^3 = 10^{18}
\]

So

\[
\text{MIN. ENERGY} = 1800 \text{ erg/cm}^2 (6 \times 10^2 \text{ cm}^2) = 1.08 \times 10^8 \text{ ergs} = 1.08 \times 10^3 \text{ J}
\]

= \(1.11 \times 10^{15} \text{ eV/cm}^2\)

(b) EACH Pt ATOM OCCUPIES CUBE OF AVERAGE SIDE:

\[
\sqrt[3]{\frac{1}{6.62 \times 10^{22} \text{ cm}^3}}
\]

= \(2.47 \times 10^{-8} \text{ cm} = 2.47 \text{ Å}\)

For 1 cm cube:

TOTAL NO. ATOMS = \(6.62 \times 10^{22}\)

SURFACE ATOMS = \(6 \left(\frac{1 \text{ cm}}{2.47 \times 10^{-8} \text{ cm}}\right)^2 = 6 (0.1634) 10^{16}\)

= \(0.983 \times 10^{16}\)

NEGLECTING DOUBLE-COUNTING OF EDGE ATOMS AS NEGLIGIBLE

FRACTION AT SURFACE = \(\frac{0.983 \times 10^{16}}{6.62 \times 10^{22}} = 1.48 \times 10^{-7}\)

\(\approx \frac{1}{10} \text{ MILLION}\)

For \(10^{-6} \text{ cm cube}\):

TOTAL NO. ATOMS = \((6.62 \times 10^{22} \text{ cm}^{-3}) (10^{-6} \text{ cm})^3\)

= \(6.62 \times 10^4\)

SURFACE ATOMS \(\approx 6 \left(\frac{10^{-6} \text{ cm}}{2.47 \times 10^{-8} \text{ cm}}\right)^2 = 0.983 \times 10^4\)

EDGE EFFECTS STILL ONLY \(\frac{1}{40}\) OF TOTAL, SO CONTINUE NEGLECT

FRACTION AT SURFACE = \(\frac{0.983 \times 10^4}{6.62 \times 10^4} = 0.148 \approx \frac{1}{7}\)
Formula given in Zangwill is:

\[ Y = Z_5 \left( \frac{E_{\text{coh}}}{Z} \right) N_s \]

Let's try it out. Use \( Z_5 \approx 0.25 \), \( E_{\text{coh}}(\text{eV}) = E_{\text{coh}}(\text{eV}) \cdot 1.602 \times 10^{-12} \text{ (eV/ev)} \)

Appox. 1/4 of bonds in bulk broken to make surface

\[ \rightarrow \text{No. density of atoms from table.} \]

Putting in all the nos. leads to values on next page.

Not very good agreement; calculated values are all \( \approx 2 \times \) too high, although systematic trends are well predicted. Reason is error in Zangwill formula, because when we break \( Z_5 \left( \frac{E_{\text{coh}}}{Z} \right) N_s \) bonds in 1 cm\(^2\), we get 2 cm\(^2\) of surface. So, correct formula is:

\[ Y' = Z_5 \left( \frac{E_{\text{coh}}}{Z} \right) N_s \]

See dashed curve on next page, which agrees very well with \( Y' \) data for liquids, but with some deviations from \( Y_{\text{calc}} \) \( \gg Y_{\text{exp}} \) over \( Z = 31-35 \) for current/semiconductor crystals, suggesting \( Z S < 0.25 \) for these, and \( Y_{\text{calc}} < Y_{\text{exp}} \) for Zn, suggesting \( \frac{Z S}{2} > 0.25 \).

\( Z = 30 \)
\[ \gamma = \sum \left( \frac{E_{\text{cm}}}{Z} \right) N_S \]

[Graph showing the atomic number vs. \( \gamma \text{ (erg/cm}^3 \) with annotations]

- Calculated from
- \( \delta = \gamma Z \)

[Handwritten notes on the graph]
\[ 1.5 \]

(a) \[ \cos \theta = \left( \frac{Y_{\text{glass-air}} - Y_{\text{glass-H}_2\text{O}}}{} \right) = \cos(150^\circ) = -0.866 \]

\[ Y_{\text{H}_2\text{O}}(g) = 72 \text{ erg/cm}^2 \]

(with geometry as -)

\[ \text{WATER} \quad \text{NON-WETTING!} \]

\[ \text{AIR} + \text{H}_2\text{O} \]

\[ \text{class} \]

\[ S^0, \]

\[ Y_{\text{glass-H}_2\text{O}}(g) > Y_{\text{glass-air}}, \quad \text{and} \quad Y_{\text{glass-H}_2\text{O}}(g) - Y_{\text{glass-air}} = 0.866 \text{ (72 erg/cm}^2) \]

\[ = 62.4 \text{ erg/cm}^2 \]

(b) Now add surfactant such that \[ Y_{\text{H}_2\text{O}}(g) = 36 \text{ erg/cm}^2 \]

This makes it EASIER TO Form THE DROP SURFACE, BUT still

equally difficult to Form the WATER-GLASS SURFACE, i.e.,

one effect: a TENDENCY TO REDUCE THE WATER-GLASS SURFACE, GOING TOWARD AN EVEN HIGHER CONTACT ANGLE.

The nas. say THIS also, as

\[ \cos \theta = \frac{-62.4}{36.0} \text{ WHICH HAS NO SOLUTION,} \]

but implies that \( \theta \rightarrow 180^\circ \) as surfactant is added.

With a more accurate model being needed in going

through this point.

\[ [1.6] \text{ I know that } \frac{x^b_y}{x^b_{Cu}} = \frac{x^b_y}{x^b_{Cu}} e^{-\frac{\Delta F_0}{kT}} \frac{x^b_y}{x^b_{Cu}} - \text{constant \( (Y^y_{Ag} - Y^y_{Cu}) \)} \]

With \( Y^y_{Ag} \approx 900 \text{ erg/cm}^2 \) and \( Y^y_{Cu} \approx 1320 \text{ erg/cm}^2 \), it is easier to Form

a Ag-MCM surface, and the above predicts \( x^b_y > \frac{x^b_y}{x^b_{Cu}} \).
\[ e^- \text{ at } 150 \text{ eV} \rightarrow \lambda_e = \frac{h}{p_e} = \sqrt{\frac{150.4}{E(\text{eV})}} \text{ Å} = 1.0 \text{ Å} \]

\[ \theta_B \text{ from condition,} \]

\[ n\lambda_e = d_i \sin \theta_{B1,n} \]

\[ \theta_{B1,n} = \sin^{-1} \left[ \frac{n\lambda_e}{d_i} \right] \]

See next page for Ni (001) dimensions, then

**Ni Spots:**

\[ d_2 = 2.49\text{ Å} \]

\[ d_1 = 2.09\text{ Å} \]

\[ d_{21} = 1.76\text{ Å} \]

\[ \theta_{B1,n} = \sin^{-1} \left[ \frac{1.0}{2.49} \right], \sin^{-1} \left[ \frac{2.0}{2.49} \right], \ldots \]

\[ = 23.7^\circ, 53.4^\circ, \phi = 0^\circ, 90^\circ \]

Also ± in polar angle

**Overlayer Spots:**

\[ d_3 = 3.52 \text{ Å} \]

\[ \theta_{B3,n} = \sin^{-1} \left[ \frac{1.0}{3.52} \right], \sin^{-1} \left[ \frac{2.0}{3.52} \right], \ldots \]

\[ = 16.5^\circ, 34.6^\circ \]

Final LEED pattern:

- \( \bullet = \text{Ni} \)
- \( O = \text{O overlayer} \)
\[ I_{\text{sm}} \propto e^{-2KL}, \quad \kappa = \frac{\sqrt{2m\phi}}{h} = 0.51 \phi^{1/2} \text{ (Å)} \]

Woodiwiss + Belcher

\[ \text{(6.30)} \]

\[ = 0.51(4.0)^{1/2} = 1.02 \text{ Å} \]

Tip at \( L = 5.0 \text{ Å} \rightarrow I_{\text{sm}} \propto e^{-2(1.02)(5.0)} = e^{-10.2} \]

\[ = 0.0000372 \]

\[ L = 5.1 \text{ Å} \rightarrow I_{\text{sm}} = e^{-10.4} = 0.0000304 \]

\[ \text{Change of } 1870 \% \]

\[ \text{A precision of } \frac{18}{10} \sim 270 \text{ should permit accurately measuring } 0.1 \text{ Å} \]