

**Physics 243A - Surface Physics of Materials/X-Ray Spectroscopies
Midterm Examination
November 18, 2014**

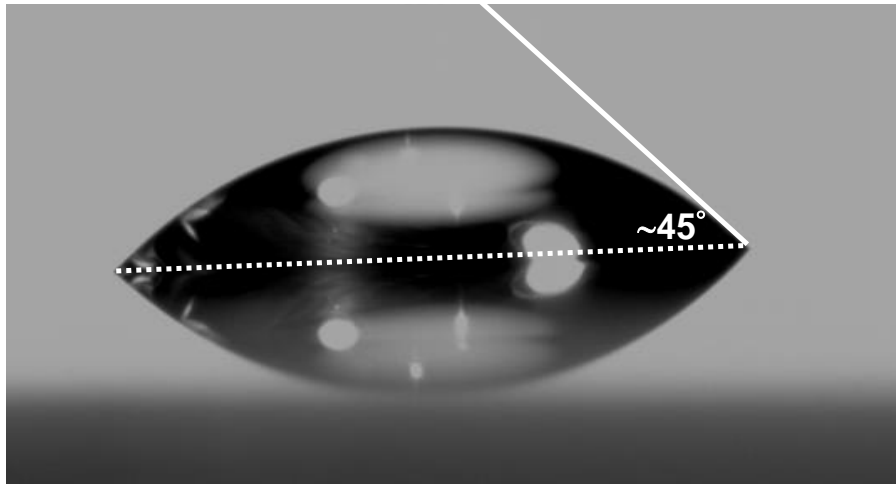
(100 points total, open books, notes, and class handouts)

Name: _____

Signature: _____

[1] (15 points)

(a) The photo below is of a water droplet on a clean glass surface at 20° C, with its mirror image also shown below the dotted line. The surface tension of liquid water in air at this temperature is 72.8 dyne/cm, and that of glass in air at this temperature is about 275 dyne/cm.



What can you say about the surface tension between glass and water? Be as quantitative as you can.

The contact angle formula, written for this problem, and then solved to get what we want, is:

$$\cos \theta = \frac{(\gamma_{SG} - \gamma_{SL})}{\gamma_{LG}} = \frac{(\gamma_{Glass-Air} - \gamma_{Glass-Water})}{\gamma_{Water-Gas}}$$

We want $\gamma_{Glass-Water}$, which is

$$\gamma_{Glass-Water} = \gamma_{Glass-Air} - \gamma_{Water-Gas} \cos \theta = 275 - (72.8)(0.707) = 223.5 \text{ dyne/cm}$$

(b) The cohesive energy of elemental Si is 4.64 eV per atom, and the atomic density is $5.00 \times 10^{22} \text{ cm}^{-3}$. Estimate the surface tension of a clean surface of Si in erg-cm^{-2} . (1 eV = $1.60 \times 10^{-12} \text{ erg} = 1.60 \times 10^{-12} \text{ dyne-cm}$).

This is a straightforward repeat of what you did in one of the problems of Set 1.

$\gamma_{Si} = [Z_S/Z] E_{coh} N_S / 2$, with $N_S = (\text{atomic number density})^{2/3}$, so we finally have

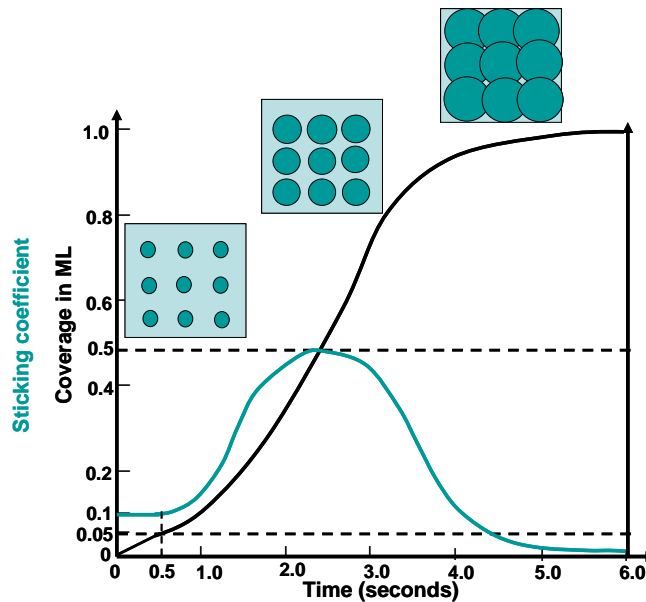
$$\gamma_{Si} = [0.25\text{-an empirical number}][4.65 \text{ eV}][1.60 \times 10^{-12} \text{ erg/eV} \times [50.00 \times 10^{21}]^{2/3} / 2 \\ = [0.25][4.65][1.60][13.57]10^{-12+14} = 1262 \text{ erg-cm}^{-2}$$

Pretty good agreement with the about 900 erg-cm^{-2} in Zangwill's Figure of liquid surface tensions, which we know will be smaller than for the s

[2] (15 points)

An atomic adsorption problem is characterized by the following kinetic model: Atoms are incident on a clean surface at a rate that would yield 1.0 monolayer (ML) coverage per second if the sticking probability were 1.0. However, the actual sticking probability is 0.1 until a coverage of 0.05 ML is reached. From this point onward, the atoms migrate to one of the atomic growth "nuclei" for islands thus created, with the sticking probability then growing from 0.1 in proportion to the island circumference available and reaching a maximum of 0.5 at a coverage of 0.5 ML. The overlayer is observed to be saturated at 1.0 ML coverage (i.e. no further atoms stick). Assuming that the islands are circular and regularly spaced, indicate how you would quantitatively calculate the coverage as a function of time from this data, and then qualitatively sketch the form of coverage versus time, indicating also what the rough relationship of the islands and their sizes should be at 0.05 ML, 0.5 ML, and 1.0 ML. It may be useful here to first sketch the sticking probability versus coverage, and then indicate how this is related to the island coverage.

The drawing below indicates the qualitative form of both curves, as well as the island nuclei for growth, although the time scale after the initial 0.05 seconds is only a rough guess.



[3] (10 points)

A certain adsorption isotherm is thought to behave as second-order Langmuir in adsorption, but as usual still first order in desorption. Without considering any sort of microscopic model, how would you analyze data for equilibrium coverage as a function of pressure at a given temperature to most easily see if the results behave according to second-order Langmuir? What sort of plot would most quickly permit checking this?

The two rates that have to be set equal for second-order Langmuir are:

$$\text{Adsorption rate} = k_1 P(1-\theta)^2 = \text{Desorption rate} = k_2 \theta$$

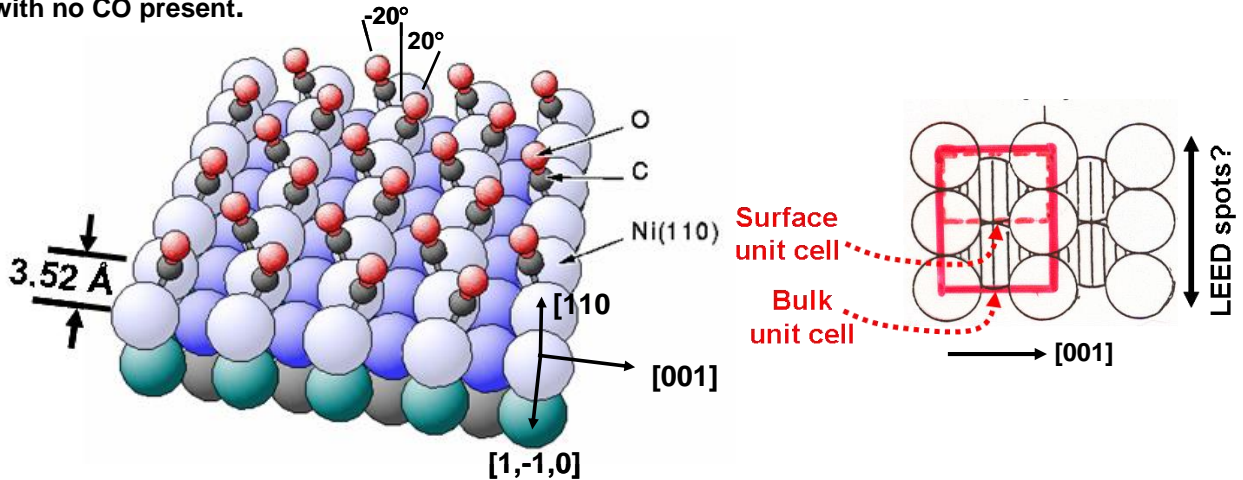
We can now rearrange this to get a function of θ that is linear in P to test for validity:

$$\theta/(1-\theta)^2 = (k_1/k_2)P$$

Thus, plotting $\theta/(1-\theta)^2$ vs P should yield a straight line of slope (k_1/k_2) . There might be other acceptable answers, but something with a straight line as the criterion is clearly the easiest to quickly interpret.

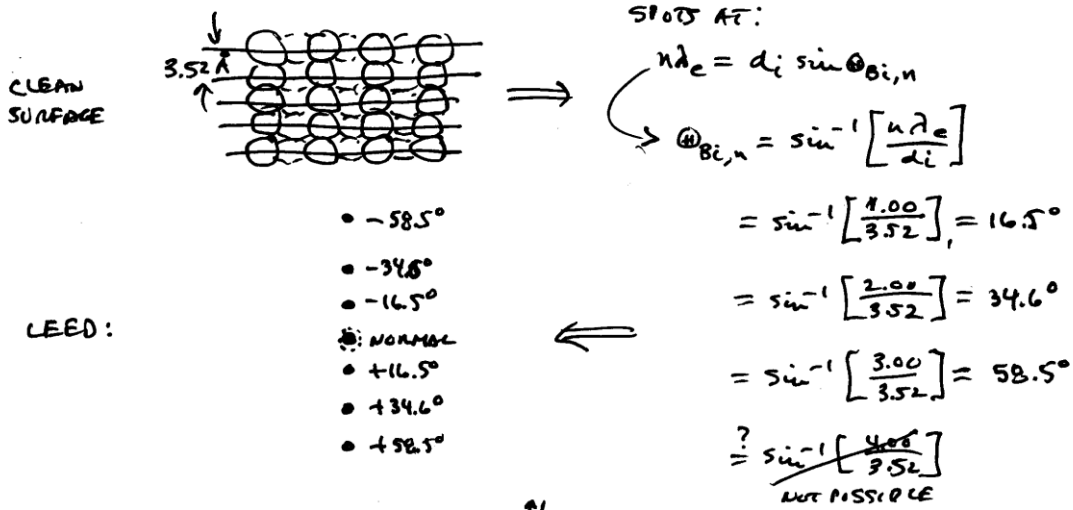
[4] (20 points)

Consider the low-temperature adsorbate structure of carbon monoxide on a Ni(110) surface shown below, in which the CO molecules are adsorbed in two-fold “bridge” sites and are tilted in opposite directions by plus or minus 20° so as to pack more tightly and yield a higher overall coverage. Also shown for reference is a top view of the (110) surface with no CO present.



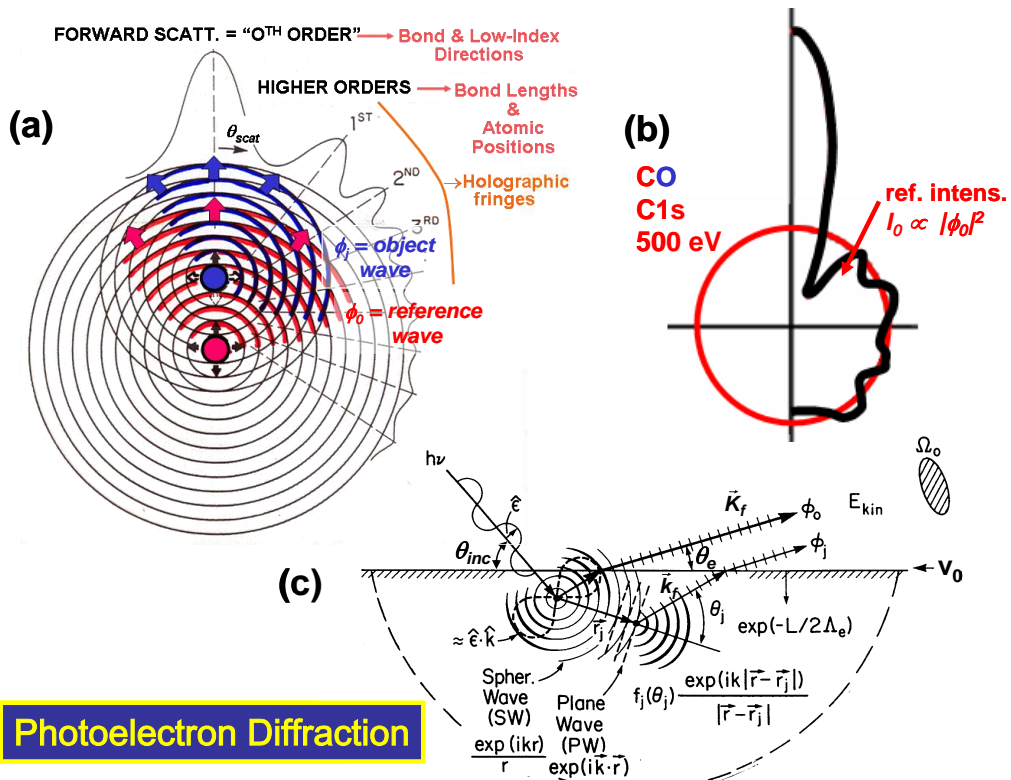
- What is the simplest name of this structure in Wood notation? First disregard the tilt of the molecules in arriving at this, counting them all as identical in arriving at the structure. This yields unit cell shown at left, and so a (1x1) structure, or more precisely Ni(110)-p(1x1)CO or more simply Ni(110)-(1x1)CO. Then consider the two tilts to be different in arriving at a second version of Wood notation. This is like having two different molecules on the surface, tilted left and tilted right, and so yields a larger unit cell, as shown above. So this would be Ni(110)-(1x2)CO.
- What is the coverage in ML relative to the top layer of Ni atoms? There is one CO molecule per surface atom, so coverage is 1.0 ML.
- Neglecting the effect of the adsorbate molecules, if 150 eV electrons are incident normal to this surface, what would be the polar-angle positions of all possible spots from the Ni(110) substrate along the direction of the arrow shown above right and in the figure below? Define the polar angle from the surface normal, as shown in the drawing below.

$$(c) \quad \lambda_c = \left(\frac{150.4}{150} \right)^{1/2} = 1.0 \text{ \AA}$$

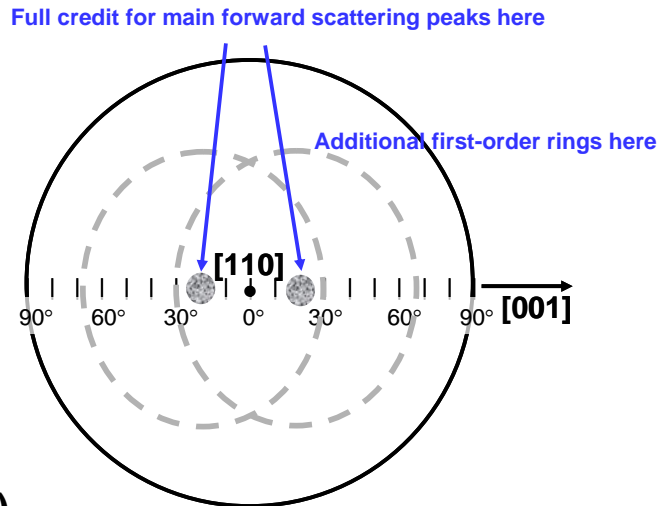


(d) Finally, from what we have said qualitatively about x-ray photoelectron scattering and diffraction, what kind of XPD pattern would you expect due to forward scattering over the hemisphere above the surface if C 1s electrons were excited by Al K α radiation. Just sketch this qualitatively in the circle below, which represents a projection of the hemisphere onto a plane, with darker areas representing higher intensity.

To help with the logic on this one, there are a couple of slides from lecture introducing XPD, as e.g.:



So the final prediction will be something like:



[5] (20 points)

Very accurate Hartree-Fock calculations have been performed for atomic argon (Ar). They yield the following values:

Total energy of Ar atom = -526.818 atomic units (1 a.u. = 1 hartree = 2 Rydbergs = 27.21 eV)

One-electron energy eigenvalues in Ar atom:

$$\epsilon_{1s} = -118.610 \text{ a.u.}$$

$$\epsilon_{2s} = -12.322 \text{ a.u.}$$

Total energy of Ar⁺ ion with 1s hole = -409.389 a.u.

Total energy of Ar⁺ ion with 2s hole = -514.880 a.u.

From these nos., calculate the relaxation energies associated with a measurement of $E_b(1s)$ and $E_b(2s)$ in eV.

$$E_b(1s) = -409.389 - (-526.818) = 117.429 \text{ au} = 3195.2 \text{ eV}$$

$$E_b^{KT}(1s) = -(\epsilon_{1s}) = 118.610 \text{ au} = 3227.4 \text{ eV}$$

$$\begin{aligned} \Delta E_{\text{relax}} &= E_b^{KT}(1s) - E_b(1s) \\ &= 320 \text{ eV} \approx 1\% \end{aligned}$$

$$E_b(2s) = -514.880 - (-526.818) = 11.938 \text{ au} = 324.8 \text{ eV}$$

$$E_b^{KT}(2s) = -(\epsilon_{2s}) = 12.322 \text{ au} = 335.3 \text{ eV}$$

$$\begin{aligned} \Delta E_{\text{relax}} &= E_b^{KT}(2s) - E_b(2s) \\ &= 10.5 \text{ eV} \approx 3\% \end{aligned}$$

[6] (20 points)

The x-ray photoelectron spectrum on the next page has been obtained by bombarding a solid sample with non-monochromatized x-rays from a Mg source. The sample contains two elements, and was prior to investigation bombarded with Ar ions to clean it. If the same spectrum is recorded with x-rays from an Al source, all peaks except those in the shaded region shift by 233 eV to higher kinetic energy, with those in the shaded region remaining fixed in kinetic energy.

Identify the two atoms involved, and the precise origins of all of the labelled peaks a, b, c..., as indicated on the spectrum.

See peak assignments below.

