# Physics 243A—Surface Physics-Spectroscopy
# Suggested answers to Problem Assignment 1
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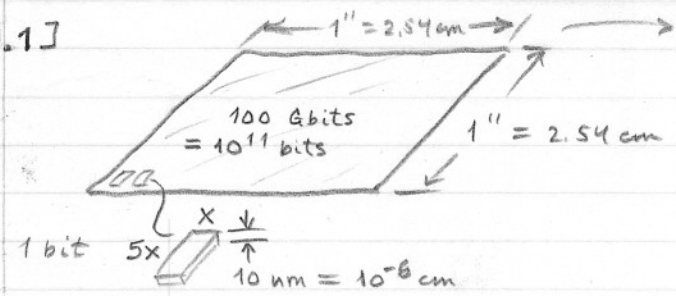
## All of PS 1

PHYSICS 243A - SURFACE PHYSICS

PROBLEM ASS'T. 1

SUGGESTED ANSWERS

[1.1]




AREA = 6.45 $cm^2$

WITH 50% OCCUPATION OF AREA:

$x(5x)\cdot 10^{11} = 0.5\,(6.45)$

$x^2 = \dfrac{0.5\,(6.45)}{5\times 10^{11}}$

$= 6.45\times 10^{-12}$

$x = 2.54\times 10^{-6}$ cm

$\therefore$ BIT VOLUME $= 5(6.45\times 10^{-12})\,10^{-6} = 3.22\times 10^{-17}$ $cm^3$

AND NO. ATOMS/BIT $= (3.22\times 10^{-17})(9.0\times 10^{22}) = \boxed{2.90\times 10^{6}}$

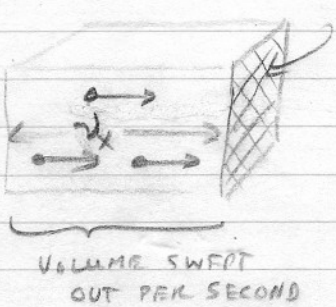
[1.2] (a) A general expression for the monolayer coverage time can be derived using the Maxwell-Boltzmann (M-B) distribution of kinetic theory, as described in any p. chem. or stat. mech. text.

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:

$$dZ_i = dn \cdot v_x \quad (2)$$




If the total number of molecules/cm3 is $n$, then $dn = n \cdot dN/N$ (as given by (1)). Substituting in (2) then gives

$$dZ_1 = n\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{m}{2kT}(v_x^2+v_y^2+v_z^2)} v_x\, dv_x\, dv_y\, dv_z$$

Integrating now over $-\infty$ to $+\infty$ in $v_y$ and $v_z$ and over 0 to $+\infty$ in $v_x$ to insure collision counting only on one side of the surface gives

$$\left(\begin{matrix}\text{Total collision rate}\\ \text{on one side per cm}^2\end{matrix}\right) = Z_1 = n\left(\frac{k_B T}{2\pi m}\right)^{1/2} \qquad (3)$$

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 stuck. Then

$$\left(\begin{matrix}\#\text{ collisions required}\\ \text{per monolayer per cm}^2\end{matrix}\right) = \frac{1}{d^2} \qquad (4)$$

$$\therefore \boxed{\left(\begin{matrix}\text{Time for monolayer}\\ \text{formation}\end{matrix}\right) = \frac{1}{P_s n d^2}\left(\frac{2\pi m}{k_B T}\right)^{1/2}} \qquad (5)$$

OR COULD USE A MORE GENERAL FORMULA WITH $P_s \rightarrow \int_0^t P(t)\,dt$

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

Or, noting that the pressure P is given by $P = nkT$, $n = P/kT$, and the time becomes finally

$$\boxed{\left(\begin{matrix}\text{Time for monolayer}\\ \text{formation}\end{matrix}\right) = \frac{(2\pi m k_B T)^{1/2}}{P_s P d^2}} \qquad (6)$$

(b) $P_s(t) = 1.0$ (OPEN AREA) $+ 0.0$ (COVERED AREA)

SO AVERAGE OVER SURFACE VALUES WITH TIME AS:

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

$$\therefore \quad \frac{dP_s(t)}{dt} = -Z d^2 P_s(t)$$

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

EQ. (3) + $n = \frac{P}{k_B T}$

$$\boxed{P_s(t) = e^{-Z d^2 t} = e^{-\frac{P d^2}{(2\pi m k_B T)^{1/2}} t} = e^{-t/\tau}} \quad (7)$$

WHERE: $\tau$ = 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 $= 10^{-9}$ torr $\left(\frac{1 \text{ atm}}{760 \text{ torr}}\right)\left(\frac{10^6 \text{ dynes/cm}^2}{\text{atm}}\right) = 1.32 \times 10^{-6}$ dynes/cm$^2$, $m = 28/(6.02 \times 10^{23}) = 4.65 \times 10^{-23}$ gm, and $d \approx 3.2$ Å (the effective diam. of CO as found in tables). Thus,

$$\left(\begin{matrix}\text{Time for monolayer} \\ \text{formation}\end{matrix}\right) = \frac{\left[2\pi(4.65 \times 10^{-23})(1.38 \times 10^{-16})(298)\right]^{1/2}}{1.0(1.32 \times 10^{-6})(3.2 \times 10^{-8})^2} = 2.57 \times 10^3 \text{ sec}$$

$\approx 43$ min (consistent with nos. given in lecture)

(ii) IF $P_s(t)$ follows (7), then the coverage is given by

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

($t/\tau = t'$, $dt = \tau\, dt'$)

$\therefore$ takes an infinite time to form first monolayer.

As another relevant number, 1/2 monolayer would be reached at $t' = 0.693\,\tau = 29.8$ min.

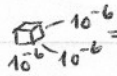
Or, 0.99 monolayers at $t' = 4.60\,\tau = 198.0$ min.

**[1.3]** (a) MIN. ENERGY = $\Delta(\gamma A) = \gamma(A_{\text{NANOPARTICLES}} - A_{1\text{ cm CUBE}})$

WITH: $\gamma = 1800$ erg/cm$^2$ FOR Pt

= 1.11 x 10^15 eV/cm^2


$\Longrightarrow A_{1\text{cm CUBE}} = 6\text{ cm}^2$




$\Rightarrow A_{\text{NANOPARTICLES}} = 6(10^{-12}\text{ cm}^2) \times \text{NO. PARTICLES} = 6 \times 10^{-12} \times 10^{18} = 6 \times 10^{6}\text{ cm}^2$

NO. PARTICLES $= (10^6)^3 = 10^{18}$

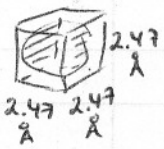
So

= 6.74 x 10^21 eV

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

(b) EACH Pt ATOM OCCUPIES CUBE OF AVERAGE SIDE $= \sqrt[3]{\dfrac{1}{6.62 \times 10^{22}\text{ cm}^3}}$

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

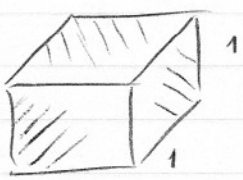



FOR 1 cm CUBE: TOTAL NO. ATOMS $= 6.62 \times 10^{22}$

SURFACE ATOMS $= 6\left(\dfrac{1\text{ cm}}{2.47 \times 10^{-8}\text{ cm}}\right)^2 = 6(0.1639)10^{16}$

$= 0.983 \times 10^{16}$

↑ NEGLECTING DOUBLE-COUNTING OF EDGE ATOMS AS NEGLIGIBLE




$\approx 4 \times 10^7$ ATOMS ON A SIDE

FRACTION AT SURFACE $= \dfrac{0.983 \times 10^{16}}{6.62 \times 10^{22}} = \underline{1.48 \times 10^{-7}}$

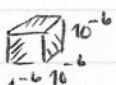
$\approx 1/10$ MILLION

FOR $10^{-6}$ 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 $\approx 6\left(\dfrac{10^{-6}\text{ cm}}{2.47 \times 10^{-8}\text{ cm}}\right)^2 = 0.983 \times 10^4$

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




$\approx 40$ ATOMS ON A SIDE

FRACTION AT SURFACE $= \dfrac{0.983 \times 10^4}{6.62 \times 10^4} \approx 0.148 \approx \underline{1/7}$ !

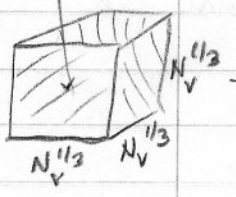
[1.4] FORMULA GIVEN IN ZANGWILL IS:

$$\gamma = Z_s\left(\frac{E_{COH}}{2}\right) N_s$$

LET'S TRY IT OUT. USE $\frac{Z_s}{Z} \approx 0.25$, $E_{COH}(erg) = E_{COH}(eV) \cdot 1.602 \times 10^{-12}$ (erg/eV)

↳ APPROX. 1/4 OF BONDS IN BULK BROKEN TO MAKE SURFACE

$N_V$ ATOMS IN CUBE

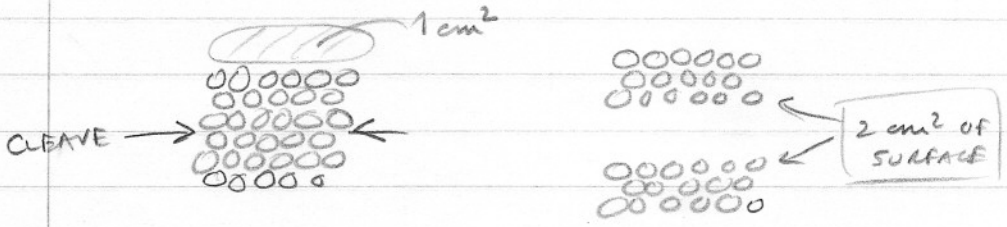



ALSO, $N_s \approx (N_V)^{2/3}$ ← NO. DENSITY OF ATOMS FROM TABLE.

PUTTING IN ALL THE NOS. LEADS TO VALUES ON THE NEXT PAGE.

NOT VERY GOOD AGREEMENT! CALCULATED VALUES ARE ALL ~ 2X TOO HIGH, ALTHOUGH SYSTEMATIC TRENDS ARE WELL PREDICTED. REASON IS ERROR IN ZANGWILL FORMULA, BECAUSE WHEN WE BREAK $Z_s\left(\frac{E_{COH}}{Z}\right) N_s$ BONDS IN 1 cm², WE GET 2 cm² OF SURFACE. SO, CORRECT FORMULA IS:

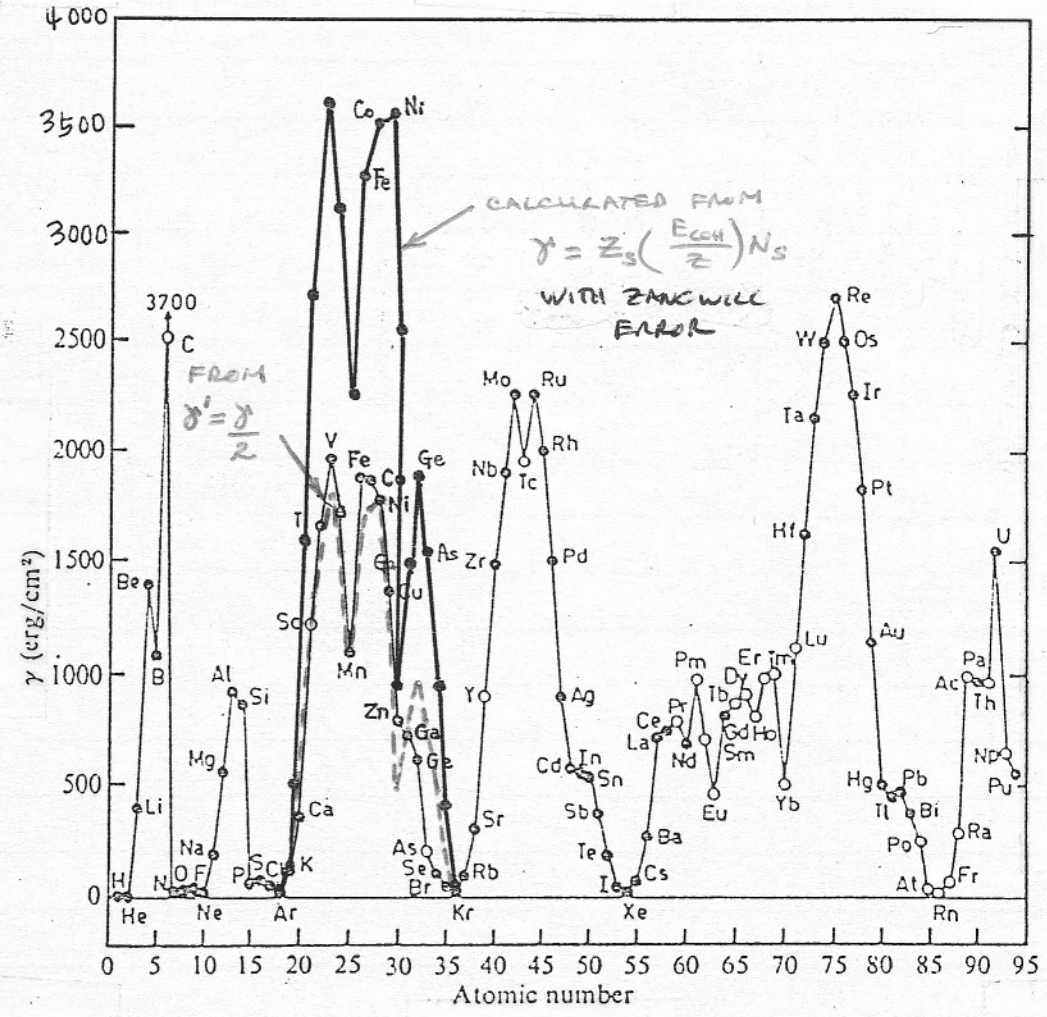
$$\gamma' = Z_s\left(\frac{E_{COH}}{Z}\right)\frac{N_s}{2}$$




SEE DASHED CURVE ON NEXT PAGE, WHICH AGREES VERY WELL WITH $\gamma$ DATA FOR LIQUIDS, BUT WITH SOME DEVIATIONS ∈ $\gamma_{CALC} >> \gamma_{EXPT}$ OVER Z = 31-35 FOR COVALENT/SEMICONDUCTOR CRYSTALS, SUGGESTING $\frac{Z_s}{Z} < 0.25$ FOR THESE, AND $\gamma_{CALC} < \gamma_{EXPT}$ FOR Zn, SUGGESTING $\frac{Z_s}{Z} > 0.25$.

Z=30

[1.4] (CONT'D.)

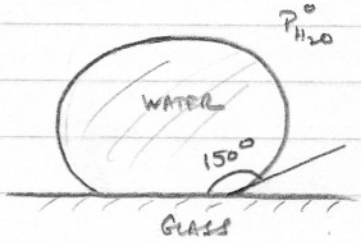

4000
3500
3000
2500
2000
1500
1000
500
0
γ (erg/cm²)
3700
C
CALCULATED FROM
$\gamma = Z_s\left(\frac{E_{coh}}{z}\right)N_s$
WITH ZINC WILL ERROR
FROM
$\gamma' = \frac{\gamma}{2}$
H
He
Li
Be
B
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Ce
Pr
Nd
Pm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
Ac
Th
Pa
U
Np
Pu
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
Atomic number

ALL $\gamma$'s POSITIVE.

[1.5] (a) $\cos\theta = \dfrac{(\gamma_{\text{GLASS-AIR}} - \gamma_{\text{GLASS-H}_2\text{O}(\ell)})}{\gamma_{\text{H}_2\text{O}(\ell)\text{-H}_2\text{O}(g)}} = \cos(150^\circ) = -0.866$

$\gamma_{\text{H}_2\text{O}(\ell)\text{-H}_2\text{O}(g)} = 72\ \text{erg/cm}^2$

WITH GEOMETRY AS —




NON-WETTING!

So, $\gamma_{\text{GLASS-H}_2\text{O}(\ell)} > \gamma_{\text{GLASS-AIR}}$, AND $\gamma_{\text{GLASS-H}_2\text{O}(\ell)} - \gamma_{\text{GLASS-AIR}} = 0.866\,(72\ \text{erg/cm}^2) = 62.4\ \text{erg/cm}^2$

(b) NOW ADD SURFACTANT SUCH THAT $\gamma_{\text{H}_2\text{O}(\ell)\text{-H}_2\text{O}(g)} = 36\ \text{erg/cm}^2$. THIS MAKES IT EASIER TO FORM THE EXPOSED DROP SURFACE, BUT STILL EQUALLY DIFFICULT TO FORM THE WATER-GLASS SURFACE, ∴ ONE EFFECT: A TENDENCY TO REDUCE THE WATER-GLASS SURFACE, GOING TOWARD AN EVEN HIGHER CONTACT ANGLE. THE NOS. SAY THIS ALSO, AS

$$\cos\theta = \frac{-62.4}{36.0}$$ WHICH HAS NO SOLUTION,

BUT IMPLIES THAT $\theta \to 180^\circ$ AS SURFACTANT IS ADDED, WITH A MORE ACCURATE MODEL BEING NEEDED IN GOING THROUGH THIS POINT.

NOTE: STATEMENT HERE LEADS TO COUNTER-INTUITIVE RESULT THAT SURFACTANT (SOAP) → LESS WETTING. IN FACT, MOST SURFACTANTS WOULD LOWER $\gamma_{\text{H}_2\text{O-GLASS}}$ VERY MUCH, GIVING MORE WETTING.

[1.6] I KNOW THAT $\dfrac{X^s_{Ag}}{X^s_{Cu}} \simeq \dfrac{X^b_{Ag}}{X^b_{Cu}} e^{-\Delta F_o/kT} \simeq \dfrac{X^b_{Ag}}{X^b_{Cu}} e^{-\text{CONSTANT}\,(\gamma_{Ag} - \gamma_{Cu})}$ (+)

WITH $\gamma_{Ag} \simeq 900\ \text{erg/cm}^2$ AND $\gamma_{Cu} \simeq 1320\ \text{erg/cm}^2$, IT IS EASIER TO FORM A Ag-RICH SURFACE, AND THE ABOVE ∴ INDICATES $X^s_{Ag} > X^b_{Ag}$;

$X^s_{Cu} < X^b_{Cu}$.

PROBLEM 1,7

NAME:

(b) -7-



(a)

$(\sqrt{2} \times \sqrt{2}) R45°$

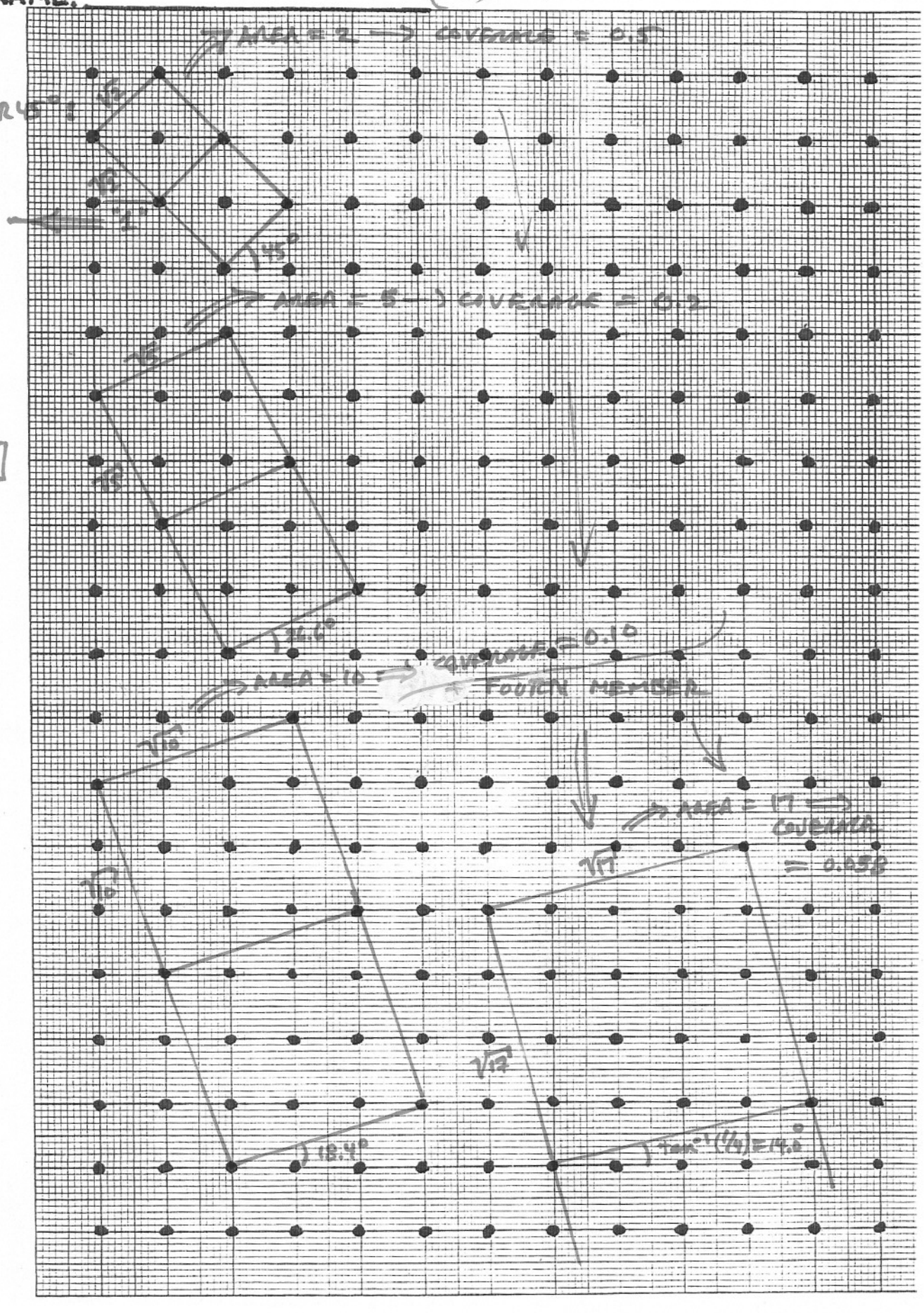
3.52 Å

FOR Ni

$\therefore$ "1" =

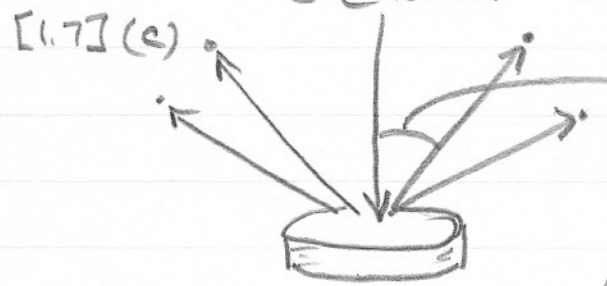
$\frac{\sqrt{2} \cdot 3.54}{2}$

$= \boxed{2.49 Å}$



de Broglie

$e^-$ @ 150 eV $\rightarrow \lambda_e = \frac{h}{p_e} = \sqrt{\frac{150.4}{E(eV)}}\,\text{Å} = 1.0\,\text{Å}$

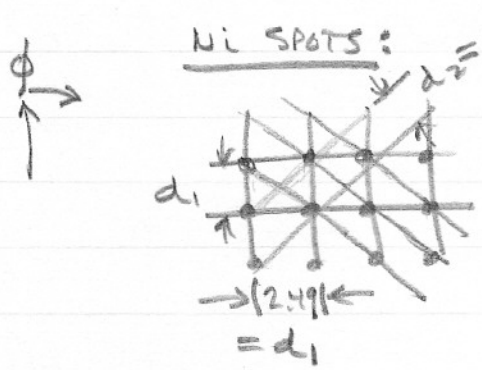



$n\lambda_e = d_i \sin\theta_{Bi,n}$

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

SEE PRIOR PAGE FOR Ni(001) DIMENSIONS, THEN

Ni SPOTS:

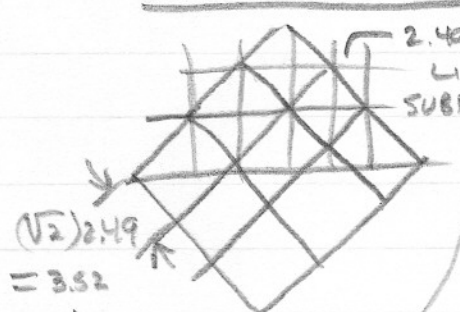



$\theta_{B1,n} = \sin^{-1}\left[\frac{1.0}{2.49}\right], \left[\frac{2.0}{2.49}\right], \ldots$ ($\sin^{-1}$)

$= 23.7°, 53.4°$ & $\phi = 0°, 90°$

ALSO ± IN POLAR ANGLE

OVERLAYER SPOTS: $d_4 =$ 2.49 – JUST LIKE SUBSTRATE




$\theta_{B2,n} = \sin^{-1}\left[\frac{1.0}{1.76}\right], \sin^{-1}\left[\frac{2.0}{1.76}\right],$

$= \boxed{34.6°}$, NOT ALLOWED & $\phi = 45°, 135°$

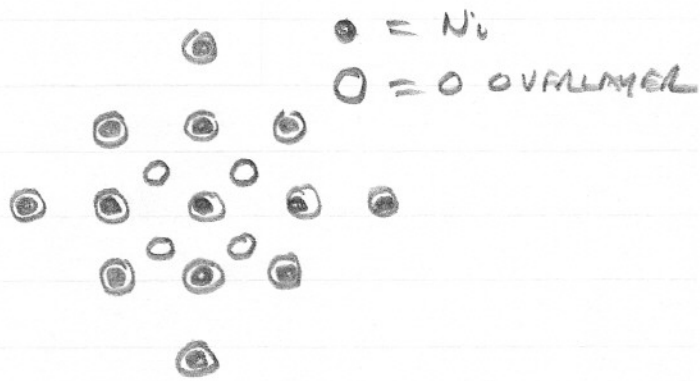
ALSO ± IN POLAR ANGLE

SAME

$\theta_{B3,n} = \sin^{-1}\left(\frac{1.0}{3.52}\right), \sin^{-1}\left(\frac{2.0}{3.52} = \frac{1}{1.76}\right),$

$= 16.5°, \boxed{34.6°}$

∴ FINAL LEED PATTERN:



[1.2] $I_{STM} \propto e^{-2KL}$, $K = \frac{\sqrt{2m\phi}}{\hbar} = 0.51\,\phi^{1/2}$ ($\text{Å}^{-1}$) ← INVERSE Å

($\phi$ in eV)

↑ WOLDMUFF + DELCHAR (6.30)

$= 0.51(4.0)^{1/2} = 1.02$ Å

TIP AT $L = 5.0$ Å $\rightarrow I_{STM} \propto e^{-2(1.02)(5.0)} = e^{-10.2}$

$= 0.0000372$

$L = 5.1$ Å $\rightarrow I_{STM} = e^{-10.4} = 0.0000304$

CHANGE OF 18%!

∴ A PRECISION OF ~ $\frac{18}{10}$ ~ 2% SHOULD PERMIT ACCURATELY MEASURING 0.1 Å