Chemical Engineering 378

Science of Materials Engineering

Lecture 21

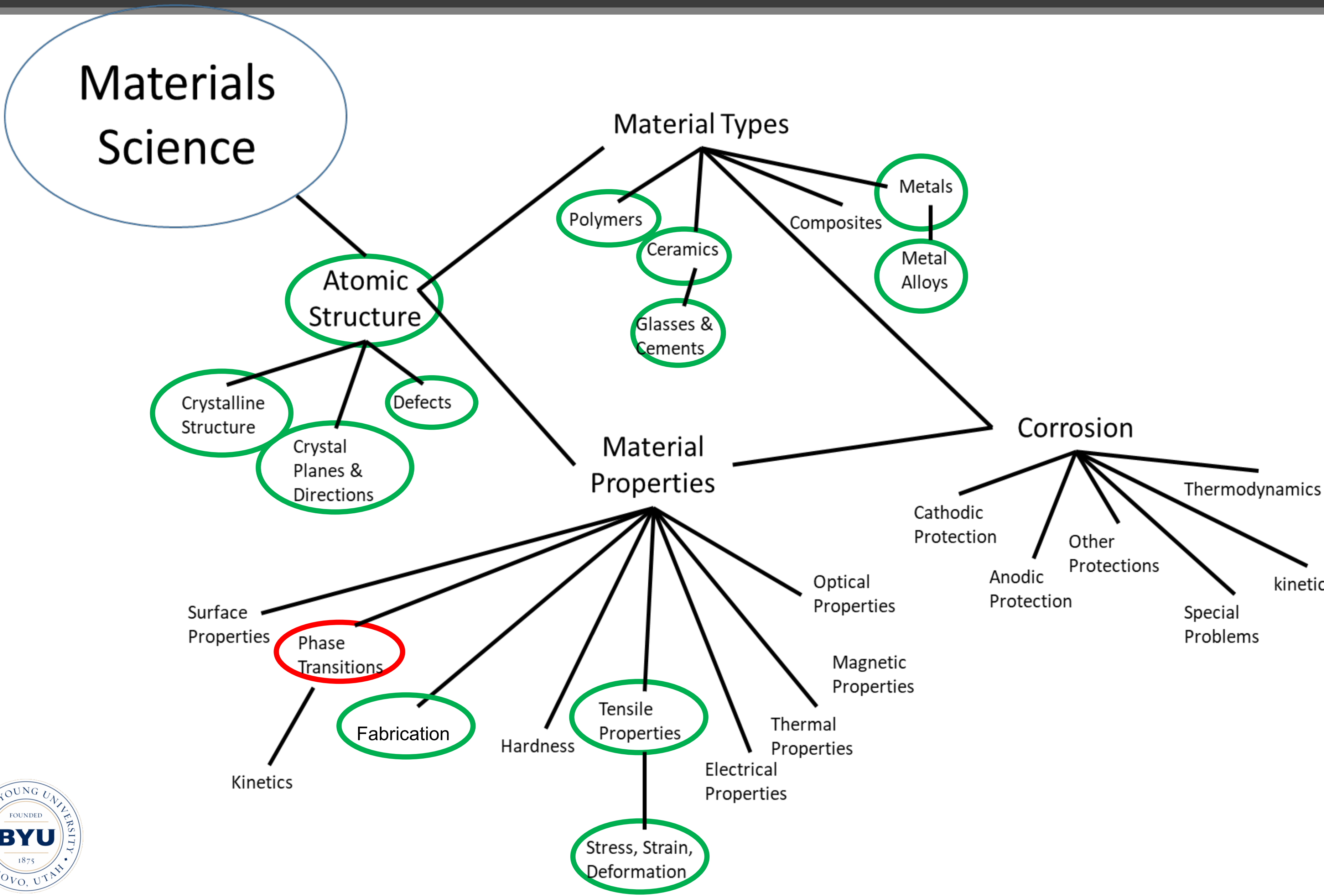
Surface Phenomena, Wetting

Spiritual Thought

"Many of you think you are failures. You feel you cannot do well, that with all of your effort it is not sufficient. We all worry about our performance. We wish we could do better. But unfortunately we do not realize, we do not often see the results that come of what we do. You never know how much good you do… Get on your knees and ask for the blessings of the Lord; then stand on your feet and do what you are asked to do. Then leave the matter in the hands of the Lord. You will discover that you have accomplished something beyond price."

President Gordon B. Hinkley

Materials Roadmap



OEP

- https://www.youtube.com/watch?v=JNd2wJSsdzM

OEP #7

Open Ended Problem #7

The Return of the King

Group work okay, Due 11/2/22 at beginning of class

(Don't be afraid to "Google" for reasonable assumptions; just provide references!)

Flame of the West

Andúril was pivotal in the defeat of Sauran, owing to the fact that Aragorn use it to both summon an undead army, as well as to defeat hordes of orcs, goblins, and even trolls. Even more notable, Andúril was a sword reforged from the shards of Narsil, the blade that originally cut the one ring from Sauron’s hand. The challenge, however, is the method of such a reforging. It required the best of elven smiths to complete this work. You, as material scientists, have the knowledge to direct the elven team in creating Andúril. For this problem, there are 3 things you must provide: 1) a description of the physics that play into reforging a broken blade on an atomic, crystalline, microstructure, and macrostructure level, 2) a specific description of HOW this process can be conducted (i.e. the steps required to do this), and 3) the final composition, microsctructures, and mechanical properties of the newly forged Andúril. Keep in mind that it must be both ductile and strong to fully work as a sword.

Surface Facts

- Atoms are in a higher energy state on the surface
- Electron orbitals are not filled
- Reactions occur more readily
- For solids: surface energy
- For liquids: surface free energy = surface tension

γ = surface energy = $\Delta G_s/\Delta A$ (units of $ergs/cm^2$ or J/m^2)

Interfacial Phenomena

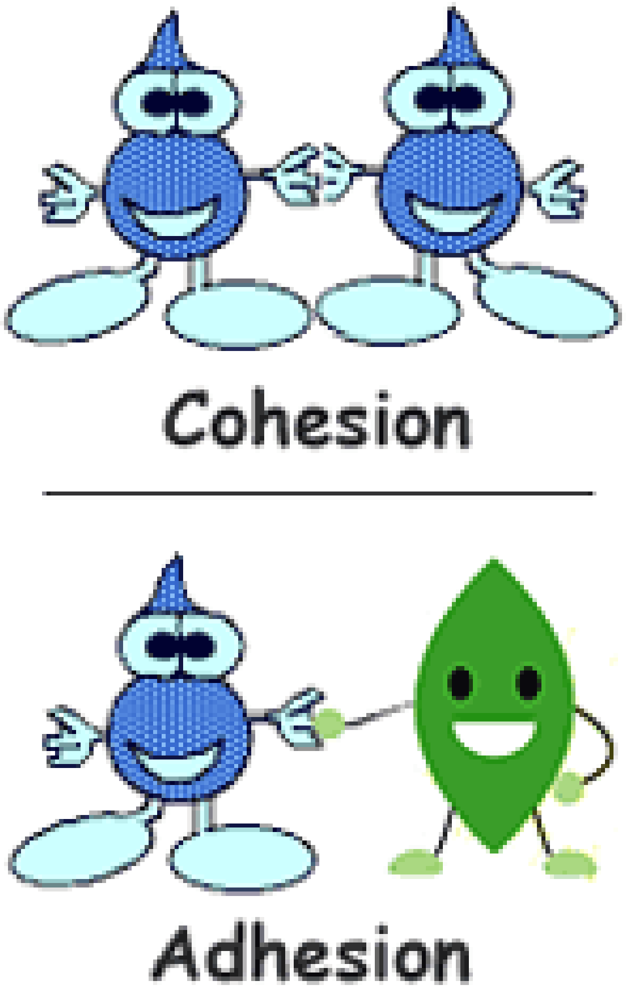
- Bubbles/Droplets
- Capillary Rise
- Cohesion/Adhesion
- Wetting/Spreading
- Colloids

Bubbles/Droplets

- Minimize surface area per volume
- Pressure drop??
  - Laplace Equation
  - $\Delta P = \frac{2\gamma}{r}$
  - Soap Bubbles
  - $\Delta P = \frac{4\gamma}{r}$
  - (2 surfaces to cross)

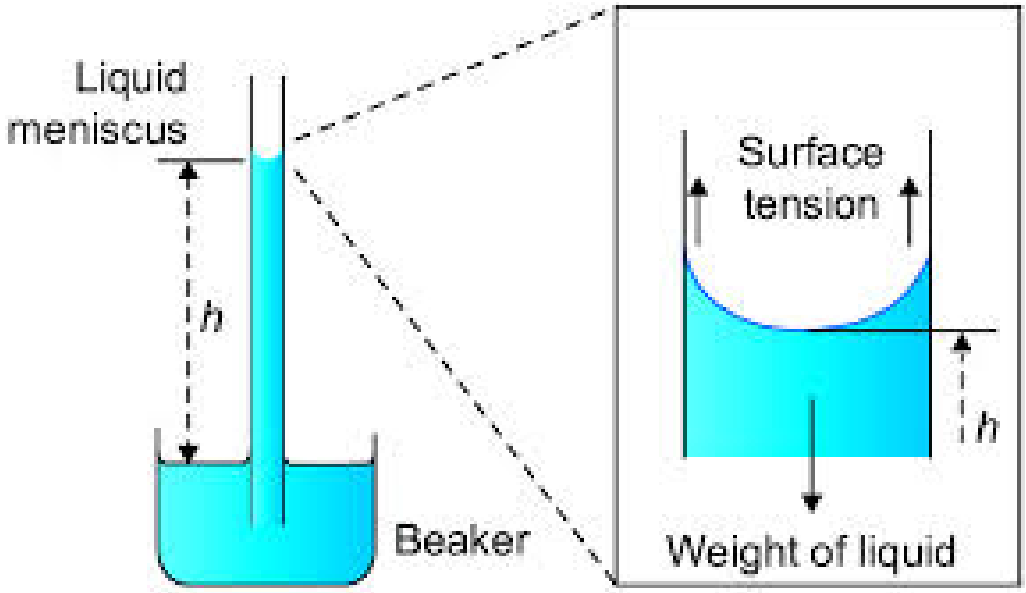
Adhesion Cohesion

- Cohesion – how well a material is bonded to itself
- Quantified by work to separate
  - Create 2 new surfaces
  - $W_c = 2\gamma_{ij}$
- Adhesion – how well two materials adhere
  - Work to separate two phases
  - $W_a = \gamma_A + \gamma_B - \gamma_{AB}$



Capillary Rise

- Rise of liquid in "capillary" or small tube
  - Caused by surface tension
    - Adhesion AND cohesion
  - Balance of pressure difference (droplet) and head due to gravity
  - $\Delta P = \frac{2\gamma}{r}$
  - $\Delta P = \rho g h$
  - $\therefore \rho g h = \frac{2\gamma}{r}$
  - If wetting is Incomplete:
  - $\rho g h = \frac{2\gamma \cos\theta}{r}$



Example

- What will be the rise in height of a column of water in a capillary of 0.1 mm diameter at 20 °C and 1 atm pressure? Assume that water completely wets the glass and its surface tension is 72.8 dyne/cm.

$$\rho g h = \frac{2\gamma \cos\theta}{r}$$

Example Solution

$h = 2\,\gamma\,\cos\theta/\rho\,g\,r$

$g = 980\ cm/s^2$

$r = 5 \times 10^{-3}\ cm$

$\rho = 1\ g/cm^3$

$\gamma = 72.8\ dyn/cm$

$\theta = 0^\circ,\ \cos\theta = 1$

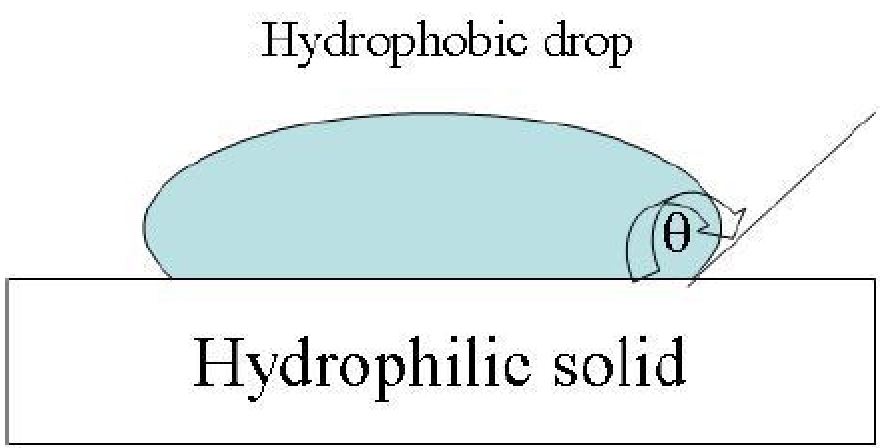
$h = 2(72.8\ dyn/cm)\ (cm\ g/s^2\ dyn)\ \cos(0^\circ)/(1\ g/cm^3)(980\ cm/s^2)\ (5 \times 10^{-3}\ cm)$

$h = 29.7\ cm$

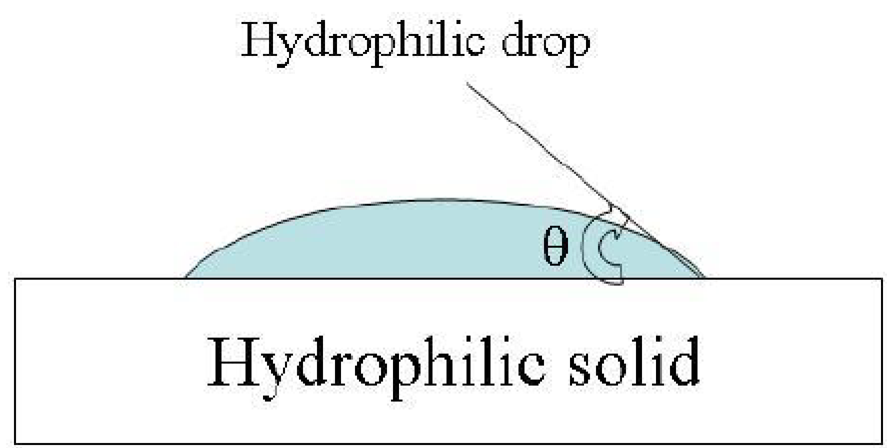
Why?

Contact Angle

- **Contact Angle is measured through the liquid phase**



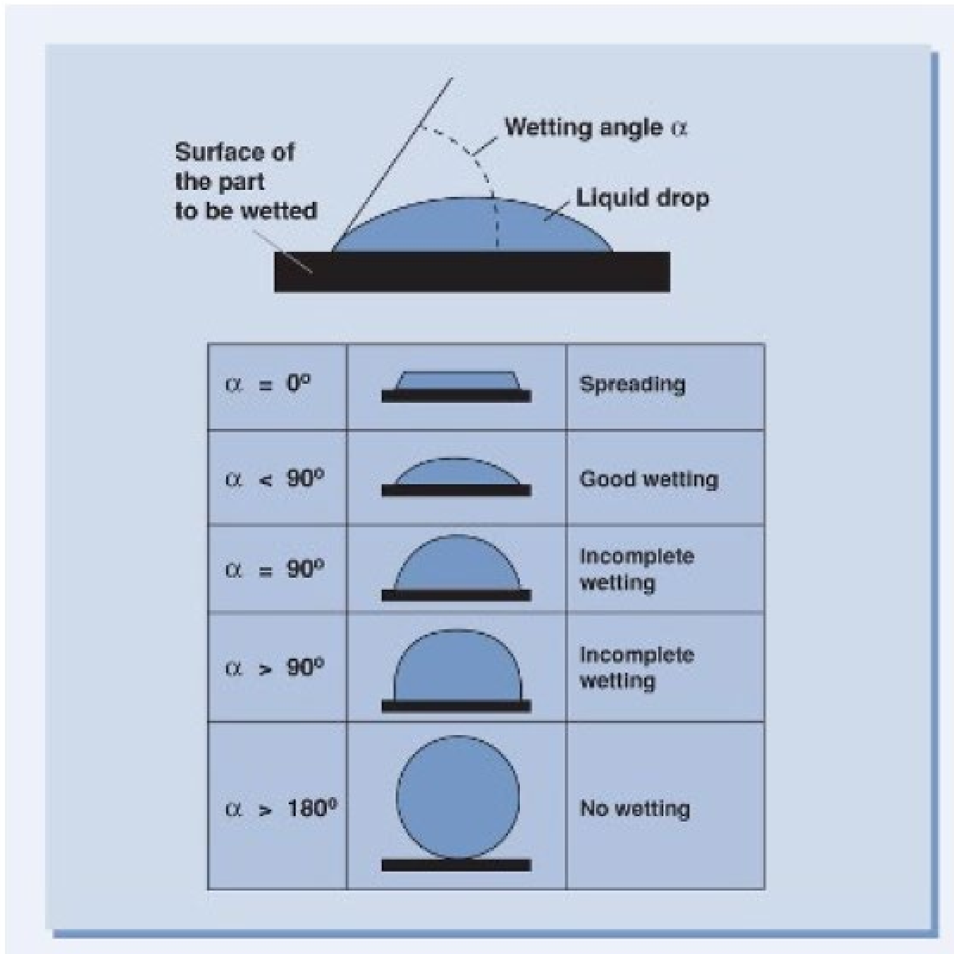
Oil or Mercury has a high contact angle, approaching 180°



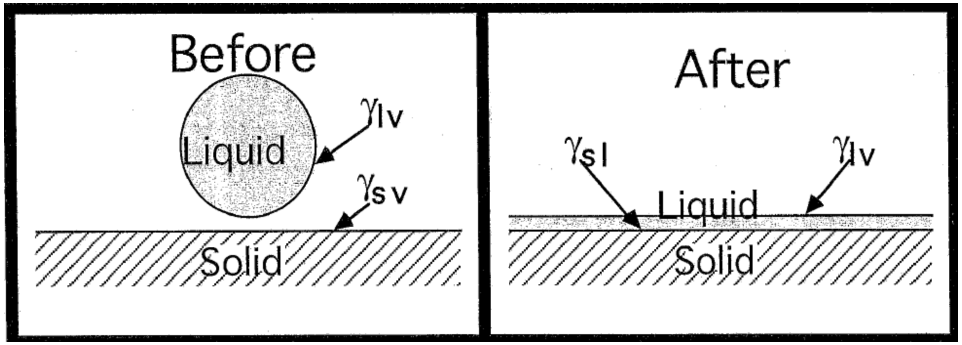
Water will have a low contact angle, approaching 0°

Spreading, Wetting

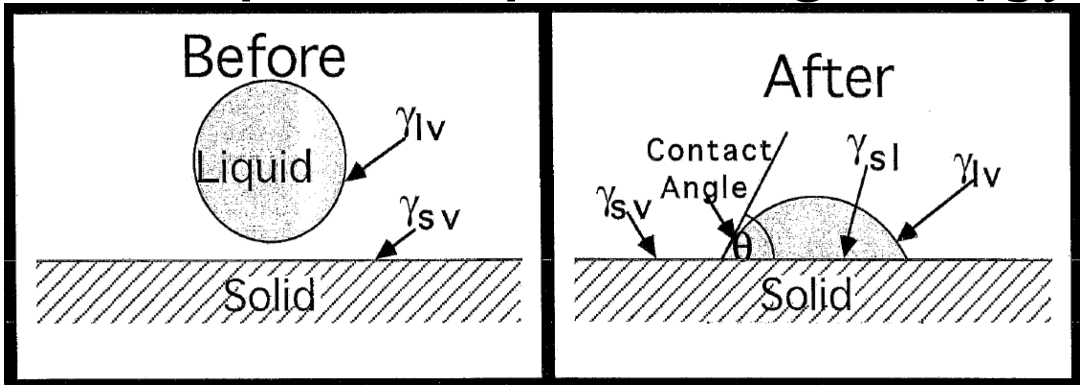
Spreading, Wetting



Spreading (S)



- Spreading occurs if: $\gamma_{sv} = \gamma_{lv} + \gamma_{sl}$
- Complete Spreading if: $\gamma_{sv} > \gamma_{lv} + \gamma_{sl}$



- Partial Spreading if: $\gamma_{lv} \cos\theta = \gamma_{sv} - \gamma_{sl}$

Surface Tension Summary

$$S = \gamma_s - (\gamma_l + \gamma_{sl})$$

when $S \geq 0$ liquids spread completely
when $S = 0$ liquids spread completely, $\theta = 0$
when $S < 0$ droplets spread only in part with contact angle θ

for $S > 0$ $\gamma_s > \gamma_l + \gamma_{sl}$
for $S < 0$ $\gamma_{sl} = \gamma_s - \gamma_l (\cos \theta)$

$W_c = 2\gamma_{ij}$

$W_a = \gamma_s + \gamma_l - \gamma_{sl}$

Surface Energy for a metal?

- Estimate the surface energy of the (111) plane of gold.
- Heat of vaporization is 334.4 kJ/mol
- Atomic radius is 0.144 nm
- Gold has FCC structure
- Atomic mass is 197 g/mol

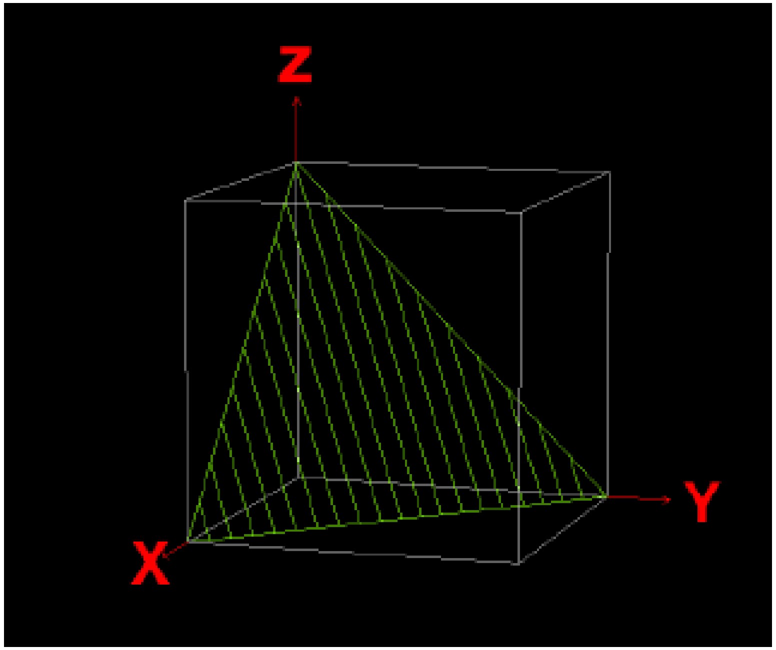
Procedure

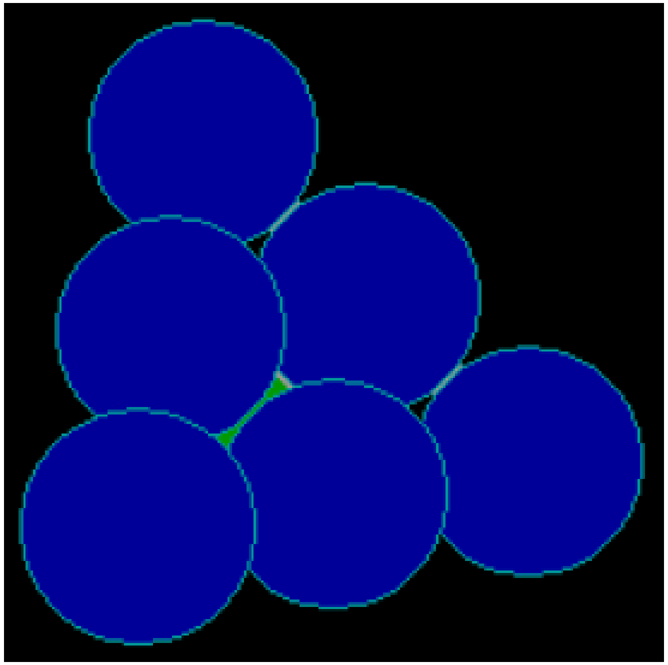
Steps:
1. Identify the energy per bond in gold (by calculation or by looking it up).
2. Calculate the bonds broken per atom by a cut parallel to (111).
3. Calculate the atoms/m^2 in the (111) plane.
4. Multiply these to get the energy of bonds broken in this plane.
5. Calculate how much new area is made.
6. Calculate energy per new area.

Basis: 1 m^2 of cut on the (111) plane.

Steps:
1. Calculate energy per bond
2. Planar density = atoms in plane/area of plane
3. Energy of bonds broken in plane
4. Number of surfaces created = 2
5. Energy per new surface area

AU → FCC, CN = 12





(111)

$$A = bh/2 = 4\sqrt{3}\, r^2$$

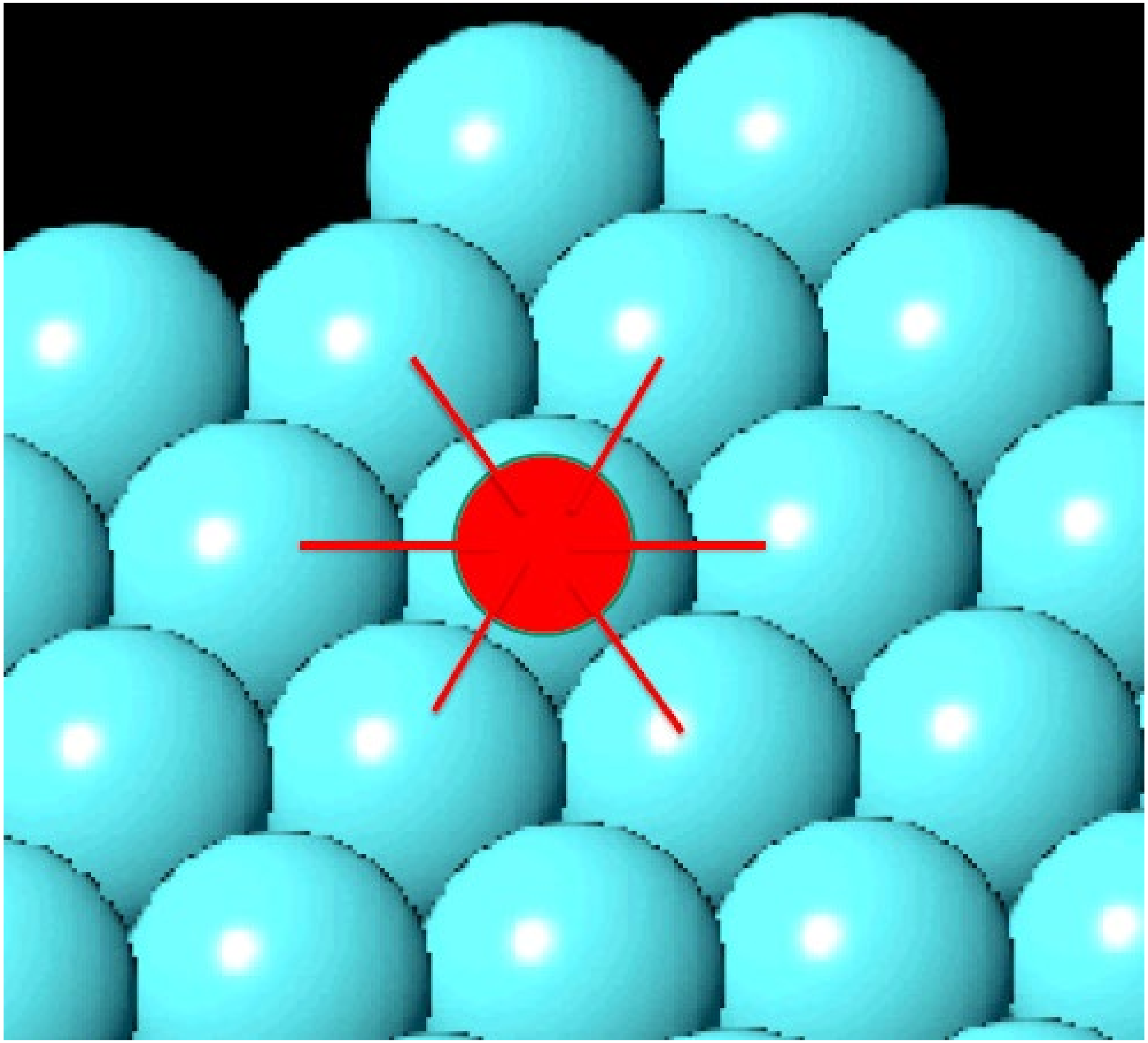
Bond Energy Calculation

- First calculate energy per bond:
  - H_v = 334.4 kJ/mol
  - Atomic mass = 197 g/mol
  - Atomic radius: r = 0.144 nm
  - For FCC: CN = 12
  - 6 bonds broken per atom = CN/2
- Energy/bond = H_v/ (CN/2) / N_A

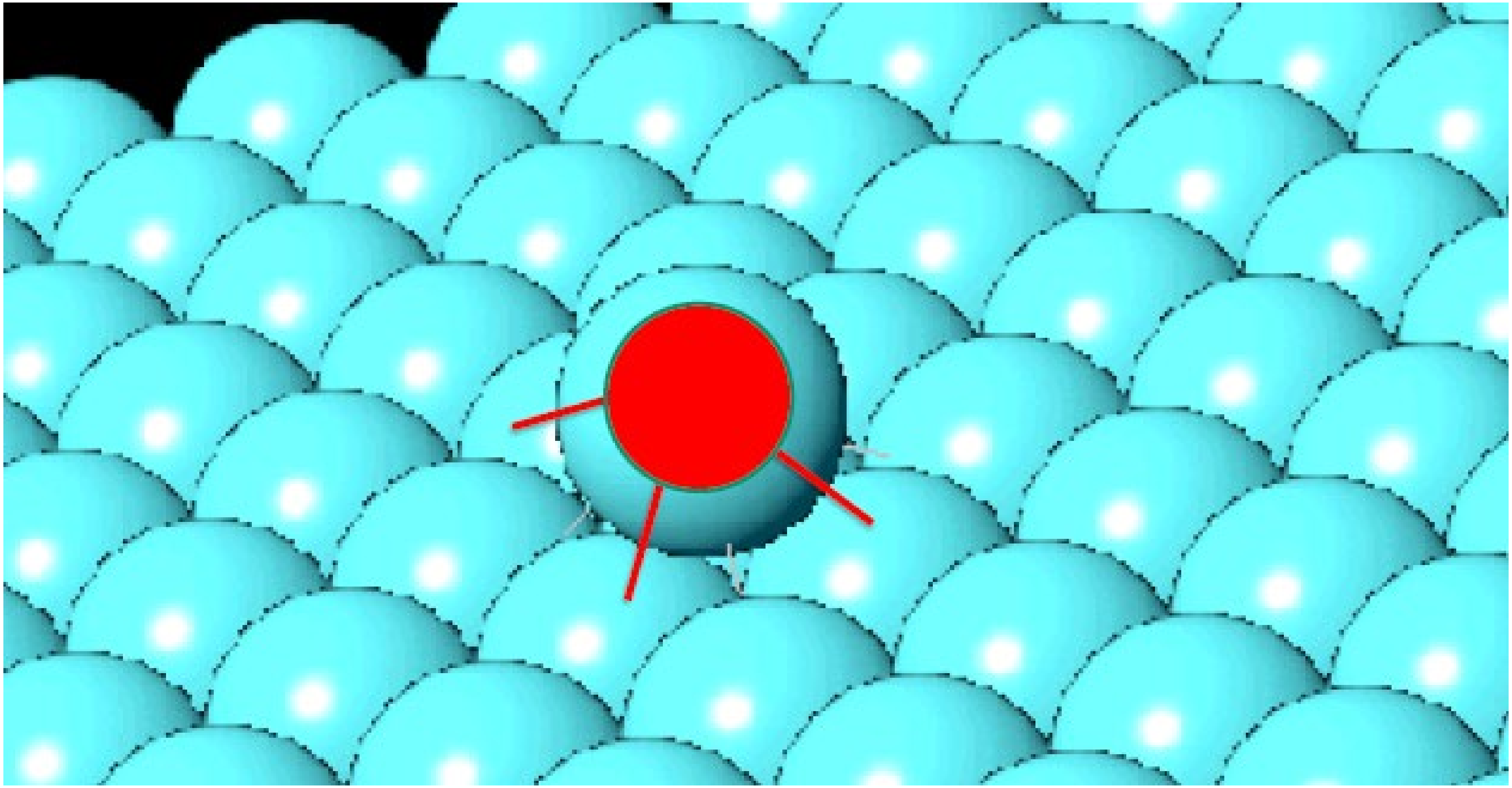
= (334,400 J/mol) /(12/2)/(6.022 x 10^{23} bonds/mol)

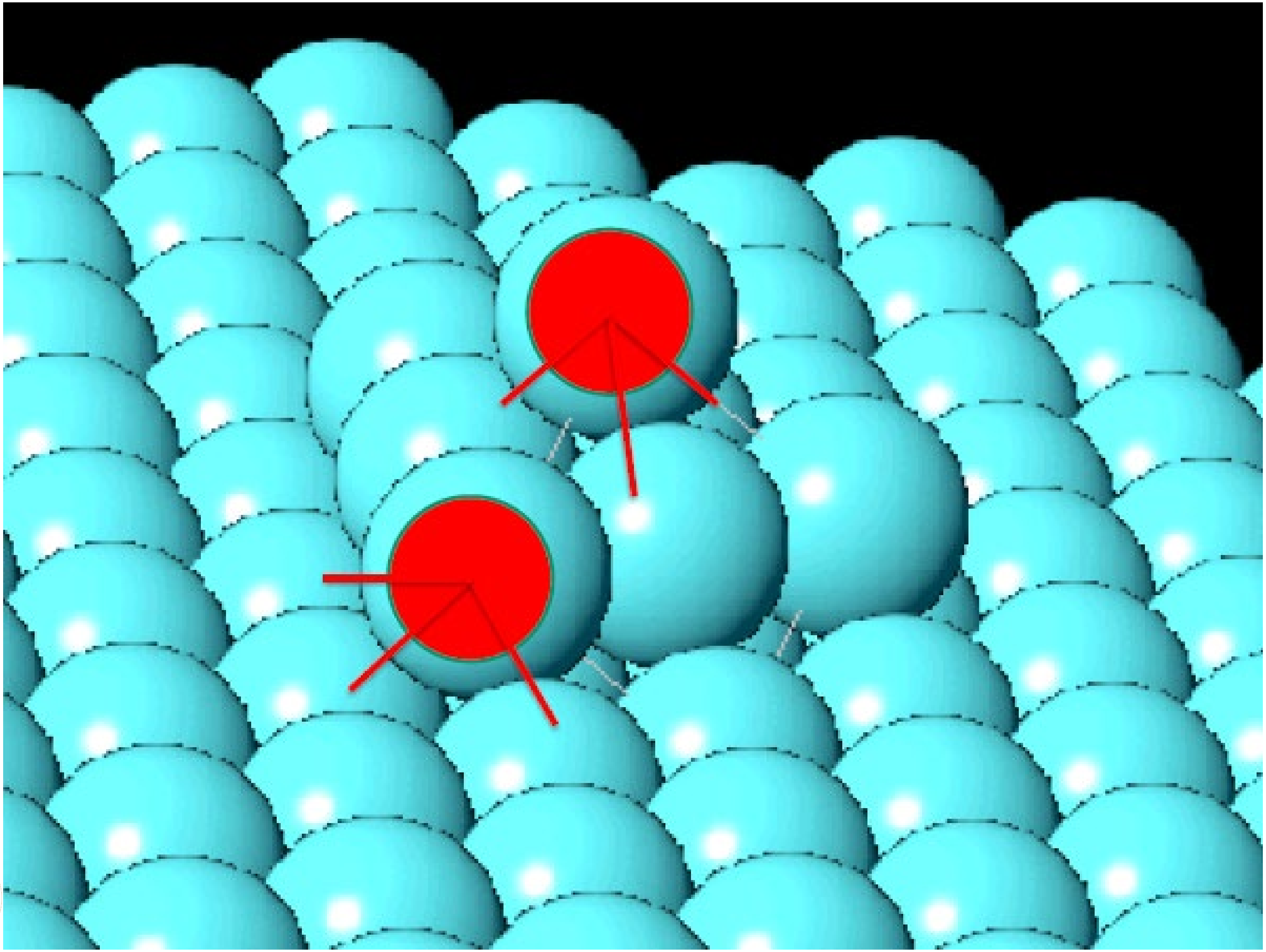
= 9.25 x 10^{-20} J/bond

Bonds per plane



3 Bonds per atom in Plane above and below





Au (111) Planar Density (PD)

- **Atoms in plane**

  3 corners, each shared with 6 unit cells = 3/6 = 1/2

  3 faces, each shared with 2 unit cells = 3/2

  Sum = 2 atoms

- **Area of plane (triangular shape); A = bh/2**

  $h = 2\sqrt{3}\,r$

  $b = 4r$

  $A = bh/2 = 4\sqrt{3}\,r^2$

- **PD = 2 atoms / $4\sqrt{3}\,r^2$**

$$PD = \frac{2\text{atoms}}{4\sqrt{3}(0.144 \text{ x } 10^{-9}\text{ m})^2} = 1.392 \text{ x } 10^{19} \text{ atoms/m}^2$$

Energy of bonds broken in this plane:

(1.392×10^{19} atoms/m^2) x (3 bonds/atom) x 9.258×10^{-20} J/bond = 3.87 J/m^2

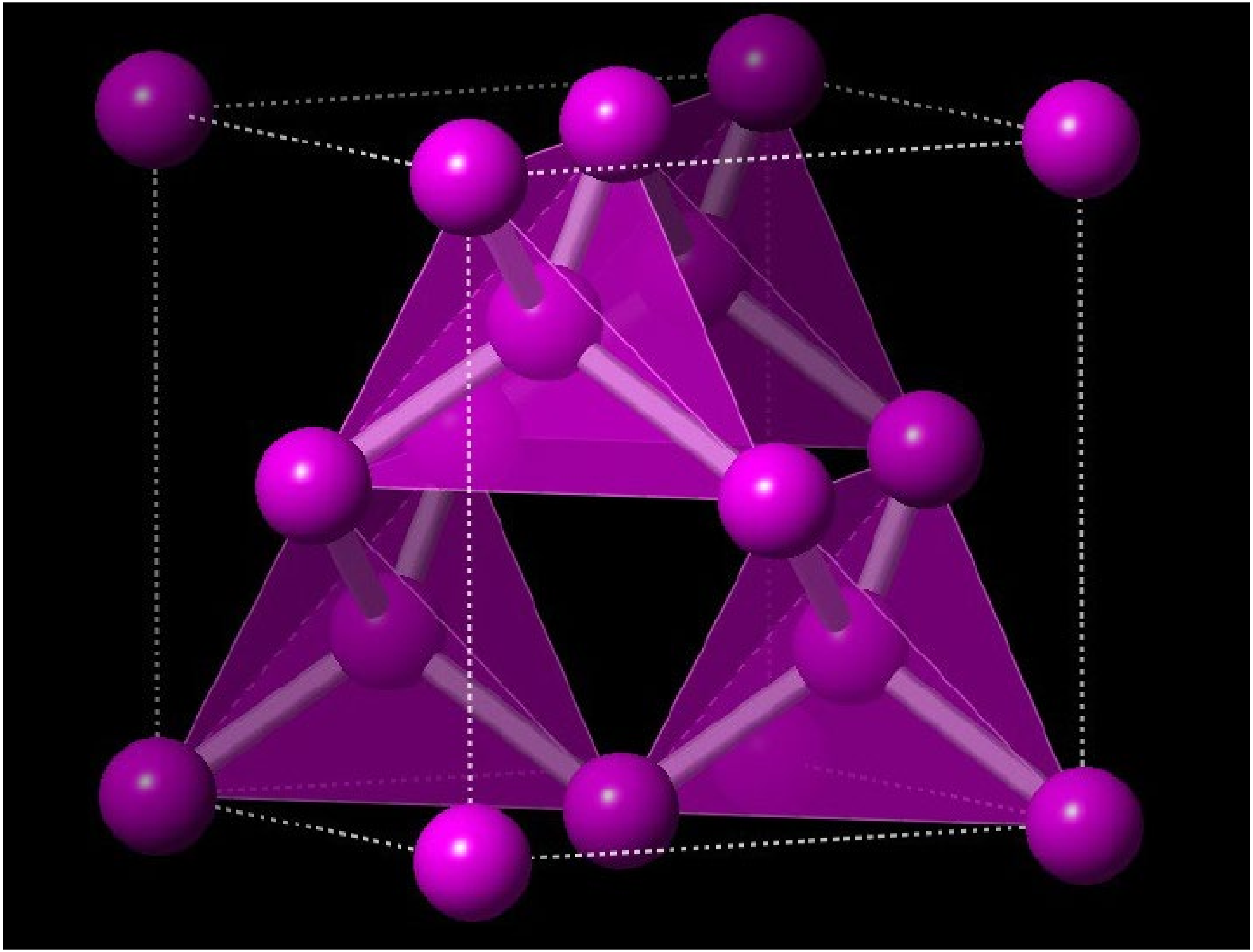
2 New surfaces created

Energy per new surface area: γ = (3.87 J/m^2) / 2 = 1.93 J/m^2

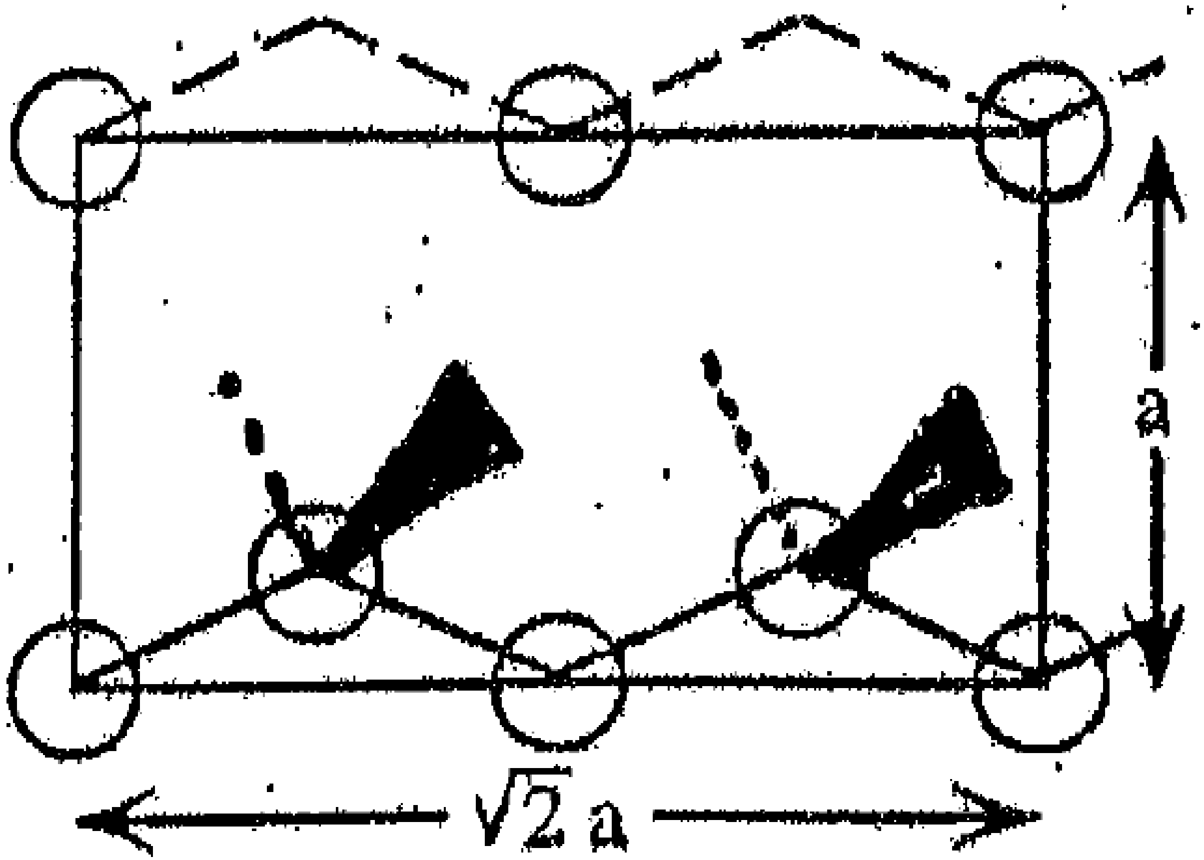
Surface Energy (Covalent Bonds)

- **Estimate the surface energy in J/m^2 for a covalently bonded crystal silicon (diamond structure) for a plane parallel to (110). The bond energy of Si-Si is 224 kJ/mol of bonds and the lattice constant *a* = 0.543 nm.**

Bond Structure (crystal)



110 Diamond



$$A = \sqrt{2}\, a^2$$

Si Surface Energy Calculations

- Each atom has 4 bonds, a slice along this plane will cut 1 bond per atom, and form 2 surfaces
- PD = 4 atoms/ $\sqrt{2}\ a^2$ = 4/ $\sqrt{2}\ (5.43 \times 10^{-10}\ m)^2$
- Energy/area = U (PD/2) / N_A

= (224,000 J/mol) (PD/2 surfaces) / (6.022 x 10^{23} bonds/mol)

= 1.78 J/m^2