**Crystal Structure**

Crystal structure = atoms arranged on a lattice defined by 3 fundamental translation vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$.

$$\mathbf{r}' = \mathbf{r} + n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$$

Atomic arrangement looks the same from $\mathbf{r}$ and $\mathbf{r}'$.

The set of points, $\mathbf{r}'$, for all values of integers $n_1$, $n_2$, & $n_3$ defines a lattice.

**Crystal structure = lattice + basis**

*Lattice and Translation vectors ($\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$) are primitive* IF any two points $\mathbf{r}$ & $\mathbf{r}'$, from which the atomic arrangement looks the same, always satisfy the above equation with a suitable choice of $n_1$, $n_2$, & $n_3$.

*Guarantees that there is NO cell of smaller volume which could serve as the building block for the structure.*

**Primitive translation vectors** are often used to define the **crystal axes** \(a, b, \& c\). Non-primitive axes may be used when they are more convenient.

**Crystal axes** \(a, b, \& c\) form 3 adjacent edges of a parallelepiped. If there are atoms or molecules ONLY at the corners of the parallelepiped, then it is a primitive parallelepiped (**primitive cell**).

**Crystal structure = lattice + basis**

**Basis** = every lattice point has a basis that is identical in composition, arrangement and orientation.


---

**Crystal Structure:**

1. What is the lattice?
2. What are the crystal axes \(a, b, \& c\) are use to describe the lattice?
3. What is the basis?
4. What symmetry operations carry the crystal structure into itself?

4. Lattice **translation** operation or crystal translation operation = displacement of a crystal parallel to itself. (The vector \(T\) connects any two lattice points.) There are also rotation and reflection operations.

\[
T = n_1 a + n_2 b + n_3 c = n_1 a_1 + n_2 a_2 + n_3 a_3
\]

The primitive cell (unit cell) will fill all the space under the action of suitable crystal translation operations; it is a minimum volume cell.

A basis of N atoms (or ions) is specified by the set of N vectors
\[ r_j = x_j a + y_j b + z_j c \quad 0 \leq x_j, y_j, z_j \leq 1 \]


**Two-dimensional Bravais Lattices (5)**

*Eric I. Altman, Yale University*

Point-group symmetry

- Square: \( |a| = |b| \), \( \gamma = 90° \) \( 4mm \)
- Rectangular: \( |a| \neq |b| \), \( \gamma = 90° \) \( 2mm \)
- Centered Rectangular: \( |a| \neq |b| \), \( \gamma = 90° \) \( 2mm \)
- Hexagonal: \( |a| = |b| \), \( \gamma = 120° \) \( 6mm \)

Crystal structure may have lower symmetry than lattice!
Three-dimensional Bravais Lattices (14)  
(shown as conventional cells)

Cubic  P or sc  \( a=b=c \)
I or bcc  \( \alpha = \beta = \gamma = 90^\circ \)
F or fcc


**bcc: primitive cell**

![Image of bcc primitive cell]

**Primitive Vectors**

\[
a' = \frac{a}{2}(x + y - z)
\]

\[
b' = \frac{a}{2}(-x + y + z)
\]

\[
c' = \frac{a}{2}(x - y + z)
\]

**fcc: primitive cell**

![Image of fcc primitive cell]

**Primitive Vectors**

\[
a' = \frac{a}{2}(x + y)
\]

\[
b' = \frac{a}{2}(y + z)
\]

\[
c' = \frac{a}{2}(z + x)
\]

fcc = simple cubic + (1/2,1/2,0) + (1/2,0,1/2) + (0,1/2,1/2)
Diamond:
an fcc cubic (space lattice) lattice with a two-point basis


Primal Basis:

\[
\begin{pmatrix}
0,0,0 \\
1/4,1/4,1/4
\end{pmatrix}
\]

Cutting a bulk crystal → Miller Indices

Two types of Miller Indices

Planes = (i j k)

Crystallographic direction = [i j k]

Plane: \( (i j k) = \left( \frac{cd}{b_x}, \frac{cd}{b_y}, \frac{cd}{b_z} \right) \)

\(b_x, b_y, b_z = \text{intersection of the plane}\)
\(The x, y \text{ and } z \text{ axes of the unit cell.}\)
\(cd = \text{constant (take } cd = \text{lowest common denominator (lcd) of } 1/|b_x|, 1/|b_y|,\)
\(\text{and } 1/|b_z|, \text{ greater to or equal to one.}\)

Intersects at 2 3 4 so \(1/2, 1/3, 1/4\) \(\text{lcd} = 12\) thus, (6 4 3)


Planes in a cubic lattice

\{i j k\} = equivalent group of planes

[ i j k] = vector defined as the distance that the vector traverses in units of the lattice vector. (direction)

< i j k > = equivalent set of directions.

Bars indicate negative values and an intercept of infinity has an index of 0.

Family of Equivalent planes \{i j k\} (cubic systems)

Cubic systems: (100) plane is perpendicular to [100] direction.

Cubic system

\[\begin{bmatrix} 0 & 0 & 0 \\ 2 & 0 & 0 \\ 2 & 3 & 0 \end{bmatrix} \times \begin{bmatrix} 2 & 0 & 4 \end{bmatrix} = \begin{bmatrix} 12 & 8 & 6 \end{bmatrix} = 2 \begin{bmatrix} 643 \end{bmatrix}\]
Ideal Single-Crystal Surfaces

**Low index** (close packed or nearly close packed) = cut along a close packed direction (i.e., where atoms are touching)

**Stepped surfaces** = Cutting along other directions

![Diagram of fcc lattice and (111), (100), (110) planes](image)

Low index planes

---

Surface unit cell vectors $\mathbf{a}_s, \mathbf{b}_s$ may be different from the bulk projection $\mathbf{a}, \mathbf{b}$.

$$
\mathbf{a}_s = m_{i1} \mathbf{a} + m_{i2} \mathbf{b} \\
\mathbf{b}_s = m_{s1} \mathbf{a} + m_{s2} \mathbf{b}
$$

$$
M = \begin{pmatrix}
m_{i1} & m_{i2} \\
m_{s1} & m_{s2}
\end{pmatrix}
$$

---

$x =$ on top, $y =$ bridge, $z =$ 4-fold hollow

---


Structure of Overlayers (Adsorbates)

Surface Unit Cell Vectors

$$a_s = m_{11}a + m_{12}b$$
$$b_s = m_{21}a + m_{22}b$$

$$M = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$$M = \begin{pmatrix} 2 & 1 \\ -1 & 1 \end{pmatrix}$$

$$p(2\times2)$$
How do we investigate the structure of surfaces on the atomic scale?

**Some Experimental Techniques of Surface Science:**

<table>
<thead>
<tr>
<th>Technique</th>
<th>Acronym</th>
<th>Species</th>
<th>Property probed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger Electron spectroscopy</td>
<td>AES</td>
<td>Electron spectroscopy</td>
<td>Surface composition</td>
</tr>
<tr>
<td>Low Energy Electron Diffraction</td>
<td>LEED</td>
<td>Electron diffraction</td>
<td>Surface structure: adsorbate arrangement</td>
</tr>
<tr>
<td>High Resolution Electron Energy Loss Spectroscopy</td>
<td>HREELS</td>
<td>Electron spectroscopy</td>
<td>Vibrational levels of the adsorbate and the surface</td>
</tr>
<tr>
<td>X-Ray Photoelectron Spectroscopy</td>
<td>XPS (ESCA)</td>
<td>Photon-Surface scattering</td>
<td>Core electronic levels (surface + adsorbate)</td>
</tr>
<tr>
<td>Scanning Tunneling microscopy</td>
<td>STM</td>
<td>Tunneling spectroscopy</td>
<td>Surface topography and electronic structure</td>
</tr>
<tr>
<td>Atomic Force Microscopy</td>
<td>AFM</td>
<td></td>
<td>Surface topography</td>
</tr>
<tr>
<td>Temperature Programmed Desorption</td>
<td>TPD</td>
<td>chemisorption</td>
<td>Binding energy of adsorbates</td>
</tr>
<tr>
<td>Secondary Ion Mass Spectroscopy</td>
<td>SIMS</td>
<td>Secondary Ion emission</td>
<td>Composition of surface &amp; adsorbate</td>
</tr>
<tr>
<td>Low Energy Ion Scattering</td>
<td>AD</td>
<td>Ion scattering (same)</td>
<td>Surface composition + structure</td>
</tr>
<tr>
<td>Reflection High-Energy Electron Diffraction</td>
<td>RHEED</td>
<td>Electrons</td>
<td>Surface and thin film structure</td>
</tr>
</tbody>
</table>
Scanning Tunneling Microscopy  
How does it work?

Consider an atom

The nucleus contains the neutrons and protons.
The electrons orbit the nucleus.

Because of Heisenberg’s Uncertainty Principle we cannot precisely know the positions of the electrons.

Instead we describe the positions of the electrons in terms of the probability that an electron is at a given location at any point in time.

The probability decays as we move further and further away from the nucleus.

Scanning Tunneling Microscopy  
How does it work?

Consider moving an electron from one atom to another

If the atoms are far apart, then we have to remove the electron from the first atom which costs us energy $IP$, the ionization potential, and then transfer it to the second atom which releases energy $EA$, the electron affinity.

We can write this as a series of chemical reactions:

\[
A \rightarrow A^+ + e^- \quad \Delta H = IP
\]
\[
B + e^- \rightarrow B^- \quad \Delta H = EA
\]

*No electrons will be transferred unless we supply energy $IP$*
Scanning Tunneling Microscopy

How does it work?

Consider moving an electron from one atom to another

If the atoms are close together, then there becomes some probability that electrons originally associated with A get close enough to B that they become associated with B. Moving from A to B in this way is called tunneling.

We do not need to supply IP to transfer an electron from A to B

If \( IP_A + EA_B < IP_B + EA_A \) then electrons tend to move more often from A to B rather than vice versa.

Consider Two Conductive Solids

When the two solids are close enough together, electrons can tunnel from one solid to the other.

The energy difference between the electrons in the two solids is determined by the voltage \( V_B \).

The electrons that flow from A to B form a current that can be measured with an ammeter.

Q: How close is close enough?
A: 1 nm

Q: How sensitively does the current depend on the distance?
A: Very strongly-

Decreasing the distance by 0.1 nm makes the current 10 times higher.
**Methods - Structural Characterization**

STM

**Tunneling**

\[ I_T = A e^{-\sqrt{\phi z}} \]

Order of magnitude change for 0.1 nm change in \( z \)

---

What happens if we sharpen one of the solids down to a point with one atom at the end?

---

The peaks correspond to the positions of the atoms!
What happens if we sharpen one of the solids down to a point with one atom at the end?

If we instead move the tip up and down to keep $I$ constant:

The images are three dimensional topographical maps of the surface.

How do we sharpen a tip so that there is just one atom at the end?

Electrochemical etching

Typical materials: tungsten, platinum-iridium alloy

Electron micrographs

KFA Julich, Germany

Technical University of Denmark
A Scanning Tunneling Microscope

Atoms on the surface of a silver crystal: Ag(111)

Surface Reconstruction

Si (100) (2x1)

Atoms on the surface of a semiconductor wafer

Courtesy of E.I. Altman, Yale University
Diffusion
Silicon diffusion on silicon  385 K

Diffusion across the rows of atoms is much slower than diffusion along the rows.

Diffusion is blocked by the other atoms on the surface

Diffusion is blocked by the steps

STM Results: Au(111) on 3 scales

Courtesy of E.I. Altman, Yale University
More Pictures of Atoms

Atoms on the surface of a gold-nickel alloy

The “whiter” atoms are gold.

University of Aarhus, Denmark

O₂ molecules on a platinum (111) surface

Sub-phthalocyananine molecules on a silver(111) surface

Wilson Ho, University of California, Irvine

University of Basel, Switzerland

An STM Image is a 3D Topographical Map of the Surface

Gold-Nickel Alloy

C₆₀ film on Ag(111)

The colors represent z

Blue is low

Black is low

Yellow is intermediate

White is high

Purple is high

An STM Image is a 3D Topographical Map of the Surface

Determining reaction mechanisms on solid surfaces by observing the individual steps

Why are we interested in solid surfaces?
All reactions involving a solid take place at its surface.
Some important examples:

- Heterogeneous catalysis - catalytic converters on cars
  \[2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2\] requires Pd or Pt/Rh surface

- Oxidation and corrosion
  \[4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3\]

- Film growth - microelectronic, data storage, etc. require ultra-thin coatings with specific structure or morphologies.
General Mechanism of a Surface Reaction

Example: \[ 2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2 \]

This cycle can repeat ad infinitum

Adsorption: \( \text{Br}_2(\text{g}) \rightarrow 2\text{Br (ad)} \) on a Cu (100)

Before Cu (100)

After \( \sqrt{2} \times \sqrt{2} \) R45°

**Adsorption**

$\text{Br}_2(\text{g}) \rightarrow 2 \text{ Br (ad)}$ on a Copper Surface

*Before*  

430 K

*After*

Atoms on surfaces move even at modest temperatures. Adsorption can cause the surface to change its shape.

Each frame = 2 sec

---

**Diffusion of Holes**

Bromine on copper at 300 K

*After*

The holes, or vacancies, rapidly diffuse, however, they cannot cross steps.
Reaction

\[ \text{Br}_2 + 2 \text{Cu} \rightarrow 2 \text{CuBr} \]

Adsorbed bromine

CuBr (111)

The reaction appears to continue to occur through the CuBr film.

The CuBr does not accumulate where it forms but rather diffuses across the surface and forms crystals elsewhere.


Diffusion

Oxygen atom diffusion on tungsten oxide WO$_3$ at 300 K
**Diffusion Along Edges**

Bromine on copper at 300 K

Atoms slide up and down the edge

---


---

**Reaction**


\[ \text{Sb}_4(t) \rightarrow \text{Sb}_4(f) \rightarrow 2 \text{Sb}_2 \]

300 K

In the gas phase, Sb exists as Sb₄.
The Future

1) Go faster

   Watch every step in a reaction in sequence.

   See chemical bonds form and break.

2) Routine spectroscopy of individual atoms

   Identify atoms and how they are bonded.

3) Assemble useful molecules and then assemble the molecules into useful structures.

   There’s still plenty of room at the bottom!
Synergism

– if it’s bad, we call it wear
-- if it’s good, we call it machining/polishing

The atomic force microscope responds to forces in nano-contacts at the nano-Newton level

Courtesy of Tom Dickinson, Washington State University
Tip – Induced Dissolution of Inorganic Crystals

Cleaved Calcite (CaCO₃) Scanned in Air

White square was scanned 3 times at $F_N = 270$ nN.

High $F_N$ scanning has no detectable effect in the absence of “corrosive” fluid.

Courtesy of Tom Dickinson, Washington State University
Higher melting and boiling point than other hydrogen compounds.

High heat capacity

High solvent power

105° polar dipole moment

Reactive $\rightarrow$ yields OH$^-$, H$^+$

Dissolution

Effect of Scanning across Step in Aqueous Solution

(just below saturation)

White square was scanned 3 times at $F_N = 270$ nN.

High $F_N$ scanning has dramatic effect in the presence of “corrosive” fluid.

No evidence for “plastic” effects (dislocations etc.).

*Courtesy of Tom Dickinson, Washington State University*
Transition State Theory

Reaction \([A] + [B] \rightarrow [AB]\) takes place at specific surface sites with site density \([a]\) through an intermediate activated state \(AB^*\) (transition state).

\[
\text{Rate (kinetics)} = [a] (kT/h) \exp(-\Delta G/kT)
\]

\(\Delta G\): free energy to form transition state

Thermodynamics \(\rightarrow\) NET Direction of Reaction Dictated by relation of \(G_1\) to \(G_2\).

Elementary Growth and Dissolution Processes

Nucleation and Diffusion along terraces and steps are major rate limiting steps in ionic crystal dissolution and growth.

Courtesy of Tom Dickinson, Washington State University
Molecular dynamics simulations were used to model two stepped \{10\bar{1}4\} surfaces of the calcium carbonate polymorph calcite. The acute monatomic steps were found to be more stable than the obtuse monatomic steps. The initial stages of dissolution from the steps were considered in vacuum and in water. In vacuum CaCO$_3$ was shown to dissolve preferentially from the obtuse step. In aqueous environment both stepped surfaces are stabilized by the presence of the water molecules although the relative stabilities remain similar. Using potential parameters that reproduce experimental enthalpies of the dissolution of calcite crystal, the formation of the double kinks on the obtuse step is shown to cost less energy than dissolution from the acute step, probably due to the lower stability of the obtuse surface. The simulations suggest that formation of the kink sites on the dissolving edge of the obtuse step of calcite is the rate determining step and this edge is predicted to dissolve preferentially, which is in agreement with experimental findings of calcite dissolution under aqueous conditions. [0163-1829(99)02030-3]

Using DL_POLY 2.9:

\[
\text{TABLE IV. Energies of dissolving calcium carbonate units from hydrated calcite surfaces.}
\]

<table>
<thead>
<tr>
<th>Surface</th>
<th>25%</th>
<th>50%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A {5 \bar{1} 8}</td>
<td>+103.7</td>
<td>+70.0</td>
<td>+88.1</td>
<td>+38.6</td>
<td>-29.9</td>
</tr>
<tr>
<td>B {3 \bar{1} 2}</td>
<td>-45.8</td>
<td>-6.0</td>
<td>+21.7</td>
<td>-19.3</td>
<td>-35.0</td>
</tr>
</tbody>
</table>

\*Adjacent calcium carbonate units dissolved.
\*Adjacent configuration, forming crenellated edge.

“Wear” Due to Linear Scanning Across Step on Calcite in Water

- Length of wear track, $\Delta L$, is linearly related to the number of double kinks nucleated.

- Courtesy of Tom Dickinson, Washington State University
Where $\sigma$ is the tensile stress at the edge of tip-sample contact (elastic contact assumed).

Rate of kink nucleation can be described as

$$ R = R_0' \exp(\alpha v* F_N^{1/3} / kT) $$

where $\alpha$ is a known function of the elastic constants of calcite and the SFM tip. Fit $v^*$, $R_0'$ to data (wear track growth rate vs $F_N$).

Rate of motion of wear track into the terrace vs. contact force
For two different solutions — curve on right is for less aggressive solution
Kinetic Monte Carlo Simulation

Daniel Bentz and Keith Jackson
University of Arizona

Reversed from our images. HERE: up DARK; down BRIGHT

Courtesy of Tom Dickinson,
Washington State University