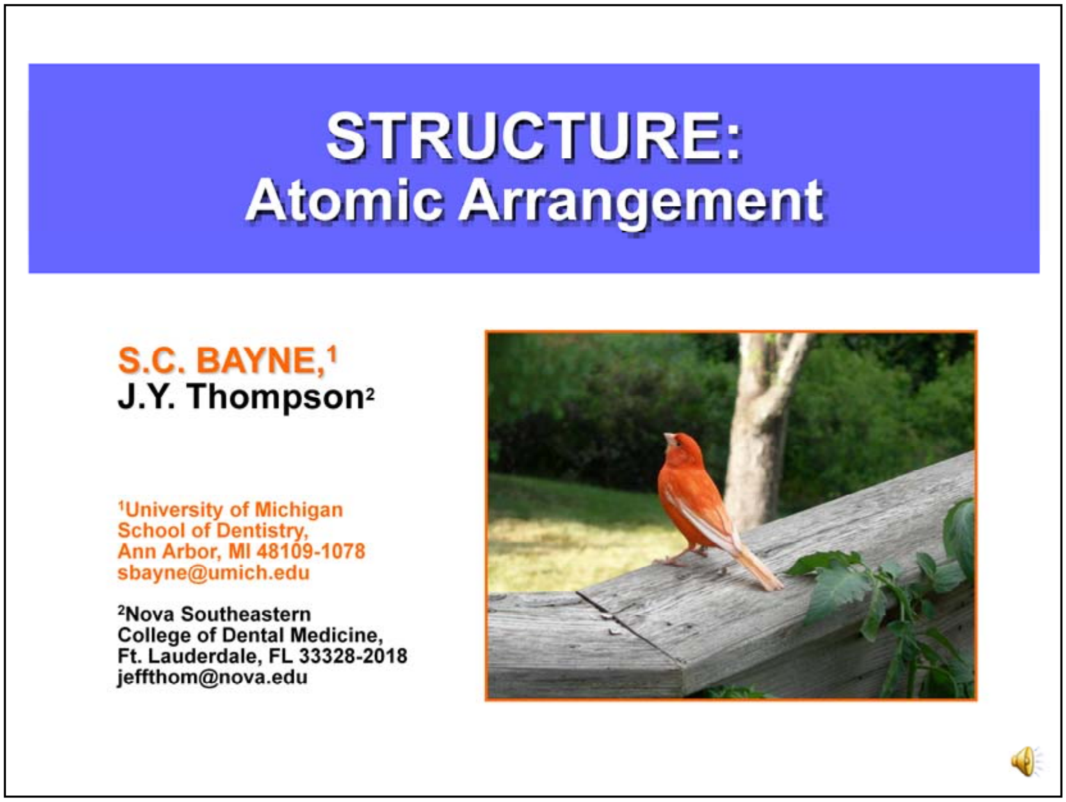

STRUCTURE:
Atomic Arrangement

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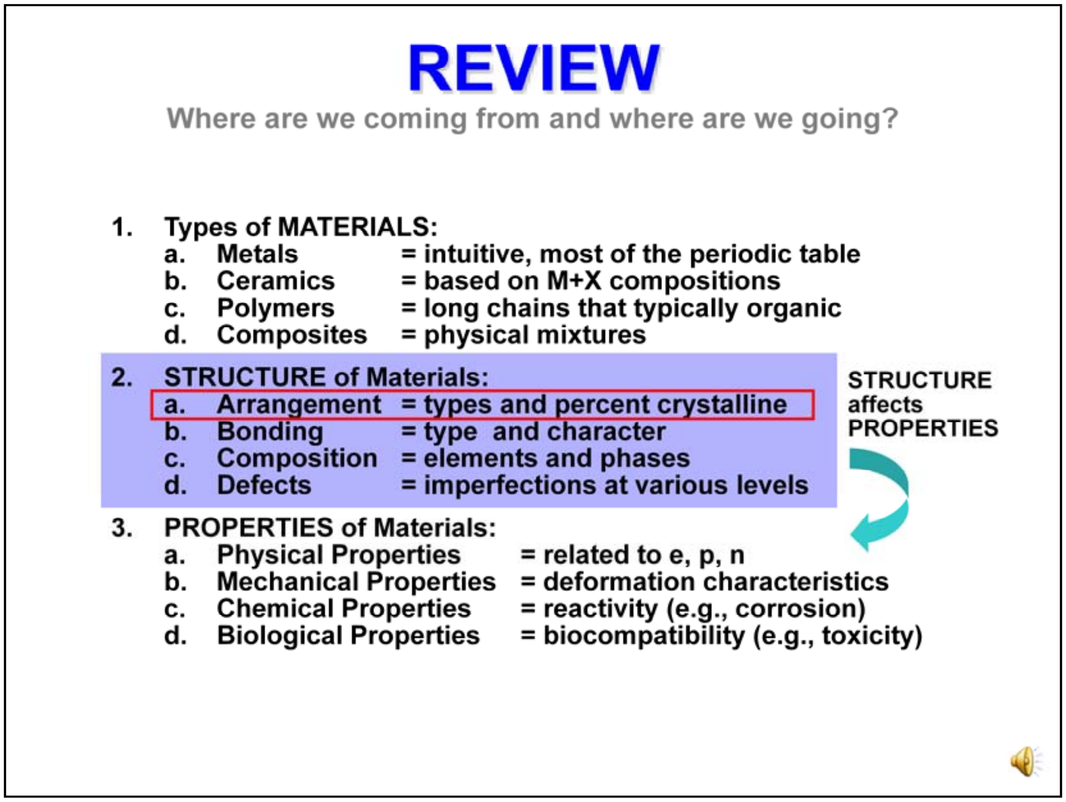
Now, let’s examine how atoms are affected as liquids transform into solids.



REVIEW

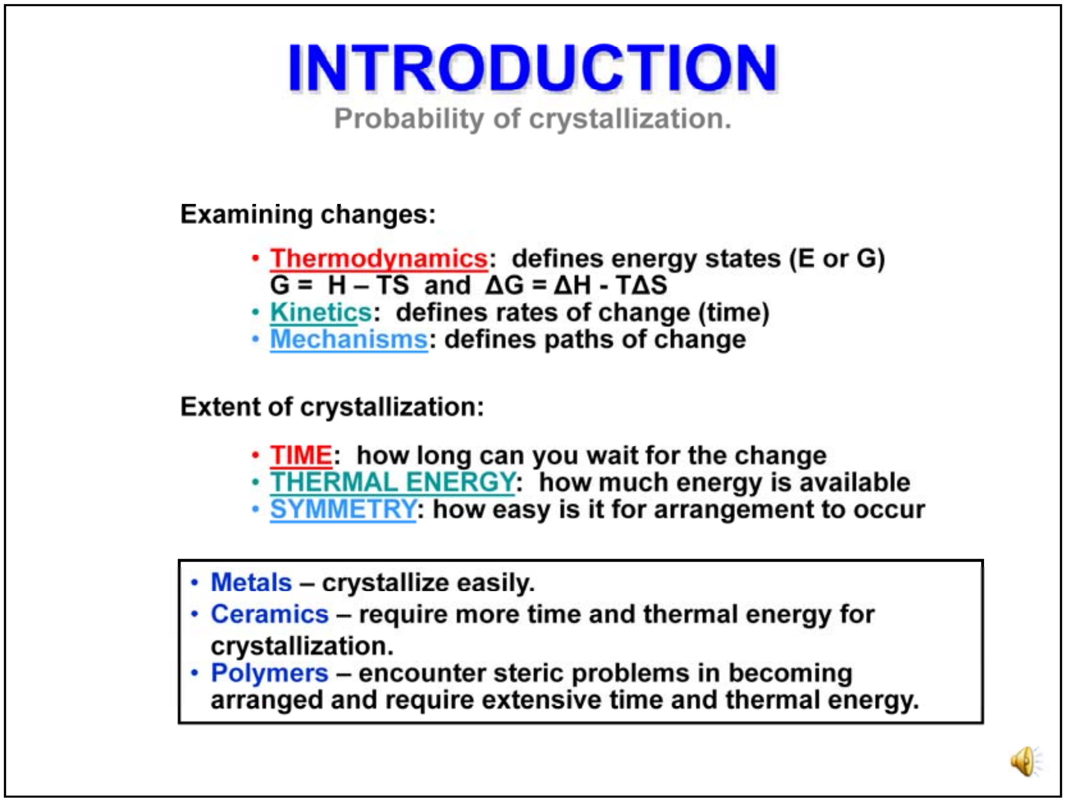
Where are we coming from and where are we going?

1. **Types of MATERIALS:**
   - a. **Metals** = intuitive, most of the periodic table
   - b. **Ceramics** = based on M+X compositions
   - c. **Polymers** = long chains that typically organic
   - d. **Composites** = physical mixtures
2. **STRUCTURE of Materials:**
   - a. **Arrangement** = types and percent crystalline
   - b. **Bonding** = type and character
   - c. **Composition** = elements and phases
   - d. **Defects** = imperfections at various levels
3. **PROPERTIES of Materials:**
   - a. **Physical Properties** = related to e, p, n
   - b. **Mechanical Properties** = deformation characteristics
   - c. **Chemical Properties** = reactivity (e.g., corrosion)
   - d. **Biological Properties** = biocompatibility (e.g., toxicity)

STRUCTURE affects PROPERTIES

Before we deal with PROPERTIES of materials, it's beneficial to remember where we have come from, and where we are going. Later, we will examine categories of materials (and dental materials) in detail. But first, we need to understand the underlying **[CLICK]** STRUCTURE (A, B, C, D – i.e., arrangement, bonding, composition, and defects) so that we can predict or interpret the resulting **[CLICK]** PROPERTIES (physical, mechanical, chemical, and biological).

[CLICK] We will start by studying arrangement within solids. Material that is arranged is called crystalline. Un-arranged material is called non-crystalline. Our starting question has to be what is the reason that crystallization should occur at all, and then, what is the barrier to the process.



INTRODUCTION

Probability of crystallization.

Examining changes:

- **Thermodynamics: defines energy states (E or G)**
  $G = H - TS$ and $\Delta G = \Delta H - T\Delta S$
- **Kinetics: defines rates of change (time)**
- **Mechanisms: defines paths of change**

Extent of crystallization:

- **TIME: how long can you wait for the change**
- **THERMAL ENERGY: how much energy is available**
- **SYMMETRY: how easy is it for arrangement to occur**

- **Metals – crystallize easily.**
- **Ceramics – require more time and thermal energy for crystallization.**
- **Polymers – encounter steric problems in becoming arranged and require extensive time and thermal energy.**

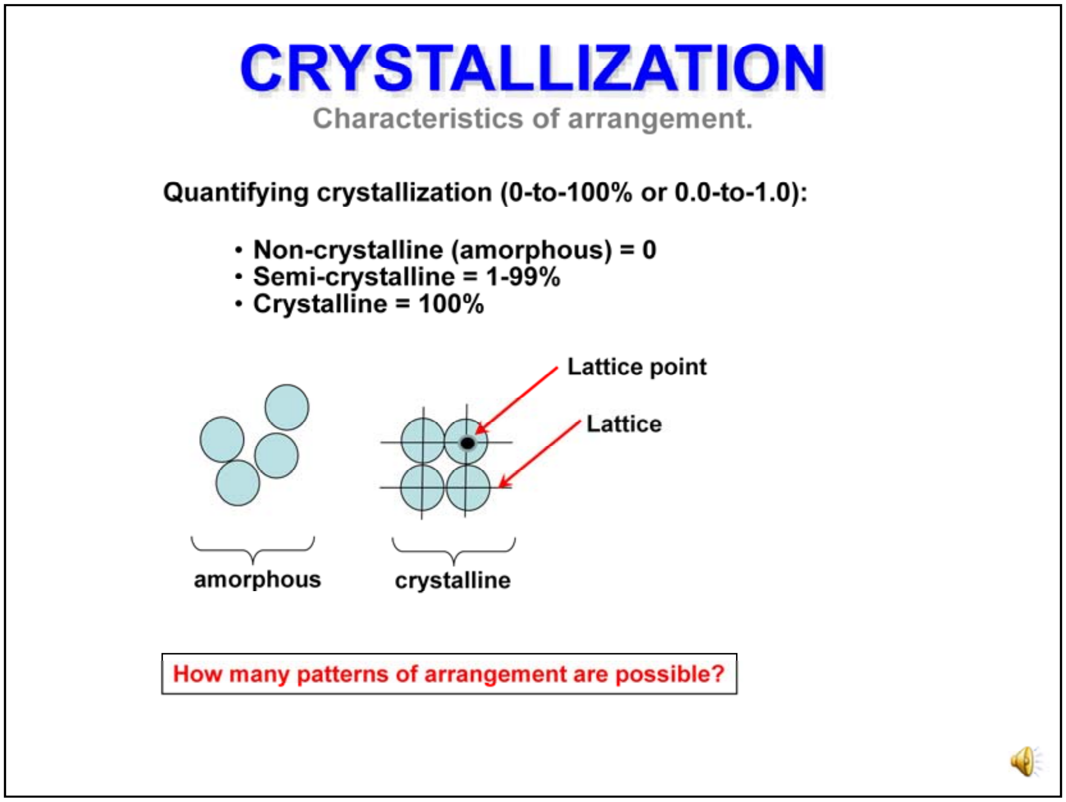
All processes that involve transformation or change-of-state are examined in terms of (1) thermodynamics, (2) kinetics, and (3) mechanisms. Let's review these terms quickly.

From physics and chemistry, you remember that **[CLICK]** thermodynamics simply considers the energy of any state and the energy differences between states. It tells you if there is a tendency toward change, but it does not consider the rate of change or possible mechanisms of change. **[CLICK]** The energy of a system is a function of its heat energy or enthalpy (H) and its arrangement energy or entropy (S). The total energy or free energy (E or G) of the system is defined as $G = H - TS$. If you compare the energies for two different states, such as the energy of the system before and after a transformation, the change in energy in thermodynamic terms is $\Delta G = \Delta H - T\Delta S$. The system will tend to go toward lower energy. In the solid state, the overall energy of any system becomes lower by arranging the atoms or molecules. While that process increases the entropy, it causes a much greater reduction in the heat energy by creating stronger and more numerous bonding opportunities. Therefore, a system wants to crystallize. It wants to lower the total energy.

[CLICK] Kinetics examines the time that a transformation takes. It could be very short (such as fractions of a second) or very long (in terms of thousands of years).

[CLICK] Mechanisms consider the path for change from one energy state to another.

[CLICK] When a liquid cools and solidifies, there is a strong tendency become arranged (i.e., crystallize). Actual crystallization depends on (a) adequate TIME, (b) available THERMAL ENERGY, and (c) sufficient SYMMETRY. **[CLICK]** Metals solidify easily. Ceramics solidify if cooling occurs slowly. Polymers are difficult to crystallize.



CRYSTALLIZATION

Characteristics of arrangement.

Quantifying crystallization (0-to-100% or 0.0-to-1.0):

- **Non-crystalline (amorphous) = 0**
- **Semi-crystalline = 1-99%**
- **Crystalline = 100%**

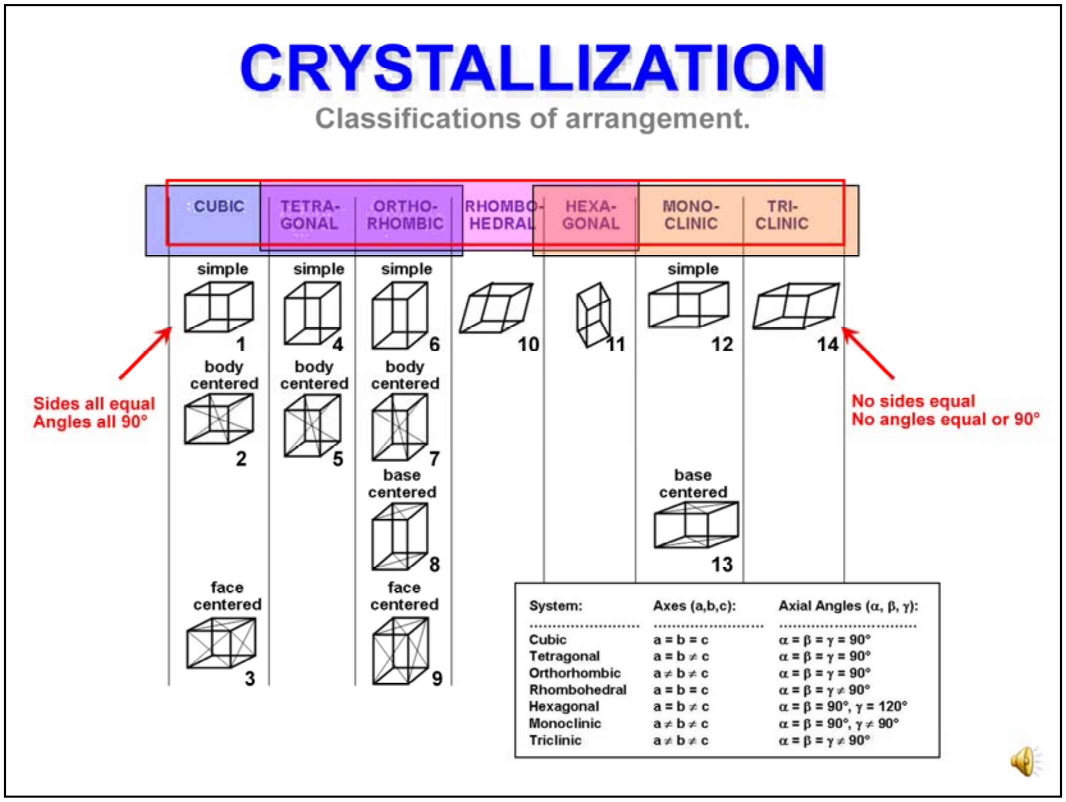
How many patterns of arrangement are possible?

Let’s use metals as our example, because their atoms and arrangements are relatively simple. Imagine atoms as spheres. Pure metals involve only a single atom type. Metal alloys are solutions (liquid or solid) of two or more metal atom types. All the rules are the same regardless of the complexity of the system.

[CLICK] Materials do not always completely transform into crystalline solids. You can get non-crystalline solid as well. The non-crystalline material is not at as low an energy as the crystalline material. We can express the extent of crystallization from 0-100% or 0-1. **[CLICK]** Non-crystalline material may also be called amorphous material. Partially transformed systems may be described as semi-crystalline and contain both crystalline and non-crystalline regions.

Now lets take some material that is **[CLICK]** dis-organized and **[CLICK]** organize it. How would you describe the order? If you were to imagine that the centers **[CLICK]** of the atoms formed a series of points (i.e., lattice points) that defined a grid (i.e., lattice) **[CLICK]**, then the pattern might be more obvious. These atoms form a square pattern. Of course, we are only examining this in 2D and the pattern is actually a 3D one. In 3D, we would call this a cubic pattern.

[CLICK] How many patterns are possible?



CRYSTALLIZATION

Classifications of arrangement.

Sides all equal
Angles all 90°

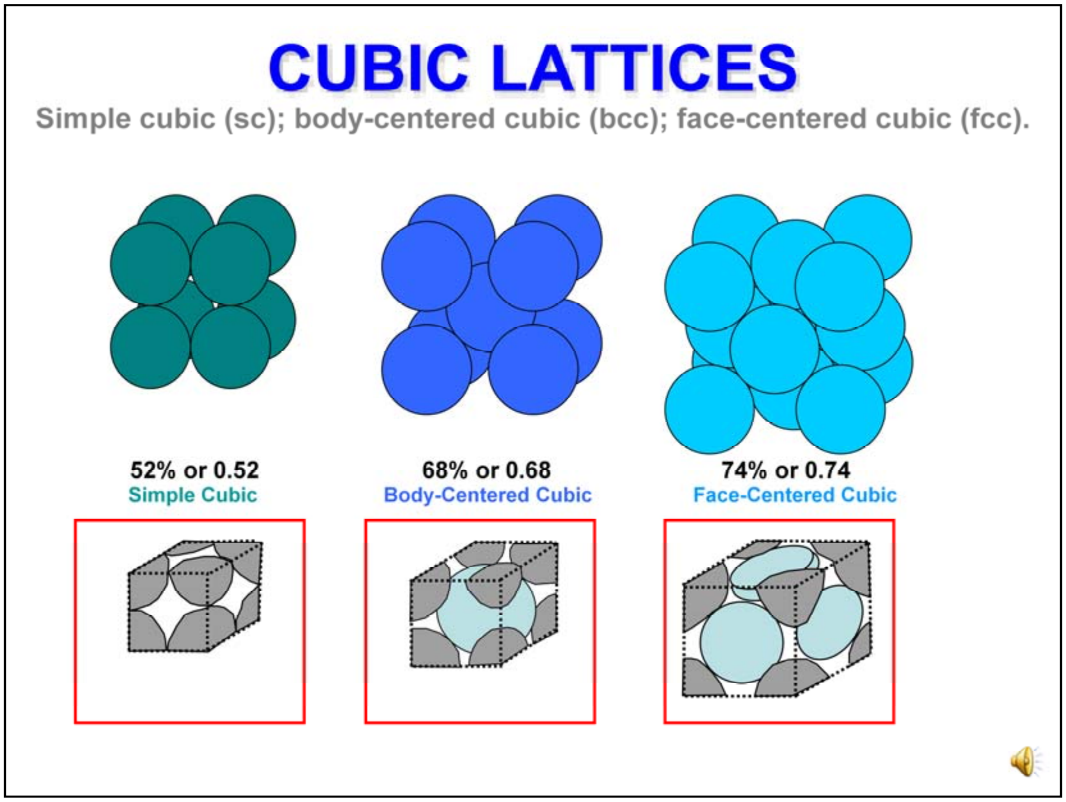
No sides equal
No angles equal or 90°

System:	Axes (a,b,c):	Axial Angles (α, β, γ):
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90°, \gamma \neq 90°$
Triclinic	$a \neq b \neq c$	$\alpha = \beta = \gamma \neq 90°$

Auguste Bravais was a French mathematician in 1848 who first figured out the number of possible arrangements. When you try to arrange atoms or anything in 3D space, it turns out that there are only 14 possibilities (called Bravais Lattices) **[CLICK]** -- and the possibilities can be clustered into 7 groups (called crystal systems) **[CLICK]**. A lattice is simply a set of points marking the positions of the atoms in the arrangement. Atoms which are close or touching each other define a repeat volume (or unit cell) that can be translated in all directions to create the arrangement.

The simplest crystal system is the cubic one. **[CLICK]** The unit cell for the arrangement has sides of equal lengths and internal angles that are all 90 degrees. **[CLICK]** The other extreme is the triclinic system in which all sides and angles are unequal. **[CLICK]** Check the table for the systematic loss of symmetry of the lattices.

Materials that can crystallize easily, usually do so because they make simple arrangements. **[CLICK]** Metals often produce cubic arrangements. **[CLICK]** Complex molecules such as polymers tend to produce monoclinic and triclinic arrangements. **[CLICK]** Ceramics are generally formed in arrangements that are intermediate in complexity.



CUBIC LATTICES

Simple cubic (sc); body-centered cubic (bcc); face-centered cubic (fcc).

52% or 0.52
Simple Cubic

68% or 0.68
Body-Centered Cubic

74% or 0.74
Face-Centered Cubic

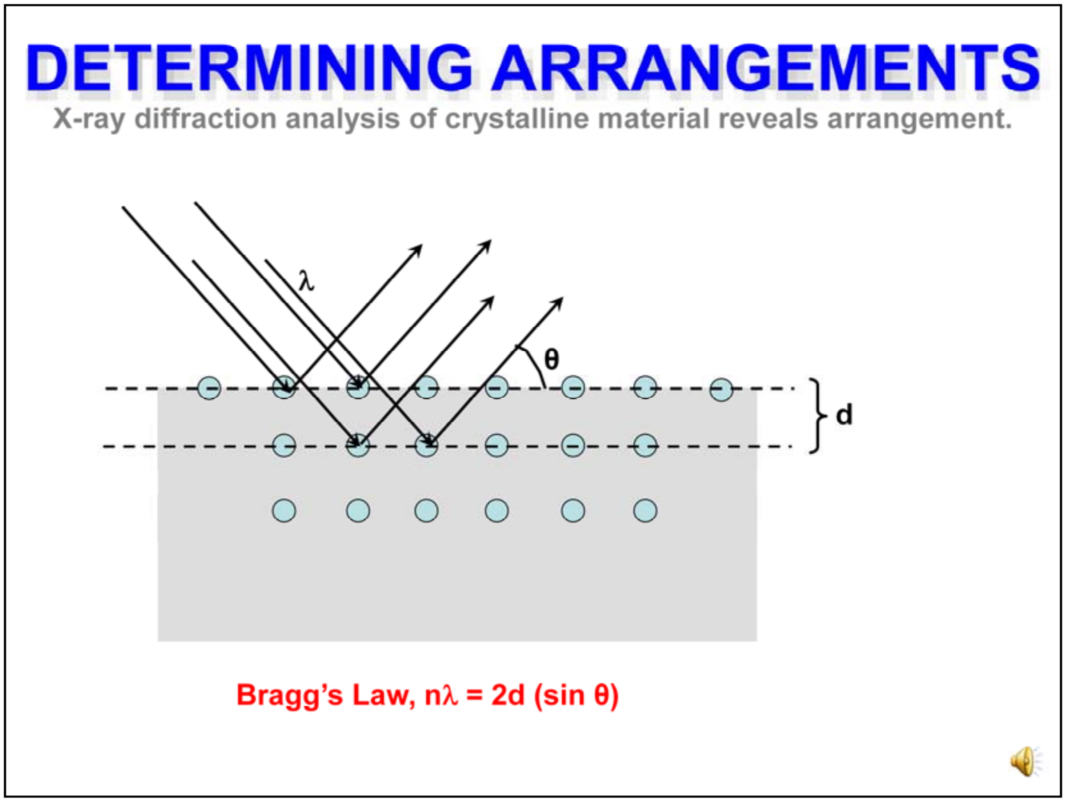
Cubic arrangements can have **[CLICK]** (1) atoms only at the corners of a unit cell, called simple cubic **[CLICK]** (2) atoms at the corners with one in the middle, called body centered, and **[CLICK]** (3) atoms at the corners with atoms in between the corner atoms along the faces, call face-centered cubic. We will use abbreviations for the arrangement types -- with simple-cubic as SC, body-centered cubic as BCC, or face-centered cubic as FCC. The abbreviations can be lower-case or upper-case and mean the same thing.

Different arrangements have different efficiencies of filling space with spherical atoms. You can begin to understand how space is filled by looking at the exact cube that is involved in repeating the pattern within a solid. **[CLICK]** The cube that is the repeating pattern is called the UNIT CELL.

[CLICK] SC arrangments fill 52% of space. BCC ones fill 68% of space. FCC ones fill up 74% of space. These are called packing efficiencies (shown as percentages). They can also be called packing fractions and represented as fractions (e.g., 0.52, 0.68, 0.74). If you know that number of atoms in an arrangement, the atomic weight, and the atomic radius, then you can calculate the weight per unit volume or density of the material. If a material crystallizes, it will be more dense than if it does not crystallize. The actual Bravais lattice type will determine the real density.

Consider a dental composite example. You want to maximize the reinforcing filler content to make it strong, but you will be limited by the arrangement type. If you use uniform sized particles and a SC arrangement, you can only incorporate 52% filler into the mix. If you can pack filler into an FCC type of arrangement, then you can get 74% incorporated. In practical terms a good mixture that is usable generally has a packing fraction of uniform filler of about 65%.

Arrangements are not affected by the absolute sizes things or the extent of the volume being filled. If you pack basketballs into the classroom in a BCC arrangement, they would fill 68% of the space.



DETERMINING ARRANGEMENTS

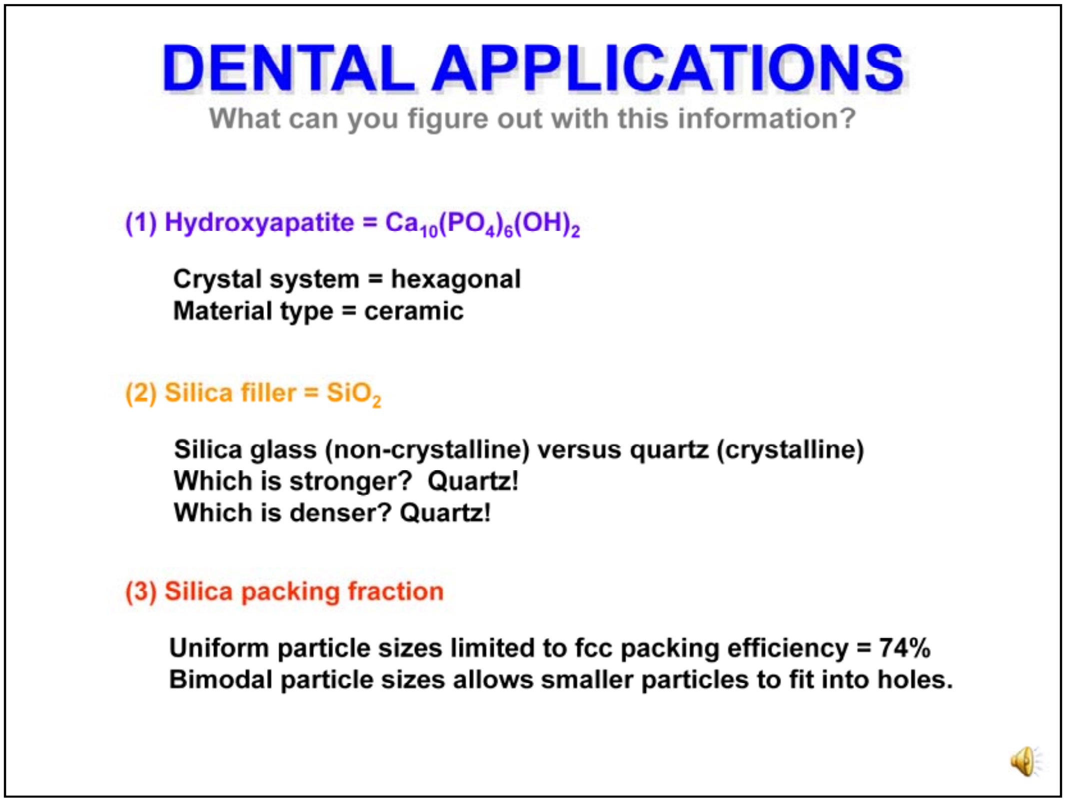
X-ray diffraction analysis of crystalline material reveals arrangement.

Bragg's Law, $n\lambda = 2d (\sin \theta)$

Imagine the solid as planes of atoms. How do you figure out what arrangement is present? **[CLICK]** You analyze the solid state structure by shooting x-rays of known wavelength **[CLICK]** into the solid at different angles, **[CLICK]** letting them bounce off of the planes of atoms, **[CLICK]** determine which angles produce in-phase reflections, **[CLICK]** and solve for the interplanar spacing. This tells you the arrangements of planes, and determines the overall arrangement.

This process is shown superficially in the figure with respect to the wavelength of the x-rays, the angle of reinforcing diffraction, and the distance between the planes. The details are not described. **[CLICK]** The formula relating the constructive angles for reflection of x-rays to unit cell dimensions is called Bragg's Law.

This is the experimental method that was used to reveal the structure for DNA and RNA. The team of Watson and Crick worked to crystalize biological material and then solve the x-ray diffraction pattern -- so they would know the relative positions of the atoms in the structure.



DENTAL APPLICATIONS

What can you figure out with this information?

(1) Hydroxyapatite = $Ca_{10}(PO_4)_6(OH)_2$

Crystal system = hexagonal
Material type = ceramic

(2) Silica filler = SiO_2

Silica glass (non-crystalline) versus quartz (crystalline)
Which is stronger? Quartz!
Which is denser? Quartz!

(3) Silica packing fraction

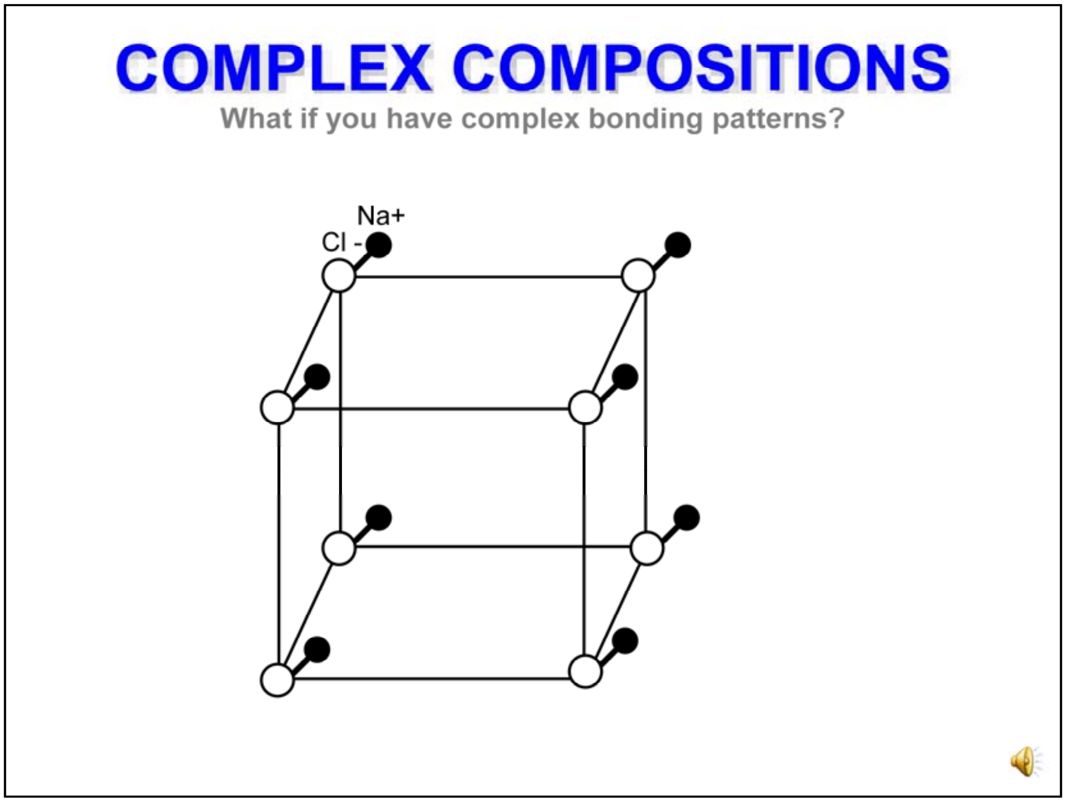
Uniform particle sizes limited to fcc packing efficiency = 74%
Bimodal particle sizes allows smaller particles to fit into holes.

Let's see if we can use this information.

[CLICK] (1) Most of enamel is made up of crystals of hydroxyapatite (or HA). The chemical formula for HA is approximately $Ca_{10}(PO_4)_6(OH)_2$. **[CLICK]** It crystallizes into a hexagonal arrangement. What type of material (metal, ceramic, polymer) would you guess that HA is? **[CLICK]** Correct. If you follow the rules, metals crystallize easily and have simple structures. Polymers are complex and hard to crystallize. Ceramics generally are in between.

[CLICK](2) Silica is a very common powdered filler used in many compositions in dental materials. **[CLICK]** It can be made to be non-crystalline (called silica glass) or crystalline (called quartz). Which one most likely has stronger mechanical properties? **[CLICK]** Right. **[CLICK]** Crystalline material is more dense than its non-crystalline analogue, and therefore you would expect it to have more bonds per unit volume to break and thus behave as stronger.

[CLICK](3) If you wanted to increase the packing fraction for adding silica fillers into a dental material what could you do? **[CLICK]** If the particles are all the same size, then you are limited to the best crystalline arrangement that is possible. **[CLICK]** However, if you incorporate smaller sized filler particles that could fit into the holes between the larger ones, then you can increase the overall packing fraction. Almost all dental composites utilize this approach.

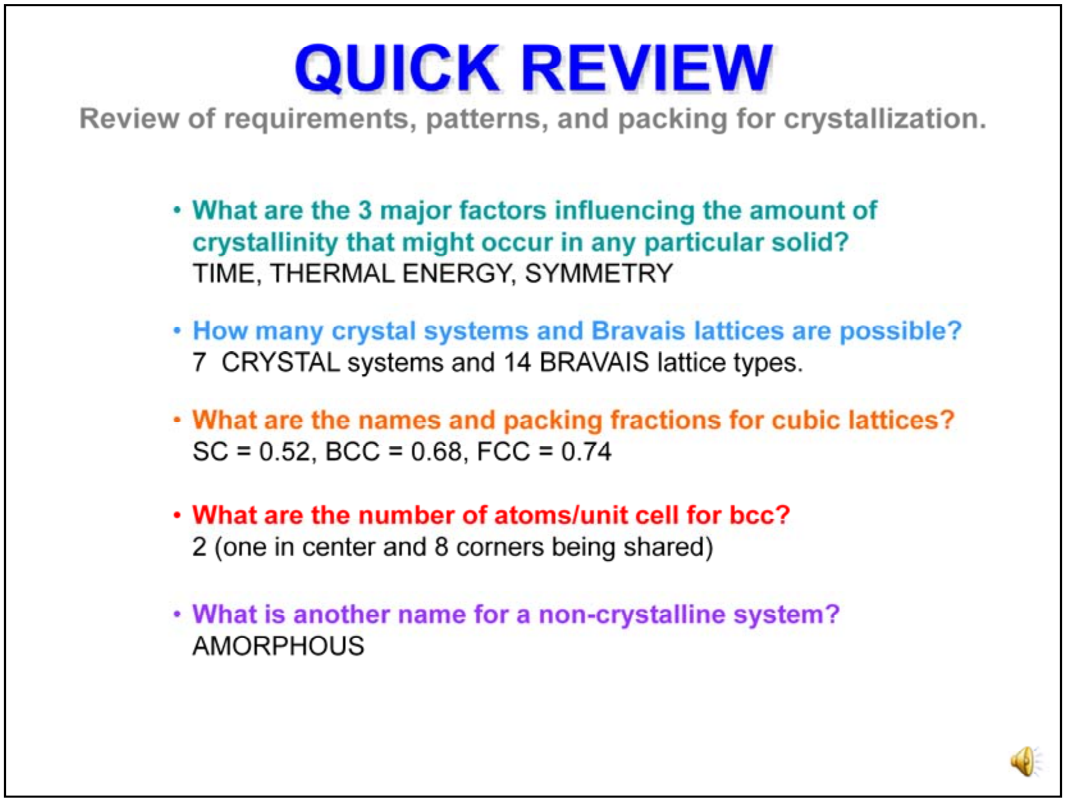


COMPLEX COMPOSITIONS

What if you have complex bonding patterns?

Complex compositions with more than one type of atom and/or more complex bonding requirements still follow all of the rules. **[CLICK]** Let’s just look at a slightly more complex situation such as NaCl. This is an ionic crystal. Every Na+1 needs to be paired with a Cl-1 ion for charge balance. **[CLICK]** Each corner of a cubic cell now has a pair of ions associated with it. All the rules and characteristics of unit cells are still the same. For this cubic cell, the packing fraction is still 0.52 (52%).

In even more complex atomic arrangements, the corners of the lattice may not be associated with a specific atom or center of an atom. However, all the rules continue to apply.



QUICK REVIEW

Review of requirements, patterns, and packing for crystallization.

- What are the 3 major factors influencing the amount of crystallinity that might occur in any particular solid?
  TIME, THERMAL ENERGY, SYMMETRY
- How many crystal systems and Bravais lattices are possible?
  7 CRYSTAL systems and 14 BRAVAIS lattice types.
- What are the names and packing fractions for cubic lattices?
  SC = 0.52, BCC = 0.68, FCC = 0.74
- What are the number of atoms/unit cell for bcc?
  2 (one in center and 8 corners being shared)
- What is another name for a non-crystalline system?
  AMORPHOUS

Here is a quick review of the concepts from this module.

[CLICK] (1) What are the 3 major factors influencing the amount of crystallinity that might occur in any particular solid?

[CLICK] TIME, THERMAL ENERGY, SYMMETRY

[CLICK] (2) How many crystal systems and Bravais lattices are possible?

[CLICK] 7 CRYSTAL systems and 14 BRAVAIS lattices.

[CLICK] (3) What are the names and packing fractions for cubic lattices?

[CLICK] simple cubic (sc) = 0.52; body-centered cubic (bcc) = 0.68; face-centered cubic (fcc) = 0.74

[CLICK] (4) What are the number of atoms per unit cell for a metal with a body-centered arrangement?

[CLICK] 2 atoms per unit cell (1 in the center and 8 corners contributing 1/8th volume each)

[CLICK] (5) What is another name for a non-crystalline system?

[CLICK] AMORPHOUS

THANK YOU

THANK YOU.