MITOCW | MIT3 091F18 lec18 300k

Big picture-- I showed you this big picture before.

We're now going to add to it.

Look at what we've done.

Ha!

Electronic structure all the way up through [INAUDIBLE],, [? Louis, ?] molecular orbital theory, how to handle multi-electrons, all these different kinds of bonding-- check.

We've covered every single one of these, and this is solid-state chemistry.

OK, but now here we are, right?

Now OK, remember we also talked about this on the very first lecture.

When you classify solids, there are two things that are really important.

One is the bonding type.

How do the atoms in the solid want to talk to each other?

How do they interact?

And that is something that we have covered in a lot of ways.

But the next is how they come together, the actual arrangement of those atoms.

And that is what we're going to talk about today and on Wednesday.

And then after exam two as we learn about X-rays, that's a way to characterize the arrangement so that you can see how they're ordered, OK?

We're going to use X-rays and do something called X-ray diffraction.

But for this week I want to just classify it.

I want to talk about the tools that we use to understand how a solid forms, how to describe the formation of a solid, how the atoms can be described.

And OK, so, of course, a solid is that which is dimensionally stable, simple definition, right?

But we can break down how these atoms arrange into two basic categories-- atomic arrangement, the order, and what we call it, right?

In the first category, it's regular.

So what that means is that everywhere I look, I have the same thing repeating.

And you know what?

It repeats over a long, long way-- like really long, OK?

So that kind of regular, long range order is a crystal.

That's a crystalline solid.

And that is going to be the topic of this week, crystalline solids.

Now, there are also solids that you can make where there isn't order.

Or maybe there's some but not much.

So, things are kind of jumbled up.

They're not regularly repeating.

They might be random, the atomic arrangement.

Or maybe there's repetition, but it's very short-range.

So things look ordered, but only for a few bond lengths, not 10 to the 23rd bond lengths, right?

Those are called amorphous solids, or also glass.

Now, as I mentioned, this is the topic of this week, and this will be covered on exam two.

This is the topic after exam two next week, OK?

So we'll talk about both of these types of solids as we go.

All right, now, OK, it turns out that nature has been thinking about order for a long, long time.

And there is a reason for this.

Because nature wants to be efficient.

This plant is like, well, I'm only going to grow this big, and I got to put as many seeds as I can on the surface of this thing.

How do I fit them-- how do I pack them in?

Well, I could fit them randomly, but it doesn't seem like I could get as many seeds on there.

What if I packed them in in some regular pattern?

What if I packed them in in some regular way?

Well, you can pack a lot more in.

And so nature has already been thinking about symmetry and order and even long-range order for a long time.

People have been thinking about this, too.

Robert Hooke, the same person from Hooke's law, in the 1600s he was all about cannonballs.

And he was like, how can I stack cannonballs?

And he tried this, right?

He's like, well, maybe if I just put them like this, is that a good way to stack them?

I don't know.

And then he sort of put them all together.

But now, he tried this, and then he tried another arrangement, and he'd be like, well, but how-- first of all, are they stable?

Do they fall over easily?

Because you don't want cannonballs falling all over the place.

But then also, did you pack as much in this way as another way?

So he was thinking about it.

And he figured out that you could pack more cannonballs in the same area or volume if you sort of switched it up, right? And then he thought, well, maybe other things have packing, too. And he thought about all sorts of things. He looked at salt crystals, and he said, they must also pack in some way, because cannonballs do. So people have been thinking about this for a long time, OK? Now, people are also inspired by regular order, right? So if you look at, for example, an Escher painting, you can see that there is a repetitive pattern here. This is a crystal of ducks, right? OK, so now, when you look at patterns like this, you have to-- well, you don't have to, but we have to in this class. We've got to figure out what is the repeating unit. What is it that is repeating everywhere? So that's the first question we need to ask. And you can see if you look at this picture, you can draw a box like that. There's a box around a light colored, dark colored duck. And now you see if you take this box and you move it over, you translate it over there, you get exactly the same thing. If you take that box and you put it up there, you get exactly the same thing. So that is a repeating unit.

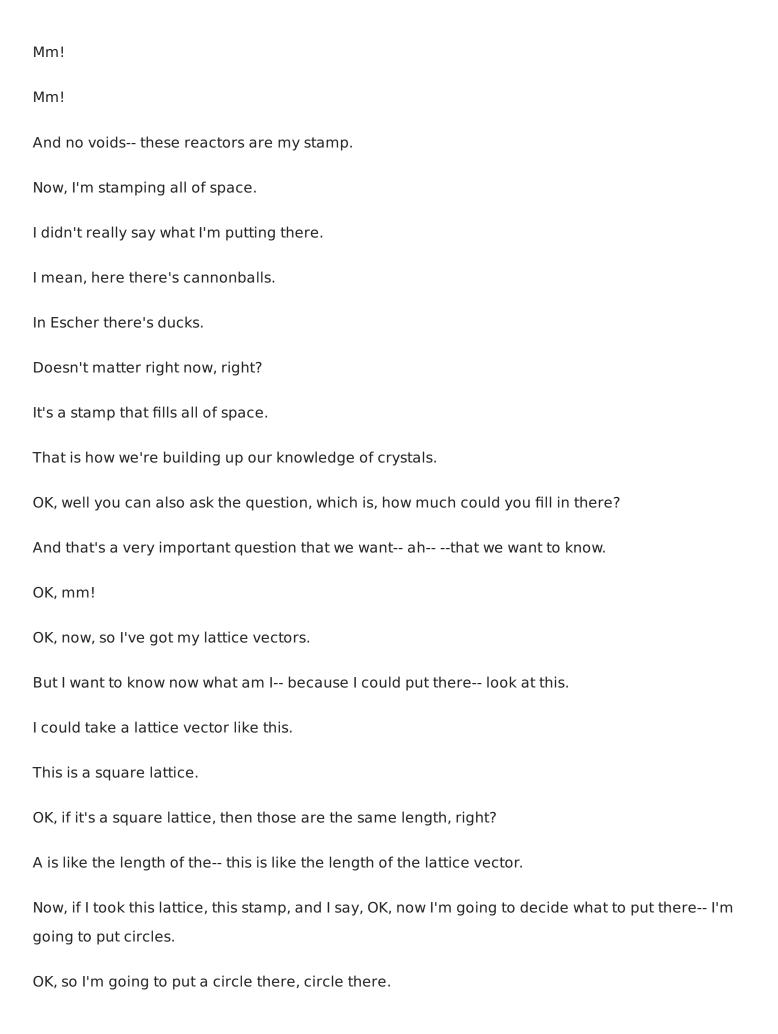
It's called a unit cell.

It's a unit cell.

Oh, we have a definition.

And it's the repeating unit in a crystal.
It's a repeating unit.
Now, it's not always obvious.
So, there's one way that I can repeat and take this and make the picture by repeating it everywhere.
But check this out I could have done that.
If you stare at that, you can see that that is also a repeating unit, right?
That is also repeating unit.
If I take this and I move it down here, I get exactly the same thing.
And I move it over there, and I can tile all of space.
I can tile all of space.
And something is really important here.
I can take these repeating units and stamp them.
Oh, I like that word.
And I can tile all of space and recreate this picture without any voids, right?
I didn't miss anything.
I filled all of space.
I filled all of space.
And that is what a crystal system is, right?
A crystal system let's write it here crystal system.
Crystal system that is a way of enumerating enumerates ways that space can be filled, OK?
Enumerates ways that space can be filled with no voids.

That's a crystal system.
OK, well, let's go back to the canons for a minute, because we can think about this first in 3D before we we're just warming up before we get to 3D, OK?
Oh, there it is.
That's a unit cell.
OK, now the thing is, so I've drawn a unit cell.
And notice what I've done.
I've taken this, and I've drawn it this way, OK?
And those vectors define the unit cell, right?
Those vectors define the unit cell.
So those are my stamps, the vectors there.
So these things here well, I went a little far there, but they should go to the center of the next cannonball.
So now these are vectors.
If I just take these, and I put them now, if I translate them over to there, then I get the next unit cell and the next one.
And I go up, and I go over, and I get all the tiling of all space.
And so those vectors are really important, and they have a name.
Those are called the lattice vectors.
Those are the lattice vectors.
I really like to think of them as my stamps, or my stamp.
It is a stamp.
Mm!



And what you do then is you put a circle everywhere that you stamp, right? OK, so I have now taken my stamp, and I've stamped everywhere. And I've put something at each place-- a circle. But I might ask a question. And this is a very important question, which is, if I have circles, what is the maximum that they can pack in for this lattice? How much can I pack? Well, you can just visualize that now. Let's grow them. A stamp means it's the same thing everywhere, right? So now if I make one of them bigger, well, I've made them all bigger, right? Because they're all the same everywhere. And if I make them all big enough, eventually they're going to touch like that. That's a special thing, because now I've grown the shape that I'm putting there to the point where it's the maximum packing, right? And so you can imagine this. The area of maximum packing is a very important parameter. And it's something that we'll talk about today with 3D crystals, which is the solids of elements in the periodic table. But if you say with this square analogy-- so my lattice is a square.

My stamp is a square.

My sides are equivalent.

And what I put there is a circle.

Then the area of maximum packing is something you can calculate, right?

Because the circle itself-- in this case, if I-- [STUDENT SNEEZES]

Gezuntheit.

If I look at it, then-- oh, that's not a good circle.

But anyway, you'll get the point here, which is that-- oh, boy-- which is that if this is the lattice vector is a, like I drew there and I'm looking at the maximum packing, then you know already that the radius of the circle is a half a.

So radius equals 1/2 a.

If the radius of the circle is 1/2 a-- if the radius of a circle is 1/2 a, then you also know what the area is.

I'm in 2D right now.

I'm in 2D.

So if I've maximized the packing of these circles on the square lattice, then the area of the circle is pi times r squared.

So 1/2 a squared equals pi a-squared over 4.

But see, I also know how much I packed it in, right?

And I'm doing this slowly on purpose, because we'll go faster when we do some of the other ones.

But I want to do the first one slow, because then we'll all be able to see what we're talking about with the simplest case.

The area of the square is a-squared, right?

And so the area of max packing is equal to pi a squared over a-squared-- pi over 4.

because the a-squared is cancelled.

So it's 78%.

This is what Hooke was-- but did I max it out, or could I do something different?

Could I pick a different lattice? What if we made cannonballs into rectangles? Bad idea. No, he stuck with spheres, but how do you pack them in? How can you arrange them in a way to change the max packing? That's what nature does with atoms, as we'll see. So for example, if I had a 2D hexagonal lattice, instead of my stamp being a square-- so if it were a 2D hexagonal lattice-- I won't do this one out. But then the max packing goes all the way up to 91%. That's a lot more per area-- max packing. So this is something that we care a lot about. It's something that we care about because, when atoms see each other in a solid, what's the first thing they want to determine? The first thing they want to do is they want to go back in here and they want to be like, which one of those can we do? Can we find some way to bond? That's what atoms do. That's what everyone does. How can we bond together? What kind of relationship are we going to have? But they want to max that out, right? And so they want to try to pack in, given the bond that they're going to have.

And that is what's going to dictate the kind of arrangement they can have in the crystal, OK?

So OK, so here we are.

And we're going from 2D to 3D.

Now, the thing is, this is not going to be an in-depth dive into symmetry and space groups and group theory.

Those are all great topics.

But I'm just going to tell you-- and it's actually kind of cool.

In 3D, there are only seven unique crystal systems.

There are only seven ways that you can do this.

You can only pack in and have no voids-- and have no voids-- you can only pack in these seven different systems where, as you can see, what's changing here?

Well, it's Cartesian coordinates, so you've got the length of each lattice vector and their relative angles, right?

That's all you're changing.

Well, sometimes you change all the angles at once, OK?

Sometimes you change only-- well, sometimes you change only a few of them.

Sometimes you make them all the same.

Sometimes you change a few.

Sometimes you have all of them be even.

And sometimes some of them are equal, some of the lattice lengths are equal but another one is different, all right?

These are the seven ways that we can fill all of space.

And there are only seven.

In this class, we're only going to focus on one, and that's the cubic system. And the reason is that this gives us plenty to work with to understand crystallography and how chemistry relates to crystallography. And there is the benefit of the fact that a lot of elements take one of these three-- actually, only two. But they take cubic symmetry. What does that mean? Well, it means that all the lattice vectors are the same. Each one has a length a. They're orthogonal to each other, which means that the angle is 90 degrees. So we've got a cube. Now, it turns out that now we say, well, how do you pack? How can I pack things together in the cubic system? And there's three different ways to do it. So what this is is it's more symmetry and more group theory and math that goes into this that Bravais figured out. And so we call these Bravais lattices. Now, what Bravais figured out-- and again, you don't need to know all the math behind this, but I want you to know these three cubic lattices. What you figured out is that from the seven crystal systems, there are only 14 ways to pack. There are 14 ways to pack. That's it, no more. That's pretty cool. There's no 15.

There's no 16.

There's 14 exactly-- 14 ways that you can, by having a lattice, which means a stamp, there are only 14 ways you can do it for the seven crystal systems.

And for the cubic system, there's only three.

So I have three types of stamp.

That's what it means, three types of stamps where I leave no voids, right?

Heave no voids.

So I can tile all of 3D space, right?

OK, and it forms a cubic unit cell, cubic unit cell.

These are the three ways-- a simple cubic, a body-centered cubic, and a face-centered cubic.

These are the three types of lattices that have cubic symmetry.

They are the only three.

So in a Bravais lattice, the difference is in a Bravais lattice what Bravais did was he enumerated-- so here we enumerate the ways space can be filled.

He enumerated the packing, all the ways that the space can be packed with, for example, packing within the unit cell.

So there's three distinct ways to pack within a cubic unit cell, OK?

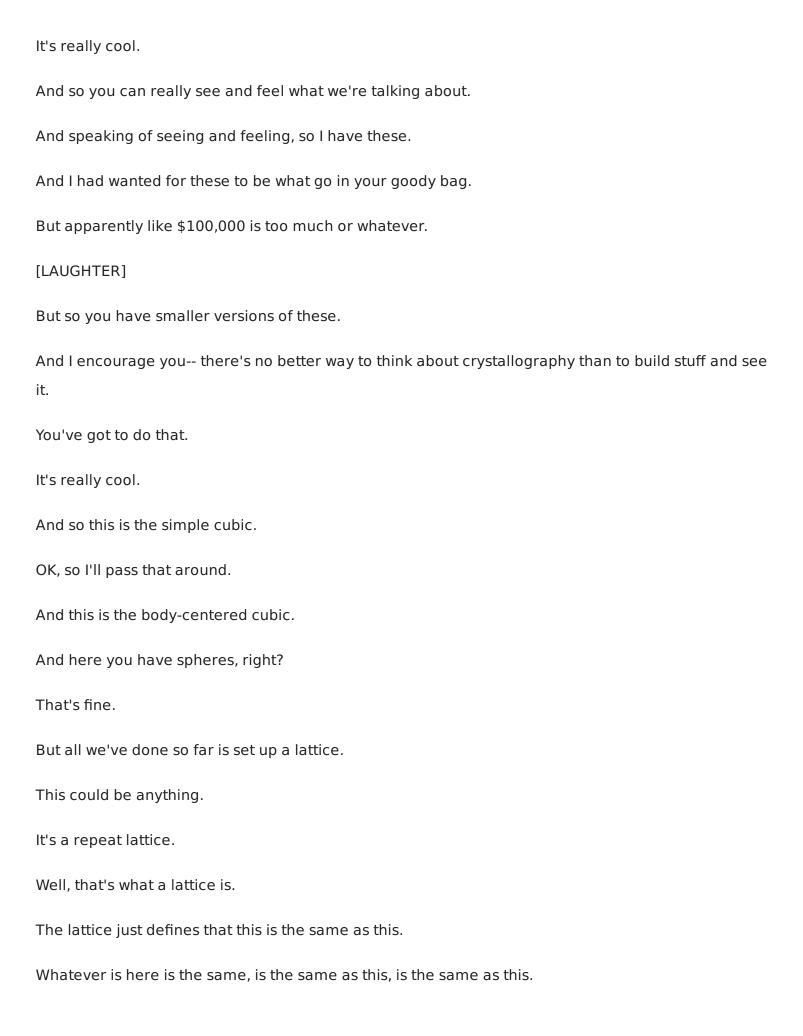
That's what we're going to bring to life today and we'll talk more about on Wednesday as well.

And what I want to do is I want to go through each one.

So we're going to go through simple cubic, body-centered cubic, face-centered cubic.

And then with each one, I'm going to talk about it, and then I'm going to show you a little video so that we can really see how the unit cell gets kind of sliced up.

And there's like a razor that comes in and slices it.



That's what we're defining here, OK?

OK, all right, now let's talk about these three.

This is a picture from [? April. ?]

These are the three systems I just talked about, the three Bravais lattices, three different ways to pack in a cubic symmetric cell.

And notice there's three ways of looking at it, right?

So here is sort of a ball-and-stick model, which makes it easy to see the bonding and the atoms.

But the space-filling model is really important here, because the space-filling model lets us think about the maximum packing.

That's really important.

Remember the maximum packing, because remember these are bonding.

Really?

These are bonding together, right?

So drawing them all the way up to where they touch, that's going to help us understand what their maximum packing can be.

So let's look at that for the simple cubic, OK?

So for the simple cubic, we'll do that here-- simple cubic.

OK, simple cubic-- oh, let's just call it SC for short.

Why not?

Now, one of the things you want to think about is, how many nearest neighbors do I have?

And I lost the-- so you can see.

Look at look at the edge and think about how many nearest neighbors-- well, you know you got six, right?

If you're in the corner there of the cube in your simple cubic, you've got six nearest neighbors. OK, that's important, right? Six nearest neighbors-- why is it important? Well, it's important because that's how many other atoms you could bond with in this solid, OK? But the other thing we want to know is the packing. Now, again, what you want to do to figure out the maximum packing is you want to think about it in the same way we did here. Think about putting something at each of the lattice points and then growing it out until they can't grow any more, right? And that's a good way to think about it. And in this case, we're going to take spheres. We're going to be taking spheres because that's how we're going to represent atoms. So we're going to be taking spheres. And we're going to grow them out and see what the packing is. Yeah, but I've got to do the same trick I did here. I've got to do the same trick I did here. I've got to write the radius of the atom in terms of the unit cell. So if the unit cell-- oh, boy. I'm going to be drawing a 3D structure. Danger! a, a, a-- that's a cube. All the sides are a. I made myself very happy.

It's a cube.
Now oh, but we have a cube.
Now, OK, here we go.
This one oh, but see, I want maximum packing.
So I'm going to grow them out.
And you can see what's going to happen as I do that.
And so you can see that in the case of a simple cubic lattice, it's just like in the square lattice.
It's just like in the square lattice, right?
When I've grown out the sphere, the radius of that sphere, the radius is r equals now, oh, wait a second.
OK, so I have 4/3 pi r OK, but that doesn't matter yet.
Don't do volume.
Think about the radius OK, the radius is just going to be 1/2 the lattice, right?
So radius is 1/2 a.
Volume is 4/3 pi 1/2 a cubed.
Now, this is important.
That is at the max packing.
OK, so I've grown these volumes out, and I've seen what the packing can be.
Now, we actually call this so now I've got the volume of an atom.
I'm pretending that these are atoms now.
No, I'm not pretending anymore.
It's real.

These spheres are now atoms.

And OK, so that's the volume of the atom, right?

And so we can write atomic packing fraction as the volume of the atom over the volume of the cell.

That's exactly what I did up here, right?

That's how we got the area of the square, the area of the circle, right?

But there's one more thing that's really important, which is it has to be times the number of atoms in the cell.

When I say cell, I mean unit cell.

It has to be times the number of atoms in the unit cell.

So it's however many atoms I have times the volume of the atom.

OK, that's good.

That's how much is inside of the cell divided by the volume of the cell, and that gives me the atomic packing fraction.

So in the case of a simple cubic, the APF, the Atomic Packing Fraction, is equal to pi over 6, which is 52%.

That's not very good, all right?

That's not-- well, I mean, it's relative.

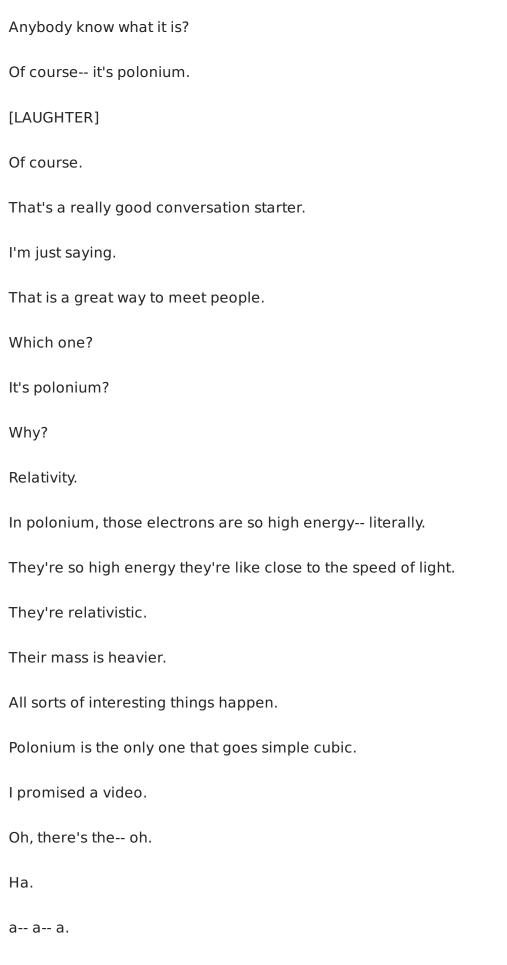
We don't know yet.

But it feels kind of low-- 52%.

So with a simple cubic lattice, all I can do in my wildest dreams is cover 52% of that volume.

That's not very-- that doesn't feel like a lot.

And in fact, when you look at the periodic table, what you find is that there's only one element-- one-that takes the simple cubic lattice.



There is a diagonal.



If we fade the others out, you can see the original group of eight particles within the array and the unit cell within that group.

We find the number of particles in one unit cell by combining all the particles' portions.

In the simple cubic unit cell, eight corners, each of which is 1/8 of a particle, combine to give one particle.

A key feature of a crystal structure is its coordination number, the number of the nearest neighbors surrounding each particle.

In a simple cubic array, any given particle has a neighboring particle above, below, to the right, to the left, in front, and in back of it, for a total of six nearest neighbors.

The body-centered cubic unit cell has a-- [END PLAYBACK]

OK, so you see-- that was so cool, right?

Like unh, unh, and you're figuring out how many atoms are in the cell, right?

Well, why didn't you just put the atom in the middle?

You could do that, but then it's not at the point, right?

So you've got to understand, the concept of the lattice is that whatever I put here, wherever my vectors go, that's what I put there and there and there.

And so we often as a standard, we say, well, OK, what did I put there?

I put an atom and then I put another atom.

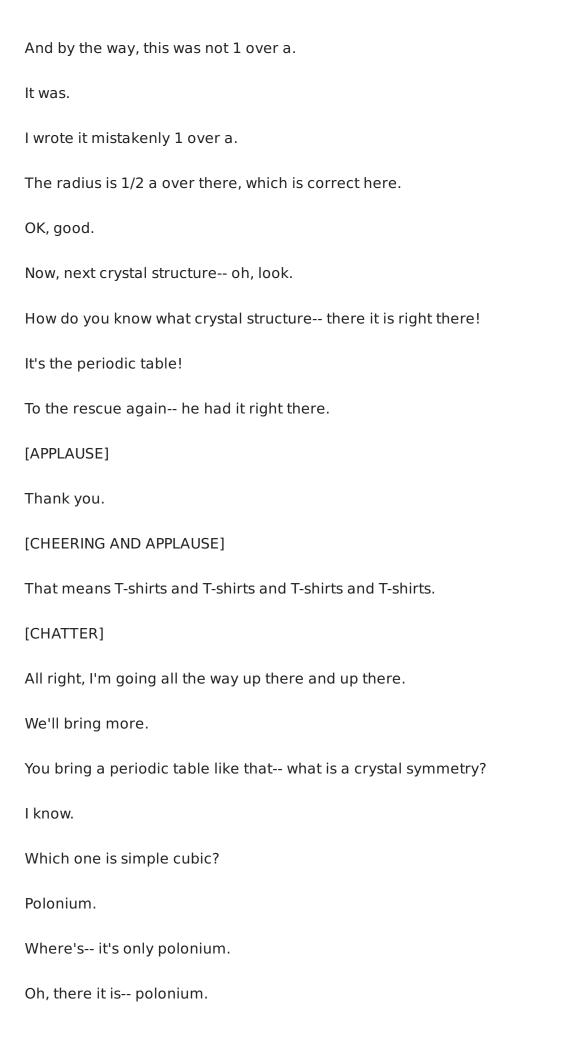
But then your unit cell is that cube.

And so we cut the unit cell, and you're like, well, how many atoms do I have in it?

Well, let's see.

I got one here, but it's shared with all these other cubes, so there's an 1/8 of an atom there and 1/8 of an atom there.

We add them all up, and you get one atom right back, which you knew-- which you knew.



Thank you for being representative of simple cubic crystals.

But now we're talking about the next kind, which is body-centered cubic.

And look, a lot more have a body-centered cubic.

And here, OK, so if it's BCC, Body-Centered Cubic, well, now you know if I take these atoms at these corners, and I add now-- there's a lattice that takes me to the middle.

Remember, my lattice is giving me this symmetry.

My lattice is giving me this.

So it means whatever I put here, I put in all the corners and I put in the middle, right?

That's BCC.

That's what BCC means.

Well, and yeah, if you grow that-- OK, so first of all, eight nearest neighbors-- eight nearest neighbors-- well, you can see that, because I've got the six, but then I've got these ones here, right?

I've got actually it's not the six.

I've got the one along the diagonal, which is kind of the point I wanted to make next.

Oh, this is BCC.

This is BCC, right?

Now, how do you see that it's BCC?

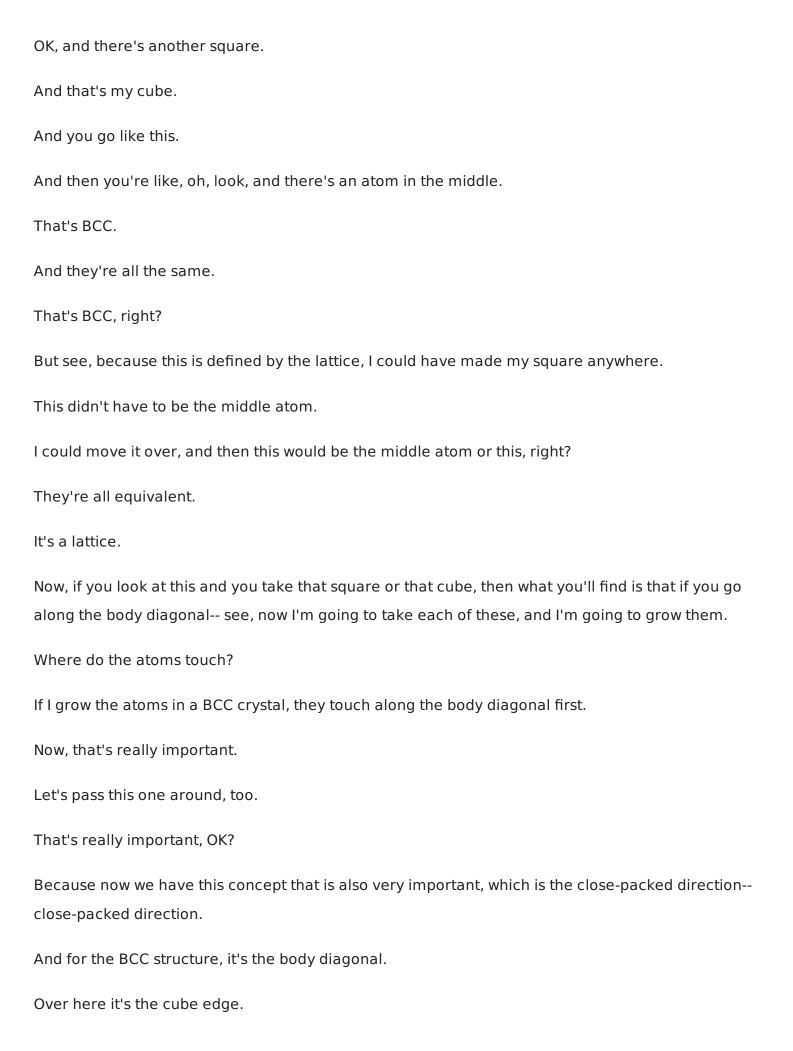
Because you stare at it and you stare at it and you build it.

You get together with friends.

You get together with friends, and you build even more.

And you see how much you can build, and then you look, and you see, look here it is.

There is my square, right?



For a simple cubic, it's the cube edge. Cube edge is the close-packed-- OK, how is that going to work? I'll do this. No, that's going to be confusing. Cube edge close-packed-- oh, that's really small. But you get my point, close-packed direction. Close-packed direction, body diagonal-- what that means is that-- and you can see it right here. If you go all the way back to this-- there it is. As I grow these-- these are the same. They're colored blue just for clarity, just you can see. But these are the same because it's a BCC lattice. And as I grow them, these all have the same radius. These are the ones that touch first along the diagonal, not those, all right? Not those. And that feeds into what the radius is of the atom. I do the same trick, and the APF is going to be 4/3 pi. And now I've got my a root 3 over 4. Why? Because a is the length of the cube. And you can see here I've got four radii, right? Two diameters of the sphere go down the body diagonal.

So r cubed, 4/3 pi r cubed, is going to be the volume of a maximally-packed sphere in a BCC lattice. So this has to be divided by the whole volume, which is a-cubed. But I'm missing something, because there's not just one. There's not just one. There's another one. There's actually two atoms in a unit cell. There's two of these. You can see that one in the middle and then that eighth, eighth, eighth. You've got two. So I've got to multiply it by 2, and it gives you 68%, is the APF. And that's why so many more structures, especially metals, are happy to be BCC. Let's watch the video again, or a different video, this one on BBC. [VIDEO PLAYBACK] - --particle at each corner and one in the center, which is colored pink to make it easier to see. With full-size spheres, you can see that the particles don't touch along the edges of the cube.

Close-packing - But each corner particle does touch the one in the center.

The actual unit cell consists of portions of the corner particles and the whole one in the center.

Eight eighths give one particle.

And the one in the center gives another, for a total of two particles.

In this tiny portion of a body-centered cubic array, you can see that any given particle has four nearest neighbors above and four below, for a total of eight nearest neighbors.

[END PLAYBACK]

OK, now it's really important, right?

Just so you see conceptually, visually how we got this, the close-packed direction for BCC is four times the radius.

I want to write that, four times the radius.

And it's that thing that we're doing now a couple of times, where you've got the radius of this sphere that you're packing in with a given symmetry.

But I've got to write that in terms of the lattice vectors, which are in this case all a, right?

So it's really easy.

But they're all a, so I've got to write it in terms of the length of the lattice.

That's how you get the atomic packing, OK?

Good, now the last one is FCC.

Look at how many elements take the FCC form.

How do you know?

You bring out the periodic table, and you look it up.

Now, many of these elements can take different crystal symmetries.

The ones that are listed are the ones that are often-- well, always the most stable one, right.

They're the most stable one.

But sometimes they can take many different symmetries if you do something like add temperature or pressure or other things to the system.

What's in the periodic table is the most stable one.

Now, the FCC is the last one that we're going to care about.

And it is the face-centered cubic.

Now, OK, so on this one, this is the face, right?

So we've got these atoms that are sharing across the face.
And then we've got these atoms here at the corners.
There's nothing in the middle now, but they're on the faces sorry, the corners and the faces, all right?
And so if you look at this, what you can see from looking at this and you've got to look at it.
Where's my cube?
Where's my unit cell?
You now know it's called the unit cell, right?
Oh, and I see.
And then there's the face atom, right?
There's a square there.
Then there's the atom in the face.
And then there's nothing in the middle.
It's not BCC, right?
But if I look at another edge of that, there's the atom in that face and so on and so on, right?
Now, what's really cool about FCC is that it's got a lot of neighbors.
And it's got more packing.
So for FCC, this is the close-packed direction.
Close-packed direction is the face, is the did I write down?
I didn't write down.
OK, that's fine.
It's the face diagonal, which is a root 2 in length.

And so the nearest neighbors is 12. And the atomic packing fraction for FCC is 4/3 pi times-- and now here we go, right? When I expand them, it's along the face that they're going to touch, right? So that's the close-packed direction. Face diagonal, that's this one here, right? So it's a root 2 over 4, right? Because again, I've got a radius and another and another and another. There's two diameters worth that go across that face. And so that's going to be cubed, OK, divided by a-cubed. Now, is there something missing? Yes. The number of atoms. If you look at a FCC crystal, and you look at the corners, each one of those shares with eight other unit cells, so there's 1/8. That gives you the one, like in our simple cubic. But now you've got all these ones sharing across faces. You've got six of those, each one sharing 1/2 atom. So that's three more. So there's 4. And this gives you a very nice packing of 74%-- 74%. Let's see what our video guy says about FCC. [VIDEO PLAYBACK]

- The face-centered cubic unit cell has a particle at each corner and in each face, which are colored yellow here, but none in the center.

The corner particles don't touch each other.

But each corner does touch a particle in the face.

And those in the faces touch each other as well.

The actual unit cell consists of portions of particles at the corners and in the faces.

Eight-eighths at the corners gives one particle.

And half a particle in each of six faces gives three more, for a total of four particles.

In this tiny portion of a face-centered cubic array, notice that a given particle has four nearest neighbors around it, four more above, and four more below, for a total of 12 nearest neighbors.

Stacking spheres shows how the three cubic unit cells arise.

Now we talk about packing.

- Arranged a layer of spheres in horizontal and vertical rows.

Note the large, diamond-shaped space among the particles.

Placing the next layer directly over the first gives a structure based on the simple cubic unit cell.

Those larger spaces mean an inefficient use of space.

In fact, only 52% of the available volume is actually occupied by spheres.

Because of this inefficiency, the simple cubic unit cell is seen rarely in nature.

Polonium!

- A more efficient stacking occurs if we place the second layer over the spaces formed by the first layer and the third layer over the spaces formed by the second.

That simple change leads to 68% of the available volume occupied by the spheres and a structure based on the body-centered cubic unit cell.

Many metals, including all the alkali metals, adopt this arrangement.

For the most efficient stacking-- Now watch this.

- --shift every other row in the first layer so the large, diamond-shaped spaces become smaller triangular spaces, and place the second layer over them.

Then the third layer goes over the holes visible through the first and second layers.

In this arrangement, called cubic closest packing, spheres occupy 74% of the volume.

Note that it is based-- [END PLAYBACK]

--on the FCC crystal, Bravais lattice.

That's what he meant to say there.

And you really see it come to life, right?

I wish I could do this somehow with the 3D models.

But you stare at the 3D models and you see that-- you know, what's interesting is the way you put it-you slide-- this is what Hooke did with the cannonballs.

You slide that base layer, and then you can stack them differently.

But it's still a cubic system, FCC, all right?

We'll pick up on this on Wednesday.