

**PROFESSOR:** OK, let us resume. I had no idea how many people would be here today, and I think I made 25 copies of the handout. And I see 25 names on the list. And that means that two people did not get a copy of the syllabus. Does anybody need a copy? That's strange. OK. All right.

We covered some introductory material, and I think we've covered enough that you can do a problem set. So it gives me great pleasure to hand out problem set number one. OK, you can think about that.

It is the sort of problem that will either take you two minutes or two hours or infinity. So don't spend too much time on it, but I would like you to put your name on it and turn it in either at the end of the hour or next time so I can make comments if there's something that's mostly right but not quite right.

Let's return to these three simple patterns that we put on the blackboard. And let me make another point about symmetry. The people who sensed that this pattern and the one on the bottom were the same because they had the same motif in them, that they had the same rectangle with one concave side. And I drew a mirror line in here because that locus, when I review this is a reflection from left to right, left the motif, as well as the entire pattern, unchanged upon making that transformation.

Is there not also a mirror line there? Worked for this motif. Why not for this motif? Well, the answer is no, that this is not a mirror line because the symmetry transformations acts on everything, and not just one little bit of space. And if I would take this chain of objects that's translationally periodic with a translation running this way, and I reflected that, I should have another chain running like this. So the direction of the translation vector is not left invariant by this reflection.

So the conclusion here, and it's a subtle one, matter of definition, almost, is that the transformation, the symmetry transformation, if it's to be a symmetry transformation, acts on all of the space, and not just on one local domain. So let me give you an

example of a pattern that doesn't involve translational periodicity. So let me try to make a star as carefully as I can.

What sort of symmetric does that have, or would it have had I drawn it more perfectly? Well, that would be a five-fold rotation axis in the middle because I could rotate through one fifth of the circle. And any of those rotations twice or three times, or just  $2\pi$  over five, would be something that maps the pattern into congruence with itself. There are also mirror lines that go from one tip of the star to the other end.

So that is an example of a pattern, non-periodic, but one that has five-fold rotational symmetry and mirror symmetry. Now, if I put that star in a box and ask, what is the symmetry of that space? There's only one operation which is common to the star and to the enclosing rectangle, and that's this mirror plane.

So the symmetry acts not just on one little part of the space, but it has to leave everything invariant. So in that sense, going to this pattern here, this is not a mirror plane because it doesn't leave the entire pattern invariant. That plane would reflect this one up to here, and we don't have anything there. So the space is not left invariant.

One further definition. We defined what we mean when we say a space or an object has symmetry. We said an object or a space possesses symmetry when there is an operation, or set of operations, that maps the space or the object into congruence with itself. Let me make another definition, and that a symmetry element-- another bit of terminology-- is the locus of points that's left unmoved by the operation. Left unmoved or left invariant.

So for some specific examples, this vertical line is a locus which is left invariant by either the five-fold rotation or any of the mirror planes passing through the points that would be true of the star. So for the star, these are all symmetry elements. For the net combination of the star and the enclosing rectangle, the only thing that leaves a space invariant is this line. The locus that's left and moved is this line, so we refer to that as a mirror plane.

Now, these may be seeming kind of definitions. Nice to have, but what use are they? We will use some of these definitions to answer a question which may seem tricky.

If we do a couple of things in sequence, for example, what is the net consequence of doing, let's say, a rotation combined with a reflection? You can answer that question by saying, what has been left unmoved? And that is the locus of whatever net transformation results from a combination of two or more. So that, again, is abstract, but we'll use that later on. Any question on this?

Let me summarize very quickly what we have found for two dimensions. We found that there are, in a two-dimensional space, three kinds of operations. There is the operation of translation, which we'll call by the vector,  $T$ , corresponding to that transformation.

And there is an operation of reflection. And the locus of the plane, in which the reflection occurs, we'll call a mirror plane. And that's a linear locus. And then, we've seen in these two patterns here an operation of rotation. In particular, in these two-dimensional patterns, we saw the rotation operation  $A \pi$ .

Now, I would put forth for your consideration something that is a profound conclusion. These are the only single-step transformations that can exist in a two-dimensional space. These are the only ones that can exist as single-step operations. We can view these as operations that result in a transformation of coordinates.

And in two dimensions, if we have some position,  $x, y$ , in the space, what the transformation of a translation does is to take  $x$  and add a constant to it. It takes  $y$  and adds, perhaps, a different constant to it. Do the operation a second time, and we'll go to  $x$  plus  $2a$  and  $y$  plus  $2b$ .

So analytically, we can look at these symmetry operations in terms of the transformation of a representative coordinate. If we have a reflection plane, and let's set up a coordinate system where this is  $y$  and this is  $x$ . We have an object here

at the location  $x, y$ , and we reflect it across this locus. It goes to  $\text{minus } x, y$ , if the mirror line runs through the origin and is perpendicular to  $x$ .

So one example of a transformation by reflection is that  $x, y$  goes to  $\text{minus } x, y$ . And this is a case where the mirror plane is perpendicular to  $x$  and passes through the origin. If we do the operation a second time,  $\text{minus } x, y$  would get mapped back into  $x, y$  again.

It comes back to where it started from. So this would be the first reflection. This would be the second reflection.

And we saw in the patterns an example of one other transformation. Let's suppose there was an operation,  $A \pi$ , at the origin, and this was  $x$ , and this was  $y$ . We started out with a motif here at  $x, y$ .

If we rotated that by 180 degrees, it would go down to a location  $\text{minus } x, \text{minus } y$ . So the operation of a 180-degree rotation is going to analytically correspond to a transformation of going from  $x, y$  to  $\text{minus } x, \text{minus } y$ . If we perform it again, it would go back to  $x, y$ .

OK, let's look at this in more general terms. In a two-dimensional space, we've got two dimensions to diddle with. We can change the sense of no coordinate. That's translation.

We can change the sense of one coordinate. That's going to be reflection. We can change the sense of both coordinates. That's going to be a rotation. That's all we can do. So these are the three basic operations in a two-dimensional space.

I gave you special cases to make things easy, but regardless of where the mirror plane is, parallel to or perpendicular to an axis or not, and whether it passes through the origin or not, a mirror plane has the operation of reversing the sense of one direction. Just the sense of one direction that is reversed. And the rotation, be it a rotation through 60 degrees or 90 degrees or 180 degrees, is always taking both coordinates. It's making a transformation of both coordinates. If you only have two

coordinates with which to play, that's all you can do.

Let's do some giant extrapolations. If we have a strictly one-dimensional pattern where there's  $x$  and nothing else, then they're only going to be two coordinates. And there are going to be only two ways we can transform coordinates.

So in a one-dimensional space, we can change the sense of no coordinate, and that's going to be the operation of translation, or we can change the sense of one coordinate, and that's going to be the operation of reflection. No rotation in a one-dimensional space.

Now, let's extrapolate in the other direction. In a three-dimensional space, the sort that we're going to be concerned with when we want to describe the symmetry of real crystals, you've got three coordinates to permute. So it follows then, without saying what they are, in 3D, there are going to be four distinct one-step operations.

And then five dimensions? Hey, that's a nice thing about mathematics. You could play any game you like. Not only that, but you make up the rules. In a five-dimensional space, there's going to be six transformations.

Would we ever want to worry about five-dimensional crystallography? Well, let me hang out a teaser and not answer the question. Yeah, there are crystals for which as many as six-dimensional symmetries are necessary. Wow. Doesn't that blow the mind? We'll return to that, and I'll explain why later on.

Another thing you might ask, why did I sneak this in? Why did I say one-step operation? Well, it's something we should worry about, and unfortunately, we will.

What if you take a motif, translate it, rotate it around a couple of times, reflect it, bounce it up and down three times, and then put it down? How do you get from the first motif to the final one there? Is there an infinite number of operations?

Mercifully, no. The number is small and very finite.

And we will systematically, in another week's time, examine specifically two-step operations. And as with many things that we'll encounter, we might not be clever

enough to think them up. But when we start putting things together into a synthesis, suddenly we're going to stumble over something we don't know how to explain, and we will have arrived, like it or not, at a new feature which we perhaps hadn't anticipated.

OK, any question at this point? All this has been in a way of general introduction. We're going to now take things more slowly and proceed one step at a time.

I would like to confine our attention for the moment on two-dimensional symmetries and examine the sorts of patterns that can exist in two dimensions, fabric patterns, floor tile, grillwork, and so on. And we've seen that, basically, there seem to be three operations, three kinds of operations, translation, reflection, and rotation. That's an infinite number of operations because we are not specifying whether or not the rotation angle is restricted to any particular value. No reason why it should be. There are lots of rotational symmetries that are absolutely lovely.

But let's build things up. And I would like to first look at the operation of translation, which we've said a great deal about to this point. Translation has magnitude. It has direction. So it acts like a vector.

But just like a vector, it has no unique origin. Perform the operation twice, and you have a position that is two translations removed from the origin. Do it three times, you have a translation that's three times out.

If a motif sits here, the motif must sit at the end of this translation in the same orientation parallel to itself. It must exist at the end of two translations. And if the operation acts on all of the space, if we say a translation is present, we really imply that there's an infinite row going to plus infinity and back to minus infinity. And there is a motif hanging at the terminal point of every vector.

Now, we can summarize this periodicity with a convenient device. Let's take some fiducial point and summarize the translational periodicity by saying that something that is hung at one point, either here, or maybe hung also off in some other direction relative to the translation, that something hung on one of these points is

automatically reproduced for us at every point. So what we have done through this device is defined something that is called a lattice point.

And this is an abstraction of the translational periodicity. There is an array of points, geometric fictions, which we have constructed. And we ascribe to this geometric fiction the property that anything hung at one of these points, be it a benzene ring or be it a Santa Claus on Christmas wrapping paper, is understood to be automatically reproduced at every other one of these points.

It is this array of fictitious points that is the proper designation of what we refer to as a lattice. So a lattice is an array of fictitious points that summarizes the translational periodicity of the crystal. It has a property to repeat that something hung at a particular disposition relative to that point and with a particular orientation is understood to be hung at every other lattice point in exactly the same way. So that is a lattice.

And this is one of the most abused terms in crystallography. We talk about the sodium chloride lattice. The sodium chloride lattice is a set of points that are placed at the corners of a cube and in the middle of all the faces.

This is the NaCl lattice. If I choose to decorate that lattice with one sodium and one chlorine, then I have atoms sitting at these lattice points. And that is the sodium chloride structure. That is the proper term for the atomic configuration. So lattice is a geometrical term, and it's an abstraction. Structure is the actual atomic arrangement.

Now, since I realize already that I am among friends, I can confess that I very often recklessly abuse the term lattice. If I talk about lattice energy, lattice diffusion, lattice vibration, I'm not talking about abstract points bobbling around or something going through this array of little points. I mean, I should talk about structure diffusion, structure energy, structure vibration. But man, that just doesn't have the established terminology, and it doesn't have the zing and music of something like lattice vibrations.

So I do it all the time. Don't tell anybody else that I said this to you, frankly. But it's never going to be stamped out. But now you perhaps are informed enough to at least blush slightly when you talk about lattice energy or lattice diffusion, realizing you're using the term incorrectly and that you know better, but everybody else does it, so you do the same thing. So that is the definition of lattice.

Now, suppose I take this space, to which I've added a first translation, and I'll call it  $T_1$ , implying that I'm going to add something else to this space, which I'm free to do. I can put in a second translational periodicity because this is a two-dimensional space. How do I do this? And the answer is very carefully because the second translation could not go in the space parallel to the first one if I put in a second translation,  $T_2$ , which is totally incommensurate with  $T_1$ .

The things blow up in my face. I don't have a lattice. I will get lattice points all over the place. So this is impossible. So if  $T_1$  is not equal to  $T_2$ , this space self destructs.

If  $T_1$  is a multiple of  $T_2$ , then if I say a translation exists of length  $T_1$ , and I add a second translation twice  $T_1$ . I've already got those lattice points. And that's nothing new. So if I want to say there's a second translational periodicity in the space, the only thing I can do is pick a  $T_2$  which is not parallel to  $T_1$ .

And then this  $T_2$  will pick up everything in the space. It's going to take these lattice points and generate them at equal intervals,  $T_2$ . But for that matter, it acts on everything in the space. So we could think of this translation,  $T_2$ , as moving this entire infinite string of lattice points separated by  $T_1$  and giving me a whole string of lattice points.

So now, having taken two noncollinear translations, those translations will imply a two-dimensional space lattice in which motifs will be hung at translations  $nT_1$  plus  $mT_2$  where  $n, m$  are integers that go from minus infinity to plus infinity. OK, so this is a two-dimensional space lattice, or sometimes it's referred to by the term a lattice net. Good term. It looks like what fishermen throw in the water to snag fish. So it is a net, in terms of something that we're familiar with in everyday life.

All right. So we've specified a space lattice, but it is a highly redundant pattern. We've got a doubly infinite set of lattice points. And the unique nature of the pattern, the structure, is going to be whatever is associated with one lattice point. So if we specify what's going on in the vicinity of one lattice point and establish that at every other lattice point, we have the entire infinite two-dimensional structure.

So let's ask now, how we can define the area that is unique to one lattice point. And there are several ways of doing this. We can specify T1, and then specify T2. We'll repeat T1 up to here. T1 will repeat to T2 over to here, and we will have defined the area that is uniquely associated with one lattice point.

So if I can tell you what's going on within the confines of this parallelogram, then I have given you the unique part of what is hung at a lattice point, and which is reproduced only by translation. And this is a very important construct. It is something that is referred to as the unit cell, or sometimes just cell for short.

And now we encounter a curious ambiguity. T1 and T2 imply an array of lattice points. And this particular choice of T1 and T2 define a cell.

But the reverse is not true. If I give you-- and what do I want to say? That a particular lattice does not specify a unique unit cell. Or, stated another way, there are many different choices for T1 and T2 that would specify the same unique area.

I could take this as a T1 prime, and then I would have a cell that looks like this. And that would also define the area associated with one lattice point. It's not clear this oblique thing with one very long T1 prime would have very much to commend it, but there are many ways, many choices, for T1 and T2, to find exactly the same lattice.

We could take this as T1, this as T2, same lattice, same array of lattice points. Take this as T1, this as T2, same array of lattice points. Take this as T1, this as T2, that's yet another choice.

So there are an infinite number of translations. Special name for this, to introduce a bit of jargon again, these are very often called conjugate translations. So all this is still nothing more than simple geometry, but if you invent some fancy words, you

really have to do that to impress your friends. Yeah, you had a question here?

**AUDIENCE:** Yeah. So you can define magnitude for  $T_1$  and  $T_2$ , all those constants. But you're changing the directions of  $T_1$  and  $T_2$ , and you're saying, even though you're changing those directions, it's still the same unit cell?

**PROFESSOR:** Yeah, provided I have some new translation like this one here, which is really this  $T_1$  plus this  $T_2$ , this would define a very, very oblique cell that looks like this. But yet, the terminal points of  $T_1$  prime and-- I need a term for this. I'll call this  $T_2$  prime. The terminal points here are going to be exactly the same as the nodes that are defined here. So they are two choices for one in the same lattice.

OK, so the implication of this is we're going to have to have rules. And some of these make common sense. You could pick, in a two-dimensional lattice, some absolutely ridiculous unit cells defined in terms of very long vectors that define a cell that is a very, very oblique cell.

So it's the lattice that's defined by this translation here. And the next translation parallel to this one would go way up to something like this. So there's a  $T_1$ . There's a  $T_2$ . This crazy cell here works. That's the area that's associated with one lattice point.

But clearly, it has absolutely nothing to commend this choice. There's nothing to be gained by using these long translations that make very extreme intertranslation angles. Your intuition would say, why would you want to do that, you dummy?

Let's take these as the translations, which is something I sort of naturally did all along. And what are we doing? We're picking the shortest translations. So there's one very common sense rule.

Another rule, getting a little bit ahead of the game, but suppose I examine the lattice that describes the arrangement of four floor tiles. If I take a lattice point right at the point of intersection of the joins between the tiles, that is a cell that is exactly square. And it's exactly square because there's a four-fold axis in that pattern that leaves things invariant after a 90-degree rotation.

So if that's the nature of a lattice, if it in fact is constrained because of the symmetry that is there to have two translations identical in length, in fact, identical in every way. Pick those as the choice of the cell to emphasize that special key feature of the lattice. So a second row, which is a second and final one, is to pick a T1 and T2 that displays the symmetry, if any, of the lattice.

Which introduces us to a feature which we'll elaborate much more later on, that the translational periodicity and the symmetry of the lattice are two things that go together. That the fact that there is translational symmetry drastically reduces the number of symmetries that you could have, the fact that there are symmetries possible for presence in a lattice restricts the number of different kinds of cells. So these are two aspects of the pattern, the symmetry that's in it and its periodicity.

OK, but these are the only two rules that we really need to pick what's called the standard cell. Take the shortest translations that are available to you, and pick translations that display the symmetry that may be present in the lattice. Any questions or comments? Any comments?

OK, I think I have time for one last major point of discussion. And what we are going to embark on now is a process of synthesis, which will occupy us for a couple of weeks. What I'm going to do is start with a translation. And this defines an infinite string of lattice points.

Now, I know that in two dimensions, I have two kinds of symmetry operations that are present, either rotation or translation. So now, I'm going to ask the question, what happens if I define a lattice, or at least one translation in a lattice, and now I add to that lattice an operation of rotation, OK? I can do that. We've seen examples of translationally periodic patterns that have rotational symmetry.

So let me suppose I add to this space a rotation operation,  $A_\alpha$ . And there's no unique origin to the translation. There is no unique location for a lattice point. So I can put the operation  $A_\alpha$  in at my designated lattice point.

Now, if I do that, all hell breaks loose because now I have a rotation operation  $A_\alpha$ . This has a translation coming out of it. That translation will be repeated up here, an angle  $\alpha$  away.  $A_\alpha$  acts on everything, so it's going to take this translation and move it over here to a location for another translation.

This is a lattice point. This is a lattice point. And this business is going to go on until it comes around full circle.

Let me focus my attention on just one of these translations, and this will be this one up here, the one that is  $\alpha$  away from the first in a counterclockwise direction. So here sits another translation, and that means this is a lattice point. At this end of the translation, the same thing is going to happen. The operation  $A_\alpha$  is moved to this location at the end of the translation. That means that anything coming out of this lattice point must also be repeated at angular intervals,  $\alpha$ .

And now I'm going to focus my attention on this translation here. And there will be a translation that goes up like this, and this is a lattice point. And now, in the words of that famous musical, there's big trouble in River City. Because we started out by saying that everything in the space was periodic at an interval,  $T$ , a translational interval,  $T$ .

This is  $T$ . This is  $T$ . This is  $T$ . Here we have a lattice point. This jolly well has to be  $T$  as well, or we've contradicted the basic assumption of our construction. Well, that's over restrictive. This doesn't have to be  $T$ , but it has to be some multiple,  $p$ , of that translation.

$p$  could be 0.  $p$  could be 5. But it has to be an integral number of translations because this translational periodicity has to work everywhere, including up on the top of this trapezohedron. So that's a constraint.

This angle is  $\alpha$ . We cannot let  $\alpha$  be arbitrary because the only way we can add a rotation operation  $A_\alpha$  to a lattice is for a value of  $\alpha$  which makes this translation be a multiple of the original one. Now, let me take this geometry, and I'm going to extract the basic constraint from it.

This is some integer,  $p$  times  $T$ . This is  $T$ . This is  $T$ . This is  $T$ . This is  $\alpha$ . Let me lickety split drop down a perpendicular to the original translation.

This is  $T$  times the cosine of  $\alpha$ . This is  $T$  times the cosine of  $\alpha$ . This total length is  $T$ . This length in here is  $p$  times  $T$ .

And now I can go away from the geometry to an equation, something you probably prefer to deal with. And what this constraint is expressed analytically is that my original translation,  $T$ , minus twice  $T$  times the cosine of  $\alpha$  has to come out equal to an integer,  $p$  times  $T$ . And there's my constraint.  $\alpha$  has to satisfy that condition.

Well, I can immediately cancel the  $T$  and write this as one minus  $2$  cosine of  $\alpha$  is equal to an integer,  $p$ . And it figures that that has to be the case because none of this construction depends on the size of the original translation that I took. And now, let me solve for the values of  $\alpha$  which are compatible with a lattice. This says that cosine of  $\alpha$  is  $1$  minus  $p$  over  $2$ . And unless that condition holds, my combination is incompatible.

So I'm going to let that stew with you until next time. But what we've set up is something where we can just plug and chug, put in different values of  $p$ . And if I start out with a value of  $p$ , and let's let  $p$  be equal to  $4$ , and then find one minus  $p$  over  $2$ , which is supposedly the cosine of an angle,  $\alpha$ . If that's  $4$ , I will have minus  $3/2$ .

And the value of  $\alpha$  obviously does not exist. Cosine of  $\alpha$  cannot get greater than  $1$ . If  $p$  is equal to  $3$ , then  $1$  minus  $3$  over  $2$  is minus  $2$  over  $2$ , or minus  $1$ . You like the way I do that arithmetic in my head just like that?

And the angle whose cosine is minus  $1$  is  $180$  degrees. And what that says is that a two-fold axis works. So I can drop a two-fold axis into a net. And what that's going to do is take my original translation, rotate it  $180$  degrees, and the second translation is going to sit here. Rotate it  $180$  degrees in the reverse direction, and then the second lattice point sits here.

And lo and behold, just as advertised, the distance between the first lattice point and the final lattice point is three translations. So I can put a two-fold axis in any lattice whatsoever because this is compatible simply with a lattice row. So one possible combination of rotation in a lattice is going to be any lattice whatsoever, and what we can add to this is a rotation operation  $A\pi$ . And we'll have two full rotation operations which are translationally equivalent.

All right. Several integers to go. We would want to try  $p$  equals 2. That's going to work.  $p$  equals plus 1 is going to work.  $p$  equals 0 is going to work. And we will find a very limited number of rotational operations that are compatible with a lattice. And this is going to give us a small number of the possible combinations of lattice and rotational symmetry in two dimensions.

So we'll pick up from there next time, and we'll very quickly determine the remaining possibilities and take a look at what the arrangement of symmetry elements look like in these lattices. OK, once again, I have some extra copies of the syllabus if somebody did not get one. And I'll have extra copies of the problem set.