PROFESSOR: Any questions before we push bravely onward? OK if there's no question on any of this I shall clean off the board. And the last thing I wanted to do in connection with thermal expansion is to examine how the macroscopic linear thermal expansion coefficient relates to the nature of the potential minimum between-- in the attraction between-- neighboring atoms. So let me suppose we have a pair of atoms separated by some distance, d, and there is a cohesive force between them or else the material would not be in a solid state. And the nature of the potential-- and I'm going to call the distance between the atoms, x-- and this is going to be the energy. And I'm measuring now relative to-- let me call this d as I did over here-- so the energy as a function of d is going to consist of a very short range, repulsive interaction, that rises very, very rapidly when you attempt to squeeze the atoms any closer than a fairly small value.

And then there'll be some sort of cohesive energy. And everybody loves to model ionic compounds because in an ionic compound this cohesive force would be purely a Coulombic force that would be, in rationalized MKS units, 1 over 4 pi epsilon zero times the product of the charges and divided by the distance between them. Taking those two potentials together, and you've all seen this many times before, there is a minimum in the energy. And then absolute zero-- that is the separation at which this atom pair would sit-- and this would be the binding energy of that ionic pair. If you carry this through to get the entire energy of the crystal, you find that the energy of the crystal goes as 1 minus 1 over-- haven't introduced this term yet, so let's hold off on that.

What I'm going to do now is to take a look at this potential and expand it around the equilibrium separation just with an empirical collection of terms. But from the shape of this well, we can see why the bond length should increase as the energy of the atomic pair increases. At absolute zero, the separation will be this equilibrium separation, d zero. But as you increase the temperature and pump vibrational energy into this pair of atoms, they will get a certain increase in energy. And as a result, the pair will be able to vibrate between these two limits. Put in some more

thermal energy by raising the temperature, and the pair will be able to vibrate between these limits-- larger limits. And so the average position of the atom, the separation of the atoms, is something that is going to increase with increasing temperature.

And that is purely a consequence of the asymmetry in this potential well. If this were a Coulombic bond, we know exactly how to model the attractive part. The repulsive part is a little harder to model because that is something that's inherently quantum mechanical. As the ion pair gets close together, the electrons start to perturb each other's orbitals. And a very common thing to do is to model this as 1 over d to the sum power n. And n is typically on the order of 8 to 12. So this is something that rises very, very steeply.

I was once at the Gordon conference where a fist fight almost broke out because somebody was giving a presentation and started from the beginning by introducing this model to the potential well. And he says, "As usual, we'll write this as a power law, 1 over d to the n." And somebody in a front row jumped up and said, "what do you mean usually? Sensible people use exponentials." And the speaker said, "No, I'm going to use a power law." That's dumb. Exponentials work better. Power laws, exponentials, power laws, exponentials. But in point of fact they're both grossly empirical and one is not better than the other. The algebra changes a little bit, but people get very, very emotionally attached to their physical models.

AUDIENCE: [INAUDIBLE] law in the exponential.

PROFESSOR: Good, you should've been there to break up the fight. If you'd gotten between them, you'd have been likely punched in the nose. [INAUDIBLE]

OK so I'm going to use the power law because as we've seen they're the same thing as exponentials. So now what I'm going to do is expand this in a purely empirical way-- measuring distance from the minimum of the potential well. So what I'm going to say is that the potential as a function of x-- and now I won't call it d because I'm going to measure distance, x, from the minimum in this well. I'm going to say V is a function of x. There is a well in which the-- which keeps the atoms

separate. I'll assume that is a parabolic potential well, so it'll go as first some constant c times x squared. Then the thing that causes thermal expansion is the asymmetry. And I want the asymmetry to increase the energy more rapidly on the side of negative x than on the side of positive x. So I'll put in a term, g x cubed. And I put a negative sign in here because I want it to go up as x becomes negative. That means the ion pairs are decreasing at separation.

And finally, a very fine touch, if x becomes very large, the potential well should soften. The edges of this are starting to level out and get lower than the purely parabolic part for very large separations. So that's what I'll use as a very simple model for my potential. This is what gives the asymmetry, and this is what gives softening. And now I'm going to ask, what is the average value of x? The probability of finding a particular x is going to be proportional to e to the minus V of x over kt.

So I can say that the average value of x is going to be the integral from minus infinity to plus infinity of the value that I'm trying to find the average of, namely x times the probability of finding that x. And that's going to e to the minus V of x over kt. And I will integrate that over x. And then I will normalize by a term which is the integral of the probability from minus infinity to plus infinity of e to the minus V of x over kt. So that's a general expression for an average. It's the thing you want to average times the probability of finding the particular value divided by the integral of the probabilities.

OK now let me do some very straightforward things and I'm just going to rattle these off very quickly. We'll expand this in terms of a series of terms. And I'm going to expand both the numerator and denominator using the approximation that e to the u is approximately equal to 1 plus u. So the numerator-- x times e to the minus cx squared over kt. I'm going to take the higher order terms and say that e to the gx cubed over kt times e to the minus-- this is a minus sign out in front-- times e to the fx fourth over kt, can be approximated by, since these are very, very small terms, 1 plus g x cubed over kt times 1 plus fx fourth over kt.

So that's going to be, if I put an x e to the minus cx squared, I'm going to have a

term 1 plus g x cubed over kt, plus f x fourth over kt. And then a very, very minuscule term, f times g times x to the 7th over kt. And I'm going to throw that out. If I look at these integrals one at a time, the integral from minus infinity to plus infinity of x e to the minus cx squared over k t, that's the first term in expansion, times dx. That's going to be zero. Because for positive x, the thing that we're integrating is plus. For negative x, the thing that we're integrating has the same exponential but has a minus sign. So that integral is zero.

So the next term I want to look at is x times gx cubed over kt. And for this I turned to my handy book of integrals. The integral from zero to infinity of x to the 2n, where that quantity is even, times e to the minus a x squared dx, is equal to, as you all know, 1 times 3 times 5 all the way up to 2n minus 1 divided by 2 to the n plus 1 times a to the n times the square root of pi over a. And proof of that the integral is left as an exercise to the reckless student. Yes?

AUDIENCE: The x cubed [INAUDIBLE].

PROFESSOR: That's why this is a 2n here. So I can say that the x cubed term is--but we don't have an x cubed term. The next term is going to be equal to x fourth. And this I'm going to drop because that's going to be x fifth.

So the integral from minus infinity to plus infinity of x to the fourth power times g over kt times e to the minus cx squared over kt dx. If I use this formula, turns out to be a very, very simple thing. It turns out to be 3/4 times the square root of pi times g times kt over c to the 5/2. And kt is to the power 3/2. So that is-- if I throw away the term in x times x fourth which is odd, that will vanish and I've then thrown out only a really large term in x to the 7th.

For the denominator, the integral that is there before us is the integral from minus infinity to plus infinity of e to the minus cx squared over kt times 1 plus g x cubed over kt. This thing is going to vanish because x is odd. And then I'll have plus fx fourth over kt. That will not vanish but it's going to be a relatively small term, so I'll go like that. Which means I just have to integrate this Gaussian factor. And that turns out to be equal to 2 times 1/2 times square root of pi kT pi times T over c.

So this is the denominator. And if I take the ratio of those two integrals, I have that the average value of x will be equal to 3/4 square root of pi times g times kt to the 3/2 over c to the 5/2, divided by the square root of pi times kt over c to the power 1/2. And if I carry through the algebra correctly, this turns out to be 3/4 of g over c squared times kt. So there is the average distance between this pair of atoms as a function of temperature in terms of characteristics of the potential. The first thing that is very gratifying is that the bond length, according to the simple model, should increase linearly with temperature. So it tells us we would expect things to expand linearly with temperature which corresponds to reality.

The next thing we'll see is that the amount of expansion goes inversely as the square. That's a strong dependence-- inversely as the square of the parabolic part of our potential. That was the c-- c was the coefficient in front of cx squared in our potential. So the stronger the bond, the smaller the thermal expansion coefficient is in proportion to the reciprocal of the square of that term. And then finally, the last important term to survive is g, the asymmetry. And the thermal expansion coefficient should increase with the first power of the term that describes the asymmetry of the potential well.

So your intuition would tell you that that's the way the thermal-- linear thermal expansion coefficient should vary. The interesting thing is that it depends more strongly on the parameter that gives the parabolic part of the potential well. And secondly, that it does predict a thermal expansion coefficient that increases-- the separation that increases with-- in proportion to temperature. And therefore there is a constant linear thermal expansion coefficient. Now all this is true at elevated temperatures. At low temperatures, thermodynamics kicks in. And it turns out that the linear thermal expansion coefficient, as does energies of vibrating atoms, must go to zero as temperature approaches absolute zero. So a typical variation of the thermal expansion coefficient with temperature is something that does this. The same way as-- the same sort of variation as things like heat capacity. And this temperature in here is on the order of the Debye temperature of the particular material.

All right, so much for linear thermal expansion. And I would now like to turn to something much more interesting. And that is physical properties that involve property tensors of rank higher than two. One of the important and more interesting of these is a property called piezoelectricity. Piezo means pressure, so the property literally means pressure electricity or pressure induced charge. Now what is the charge? First of all, this does not describe a property where-- if I were to pick up a chunk of crystal, and I drop it because I just got an electric charge. These are not mobile charges, these are bound charges. And the reason for the induced charge is the fact that we are squeezing or stretching an ionic material, and that's moving charged ions around. So what we're going to do if that process involves motion of charged ions is to induce a dipole moment per unit volume.

I have a little primer on some quantities in electromagnetic theory and I-- I brought them with me upstairs to look them over and I forgot to bring them down. But I don't think we'll need them in what's left of this hour. So let me say that for matter and bulk, the quantity that is involved in piezoelectricity is the polarization. And polarization is dipole moment per unit volume. And a dipole moment, to refresh your memory, is that if I have a positive charge plus q and negative charge minus q separated by a distance, d. The dipole moment, which I'll indicate by a lowercase p, has a vector quality and it's equal to the magnitude of one of these charges times the distance between them.

And we'll define the distance as going from the positive charge to the negative charge. That's a crazy way of defining a pair of charges of equal but opposite sign. The reason for defining a quantity like the dipole moment is that this combination of charge and separation of the charges comes up in all sorts of problems in electrostatics and electrodynamics. And this is the delight of people who teach elementary physics. You are given, on the first quiz, a question that says-- calculate the electric field that is created by a set of dipoles on the Great Court which spell out MIT.

And we can come up with all sorts of crazy configurations of dipoles and then calculate the field that they produce. And the field turns out to be something that

always involves the product of charge and separation in a vector sense. Probably the best illustration of this would be if I have a dipole charge plus q, charge minus q, separated by d. And I put it in the electric field. The electric field, which is defined as the force per unit charge on a positive charge is going to pull the positive charge this way. And it's going to pull the negative charge this way. And what that's going to do is to place a torque on the dipole. And that torque is going to be equal to a vector product of the electric field and a vector. You can express it in terms of the separation of charges defined in a vector sense going from the positive charge to the negative charge.

So there's an example of how the torque on a dipole directly involves the product of charge and the separation between them and the angle between the field and the dipole. So it's a useful quality and, without further apology, we will use it in our discussion. Now polarization-- dipole moment per unit volume-- is just going to be the dipole moment of one dipole pair times the number of them per unit volume. And that will be a macroscopic measure of polarization.

OK, if we subject a piece of material that contains ions to a stress- so here is a stress tensor, sigma ij. Let me call it jk. We will create reorientation of the dipoles. We will have a polarization, a dipole moment per unit volume. This will be a vector because there will be some net dipole moment per unit volume. And that will just be the sum of all the little individual dipole moments on the ions-- ion pairs. And if the stress is not too large, every component of polarization is going to be given by a linear combination of every one of the components of stress. So we will have an array of coefficients, d ijk The i goes with the P and the j and k goes with the elements of stress.

This is something that's called the direct piezoelectric effect. It's the basis of a lot of every day devices-- pick ups on the old records which nobody uses anymore, cigarette lighter which nobody uses anymore because everybody's quit smoking-- but worked the cigarette lighter, in some of the more modern incarnations of the lighter, was the piezoelectric effect. It's important to note that the charges that are involved in the piezoelectric effect are bound charges. Again you can't get a shock

by picking up a piece of a strongly piezoelectric material like quartz. Might say then, well if there's no spark, how could a piezoelectric material in a cigarette lighter cause the lighter fuel to ignite. The charge doesn't move. How could there be a spark? How could the lighter fluid be ignited? Anybody got an idea?

Charge can induce current flow in circuit elements that are removed from the charge. So if you have a little capacitor in the lighter that is near the piezoelectric element that will develop the charge, you can induce current flow in a circuit as a result of that capacitor experiencing the electric charge of the piezoelectric induced charge. And that's how the little piezoelectric cigarette lighters worked. OK, this stress-- array of stress elements, nine of them, constitutes a tensor of second rank. Polarization is a vector per unit volume. This is a tensor of first rank. This is a tensor of second rank. Therefore it follows that this array of coefficients, d ijk will be three equations involving all nine elements of stress.

So it'll be a total of 27 coefficients in the array. And this array constitutes a tensor of the third rank. So this is clearly a property tensor which relates a generalized force-- the stress tensor to a generalized displacement, which is the dipole moment per unit volume. Since this is a property of a crystal, that tensor is subject to symmetry restrictions. In particular, if there is some direction, cosine scheme Cij, that corresponds to the operation of a symmetry element, then it follows that if we evaluate the new tensor elements, d ijk prime in terms of the old elements, that is going to be a transformation of the form Cil, Cjm, Ckn times all 27 of the original tensor elements, d lmn. And the l, m, and n are dummy indices, just as with our second rank tensors. And the ijk are real indices that go with the subscripts on the particular tensor element.

So there are 27 coefficients. And each transformed element is going to be a sum therefore of 27 coefficients times-- each times three direction cosines. So each transform tensor element is going to be given by a sum of 3 times 27 quantities. And to do the complete transformation would involve doing it 27 times. So 3 times 27 squared is the number of terms that we're going to have to write down to transform the entire tensor. Not a terribly encouraging prospect unless you use the

method of direct inspection, namely that the tensor transforms like the product of the corresponding coordinates. And then it works fairly quickly, particularly for symmetry transformations, where there are a lot of zeros in the direction cosine scheme.

So we're going to have to do this for each of the crystal-- crystal point groups. So we're going to have to do this exercise of 3 times 27 times 27 times the 32 point groups that exist, which becomes an even more daunting task. But let's do one such transformation and let me show you that it, in fact, it's going to go fairly easily. So let me follow the tracks of what we did with second rank tensors and examine the restrictions imposed by inversion.

OK so the transformation of the axes, as we've seen before, that's produced by 1 bar. That's going to take x_1 and change its direction to minus x_1. It's going to take x_2 and change its sense to an x_2 prime that points in this direction. And take x_3 and change its sense to something that points down here. So that's x_3 prime. So the relation between the axes, before and after inversion, is that x_1 prime equals x_1-- minus x_1-- x_2 prime is equal to minus x_2. And x_3 prime is equal to minus x_3. And we've seen this before. It's deja vu all over again.

So C_{ij}, the direction cosine scheme, is equal to minus 1, 0, 0. 0, minus 1, 0. 0, 0, minus 1. So let's transform a representative tensor element for a change of axes that corresponds to that direction cosine scheme. And that's the same as physically inverting the crystal and demanding that the property be unchanged if that is a symmetry transformation which leaves the crystal invariant. So if we look at some d_{ijk} prime, that's going to be C_{il}, C_{jm}, C_{kn}, d_{lmn}, where this is a sum over the index l, the dummy index m, and the double index n, from 1 to 3.

If we sum over C_i something, the only term of the form C_i something, regardless of what i is, is going to be the diagonal term C_{ii}, the diagonal direction cosine C_{ii}. In other words, if i were 1, the only term of the form C_1 something that is non-zero, is C_{11}. If I sum over m, the only term that is non-zero is C, with m equal to j. So this is going to be C_{jj}. And if I sum over n, the only term that is going to be left is C_{kk}. And

all this will be times d ijk, the single tensor element. Regardless of the values of i, j, and k, they are all equal to minus 1. So the operation then of inversion, then says that for the transformed crystal, d ijk prime for any i, j, and k, is going to be equal to minus d ijk. But if this is a symmetry transformation, the tensor element has to be the same before and after. And the only number which can be equal to the negative of itself is zero. So we have, with one swell foop, transformed 27th tensor elements-- each one of them a sum of 27 elements in the original tensor.

So the conclusion is, if a crystal has the operation of inversion, all d ijk vanish. What does that mean? Means the property just doesn't exist. So no crystal which has an inversion center can display piezoelectricity. Which means that none of the 11 Laue groups can be piezoelectric. And the only point groups for crystals that can be piezoelectric are the 32 minus 11 equals 21-- and this isn't even one of my good days-- acentric point groups-- the noncentrosymmetric point groups.

And, these, in principle, can be all different. So we can't get away with just looking at the restrictions of Laue groups as we did with second rank tensors. We're going to have to look at every one of the point groups that have no inversion center. And these can, in principle, be different, and they usually are. Let me give you a physically-- physical feeling for why the piezoelectric effect cannot exist for a crystal that has an inversion center in it. Let's suppose we cut a wafer from our single crystal, regardless of orientation. And we subject it to a compressive stress.

We will see-- and I've got a primer on some simple electrostatics that may be useful-- that a polarization in the x1 direction manifests itself as a charge per unit area on the surface and an opposite charge on the other surface. So P1 corresponds, numerically and physically, to a charge per unit area on a surface that's normal to x1. OK now let's suppose that that crystal has an inversion center in it. And that means we should be able to invert the crystal and measure exactly the same charge per unit area. Well, if this is surface a, and this is surface b, we can imagine ourselves doing the thought experiment in which we invert the crystal.

So this surface becomes b and this surface becomes a. And we apply the same

sigma along x1-- a compressive stress. It's really doing exactly the same thing that we were doing before-- inverting the crystal. And now we say that the property has to stay the same. So now we are demanding that surface b have a positive charge per unit area, and surface a develop a negative charge per unit area-- completely the reverse of what happened here. But yet what we're doing is just squeezing the plate. The crystal can't tell which side is up, which side is down. We're applying the same compressive effect. So these two distributions of charge are not the same and can be the same only if that charge is zero. So physically we can see why the crystal can't be piezoelectric.

If you don't like to invert the crystal-- if you can't do that physically-- one thing we can do is leave the crystal alone and invert the compressive stress. So this is sigma top and this is sigma bottom which is exactly equal to it but opposite in direction. If we invert the stress relative-- relative to the crystal-- then what we've done is to take sigma top-- leave the crystal alone-- so this is now the sigma that was squishing the top. Here's the sigma that was squishing the bottom and well, that's clearly doing the same thing. So inverting the stress, relative to the crystal, is the same as inverting the crystal relative to the stress. And nothing is supposed to happen but clearly the sign of the charge is going to be reversed. So that just won't work. The charge has to disappear.

OK this is the direct piezoelectric effect. It can exist only for crystals that lack an inversion center. Let me mention some other piezoelectric effects. So we mentioned that a polarization, given by a third rank tensor times an applied stress, sigma ij, is the direct piezoelectric photoelectric effect. However, if we have a stress, we also have a strain. So another piezoelectric effect, which is not dignified with a name, is that we can apply a stress that creates a given state of strain. And we again, we'll get a polarization per unit-- a charge per unit area of polarization.

And this is a set of coefficients which are represented by e. And we can write a tensor relation of this sort-- that components of polarization, charge per unit area, normal to axis xi, is given by a linear combination of every one of the components of strain. This is something that is not dignified by any name. And clearly, the

piezoelectric coefficients, e, have to be related to the piezoelectric coefficients, d, by the elastic constant somehow-- unless we are doing the same thing. We've got to create a stress, operationally, in order to create the strain. So a stress creates a strain. And that has to describe the same polarization if we've done the same thing. So the e's and the d's have to be related.

Another piezoelectric effect involves a applying an electric field. And if we apply an electric field, we will in general create a strain. This direct piezoelectric effect is three equations that involve a linear combination of nine elements of stress. This piezoelectric relation here is going to involve writing an equation for each of nine elements of strain. And there would be three components of the electric field vector. So it'll be three this way. So both of these relations involve 27 elements.

So again we're going to have a third rank tensor because the electric field is a vector-- strain is a tensor. And now the mind boggling thing that I will leave you with is exactly the same set of coefficients, d ij describe both effects. And this effect is given a special name. This is called the converse piezoelectric effect. And it's not at all clear how strain, in terms of electric field, should be described in terms of the same array of 27 numbers as polarization per unit volume in terms of stress. And that is an argument that is based on thermodynamics. So that's a good place to quit. We'll have some fun in looking at a few symmetry restrictions imposed on the acentric point groups, 21 of them. We're not going to do all 21. If you know how to do one or two, and marvel over the results, you can do them all.

But one thing that we'll be asking is how can we represent the variation of the piezoelectric effect with orientation of the crystal. And the answer is we can't. We can't. Because what is the direction of what we're doing? There are nine elements of stress, not just three components of a vector which defines an orientation. There are nine parameters here. And there are three components to the charge per unit area-- that's a vector. So all that one can do for these higher ranked tensors is to look for a special, generalized force. And then perhaps for a very special form of that generalized force, that tensor, look at how the polarization changes. But you're going to have to look at six different representation surfaces-- each one which will

describe a different piezoelectric effect. So this will become less simple in many respects. But correspondingly, more interesting because we'll have some really wild, mind boggling representation surfaces for piezoelectric effects. OK so we'll stop there and resume on Thursday. And I'll let you get back to the MRS if that's where you earlier today.