

**PROFESSOR:** Build things, what we'll do is this stuff will go on the web. Usually, we put it up the night before. We had some problems with Stellar, but normally, you can actually see the lecture notes the night before on the web as a PDF. And there will always be a paper copy for you here as well. Let me go through a few practical things.

So you know who we are. We have no TA this year. Normally, we have a TA. Because it's an off year, we're actually going to run this with students out of our own group. Because there are five lab sessions, and there you will have students from our own group helping you.

We will meet here for the lectures, 1390, but the labs will be in 1115. There'll be five of them, and we'll announce them well ahead of time. There is a course website which is on Stellar.

There's not much on there, like I said, because we had some problems with it. But for later in the day and tomorrow, you'll see course materials being uploaded on there. This is where extra readings, for example, will be uploaded or links to readings, in case we can't post them ourselves.

Grades are determined by five problem sets. So there are five lab sessions. The way they work is that instead of coming to class, we meet in the lab. And we give you an assignment, modeling assignment, and you start it there.

And then you will never be able to finish it in that 90 minutes, but then you take it home. And typically, you have two to three weeks for it to be due. So think of it as an extended homework problem.

We start you in the lab, because we feel it's important we solve the practical problems. You have to get a cold running or something to do the modeling. So once that's done, you can just take it home and finish it there.

And we will give you computer access, so you don't need your own computing resources of where to run that. So we'll work that all out in the first lab. And so because of that, there's no final exam in this course. I wouldn't really know what to ask.

There's one thing. We really like students, if you're a graduate student, to register for credit, so not just listener status. This is a course that's not required in any program. So the only way these courses stay alive is if people actually register for them.

It's a sad thing, but the university administration only counts registered students in a class. So if we don't do this, we have 20 people sitting here, but on paper, my dean tells me I only had three people in class, and that's how it's counted in the department. So we really want people to register. Also, that forces you to do the problems, and I feel in a modeling course, there really isn't much use if you don't do the problems.

Postdocs, of course, can't really register, so those are free to just come and listen. But I hope if your postdoc or anything else, visitor, that you also come to the labs to do those. I think we have about 20 seats, so we'll be fine with that. OK.

We don't have a very specific course text, but like I said, in some case, we'll give you review articles. We'll give you handouts. There's a few good books though that you may want to browse through on occasion.

So depending on what's your main interest, the book by Allen and Tildesley is an old classic on computer simulation of liquids. In the end, it's really a book on molecular dynamics. It's quite old by now, but it's a very good basis to start from. It doesn't have the most advanced algorithms or new techniques in it per se, but it's really still a very good book.

Rob Phillips wrote a newer book on, essentially, modeling which both contains continuum and atomistic modeling. That has a heavy slant on mechanical behavior. So if you're more interested in that, that may be a book that you want to look into. Jensen is one of my favorites, although it's heavily chemistry focused, modeling of molecules and so, but it's actually very clearly written.

And Thijssen is a great book if you want to focus on ab initio methods and quantum mechanics, which we'll do later in the course. And Frenkel and Smit is my favorite for statistical mechanics, if you want to learn about the statistical mechanics of molecular dynamics and Monte Carlo methods and things like that. This is really a very, very good book, very thoroughly done. OK.

So I should say a few words about the course objectives. When we designed this course, we deliberately made it a somewhat introductory and overview subject. We wanted this to be a course that was not for experts. So if you already know everything about ab initio methods and molecular dynamics and Monte Carlo, you may actually start getting bored after a while. We really wanted this to be a course that an average graduate student, somebody who was doing experimental research for example, also could take.

So what we mainly try to do is teach the tools of modern computation materials science and how they can be applied to diverse materials problems. So we will give you technical details of the tools but only to the extent that you need them to understand how you can apply them. OK? So we will, of course, tell you, for example what molecular dynamics is, what the basis is of it, what some of the basic algorithms are. But we will not go into the very detailed, novel algorithms to make it a factor of too fast or something like that. So we will not do a lot of detailed algorithmic work in the course.

So there is a heavy focusing on understanding the physics that goes in and because of that the physics and the applications that can come out. So because of that, you will occasionally see us teach materials theory rather than computation. Because in some cases, I feel the hard part of computation is knowing what to compute, and for that, you need some basic materials here. Like when I do a case study on diffusion, towards the end, I may have to tell you a little bit about diffusion theory, activation barriers and correlation factors, because then we can actually connect that to the things we can calculate.

So you should think of this as a course in modeling towards material science and materials application. We do very little purely numerical work, actually almost none to speak of. OK. So the way I see atomistic modeling is really as the integration of these four basic fields-- physics, mathematics, computer science, and material science, and that's how we'll tend to approach it.

Let me go through the calendar, because it gives you a broad outline of the course. This calendar is always subject to change. Even though we teach this with two people, we never seem to be able to get our travel schedules coordinated. In some cases, we also slip a little, but the gross outline will remain the same.

Essentially, there's the first section, which I would say is energy descriptions which is essentially from here to here. This is energy methods. And it starts with more empirical methods, potentials things like embedded atom method, and then it goes into ab initio.

So this is largely DFT, although we do some quantum chemistry. We give it some quantum chemistry basis as well. After that, it's really finite temperature techniques. So we do Molecular Dynamics, MD, and that runs into coarse-graining theory and Monte Carlo. So this is really finite temperature.

OK, and after that, it really is a-- I'll be honest-- a set of random topics. We do case studies. Last year, I did one on hyperdynamics which is accelerated molecular dynamics. We did one on diffusion. This year, we have great ambitions to do one on Green-Kubo relations and how you can extract transport properties.

We have a great lecture from Chris Wolverton, which we've done every year, which students really like. Chris is the Head of Scientific Computing in Ford Motor Company and gives a lecture on how they use even first principles calculation and modeling in general, in Ford and has a brilliant case that. It's really fascinating lecture, how they saved the company millions. It's a great story how they saved the company millions by doing quantum mechanics. So stay tuned for that.

So that's roughly how we work. As you can see, there are labs interspersed-- three, four, where is number three? Here we go. Essentially, one on generic modeling which is really getting you introduced to building cells, and we do this with potential models.

Two on density functional theory, one on the molecular dynamics, and one on Monte Carlo and coarse-graining methods. So that's roughly how the course will work. So there are any questions on the schedule or topic coverage in the course? Yes?

**AUDIENCE:** How long are the labs, and when do they take place?

**PROFESSOR:** Well the labs, so they start-- they are essentially during lecture time, but then you will have to continue it on own. So we get you started on the problem, introduce you, show you where the codes are, how to run them. And typically, in the earlier labs that are not computationally intensive, like the first one, you can really run things and the answer comes back in no time. So we actually get some results already in class and discuss them.

On some of the computationally more intensive ones, like DFT, there'll be less of that and more time that you need to spend afterwards with them. OK? They tend to have about a due date that's two to three weeks after the actual lab. OK? Any other questions? OK.

So I wanted to talk a little about the growing importance of modeling. I started computational modeling in 1988, when it was a rarity, especially in material science department. Now, you see it everywhere.

It's one of these enormously growing fields. You'd be surprised, but even atomistic level modeling is probably now more intensively done in industry than it is in academia. We think of it as a broader academic subject, but it really has taken a foothold in corporations.

I wanted to show you a few examples of how I think that really showed the impact of modeling, where modeling is used to make important decisions. This is a picture from the ASCI Program. When the US was planning to sign the Nuclear Stockpile Treaty, which meant that-- the nuclear stockpile treaty is basically that you cannot test nuclear missiles anymore by setting them off. Because essentially that's so the US was concerned how could we verify the reliability of nuclear missiles, because they're essentially going to sit for 100 years in their silo.

And there was an enormous program in the US for, literally, they would just blow one up once in a while to see if it still works, and now, they can't do that anymore. Although, the US has actually not ratified the Nuclear Stockpile Treaty, they still are sticking with it. And some, I don't know, smart people decided what are we going to do with all this money which was several hundred million dollars.

So they decided, well, we're going to model the reliability of nuclear missiles, and that led to what's called ASCI Program, the Advanced Simulation Computing Initiative, which is literally one of the largest computational modeling programs in the world now. It's definitely not all atomistics, but there definitely is a large atomistic component on it. And the whole idea was, as they call it cynically, it's modeling from button to boom. So they model everything-- aging of plutonium, aging of corrosion of the alloys, corrosion of the electronics.

Whether actually the time is actually ripe for that is another question. Whether you can reliably model all these things is another question. But just another example that computing has taken on a quite important role.

Here's my favorite. This is-- or was, I don't know if was-- this was the largest computer for a while, the Earth Simulator, in Japan. When it came out, it was the largest computer. I think it eclipsed the fastest computer in the US by a factor of five, when it came out, and it's solely used to model environmental processes. The whole idea was that the Japanese had the ambitious idea that they really wanted to use this for predicting climate change in the end. There's other work done, but that's its main purpose.

I think now Blue Light that's being built, but that is actually not quite active, in Livermore, will be bigger than this. But again, you see enormous computational resources spent. This is I think like several hundred million dollar setup, enormous computational resources being set up to deal with what's in the end the very important problem, environmental change. OK.

People usually don't believe me, but I once in my head made up a list of companies where I knew they were doing first principles modeling in companies, and this is not a complete study. This is just the ones that I visited, that I know of. There's actually not a complete study out, and I'll put the link on the web, this study that was sponsored by the National Science Foundation and the University of Loyola. Where literally a panel for two years visited companies all around the world and looked at what they did with modeling.

And so there's an enormously comprehensive list there of the kind of work that's being done in companies with computational modeling on materials. But again, so you see a lot of big companies in here actually. The largest groups that I know of are probably at Motorola, Siemens, Ford, Nippon Steel, and I think these days at Toyota as well. These all have very substantial groups in atomistic modeling on materials.

OK. So this course is supposed to be interactive. We used to have this course in a small room. This is a bit of an unusually big setting for us. So normally, like there's not enough seats for people which makes us feel much better. So this is supposed to be somewhat interactive. So like MBA classes do, they ask you questions, and you're supposed to answer.

Why are you here in the end? Why do you think modeling is useful? I know there's some familiar faces here, people who did for the research, but what do you think-- what's so useful about it?

Why do you think companies do it? Because anything companies do is because it makes them money, or it saves them money. So what's so great about it? Too early in the morning for that. Huh? What can you do better or faster, or what is it that you cannot, maybe, unless you do it with modeling? Yes, sir.

**AUDIENCE:** You can set exact variables. Like in your experiment, you might think, if you're trying to set variables, that they're changing a little bit.

**PROFESSOR:** You hit the nail right on. That's actually number one. It's not the one you usually bring up, control. The number one reason people use modeling is control.

In essence, think of it as doing experiments in a controlled environment. OK? So because you have anomalous control, you can very quickly understand what goes on in your systems, assuming that the answer that comes out is right. That is the number one reason, to solve, to isolate phenomena by controlling the variables. But what else do you think? There's usually one that people always bring up right away.

**AUDIENCE:** To do the experiment.

**PROFESSOR:** You don't have to do the experiment. So to predict things without having to do the work of the experiment, and that's definitely becoming more and more an important role. OK? It's still done less than you think. Most modeling is still done on materials that have already been made and that people have already done the experiment on and that they're trying to understand. But more and more what you bring up which is trying to predict truly before you actually do the experiment, the virtual searching for materials is playing a more and more important role.

Let me show you a few examples that point this out. There's another one that we didn't bring up, and it's using modeling where you cannot do the experiment or where it's really very hard or very expensive to do the experiment. And here's one, this is from Alfie's group, which is, I think, Cambridge or--

**AUDIENCE:** London.

**PROFESSOR:** London, close by. OK. Where knowing what the composition is of the mantle in the Earth, both the composition and the phases that are present, is an enormously difficult problem. But it's one of these actually quite literally hot problems in materials geology.

We know that there's iron and magnesium and oxygen and silicon and a few other things, but in the end, we really don't know what phases they form, what their elastic properties are, and things like that. And the experiments are really hard. Somewhere in the mantle, pressures are I think anywhere from 50 to maybe 300 gigapascals. These are really hard experiments to do.

And I was yesterday at the University of Illinois in the Department of Geology, and they showed me the way they do high pressure experiments with diamond anvil cells. You need about a 1/4 to 1/2 a carat diamond, first of all, so these people have a safe in their lab, it's pretty cool, where they're diamonds sit. And then you have to make really small samples, pushed very hard on them with a diamond anvil. OK?

So you're really pushing on it. This sits in an enormous container, because you have to keep a hundred gigapascal on this thing, and then you have to characterize it. Can you imagine? So you have this enormous holder, because you're putting it under 100 GPa, and you've got to see inside.

So they're really hard experiments to do. You can't really control the temperature very well. So this is where modeling is great, if you believe the answers. So a lot of people do computational quantum mechanics on phases under high pressure.

High pressure is trivial in computation. Just push on it, you change the lattice parameter, and you constrain it. You control the variable, and you have high pressure. 300 gigapascal, no problem. OK.

This one I particularly like. There was an article in the *New York Times*. This is when science made the *New York Times* which doesn't happen too often, in 1999. The people had basically been able to visualize electron densities, orbitals, and that's the left picture.

This is I think in copper oxide. I forgot what this is. In some copper oxide, where they literally were able to visualize the orbitals, and they look like d orbitals, don't they? This is actually one of these things that is quite an experimental feat. It made the *New York Times*, because people could do it experimentally.

This is trivial computationally. When you do computational quantum mechanics, you will get orbitals and orbital populations. That doesn't mean that the experiment is useless. OK? Because the experiment could be the critical verification of what you do in your theory, but I'm just showing you that these things have an enormously different level of complexity.

And if you're ever going to use both computations and experiment, the one key thing that will put you ahead is understanding what is most efficient for a given problem, either computation or experiment. Because the complexity of either has no relation to each other. So for some problems, computation is extremely efficient, and experiment is really hard, and for some problems, it's the other way around. And understanding where to use what, if you're going to use both, I think is the thing that would really get you ahead. And unfortunately, most of the time, that doesn't happen, because usually people only do one of the two.

Here, for example, this is actually from Professor Marzari, the electron density in lead titanate which is a perovskite, a ferroelectric. So you see beautiful orbitals without the graininess of experiments. The other thing is, sometimes, you can do things fast computationally.

This is out of my own work. One of the areas we work in is predicting crystal structure. Typically, getting a phase diagram of a material used to take about a PhD thesis. It takes you that long to make all the samples, do the structural analysis, get the phase boundaries.

In about a six month time frame, we ran 15,000-- it says 10,000. We were up at 15,000-- first principles calculations to find the structures, the ground-state structures in 80 metallic systems, 80 binary metallic systems. So in some sense, we did 80 PhD theses in about six months.

So there are certain things that you can now solve more efficiently computationally than experimentally. And I think it makes sense, like let's say you are looking for structure of material, to first do the computation, and then when you need to resolve issues, then do the experiment, rather than first blindly do the experiment. And we'll talk a little more later about these things.

Control, we already talked about control. That's the number one. Here's one of the first examples of where I saw that applied. In the early '80s, aluminum lithium was one of the key alloys that people thought of for airframes. Because of course now, airframes are aluminum copper.

If you want to make it lighter, you have to go to lighter elements. Well, lithium is the lightest solid element. So substituting the copper away and using aluminum lithium alloys was supposed to make really light alloys. It didn't pan out, because they're not very weldable. So you actually find very little aluminum lithium on airplanes these days.

But the key issue in aluminum lithium is that-- this is the stable phase diagram. So there's an FCC solid solution in equilibrium with a compound, but what actually strengthens the material is a metastable precipitate which is in here. And because it's metastable, it's very hard to study, because to study it, you need to make it big. To strengthen the alloys, you have to keep it small. But to study it, like with microscopy, you need to make it big enough.

But the problem is you can't anneal the precipitate, because it's metastable. If you anneal it to long, it goes away. OK. So this was a great one for computation. In computation, something that's metastable, you can easily make it stable by not letting the system evolve to whatever is stable, and that's what was done here.

This is a calculated phase diagram completely from first principles with the stable equilibria in solid lines and then the metastable equilibrium, this was the precipitant phase. And so you can just isolate this thing and look at it separately. OK. Let me skip that one.

You can use computation often to prove or disprove hypotheses in cases where it's hard to see experimentally. A really ongoing and long story has been the defect in silicon. How do vacancies or interstitials look like in silicon? The reason that they're a little odd is because it's such an open structure. Whereas in a close-packed metal, a vacancy is just taking an atom out, and interstitials, you're just taking putting one in the interstitial position.

But because in silicon it's such a close-packed and covalently bonded network, every time you take an atom out, you can actually have quite a bit of rearrangement of the other atoms. So it's quite an old problem, and it's probably a problem where computation has made considerable impact. If you have an idea for how the vacancy or interstitials should look like, you can test it computationally. You can calculate its energy and compare it to other potential arrangements. OK.

This is my last piece of philosophy. After that, we'll start doing real work. But this is one that if you didn't remember anything from the class except one thing, this is the one I want you to remember. If you do modeling, and people will come up to you, and they will call it simulation, and modeling is not the same as simulation. You should keep that in mind.

We actually do computation. Maybe we do modeling. We rarely ever do simulation. We sometimes do simulation.

The reason is that reality is very often too complex to simulate. OK? So rather, what we do is we isolate parts of reality. OK? We say, this subset is important, and we do computation on that. And what that means is that you will very often have to make judgments. OK?

Like if you're going to study corrosion, let's say you're going to study corrosion of a high strength steel. There is no way in hell you're going to simulate that, because you don't even know what the relevant variables are. You don't even know what the relevant environments are. OK? So what you're going to have to do is learn a lot about the signs of corrosion, and take one isolated element, maybe surface attack by chlorine or something like that or hydrogen going in and locally embrittling the material. So you will never just take your high strength steel, put it in a computer, and wait for a long time, because you don't even know what environment to impose on that system. OK?

So rarely do we do simulation to solve complex problems. Sometimes, we will isolate a piece and then simulate on that, but we rarely simulate the full reality. And because of that, it's really important that you know the signs of the field you work in. OK? You cannot have impact with computation without understanding your field of application, period, because you will never know what to compute. OK?

So I think if you want to remember one thing, that's the one. The hardest part of computing is knowing what to compute. OK? Everybody can learn molecular dynamics. Everybody can learn ab initio methods, but using them in an intelligent way becomes the hard part. And I like the quote from Frank Jensen, computers don't solve problems, people do, to paraphrase something.

OK. I'm going to skip this. I'll let you read this, an article we put on the web from James Langer. People are trying to establish computing as the third branch of science. There's experiment, there's theory, and there's computing, and it's an interesting article. OK.

So let me get to the real science that we can do today, at least a little bit. So the first maybe a few weeks or so, we're going to talk about energy models. And the reason we start with energy models is because I feel that, unless you have an adequate energetic description of your material, you really don't know if what comes out of your computations is actually right or relevant. So typically, people distinguish empirical energy models from ab initio or quantum mechanical, so this is what we sometimes call ab initio, or first principles. In some sense, in empirical models, all you do is you take some form for the energy, and you fit it to any data you may have, and sometimes, that data is quantum mechanically computed.

In quantum mechanics, you leave the fitting aside, and you go straight to just solving the Schrodinger equation for whatever problem you're trying to solve. And there are methods in between which are semi-empirical which are essentially quantum mechanical in form but empirical in the parameters. Essentially tied binding fits into these, things that the chemists often do, like MINDO and INDO. So these are effectively, you could think of them as parameterized Schrodinger equations almost, where the overlap integrals between wave functions are not computed but are parameterized. So you save a lot of time.

Personally, I believe that that middlefield is losing in importance considerably. I think if we'd given this class 10 years ago, we would have talked a lot about that. Because people see that as a way of like, well, it's much faster than ab initio, but you keep some of the accuracy of it.

I think that's less and less true these days. You don't keep as much accuracy as you usually want to, and it's not as much faster anymore. So while there are obviously still problems where this is important, more and more people just do the ab initio, period. Computers are cheap these days.

The reason we teach you about empirical models is because, first of all, you will encounter, and if you're going to do really, really large problems, they can be quite useful. And also, they are really great handle I find to teach you some of the essential energy physics that you need to deal with when studying different materials, and so that's why I spend 2, 2 1/2 lectures on empirical models. OK. And so obviously, keep the obviously in mind, that if you work with potentials, you have no information about electrons. You just have energies as a function of position.

If you work with semi-empirical and quantum mechanics, you also have more information. You know something about the electronic structure of the material. Which one is best, I think that's an irrelevant question, depends what you can afford. OK.

So essentially, what you want if you want to do an empirical modeling method is that you want to have the energy as a function of all the nuclear coordinates. That already itself implies an assumption, because the energy is actually a function of the nuclear and the electronic coordinates. Typically, what we do is we variationally remove the electronic coordinates, and that's essentially what's called the Born-Oppenheimer approximation. If you think if your atom-- if you have a bunch of atoms together. So you have a set of coordinates that describe the positions.

People think that the energy is uniquely determined by that set of coordinates, but that's actually not true. Because you have electronic states, and in many cases, for a given state of the nuclei, you can have multiple electronic states. OK? There'll be a ground state, but you can be in excited states as well.

What the Born-Oppenheimer approximation essentially assumes is that, for any set of nuclear coordinates, you are always in the electronic ground state. So  $E_R$  is derived from  $E_R \psi$  by essentially variationally removing  $\psi$  by minimizing over  $\psi$ . OK? So what's the physical implementation here? If you're in a stationary configuration, and you wait long enough, this is probably OK. If your atoms sit there frozen in some position, if you wait long enough, the electrons will go to the ground state, especially when you're at 0 temperature.

Where it can wreak havoc is in certain molds of dynamics, because what you're really assuming is that, if you move your atoms, your electrons follow infinitely fast. OK? Because if you move the atom a little bit, the energy change is the energy change when the electrons relax immediately to the ground state, as you move the atoms. OK? That's essentially the Born-Oppenheimer approximation.

So when is this not going to be true? It's when the atoms move really fast, or the electrons move really slow, and there are cases like that. This is one of these approximations that we want to believe is always true, because it's very hard to do anything else. So we kind of kid ourselves, because it's very hard to verify as well. But there are long-lived excited states in materials.

There are defects in semiconductors, for example, EL2 in gallium arsenide was a famous one that has very long-lived excited states, where there are essentially two Born-Oppenheimer surfaces. Let's call one the ground state one, and then there's another one that's the excited state one. And the interesting thing was they gave you different nuclear coordinates. So if you minimized it under one equipotential surface and under the other one, you ended up in a different nuclear configuration. So you see then, you have a problem.

You can find the lowest energy configuration of the nuclei, unless you know what the electrons do. So you now have a coupled problem. OK? So that's a non-obvious violation of the Born-Oppenheimer approximation. In fast dynamics, things that move fast, like protons. The lightest nucleus or protons can move very fast, and in some cases, the electrons won't follow fast enough.

In insulators, let's say you studied diffusion of charged ions in insulators. OK? So I work on battery materials. It's all about lithium plus diffusion, lithium ions diffuse. Well, if the ion diffuses-- if the ion hops very fast, but I'm in an insulator, maybe the electron won't follow fast enough. OK? So I'm going away from the Born-Oppenheimer surface there. OK?

So this problem actually appears more than you think. It's just that we don't know how to deal with it. So we like, shush, remove it from our thoughts.

The other obvious violation of Born-Oppenheimer is when you're at nonzero temperature. When you're at nonzero temperature, you have a finite probability to actually occupy the higher level electronic citations, so the higher energy electronics states. That's not a really big problem. It is technically a violation of the Born-Oppenheimer approximation, but essentially, it's easy to solve.

You can replace this minimum. So minimizing it by statistically averaging over the right levels by literally doing a statistical weighting of how the levels are populated. Then, they do a statistical mechanics approach, and we'll talk much more about these things when we talk about coarse graining methods in the later part of the course. So temperature isn't a big deal for Born-Oppenheimer. OK.

So here's what we're going to do on potentials. There are as many different potentials as there are people. Everybody has their favorite one. So we're going to pick and choose, and I'm mainly going to pick and choose based on the materials physics I can teach you with them.

So we're going to talk about a few particular forms and the physical limitations that they introduce, and I'm going to start with pair potentials, because they're the obvious one. That'll be today, and then that'll obviously lead us, the failures of those will lead us into many body potentials and pair functionals. This one will be particularly relevant for covalent delocalized materials, like metals, and this is for delocalized-- sorry. Sorry, covalent localized. So we're mainly going to talk about the form of these things. I'm not going to spend a whole lot of time talking about the detailed parameters you put in. OK.

So here's pair potentials. Obviously, what are you really saying when you use pair potentials to model something? You're saying that, if I have a bunch of atoms together, I can sum their energy from pairwise interactions.

So you're saying that this interaction between these two atoms has nothing to do with whether this atom or that atom is present. That's essentially the physics of what you're saying. You're summing the energy. In some cases, you take a constant, and then simply a sum of interaction potentials that only depend on the distance between two atoms.

Pair potentials pretty much always have the same form. They are attractive at intermediate to long distance, and they are repulsive at short distance. And they have to be repulsive at short distance, because otherwise, your system collapses into itself.

**AUDIENCE:** Sorry. I left my phone. I just don't see it. Sorry to interrupt.

**PROFESSOR:** You left what?

**AUDIENCE:** My phone. I'm sorry.

**PROFESSOR:** I didn't see a phone.

**AUDIENCE:** Sorry. Sorry.

**PROFESSOR:** No problem. OK. Every lecture will have something like that. Something odd happens. We do it deliberately. No.

One issue, practical issue with potentials, is that you have to truncate them. OK? Because you want to keep this pairwise distance not out to infinity. Most potential is just the form they have. They slowly decay, and people do all kinds of tricks.

The problem is if you say, I'm only going to truncate up to here, that you have this discontinuity. Let me see if I can make a wide slide, if I remember how to do this. Ah, magic. OK.

So let's say I truncate the potential here at this distance. Then essentially, my potential really looks like this. I have this discontinuity in it which is not very good. Because whenever atoms move in and out of this range, they actually have a strong energy jump, as they move in and out of that range.

So people do all kinds of tricks. You can smooth this, like attach some spline to it that smooths this out to zero. Sometimes, you want to have literally zero at some distance. Sometimes, you also like zero derivative, so you have continuous forces.

Some people use shifted potentials which is kind of cute. If you know that this has some value, let's say epsilon here, you just shift the potential up by epsilon. So now, it's zero at your cutoff, but of course, the force would still be discontinuous, because the force would be the derivative. OK.

The most simple potential form that you'll sometimes see used is the Lennard-Jones potential which has an  $R$  to the 6th which is the attractive part. OK? That gives you the attractions and has the negative sign in front, and the  $R$  to the 12th which gives you the repulsion. The  $R$  to the 6th term can actually be physically justified. It comes from the interaction between fluctuating dipoles.

If you have an atom here with its electron cloud and an atom here, and if these are inert atoms, so with filled electron shell, so there's no covalent bonding going on with them. So these are either ions with a filled shell, or they're noble gases. Then, there is no direct covalent interaction, so the interaction you get is from fluctuating dipoles. So at some point, there's a dipole that, just from fluctuations, that sets up here, and that will induce a dipole in the other electron cloud.

And so the interaction between these dipoles and these dipoles, if you actually look at it, gives you an  $R$  to the 6th. So this piece is physically justifiable, and that's where Lennard-Jones got it from. It's essentially the form of what's called a Van der Waals interaction which is the interaction between inner shells.

So where does the R to the 12th come from, you think? Obviously, you need something steep to get that. Otherwise, the ions fly into each other. You need this steep repulsive part when the ions come very close together, and essentially what the physics of it is the Pauli repulsion. As the electron clouds come into each other, remember, the electrons cannot occupy exactly the same quantum state.

And so as you bring them closer, you're almost forcing them to occupy the same quantum state, but why R to the 12th? It's really because it's the square of R to the 6th. There is no physical justification for R to the 12th. Lennard-Jones used it, because it makes the math of some things you want to do with it easy, because it's the square of R to the 6th. So if you like R to the 10th, R to the 14th, R to the 16th, go ahead.

People always take the Lennard-Jones potential, because it's there. And like I said, the R to the 6th, I grant you that. Maybe you should keep that. That is a true Van der Waals interaction, but the R to the 12th, there is no reason that it should be R to the 12th. OK? Anything, sometimes you actually want steeper potentials, so you make it like R to the 20 or something or whatever.

OK. The other thing is that people use the Lennard-Jones potentials to attract atoms together that has nothing to do with Van der Waals interaction, to actually look at things that almost have some covalent interaction. And then there's actually no reason to keep the R to the 6th. OK? Because the R to the 6th is really only physically justifiable for Van der Waals terms. OK.

The interesting thing about Lennard-Jones, it's actually the simplest potential, because it only has two parameters. There's essentially A and B, or if you renormalize the potential, there's an energy scale, and there's a length scale. So you see, if you write it in this form, you see that the potential is in units of epsilon, and the length, or the sigma which is the distance-- I'm sorry, the R which is the distance is in units of sigma. OK? So what that means is that there's essentially only one Lennard-Jones system in the world.

You will see tabulated Lennard-Jones parameters for a lot of materials, but if you think of it, the energy scale of your potential sets the temperature scale of the system. And the length scale sets the volume or therefore the pressure scale. So if you take one Lennard-Jones system at a given temperature and pressure, that will always be the same as a Lennard-Jones system without the parameters but at another temperature and pressure. So there's a unique transformation going between all Lennard-Jones systems. Yes, sir.

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** No. Sometimes, people leave out that factor of 2. I'm sorry?

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** I'm not sure. I think the reason the factor 2 is there, if you differentiate it, and that way you find the minimum is exactly at sigma. OK? Because if you differentiate the 12, you get a factor of 12. If you differentiate the 6, you get a 6.

You could leave 2 out, but then sigma is not the value where the potential is minimum. That's the reason people put sigma there, because I think-- I may be wrong-- but I think in this form, this is sigma. OK? And I actually think that this is epsilon, but I should verify that.

So there is essentially only one Lennard-Jones. Ah, there's Lennard-Jones. I forgot his picture. I think it's sir now, Sir Lennard-Jones, I think. OK.

Usually, two parameters is just not enough in a potential, and the reason is that usually you want to mimic at least three properties of a material. Its length scale which is its largest parameter, its energy scale which you can think of as its cohesive energy which is the potential depth, but you also want to get its elasticity right. OK? And so that's three fundamental properties to get right, because its elasticity tells you its response to any perturbations. And the problem is that a Lennard-Jones potential only has two parameters. You cannot fit three things with two parameters.

So most people will go to things with three parameters, usually, so they can get these three things right. And one classic is a Morse potential which has  $D$  which sets the energy scale,  $R_0$  which sets the length scale, and  $\alpha$  which sets the elasticity scale. Because you can see  $\alpha$  sets in some sense the curvature of the potential. It's what you multiply with the distance differential. OK? So  $\alpha$  will be a measure of the elastic behavior.

In particular, in oxides, the form that's most popular is what's called a Born-Mayer or a Buckingham potential which is essentially a decaying exponential, a Van der Waals term, and then the second order term in Van der Waals perturbation theory which is the  $R$  of the 8th parameter. The weird thing about this potential that you have to be somewhat careful about is that it diverges at short distances if you plot it. If you plot the exponential, that goes to a finite value of  $A$  when  $R$  is 0.

So the exponential to something like this, and this is  $A$ -- it's actually a lot steeper in reality. Typically,  $A$  is very large, but these terms, these  $R$  to the 6th and the  $R$  to the 8th--  $1$  over  $R$  to the 6th and  $1$  over  $R$  to the 8th diverge and  $R$  goes to 0. So they, on the other hand, look like this, where this goes to minus infinity. So when you add the two up, you get something like this. I'm sorry. This is supposed to go down.

So if you look only up to here, this potential looks fine. But if you go past it, if you in some sense go into the core, the potential diverges, and you may think that's silly. You never go there, but you sometimes do because of numerical issues.

Sometimes, what happens in say a simulation is that, when you start-- let's say you do something molecular dynamics which is essentially evolving atoms according to their force. You may start in a configuration very far from equilibrium. So in the initial steps, atoms move with tremendous force, and so because of that, they can literally just overshoot and shoot into each other.

And what you see is that actually the state with two atoms on top of each other is a highly bonded state in this kind of potential. So you will never escape it. You were really just put atoms on top of each other. And trust me, if you work with Born-Mayer potentials, and you're not careful, you will see that. You will see atoms sitting on top of each other, exactly because of this problem.

OK. I got some Morse potential parameters out of a book. It's probably rather useless. Nobody would use this anymore for metals to be honest, because I'll show you a bit later why. These pair potentials are not very good for metals. Yes.

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** You're asking about how to calculate.

**AUDIENCE:** [INAUDIBLE]

**PROFESSOR:** Let me come to that. That's a question I will specifically address, but thank you. I wanted to show you the difference between a few potentials for a specific bond. This is the CH bond in methane, and so they're all fitted to have the same bonding energy and the same modulus. So the same bond distance, the same bonding energy, and same modulus, and this is the exact curve in the solid line.

The dash dash dotted is the Morse potential. That's actually the one that's very close to the exact line. Let's see if I get this right. This is just a harmonic potential.

So this is something like what they call P2. This is sort of  $K \times \Delta R^2$ , where  $\Delta R$  is the distance away from the equilibrium bond in geometry, and P4 is a 4th order polynomial. So that would be  $K + L \Delta R^4$ .

And I think the interesting thing is that near the minimum they all look the same. They pretty much have to. They have the same position in the minimum, and they have the same curvature. OK?

So if you're only going to be looking at very short displacements around the equilibrium, actually just your quadratic is fine, and you'll see that often. People who model small deformations in organic systems in polymers and so will often just use spring models, essentially a harmonic potential. So to decide what potential you need, you should think about how far you want to go away from equilibrium.

If you go very far away from equilibrium, obviously, this Morse potential does a fine job. If you stay very close to equilibrium, you may not want to put in that effort. It's much easier to work with a spring model than to actually work with a Morse potential. It's much faster to evaluate a quadratic.

I always thought I should put a section in my lectures on how to fit potentials, and every time, I look up papers, and I can never find anything systematic. So I think the rule is you fit to anything you can get your hands on. And as we'll point out later more carefully, since potentials only have a limited region of applicability, you want to fit as close as possible to the things you're going to calculate, to the environment you're going to calculate, but so in theory, that could be anything. There's the obvious candidates.

You always want to get the length scale and the energy scale pretty much right and the stiffness, here sort of obvious. In some cases, you want to get low symmetry environment right. So if you only fit to crystal structures, you may have very poor reproduction of low symmetry things, like surface energies or what goes on in a liquid. And so in some cases, people explicitly fit to that.

I wouldn't worry too much about this. This is going to become a lot clearer, as I talk to you about the physics that's missing in pair potentials and how you correct to that. OK. So I tried to find what I thought is maybe the first example of computational modeling with potentials. It's probably not the first, but I think maybe one of the first that was done on computer.

This was done by Vineyard's group, and it's essentially studying radiation damage in copper. This is from 1960. I don't know if you remember punch cards for computers. I think this is from before punch cards.

But they managed to program a small molecular dynamics, and essentially what they're doing is they have a crystal of copper, and they're shooting-- I think they're shooting some ions in it to actually see the orbit that the radiation damage falls. So you knock out atoms, and you show the displacement. Ironically, this is a simulation people still do these days. Molecular dynamics on radiation damage, so 1960. OK.

So let me talk a little about the obvious problems with pair potentials, and this is one of the things that we're going to then show you in the lab. We are actually going to make you demonstrate this in the lab, and once you understand the physical limitations of pair potential, you'll see that the solutions which is pair functional methods or cluster potential are actually quite obvious why they came about. And when I talk about failures of pair potentials, I don't talk about failures of the parameters. I talk about failures of the form, and there's a lot of people who say, well, if this doesn't work, I just need to change my parameters in my potential. There are certain things that you can never get right with pair potentials, because they are in violation of the particular form which is a pairwise interaction.

So one is, obviously, that pair potentials count bonds. That's what you should keep in mind. They really essentially sum-- the cohesive energy on an atom is largely determined by how many things are around it, because it literally sums bonds around it. It doesn't care much about the organization of atoms.

So if you take this triangle, let's say these bonds are one Angstrom, or I take this chain, where the bonds are one Angstrom. OK? Here, I have four atoms, here I have three, but there are three bonds in each case. These have essentially the same energy in a pair potential model. OK?

The only thing that would distinguish them is longer range interactions, but that's not the physics that in many cases makes this different. OK? The physics that in many cases makes this different, for example, could be angular or bonding or could be that the presence of this truly influences the bond between these two. And we'll actually show you how to solve both problems. They're actually different problems that lead to different solutions.

Another nice example, if you take a ethylene molecule, let's say you were trying to model that with pair potentials. If I flap these bonds here, so I bend open the hydrogens, that really doesn't cost me any energy, if I have a pair potential. OK? Because the pair potential just measures this distance and this distance. So if I just flap this open, that distance stays the same. OK? Only if you had some indirect interaction between these hydrogens would you pick up that energy difference.

But you see, if you made a potential between the hydrogens, you'd be putting the wrong physics in. Because the reason that energy changes, as I change that bond, has nothing to do with the interaction between the hydrogens. But it has all to do with the hybridization of the carbon, that the carbon is  $sp^2$  hybridized and one certain bond angles. OK? So it's not because you can fix it with pair potentials that you fix it right.

OK. The other thing you will see is, if you use pair potentials, and you look say for low energy crystal structures, you will almost always end up in close-packed systems. And the reason is that in pair potential models, atoms try to maximize their coordination, because really you sum the energy pairwise coming from atoms around you. So if you have a negative bonding energy with atoms around you, you try to get as many as you can around you, so you will maximize coordination.

The ground states of most potential models for elements are HCP Hexagonal Close-Packed and FCC Face-Centered Close-Packed. OK? So it's extremely hard to stabilize things like a diamond cubic structure which is an open structure. I don't know if you have a picture for it.

The other thing which is maybe more obvious, but pair potentials are not stable against shear, and now you could argue most materials aren't stable against shear. But if I take the square of atoms-- let's say this is just a piece of a lattice. OK-- if I shear this, I can shear this and keep all these distances the same.

So in a nearest neighbor pair potential, all the energy has not changed. So if the energy has not changed, that means that my elastic constant in shear is 0. OK? Now, you could say, this is why real materials form square lattices and simple cubic lattice, and that's actually true. But a real material has some amount of resistance against shear, even in a square configuration. And here you see by construction, it doesn't have any resistance. OK.

What I'm going to do is try to break down what in different materials classes, like metals or organic solids, what the failures of pair potentials, and then we'll go into what the remedies are for that. So in metals, the main thing is this problem. That if you do a pair potential model, and you look at the bonding energy of this red atom, it's really essentially six times the single bond energy of the red with the white one. And so that's why for pair potentials, people say that cohesive energy scales with  $Z$  which is the coordination number.

And if you do quantum mechanics or even more approximate theory but that have the essentials of hybridization in them, you find that actually for metals-- and with metals, I mean things that have covalent delocalized bonding, which you call metallic bonding-- the cohesive energy of an atom goes like the square root of  $Z$ . OK? So it's not linear in  $Z$  at all. So if you have more bonds, you start gaining less and less incrementally, and you can see that.

I made a picture here. This is out of a, I think, what's really a great article, if you want to read more about this. It's a review article on the embedded atom method. We'll put this on the restricted side of the course website.

This is actually for nickel, the cohesive energy per atom as a function of the coordination it's in. So of course, 12 here, this is the FCC solid. 2 is the dimer. So this is just two atoms in the gas phase, and what do you think is 11? How do you get 11?

This is actually experimental data. 11 is from the vacancy formation energy. If you make a vacancy in a crystal, the atoms around it are 11-fold coordinated instead of 12. In FCC, you have 12-fold coordination, but if you take an atom away, those atoms around there have 11-fold coordination. So this comes from the vacancy coordination.

Now, there's three points here. They drew a square root through them. You probably could draw other things, but what we do know from quantum mechanics is that essentially the first order is square root of  $Z$  behavior and now  $Z$  behavior. You can also see that in silicon. This is a slightly confusing graph, but this is the energy per bond in red for silicon in different coordinations. OK?

So what you see is that the energy per bond actually goes down as you make more bonds. So even though as you coordinate an atom with more atoms around it, the total cohesive energy may go down. If you divide that energy by the number of bonds, that number becomes smaller and smaller. OK? It's almost like an atom in a covalent bonding has only so much bonding power to give, and if it only bonds to one atom, it gives all its bonding power to that one atom. If it has to bond to a lot, it has to divide that between all those.

So this is an important concept to remember, that in covalent materials, cohesive energy is not linear in coordination. Bonding strength gets weaker, as you add more bonds, and we'll come back to that. This is important when you go between-- when you make potentials in one coordination environment and start using them in another one.

Here's a quantum mechanical result for aluminum. So this is the cohesive energy, again, as a function of the coordination number. So this is actually a calculation, and again what you see is that, even though as you coordinate more the cohesive energy goes down, but it doesn't go down linear. If you want to think of it, the increment you're getting from adding a bond starts getting smaller and smaller.

If you go from one to two, you could say this is your bonding energy. This is the extra energy you get. If you go from 11 to 12, all you gain is this. So the bond energy, when you go from the 11 to 12 is much smaller than the bonding energy when you go from 1 to 2. OK? So the cohesive energy with coordination is a convex function. That's important to keep in mind.

And of course, you cannot get that with pair potentials. With pair potentials, this will essentially look linear. Now, what's the slope of it in pair potentials? It's a trick question. What's the slope of that line?

Well,  $Z$ 's the coordinate, so I need the factor in front. See, the problem is you don't know. This is in the end the fundamental problem. It depends on where you fit it.

If you fit from 11 to 12-- if you fit from 11 to 12, then this is your slope. Then, you're going to have this curve. If you fit from 1 to 2, you're going to have this curve. And do you see that they really give substantial error when you go away from the coordination in which you fit?

I'm going to show you that with the last result. This is basically saying the same thing. What I took here, this is out of Anders Karlsson's paper which is on our reference list, which we've put on the web. This is a great review paper on potentials, and not just pair potentials. And we give with every main topic-- not every lecture-- with every main topic, we have a list of references, and they just go on the Additional Materials on the Stellar website.

This is the pair potential for copper fitted to different properties. The lowest one is the one fitted to the dimer, to the molecule. So this is just a copper-copper dimer. You see, it's the strongest of them all. It's the strongest of all the potentials, and why, because there's only one bond. OK? You remember, all the bonding energy goes in that one bond.

The equation of state, that's essentially looking at the cohesive energy of the solid as a function of lattice parameter. So this one, that's almost the smallest one. That's the solid. See, a lot smaller, because you're counting now bond strength in coordination 12, where every bond is weaker. So you try to map that onto a pair potential, and you get, in some sense, a much weaker interaction per pair.

And what Anders Karlsson did, he also extracted it from phonons. This is actually one. It's really small and from defects, and the defect one even has a different minimum. Actually, they all have a different minimum.

So what this is telling you, what I'm trying to demonstrate, is that for metals and for anything that's actually covalent, but this is worse for covalent delocalized, your potential is extremely environment-dependent. It's essentially coordination-dependent. OK? And we show you in the next lecture how that shows up in certain physical properties and then how you solve that. Because turns out, there's a very elegant solution to the problem, and I think you can already see where we're going to take this.

The problem is that our bonding energy is linear in coordination with a pair potential. So all we need to do to fix this problem is to make it nonlinear, and that leads you into what are called pair functionals, rather than pair potentials. And things like there's a whole class of methods, things like the embedded atom method, glue models, effective medium theory, they all go by different names, are essentially pair functional models.

There are still things that count the coordination around you in some form or another. It's just that they make the energy evolve nonlinear with that coordination, and they're very elegant methods. They're still empirical methods, but very elegant methods that solve the essential problem of pair potentials without a lot of extra work, and so we'll talk about that on Thursday.

So I'll end here. I'll be happy, if there are questions, I'd be happy to take questions. Professor Marzari and I will be here for a few more minutes, if there's anybody that has questions about how the course will run in general.