Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 20 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

Wisconsin Initiative for Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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May 2014

Chapter 8.

Atomic Size Matters

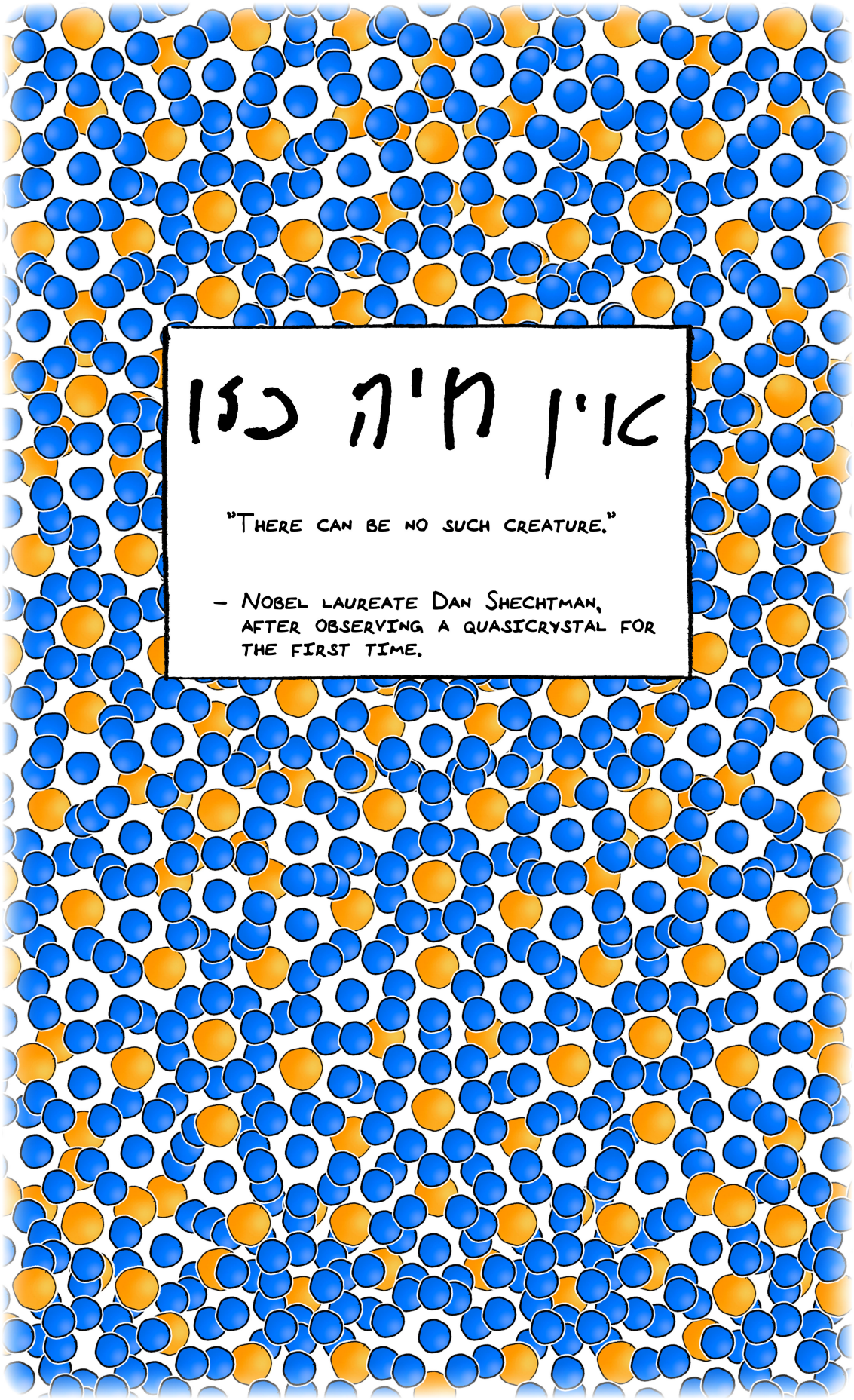
A comic book–style interpretation of some of the previous work, presented here for a more general audience.

Chemical Pressure and Its Applications to the Tsai-type Quasicrystal

– or –

Atomic Size Matters

Veronica M. Berns

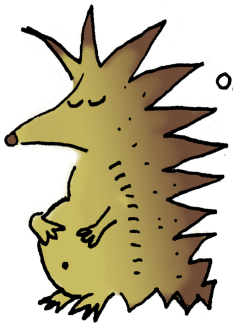

אין מיה כזו
"There can be no such creature."
– Nobel laureate Dan Shechtman, after observing a quasicrystal for the first time.

TO SCIENCE, FOR THE INSPIRATION
AND TO MY FRIENDS AND FAMILY, FOR THE MOTIVATION

THERE ARE SOME THINGS THAT SCIENTISTS KNOW FOR SURE ABOUT THE WORLD.

THINGS WE CAN MEASURE DIRECTLY, LIKE ACCELERATION DUE TO GRAVITY

9.8 m/s →



OR THE GESTATION PERIOD OF A PORCUPINE

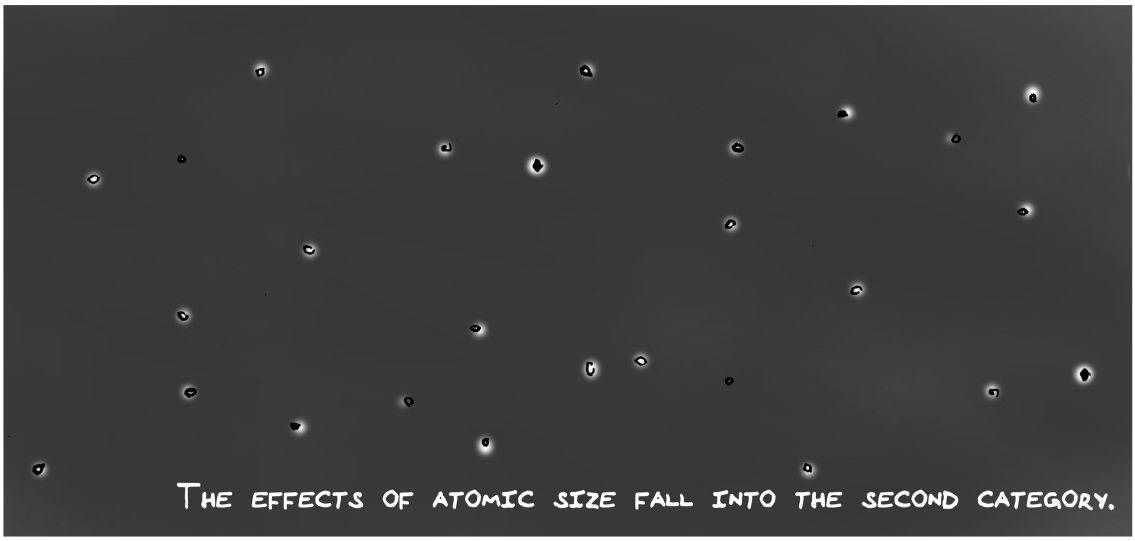
← 213 days

AND THERE ARE SOME THINGS WE ARE PRETTY SURE ABOUT BECAUSE OF A COMBINATION OF EVIDENCE FROM DATA AND, WELL...

...A HUNCH.

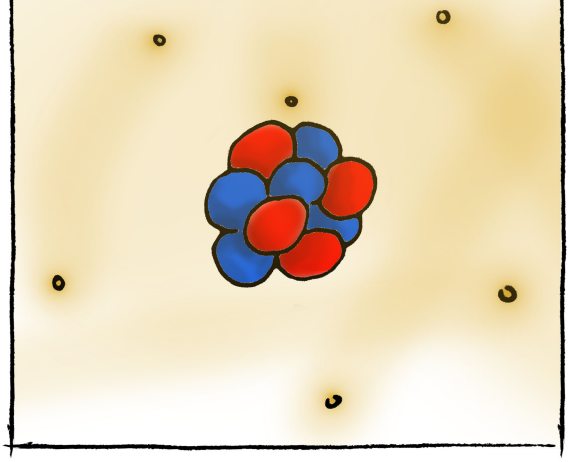
LIKE GLOBAL WARMING OR THE BIG BANG.

WE CAN NEVER BE 100 % CERTAIN, BUT MOST SCIENTISTS AGREE ON THOSE THINGS.



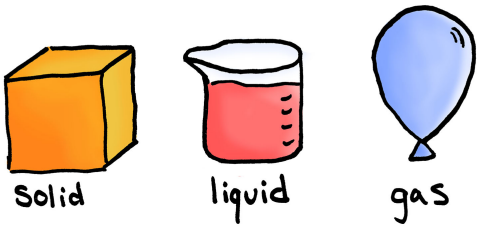
THE EFFECTS OF ATOMIC SIZE FALL INTO THE SECOND CATEGORY.

ATOMS CAN BE THOUGHT OF AS HARD SPHERES. THEY AREN'T, BUT YOU CAN THINK ABOUT THEM THAT WAY SOMETIMES, TO SIMPLIFY THINGS.

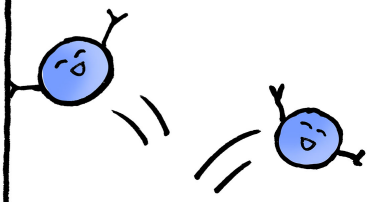


EVERYTHING IS BASICALLY A PILE OF ATOMS.

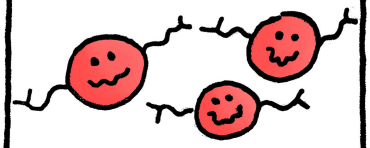
WHETHER WE CALL THAT PILE A SOLID, LIQUID, OR GAS DEPENDS ON HOW CLOSE TOGETHER THOSE ATOMS ARE AND HOW FAST THEY ARE MOVING.



THE FAST ONES FLY APART FROM EACH OTHER. THESE ARE GASES.



LIQUIDS' ATOMS ARE CLOSER TOGETHER AND SLOSH ABOUT IN THEIR CONTAINERS.

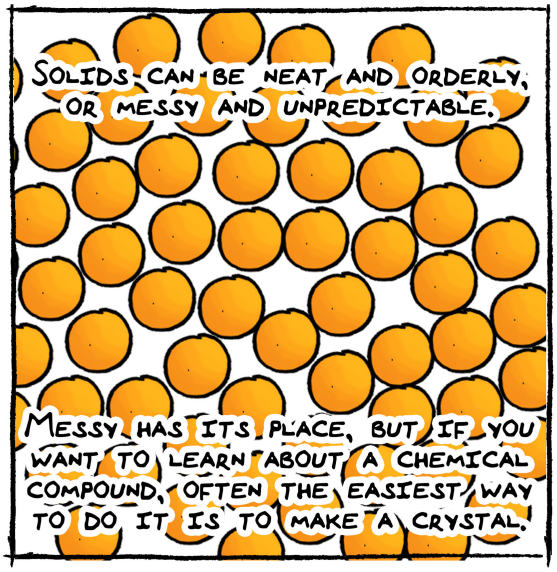


AND THEN THERE'S SOLIDS.

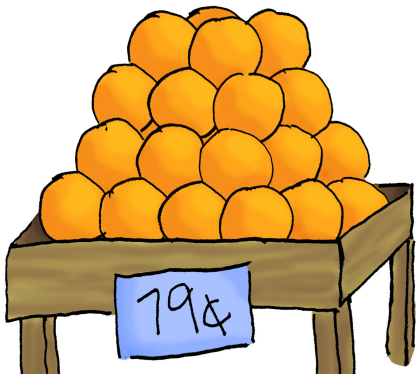
SOLIDS HUDDLE TOGETHER AND THE ATOMS MOVE SLOW.

SO SLOW THAT WE OFTEN ROUND DOWN TO SAY THEY AREN'T MOVING AT ALL.

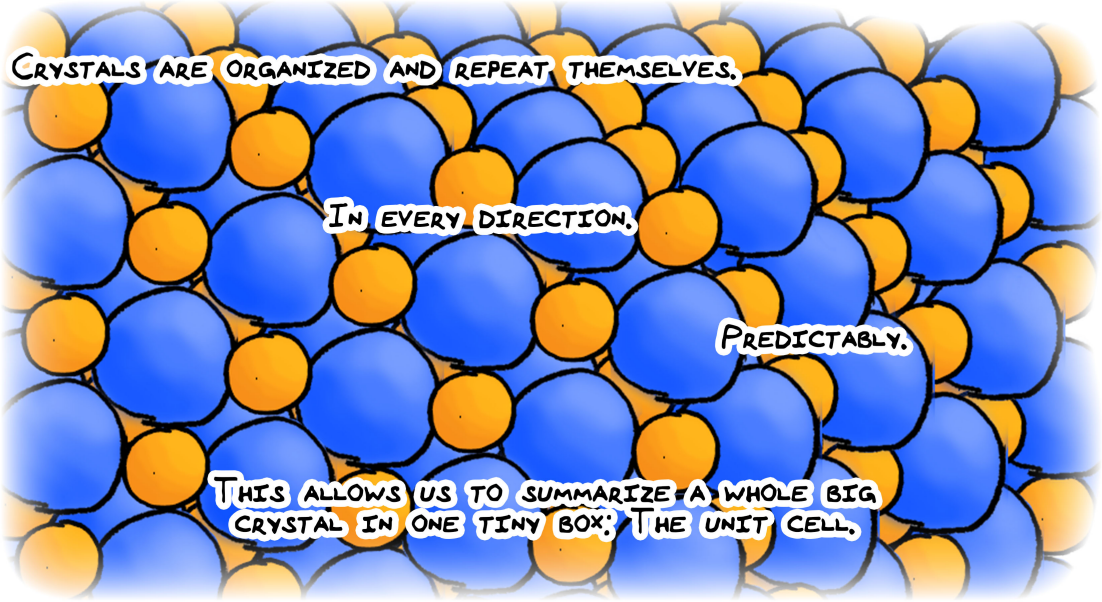
SOLIDS CAN BE NEAT AND ORDERLY, OR MESSY AND UNPREDICTABLE.



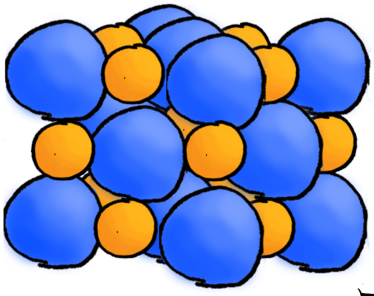
MESSY HAS ITS PLACE, BUT IF YOU WANT TO LEARN ABOUT A CHEMICAL COMPOUND, OFTEN THE EASIEST WAY TO DO IT IS TO MAKE A CRYSTAL.

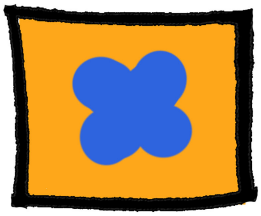


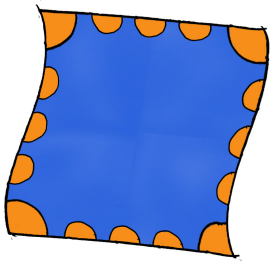
IN CRYSTALS, ATOMS PACK ORDERLY AND TIGHTLY, LIKE ORANGES IN A GROCERY STORE DISPLAY.



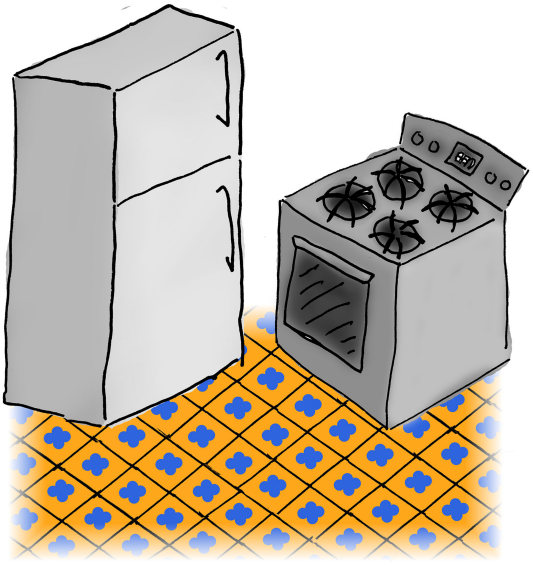
The unit cell is the smallest region that repeats itself in every direction.

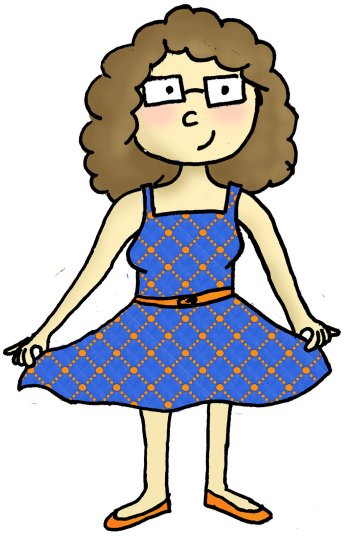


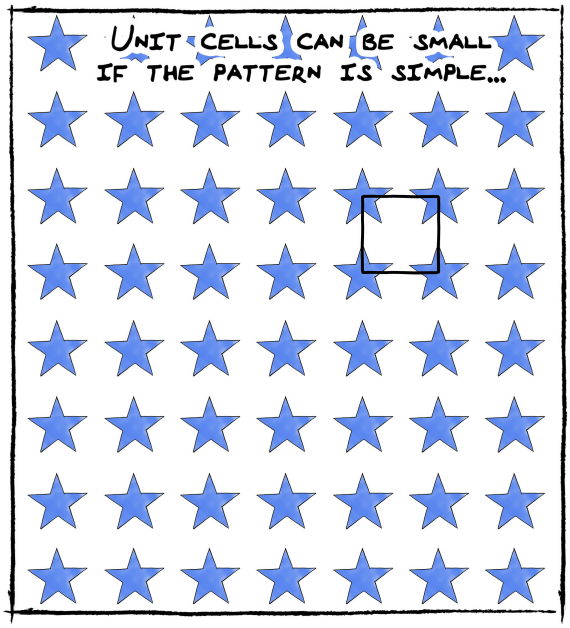


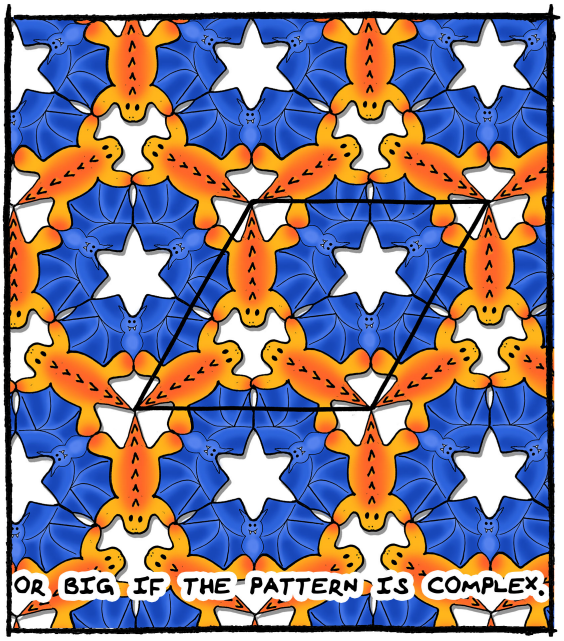


Like a decorative kitchen tile, or a patterned swatch of fabric.

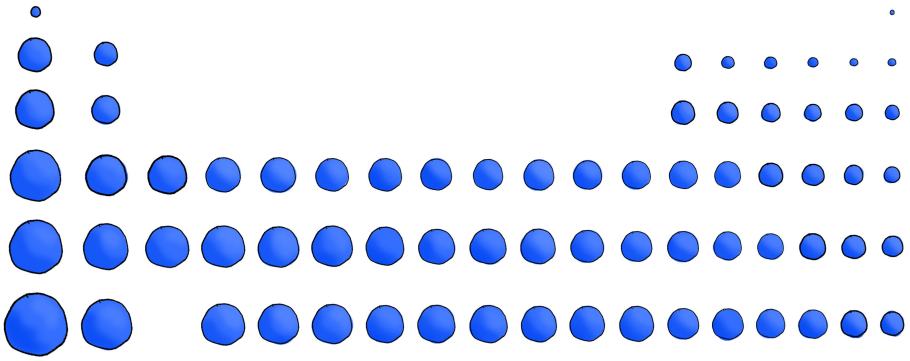






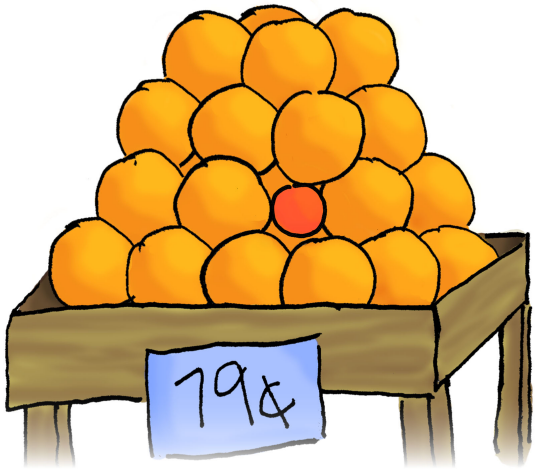


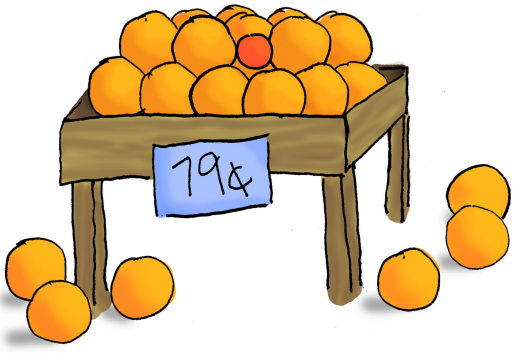
ONE FACTOR THAT CONTRIBUTES TO HOW COMPLEX OUR ATOMIC PATTERN WILL BE IS THE SIZE OF THE ATOMS. ATOMIC SIZE IS GOVERNED BY AN ELEMENT'S SPOT ON THE PERIODIC TABLE.



IT MAKES INTUITIVE SENSE THAT WHEN YOU HAVE DIFFERENT SIZE SPHERES PACKING TOGETHER THINGS WILL GET INTERESTING.

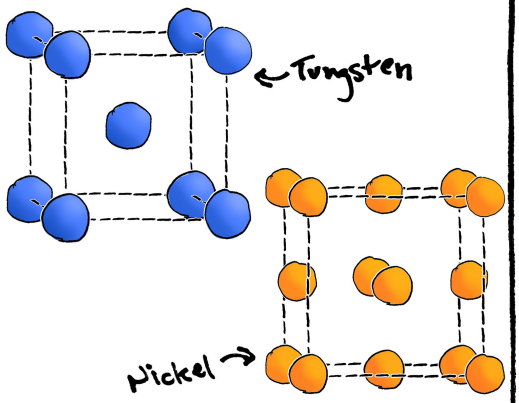
CONSIDER MIXING TANGERINES WITH YOUR ORANGES.



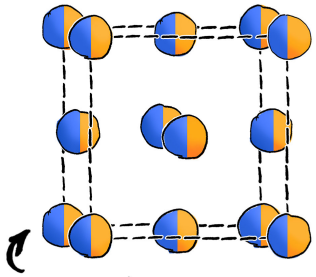


SIZE AND STRUCTURE HAVE A STRONG RELATIONSHIP, IN CITRUS AND IN SCIENCE.

METALS NATURALLY PACK TOGETHER VERY SIMPLY.

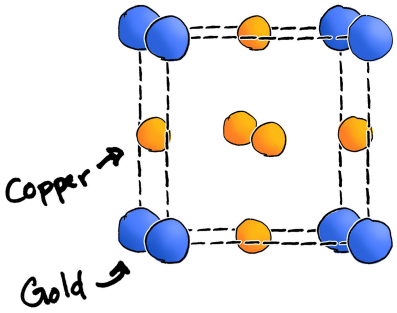


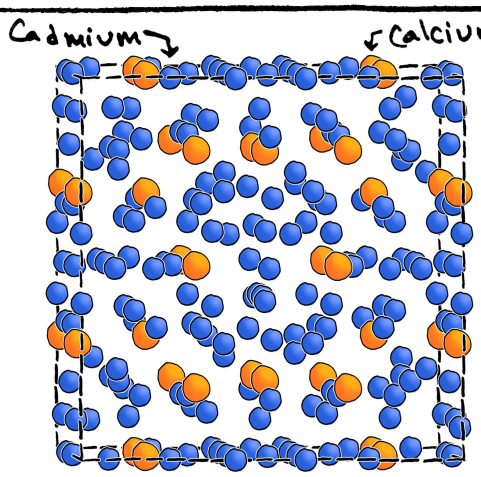
SOME METALS WE CAN MIX TOGETHER WITHOUT ADDING ANY COMPLEXITY.



Each of these atoms has a 50/50 chance of being nickel or palladium

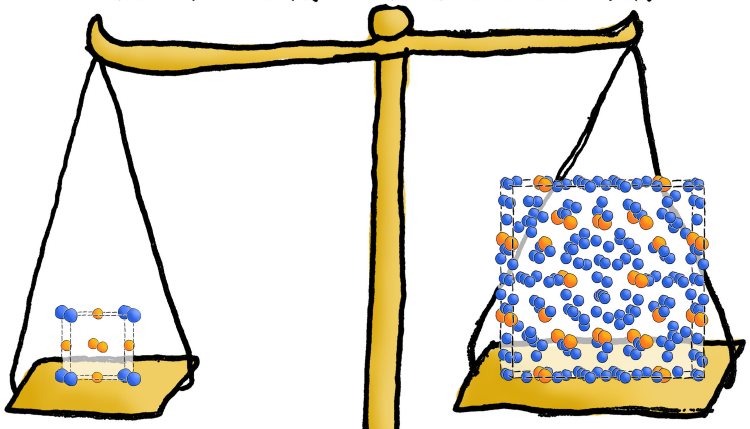
WE CAN GET SOME REALLY SIMPLE PATTERNS LIKE IN $AuCu_3$...



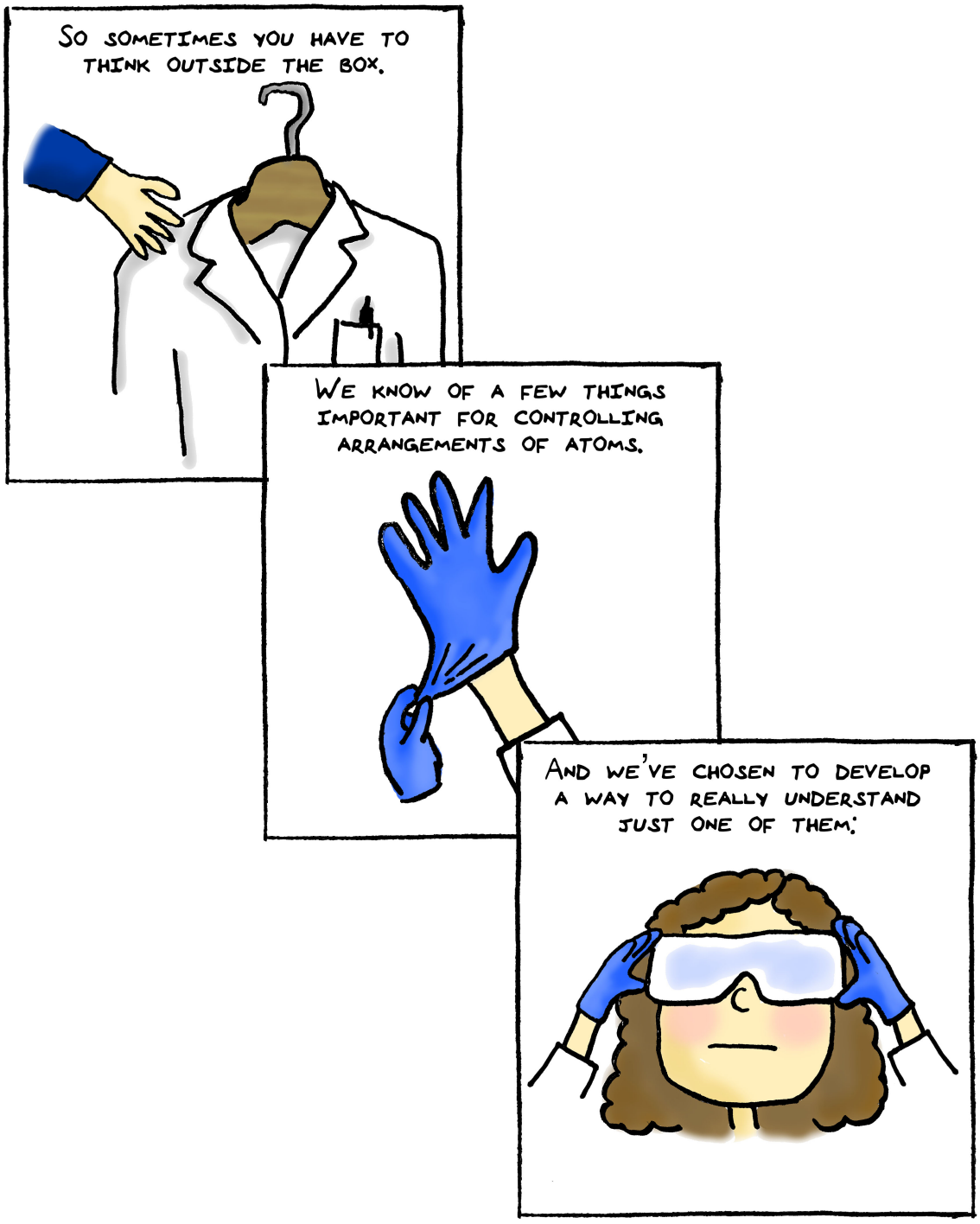


...OR WE CAN FIND REALLY COMPLEX ARRANGEMENTS LIKE $CaCD_6$.

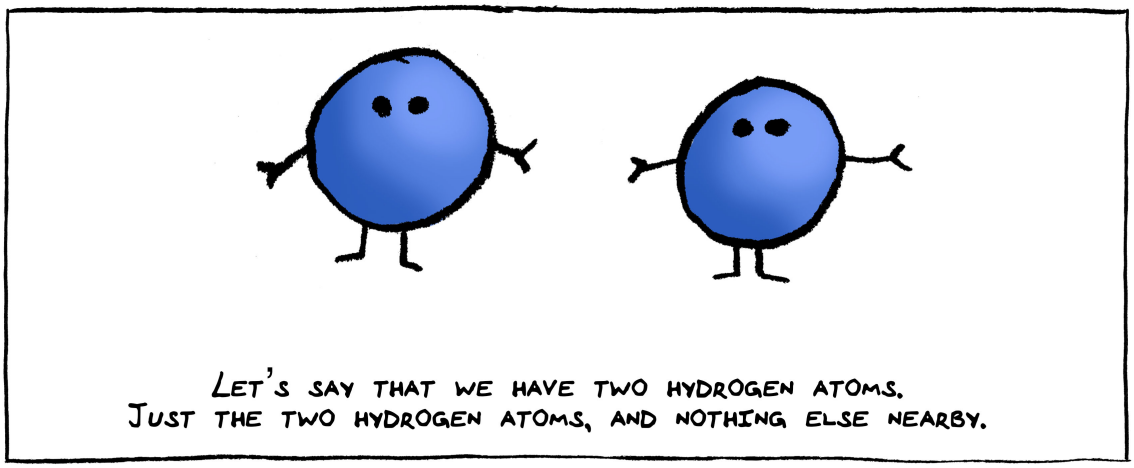
THE CATCH IS THAT WE REALLY DON'T UNDERSTAND HOW TO CONTROL WHICH ONE WE GET.



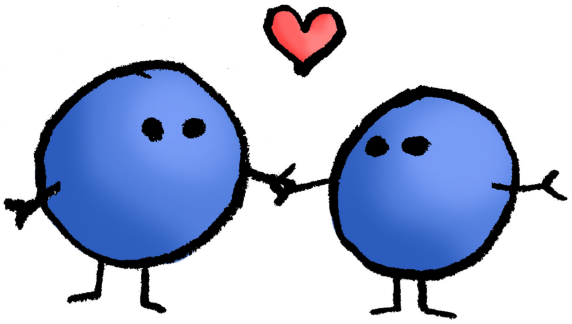
INTUITION TELLS US THAT ATOMIC SIZE MUST BE IMPORTANT SOMEHOW, BUT IT'S REALLY HARD TO DESIGN AN EXPERIMENT TO DETERMINE THE INFLUENCE THAT SIZE HAS ON STRUCTURE.


So sometimes you have to think outside the box.
We know of a few things important for controlling arrangements of atoms.
And we've chosen to develop a way to really understand just one of them:
Size.

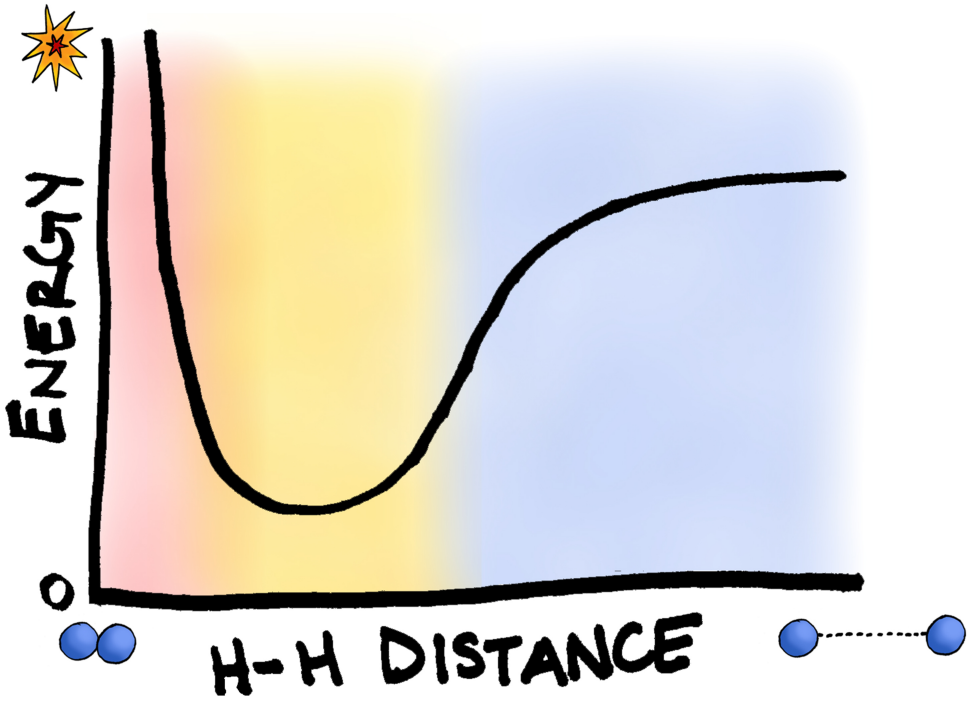
FOR PEOPLE, WE KNOW THIS BECAUSE TAKING A NAP FEELS SO GOOD.
FOR BONDS, WE KNOW THIS BECAUSE WE
CAN CALCULATE A BONDING POTENTIAL.



THE BONDING POTENTIAL TELLS YOU HOW MUCH THE HYDROGENS
BENEFIT FROM BEING NEAR ONE ANOTHER: FROM CHEMICALLY BONDING.

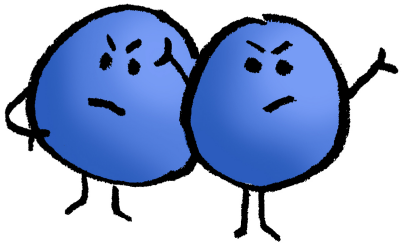


We can represent this potential as a graph of energy versus the distance between the atoms. And everything seeks the lowest energy possible.



This graph is best understood in three parts:

Too close.

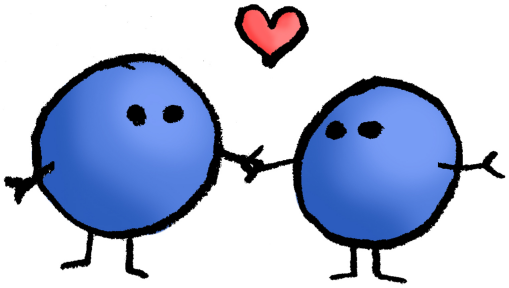


The nuclei start to feel each other's positive charge too much, and energy sky rockets.

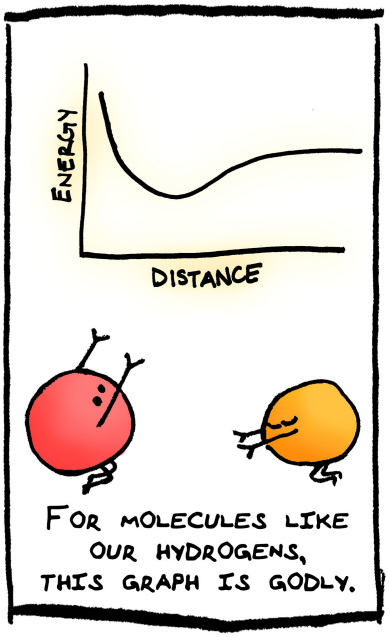
What other hydrogen?

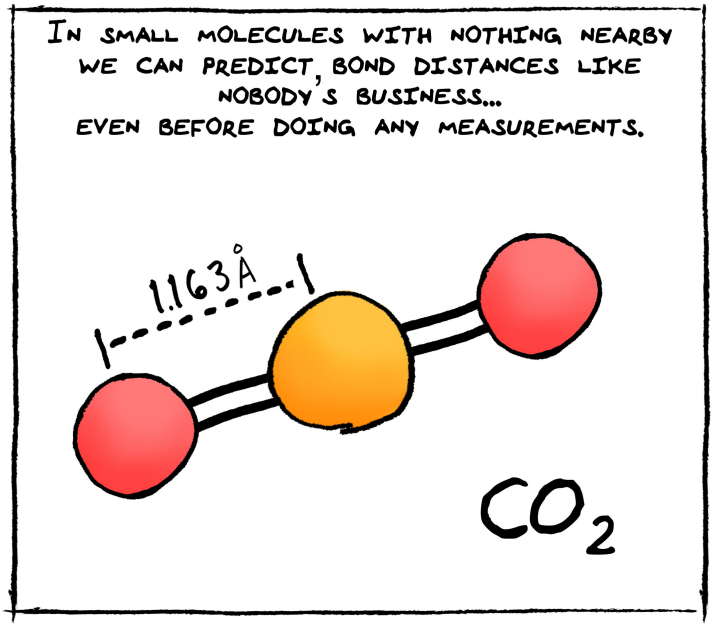
Too far away and the atoms don't notice one another

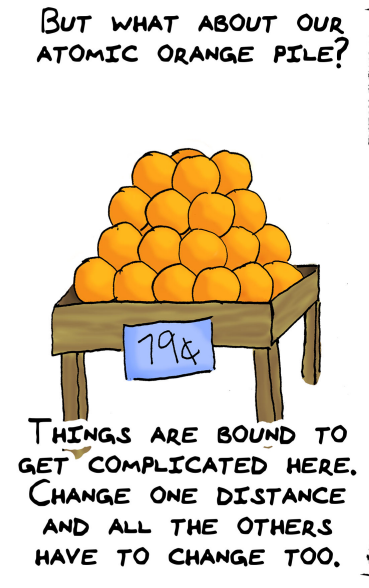
Goldilocks.

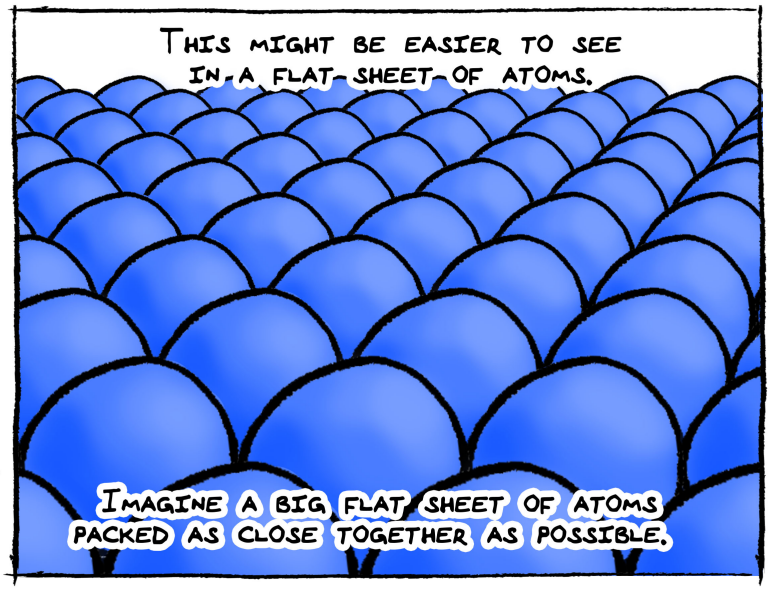


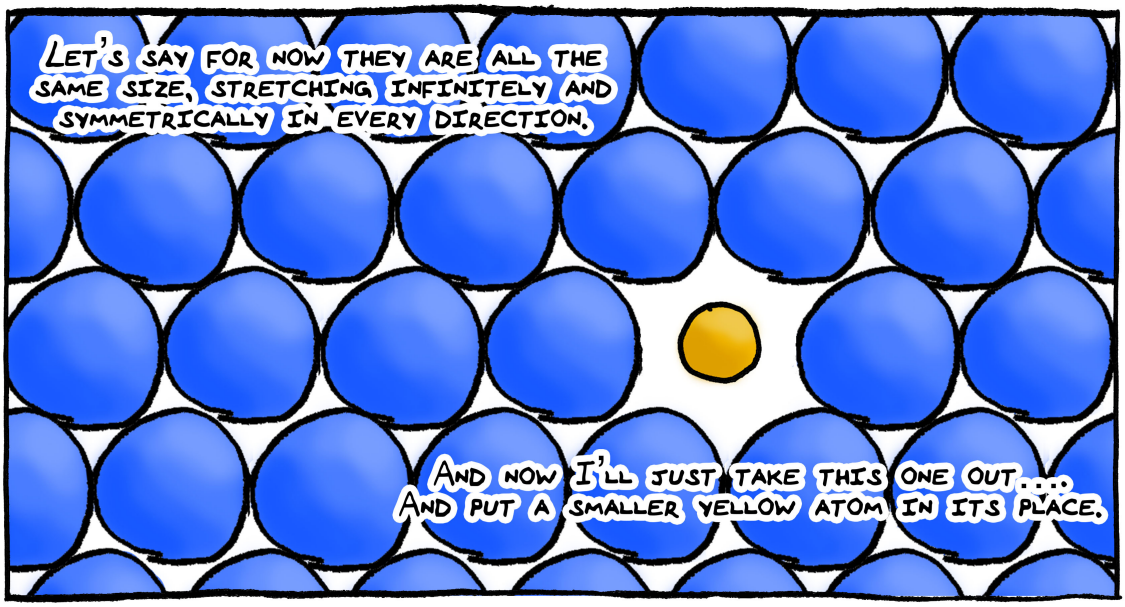
In a range of bonding distances, the energy plummets as the atoms favorably bond.


ENERGY
DISTANCE
FOR MOLECULES LIKE OUR HYDROGENS, THIS GRAPH IS GODLY.


IN SMALL MOLECULES WITH NOTHING NEARBY WE CAN PREDICT BOND DISTANCES LIKE NOBODY'S BUSINESS...
EVEN BEFORE DOING ANY MEASUREMENTS.
1.163 Å
CO_2


BUT WHAT ABOUT OUR ATOMIC ORANGE PILE?
79¢
THINGS ARE BOUND TO GET COMPLICATED HERE. CHANGE ONE DISTANCE AND ALL THE OTHERS HAVE TO CHANGE TOO.

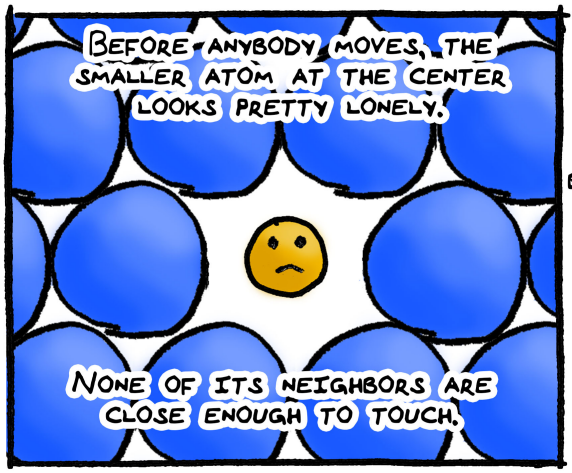

THIS MIGHT BE EASIER TO SEE IN A FLAT SHEET OF ATOMS.
IMAGINE A BIG FLAT SHEET OF ATOMS PACKED AS CLOSE TOGETHER AS POSSIBLE.


LET'S SAY FOR NOW THEY ARE ALL THE SAME SIZE, STRETCHING INFINITELY AND SYMMETRICALLY IN EVERY DIRECTION.
AND NOW I'LL JUST TAKE THIS ONE OUT... AND PUT A SMALLER YELLOW ATOM IN ITS PLACE.

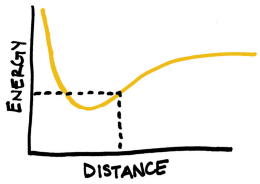
What do you hypothesize will happen?

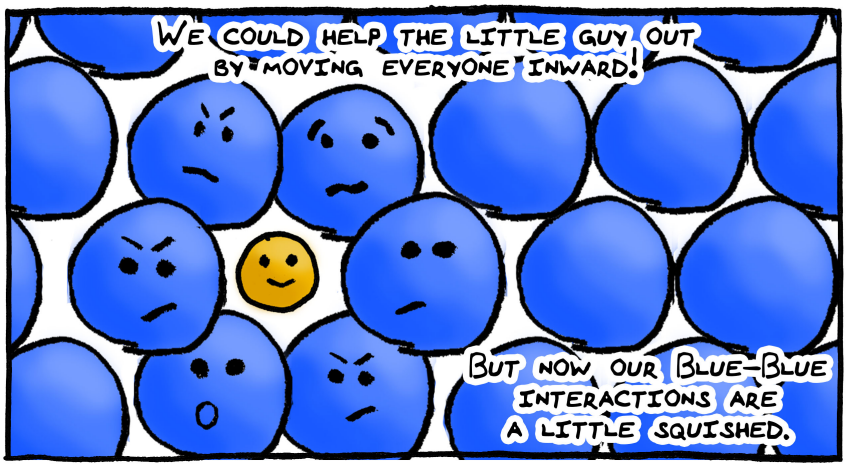
Let's think about it:

Well, poop. That's not optimal.

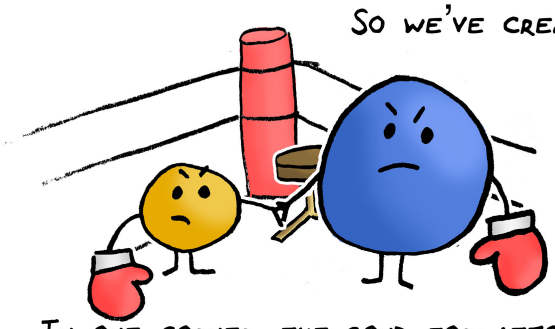


Put in terms of a two atom potential for the small atom and one of its bigger neighbors, we'd be here:

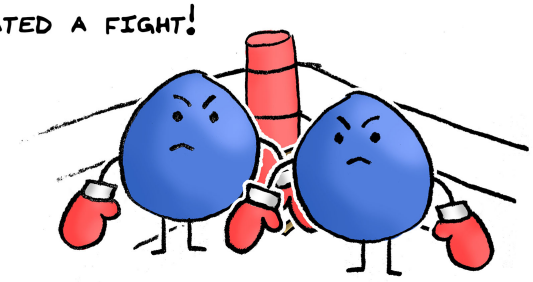




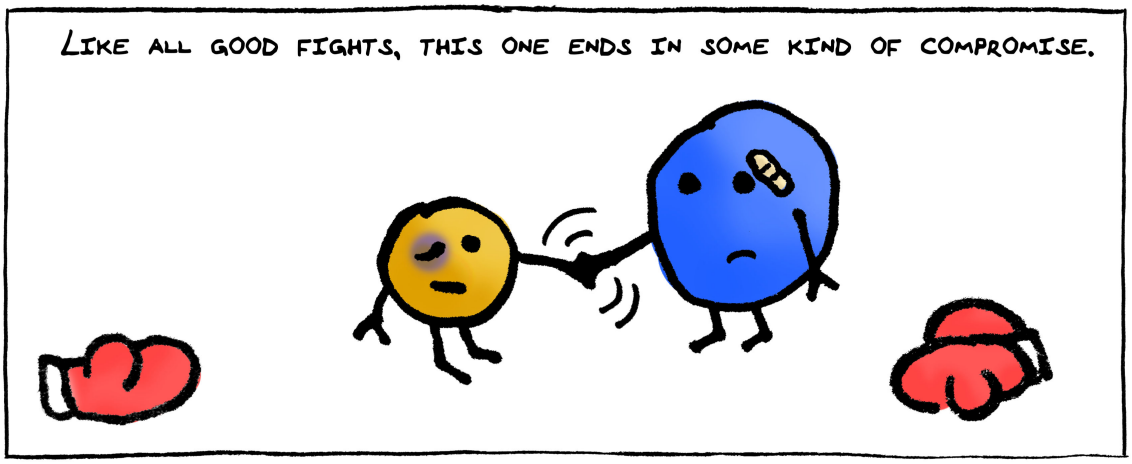
So we've created a fight!

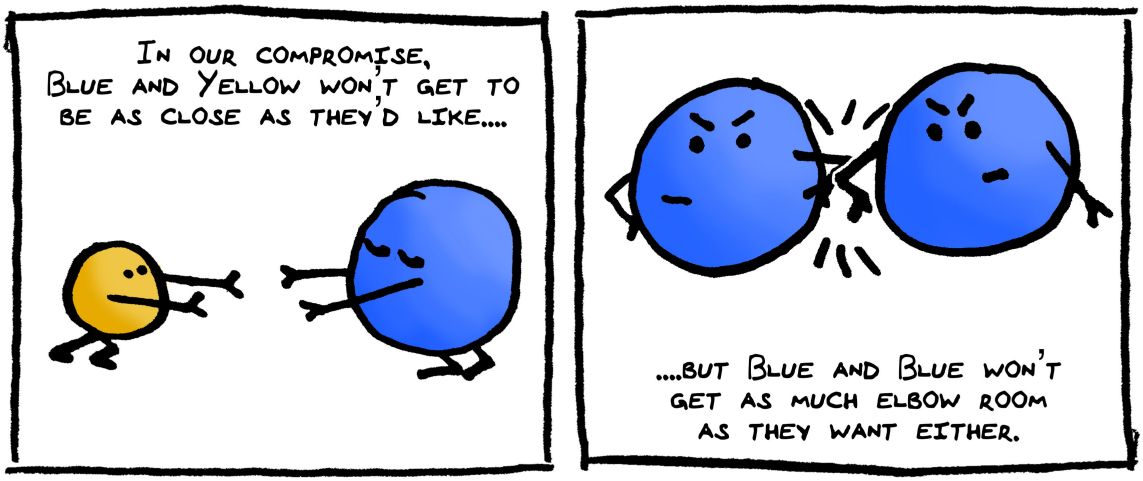


In one corner, the bond formation between Yellow and Blue...



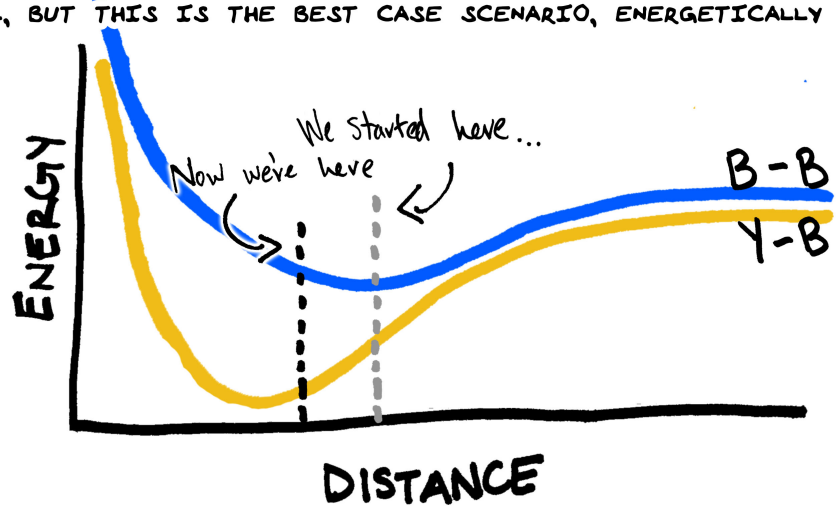
In the opposite corner, Blue's need to keep its distance from other big atoms.



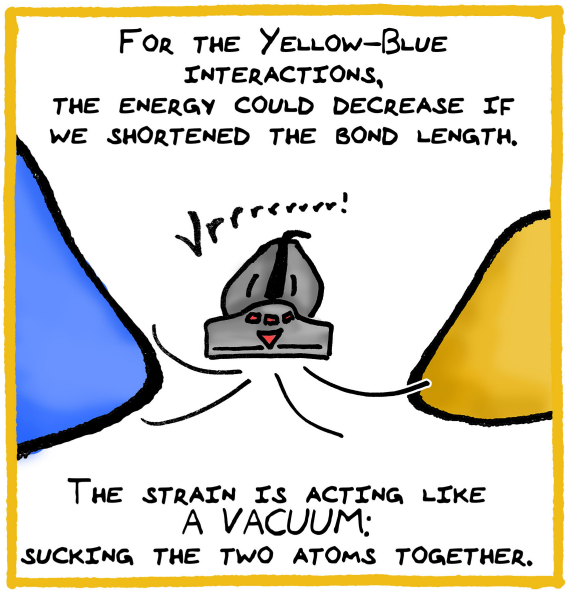


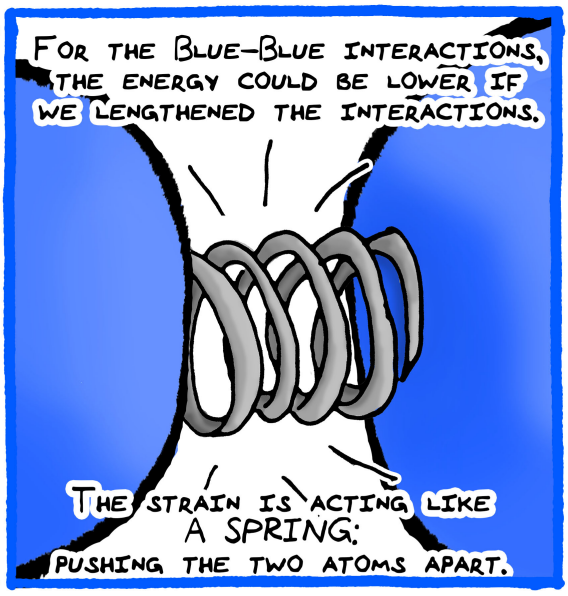
What does this compormise mean on our energy-distance graphs?

At the black line, after we move everyone inwards a little, neither curve is at its lowest point. Both interactions aren't optimal, but this is the best case scenario, energetically speaking.

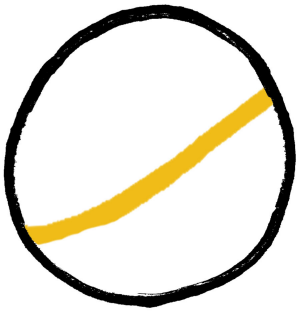


Being held at a non-optimal energy creates strain. Let's take a closer look at what it means to be strained in our example:

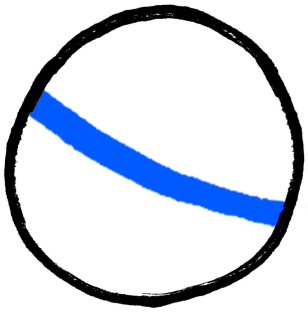




THE QUICK-AND-DIRTY WAY TO TELL IF WE'VE GOT A VACUUM OR A SPRING IS TO LOOK AT THE SLOPE OF THE LINE.

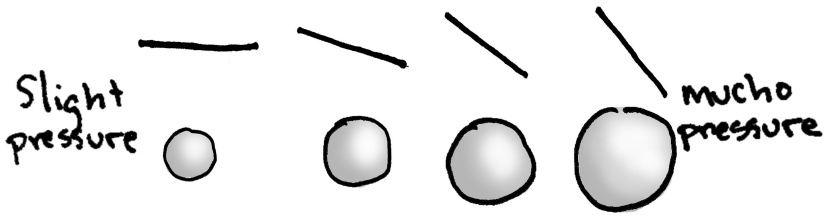


IF THE LINE TILTS THIS WAY, WE'D NEED TO SHORTEN THE BOND.

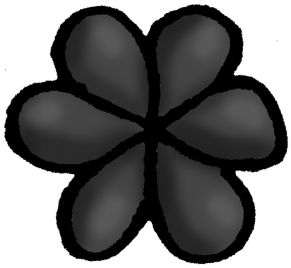


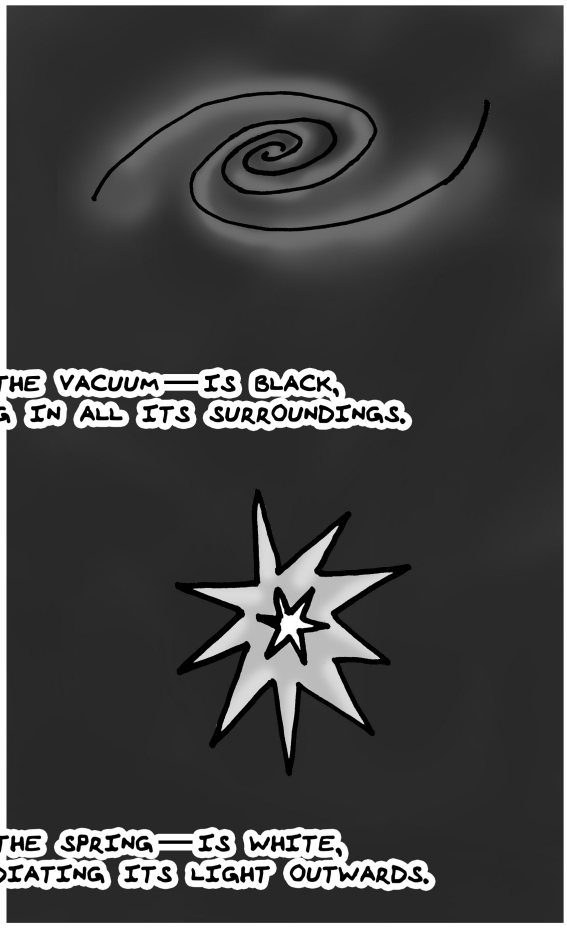
IF THE LINE TILTS THIS WAY WE'D NEED TO LENGTHEN IT.

THE SLOPE OF THE LINE TANGENT TO THE CURVE TELLS US THE SIGN OF THE STRAIN AND THE DEGREE OF TILT TELLS US HOW STRONG IT IS.

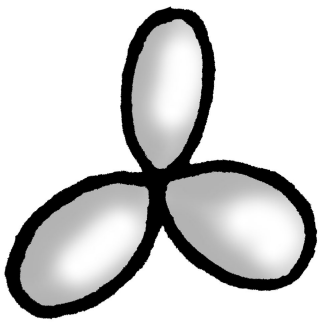


WE'VE DECIDED TO CALL THE STRAIN CHEMICAL PRESSURE, AND WE DRAW IT LIKE THIS:

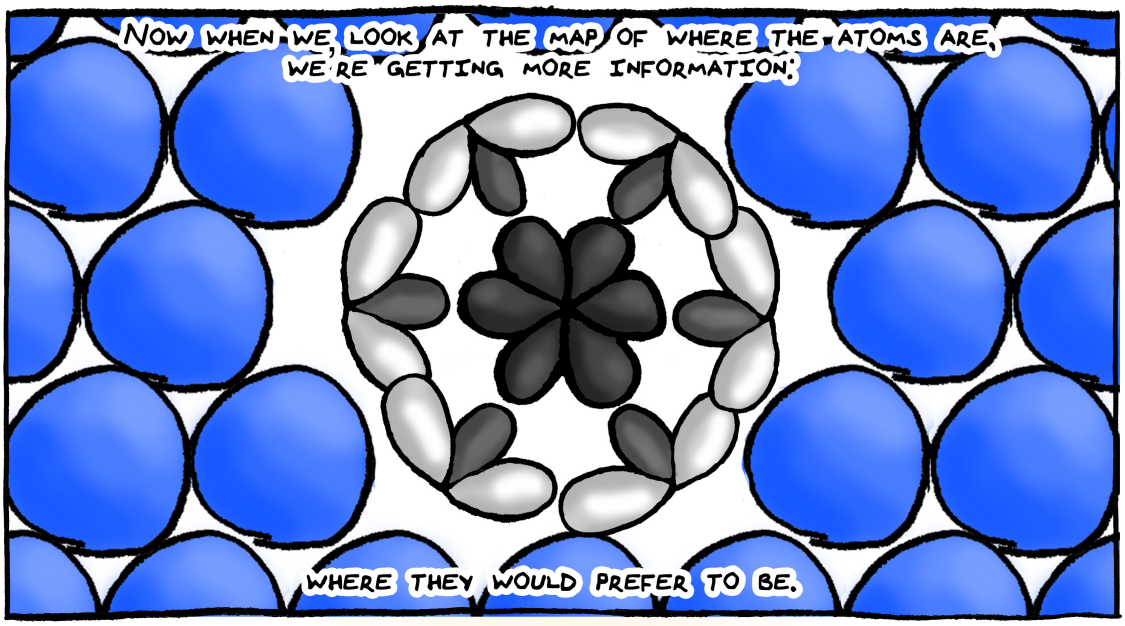




NEGATIVE PRESSURE — THE VACUUM — IS BLACK, LIKE A BLACK HOLE, SUCKING IN ALL ITS SURROUNDINGS.



POSITIVE PRESSURE — THE SPRING — IS WHITE, LIKE A WHITE HOT STAR, RADIATING ITS LIGHT OUTWARDS.



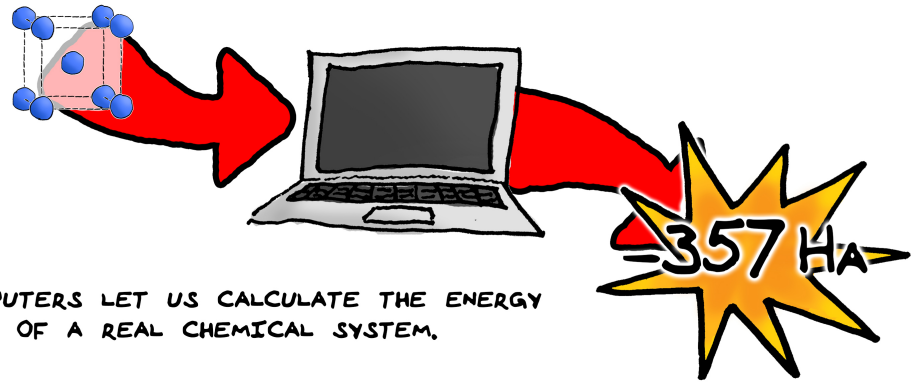
BUT WHAT ABOUT THE ORANGES? CAN WE EXTEND THIS IDEA INTO 3-D?

YES, YES WE CAN.

So much is possible with computers.

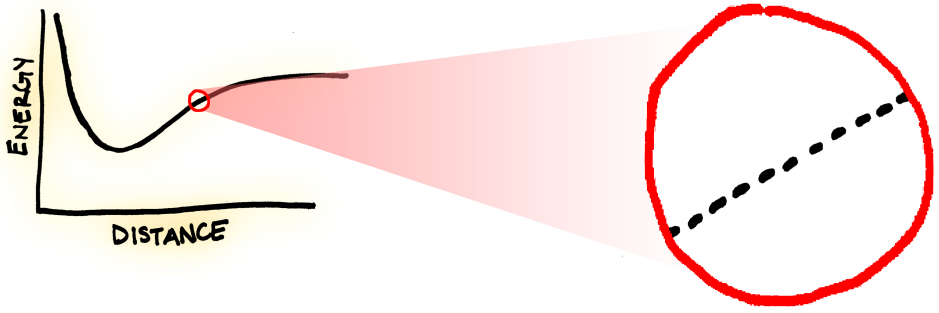
They let you watch cat videos, listen to podcasts, and fight battles with lasers in outer space.

Turns out they are pretty helpful when it comes to chemistry too.



Computers let us calculate the energy of a real chemical system.

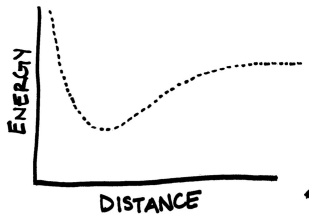
This gives us the data for our all-important energy-distance diagram...



But here's the bad news:

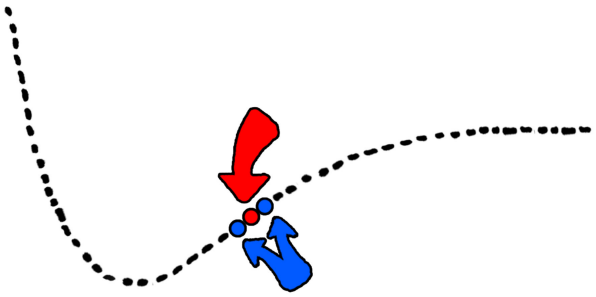
They do it one point at a time.

Each point needs between a few hours and a few days for the calculation to finish.

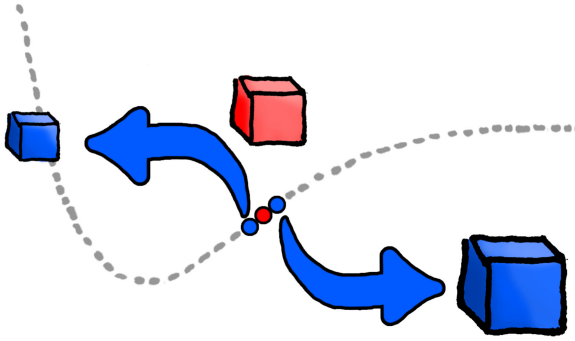


...But remember, we don't need the whole curve.

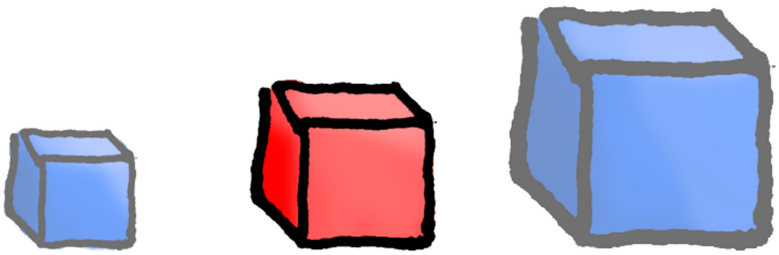
Since the slope of the line tells us everything we need to know,



all there is to do is calculate the energy at two points, one on either side of the one we care about.

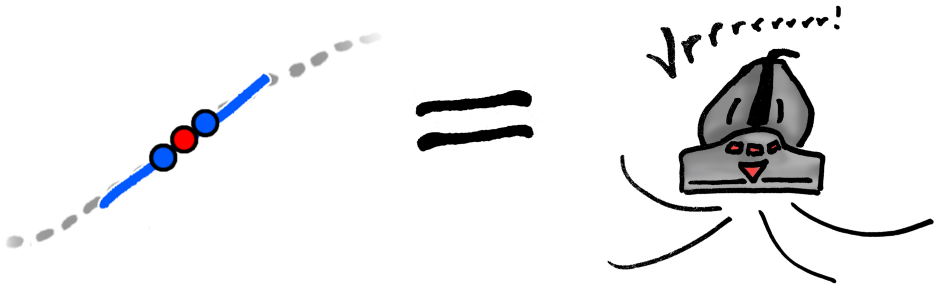


Practically speaking, this means we are going to make a Small Version of the unit cell that artificially shortens everything to get the energy at point #1, and then a Big Version that lengthens everything to get the energy at point #2.

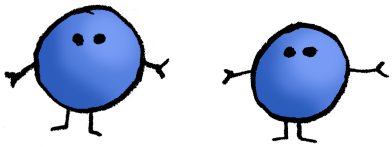


Note: the Small Version and the Big Version don't actually exist. We can only make them because we are inside a computer.

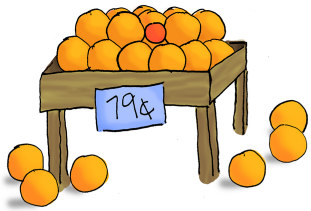
Once we have the energies for Big Version and Small Version, all we need to do is draw a line and determine if our leftover tension is a vacuum or a spring.



Up until this point, the 3-D seems a lot like our 2-D example. Here's the difference:

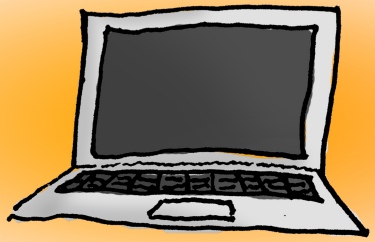


In 2-D, it was enough to look at one atom pair at a time.

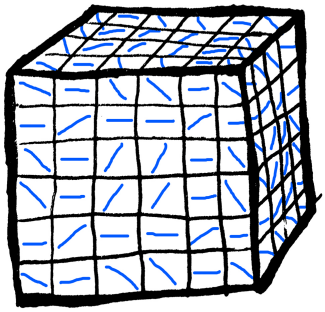


In 3-D, we anticipate that every interaction will influence all of the others, in every direction.

In 3-D, we need to make an energy - distance diagram for every point in the structure in the Big Version and the Small Version, because we can't move just one atom. Now for the good news:

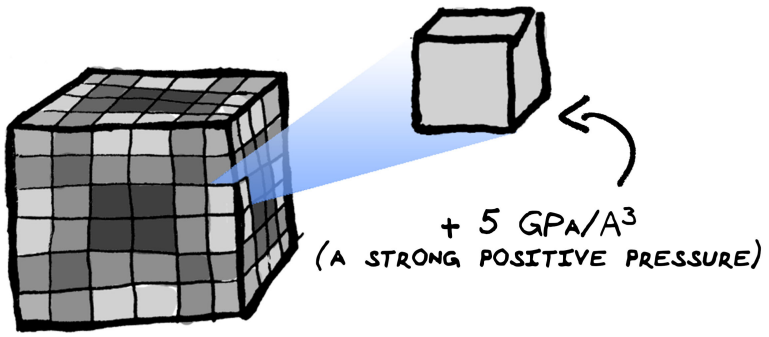


The computer gives us an energy for every point in the structure at the same time. Thanks, computer!



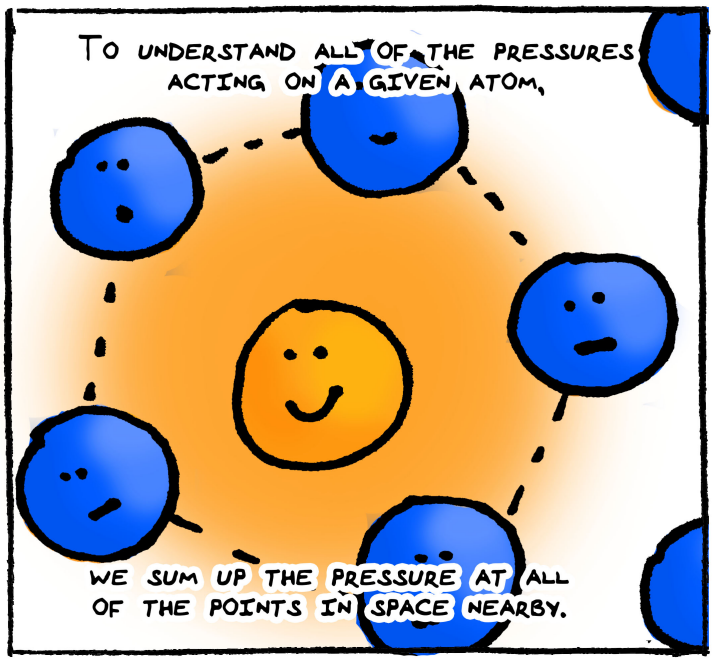
We can draw that line between Big Version Energy and Small Version Energy for every one of these points simultaneously.

And we end up with an array of vacuums and springs of varying intensities.

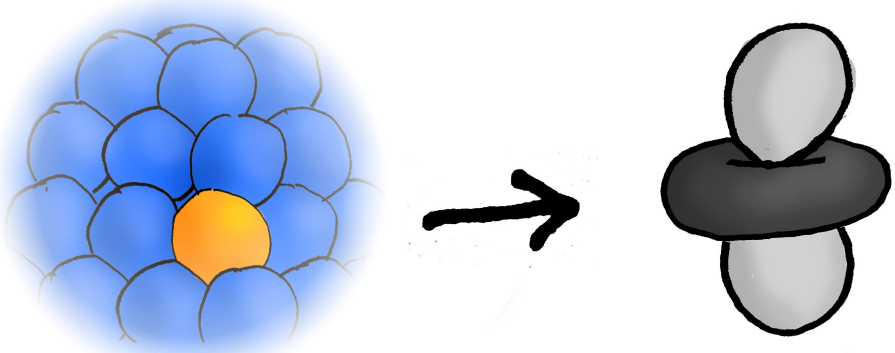


But this just gives us a map of where pressure is high and low. How can we turn this into a picture that emphasizes how the atoms might react to the pressure?

The answer requires some fancy scissors.

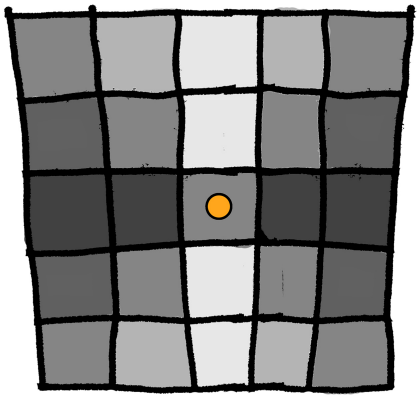


It turns out that the way we cut the map into separate atoms has to be pretty involved.

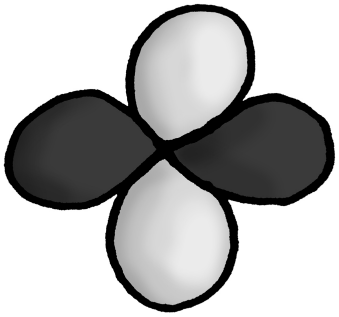


But simply put, we take all of the points within the atom's reach, turn it into an interpretable 3-D object that corresponds to the sign and intensity of the pressures in all directions.

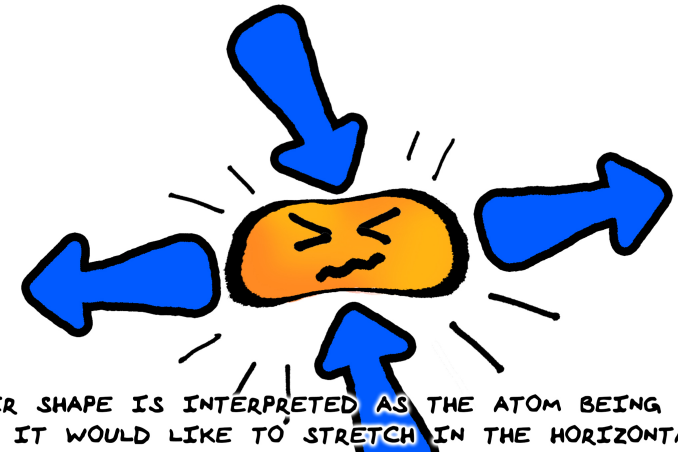
Let's take a quick 2-D example to see the concept:



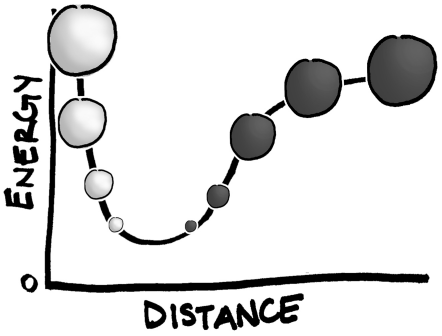
This map has positive pressures above and below the atom at the center, but off to the left and right, we see dark regions.



That map would sum up to this object – a clover that alternates black and white petals.

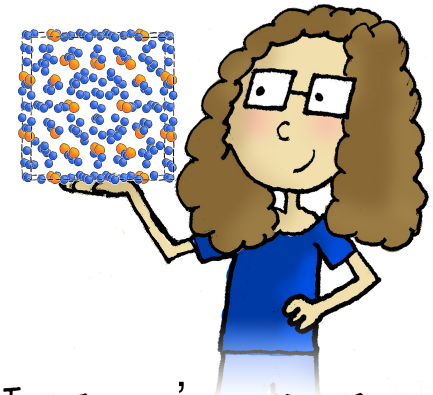


This clover shape is interpreted as the atom being squished vertically, but it would like to stretch in the horizontal direction. If we moved to three dimensions, we would have information about pressure above and below the surface of this page too.

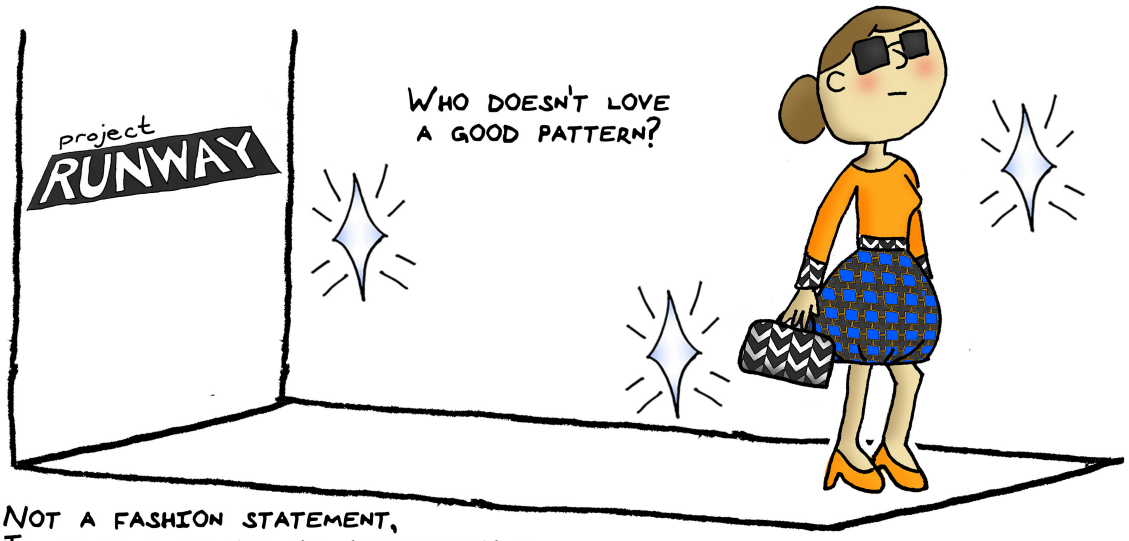


Up until this point, we've looked at the inner workings of Chemical Pressure, a tool that we can use to understand how the size of an atom can influence a 3-D crystal structure.

It's a pretty powerful tool. We've been able to use it to explain the formation of many complex atomic arrangements.

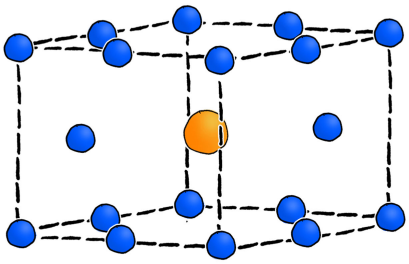


I think we're ready to see what this puppy can do.



NOT A FASHION STATEMENT,
I MEANT A SERIES OF OBSERVATIONS
THAT WE THINK IS MORE THAN A COINCIDENCE.

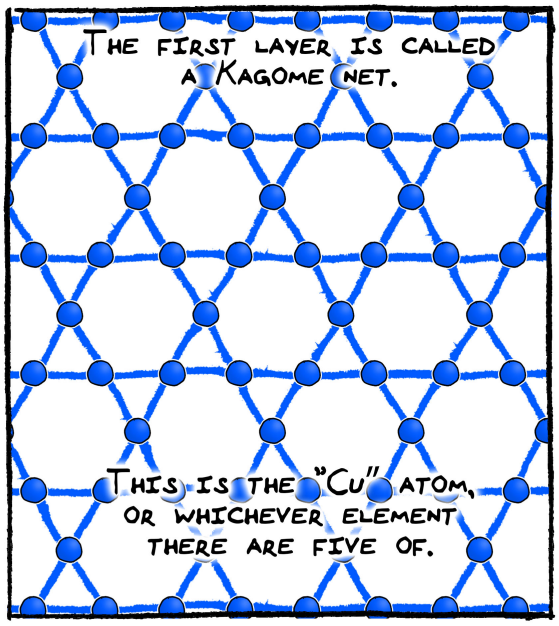
IN THIS CASE, WE FOUND A PATTERN IN WHICH
DIFFERENT COMPOUNDS TAKE ON ONE PARTICULAR STRUCTURE:

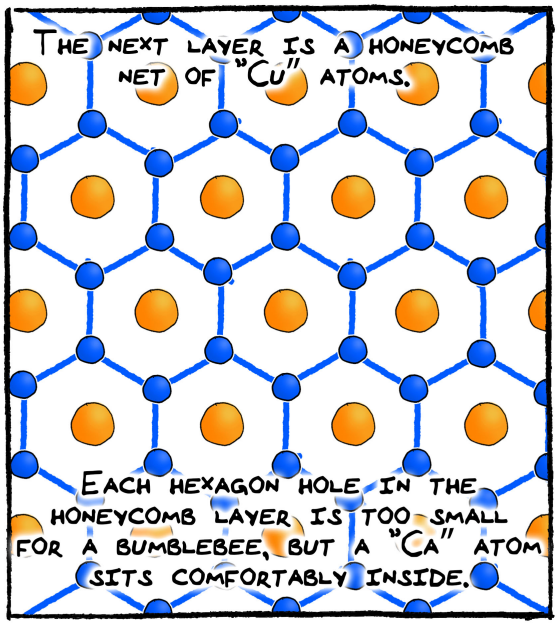


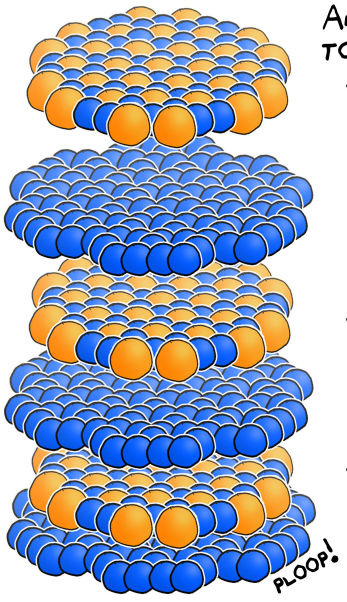
LOTS OF INTERMETALLICS
MAKE THIS STRUCTURE TYPE.
IT'S ALL THE RAGE THIS SPRING.

WE CALL IT "THE $CaCu_5$ TYPE", WHICH DOESN'T MEAN THAT IT ABSOLUTELY HAS TO CONTAIN CALCIUM OR COPPER, IT JUST MEANS THAT THE FIRST TIME WE SAW THIS STRUCTURE, THAT'S WHAT WE HAPPENED TO BE LOOKING AT. THE ESSENCE OF THE $CaCu_5$ TYPE IS THE SPECIFIC ATOMIC POSITIONING.

THIS STRUCTURE IS MADE UP OF TWO FLAT LAYERS, AND THEY ALTERNATE:







AND THE LAYERS STACK TOGETHER, ALTERNATING STUFFED HONEYCOMB,

KAGOME,

STUFFED HONEYCOMB,

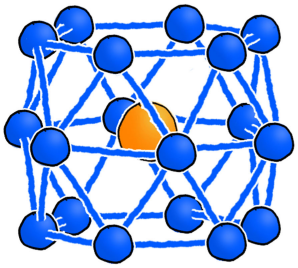
KAGOME,

STUFFED HONEYCOMB,

KAGOME,

HONEYCOMB... UNTIL...INFINITY.

IF WE LOOK AT THIS FROM CA'S PERSPECTIVE, WHAT WOULD WE SEE?



THAT ATOM GETS A NICE LITTLE BASKET TO SIT IN: HEXAGON ABOVE, HEXAGON BELOW, AND A NICE HUG FROM A HEXAGON AROUND THE CENTER TOO.

SO WHAT'S ALL THIS TALK ABOUT A PATTERN? LET'S CHECK OUT THE PERIODIC TABLE:

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 In	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

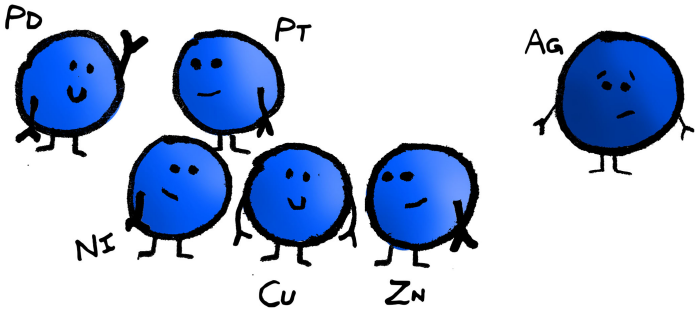
*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cu	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

IF WE KEEP THE CALCIUM ATOM A CALCIUM ATOM, THEN ALL OF THESE BLUE METALS STANDING IN FOR "Cu" WOULD GIVE US THE $CaCu_5$ TYPE. FOR EXAMPLE, $CaNi_5$ MAKES THIS STRUCTURE, BUT $CaAg_5$ DOESN'T.

WHAT DOES THIS MEAN?

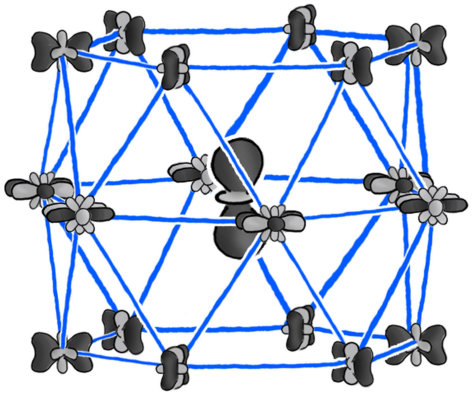
WE'RE SEEING THE VERSATILITY OF THIS STRUCTURE TYPE.

THERE'S SOMETHING ABOUT ALL FIVE OF THESE METALS THAT JUST WORKS WHEN WE COMBINE THEM WITH CALCIUM IN A 5:1 RATIO.



COULD THAT SOMETHING BE...SIZE?

Let's look at what a chemical pressure plot of $CaPd_5$ has to say.



The large black peanut shape in the center implies the calcium is experiencing negative pressures, and it wants to be closer to the atoms in the Kagome nets above and below.

The pressures between Ca and the honeycomb net are positive, indicated by the white doughnut shape in the middle.

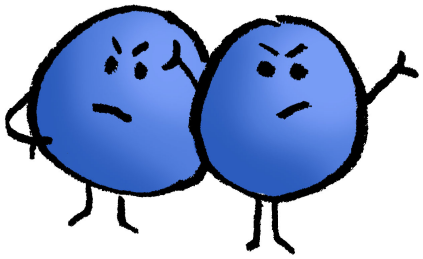
We can tell this positive pressure is not as strong as the negative pressure: The size of the lobe is proportional to the magnitude of CP.

Calcium experiences an overall negative CP.

With a black hole at the center of the basket, why doesn't it implode?

Take a close look above. The negative pressure at the center is countered by a positive pressure between the palladium atoms of different layers.

The palladium Kagome rings can't even contract around the calcium because those Pd–Pd contacts are already too close.



We've got another fight! But that's not a bad thing.

We know that this compound actually exists in the real world, and everything will inherently have a little bit of strain in it.

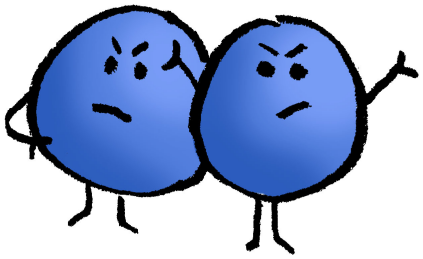
This strain is only meaningful when we compare it to the strain in similar compounds.

(This is where it gets really fun.)

Knowing that the calcium atom is a little too small for its palladium basket,

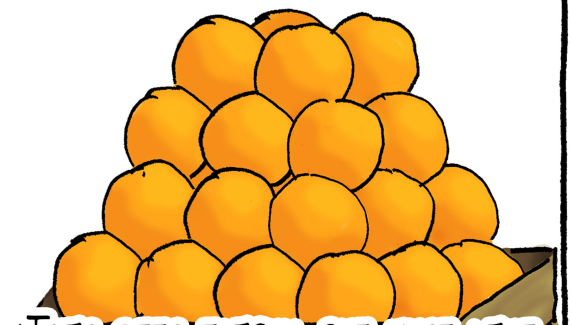
What do you think would happen if we put larger atoms in place of palladium?

We already know the atoms making up the cage are squeezing together as tightly as possible.



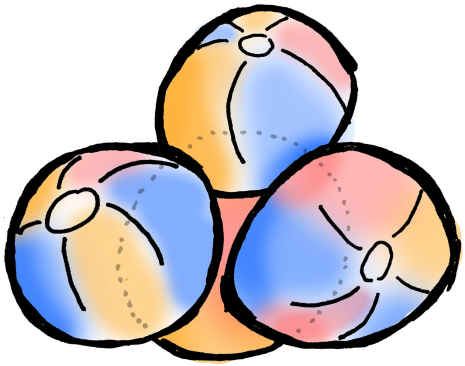
If we make those atoms bigger, we predict that they'll be even more stressed out!

But what effect will that have on calcium, which obviously stays its same size?



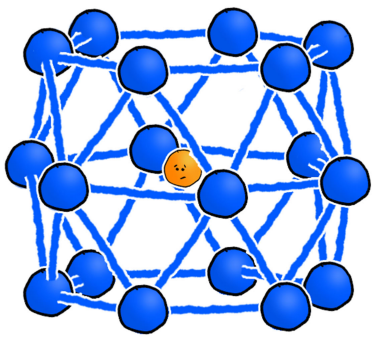
This gets tricky, but just like a stack of 18 oranges is bigger than a stack of 18 tangerines, if we use larger atoms, the cage will be bigger, making for a bigger hole for calcium to sit in.

Therefore the amount of empty space between something like a couple of beach balls is much bigger than the empty spaces between our dear citrus fruits.



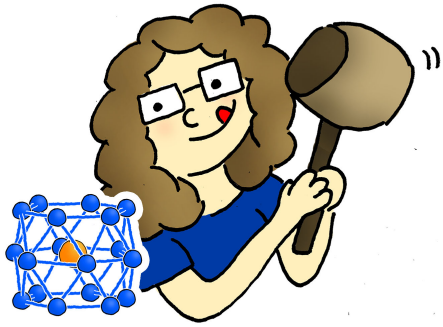
But wait!

Didn't we say we wanted a SMALLER hole for our tiny calcium atom to sit in?



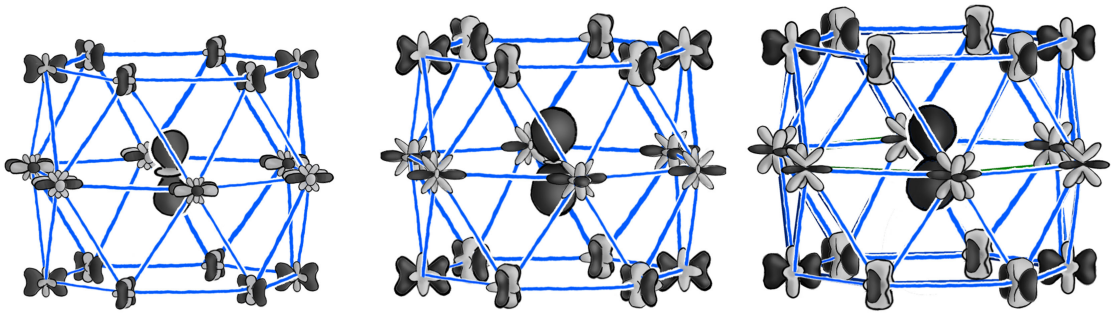
This bigger cage idea is going to ruin everything!

Well, yes, a smaller atom would make this ONE situation better. But we're interested in taking our understanding even further.



And some things have to break before we can totally understand them.

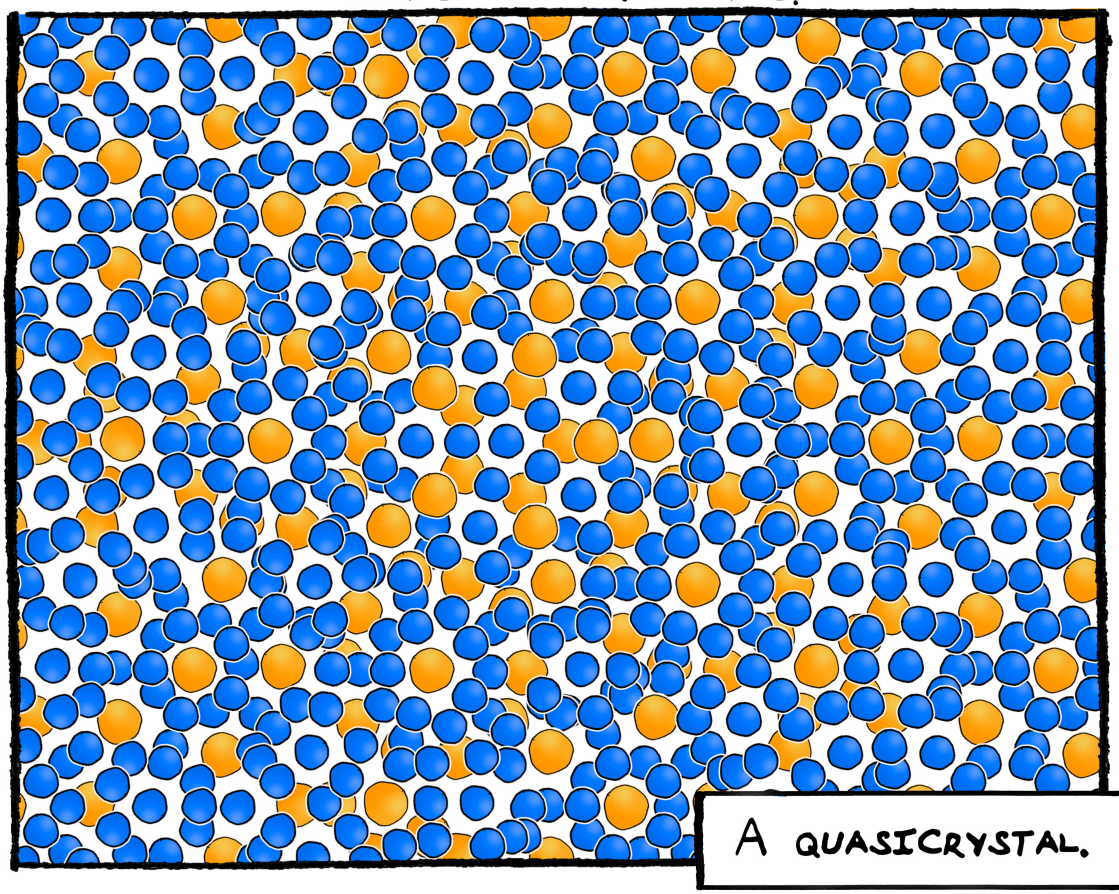
Ok let's do this, let's get to the real data! Here we compare the familiar $CaPd_5$ with hypothetical compounds "$CaAg_5$" and "$CaCd_5$".



Just like we had guessed, the bigger the transition metal, the more intense the negative pressure is inside that basket.

In the hypothetical "$CaCd_5$", calcium is experiencing quite the vacuum! No wonder "$CaCd_5$" has never been made.

What do we observe instead?



A quasicrystal.

QUASICRYSTALS ARE THE

REBELS OF THE CRYSTALLINE WORLD

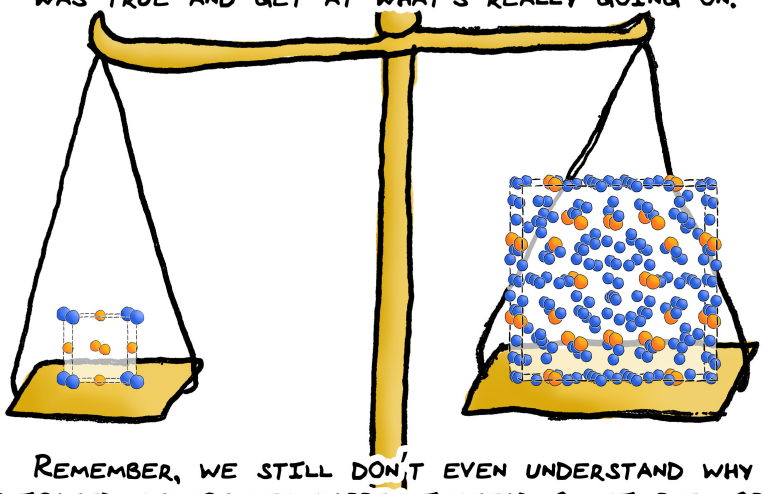
THEY'RE ROTATIONALLY SYMMETRIC, BUT NOT TRANSLATIONALLY SYMMETRIC.

THEY CAN BE PERIODIC IN ONE DIRECTION, BUT NOT PERIODIC IN EVERY DIRECTION.

THEY DIFFRACT, BUT YOU HAVE TO USE MORE THAN 3 DIMENSIONS TO SOLVE THEIR STRUCTURES.

QUASICRYSTALS BREAK ALL THE RULES, AND THEY DON'T GIVE A #@$&.

STUFF THAT BREAKS RULES IS OFTEN THE MOST INTERESTING STUFF TO STUDY, BECAUSE IT LETS YOU REVISE WHAT YOU THOUGHT WAS TRUE AND GET AT WHAT'S REALLY GOING ON.



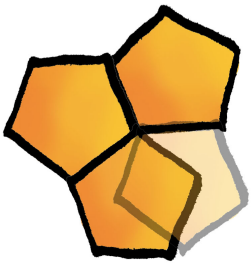
REMEMBER, WE STILL DON'T EVEN UNDERSTAND WHY COMPLICATED STRUCTURES HAPPEN INSTEAD OF SIMPLER OPTIONS.

WE WANT SOME RULES.

BUT WE'RE ONLY GOING TO GET THEM IF WE TAKE A CLOSER LOOK AT THE REBELS, THE RULEBREAKERS, THE WEIRD STUFF ON THE FRINGES OF OUR CURRENT UNDERSTANDING.

WHAT DO WE KNOW SO FAR ABOUT QUASICRYSTALS?

QUASICRYSTALS HAVE ROTATIONAL SYMMETRIES THAT ARE INCOMPATIBLE WITH TRANSLATION.



ONLY 2-, 3-, 4-, AND 6-FOLD PATTERNS CAN HAVE UNIT CELLS.

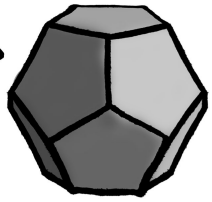
WHY CAN'T WE HAVE 5-FOLD PATTERNS?

UNLIKE HEXAGONS, SQUARES, AND TRIANGLES, YOU CAN'T COMPLETELY COVER A PLANE WITH ONLY REGULAR PENTAGONS OR OCTAGONS.

YOU'LL END UP WITH WEIRD SHAPES OF EMPTY SPACE. GRAB SOME TANGRAMS AND TRY IT.

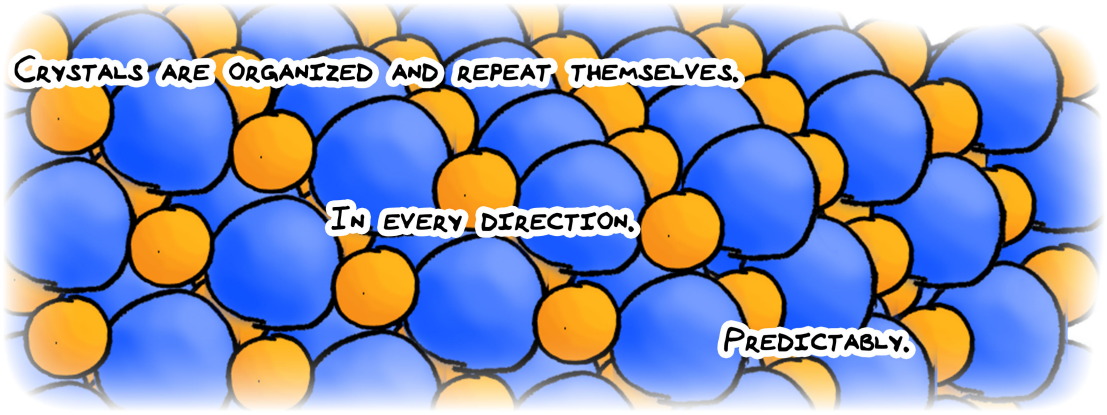
WE'VE FOUND QUASICRYSTALS THAT HAVE 5-, 7-, 8-, 10-, EVEN 12-FOLD SYMMETRIES.

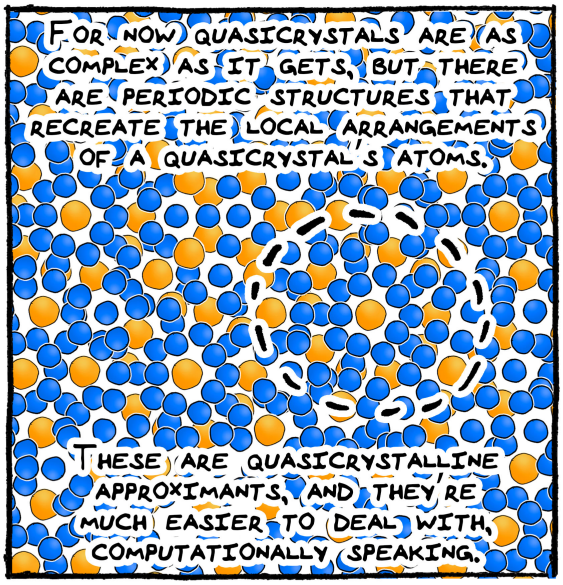
Some of them look like this

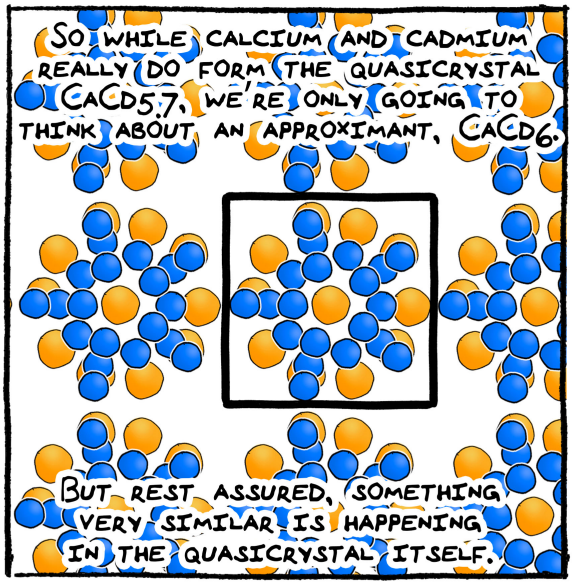


THEY DON'T HAVE UNIT CELLS, BUT THEY'VE STILL GOT SYMMETRY.

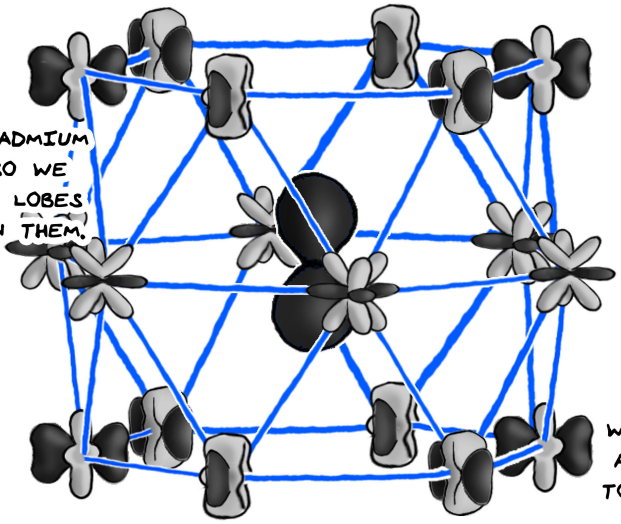
I'VE SAID IT BEFORE, BUT IT IS WORTH (AHEM) REPEATING...





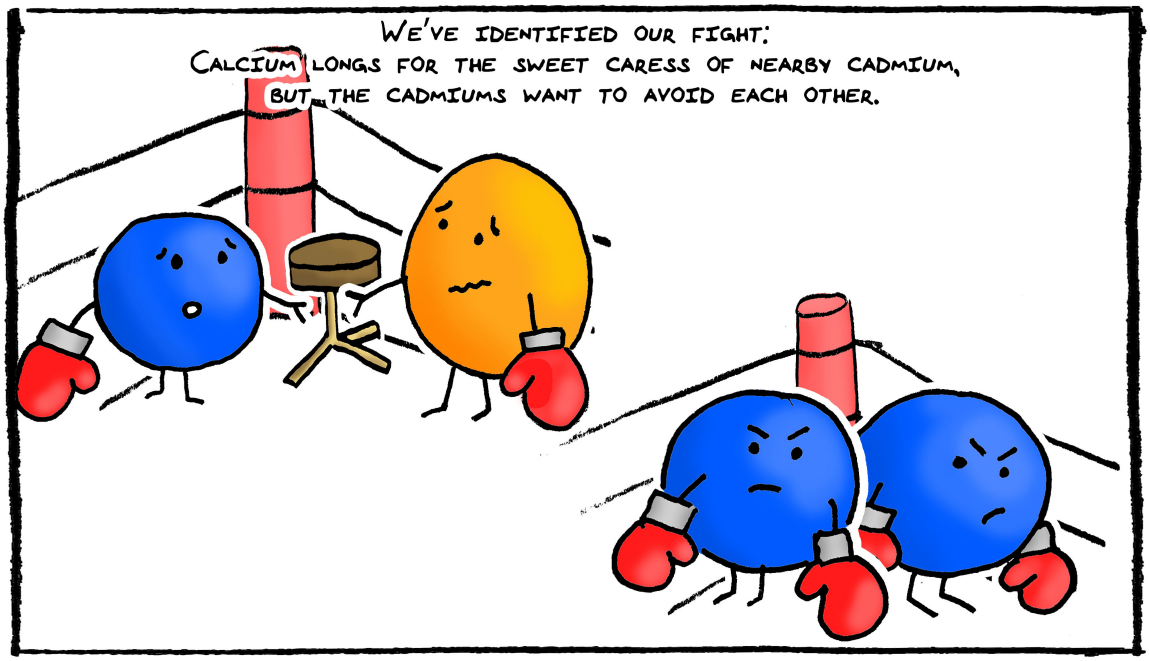


When we looked at the hypothetical $CaCd_5$ compound, we noticed that there was a vacuum in the center.

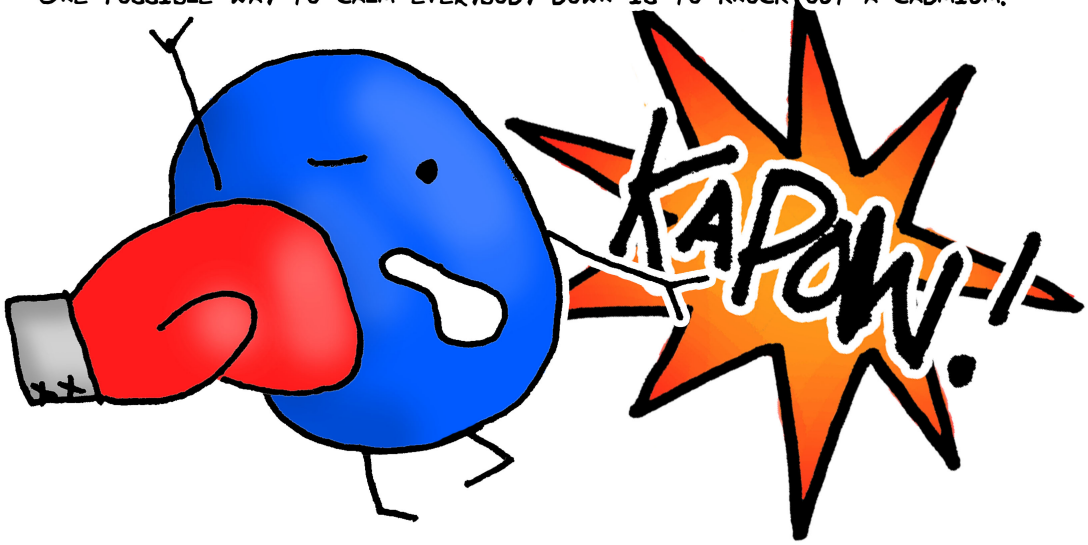


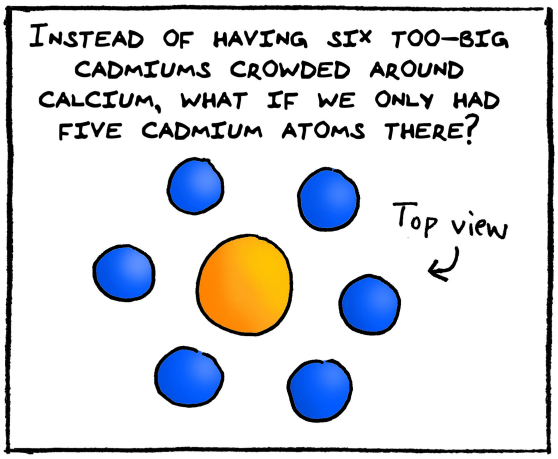
Calcium wants cadmium to be closer, so we see large, black lobes pointing between them.

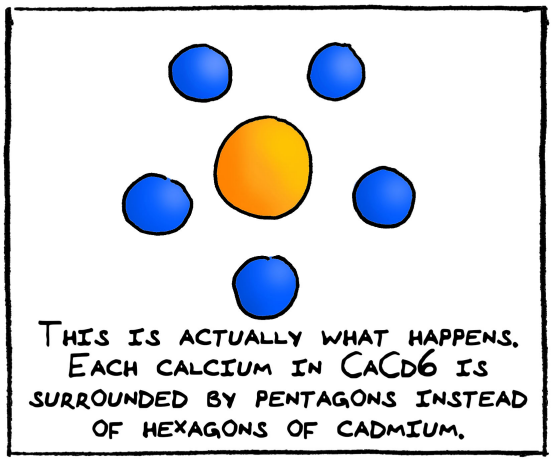
This force is opposed by cadmium–cadmium repulsion... those lobes are white, meaning the atoms are already too close together.

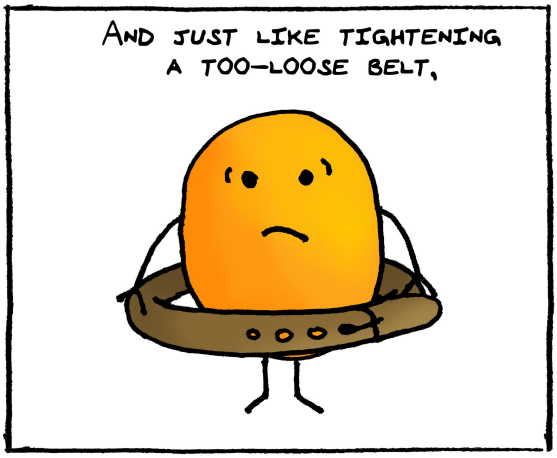


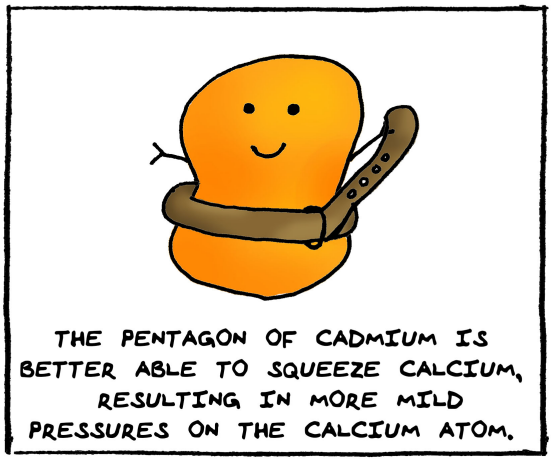
One possible way to calm everybody down is to knock out a cadmium.



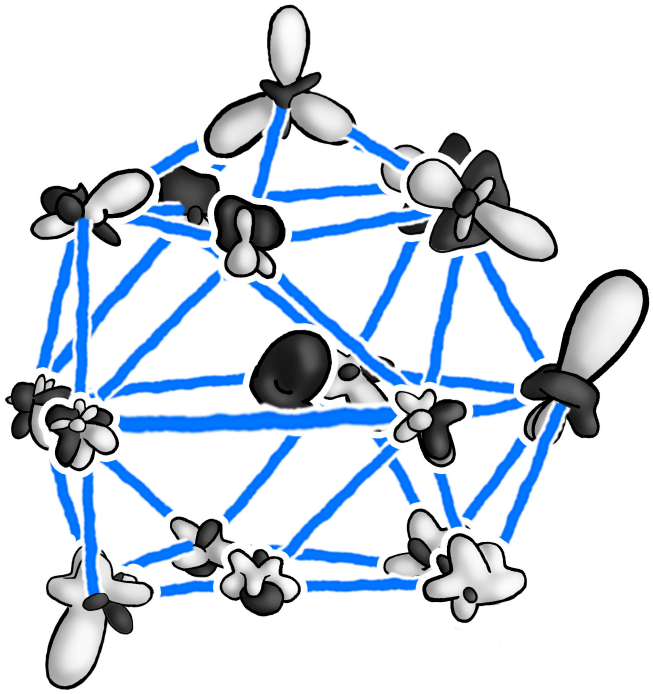






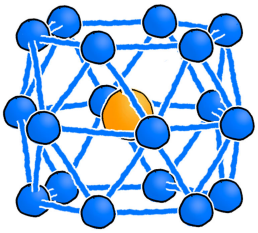


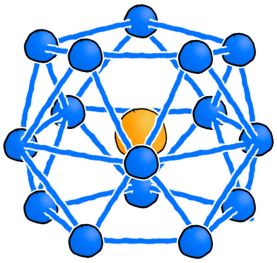
Cadmium is pretty happy with this arrangement too; there's fewer neighbors to bump into. Here's what the CP looks like:



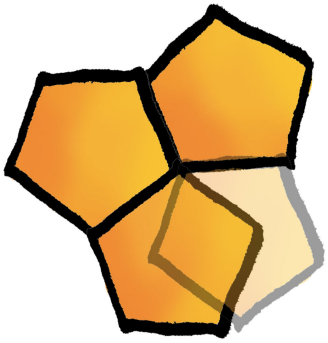
Now it's smooth sailing, right? The CP is better, Calcium has a pentagonal belt, and cadmium mostly stopped hitting itself.

We've got a problem with periodicity.
The very thing that pleases our compound upsets the periodicity of our structure!



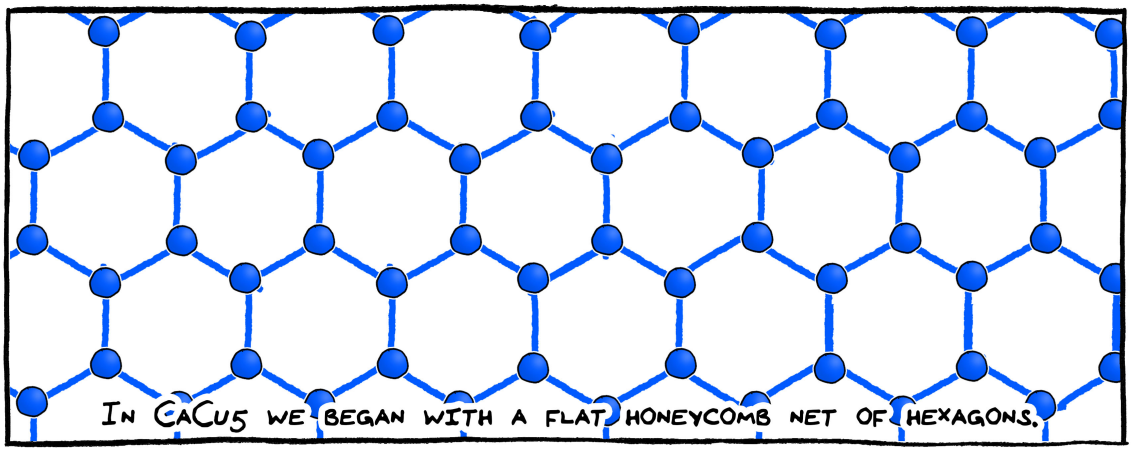


Instead of those infinite hexagonal nets,
our new compound demands infinite pentagonal nets.

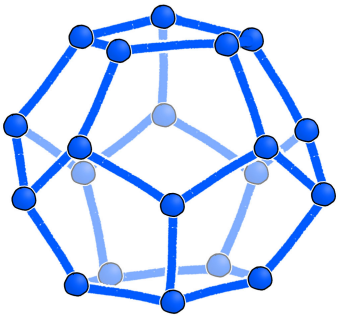


And we know that you can't have 2-D pentagonal tiles.

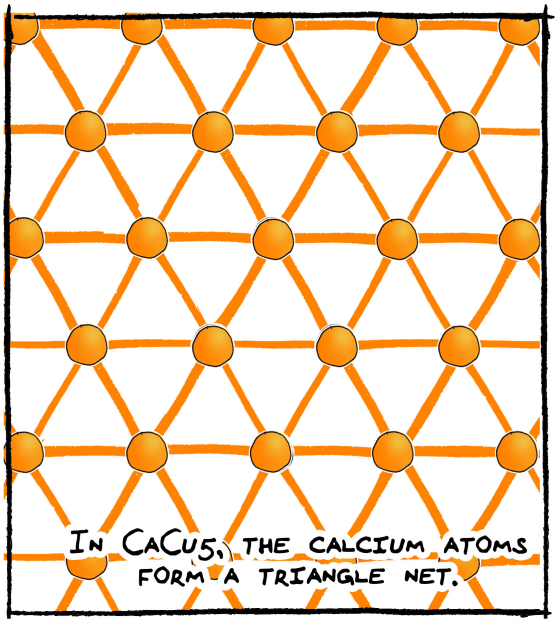
But we never said anything about 3-D pentagonal tiles.



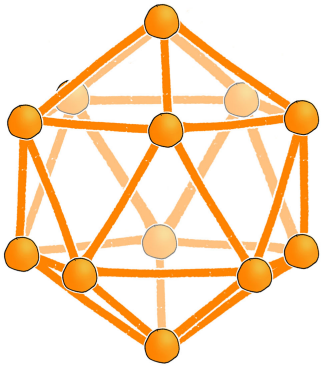
In $CaCu_5$ we began with a flat honeycomb net of hexagons.



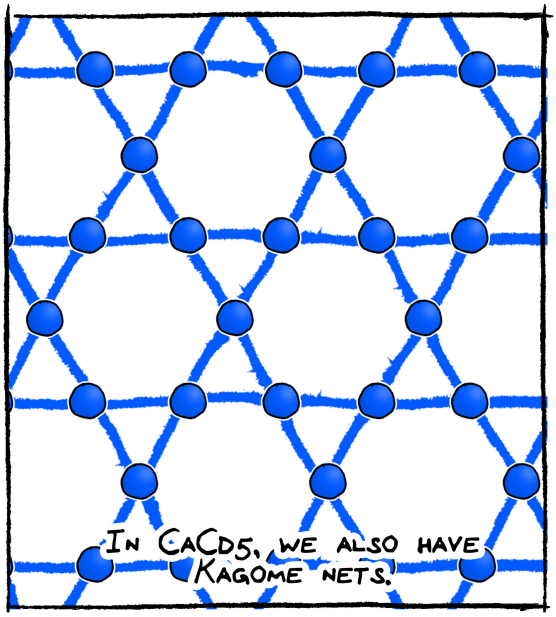
In $CaCd_6$ we'll begin with a dodecahedron:
A shape with 12 pentagonal faces.



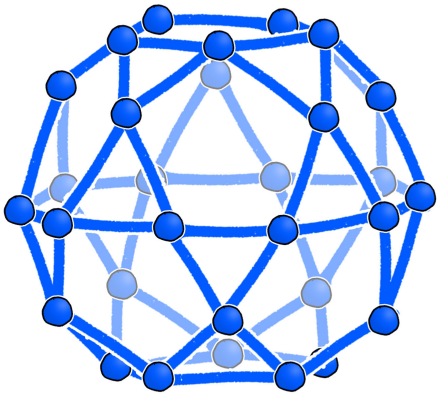
In $CaCu_5$, the calcium atoms form a triangle net.



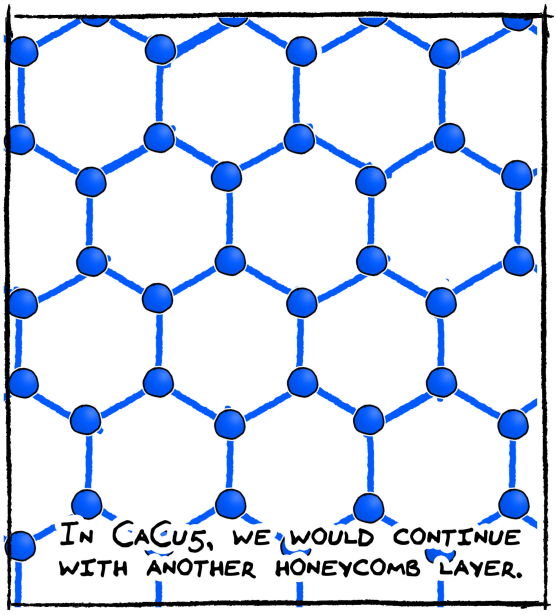
In $CaCd_6$, calcium atoms form an icosahedron: a shape with triangle faces.



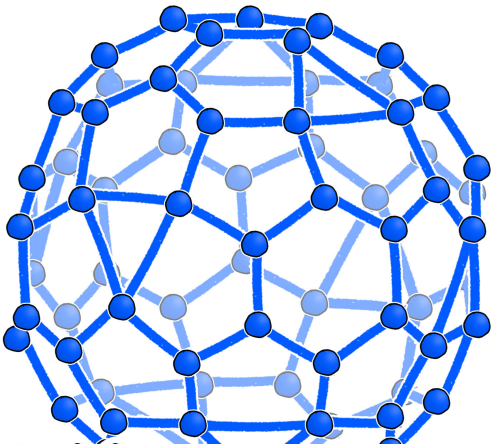
In $CaCd_5$, we also have Kagome nets.



In $CaCd_6$, we have icosidodecahedra: five-pointed stars, not six.

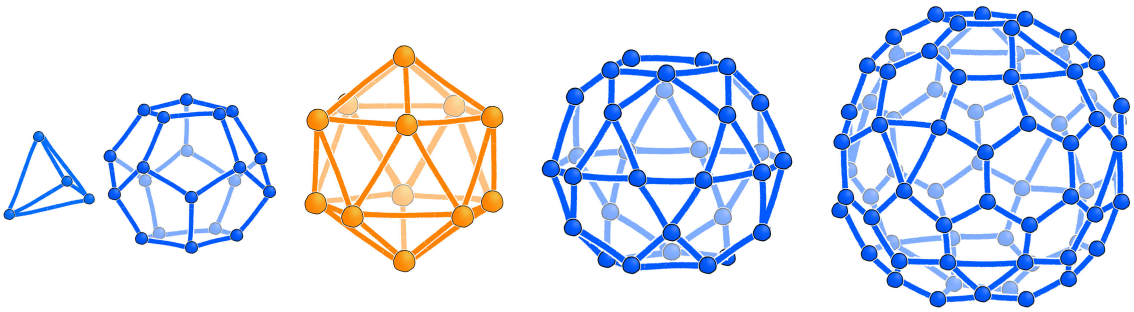


In $CaCu_5$, we would continue with another honeycomb layer.



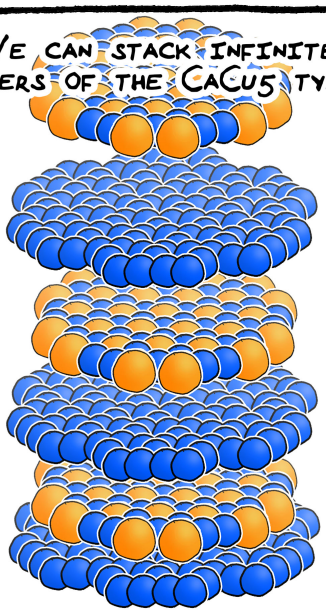
In $CaCd_6$, we terminate our cluster with a truncated icosahedron: a solid with some faces pentagons, some hexagons.

This is our Tsai-type cluster.

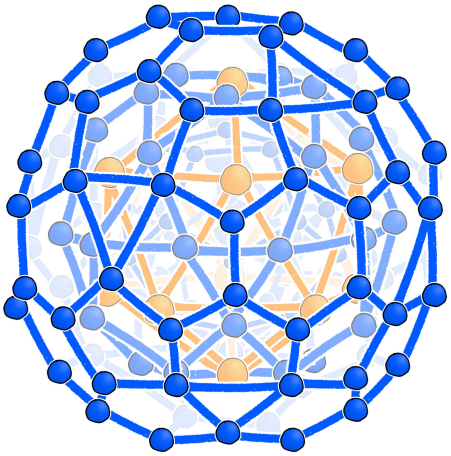


A dodecahedron inside of an icosahedron inside of
an icosidodecahedron inside of a truncated icosahedron
(with a tiny tetrahedron in the center, to fill the empty space).

We can stack infinite layers of the $CaCu_5$ type.



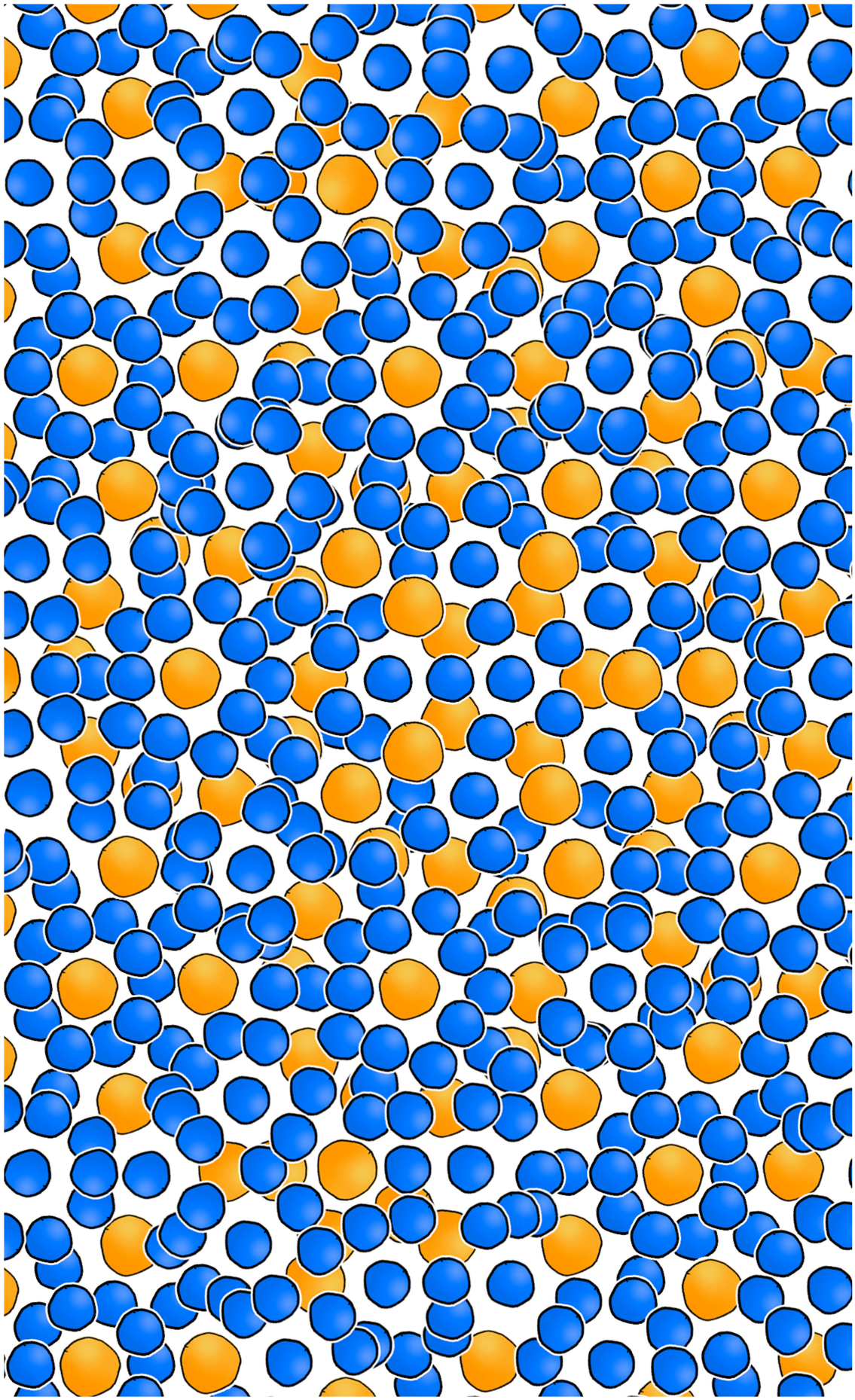
Our cluster ends here.

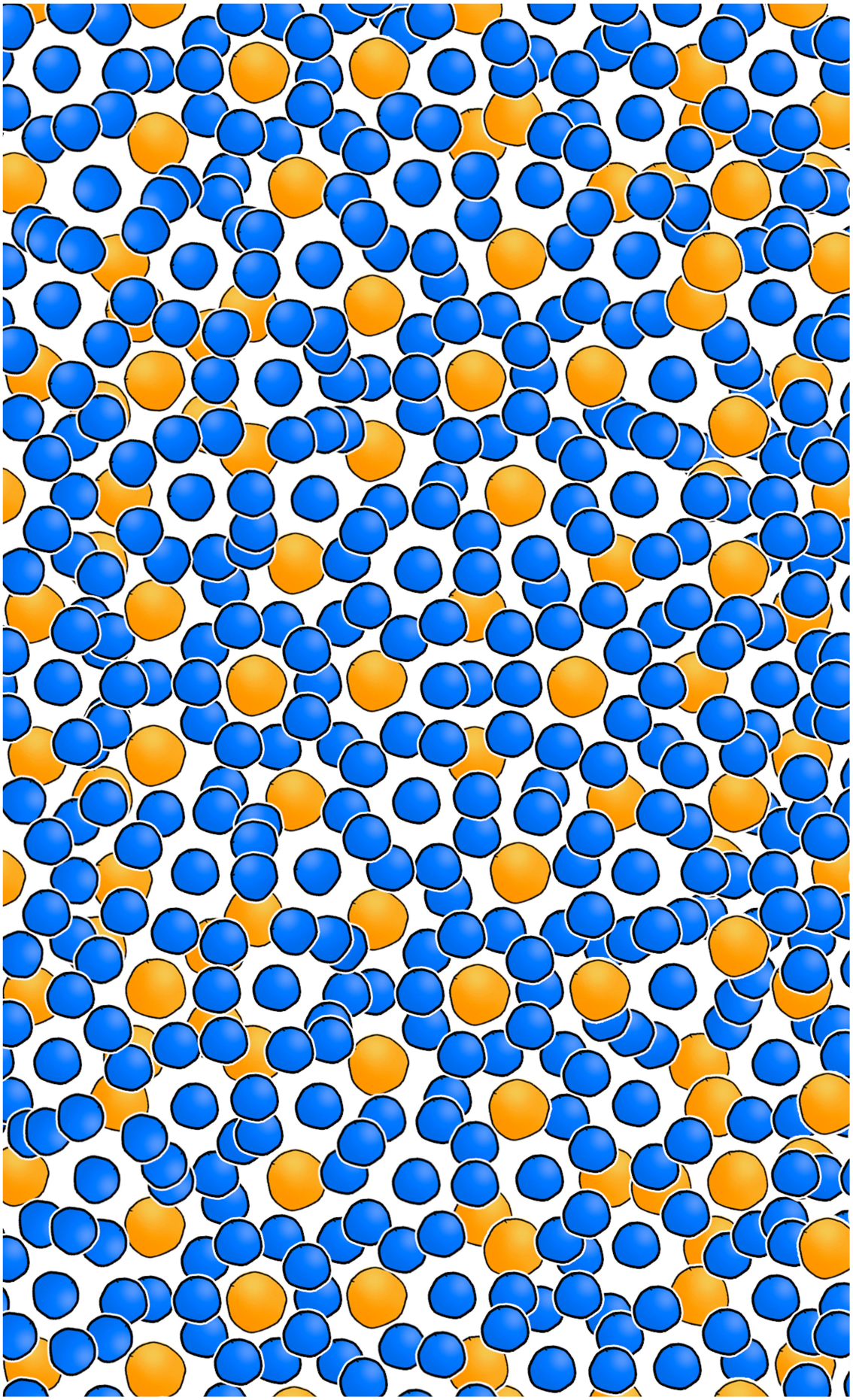


To make $CaCd_6$, we pack these clusters together periodically.

But now that we understand the pieces of the puzzle,
and why they are doing what they are doing,
and that calcium really needs those pentagons,
you can imagine an infinite array of little five-fold blocks.
You can imagine them making five-fold
patterns that never repeat themselves.

You can imagine a quasicrystal.



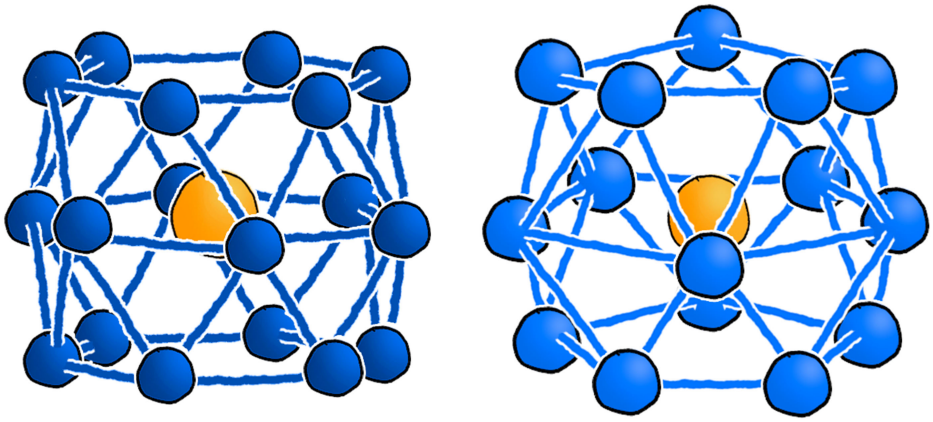


The relationship of the simple CaCu5 type to the complex Tsai-type quasicrystal is just one example of a structural remix.

Just like a DJ cuts up old songs to make new ones, we cut up a simple structure and made a more complicated one.

Wiggy wiggy wiggy

Similar structural things were happening in both compounds.



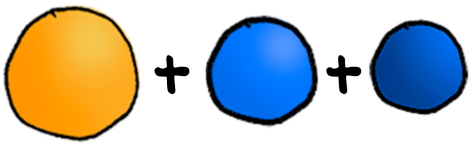
But when you change the sizes of the atoms involved, you stress out the material, and you might get something totally new.

But often times, there is a connection between the simple and the complex.

This happens for a lot of compounds. We've only scratched the surface.

By understanding these connections, we have better footing to manipulate a compound and create something we've never seen before.

Ca and Pd form the CaCu5 type. Can you imagine adding a little palladium to our calcium and cadmium?



We might get a new compound! And it might be a whole new structural remix!


NOW THAT WE'VE THOUGHT A LOT ABOUT THIS TINY PIECE OF THE UNIVERSE WE LIVE IN, IT'S TIME TO TEST OUT OUR THEORIES BY TRYING TO MAKE NEW THINGS.
THERE ARE SO MANY COMPOUNDS THAT MIGHT EXIST, AND WE WON'T KNOW UNTIL WE MAKE THEM.
ISN'T IT WONDERFUL?
THERE'S SO MUCH TO DO.
SOLID STRUCTURES ARE FULL OF POSSIBILITIES.

It's a beautiful world
out there, my friends.

Let's go exploring.

Abridged and Annotated Bibliography

These are certainly not the only materials referenced throughout my work on this project, but they are perhaps the most relevant to someone wanting to learn more about the science behind this comic. I've written a short summary of each, so you know what you're getting into before you get into it.

The number of papers developing the CP method should tell you that science isn't straightforward. We've had to go through a lot of potential methods before settling on the current one. This doesn't mean previous iterations are wrong or bad, we're just trying to figure out the best way to measure something that has never been measured before. So chances are good we'll end up modifying the current method too. That's just how it goes.

Sands, Donald E. Introduction to Crystallography. Dover Publications: Mineola NY, 1975.

This was the first book I ever read about crystallography. I don't explicitly talk much about this technique in the pages of this comic, but if the structures of materials caught your attention, this is a great little book. Crystallography is how we know what materials look like on an atomic scale. Someone (not me!) discovered every one of the structures in this comic with a crystallography experiment. X-rays go in to a crystal, bounce around a little, and then diffract outwards in interpretable patterns. It's these patterns that give us very precise placement of the atoms in the crystal.

Hoffmann, Roald. Solids and Surfaces: A Chemist's View of Bonding in Extended Structures. Wiley-VCH: New York, 1988.

Ideas behind chemical bonding are all based on where electrons are, and how much energy they have. Many chemists have a good handle on "chemical bonds" in molecules, but in 3-D solids, there are a lot of electrons flying around. This book offers a beautiful explanation of the techniques behind thinking about electrons in solid materials. Additionally, Professor Hoffmann is very talented* when it comes to communicating technical material, and this book is no exception. Every chapter feels like going on a splendid little adventure with a very knowledgeable* friend.

*Severe understatements

Fredrickson, Daniel C. Electronic Packing Frustration in Complex Intermetallic Structures: The Role of Chemical Pressure in Ca_2Ag_7. Journal of the American Chemical Society. **2011**, vol. 133, pg. 10070–10073.

Coca-Cola Classic. Action Comics. Star Wars Epsiode IV. CSI: Las Vegas. This paper. This is the original introduction to the idea of chemical pressure, calculated with Hückel theory instead of the current method that uses Density Functional Theory (DFT). Practically speaking, all that means is that it is less accurate, but easier to use because we don't have to worry about the fancy scissors and cutting up space. This paper lays out the methods and ideas behind chemical pressure, and then applies them to a calcium-silver compound, Ca_2Ag_7.

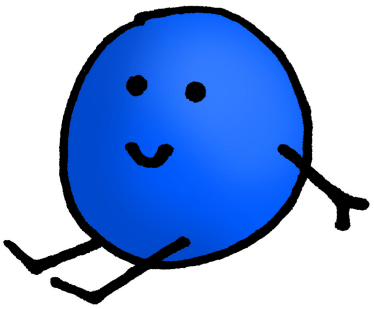
Fredrickson, Daniel C. DFT-Chemical Pressure Analysis: Visualizing the Role of Atomic Size in Shaping the Structures of Inorganic Materials. Journal of the American Chemical Society. 2012, vol. 134, pg. 5991–5999.

A follow-up to the previous paper, this one introduces chemical pressure powered by DFT. It goes through the same example, Ca2Ag7. Just like the compound in this comic, Ca_2Ag_7 is based on the $CaCu_5$ type: strontium and silver form $CaCu_5$-type $SrAg_5$. Calcium is smaller than strontium, and the Ca_2Ag_7 type provides a few close Ca–Ag contacts to make up for the stresses we see in $CaCu_5$-type $CaAg_5$.

Engelkemier, J.; Berns, Veronica M.; Fredrickson, Daniel C. First-principles elucidation of atomic size effects using DFT-chemical pressure analysis: Origins of $Ca_{36}Sn_{23}$'s long-period superstructure. Journal of Chemical Theory and Computation. **2013**, vol. 9, pg. 3170–3180.

This paper tells another story about chemical pressure in a calcium-tin compound. Again, calcium isn't the right size for a simple structure, and everything is happier in a more complicated arrangement. In this case, the hypothetical simple structure has chains of tin tetrahedra with calcium in the middle, but the Ca atoms are held too close together for this compound to exist. The structure that we actually can make out of calcium and tin occasionally incorporates an octahedron that gives calcium more room. This paper also has a bunch of cool math and develops the theoretical methods behind chemical pressure, and chronicles a drastic improvement to our "fancy scissors".

Berns, Veronica M.; Fredrickson, Daniel C. Problem Solving with Pentagons: Tsai-Type Quasicrystal as a Structural Response to Chemical Pressure. Inorganic Chemistry. 2013, vol. 52, pg. 12875-12877.



The last few pages of this comic are pretty much straight from this paper, but the paper goes into more detail. It shows the chemical pressure pictures for the hypothetical CaCu5- type "CaCd5" and compares them with the chemical pressures of the quasicrystal approximant CaCd6. The ultimate conclusion is that the pressures on the calcium drive the transformation into a quasicrystalline approximant: the CaCu5 type is based on hexagon rings, and CaCd6 is based on pentagonal rings. The quasicrystallinity comes from trying to cram a bunch of pentagons together to fill space.

Berns, Veronica M.; Engelkemier, J.; Guo, Yiming; Kilduff, Brandon J.; Fredrickson, Daniel C. Progress in Visualizing Atomic Size Effects With DFT-Chemical Pressure Analysis: From Isolated Atoms to Trends in AB5 INtermetallics. Journal of Chemical Theory and Computation. Year, vol. pg.

Occasionally we find the need to update the methodology of the chemical pressure technique. This paper brings us ever fancier scissors, but more importantly it corrects for a distortion in our chemical pressure maps that we didn't know we had. This was due to a mismatch in the grids during the calculation. Once we realized we were inadvertently distorting the grid, we fixed it. This paper shows that our old method gave us a nonsensical story for compounds in the MgCu2 type, but our new method allows us to analyze these structures that were once troublesome.

Takakura, Hiroyuki; Pay Gómez, Cesar; Yamamoto, Akiji; De Boisseau, Marc; Tsai, An-Pang. Atomic Structure of the Binary Icosahedral Yb-Cd Quasicrystal. Nature Materials. 2007, vol. 6, pg. 58-63.

Tsai, An-Pang; Pay Gómez, Cesar. Quasicrystals and Approximants in Cd-M Systems and Related Alloys. In Handbook of Metal Physics. Elsevier, 2008.

We often rely on periodicity to get atomic positions out of crystallography experiments, but these guys figured out how to get a structure for a quasicrystal. The short paper from Nature Materials talks about why it was necessary to do this in 6 dimensions (the TL;DR answer is "math"), but the book chapter gives a great overview of the whole family of related compounds we've found, some of which we're able to understand with our humble 3 dimensions, like CaCd6.

Shadle, Albert R. Gestation Period in the Porcupine, Erethizon dorsatum dorsatum. Journal of Mammology. 1948, vol. 29, pg. 162–164.

If you look up the gestation period of a porcupine on Wikipedia, it will say 113 days. That was the belief in 1928, based on the time between someone's observation of a lady porcupine mating with a man porcupine, and that lady-pine giving birth. But in 1948, Albert Shadle changed our understanding of porcupine gestation with a very controlled experiment. He isolated a pair of lady porcupines, and later introduced a male. After they bred, the females had no other contact with males, and it took 209 and 217 days for the porcupine babies to be born. Ideally he would have gotten more than two data points, but later studies confirmed his observations, suggesting that the estimation of 113 days was incorrect.

Thanks!

This comic book couldn't have been made without the help of so many people. Number one is Professor Danny Fredrickson, my PhD advisor and the guy who so brilliantly captains the CP ship. Of all the things I will take away from grad school, your kindness and engouragement has meant the most.

I'm beyond lucky to have had Kale Engelkemier as my coworker on the CP code. They've also helped edit this book, and been a fantastic friend for the past three years.

Yiming Guo is a brilliant scientist and an all-around great person who has with Kale written a lot of the CP programs.

To Kale, Yiming, and the rest of the Fredrickson Group- Brandon Kilduff, Vince Yannello, Anastasiya Vinokur, Katie Hilleke, Rie Fredrickson, Amelia Hadler, Arthur White, Nick Harris, Mike Sapiro, and Tim Stacey: I couldn't have dreamed up a better group of passionate and inspiring people to work with. May you jump and always go.

Ashlan Musante lent her scientific and creative mind as an editor. Josh Klemons is a bit more removed from the world of science, but he's been amazing at helping edit as well.

Another big thanks to my many draft-readers and encouragement-providers. Especially Max.

And finally, the last thank you goes to you, for jumping into this little bit of the scientific world. I set out to make something that would bring the joy and wonderment of cutting-edge science to more people, and your curiosity was the last piece of the puzzle.