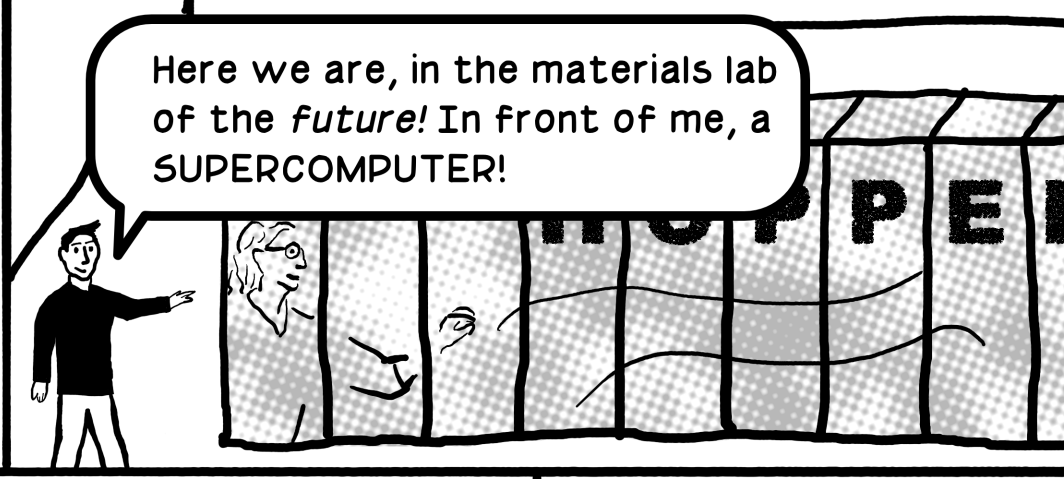
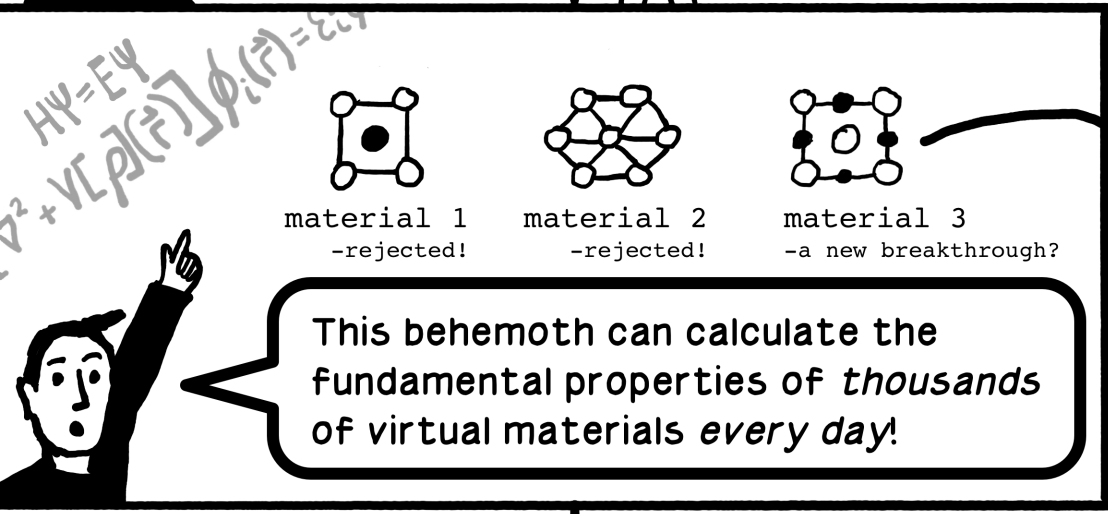
Materials stability & Nature's bike shop

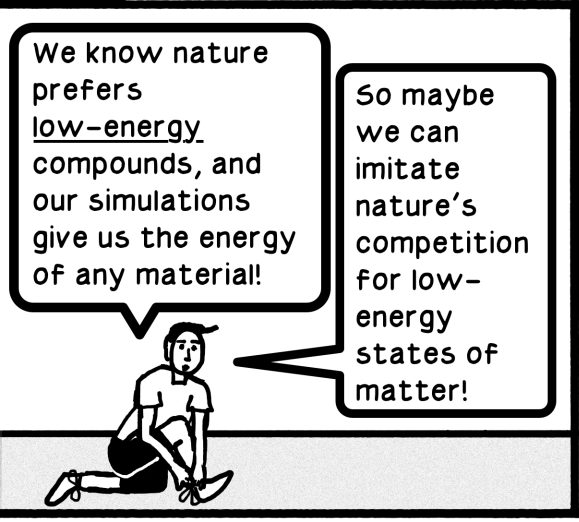
A comics guide* to predicting new materials!

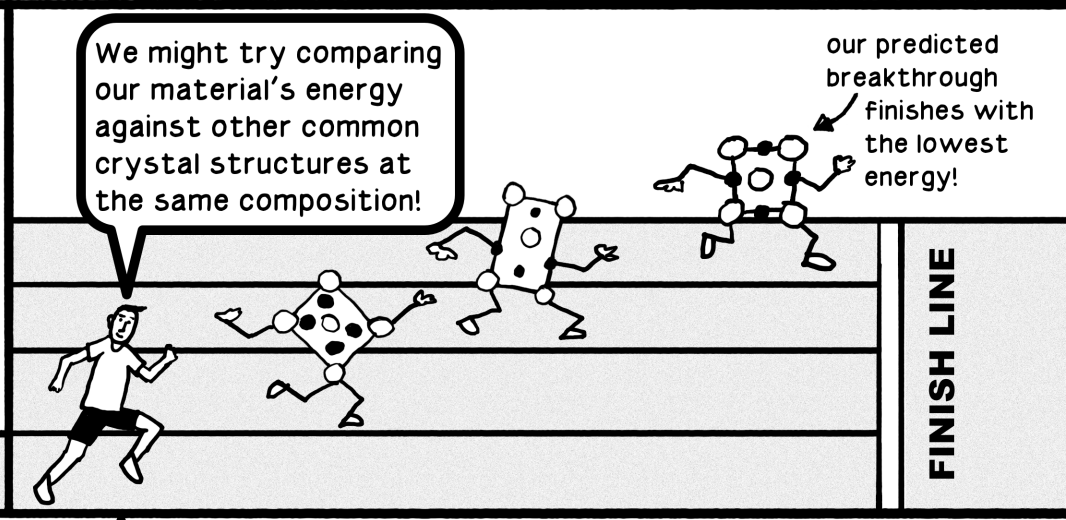


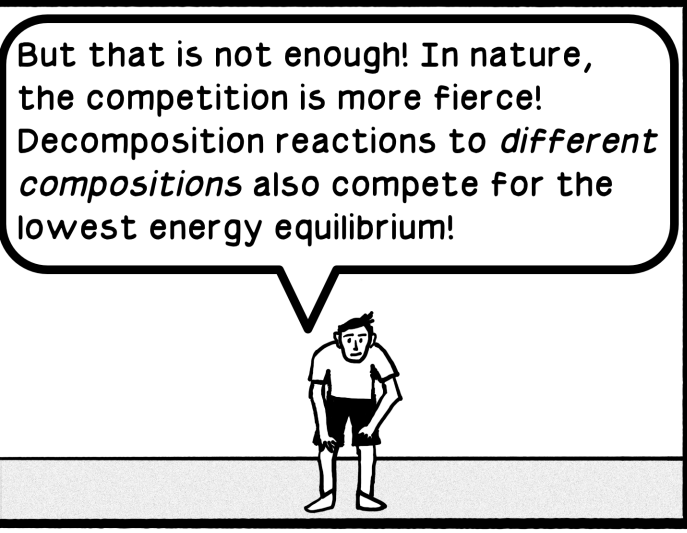
by Anubhav Jain

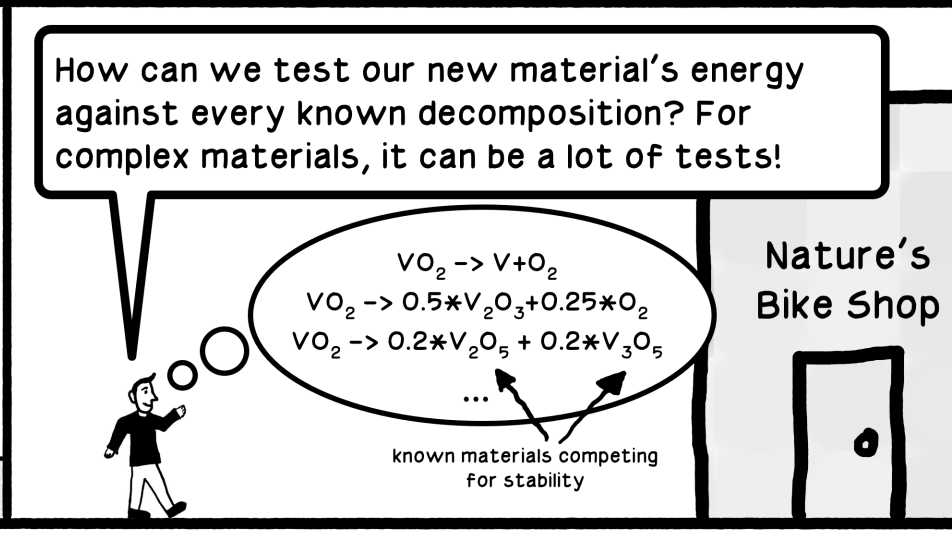












*Inspired by Scott McCloud's *Understanding Comics*

Comic font: Basic Comical NC by Jayvee Enaguas

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www.hackingmaterials.com

Here we are in Nature's bike shop! Nature, perhaps you can tell us about how your business operates!

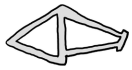
Nature!

Sure! We have a stockroom containing wheels and bike frames. Depending on how many of each we have, we assemble unicycles or bicycles to sell at a profit!

Here's our profit sheet!



wheels
no profit [$0/part]



frames
no profit [$0/part]



unicycles [wheel+frame]
$20 profit [$10/part]



bicycles [2 wheels+frame]
$30 profit [$10/part]

Our goal is to maximize profit based on stockroom composition!

If stockroom contains...	*We will make/earn:*
2 wheels + 1 frame	bicycle [$30=$10/part]
2 wheels + 2 frames	2 unicycles [$40=$10/part]
3 wheels + 1 frame	bicycle+wheel [$30 = $7.5/part]

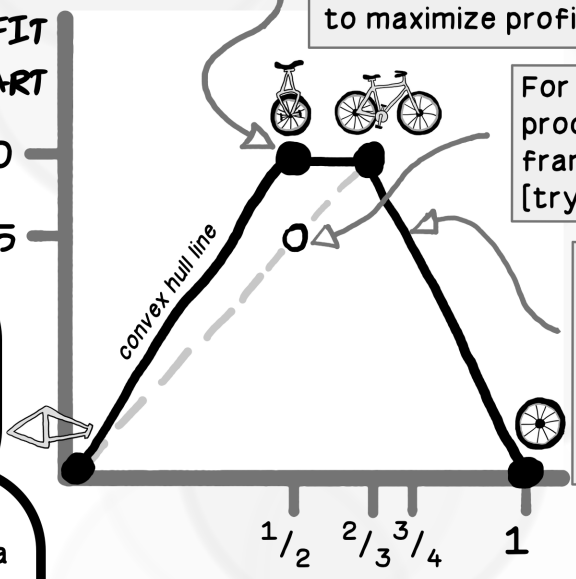
So Nature's products and her profit depends on the *starting ratio* of wheels to frames! What's her strategy?

Let's plot the profit for all known products versus the fraction of wheels they contain as solid black dots!

Next, connect those profits via a black convex hull line, like a rubber band snapping over pushpins!

The final plot tells us the most profitable products for different stockroom compositions – we just need to follow the convex hull!





At a wheel fraction of 0.5 [example #2 above], the unicycle falls on the convex hull. So that's what Nature should make to maximize profit, giving $10/part as found earlier!

For comparison, at that *same fraction* of 0.5, producing a mixture of bicycles and leftover frames would earn only $7.5/part! [try the math with 2 frames and 2 wheels]

For a wheel fraction of 0.75 [example #3 above], the convex hull connects bicycles and wheels. The profit from this mixture is $7.5/part. *So a new product at this ratio [like a tricycle!] must earn over $7.5/part in order to be sold at Nature's bike shop!*

Okay ... but what does all this have to do with chemistry?



Here we are in an experimental lab, trying to apply lessons from Nature's bike shop to *chemistry!*

glovebox!

Looks like a PhD candidate is mixing Fe and P in a sealed glovebox .... can we *predict* the result?

Bike shop convex hull

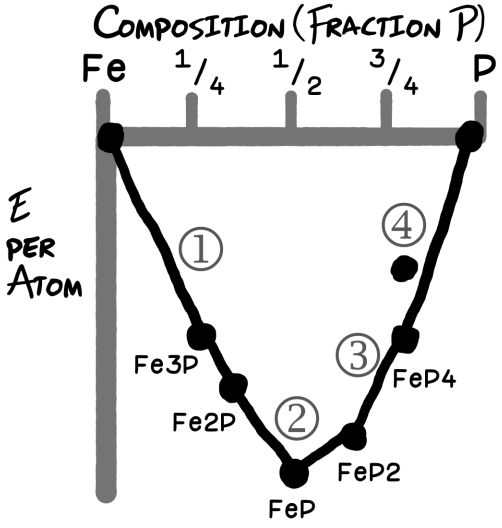


Fe-P convex hull



Yes! But first we need to turn our convex hull upside-down!

"Interpreting the Fe-P convex hull"



① Like in the bike shop, each point represents a product that Nature can make. Once again, the convex hull connects points like a rubber band over pushipins. On the y-axis, we plot the [computed] energy per atom.

② FeP – with a single Fe and a single P – is like Nature's unicycle! FeP2 is like a "bicycle". Points on the convex hull cannot be decomposed to other products to reduce energy; they are thermodynamically stable!

③ At a ratio of Fe:P = 1:3, there exists no stable FeP3 phase ["tricycle"]. Energy is minimized by forming a mixture of FeP2 and FeP4. To predict a new FeP3 phase, we should find a structure with energy below the convex hull [not just the lowest-energy FeP3 structure!]

④ Multiple crystal structures – with different energies – can be compared at the same composition. The two FeP4 points are like two models of a 4-wheeled bike! [one is stable, the other metastable]

So compounds <u>not</u> on the convex hull can be decomposed to reduce energy!

The "<u>e above hull</u>" measures this decomposition energy. It's *<u>how much</u>* Nature can profit by choosing different products!

FeP4

Of course, Nature can't always maximize profits [minimize energy]. When she is in a time crunch, whatever is easiest to assemble gets shipped out the door! Thus *<u>metastable materials</u>* that are not on the convex hull can still exist due to kinetic factors!

<u>Temperature</u> is another consideration; it reduces the cost of "manufacturing" some products more than others, <u>modifying energies</u> and the hull. Here in the cold, it doesn't matter so much!

But at high T, phases with high entropy [like gases!] have their energies greatly reduced! So we must create our hulls using energies relevant at high T!

Due to these effects, it is generally OK to accept a bit of instability when predicting compounds! [e.g., about 50-100 meV/atom "e above hull"]

But go too far, and you're likely predicting *<u>nonsense!</u>*

Perhaps you're wondering what to do with more than 2 components?

Fortunately, convex hulls can be applied to systems with *any* number of components – we just need to add another dimension!

For example, let's say Nature adds another part for building products – the basket!

Now Nature also sells...

Unicycle w/basket [$25 profit]

Bicycle w/basket [$55 profit]

First, we plot Nature's products on a triangle: the closeness to a vertex is the fraction of that component!

The "unicycle w/basket" has equal amounts of each component!

But the "bicycle w/basket" has more wheels!

The bottom edge is like our first convex hull!

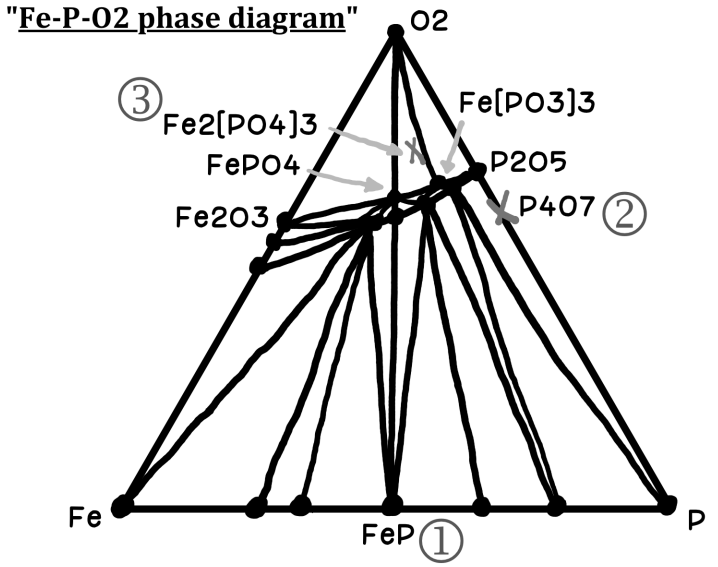
We can't see the profits on this 2D plot, so pretend we stick up *tent poles* at each product. The height of the pole is the profit per part.

The convex hull is like *stretching a tent* over the poles – only the stable materials will touch the tent!

A 2D plot only shows the "outline" of the tent from above as lines. Unstable points that do not touch the tent are indicated by a different symbol or color [in this case, a gray 'X']

The unicycle with a basket is <u>unstable</u> because with equal amounts of all parts, the bicycle with basket along with a leftover frame and basket is the most profitable combination! Try the math with 2 of each part...

Going back to chemistry, we can use the same idea to create phase stability diagrams for *ternary* systems!

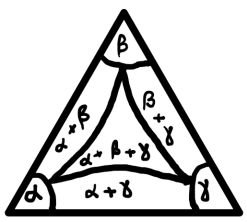


① Like always, stable compounds like FeP are marked by circles and intersect the lines [the convex hull surface]

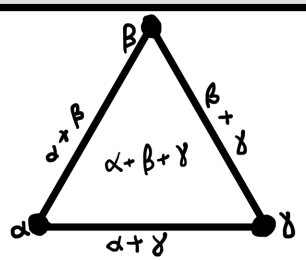
② Unstable compounds on a line segment decompose to its two endpoints, like P4O7 -> P + P2O5

③ Compounds inside a triangle decompose to its three vertices, like 4Fe2[PO4]3 -> 6FePO4 + 2Fe[PO3]3 + 3O2

Note that these phase stability diagrams can appear different than experimental diagrams because no solubility is taken into account. Single-phase regions are always points, two-phase regions are always infinitesimal lines, and all finite areas are 3-phase regions!

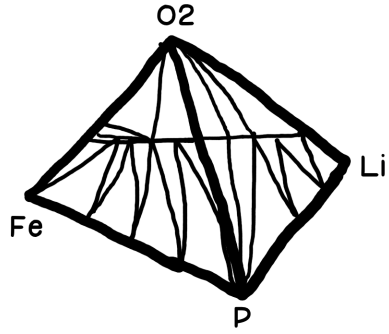


Experimental



Computational

One can even add *more* components. For example, a 4-element phase diagram is plotted as a 3D tetrahedron with elements at each corner and energy in a hidden 4th dimension! This is difficult to read but the analysis is straightforward.



The convex hull algorithm computes the most stable decomposition, regardless of number of elements!

So there you have it! Computational phase diagrams in a nutshell!

TAP TAP

Yes?!

But everything you've told us is for fixed starting compositions! Sometimes, the element ratios depend on the environment!

Oxygen sneaks in from the air! Chemicals come from a concentrated solution! How can we take this into account?

I see your point... *but it's still like the bike shop!*

However, let's imagine some of Nature's parts aren't in her supply room. Instead, she must *buy* parts from an open market!

WHEELS FOR SALE!

If Nature no longer starts with wheels, she must subtract from her profit the total cost of buying wheels when deciding what products to sell!

$$P = R - cN$$

P: PROFIT; R: REVENUE; c: COST PER WHEEL; N: NUMBER OF WHEELS

Let's see what Nature produces from a frame depending on the cost of wheels!

CASE 1: $1 WHEELS!

unicycle
$20 - [1*$1]
= $19 profit

bicycle
$30 - [2*$1]
= $28 profit

When wheels are cheap, make bicycles!

CASE 2: $15 WHEELS!

unicycle
$20 - [1*$15]
= $5 profit

bicycle
$30 - [2*$15]
= $0 profit

But if wheels are expensive, unicycles are better!

Thus, whomever controls the price of wheels controls Nature's products!

"Price of wheels"

$0 $10 $20

BICYCLES UNICYCLES FRAMES

Things are similar in chemistry! When an element is open to the environment, we need to minimize the grand potential [energy "cost" when "purchasing" open elements!]

$$\phi_G = G - \mu N$$

ϕ_G: GRAND POTENTIAL; G: GIBBS FREE ENERGY; μ: CHEMICAL POTENTIAL; N: AMOUNT OF ELEMENT IN PRODUCT

The chemical potential of an open element is like its "*cheapness*" on the free market!

A good experimentalist is like a corrupt tycoon, fixing the price of these elements to get what they want!

μ_{O2}

Fe_2O_3
Fe_3O_4
FeO
Fe

CASE 1: HIGH μ_{O2}

I'm synthesizing in air at low temperatures – oxygen is cheap! Metals will absorb lots of O2!

crucible containing Fe_2O_3

CASE 2: LOW μ_{O2}

I'm synthesizing under an inert gas atmosphere at high temperature! Oxygen is expensive to obtain! Less O2 will be absorbed! *Muahahahaha!*

sealed tube containing FeO

Open phase diagrams look like regular phase diagrams with the same number of closed elements!

A series of these diagrams is shown at different chemical potentials of the open elements to give a full view of the system!

V closed, O2 open* – a series of points!

$\mu O2 > -0.9$ • V_2O_5

$-1.4 < \mu O2 < -0.9$ • V_3O_7

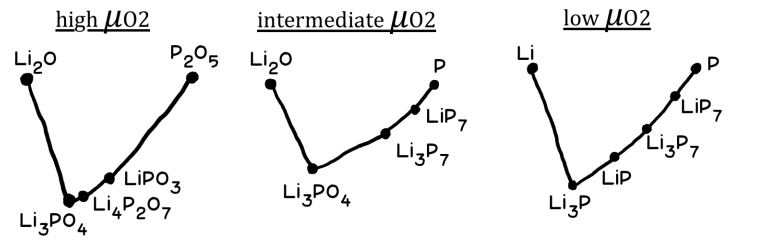
$-2.2 < \mu O2 < -1.4$ • VO_2

$-2.4 < \mu O2 < -2.2$ • V_3O_5

$-4.2 < \mu O2 < -2.4$ • V_2O_3

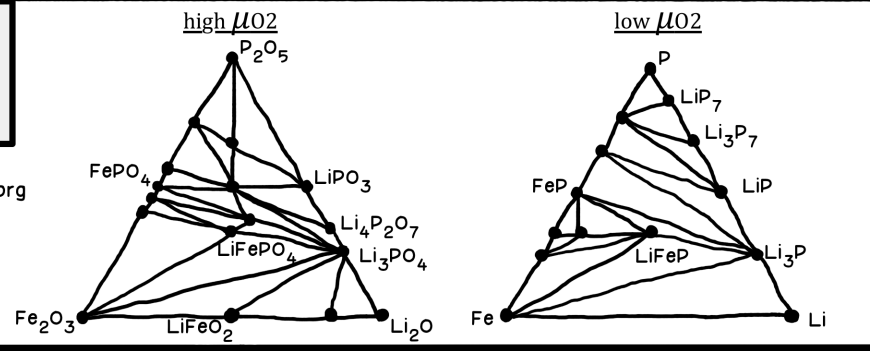
$\mu O2 < -4.2$ • V

Li & P closed, O2 open* – a series of 1-dimensional lines! As oxygen becomes less cheap, oxides disappear!



Li & P & Fe closed, O2 open* – a series of 2D ternary plots!

* Data from www.materialsproject.org [May 2014]



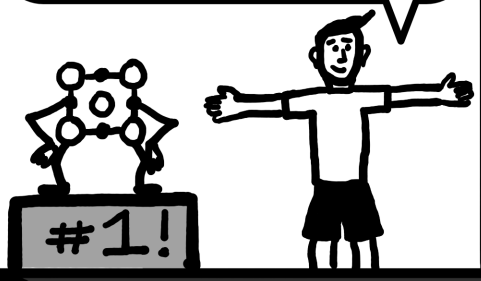
Note that if a compound is *stable* on a closed phase diagram, opening an element to the environment can make that compound unstable!

But the *reverse* is not possible! An unstable compound cannot be made stable by opening one of the elements!



Whether your environment is open or closed, or you have two elements or four, remember that the race for stability involves more than just structure polymorphs!

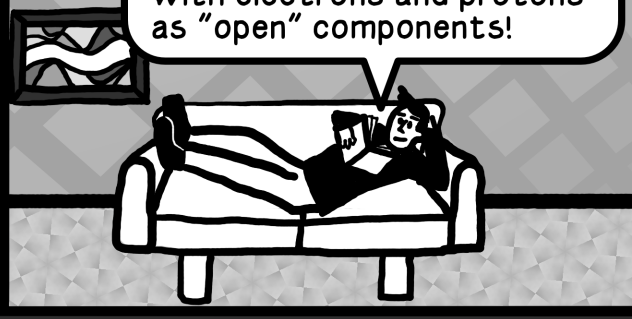
With convex hulls, we simultaneously evaluate *all* decompositions!



And there's plenty more to learn!

For example, *Ellingham Diagrams* are another way to visualize stability under temperature and pressure.

And *Pourbaix Diagrams* are essentially phase diagrams with electrons and protons as "open" components!



Nature's Bike Shop



Bye! Good luck!



Hope you enjoyed touring Nature's bike shop and our phase diagram explorations!

For more information, including how to test your own compounds for stability, check out:

www.hackingmaterials.com/pdcomic

See you next time!

