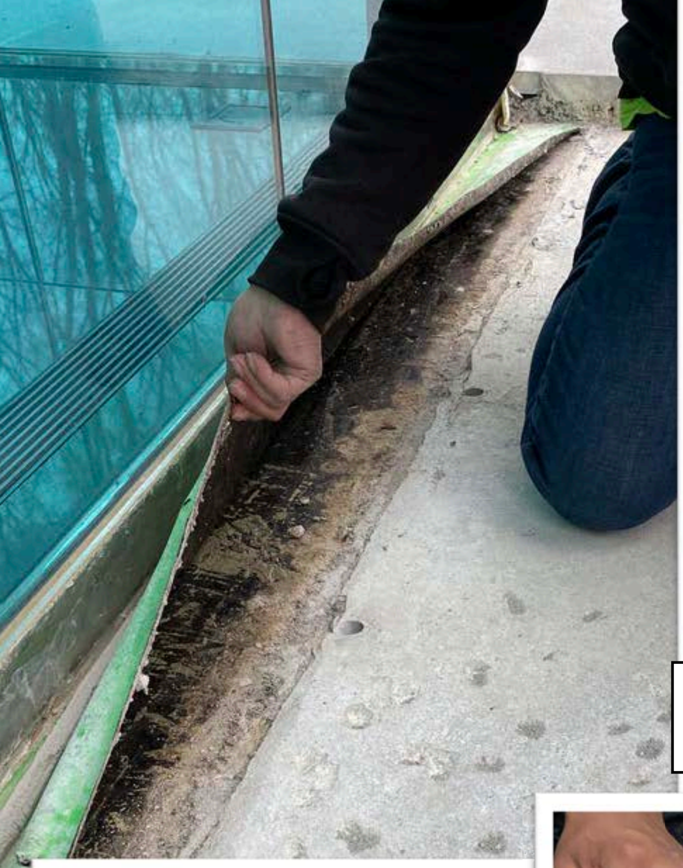
The Pleasure of Finding Things Out About Adhesion

J. Foster Lyons

August 5, 2024. Westford, MA
www.FosterLyons.com

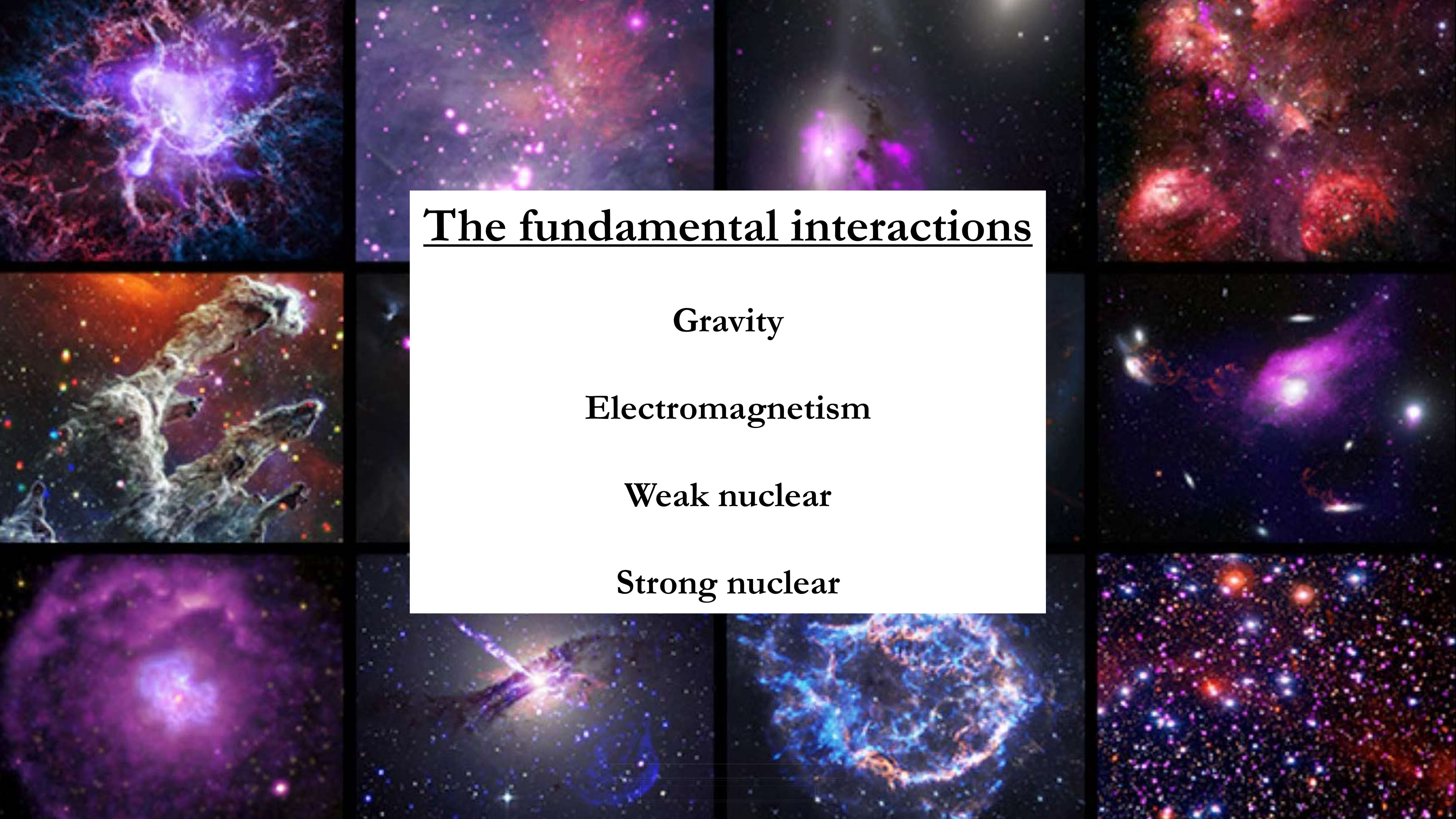
Painting: Jacob Peter Gowy, The Fall of Icarus (1635-7), Museo del Prado, Madrid.



I shouldn’t be assigning blame….



…if I can't explain this.



The fundamental interactions

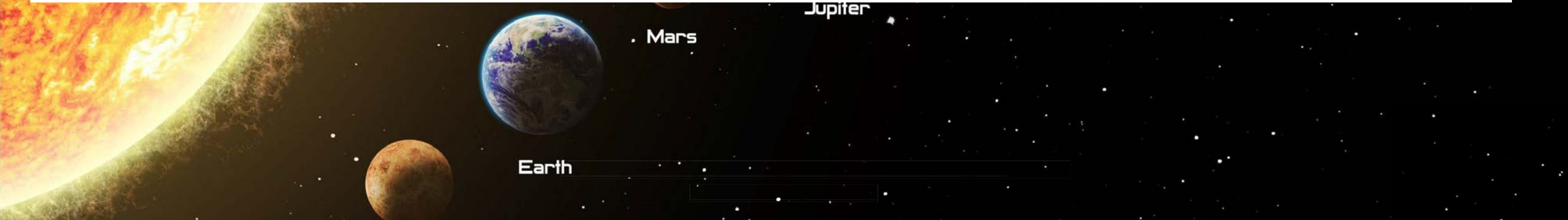
Gravity

Electromagnetism

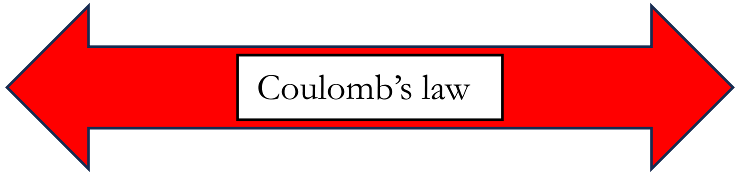
Weak nuclear

Strong nuclear

	Relative strength	Range	Interaction
Gravity	1	infinite	attraction only
Electromagnetic	10^{36} ?!!!	infinite	attraction and repulsion
Weak nuclear	10^{33}	10^{-18} meters	attraction and repulsion*
Strong nuclear	10^{38}	10^{-15} meters	attraction and repulsion



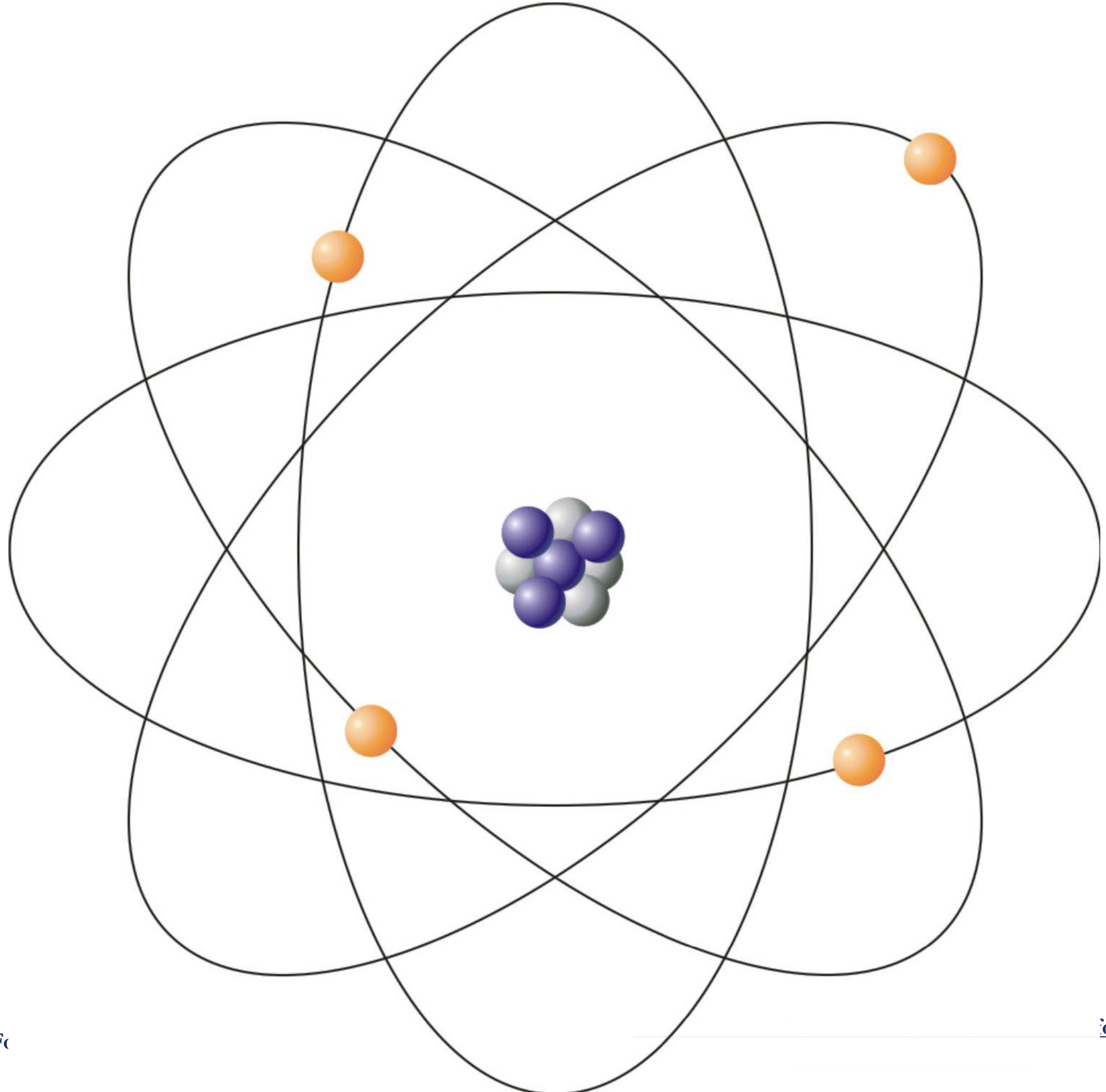
If we consider only the electrons
in these pitchers of water.



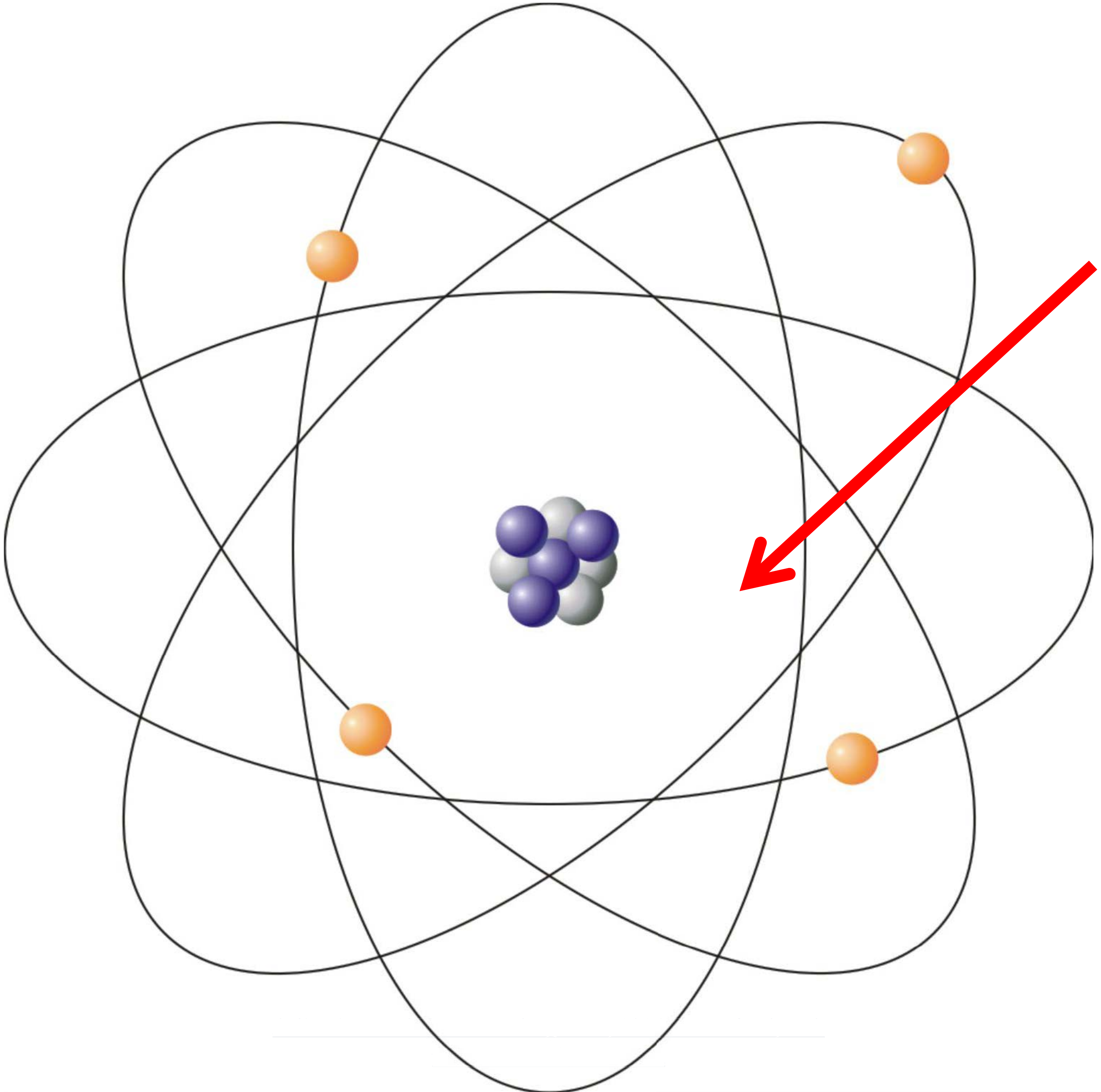
~ 1.0 x 10^{25} lbs

(FYI, Earth ~ 1.0 x 10^{25} lbs)

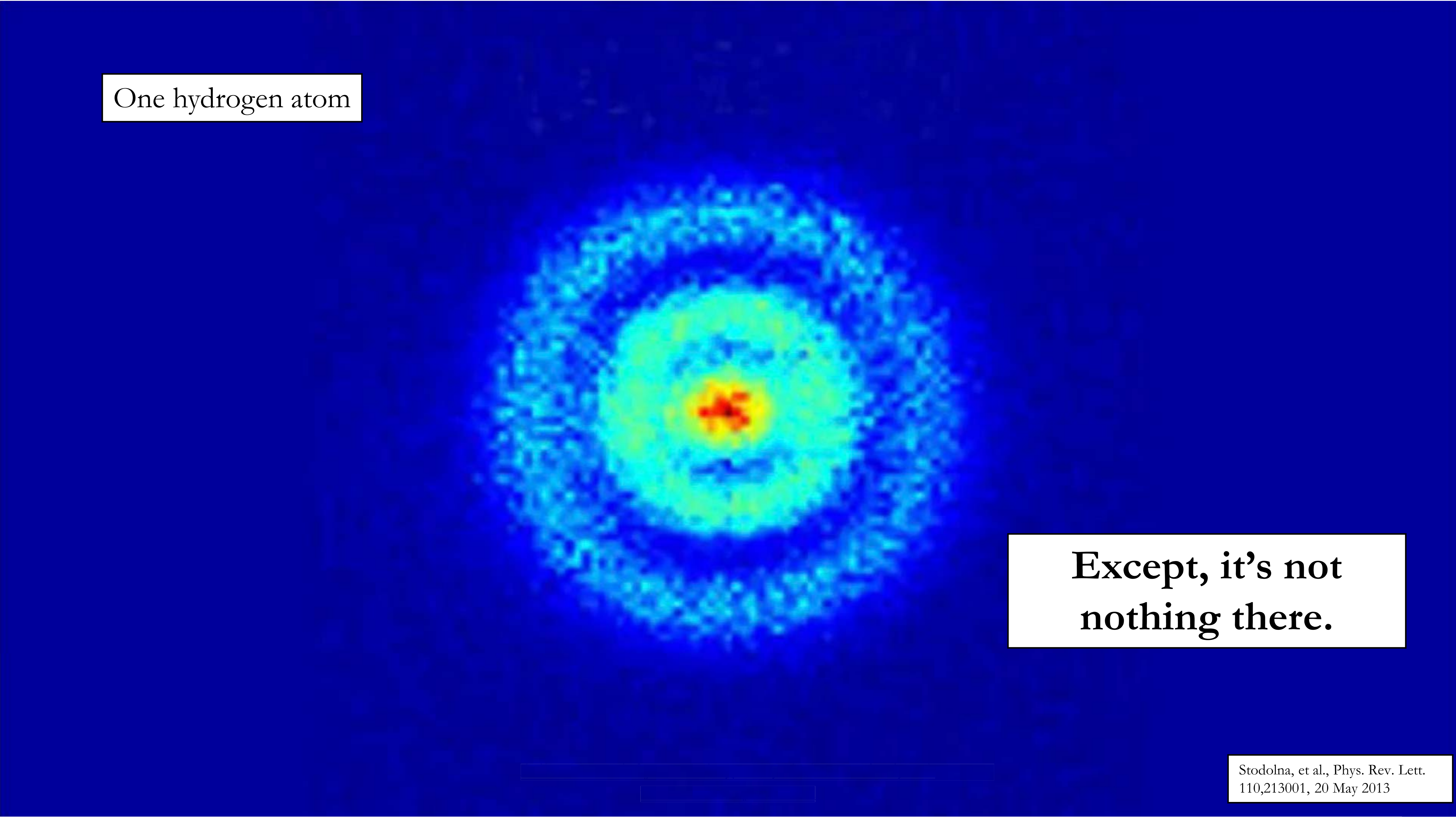
Usually, electromagnetic forces balance each other out and gravity dominates.
But….
At atomic scale, electromagnetic forces are TOTALLY, TOTALLY dominant.



Imagine yourself at
this size
-
were electromagnetic
forces TOTALLY dominate



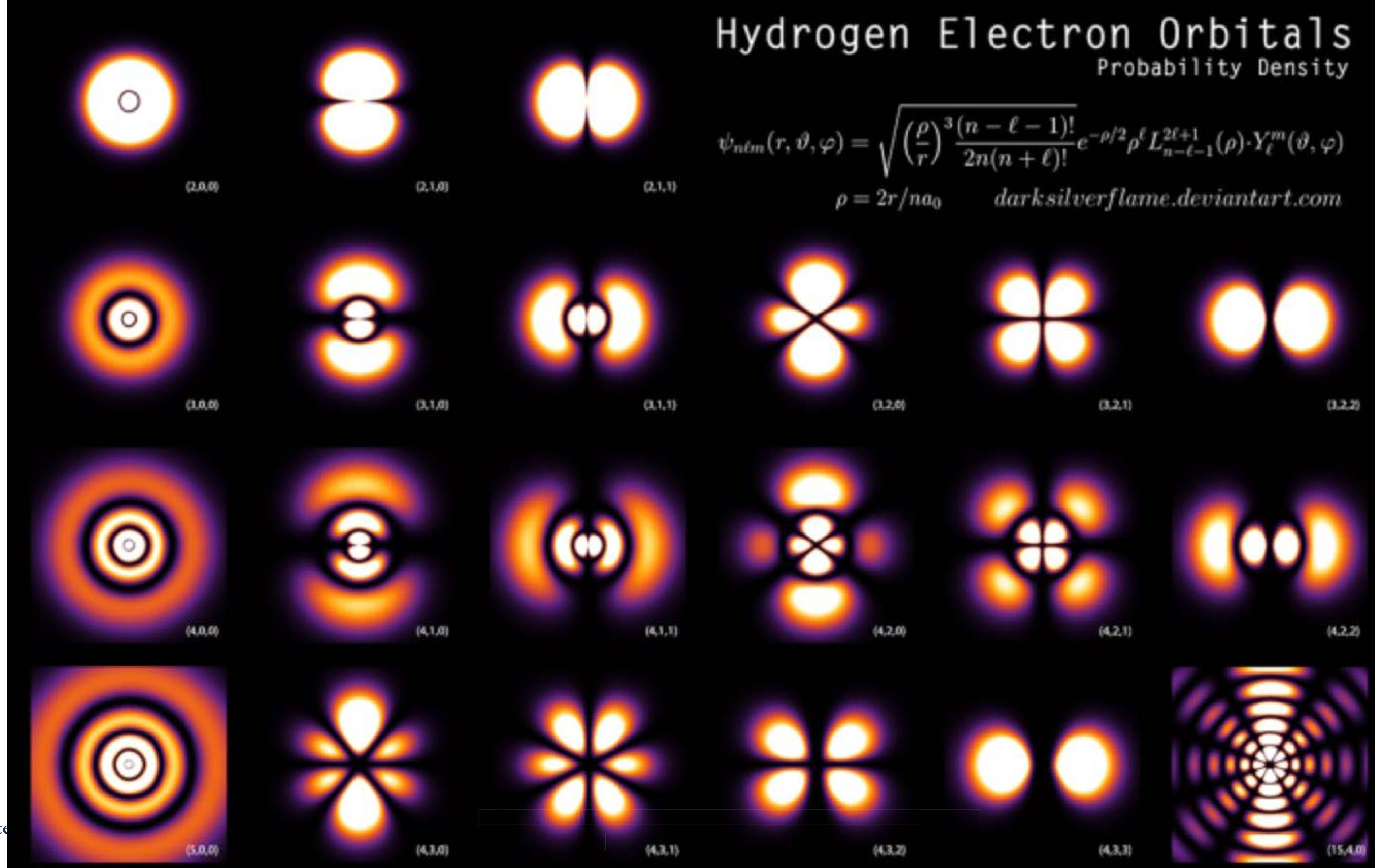
Lots, and lots of nothing here.



One hydrogen atom

Except, it’s not nothing there.

Stodolna, et al., Phys. Rev. Lett. 110,213001, 20 May 2013


Hydrogen Electron Orbitals
Probability Density
$\psi_{n\ell m}(r,\vartheta,\varphi) = \sqrt{\left(\frac{\rho}{r}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) \cdot Y_\ell^m(\vartheta,\varphi)$
$\rho = 2r/na_0$
darksilverflame.deviantart.com
(2,0,0)
(2,1,0)
(2,1,1)
(3,0,0)
(3,1,0)
(3,1,1)
(3,2,0)
(3,2,1)
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(4,0,0)
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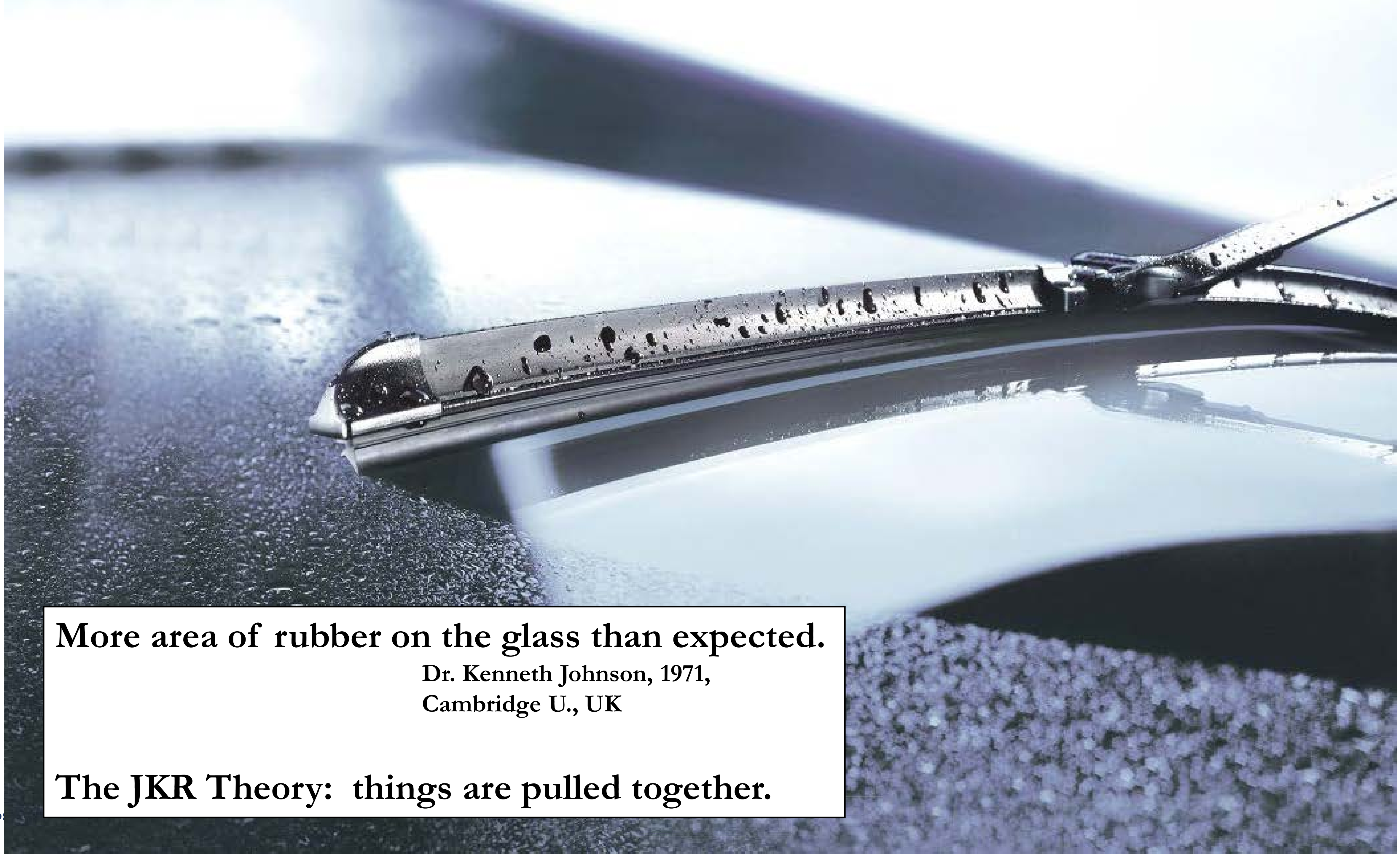
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)
(15,4,0)

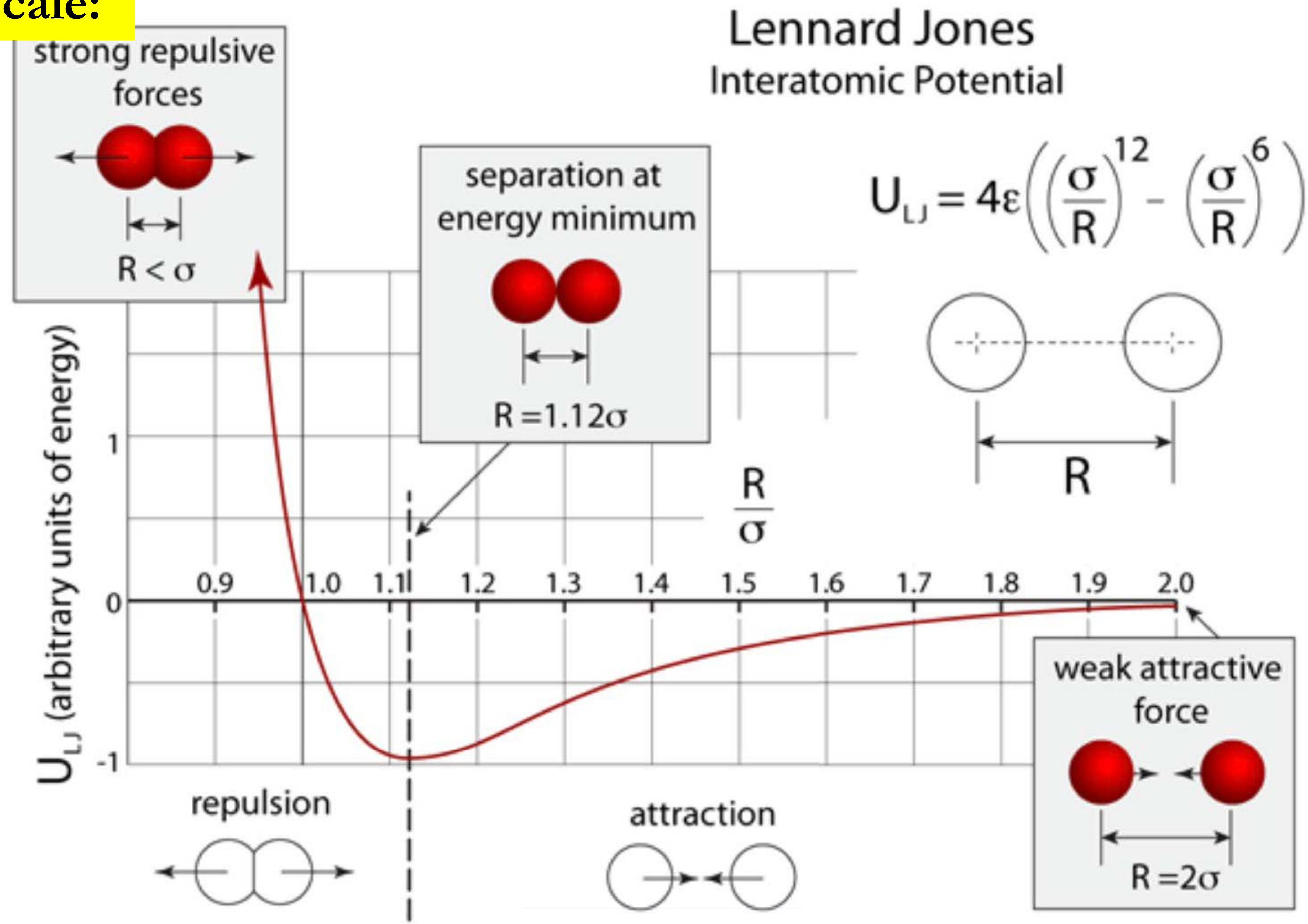


More area of rubber on the glass than expected.

Dr. Kenneth Johnson, 1971,
Cambridge U., UK

The JKR Theory: things are pulled together.

Atomic scale:



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https://physicsatmcl.commons.msu.edu/lennard-jones-potential/

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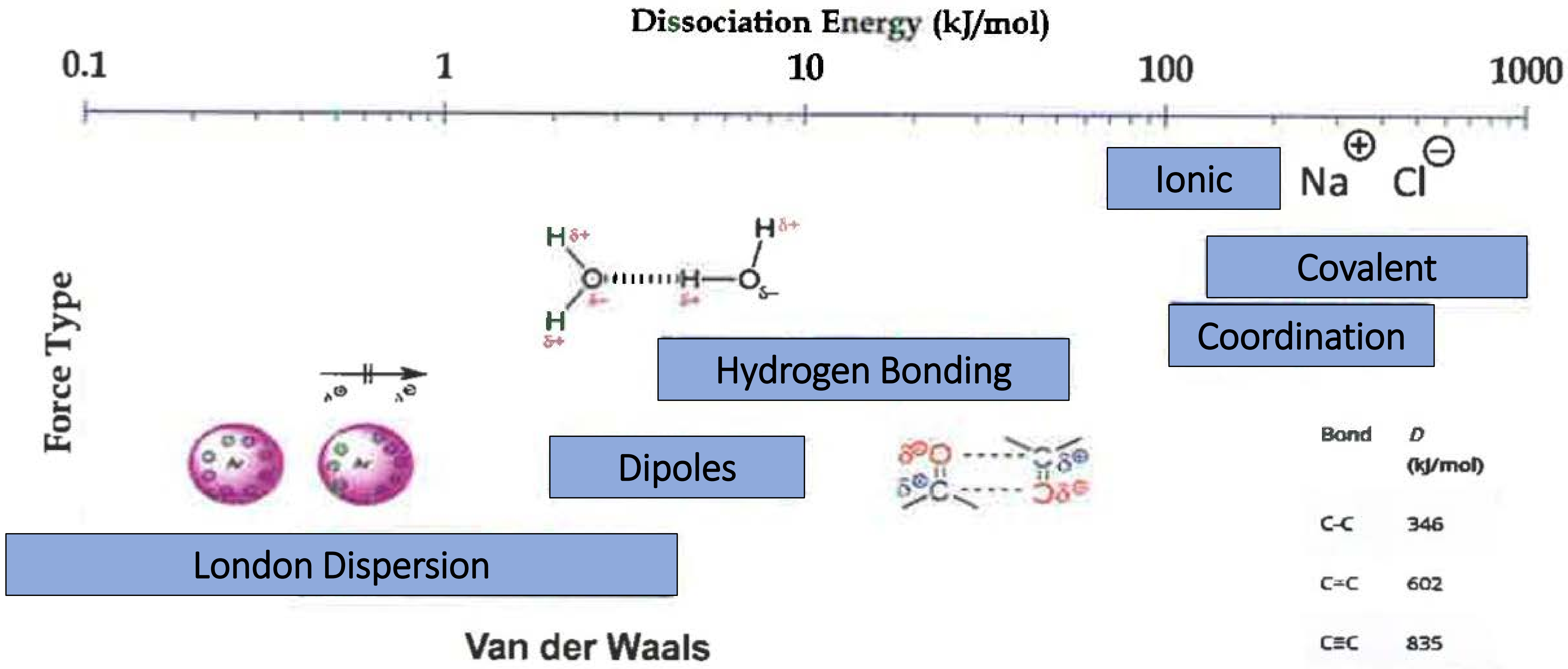
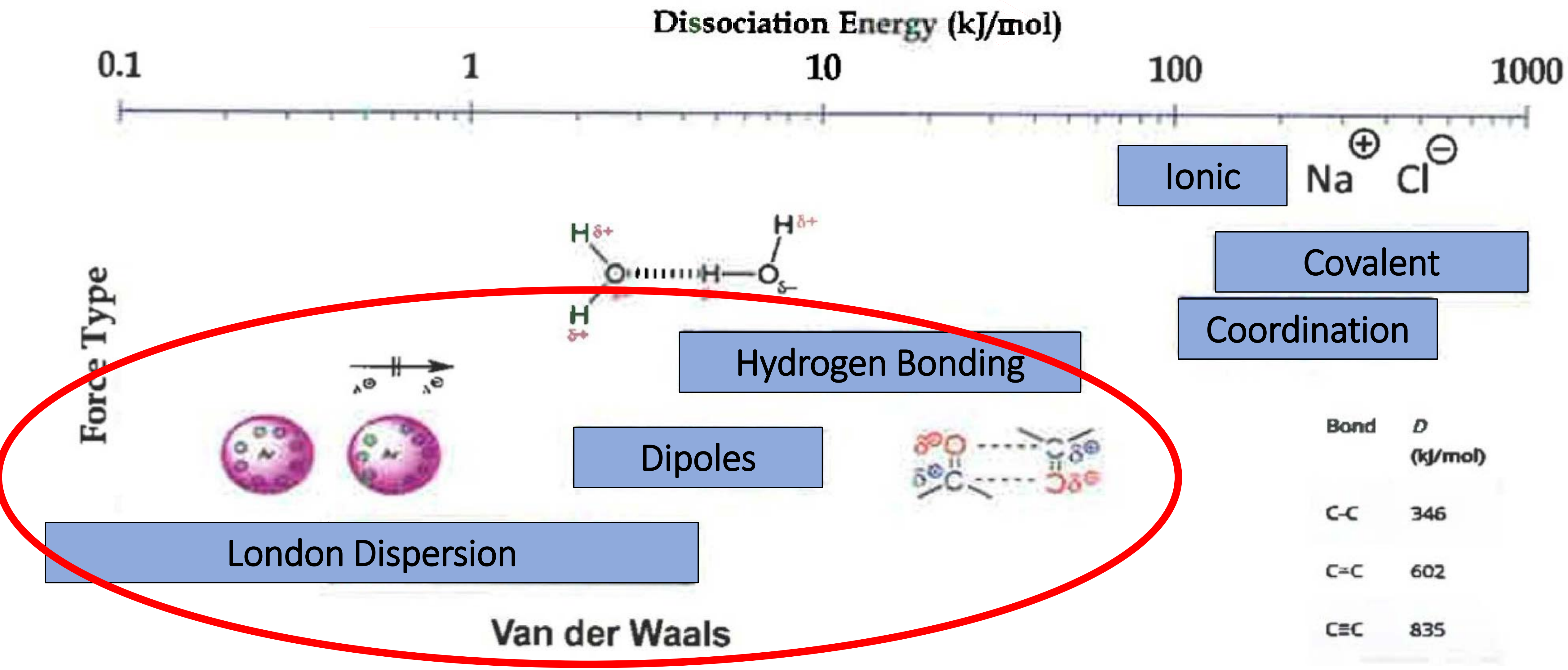

Dissociation Energy (kJ/mol)
0.1
1
10
100
1000
Ionic
Na
Cl
Covalent
Coordination
Hydrogen Bonding
Dipoles
London Dispersion
Force Type
Van der Waals
Bond
D (kJ/mol)
C-C 346
C=C 602
C≡C 835



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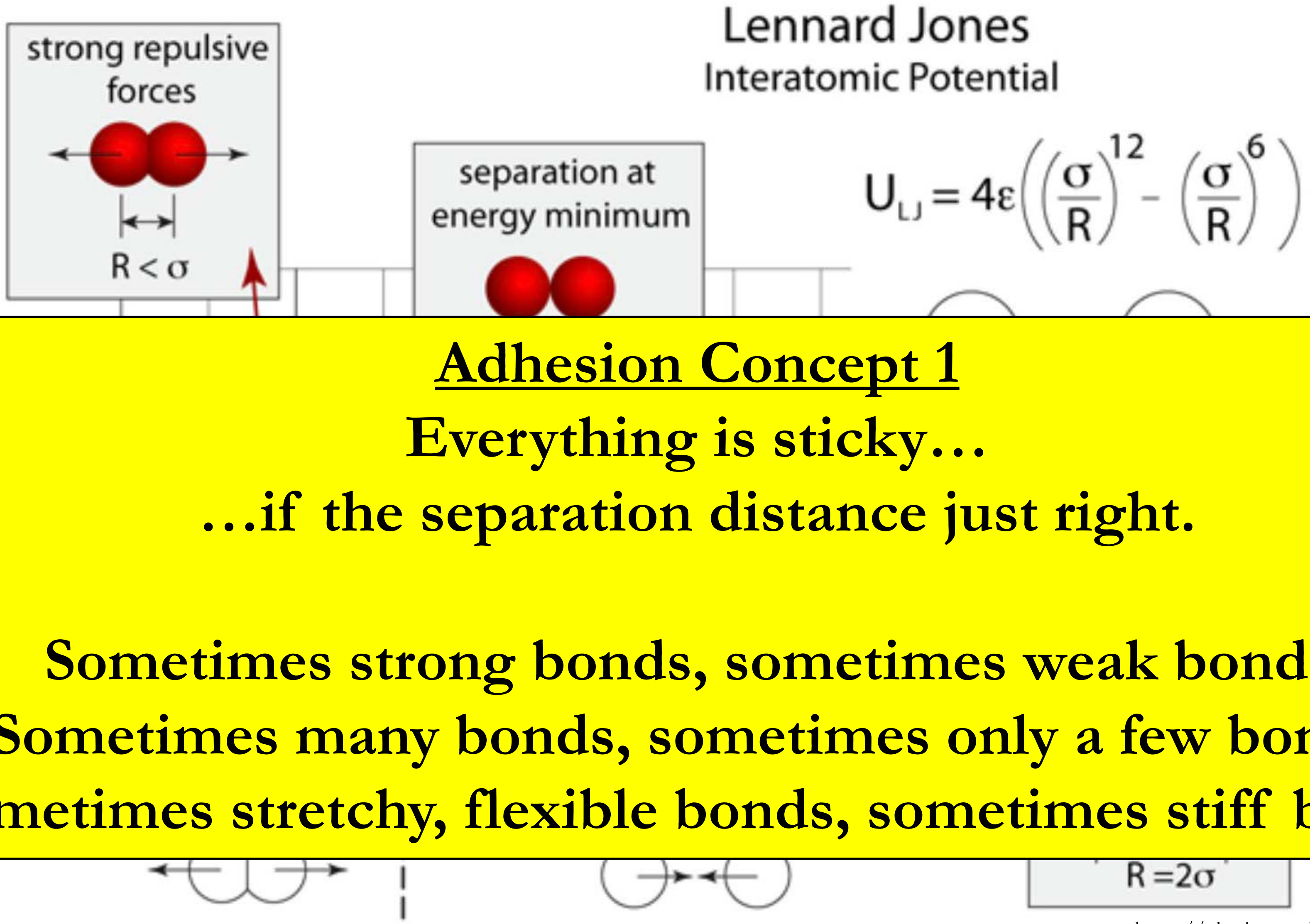


<u>Adhesion Concept 1</u>

Everything is sticky…

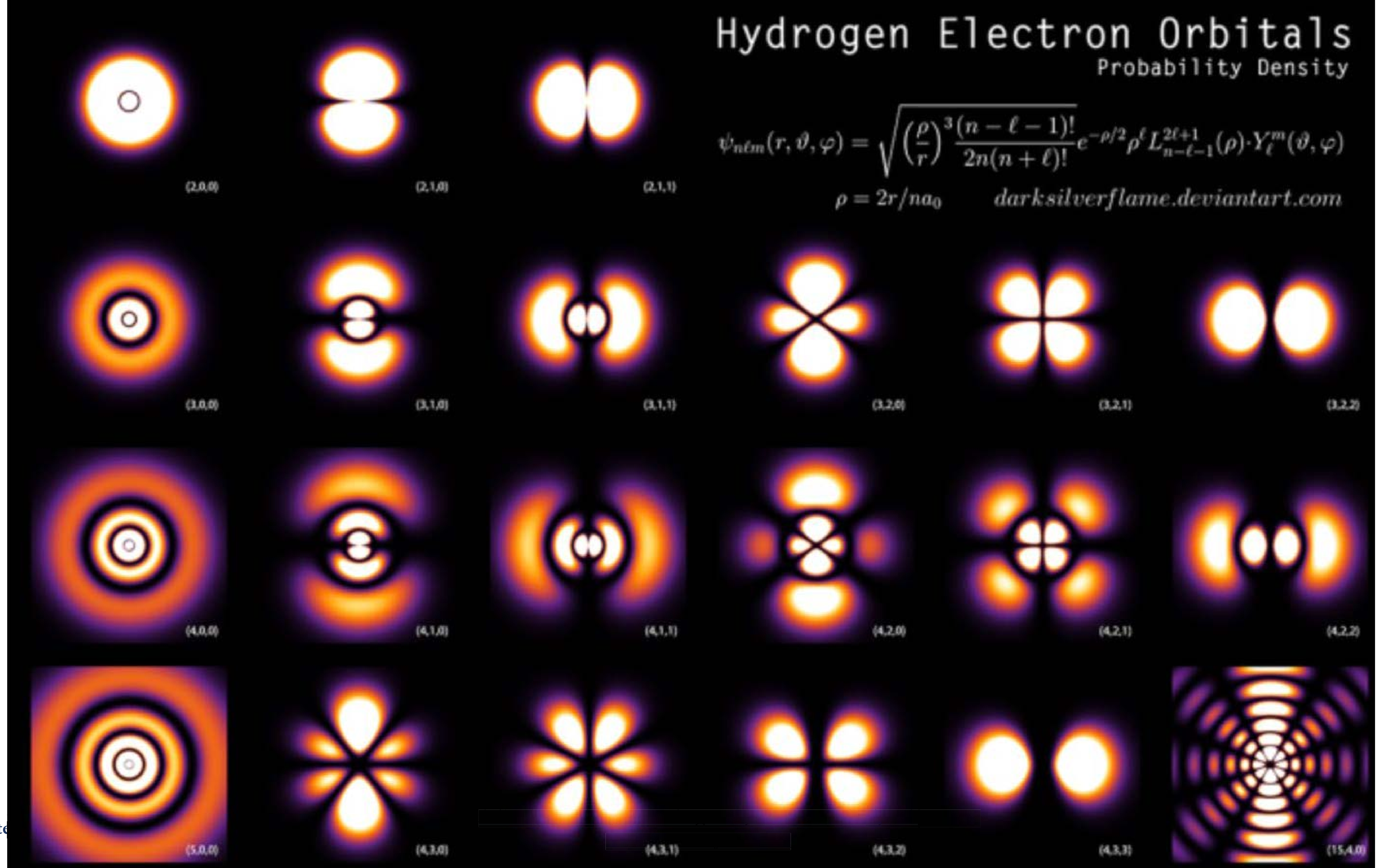
…if the separation distance just right.

Sometimes strong bonds, sometimes weak bonds.

Sometimes many bonds, sometimes only a few bonds.

Sometimes stretchy, flexible bonds, sometimes stiff bonds.

https://physicsatmcl.commons.msu.edu/lennard-jones-potential/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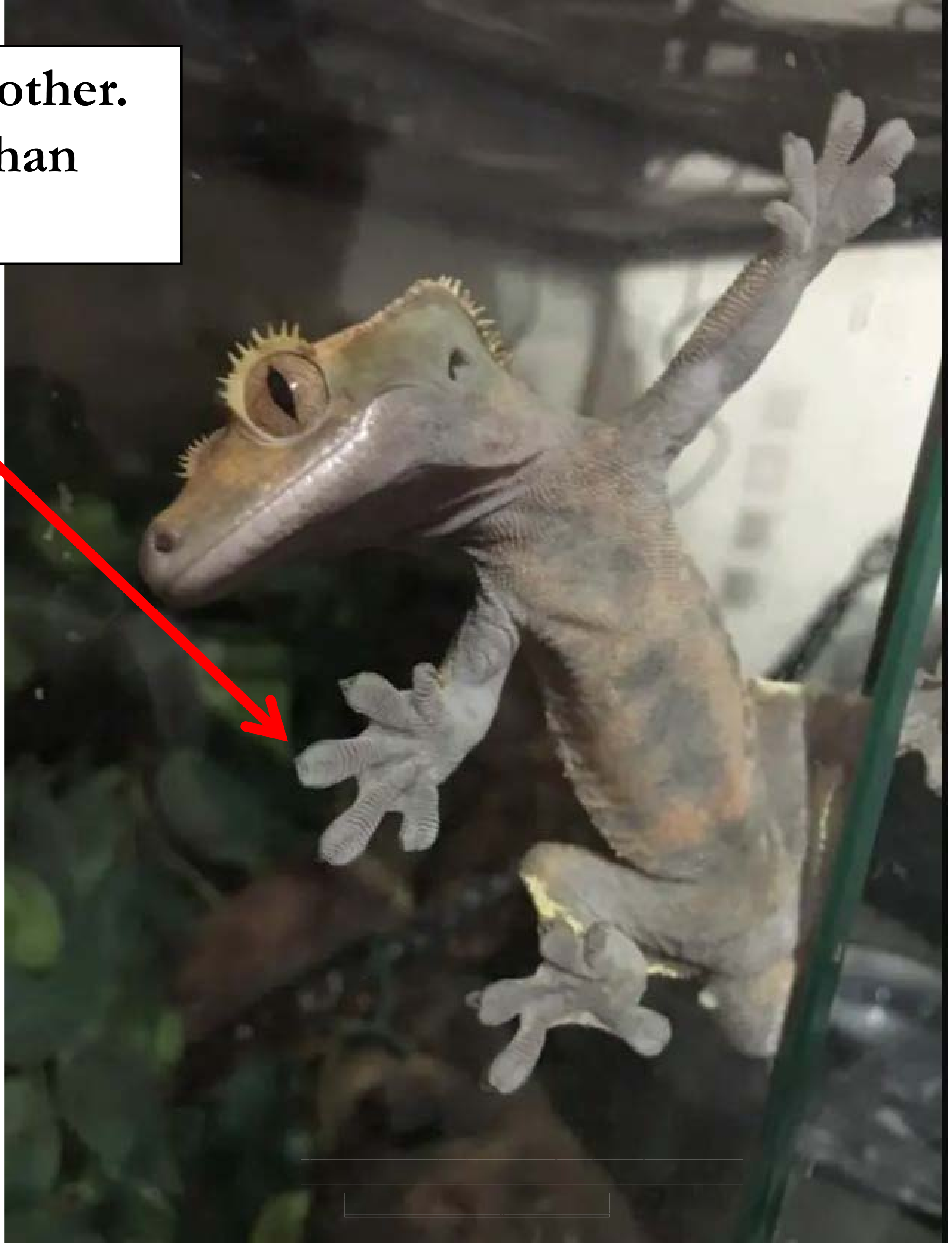
(4,3,2)
(4,3,3)
(15,4,0)

Just one thing close to another. About 4x more strength than needed.



FYI – Geckos can't climb on Teflon. Unless it's wet.

Also, they stay stuck after they die.

Mirrors:
Just metal close to glass.

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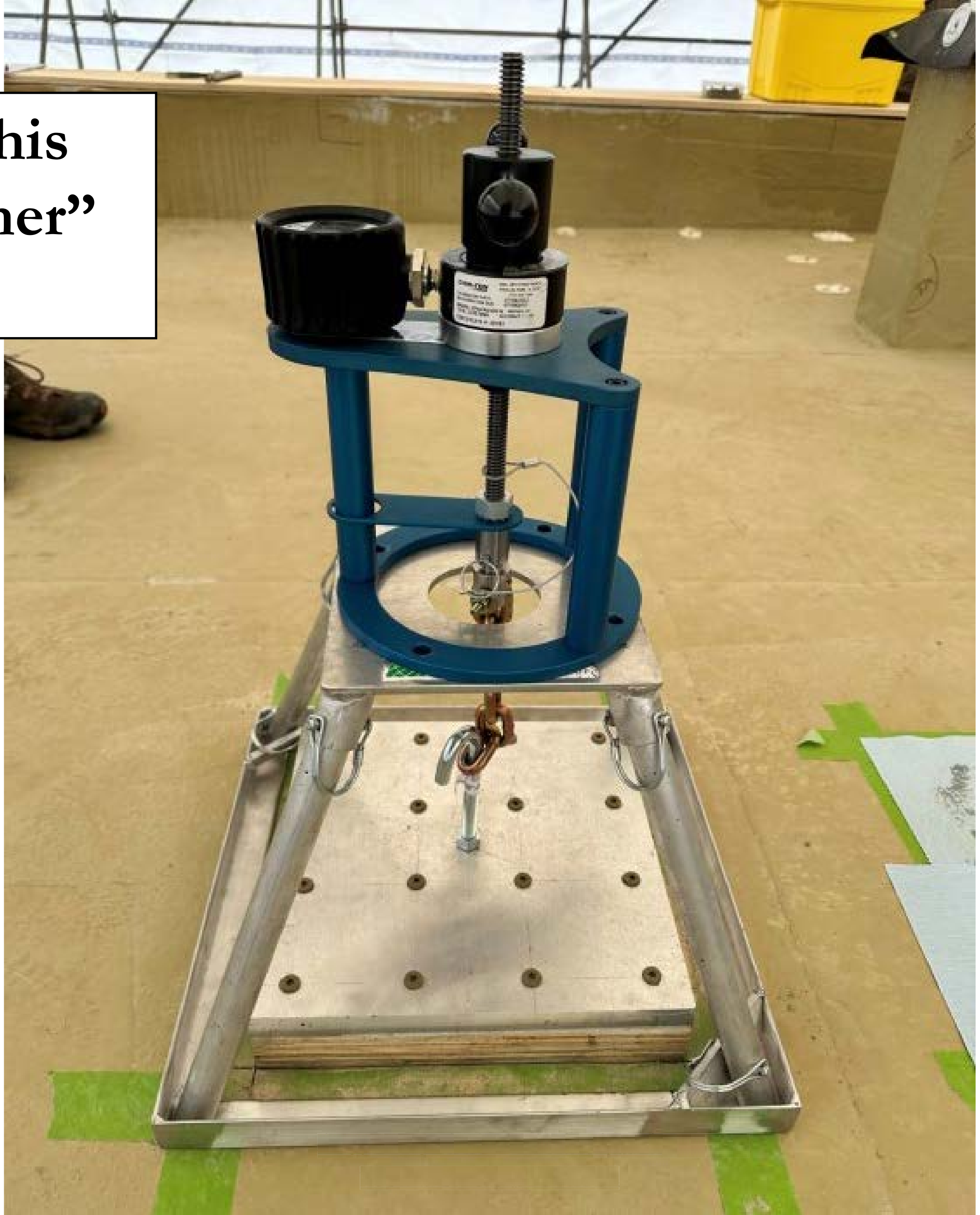
How strong is this ”just close together” bond?



Summer Camp, 2023

Dr. Matt Dupuis
SRI Consultants

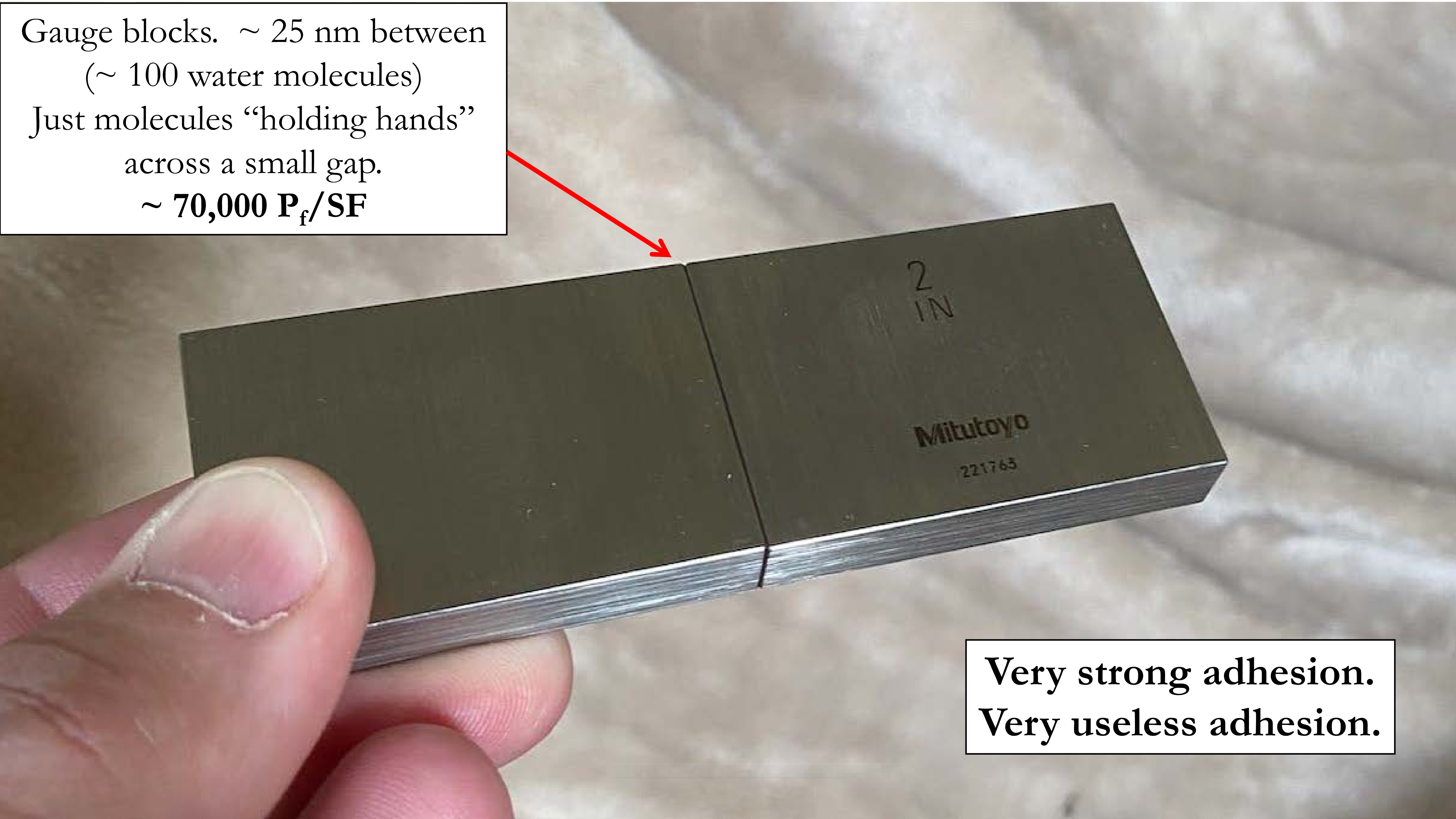
> 2,000 P_fSF

“We stopped pulling”

So, that’s <u>really</u> strong.

(BTW, this adhesion is much different and more than “just close together”)

Gauge blocks. ~ 25 nm between
(~ 100 water molecules)
Just molecules “holding hands”
across a small gap.
~ 70,000 P_f/SF



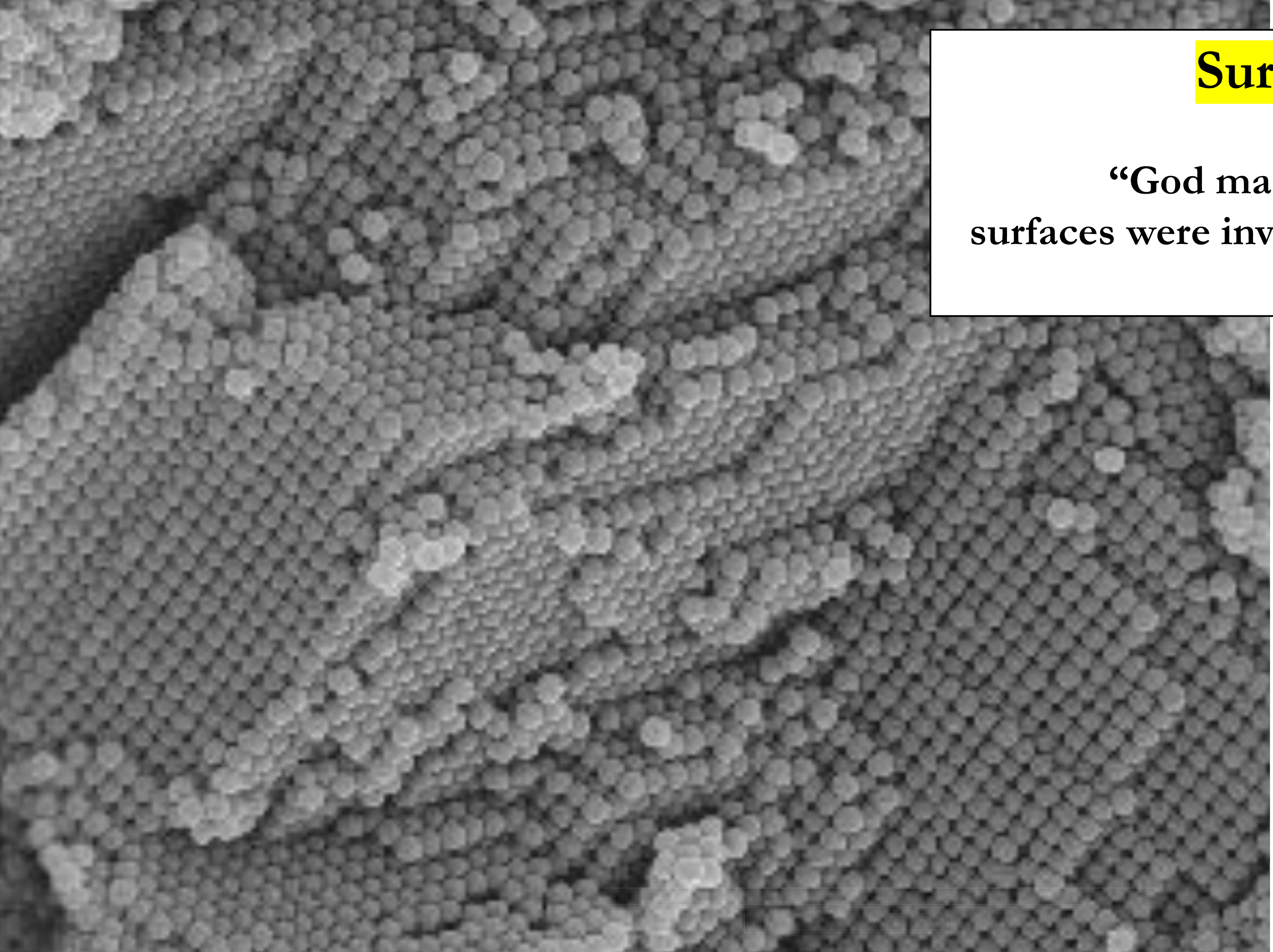
Very strong adhesion.
Very useless adhesion.

Just glass.
Hercules couldn't pull this glass bottle stopper out.

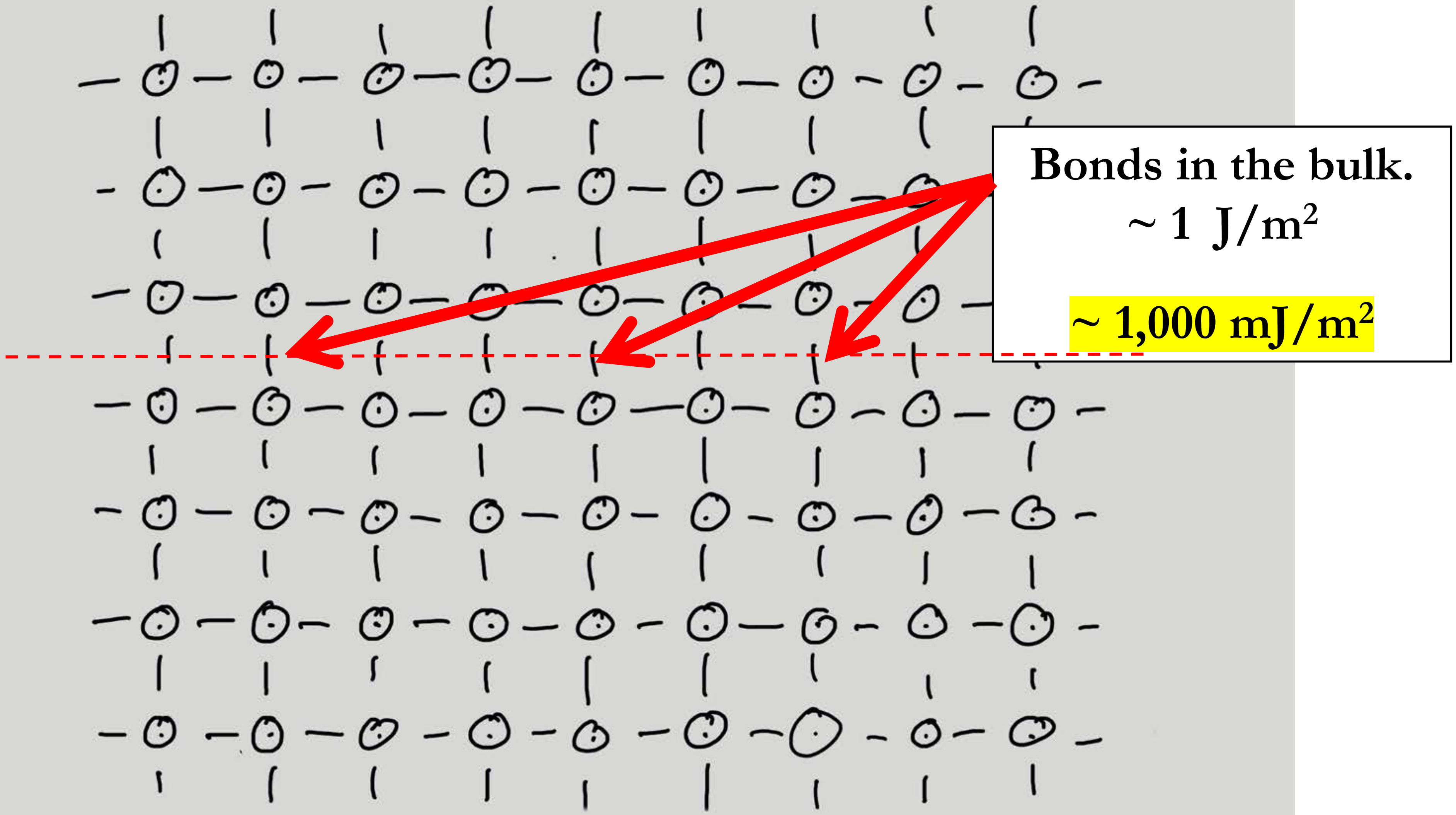
(But a small child can easily twist it out.)

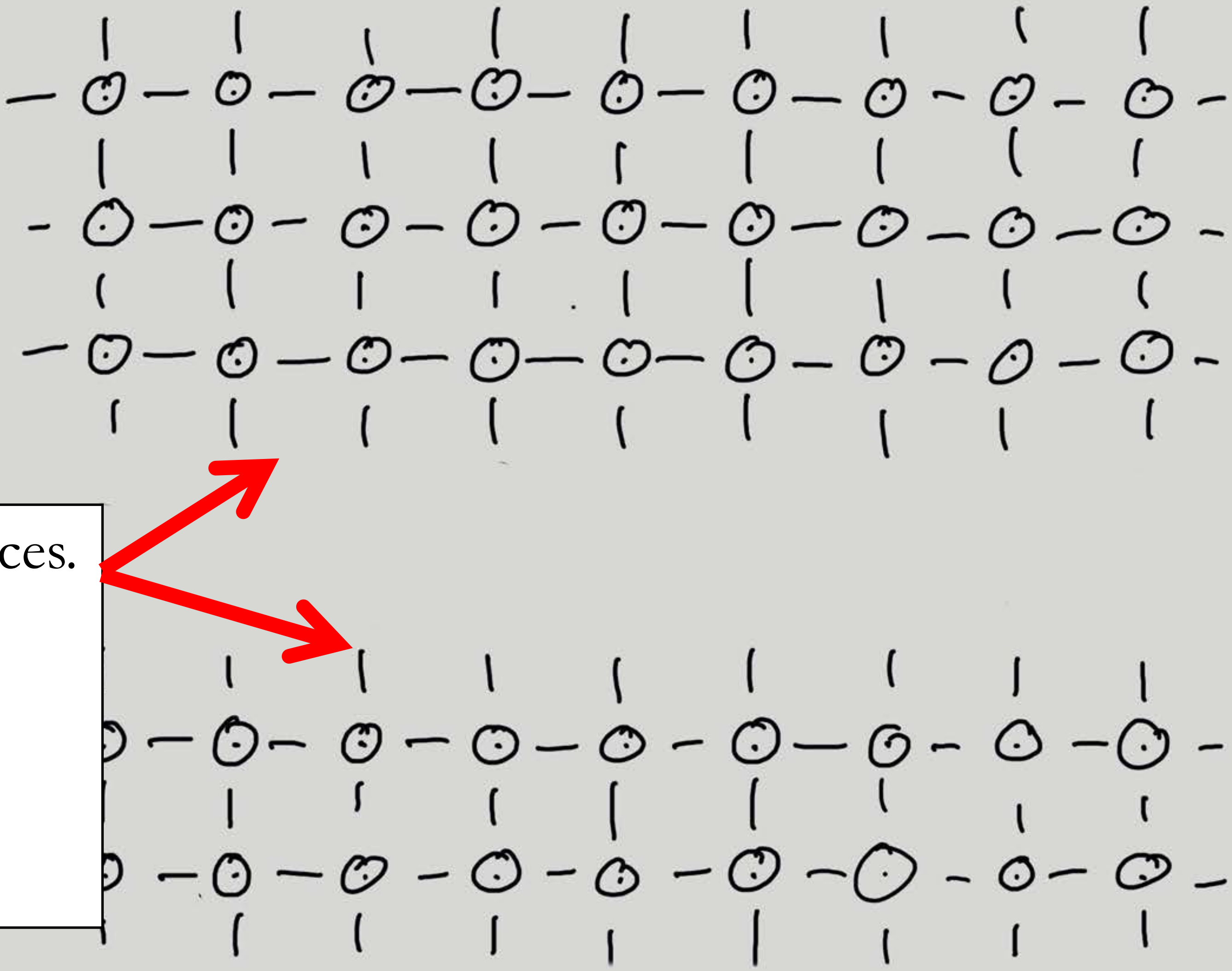
Surfaces

"God made the bulk;
surfaces were invented by the devil."
- Wolfgang Pauli



Opal.
(Fancy quartz)
$SiO_2 + H_2O$


Bonds in the bulk.
~ 1 J/m²
~ 1,000 mJ/m²



Two newly created surfaces.
~ 0.5 J/m²

~500mJ/m²

Surface energy!

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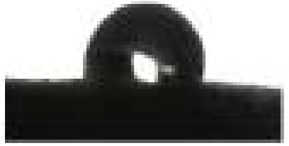
Metal Surfaces (High Surface Energy)

mJ/m²	Surfaces
1103	Copper
840	Aluminum
753	Zinc
526	Tin
458	Lead
700-1100	Stainless Steel
250-500	Glass
72	Water
36 – 70	Concrete
30 – 300	Wood
33	Olive Oil

Plastic Surfaces (High Surface Energy)



mJ/m²	Surfaces
50	Kapton® Industrial Film
47	Phenolic
46	Nylon
45	Alkyd Enamel
43	Polyester
43	Epoxy Paint
43	Polyurethane Paint
42	ABS
42	Polycarbonate
39	PVC Rigid
38	Noryl® Resin
38	Acrylic

Plastic Surfaces (Low Surface Energy)

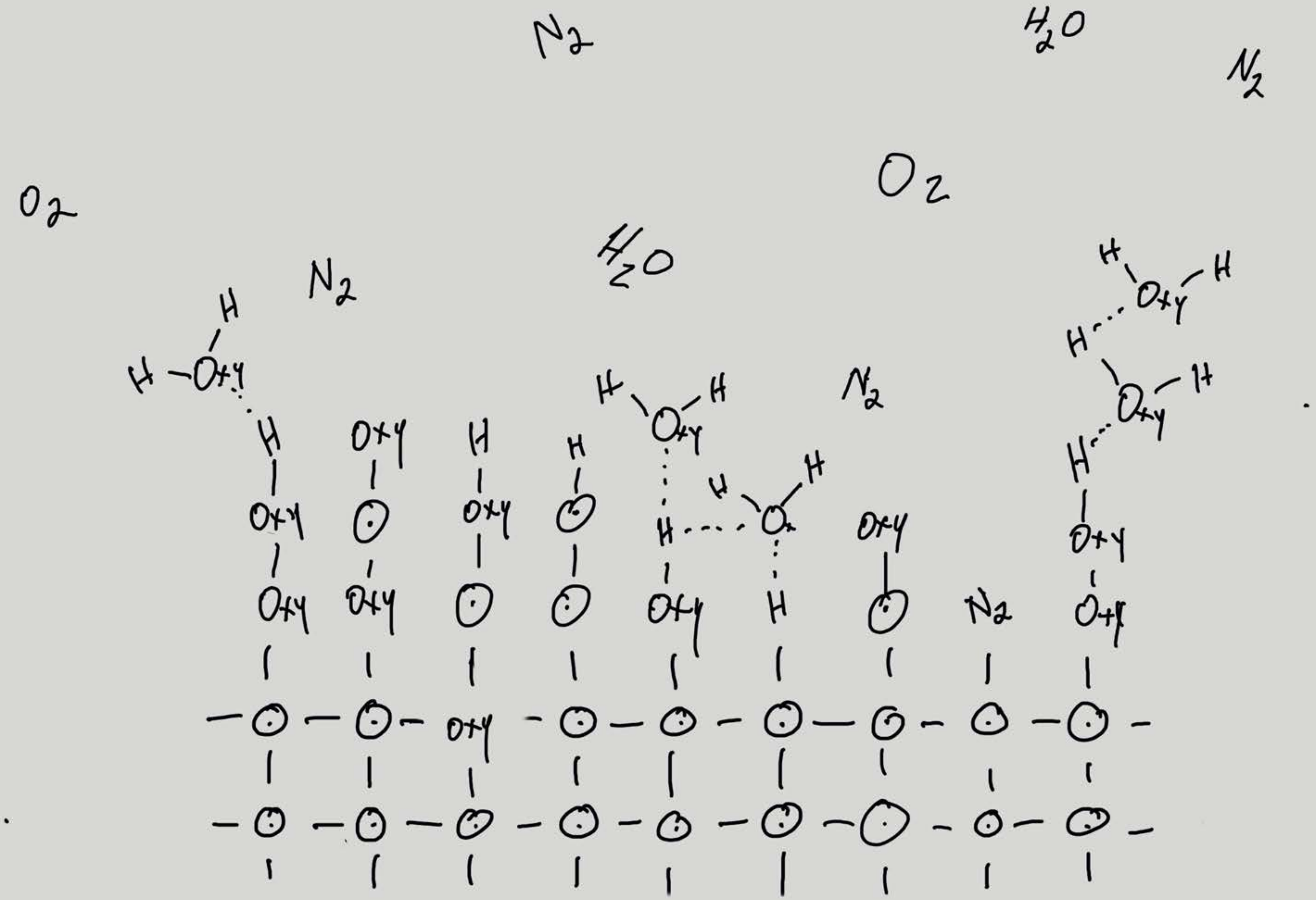
mJ/m²	Surfaces
37	PVA
36	Polystyrene
36	Acetal
33	EVA
31	Polyethylene
29	Polypropylene
28	Polyvinyl Flouride Film
18	PTFE Fluoropolymer
+/- 24	Silicone

https://www.horaetape.com/what-is-surface-energy-does-surface-energy-affect-bonding/

1 or 2 seconds later.

~ 0.1 J/m^2

~ 100mJ/m^2



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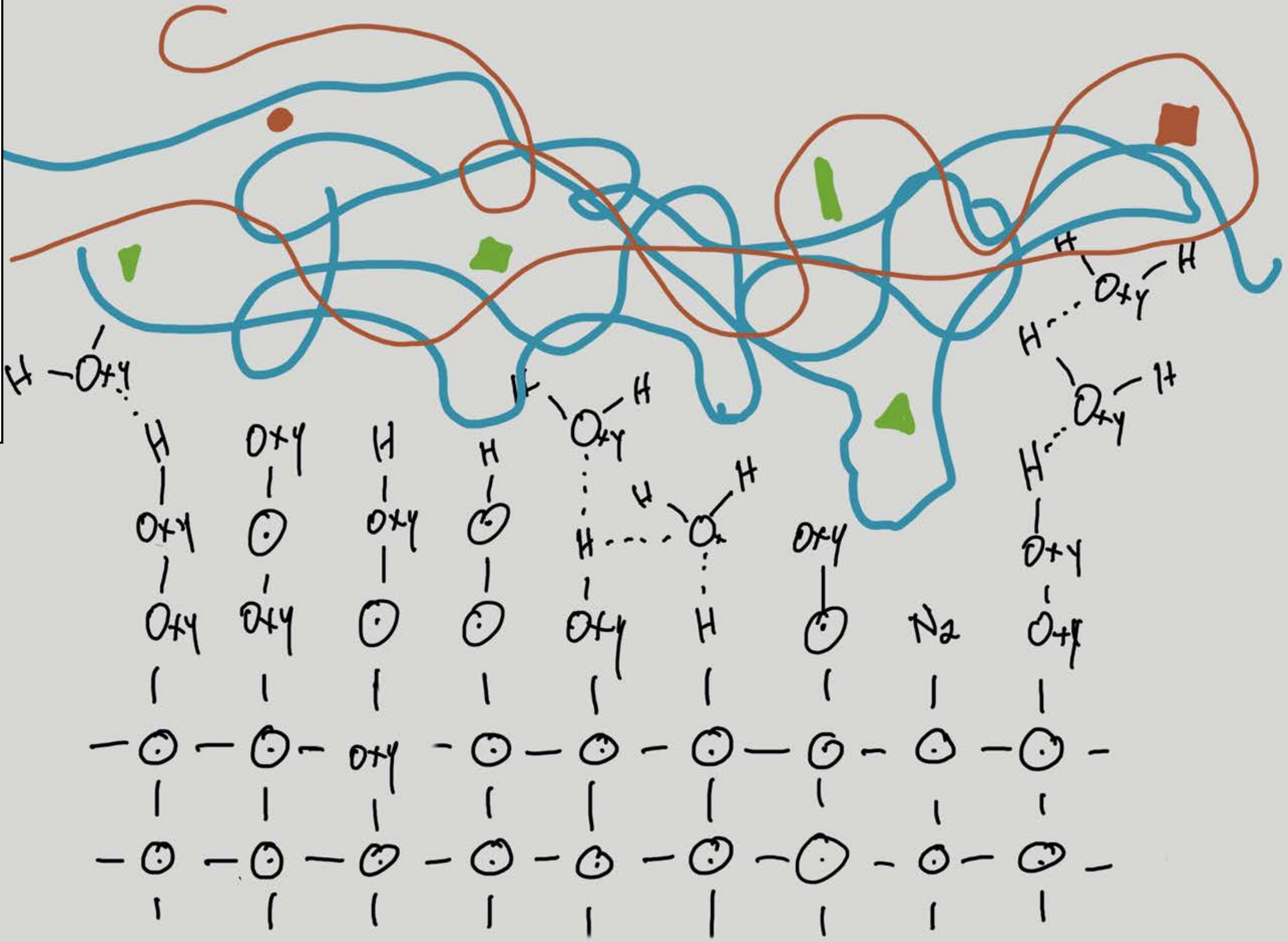
These sparks are the new surface burning.

Minutes later.

~ 0.05 J/m²

~ 50mJ/m²

(typical surface energy of plastics)



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~ 500,000 mJ/m2

10,000 X increase!?

(ASTM D-3330)

Typical "strengths" of adhesion:

Surface bond adhesion: < 500mJ/m^2 (weak)

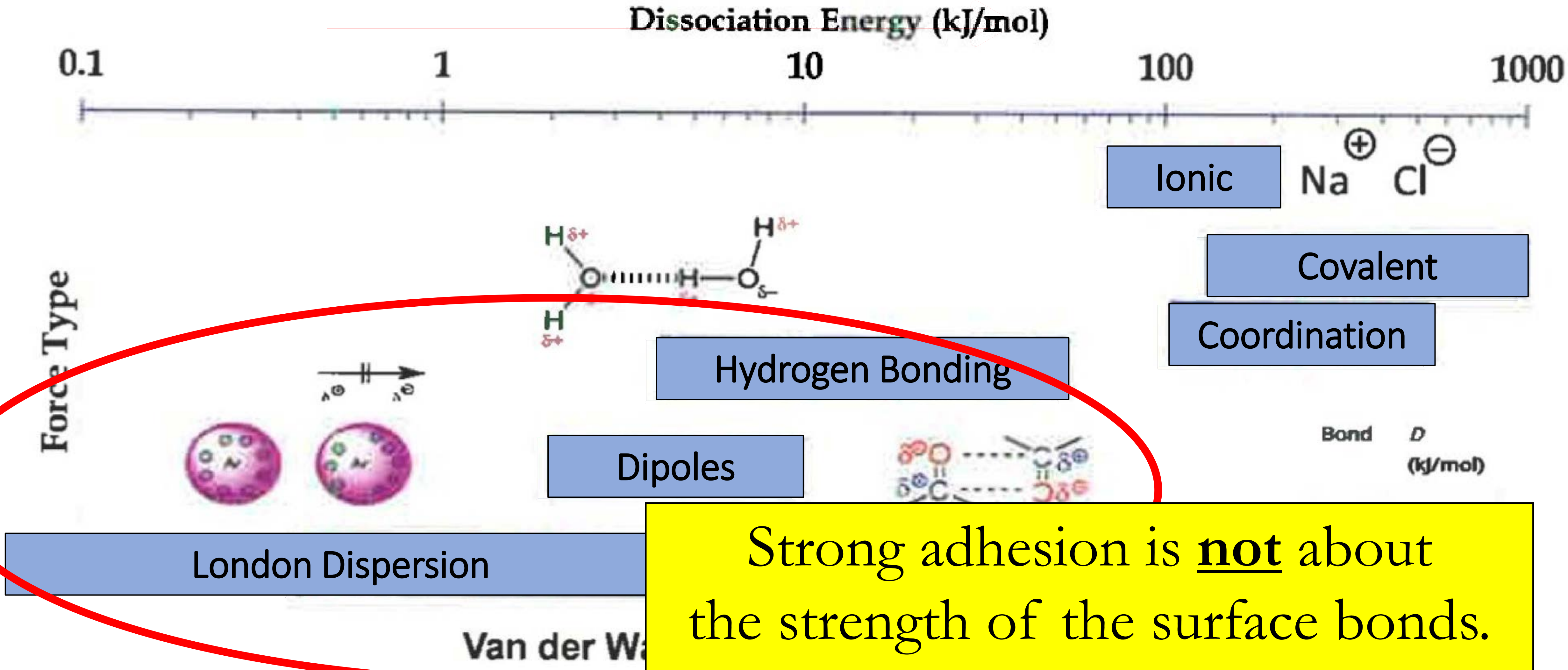
10x to 100x increase

Intrinsic adhesion: 500 to 50,000 mJ/m^2 (modest)

10x to 10,000x increase

Practical, strong adhesion: >50,000 mJ/m^2 (strong)

~ 3x Post-it-Note peel strength



Strong adhesion is **not** about
the strength of the surface bonds.
But… there must be some.

Adhesion Concept 2

Atom-to-atom **surface bond adhesion is necessary but, insufficient** for *strong*, *practical* adhesion.

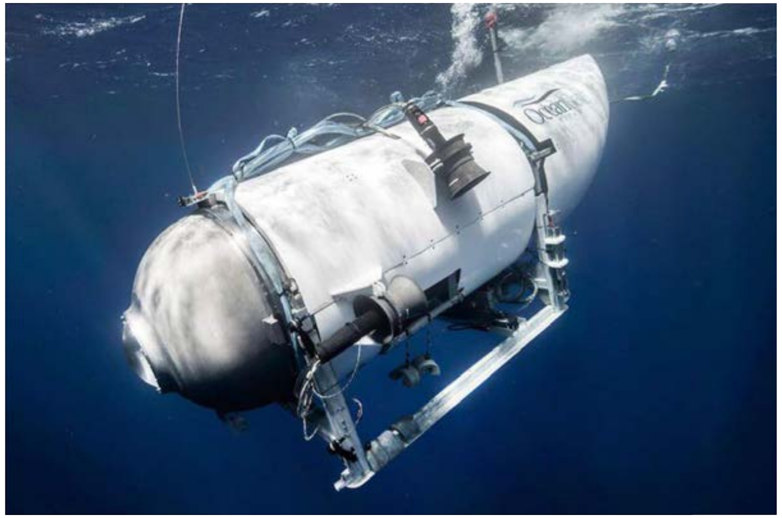
Surface energy is almost insignificant regarding strong adhesion.

1: **Everything is sticky.**

Polymers

50,000 BC
Birch tar

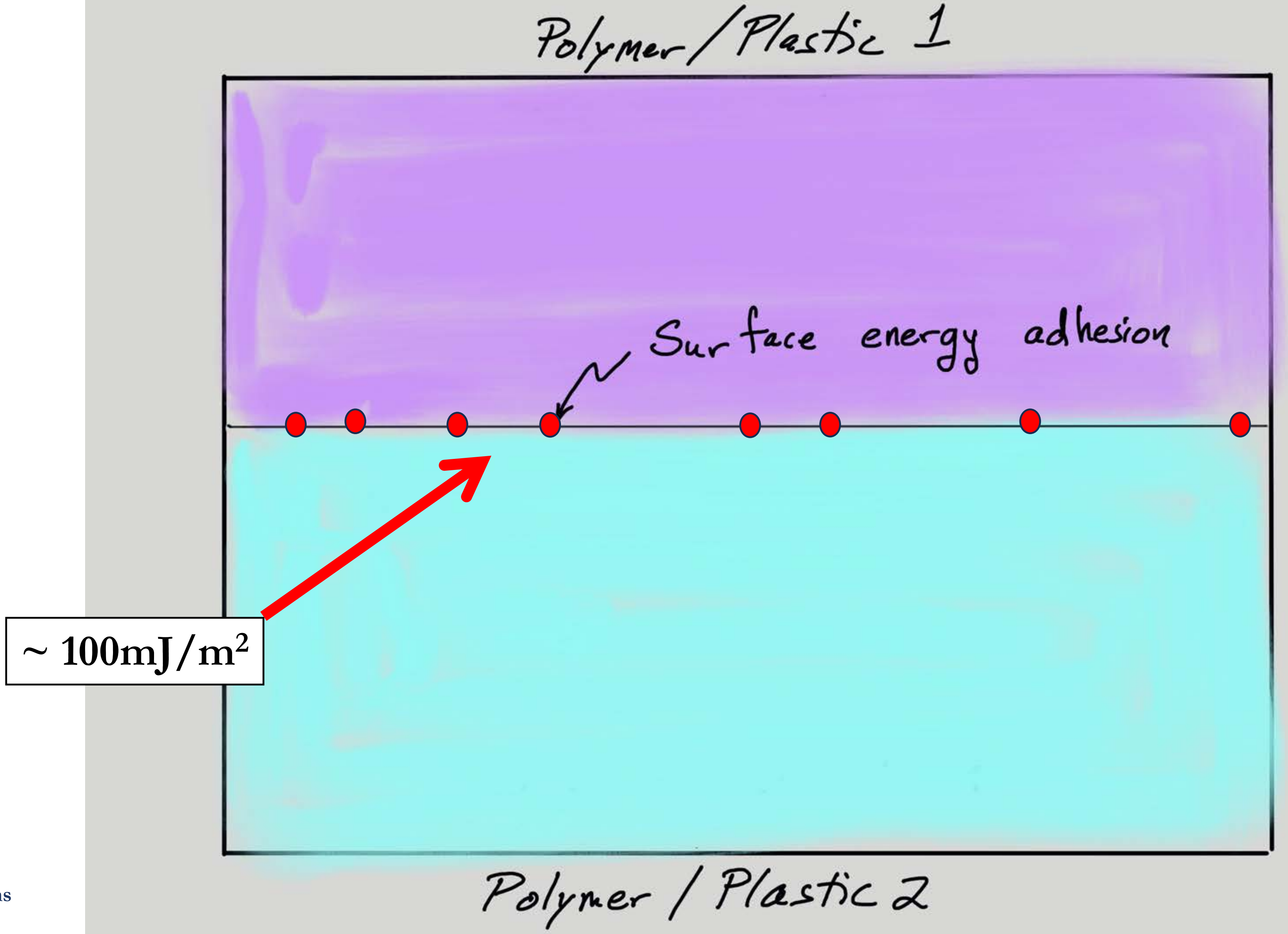
1,400 BC
Bee's wax



2024
Epoxy

100% of our strong adhesives are polymers or very long chain molecules.
Most organic (carbon), some inorganic (silicone or alumino-silicate).

Painting: Jacob Peter Gowy, The Fall of Icarus (1635-7), Museo del Prado, Madrid.



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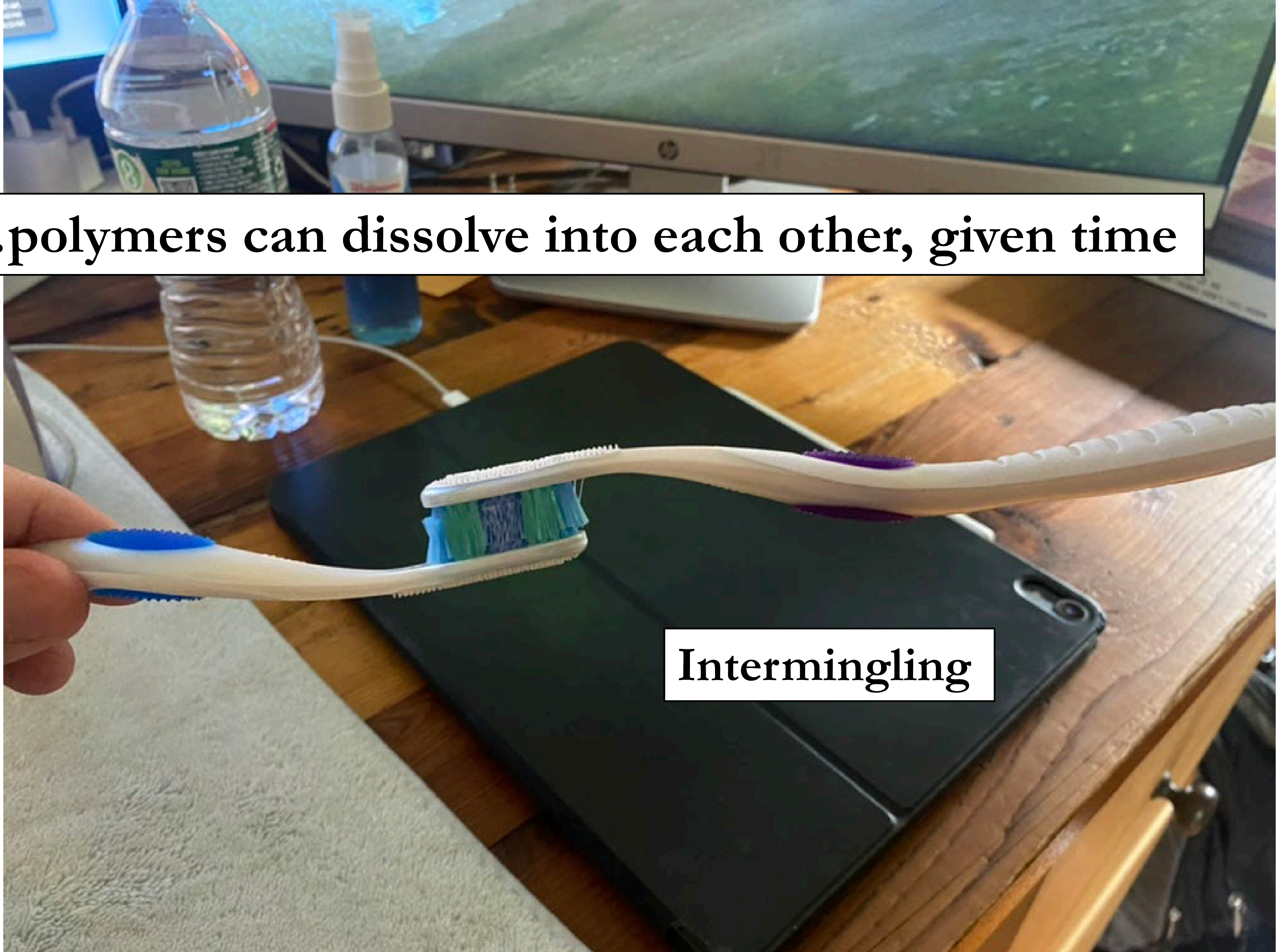
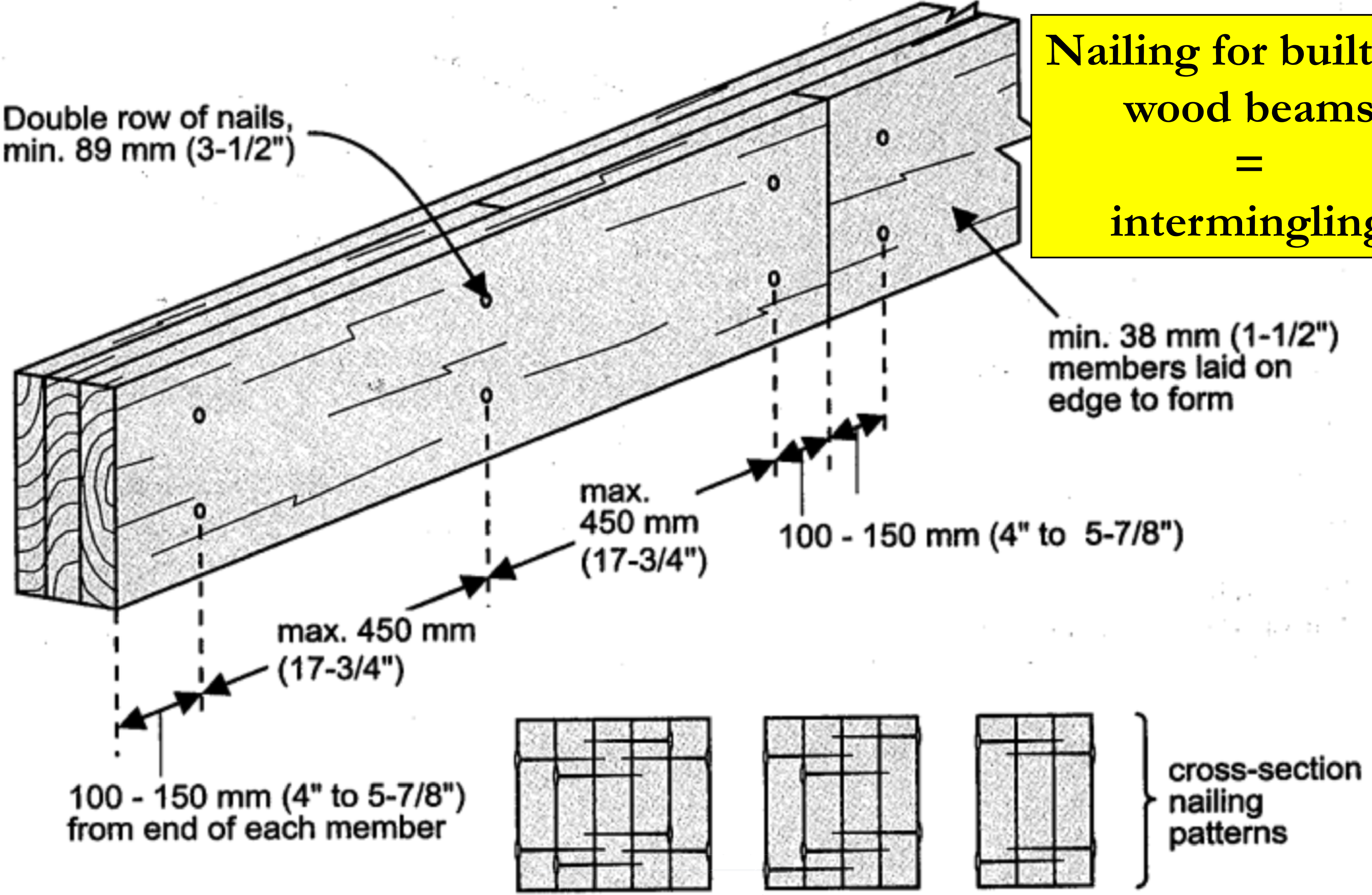
But…
polymer surfaces are fuzzy.
And, the fuzz is wiggly.

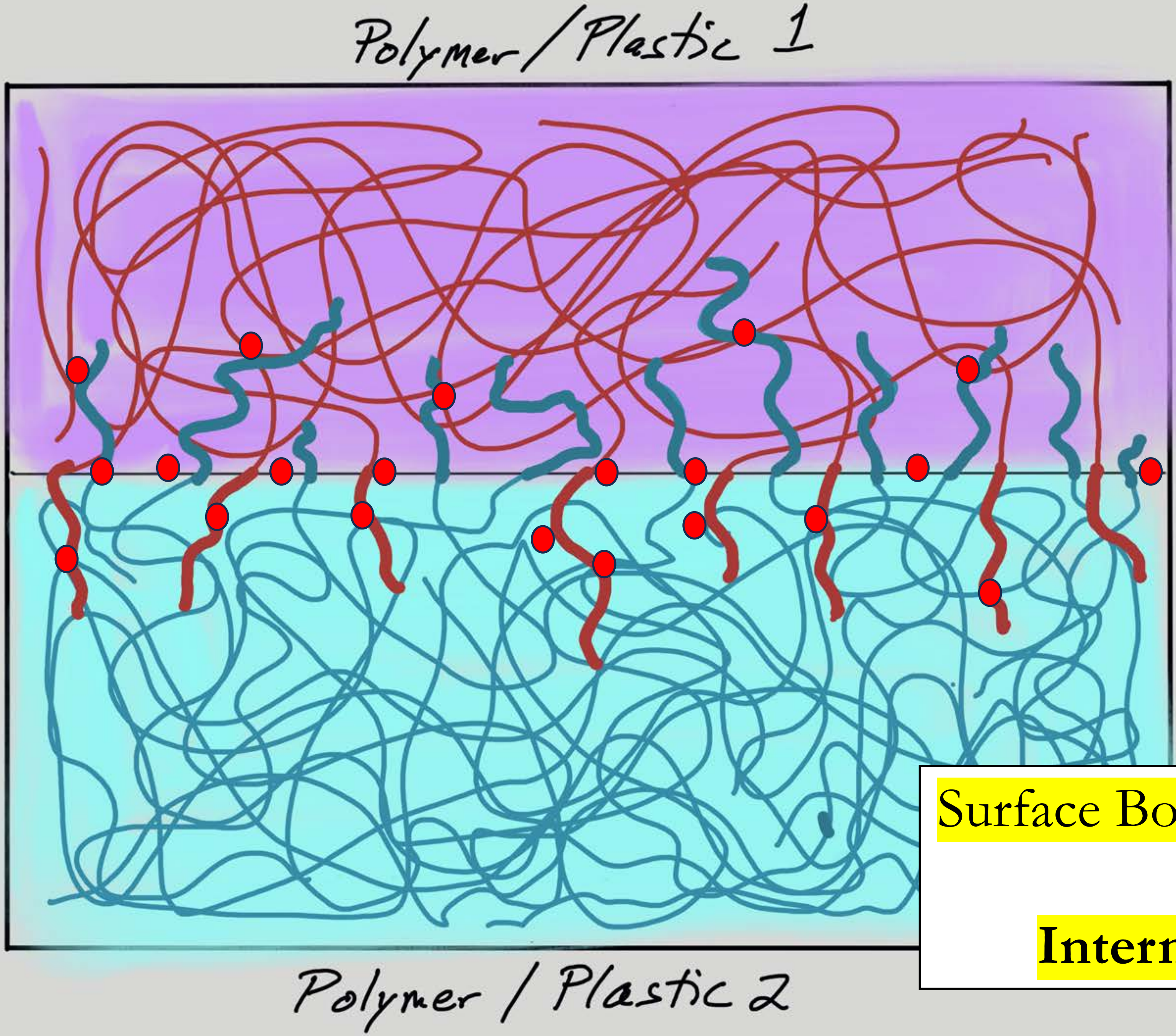
Some more fuzzy. Some less fuzzy.
Some long fuzz. Some short fuzz.
Some very wiggly. Some not so wiggly

And…polymers can dissolve into each other, given time



Nailing for built-up wood beams = intermingling





Surface Bond Adhesion
+
Intermingling

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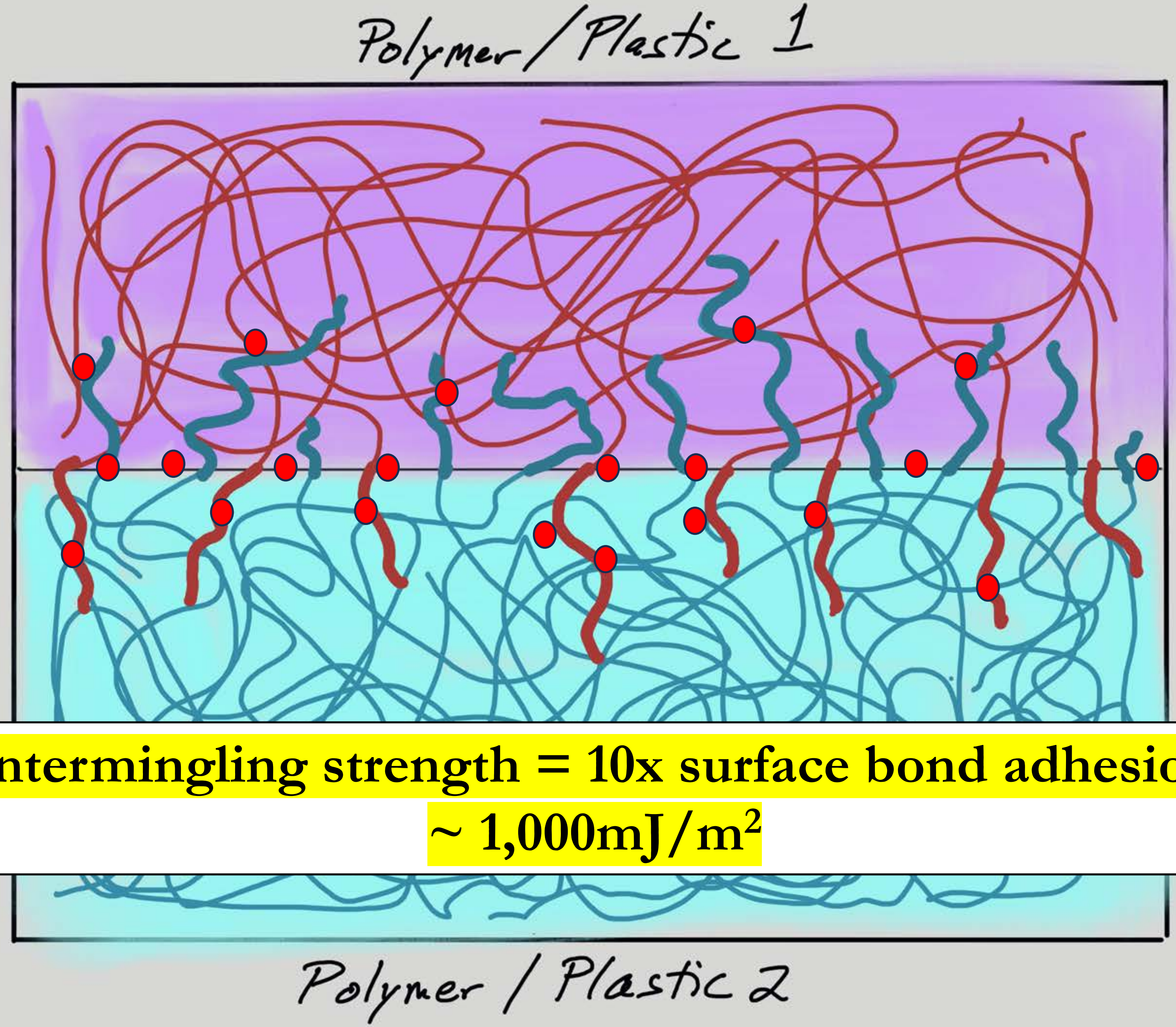

Intermingling strength = 10x surface bond adhesion
~ 1,000mJ/m^2

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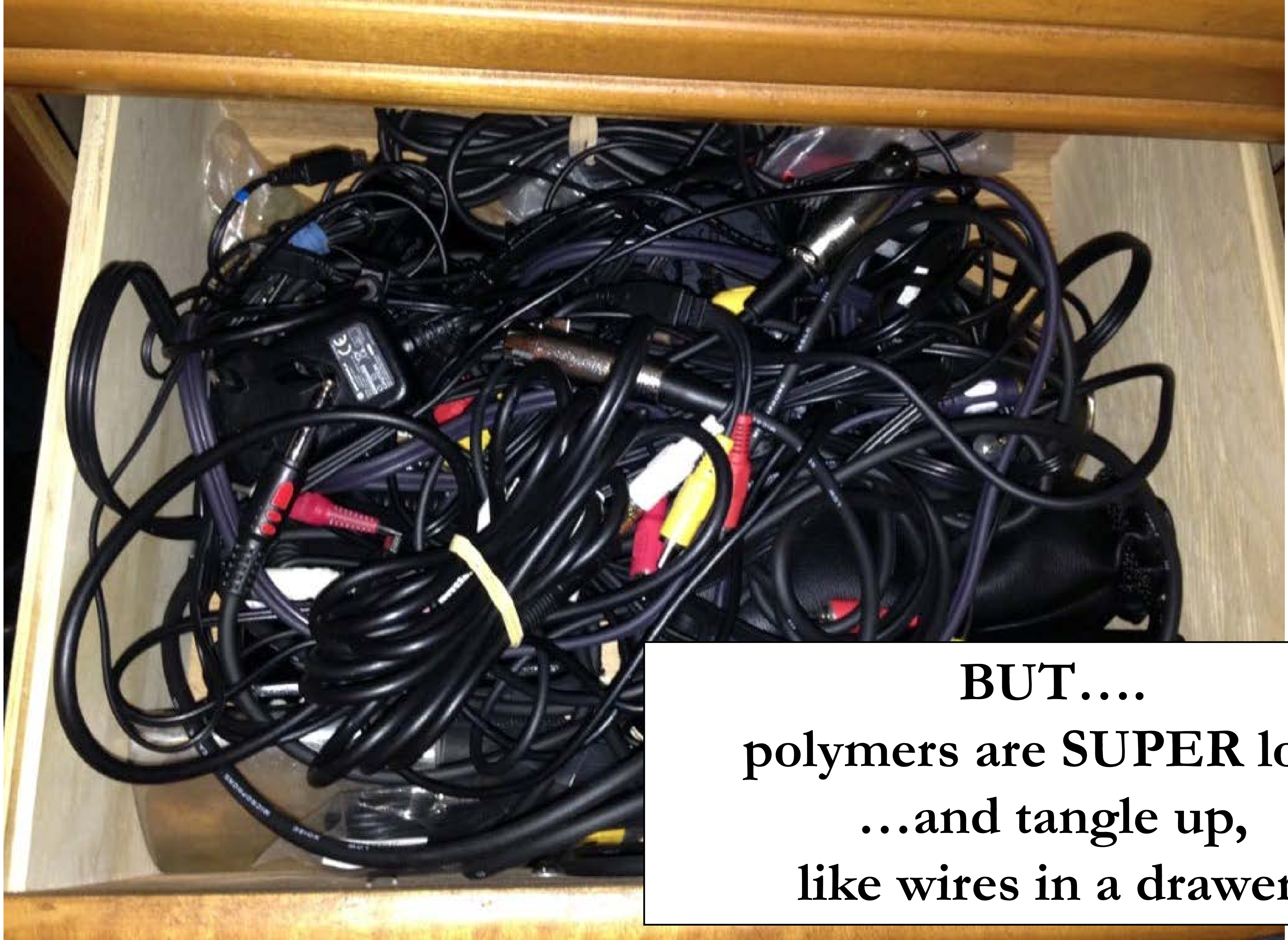
Adhesion Concept 3

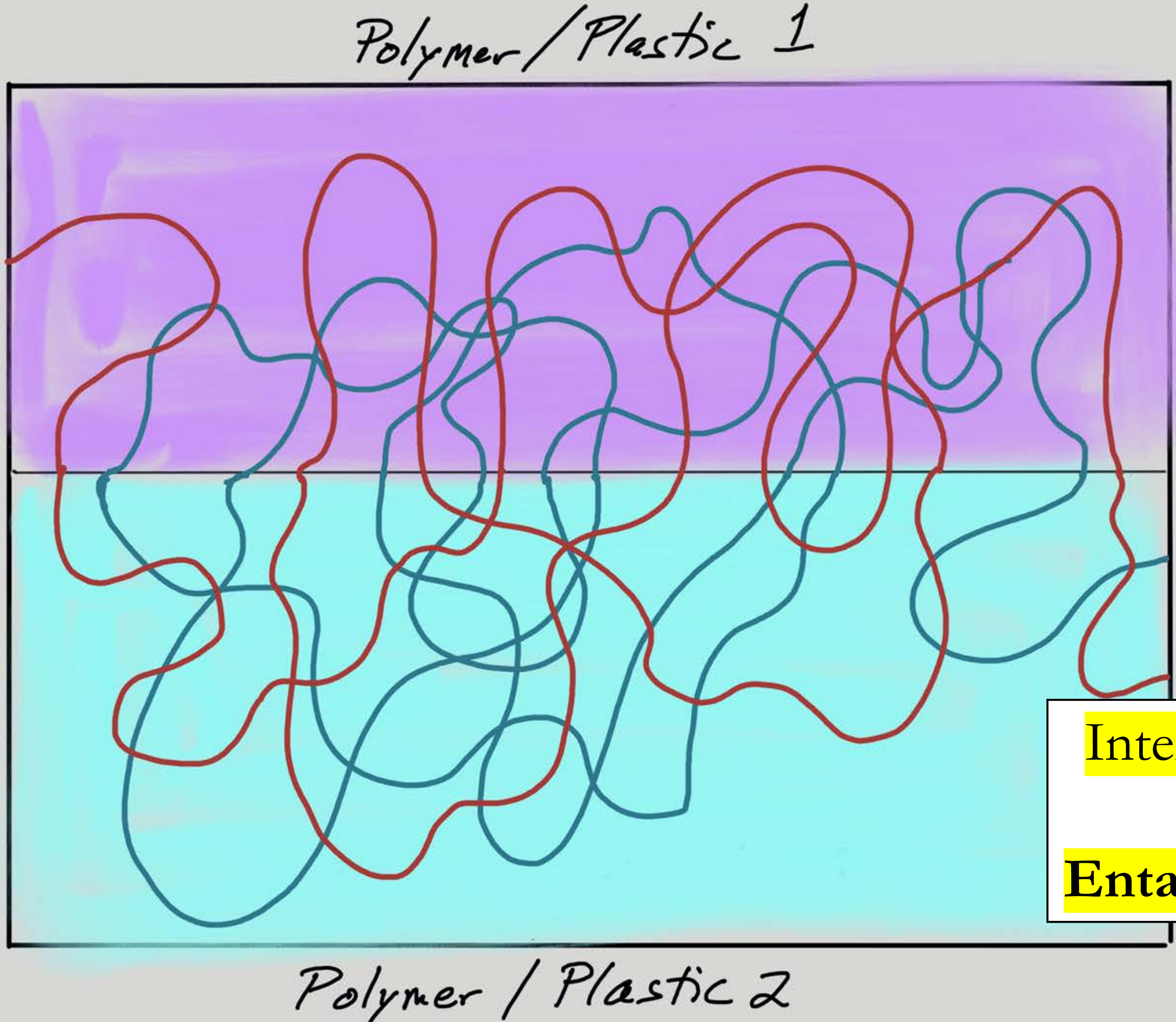
Intermingling of long polymer molecules across the interface increases the strength of weak surface bond adhesion up to something moderately strong (~ 10x increase).

2: Surface bond adhesion is necessary but insufficient.

1: Everything is sticky.



BUT….
polymers are SUPER long
…and tangle up,
like wires in a drawer.



Intermingling
+
Entanglement

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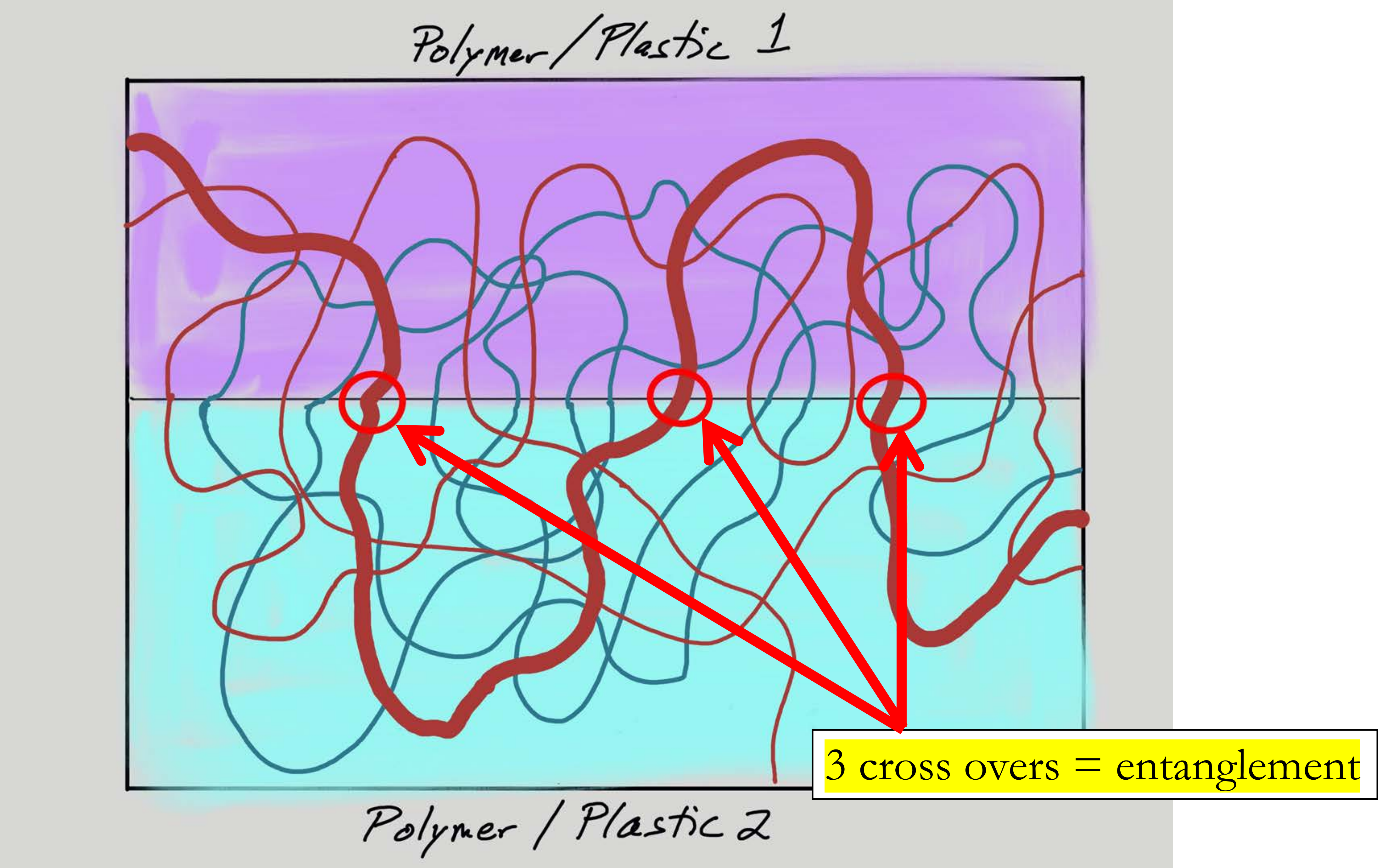
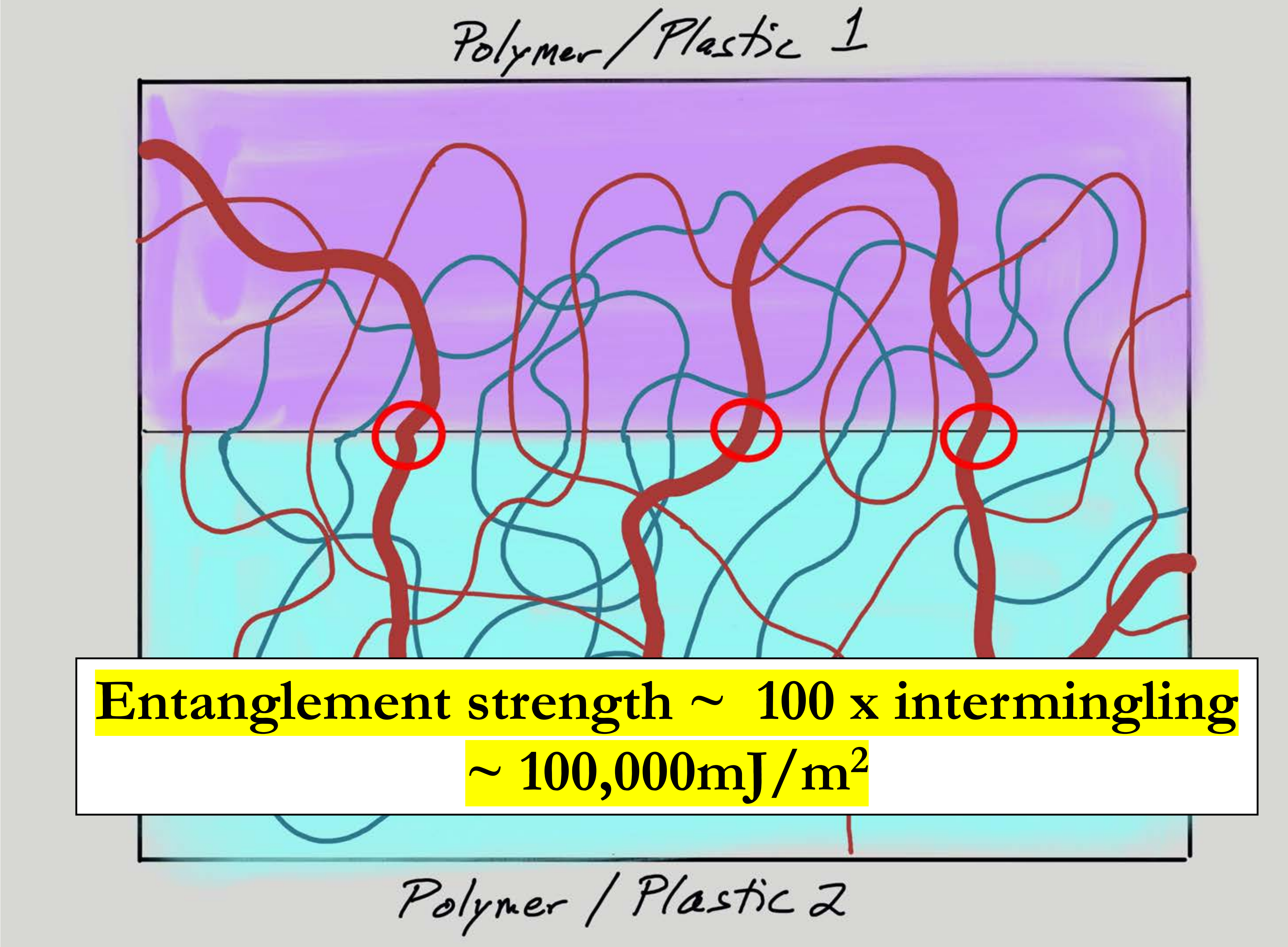

Polymer / Plastic 1
Polymer / Plastic 2
3 cross overs = entanglement



Entanglement strength ~ 100 x intermingling

~ 100,000mJ/m^2

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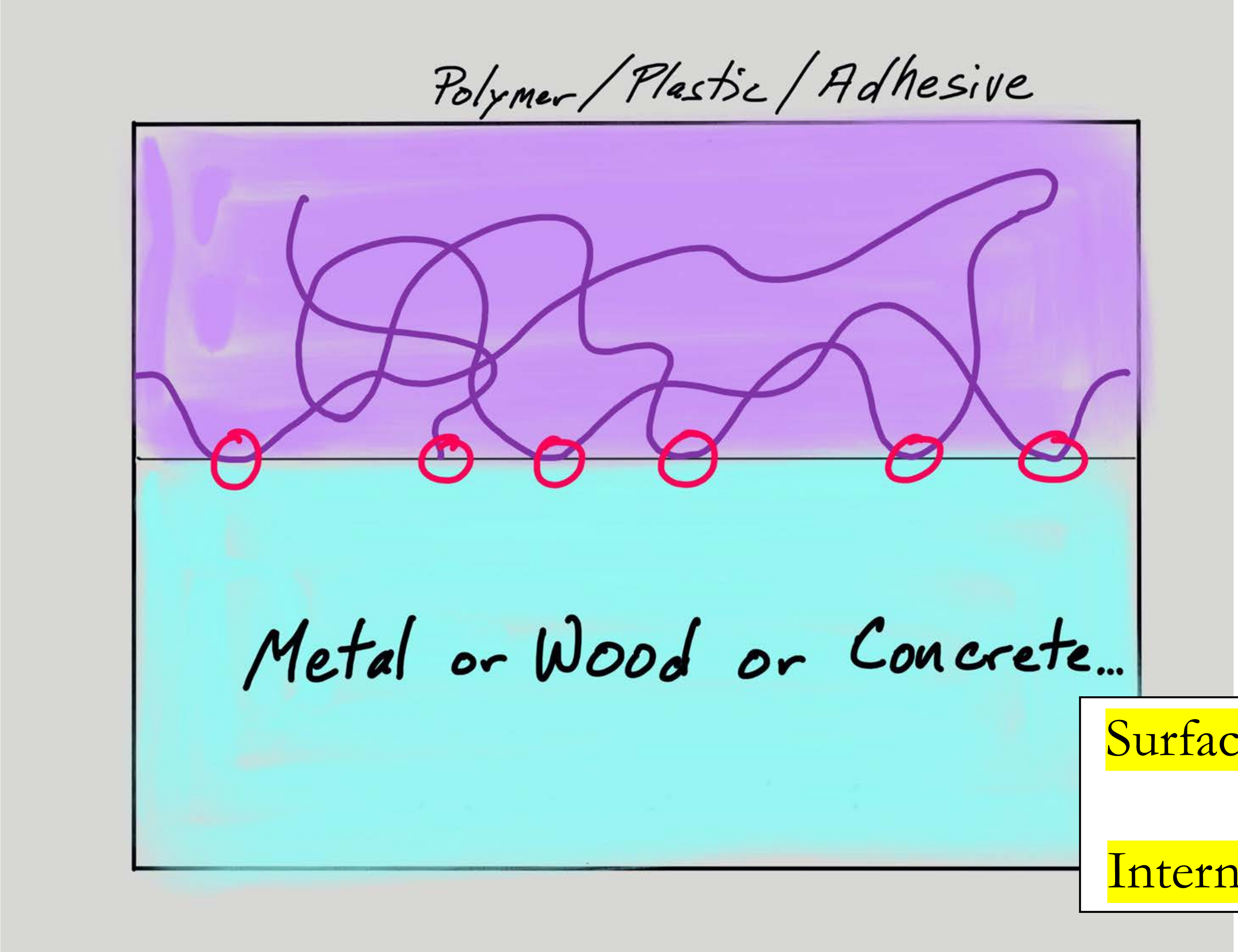
Adhesion Concept 4

Entanglement of long polymer molecules increases the strength of surface bonding adhesion plus intermingling to something truly strong & useful (~ 100x increase over intermingling).

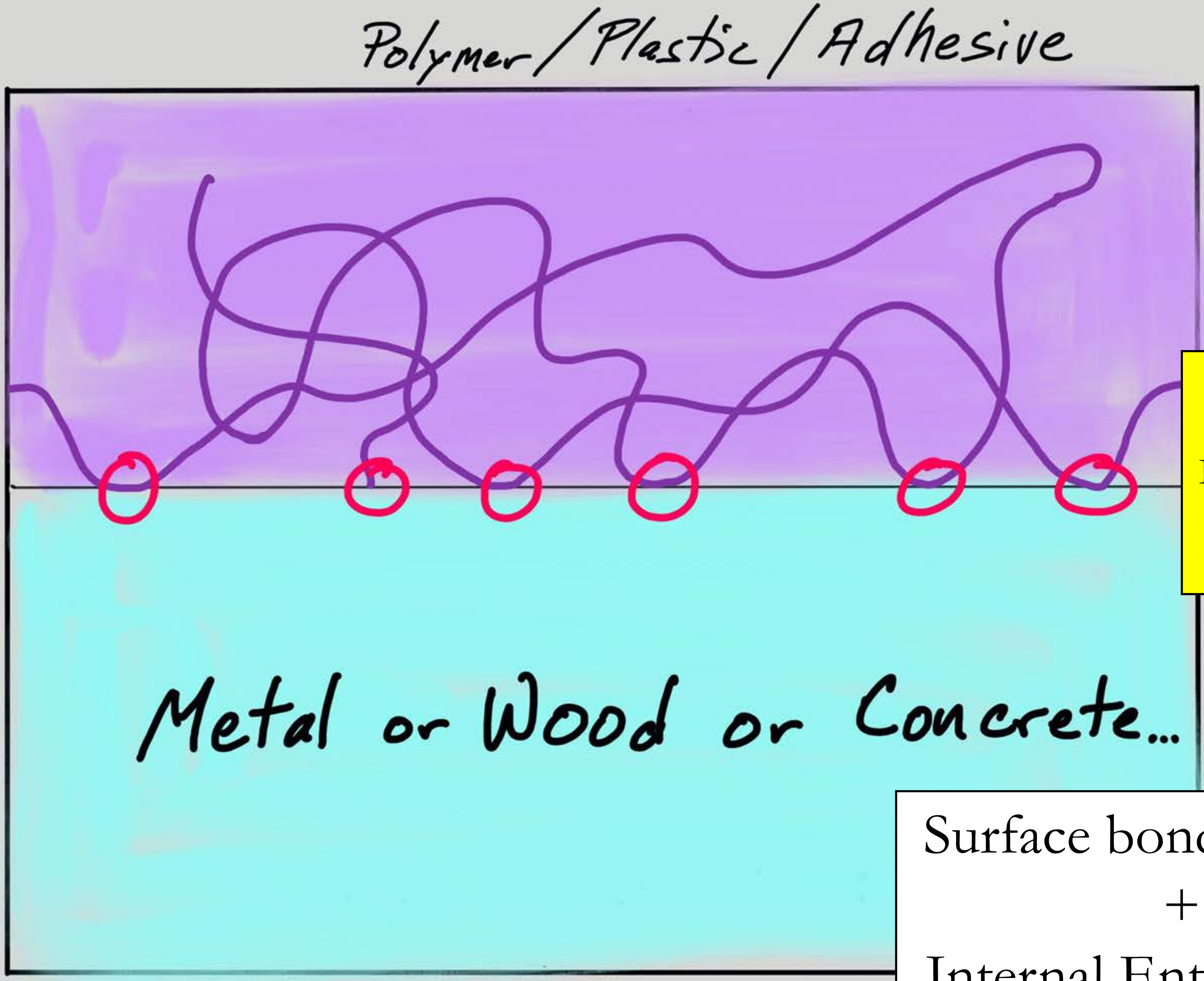
3: Intermingling creates modestly strong adhesion. (~10x surface)

2: Surface bond adhesion is necessary but insufficient.

1: Everything is sticky.



Surface bond adhesion
+
Internal Entanglement



How many bonds?

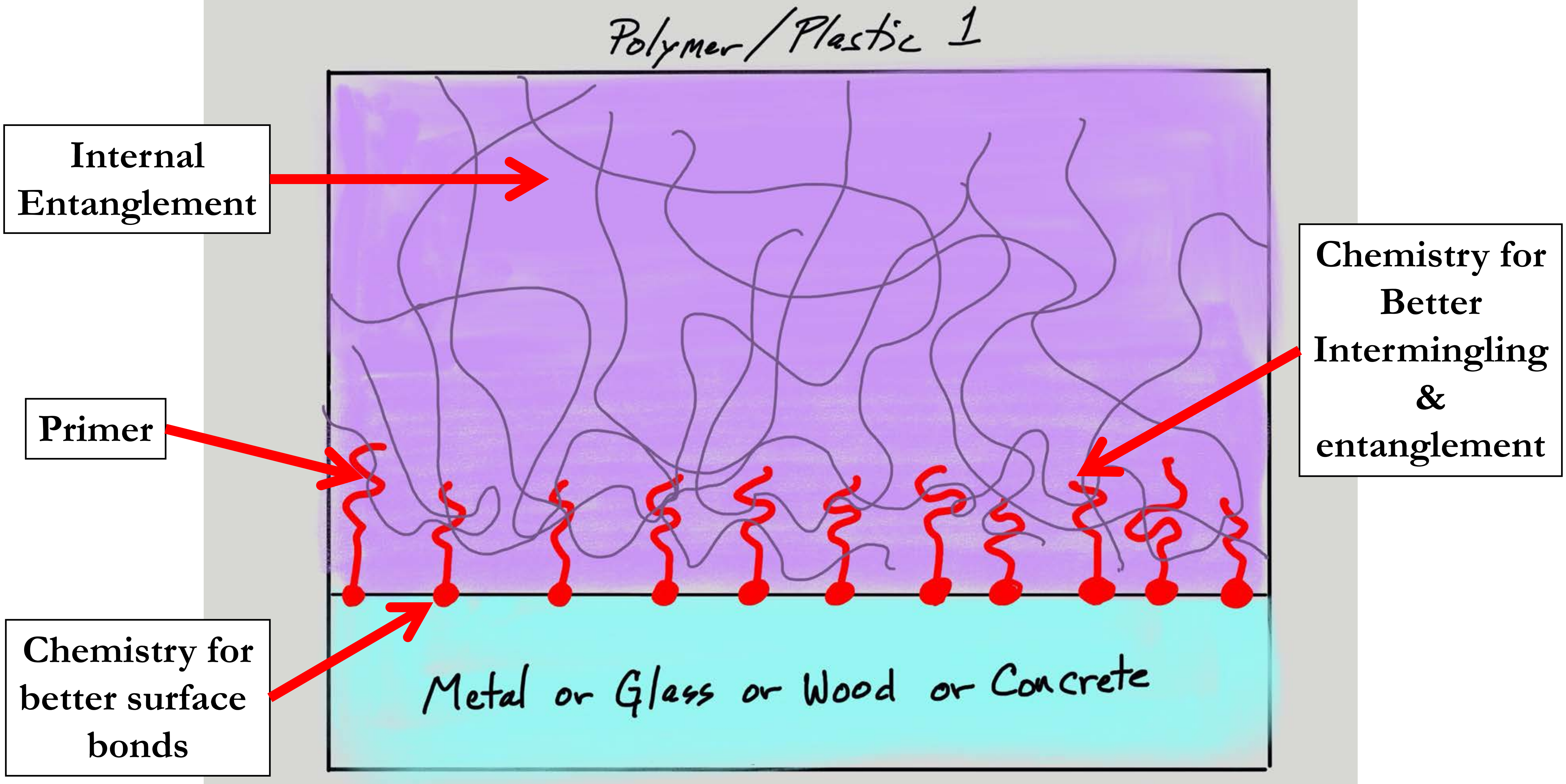
If strong bonds: ~1%

If weak bonds: >1%

Surface bond adhesion

+

Internal Entanglement



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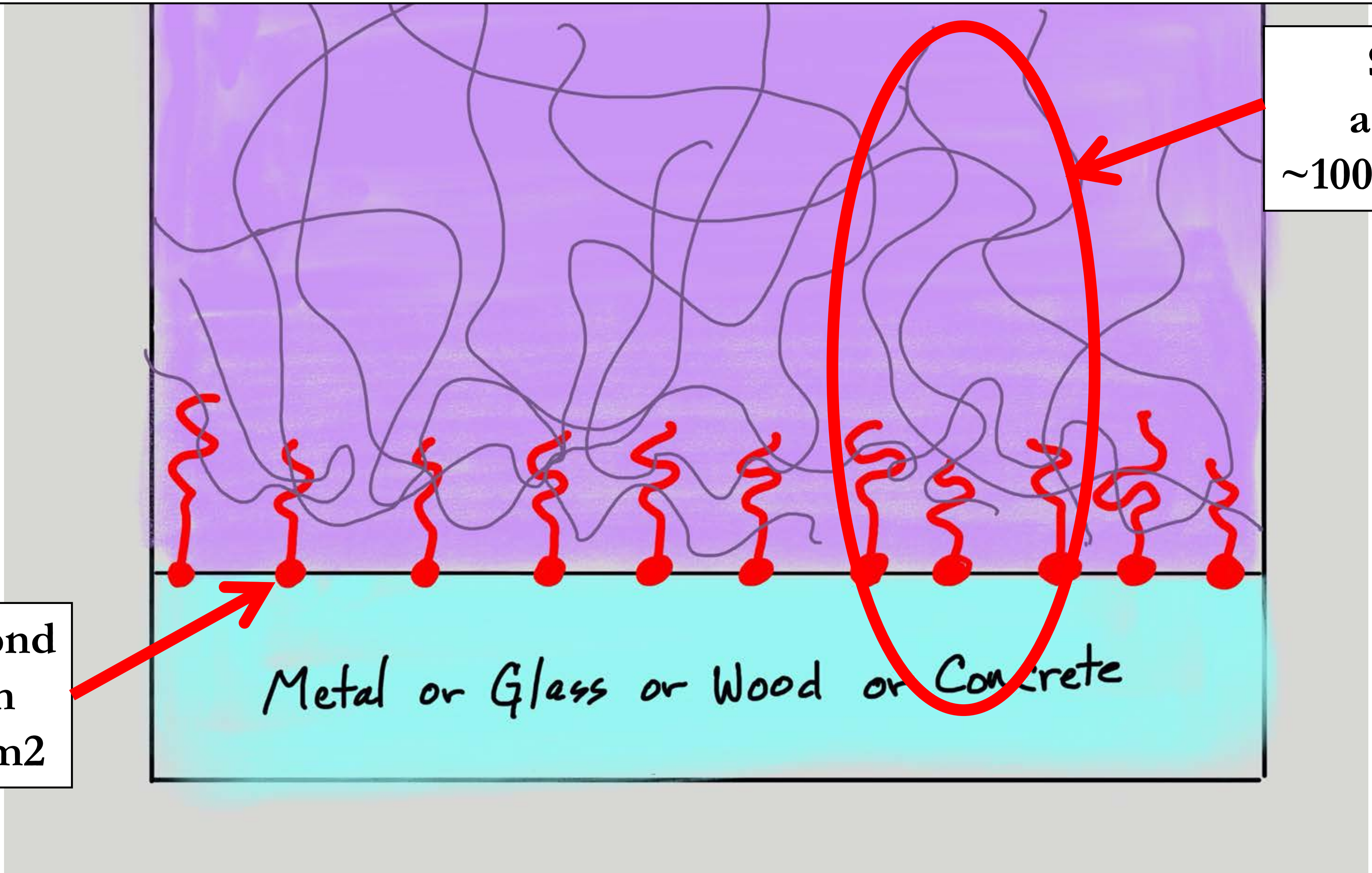
How does all this intermingling and entanglement increase adhesion strength?



System adhesion ~100,000mJ/m2

Surface bond adhesion ~100mJ/m2

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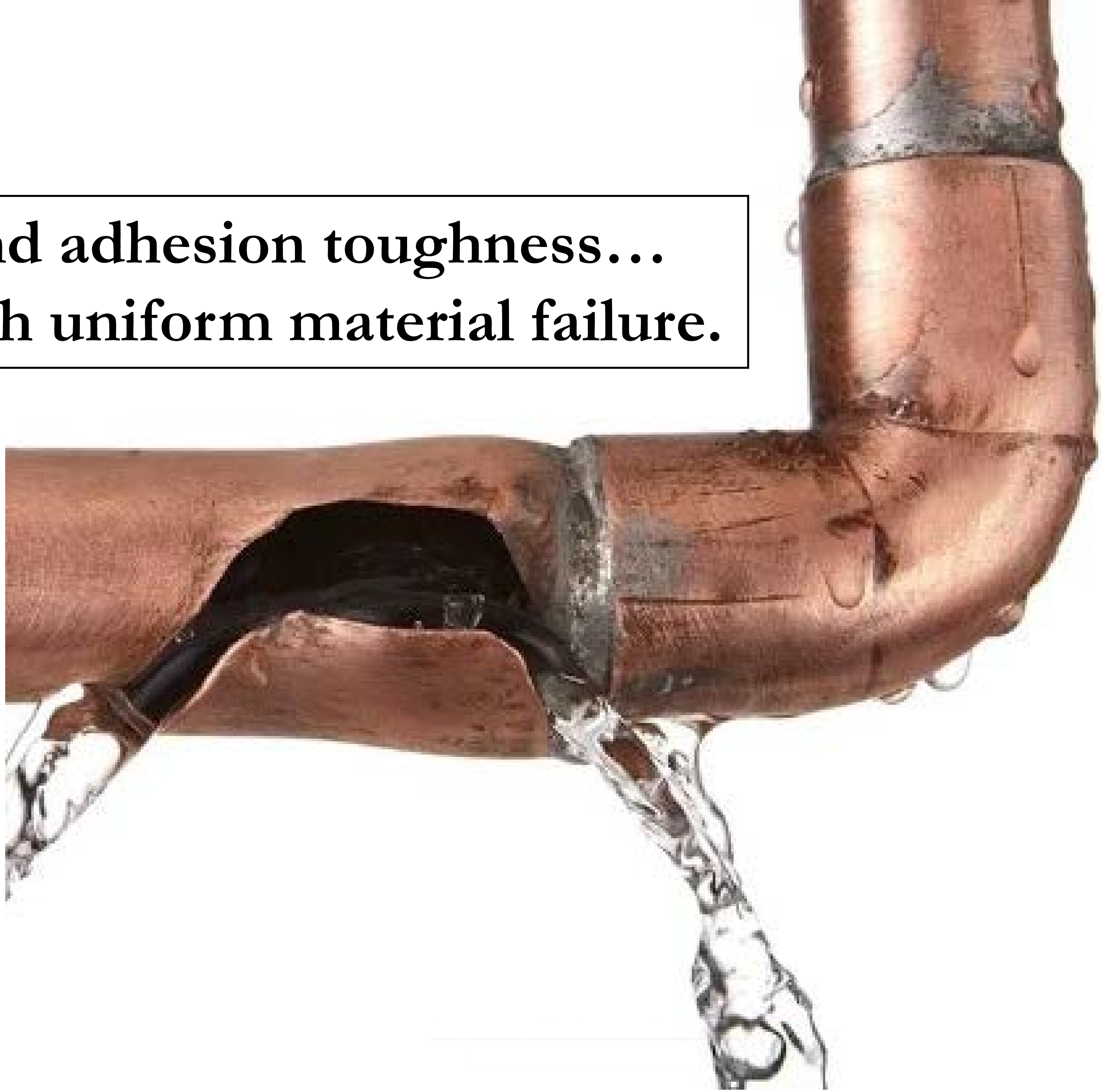
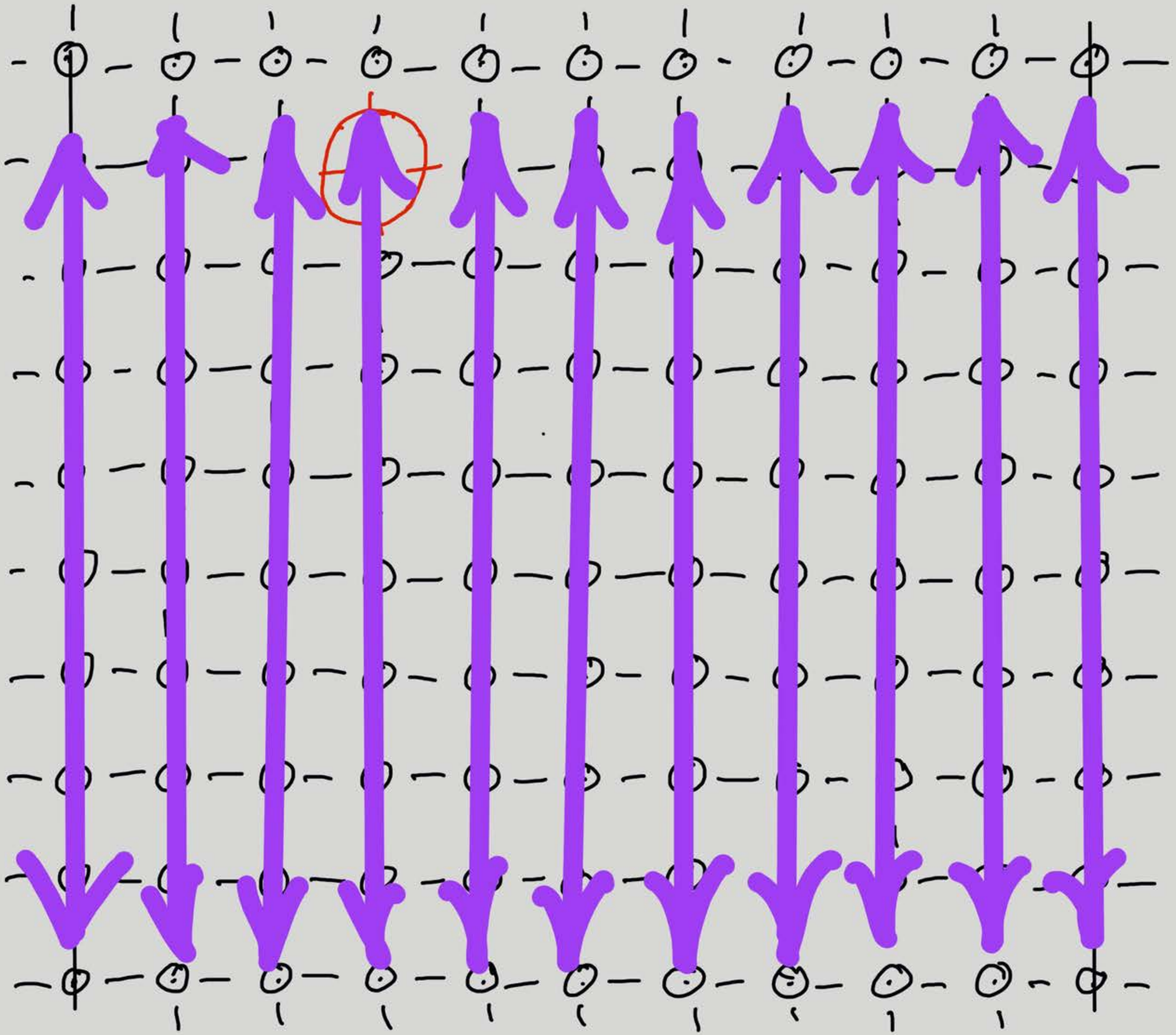
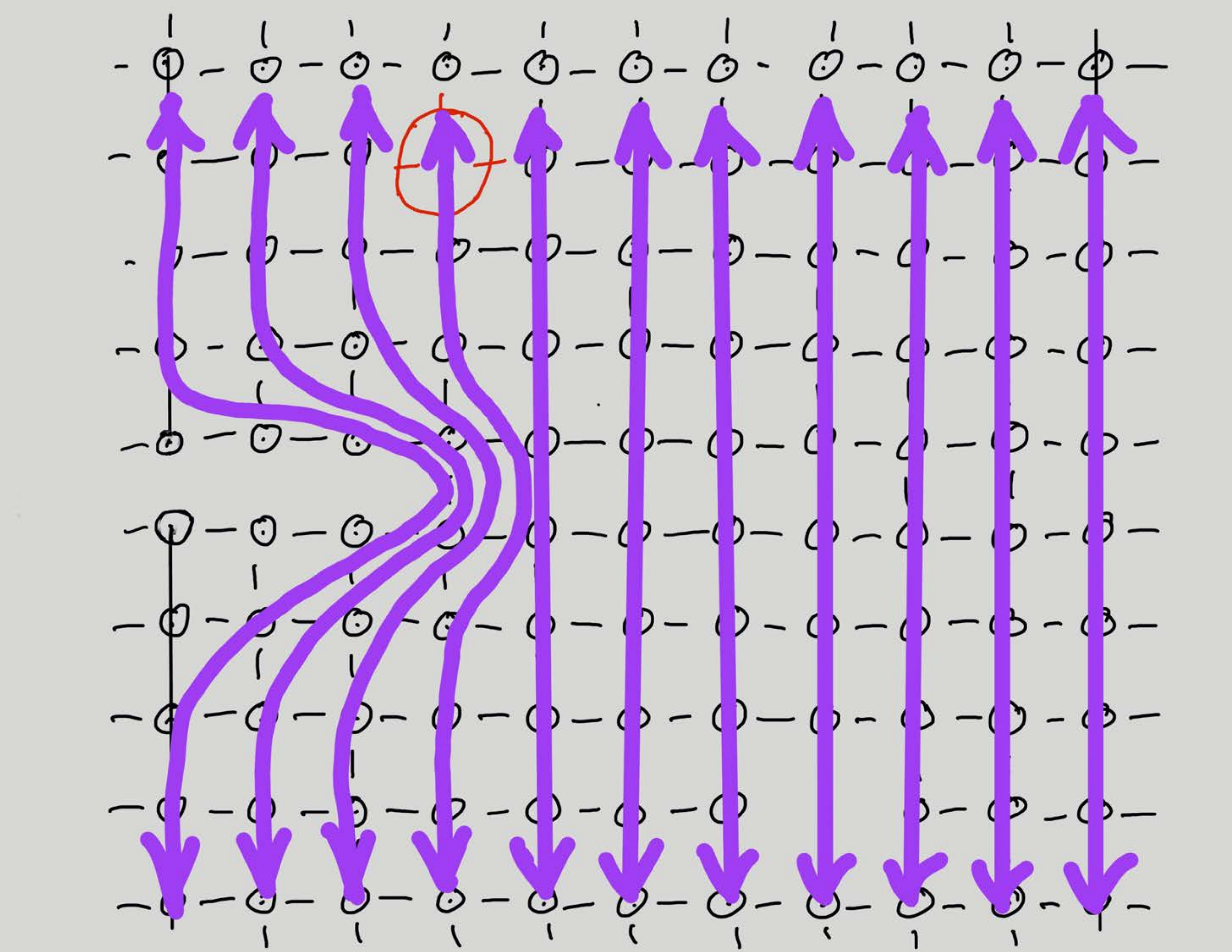
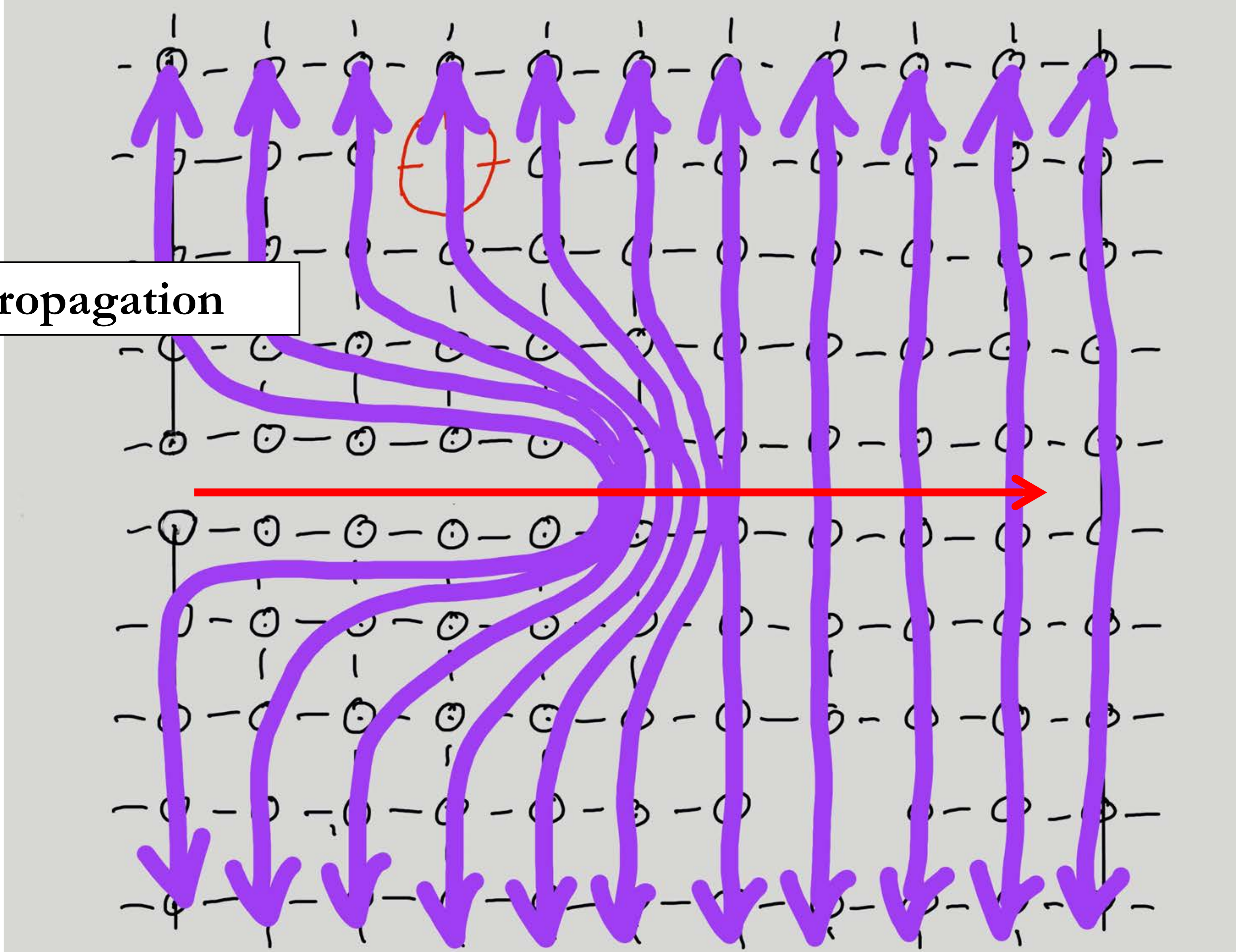
To understand adhesion toughness…
….start with uniform material failure.







Crack Propagation



Adhesion Concept 5

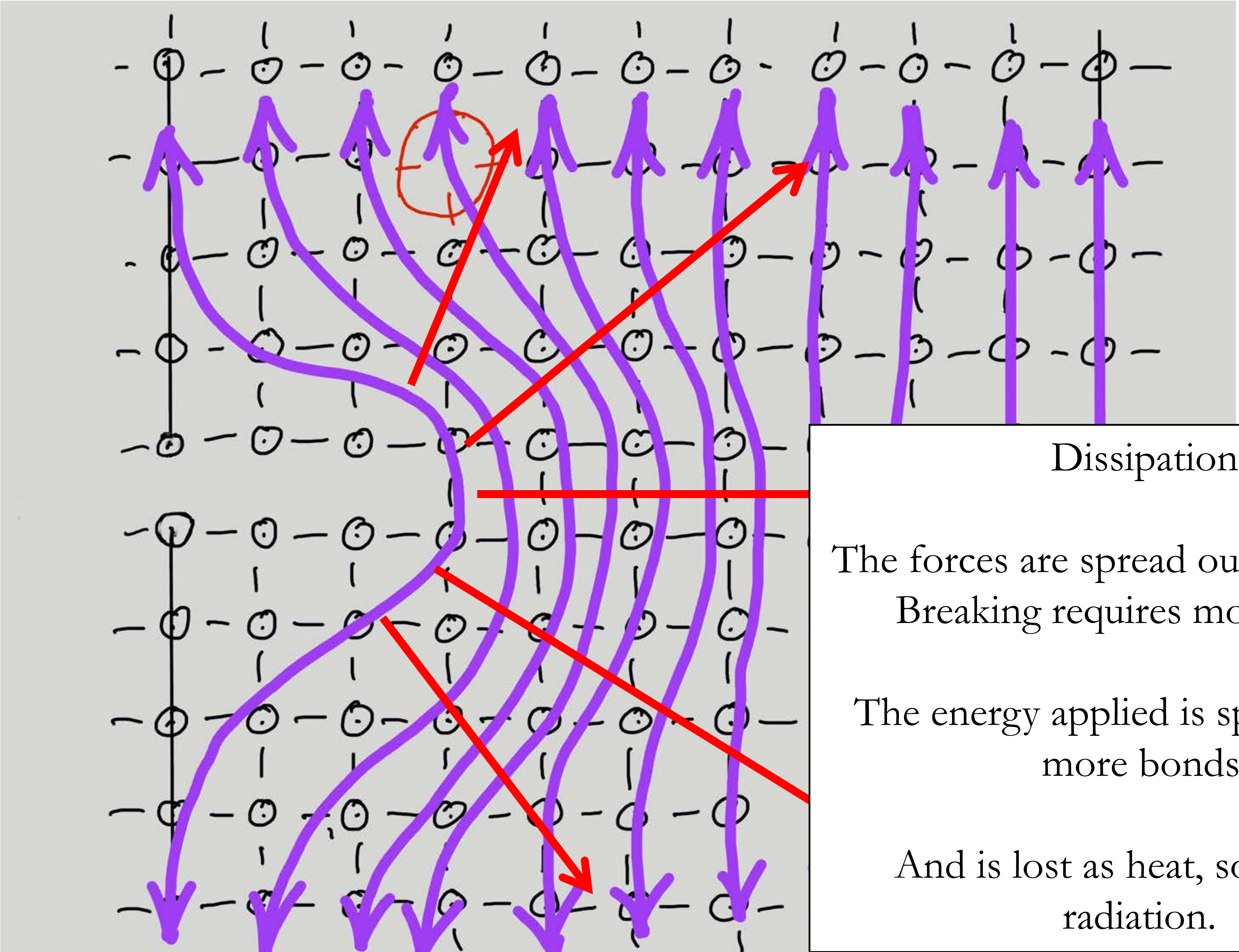
Adhesion failure is always crack propagation.

4: Entanglement creates strong, useful adhesion. (~100x intermingling)

3: Intermingling creates modestly strong adhesion. (~10x surface)

2: Surface bond adhesion is necessary but insufficient. (Weak)

1: Everything is sticky.

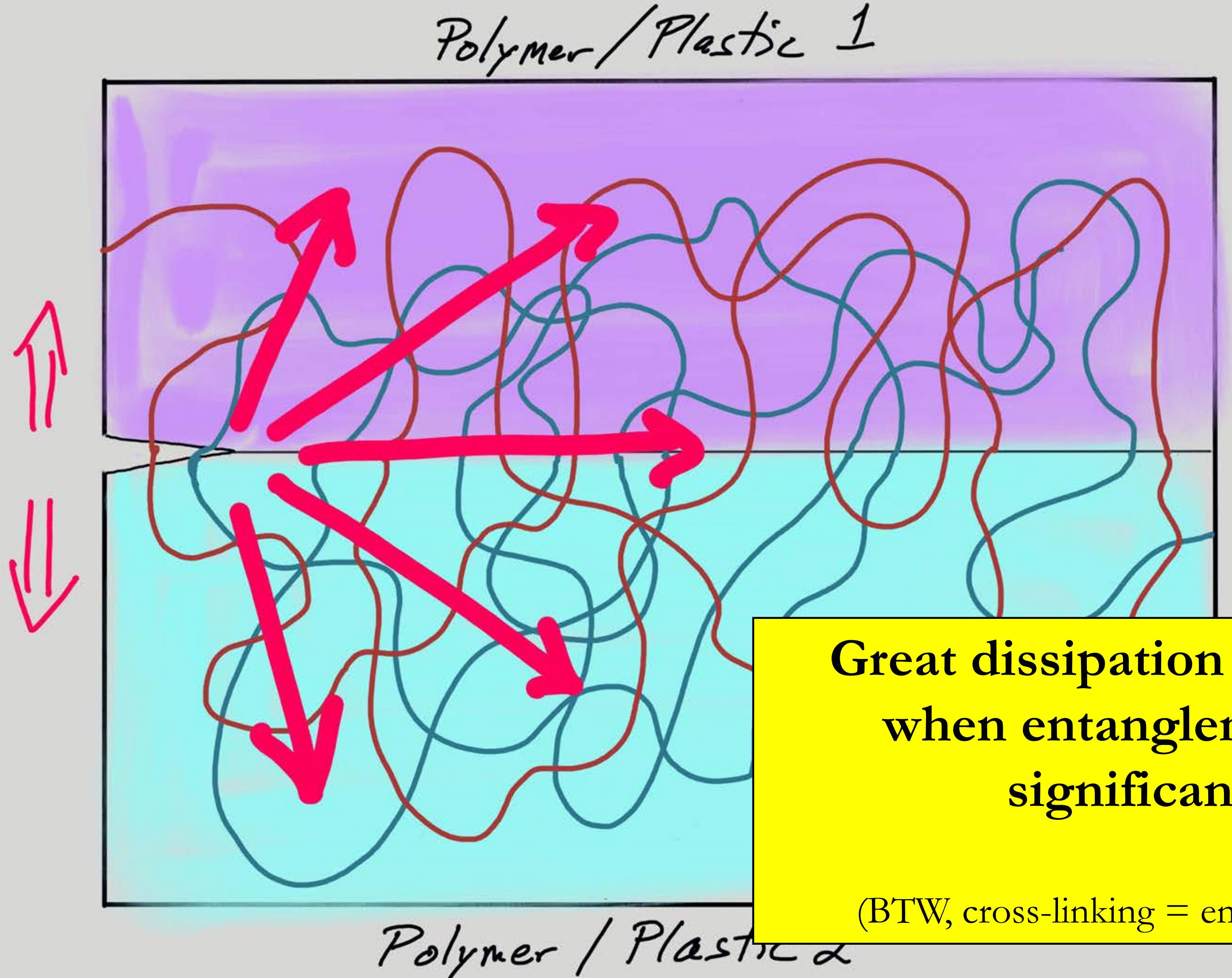


Dissipation

The forces are spread out - dissipated. Breaking requires more energy.

The energy applied is spread across more bonds.

And is lost as heat, sound, and radiation.



Great dissipation of forces when entanglement is significant.

(BTW, cross-linking = entanglement)

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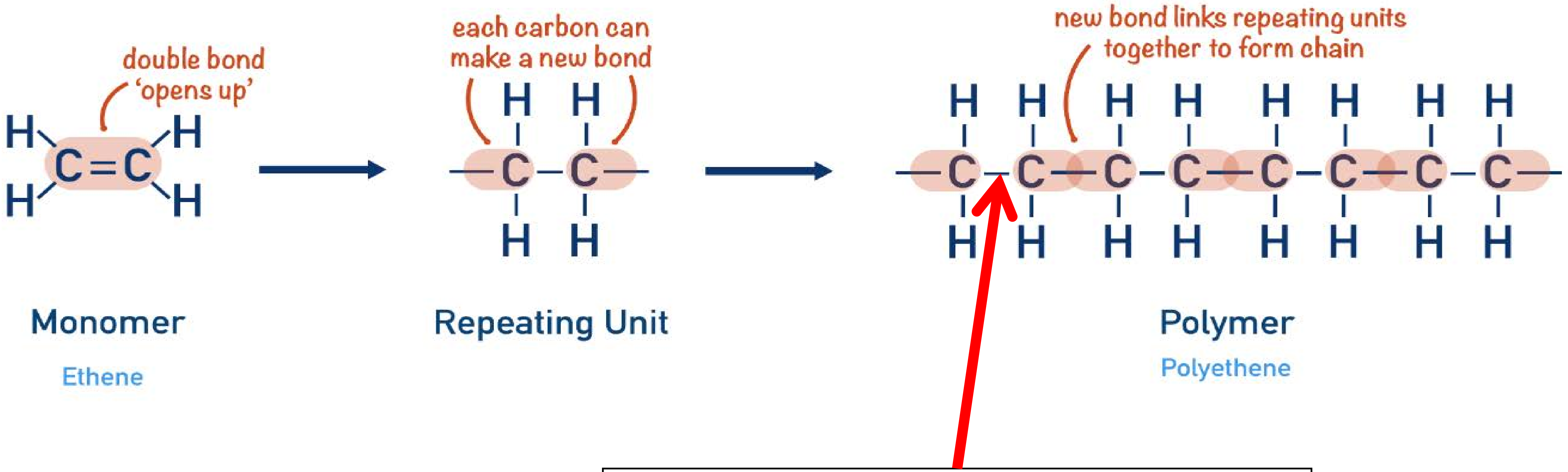
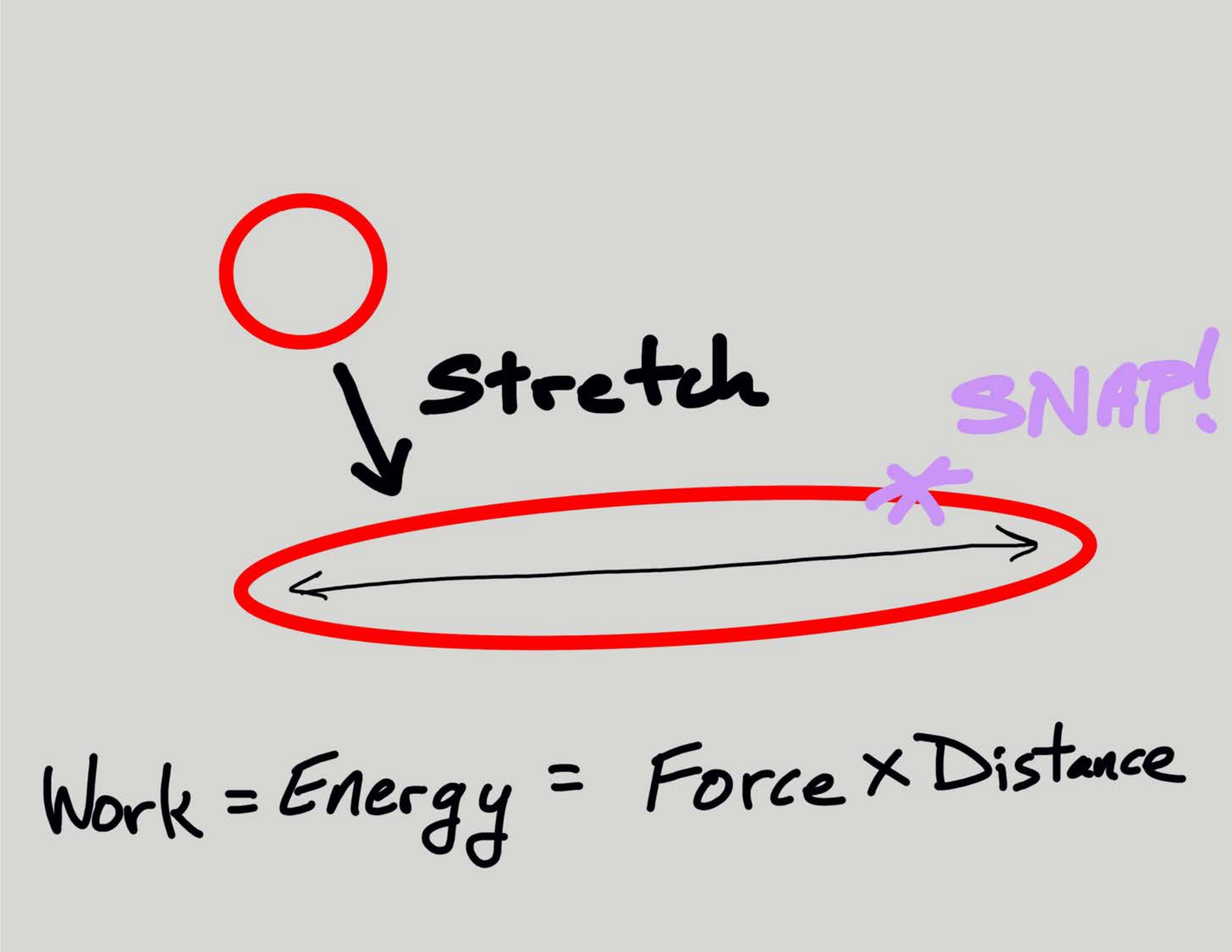
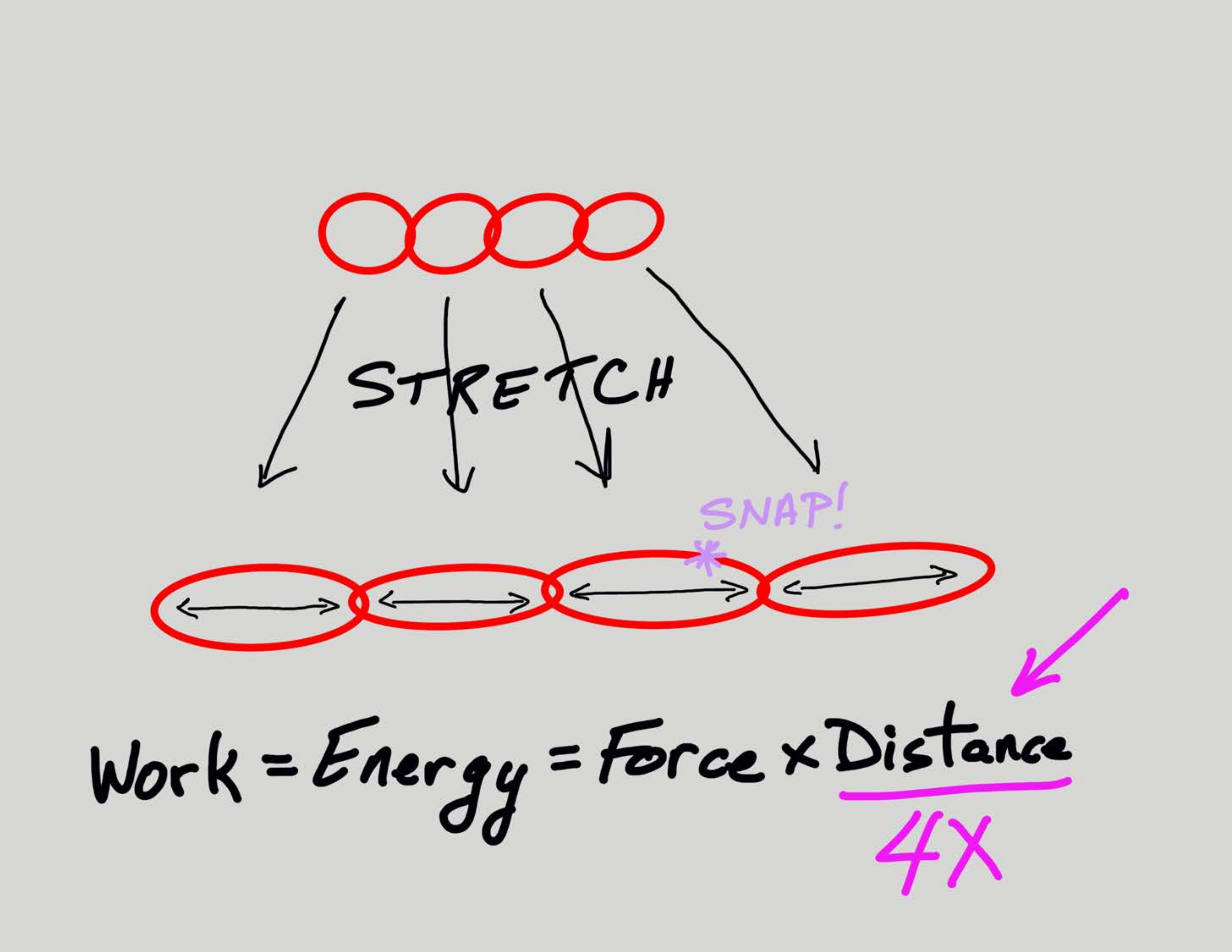
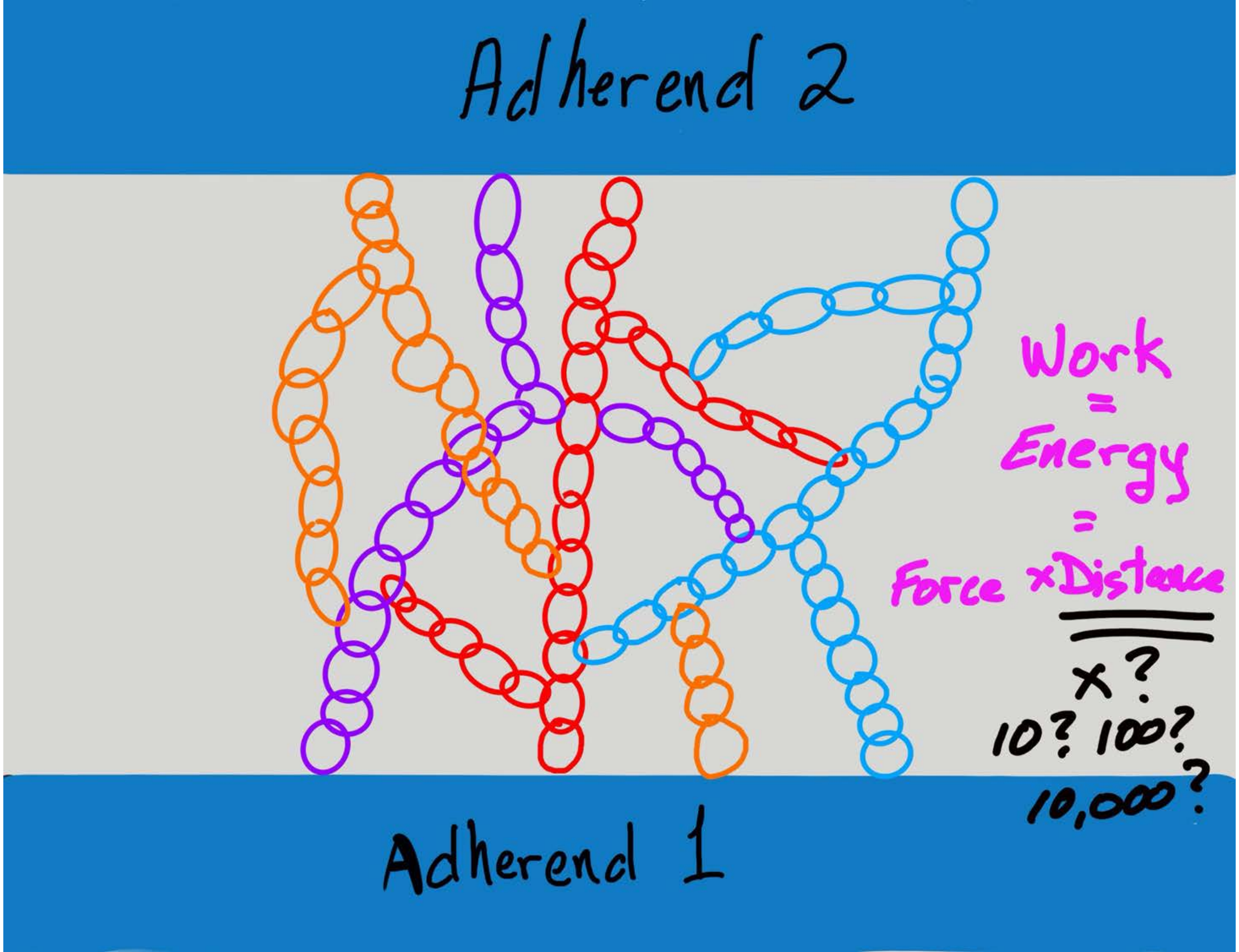


Every bond is like a rubber band.


Stretch
SNAP!
Work = Energy = Force x Distance


STRETCH
SNAP!
Work = Energy = Force × Distance
4X



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Insanely strong in straight pull (butt pull).

Zero intermingling. Zero dissipation.

Easy crack propagation.

Zero useful adhesion.


Non-stick?

Very weak (wet) polymer.
Weak but enough surface bonds.
Great internal entanglement.

GREAT dissipation.
Diminished crack propagation.

Modestly strong adhesion

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Weak polymer.
Weak but enough surface bonds.

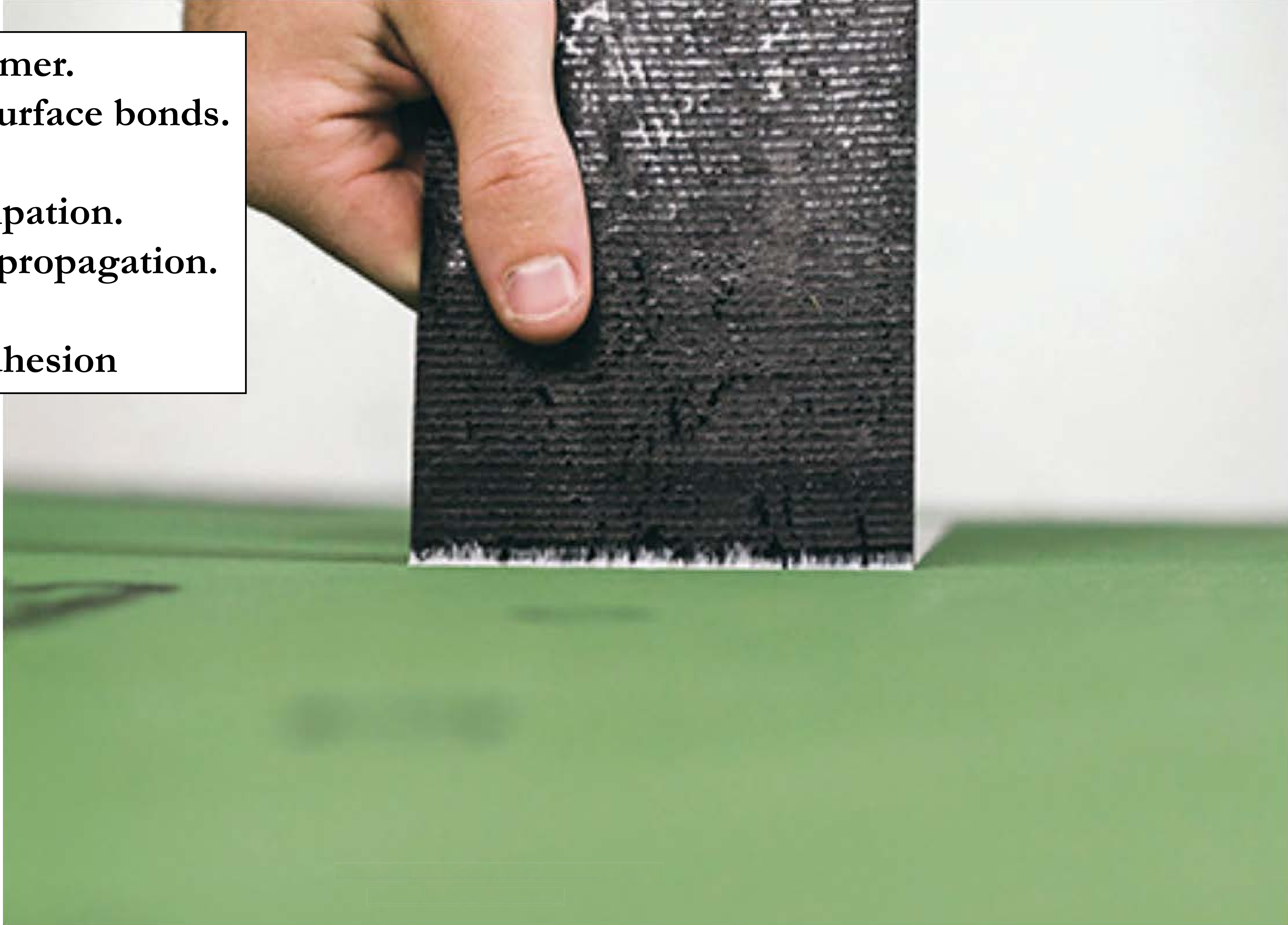
GREAT dissipation.
Diminished crack propagation.

STRONG adhesion

Weak polymer.
Weak but enough surface bonds.

GREAT dissipation.
Diminished crack propagation.

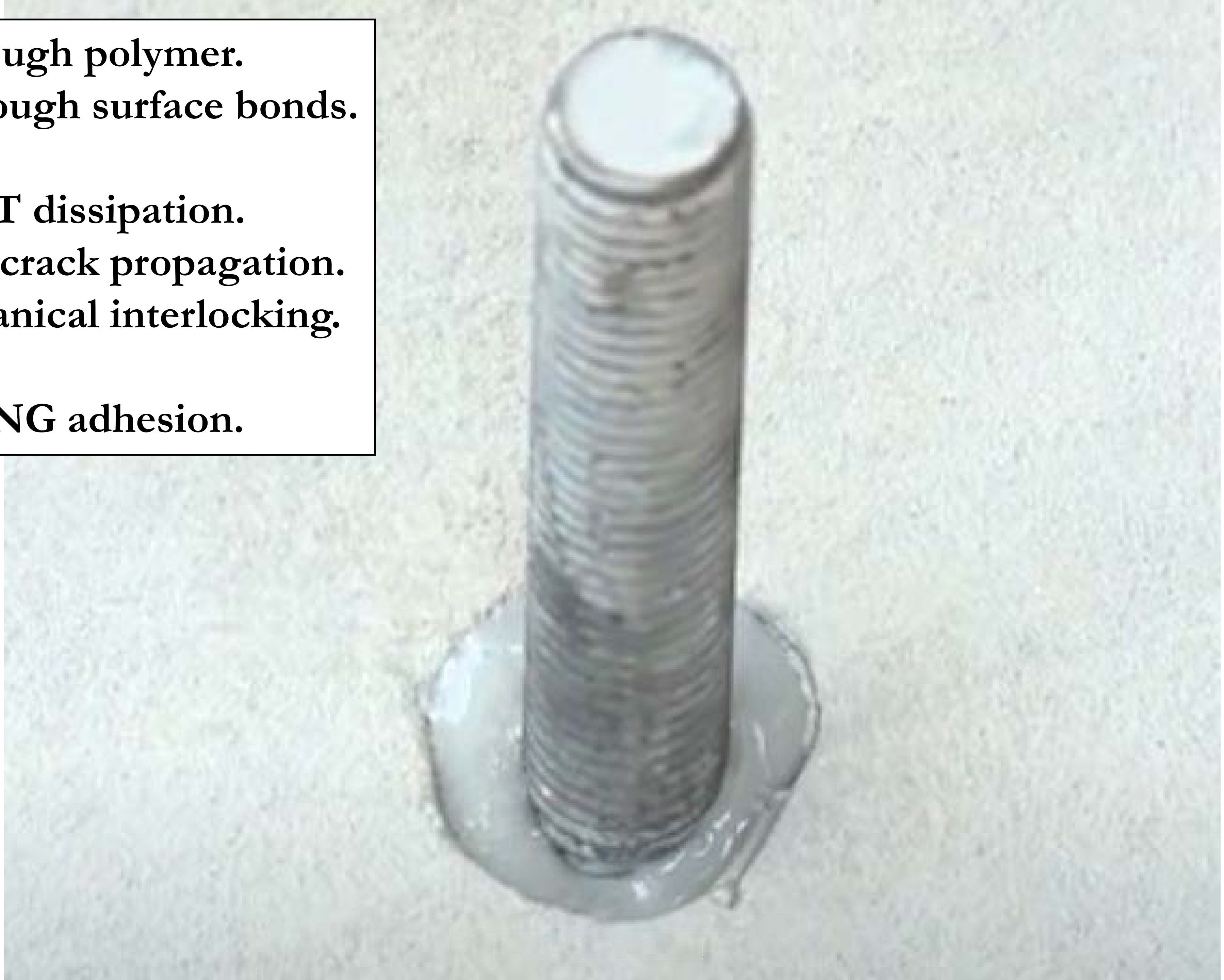
STRONG adhesion



Very tough polymer.
Weak but enough surface bonds.

GREAT dissipation.
Diminished crack propagation.
Some mechanical interlocking.

STRONG adhesion.



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Adhesion Concept 6

Dissipation of forces, promoted by entanglement and intermingling, mitigates crack propagation.

5: Adhesion failure is always crack propagation.

4: Entanglement creates strong, useful adhesion. (~100x intermingling)

3: Intermingling creates modestly strong adhesion. (~10x surface)

2: Surface bond adhesion is necessary but insufficient. (Weak)

1: Everything is sticky.

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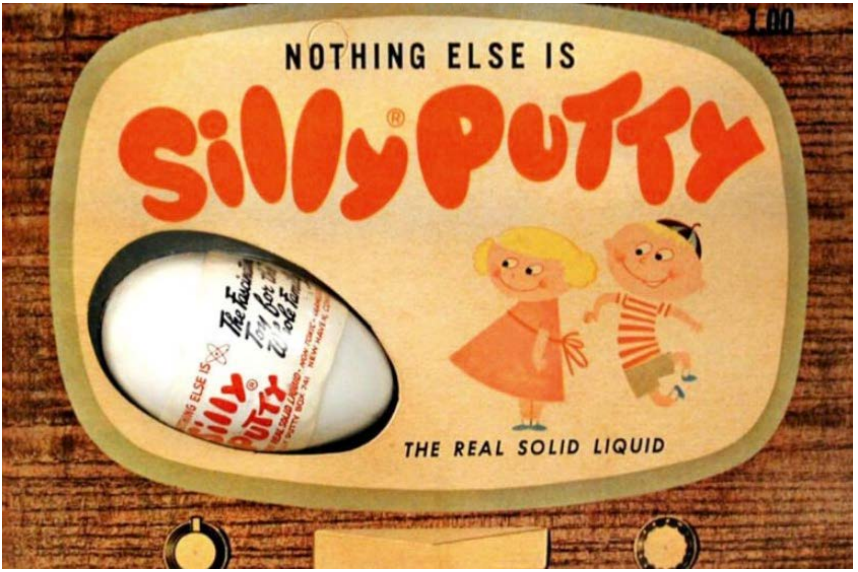


Infinite chemical combinations.

Infinite mixture ratios.

Infinite variety of physical properties.

Infinite variety of adherends.

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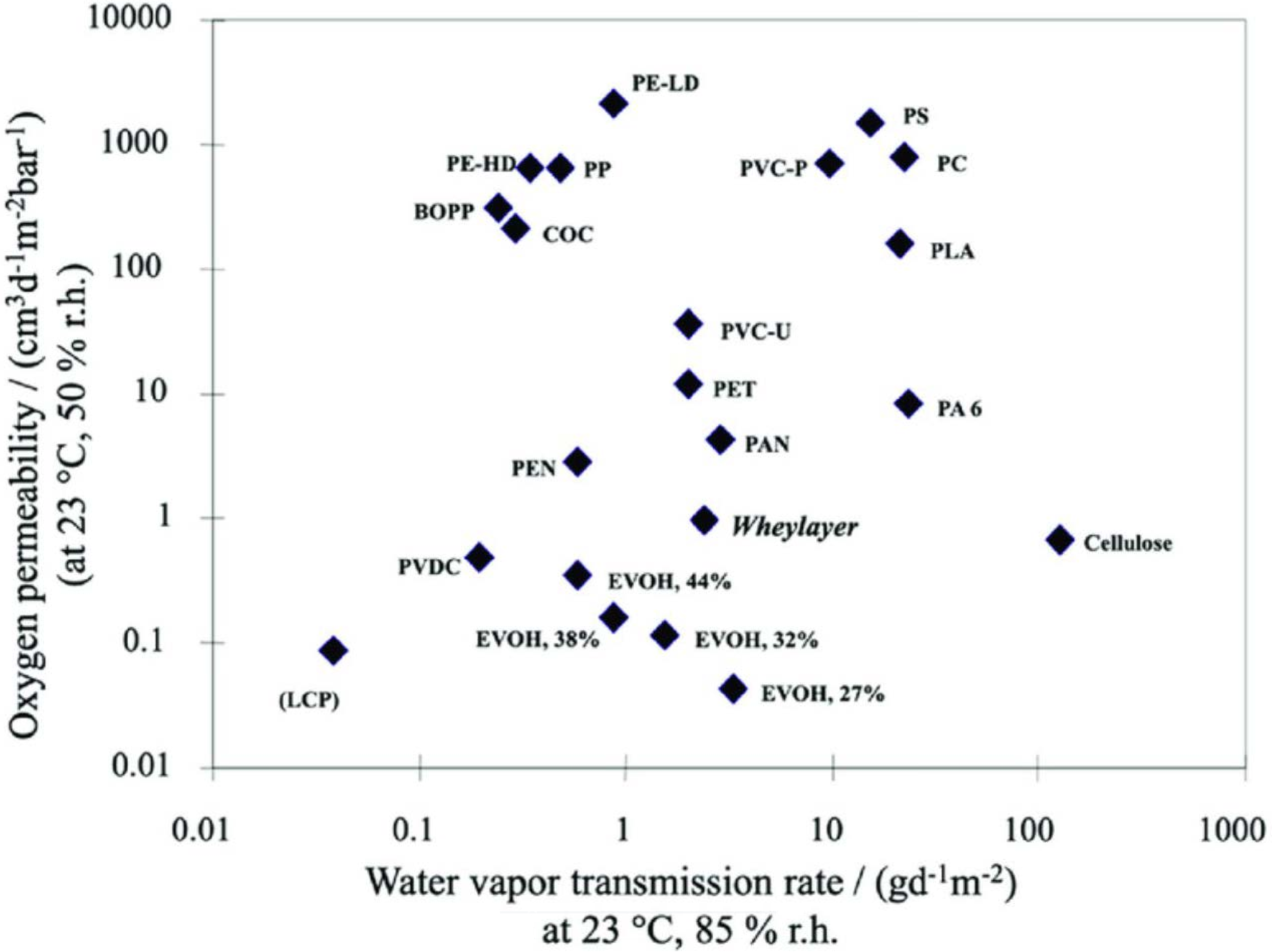
Time is also a factor.

Same as temperature.

Fast = brittle
Slow = relaxed (not brittle)

Cold = brittle
Hot = relaxed



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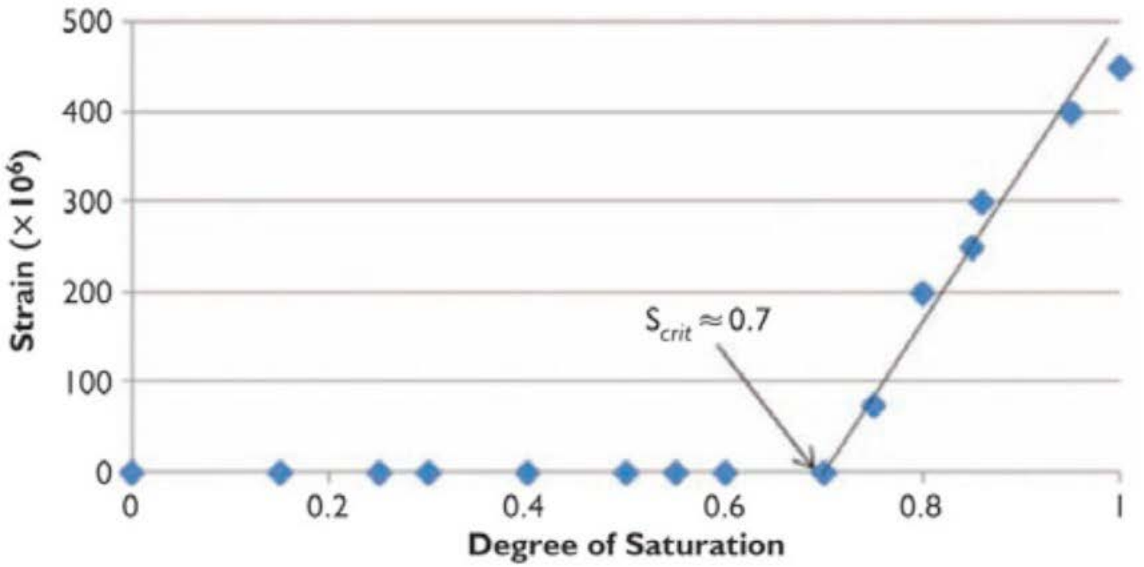
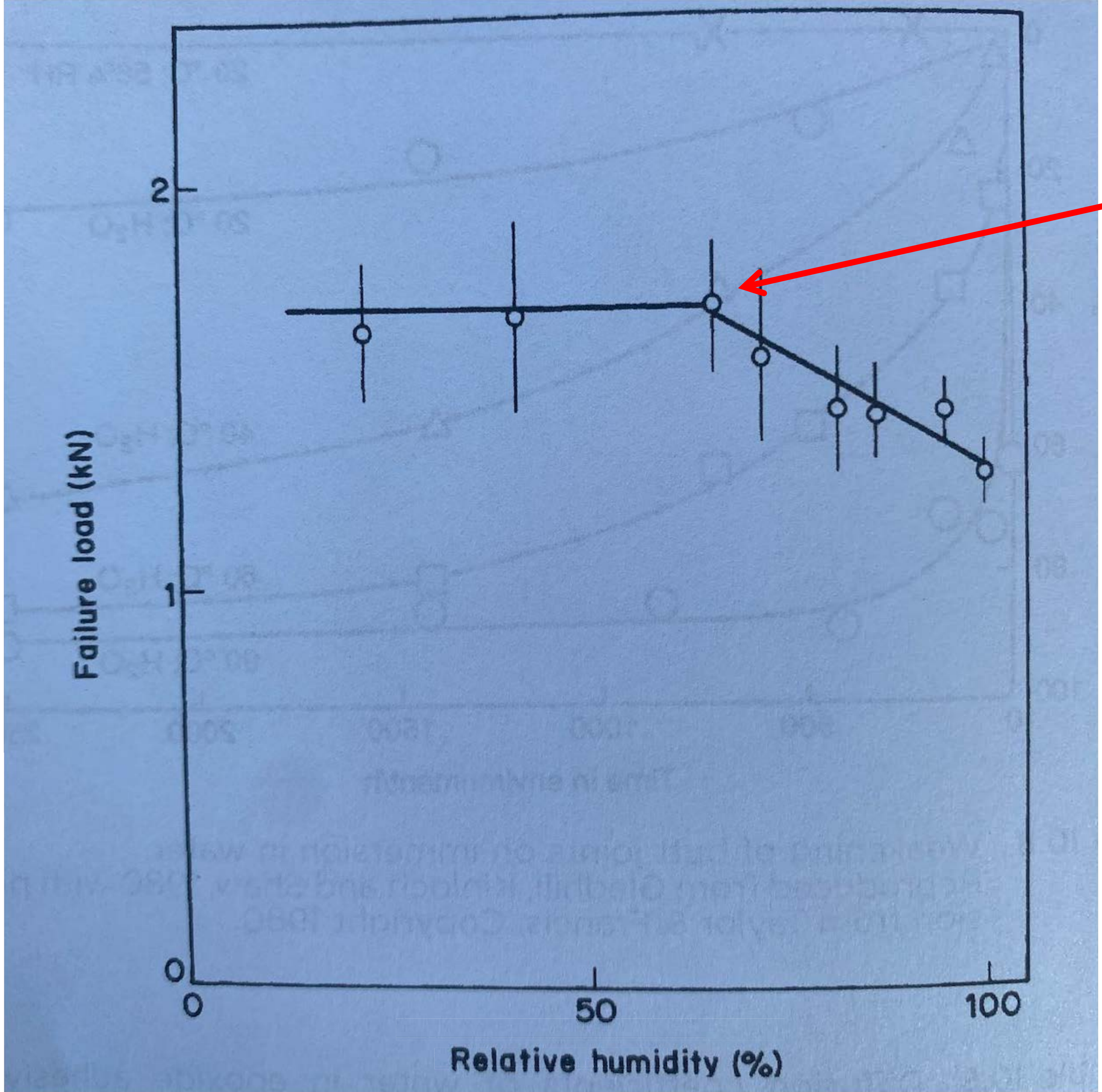
BSI-047 Thick As A Brick

By Dr. Joseph Lstiburek



From Mensinga, P. 2009. “Determining the Critical Degree of Saturation of Brick Using Frost Dilatometry.” Master of Applied Science in Civil Engineering Thesis, University of Waterloo, Waterloo, ON, Canada.



RH_{Acrit} ?

~ 60%

Brewis, Comyn, Raval, Kinlock, 1990

Adhesion Concept 7

The quality of force dissipation is a function of the chemical and mechanical characteristics of the system's materials, AND temperature, AND speed of force application.

Adhesion Concept 6

Dissipation of forces, promoted by entanglement and intermingling, prevents crack propagation.

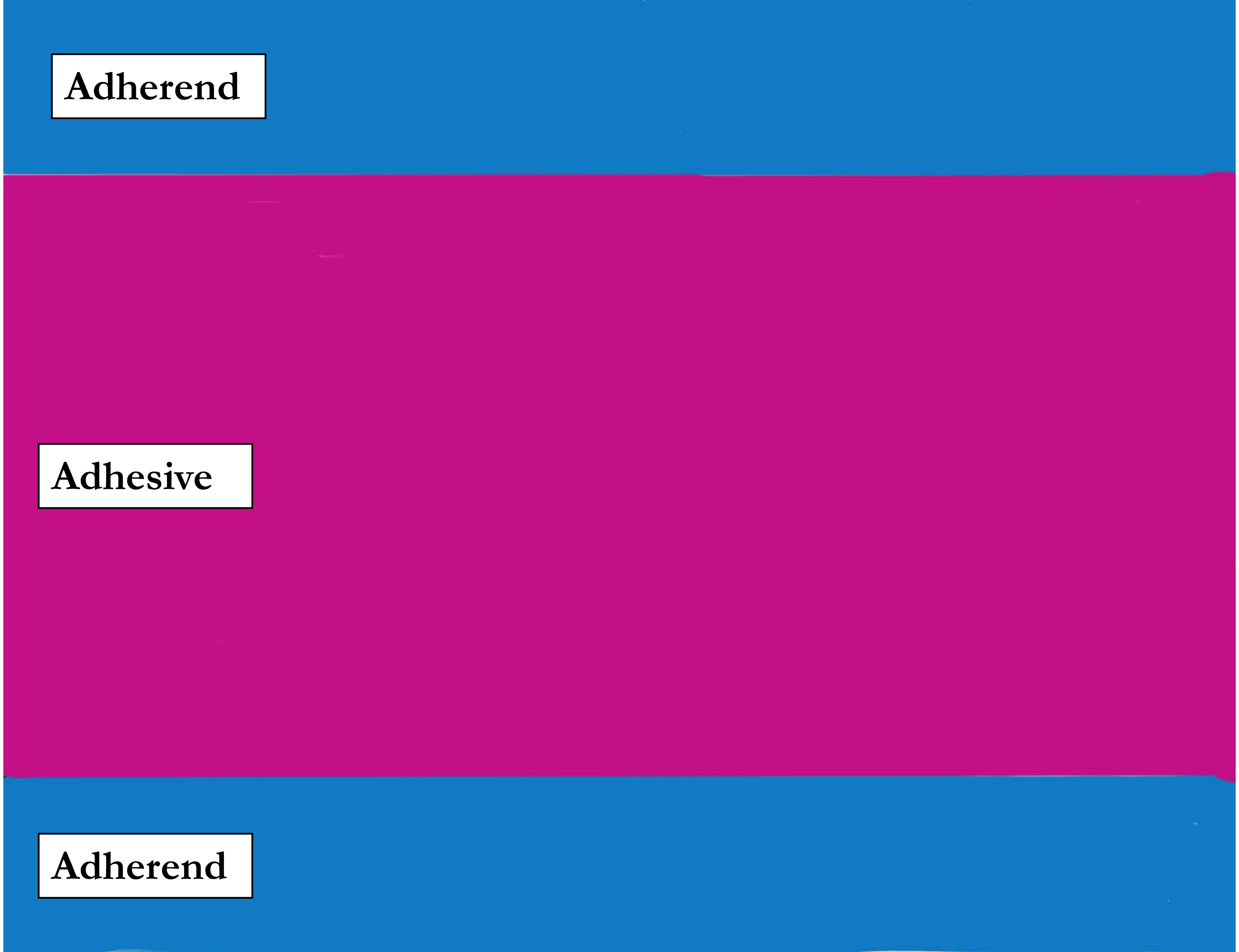
5: Adhesion failure is always crack propagation.

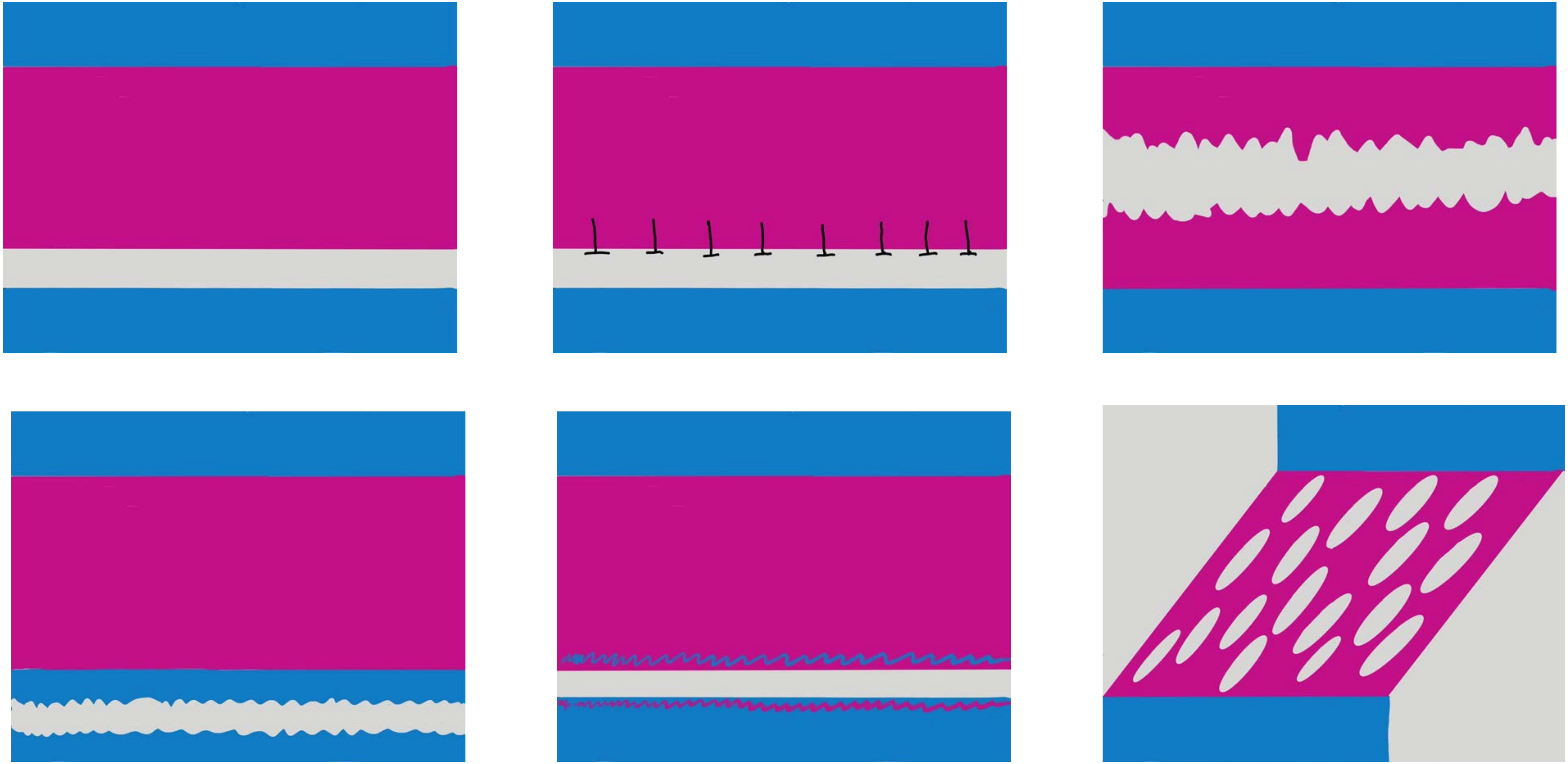
4: Entanglement creates strong, useful adhesion. (~100x intermingling)

3: Intermingling creates modestly strong adhesion. (~10x surface)

2: Surface energy adhesion is necessary but insufficient. (Weak)

1: Everything can bond to everything.


Adherend
Adhesive
Adherend



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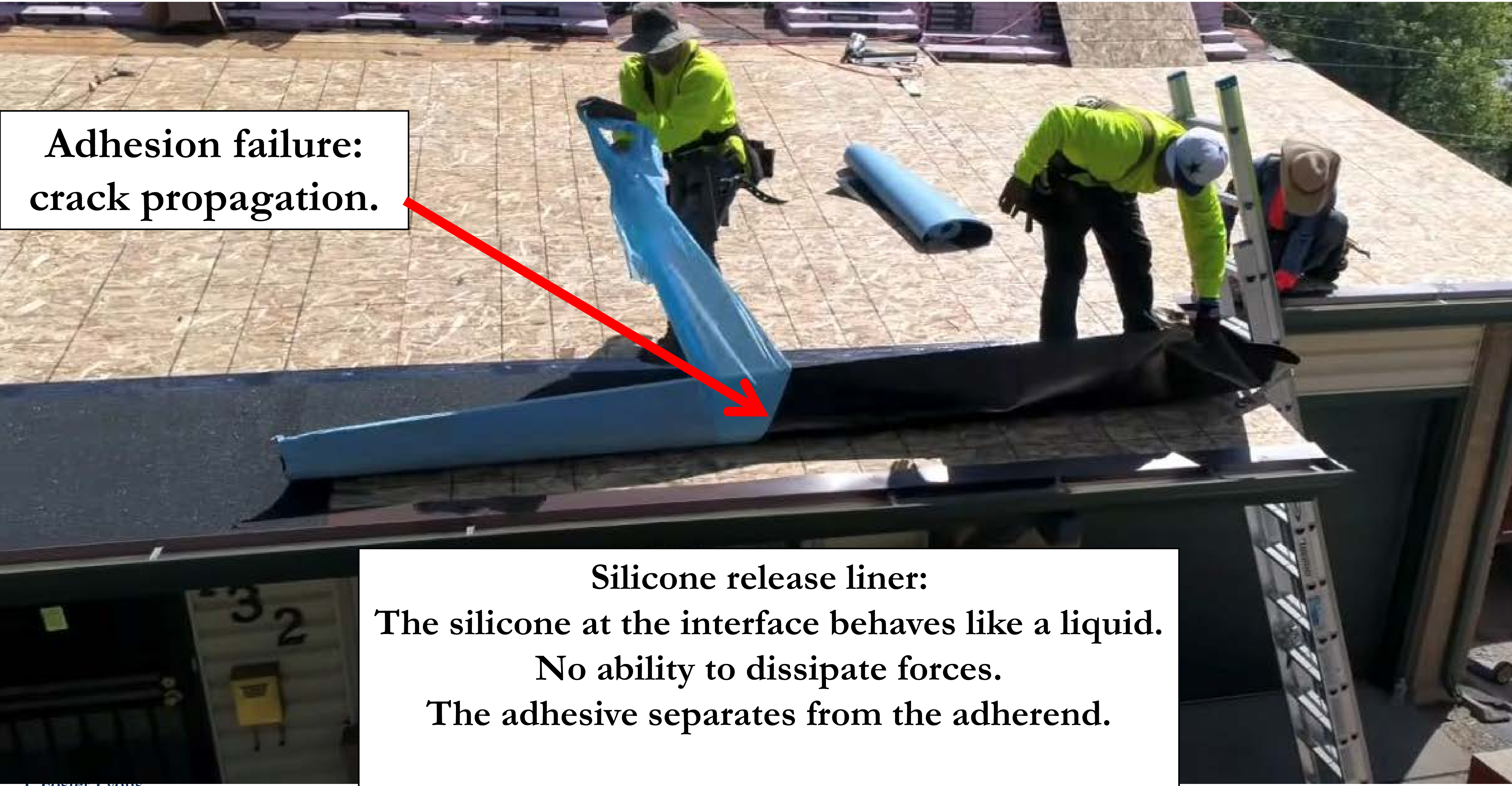
August 5, 2024. Westford, MA
www.FosterLyons.com



Adhesion failure: crack propagation.

Silicone release liner:

The silicone at the interface behaves like a liquid.

No ability to dissipate forces.

The adhesive separates from the adherend.

(BTW, Teflon is useless as release liner.)

Adhesion failure:

Very little **surface bond adhesion**
No **intermingling**
No **entanglement**

The surface is crystalline, not fuzzy.
Also, not smooth = easy to start a crack.

Zero dissipation.
Cracks propagate easily.
Separation at the interface.

Adhesion:

Surface bond adhesion only.

Aluminum on glass.

Failure:

Water diffuses along the interface, and "bumps" the aluminum off the glass.

Permittivity !

A relative measure of chemical polarity

Conjugated polymers	100,000
Barium titanate	1,200
Titanium dioxide	129.5
Water	80
Hydrogen peroxide	60
Ceramic (MgTa2O6)	28
Ethanol	24.3
Ammonia	16.5
Acetone	17.7
Silicon	11.5
Marble	8
Diamond	7
Glass	6.85
Neoprene	6.7
Concrete	4.5
Bakelite	4.2
Plexiglas (PMMA)	3.2
Rubber	3
Teflon (PTFE)	2.1
Air (Dry)	1.0005
Vacuum	1

Easy to polarize

Hard to polarize

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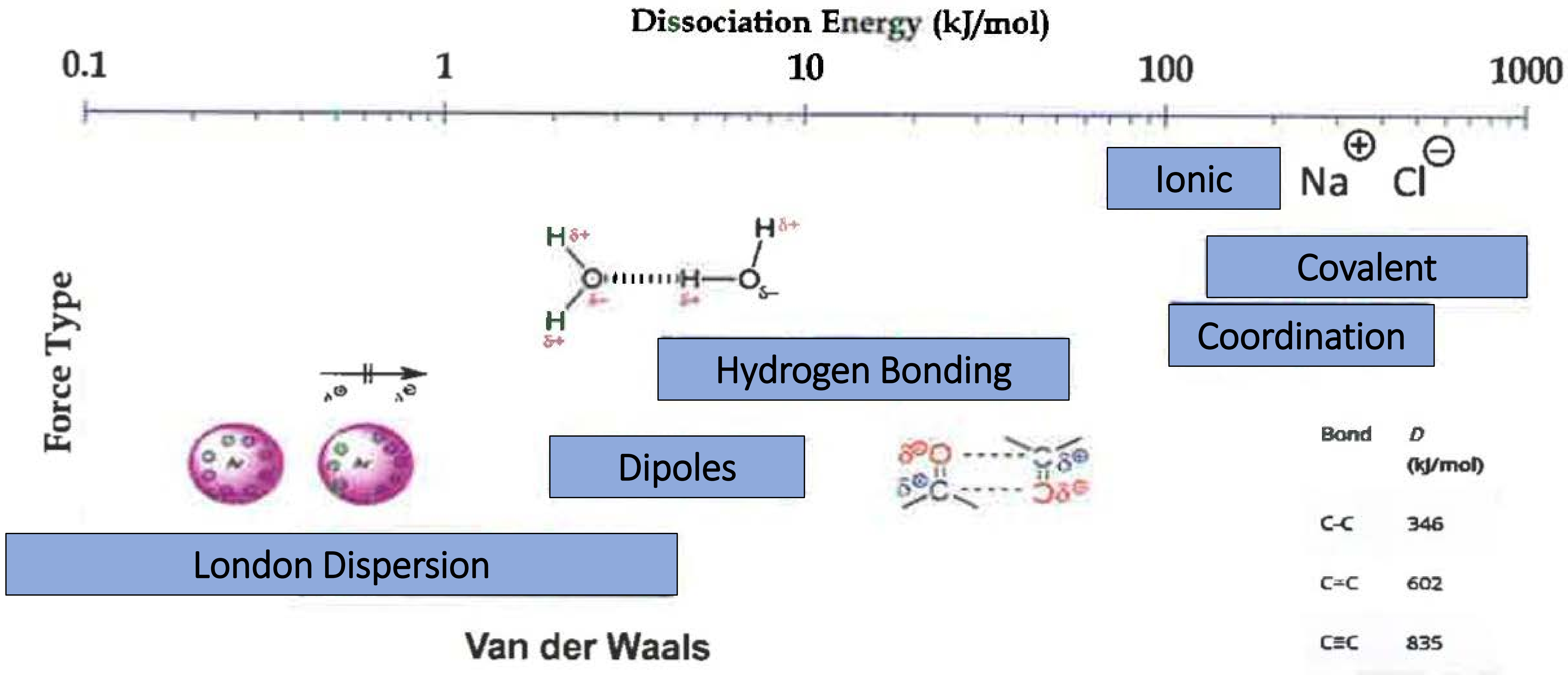
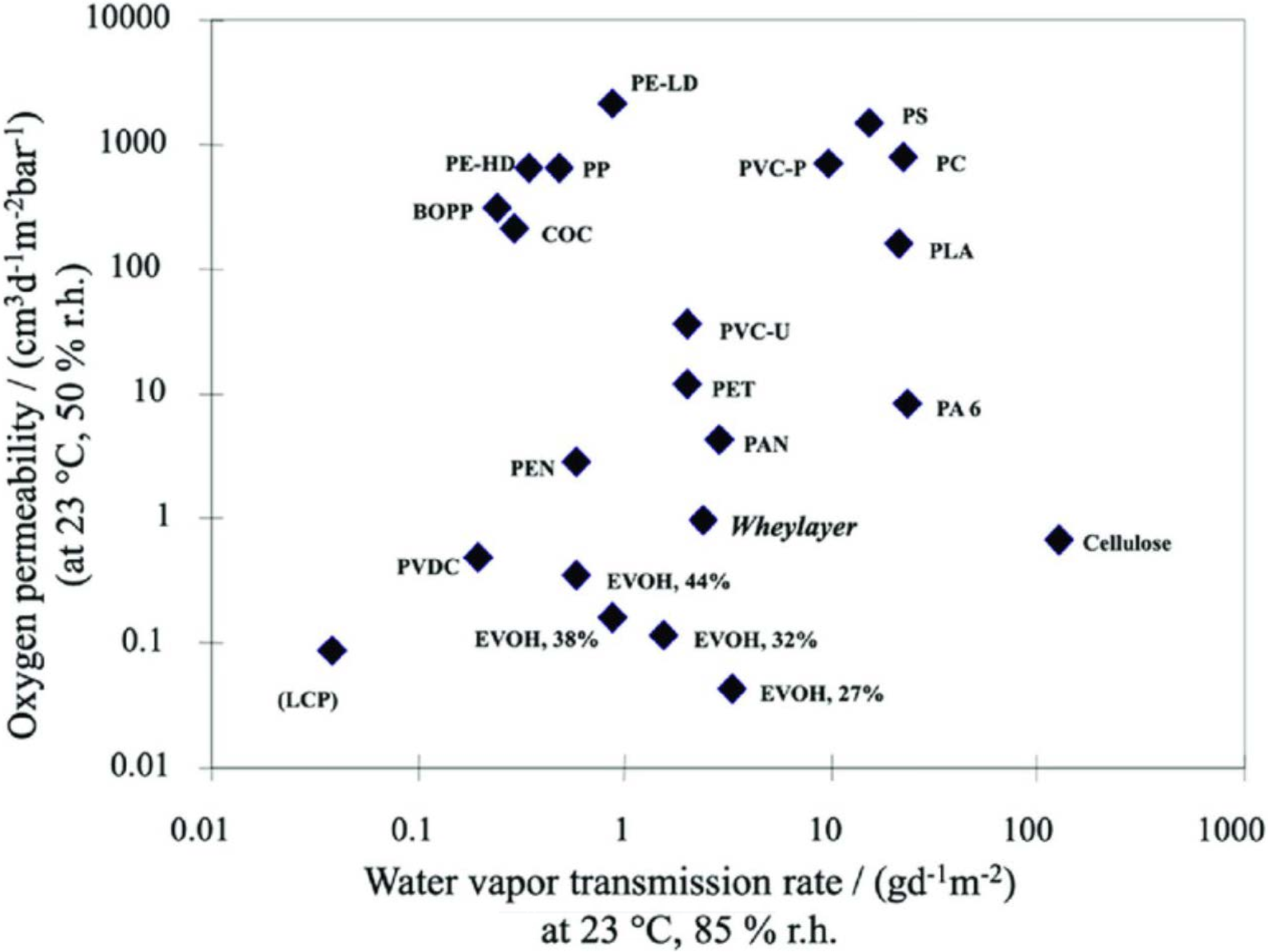

Dissociation Energy (kJ/mol)
0.1
1
10
100
1000
Ionic
Na
Cl
Covalent
Coordination
Hydrogen Bonding
Dipoles
London Dispersion
Force Type
Van der Waals
Bond
D (kJ/mol)
C-C 346
C=C 602
C≡C 835



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Adhesion:

Typical, weak surface bond adhesion

+

not much intermingling

+

very little entanglement across interface

Not failure but, almost.

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Failure! without a significant force.

Adhesive material still on the concrete.

Not a loss of surface adhesion.

Loss of structure within the adhesive. But, near the interface.

Maybe:

- Re-emulsification
- Polymer breakdown

2 adhesives:

stiff, inorganic polymer

flexible, organic polymer

Failure at the interface (mostly).

Likely:

Surface bonds lost

Possible:

Simple crack propagation (shrink)

Polymer breakdown

(loss of dissipation ability)

Polymer cross-linking increase

(loss of dissipation ability)

J. Foster Ly
Westford, MA
Lyons.com

No adhesive (paint) on the concrete.

Surface bond adhesion failure.

It breaks off in large chunks because the entangled polymer is still functional (mostly) but brittle.

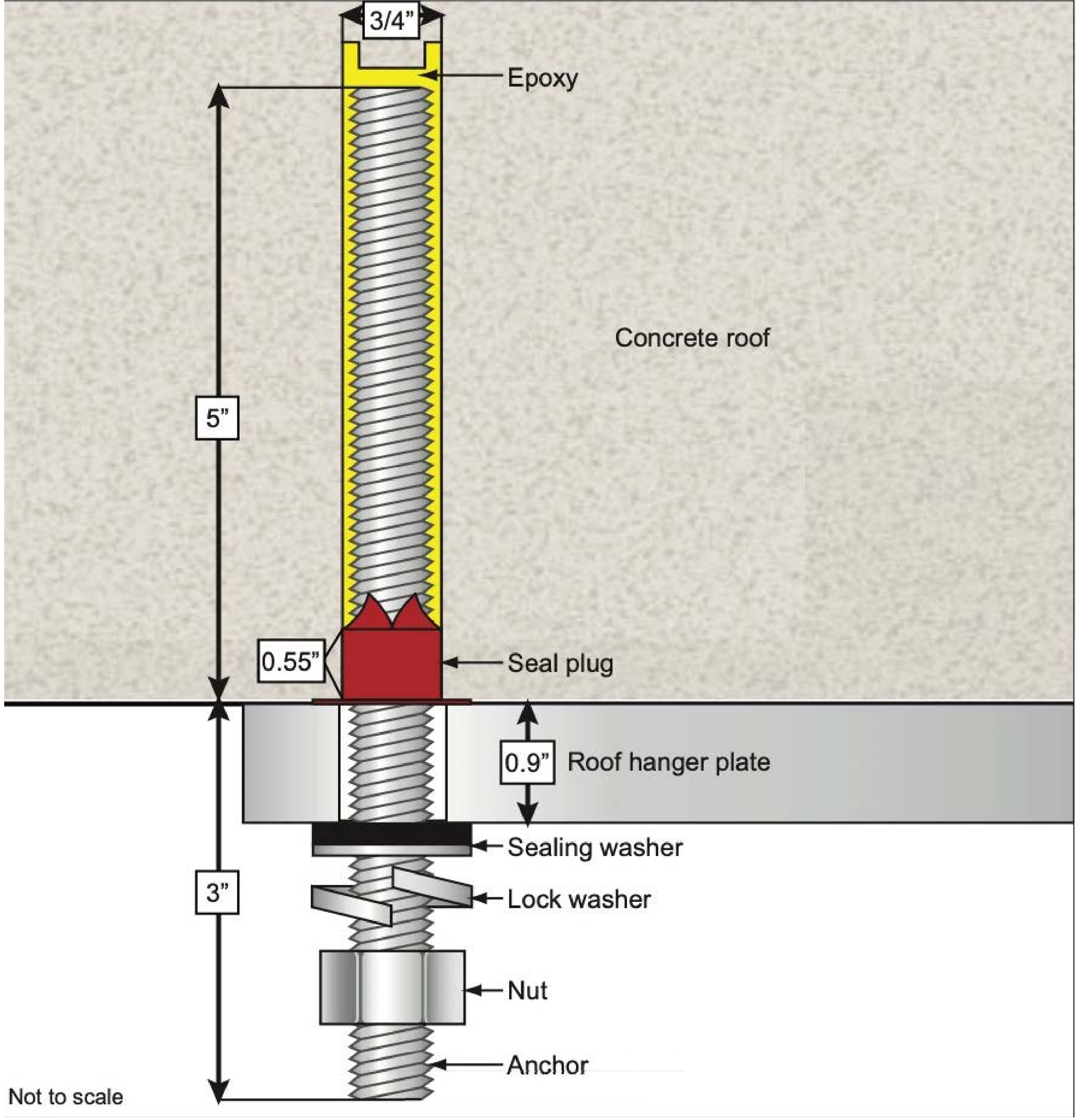
Vapor pressure doesn't "push" the paint off.
Individual water molecules replace the bonded paint molecules.
Water vapor then fills the space between adherend and paint.
The bubble increases the forces at the crack.

Same.
But thicker,
flexible paint.

Boston Tunnel Ceiling Collapse 2006

Anchor bolt adhesive failure.

Original adhesive cost: $1,287.60
Repair: $54,000,000.00



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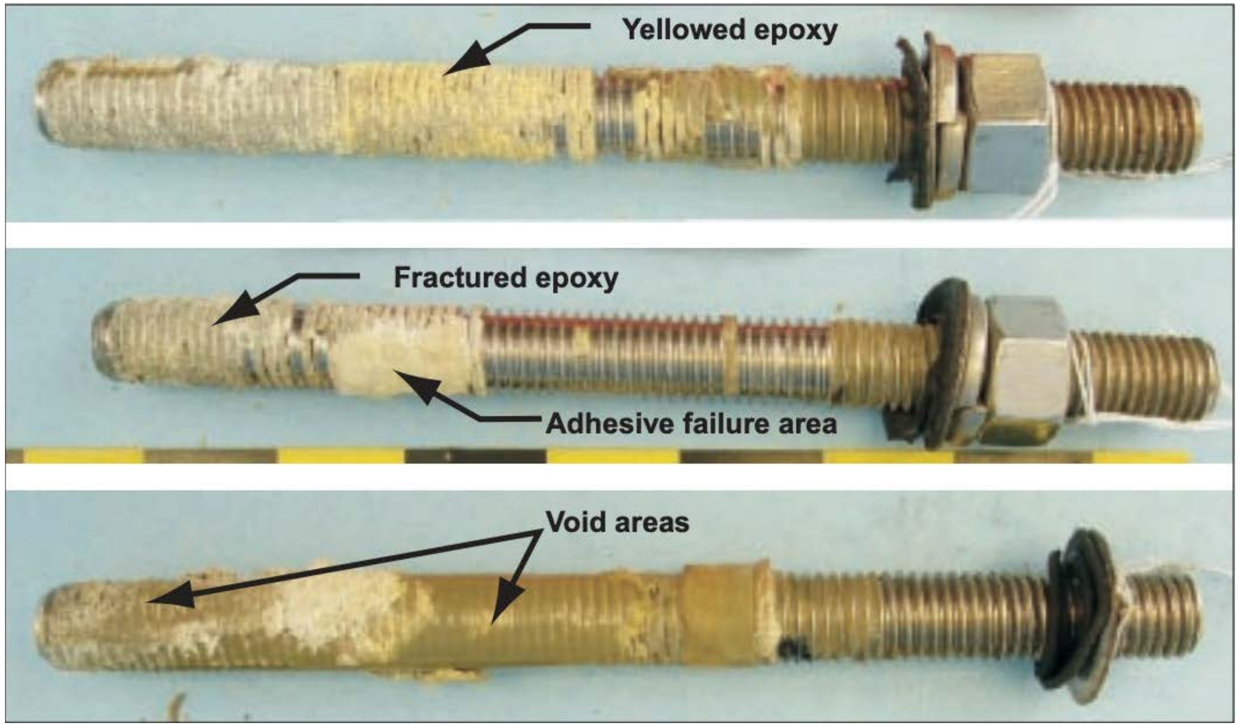

Bad material rheology. Mostly.

Not enough entanglement (cross links).

Short term load: pass
Long term load: fail

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Thank you for your time!

Questions?