Mechanical and Rheological Properties

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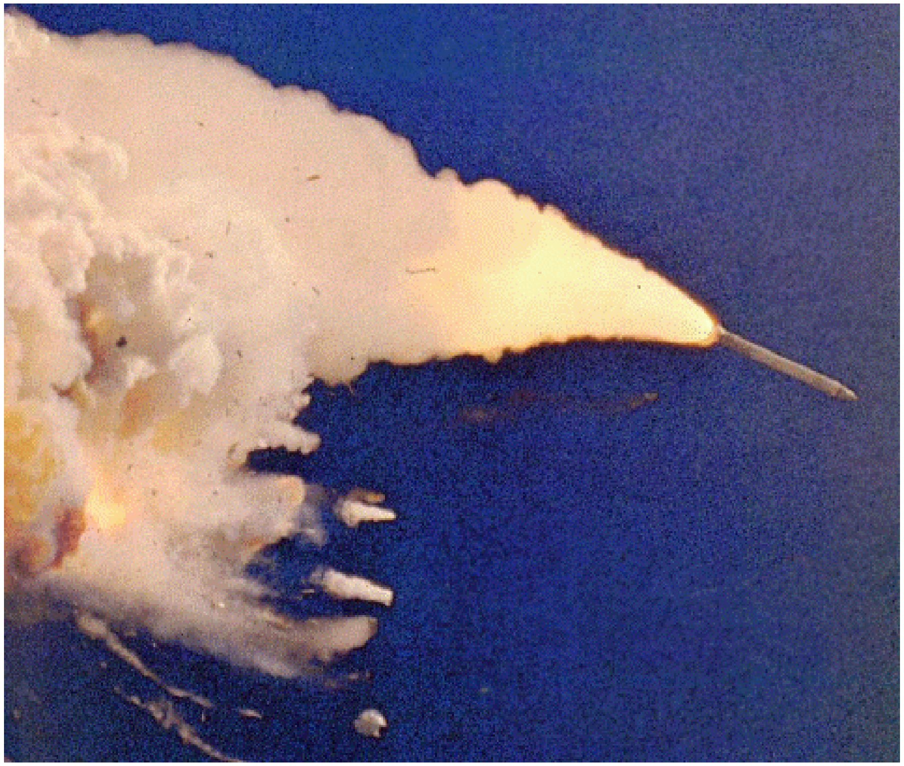
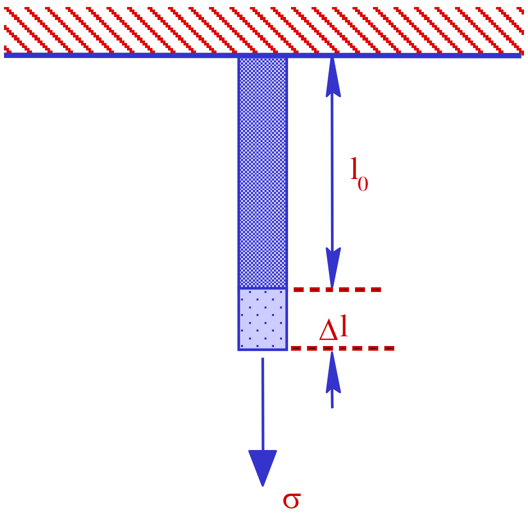


Mechanical and Rheological Properties

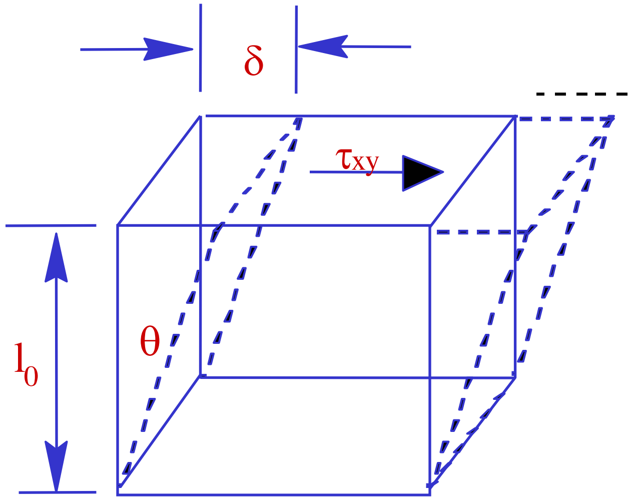
MECHANICAL PROPERTIES OF SOLIDS

Extension



Hooke's law $\sigma = E\varepsilon$

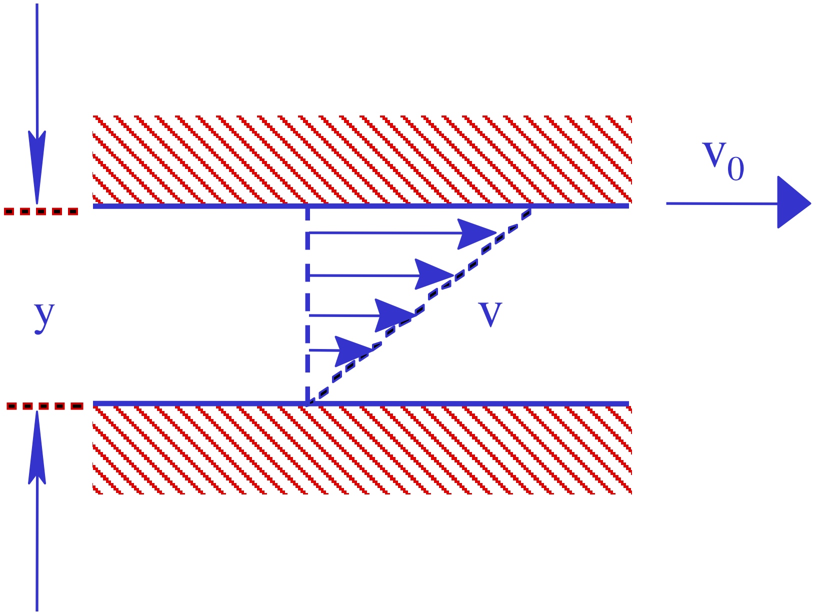
Shear



Hooke's law $\tau_{xy} = G\,\gamma_{xy}$

Mechanical and Rheological Properties

RHEOLOGICAL PROPERTIES OF FLUIDS



Newtonian fluid

$$\tau_{xy} = \eta\dot{\gamma}$$

Overview

POLYMERS TREATED AS SOLIDS

Strength
Stiffness
Toughness

↓

POLYMERS TREATED AS FLUIDS

Viscosity of polymer melts
Elastic properties of polymer melts !!!

↓

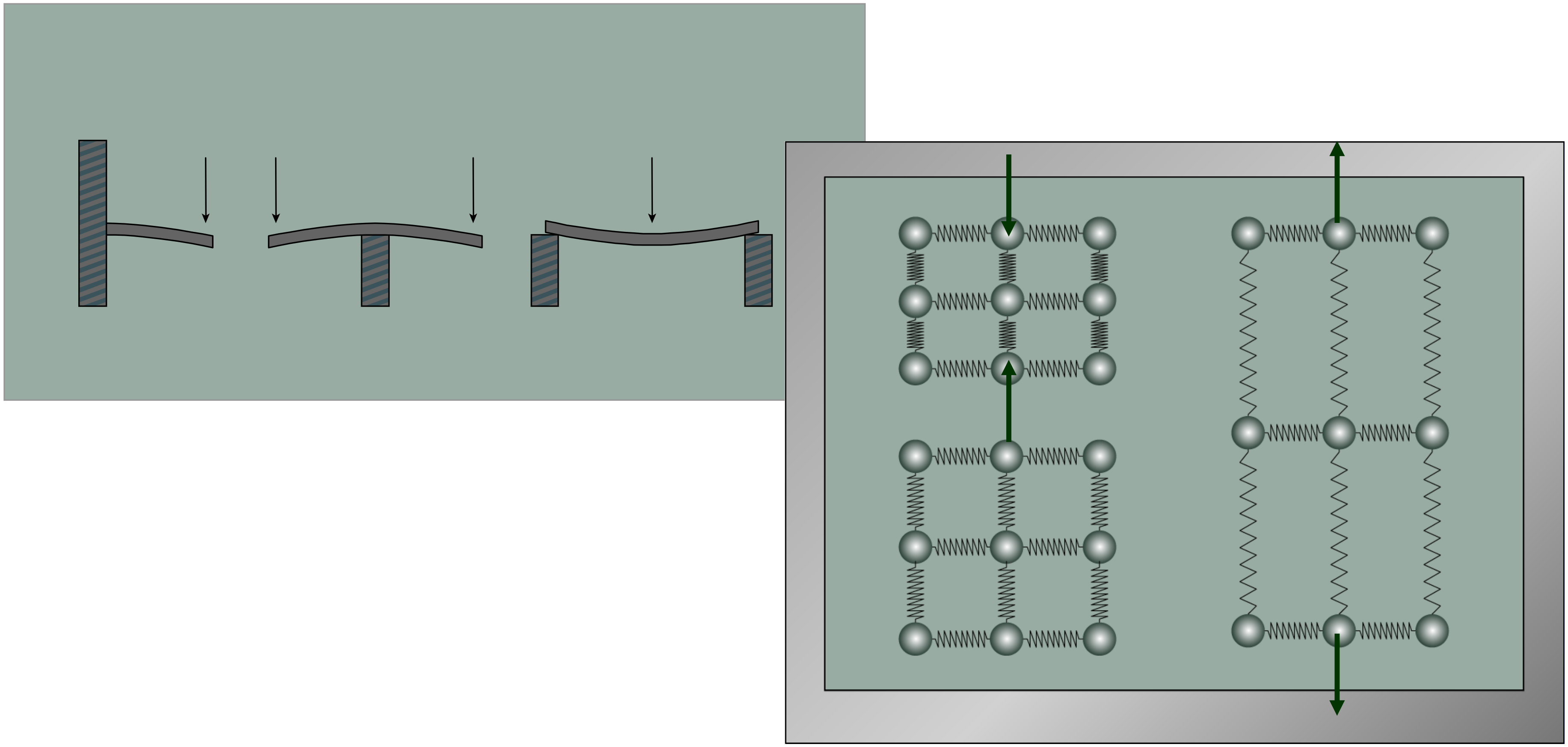
VISCOELASTIC PROPERTIES

Creep
Stress relaxation
Relaxation Processes

Stresses and Strains

(or why you don’t fall through the floor)

How does an inanimate object support a load ?

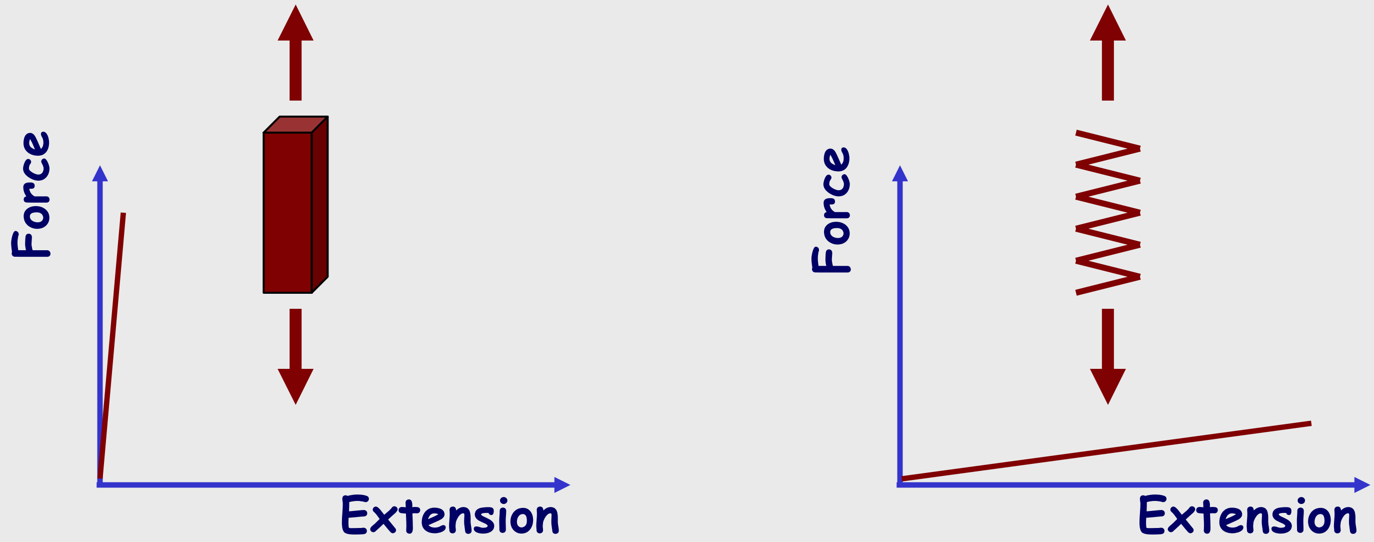


Hooke's Law

In 1676 hooke published "a decimate of the centesme of the inventions I intend to publish" (!!!). Included "the true theory of elasticity or springiness"

ceiiinosssttuu

As the extension,so the force



Questions : slope depends upon shape as well as the material being stretched - can we obtain a material property -stiffness ?

how linear is the response of real materials ?

Thomas Young and Young's Modulus

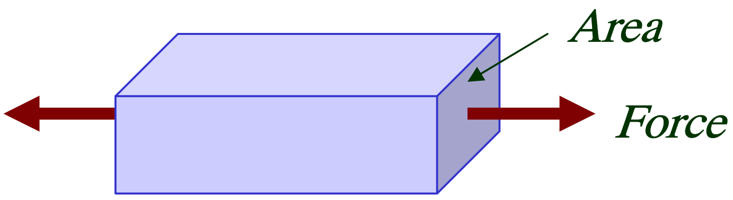
Young's definition of the modulus (~1800) given his name reads;

"the modulus of the elasticity of any substance is a column of the same substance, capable of producing a pressure on its base which is to the weight causing a certain degree of compression as the length of the substance is to the diminution of its length".

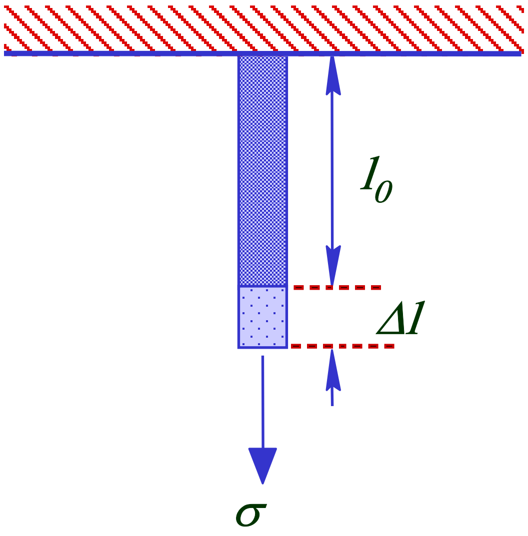
Amazingly enough, later in life he made major contributions to deciphering Egyptian hieroglyphics. After reading his own work hieroglyphics probably seemed easy.

Stress and Strain

But to be fair to Young, he was wrestling with a concept that needed the definition of stress and strain to be expressed in a simple form. These definitions were not to come until some years later, when Cauchy perceived that the load on an object divided by its cross-sectional area is a measure of the force at any point inside a material, rather like how we describe the pressure exerted by a gas on the walls of its container. Strain was defined as the normalized extension, the change in length divided by the original length of the object.



Stress = Force/Area



Strain = $\Delta l / l_0$

Stress

$$\sigma = F/A$$

This in itself is a useful concept

e.g. BRICK 3"x 4" ; LOAD OF 200lbs

Stress = 16.67 lbs/sq.In.

BRIDGE 20' x 5' ; LOCOMOTIVE ~ 100 TONS

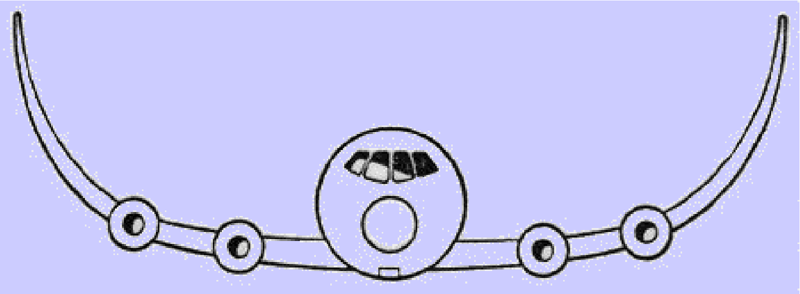
$$\text{Stress} = \frac{100 \times 2{,}240}{5 \times 20 \times 144} = 15.6 \text{ lbs/sq in}$$

Strain

Now define strain ;

$$\varepsilon = \Delta l / l_0$$

Aircraft with strain of 1.6 % in wings



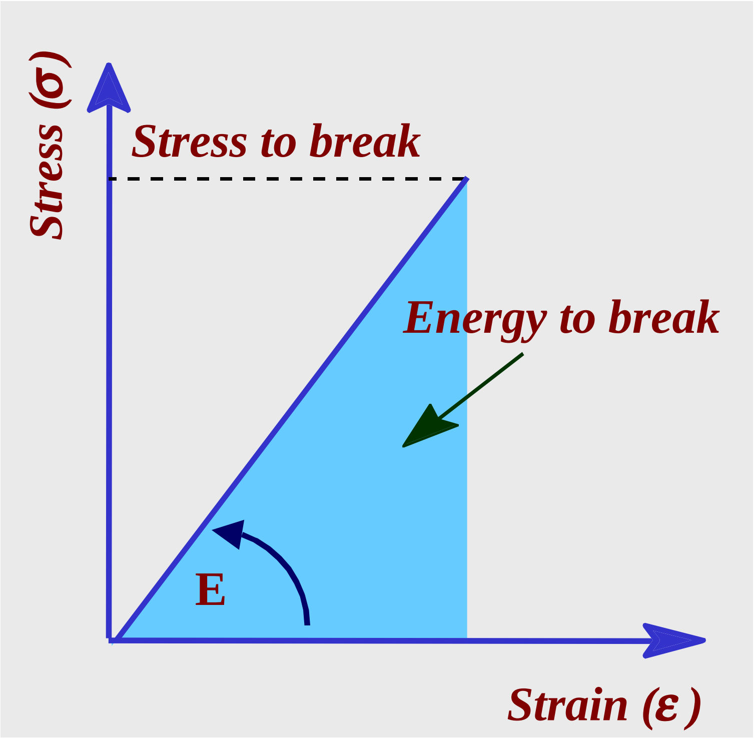
Building on this, Navier finally came up with the modern definition of Young's modulus, stress divided by strain, in 1826, and we now write Hooke's law in the form given opposite.

Hooke's law

$$\sigma = E\varepsilon$$

Stress = Young's Modulus x Strain

The Elastic Properties of Materials



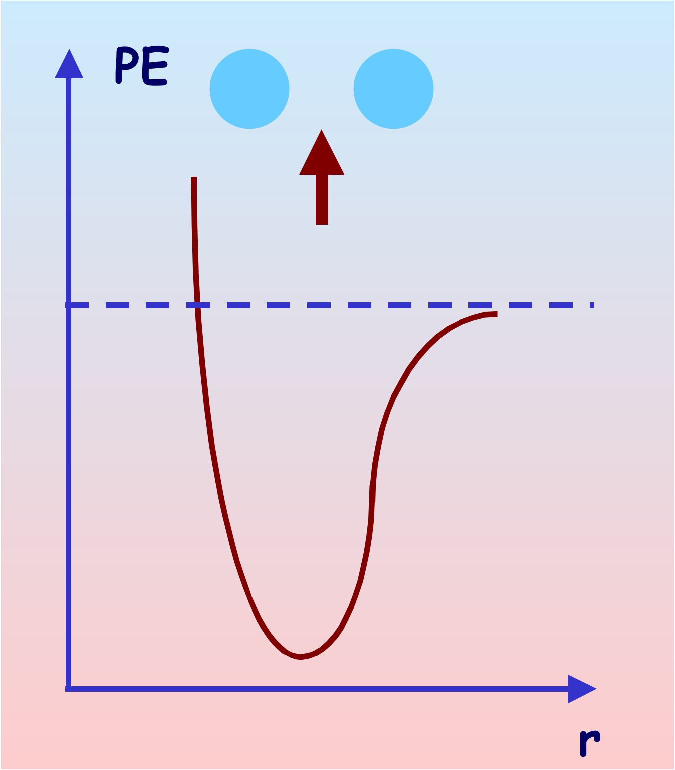
Hooke's law for an ideal material.
But real materials aren't perfect!

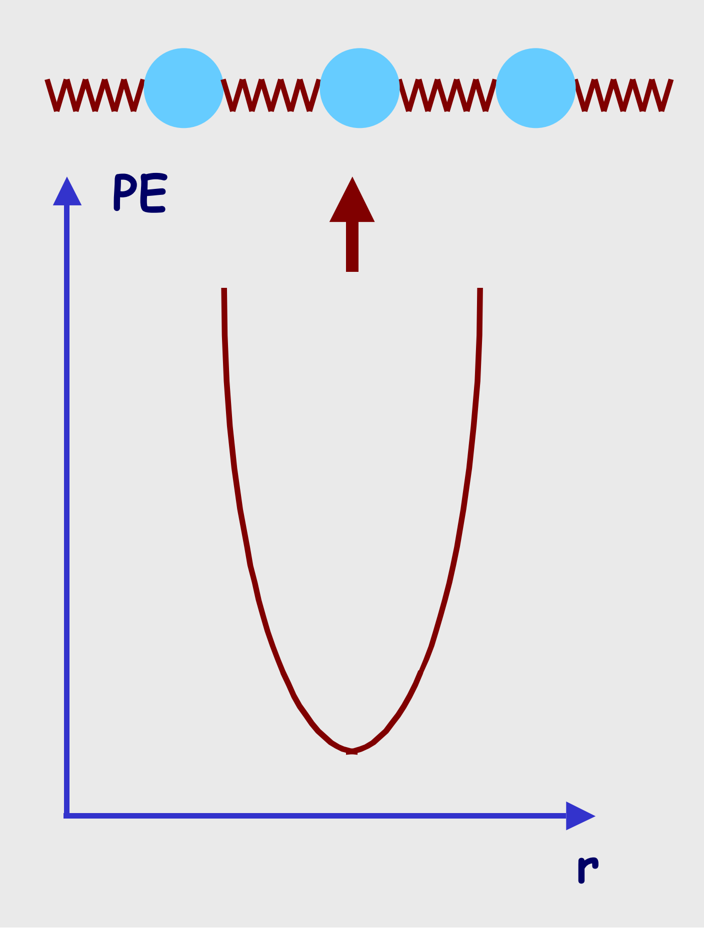
Let's consider the properties of an "ideal" material first, then come back to the stiffness, strength and toughness of real materials.

Hooke's Law - an Approximation

It is important to realize that even if we had a perfectly ordered material with no defects whatsoever, then we would still get deviations from ideal linear behavior. To see why this is so let's consider a simple model, a one dimensional array of atoms linked together by ordinary chemical bonds

Now let's look at the forces between just two of these atoms taken in isolation





When arranged in a lattice, however, the atoms have neighbors on both sides and if you sum the contributions from each of these then locally the potential energy curve has a "U" shape that at least near the bottom part of the curve can be approximated by a simple quadratic function of the form

$$PE = k''x^2 = \frac{k}{2}x^2$$

where x is the displacement of the bond from its minimum energy position and the factors k" and k are constants (we use k/2 to get our final answer in a simple form). However, this is only an approximation and the PE can be represented more accurately by a power series

$$PE = \frac{1}{2}kx^2 + \frac{1}{3}k'x^3 + \cdots$$

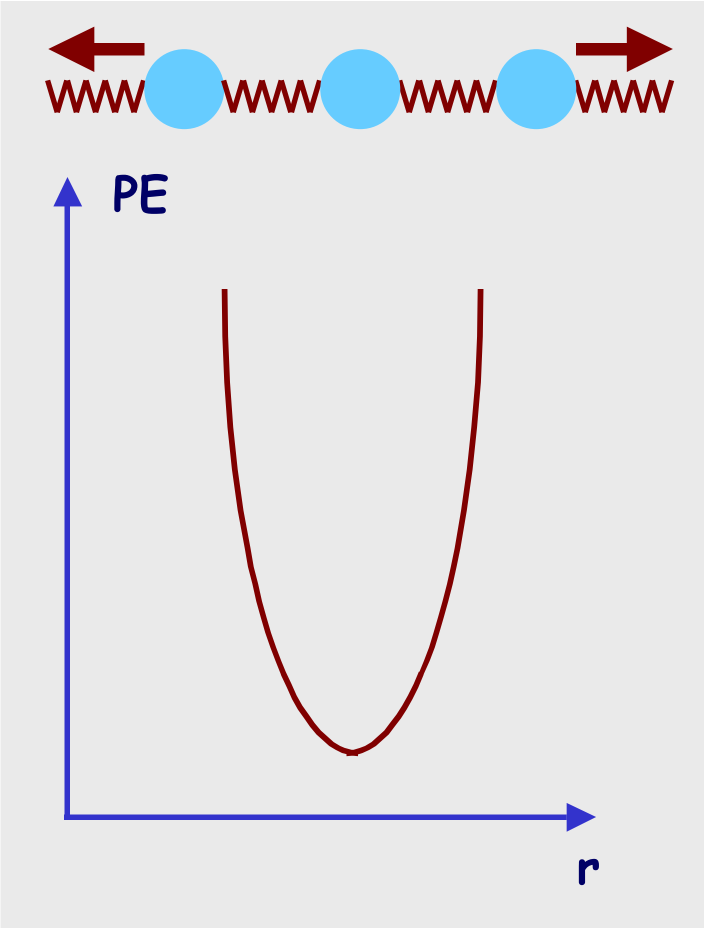
The restoring force is equal to the first derivative of the PE with respect to x, the displacement (think about it; energy is force times distance, so differentiating with respect to distance gives you a force). Differentiating the power series for the PE with respect to x gives us;

$$f = kx + k'x^2 + \cdots$$

Or, normalizing the displacement with respect to the original length of the bond we can write this equation in terms of the strain, Δl

$$f = k\Delta l + k'\Delta l^2 + \cdots$$

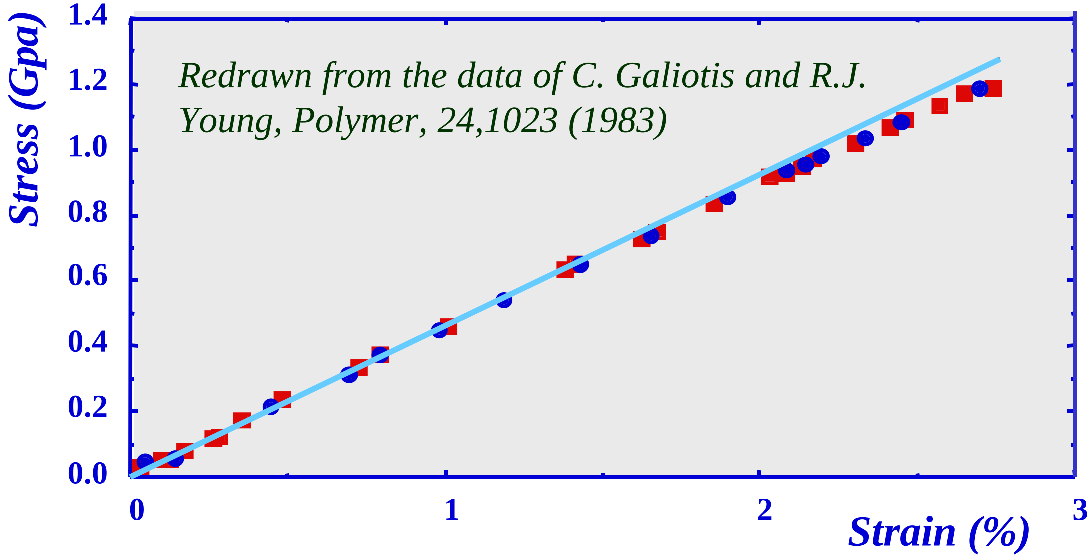
Clearly, for small strains we can neglect higher order terms (if the strain is 2%, then $\Delta l = 0.02$ and $\Delta l^2 = 0.0004$).



An Almost Ideal Material

Hooke's law obeyed up to deformations ~ 2%. Deviations beyond this could be due to defects as well as non linear terms in the force/extension equation

POLYDIACETYLENE SINGLE CRYSTAL



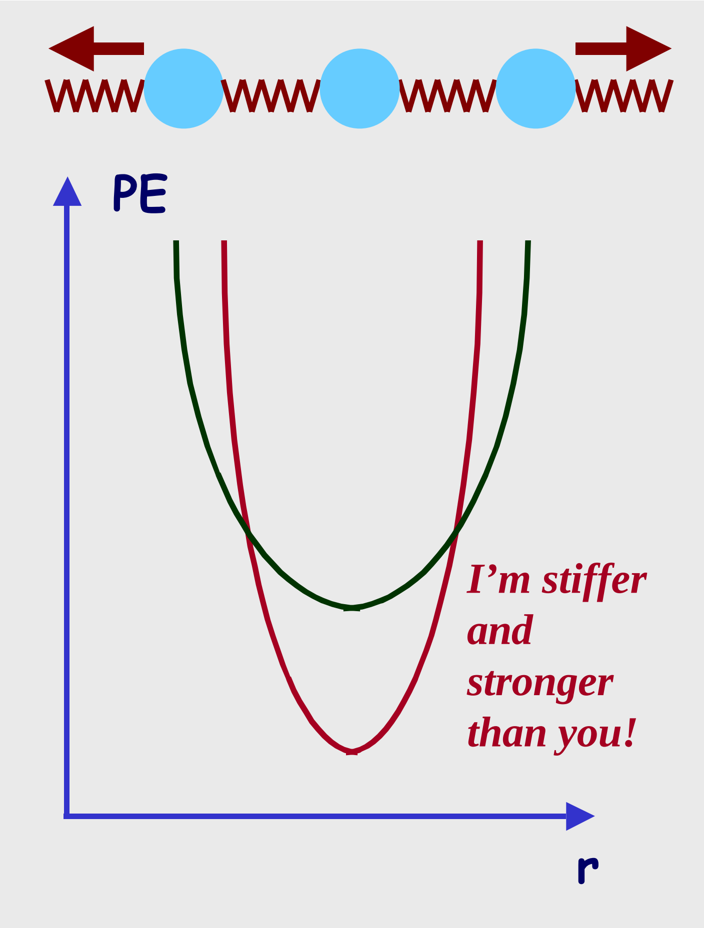
Redrawn from the data of C. Galiotis and R.J. Young, Polymer, 24,1023 (1983)

Cohesion, Strength and Stiffness

Stiffness of an ideal material ~ related to the stiffness of the chemical bonds within the system. The stiffness of each bond is given by the slope of the potential energy curve.

Strength of an ideal material ~ related to the cohesive strength of the bonds, proportional to the depth of the potential energy well.

A strong stiff material should have a deep, narrow potential energy curve.

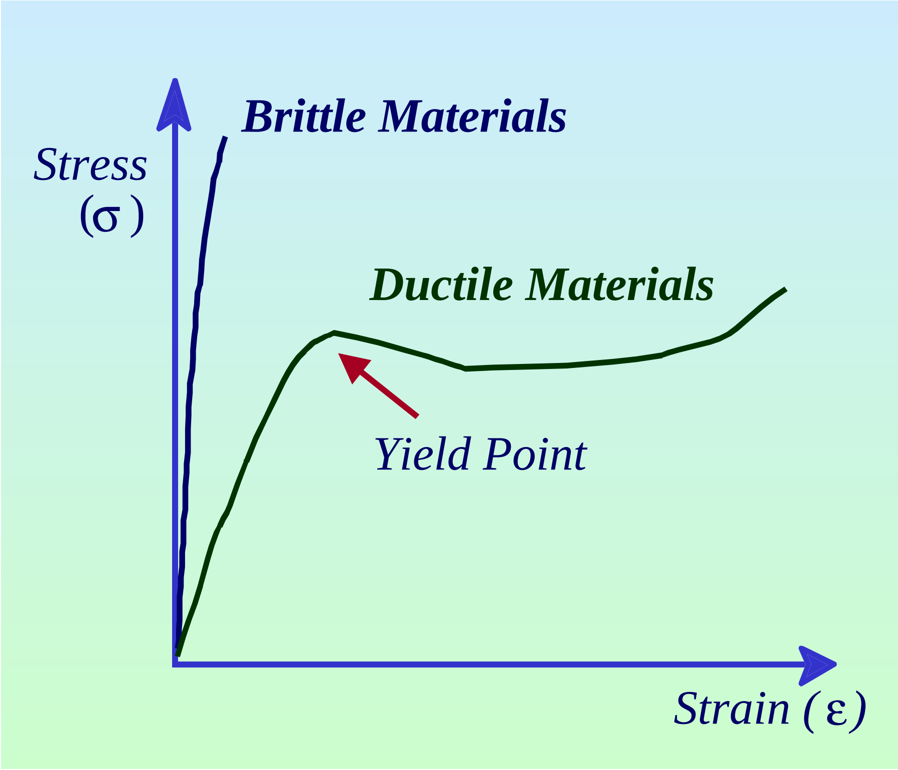


Elastic and Plastic Deformation

REAL MATERIALS

Some brittle* materials, like ceramics, at first glance appear to be almost ideal in their behavior. But, these materials are usually nowhere near as strong as they should be (more on this later).

Even more drastic deviations from ideal behavior are observed in ductile materials (e.g. many metals), where a *yield point* occurs well before fracture.



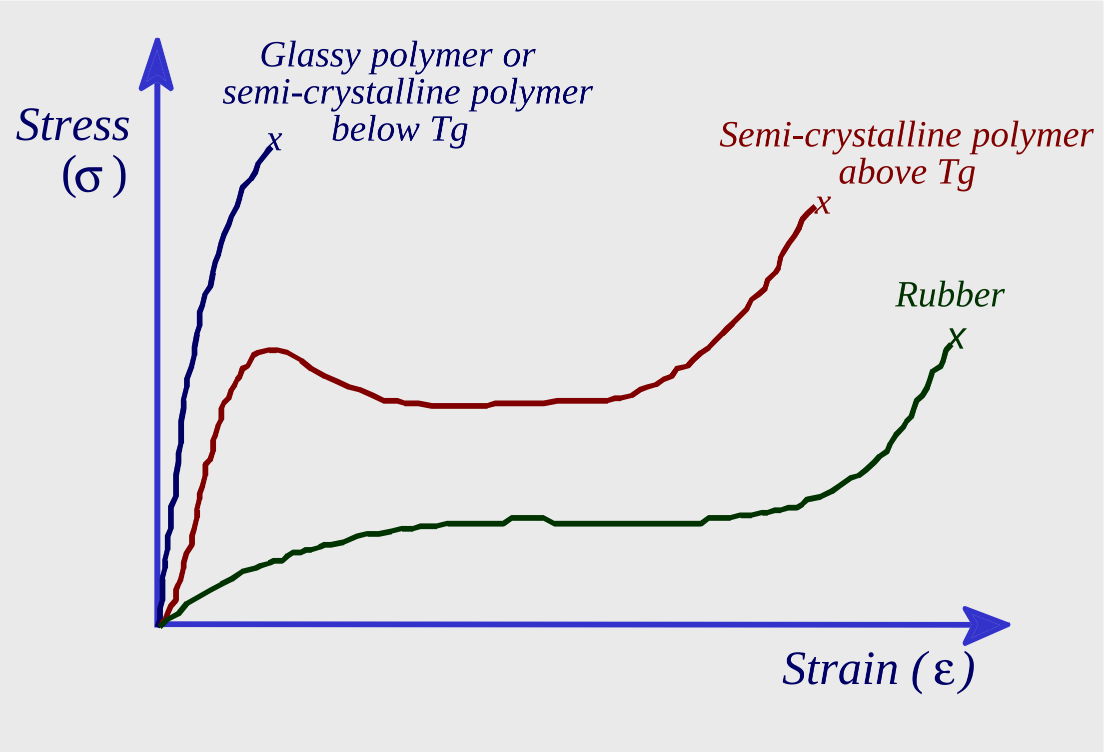
** The word "brittle" to most people implies poor impact resistance. As we will see, it's a bit more complicated than this and in general brittle materials have poor resistance to the propagation of cracks.*

The Stress/Strain Characteristics of Polymers

For glassy and semi-crystalline polymers we see this type of brittle and ductile behavior.

For elastomers, however, elastic but non-linear behavior is often observed up to strains of 500%!

Furthermore, even in the initial apparently Hookean regions of the stress/strain behavior of polymers *anelastic* (time dependent) responses are usually observed!



Stiffness

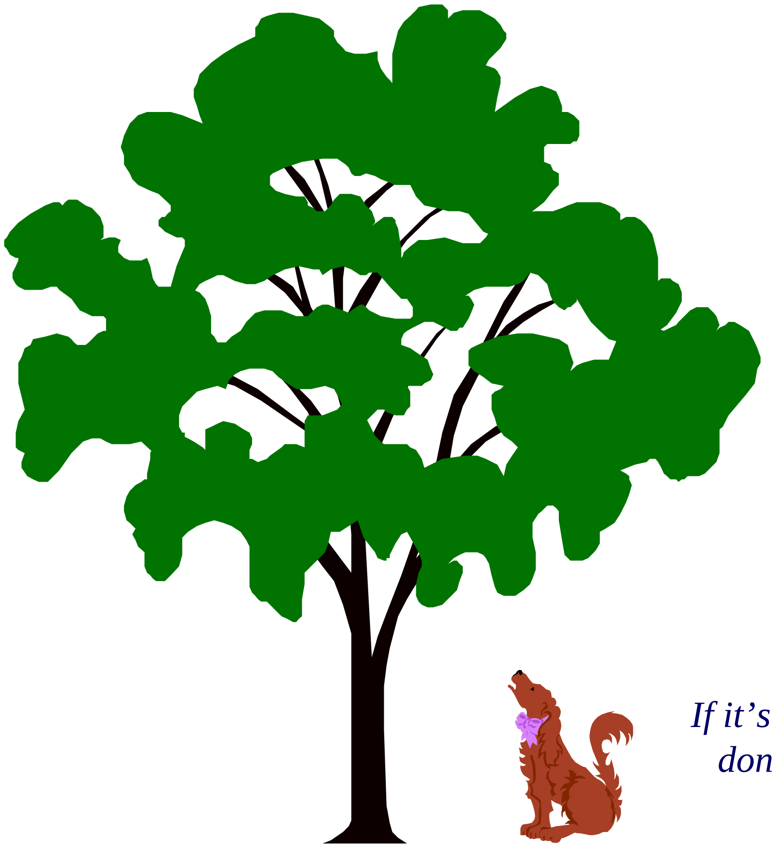
We'll get to the complications later - first consider the modulus as defined by the initial slope of the stress/strain curve.

Material	*E (lbs/sq. inch)*	*E (MPa)*
Rubber	*0.001 x 10^6*	*7*
Polyethylene	*0.2 x 10^6*	*150*
Wood	*2.0 x 10^6*	*14,000*
Concrete	*2.5 x 10^6*	*17,000*
Glass	*10.0 x 10^6*	*70,000*
Steel	*30.0 x 10^6*	*210,000*
Diamond	*170.0 x 10^6*	*1,200,000*

Polymers aren't very stiff!

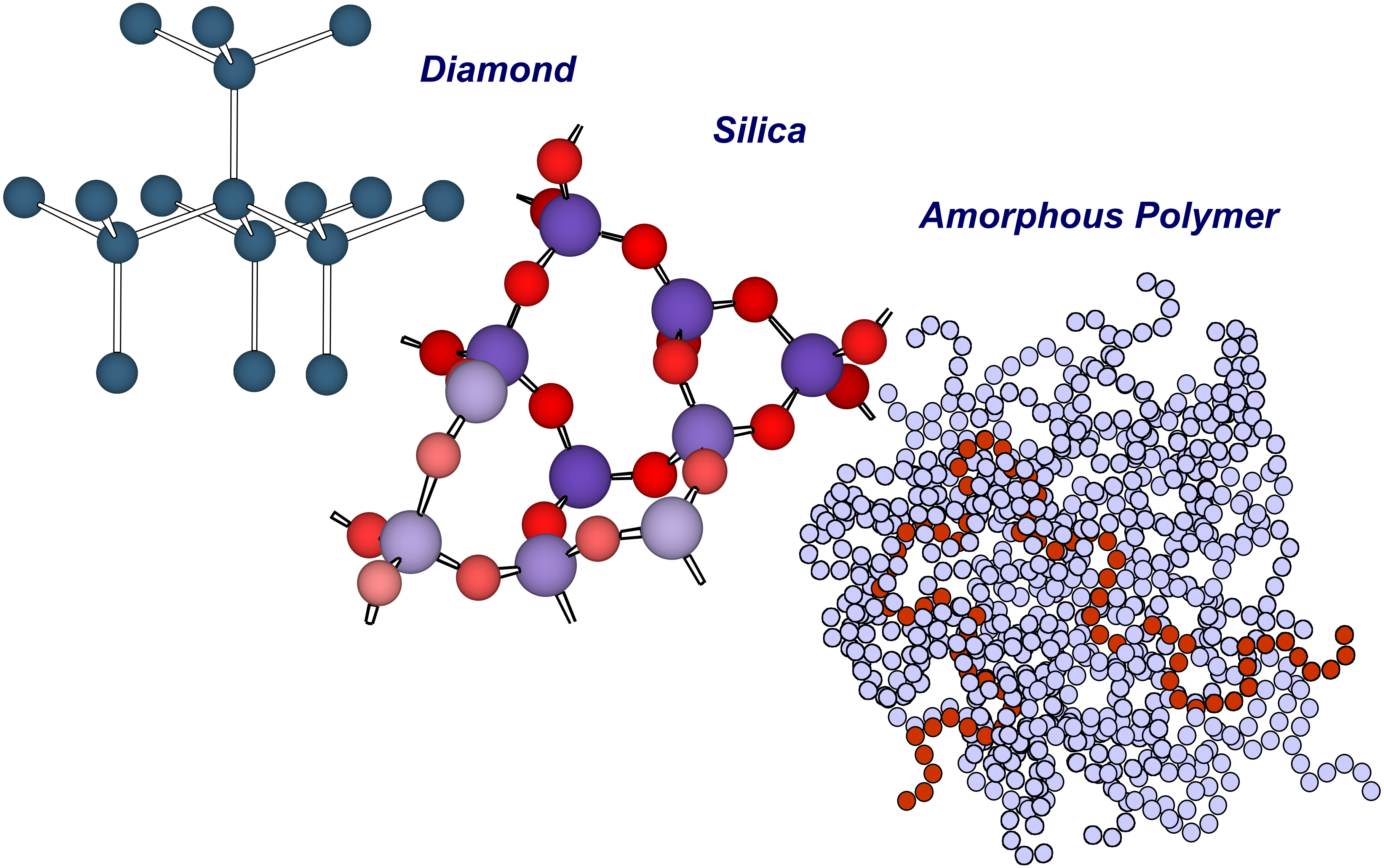
Polymers aren't very stiff! (Modulus of polyethylene ~ 150 Mpa).

Even a glassy polymer like atactic polystyrene has a modulus of only about 3,000 MPa (about 1/20th that of window glass).



If it's polyethylene, don't go near it

Stiffness and Structure

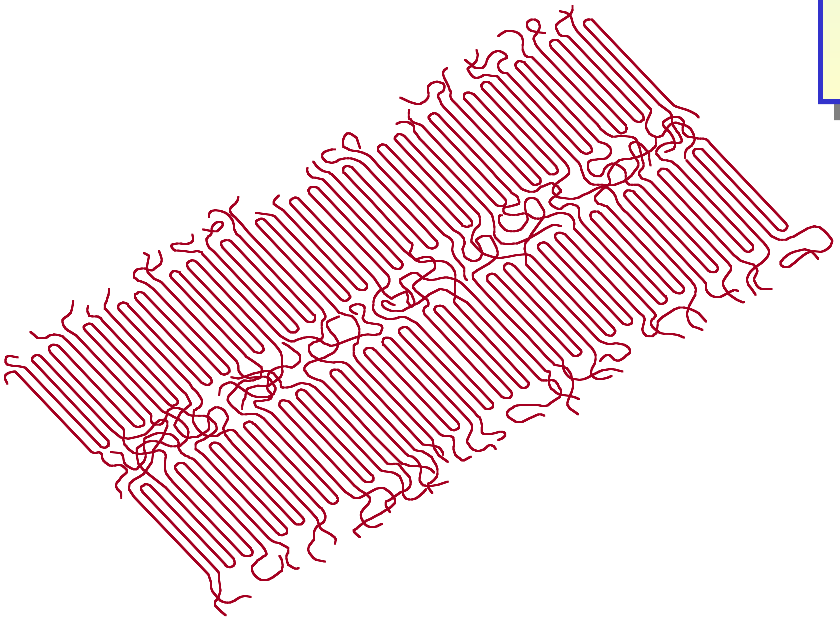


Stiffness of Polymers

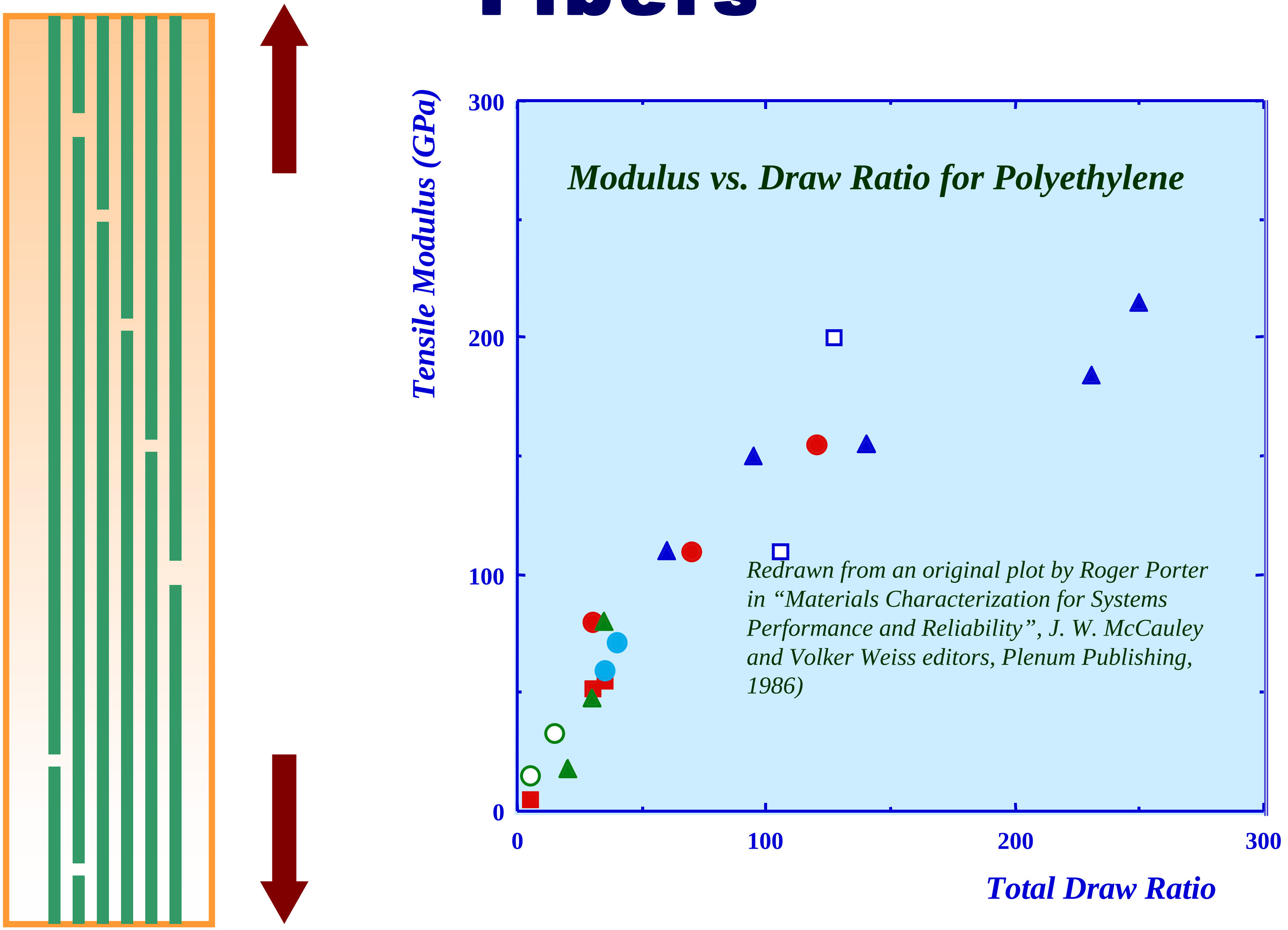
FACTORS:

- Crystallinity
- Cross Linking
- Tg

Polymer	E (MPa)
Rubber	7
Polyethylene	
High Density	830
Low Density	170
Poly(styrene)	3100
Poly(methyl methacrylate) (Plexiglas)	4650
Phenolic Resins (Bakelite)	6900



Fibers


Modulus vs. Draw Ratio for Polyethylene

Redrawn from an original plot by Roger Porter in “Materials Characterization for Systems Performance and Reliability”, J. W. McCauley and Volker Weiss editors, Plenum Publishing, 1986)

Tensile Strength

Material	TS (psi)	TS (MPa)
Steel piano wire	450,000	3,000
High - tensile steel	225,000	1,500
Aluminium alloys	20,000 - 80,000	140 - 550
Titanium alloys	100,000 - 200,000	700 - 1,400
Wood (spruce),along grain	15,000	100
Wood (spruce),across grain	500	7
Ordinary glass	5,000 - 25,000	30 - 170
Ordinary brick	800	5
Ordinary cement	600	4
Nylon fiber	140,000	950
Kevlar 29 fiber	400,000	2,800

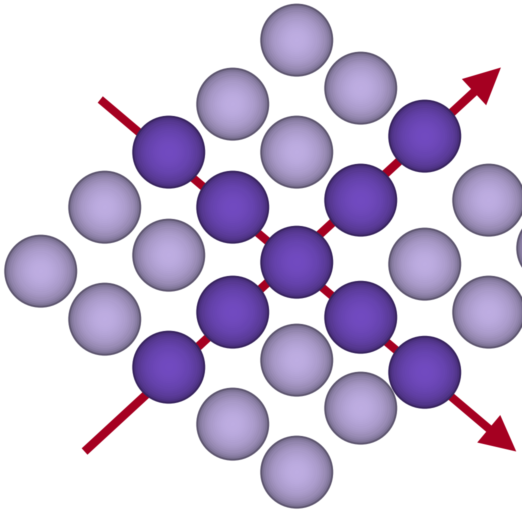
QUESTION USUALLY ASKED
WHY IS ONE MATERIAL STRONGER THAN ANOTHER?

QUESTION SHOULD BE
WHY ISN'T ANY MATERIAL AS STRONG AS IT SHOULD BE?

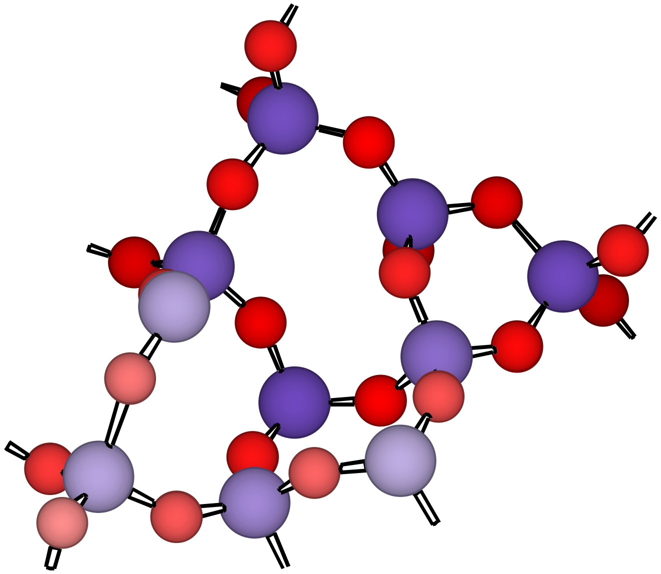
How Strong Should Materials Be?

Material	*Theoretical Strength*	*Measured Strength*
Glass	*~2 x 10^6 p.s.i.*	*~ 25,000 p.s.i.*
Steel	*~5 x 10^6 p.s.i.*	*~ 400,000 P.S.I (Best)*
Polyethylene Fibers	*~ 25 Gpa*	*~ 0.35 GPa (Tensile drawing)* *~ 4 GPa (Gel spun)*

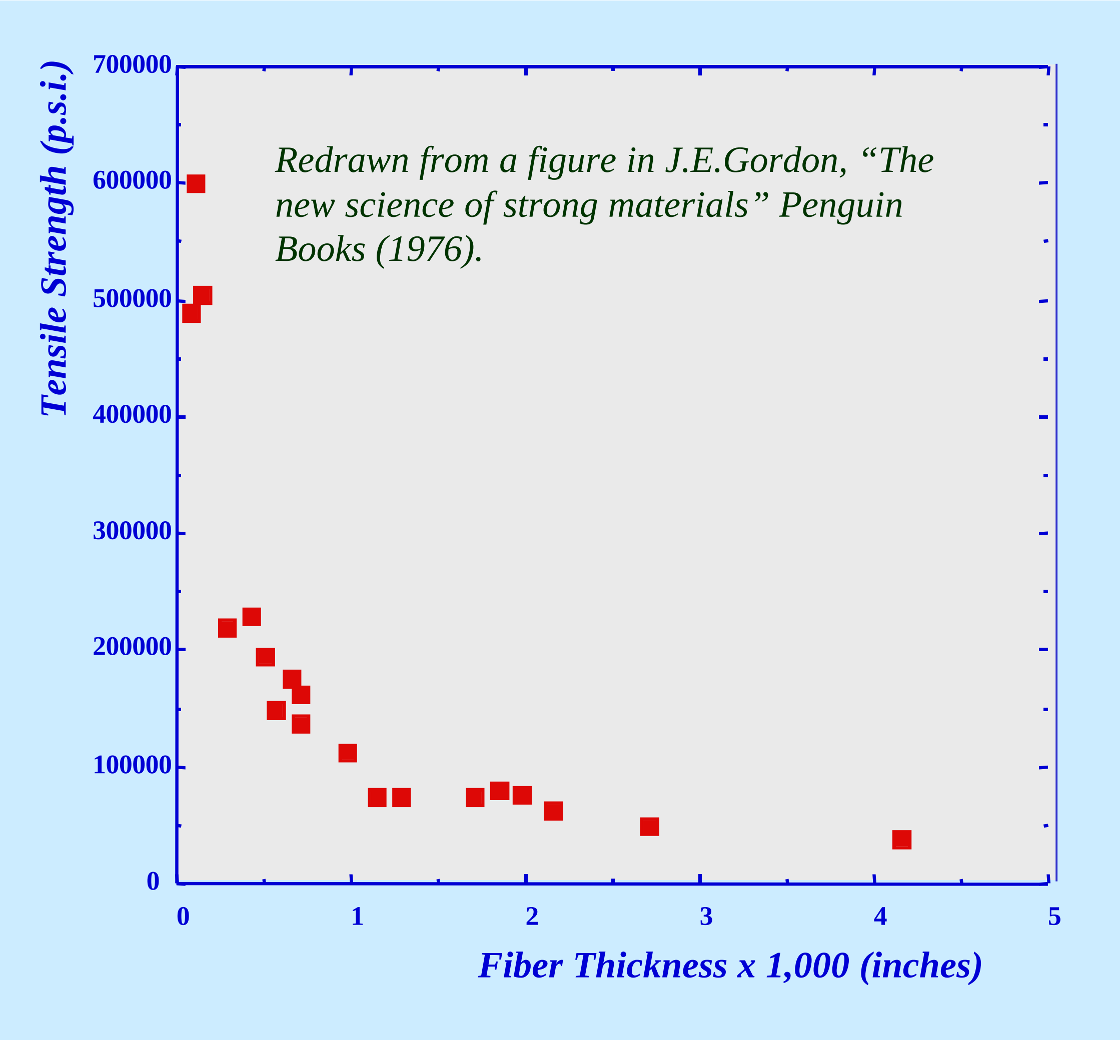
Brittle vs Ductile Materials



I can slip this way or that, but you can't!

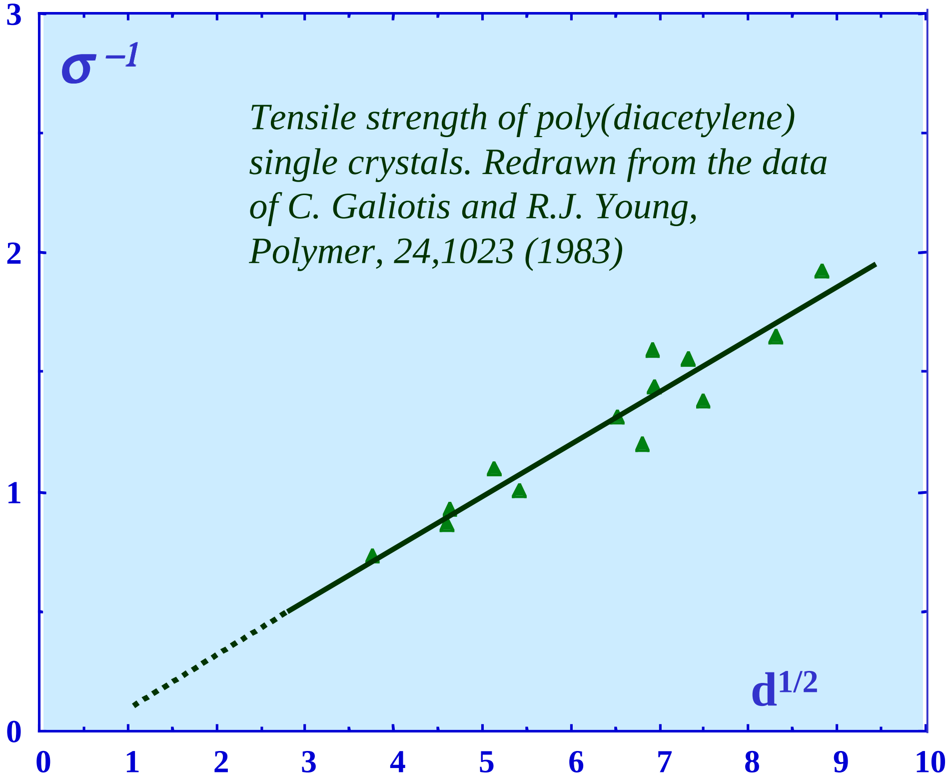


The Strength of Glass

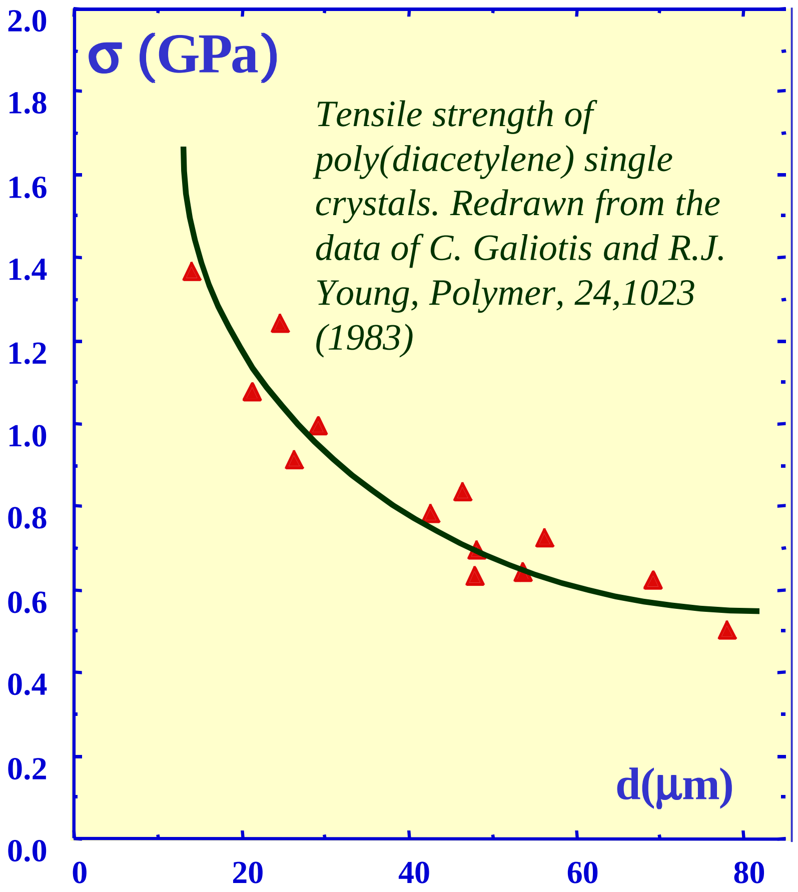


Redrawn from a figure in J.E.Gordon, "The new science of strong materials" Penguin Books (1976).

Poly(diacetylenes)

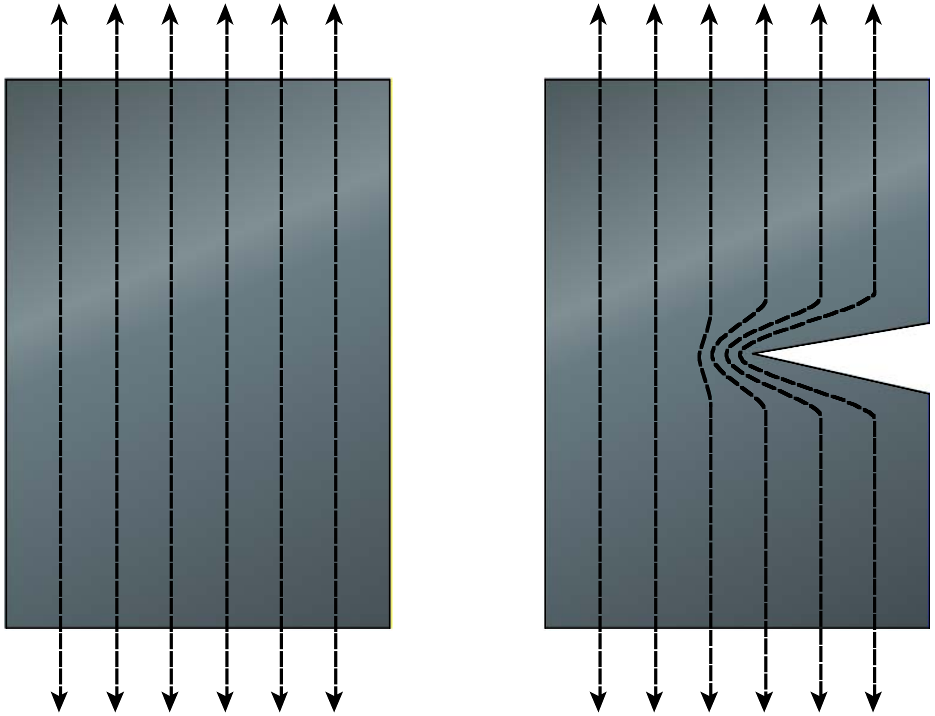


Tensile strength of poly(diacetylene) single crystals. Redrawn from the data of C. Galiotis and R.J. Young, Polymer, 24,1023 (1983)



Tensile strength of poly(diacetylene) single crystals. Redrawn from the data of C. Galiotis and R.J. Young, Polymer, 24,1023 (1983)

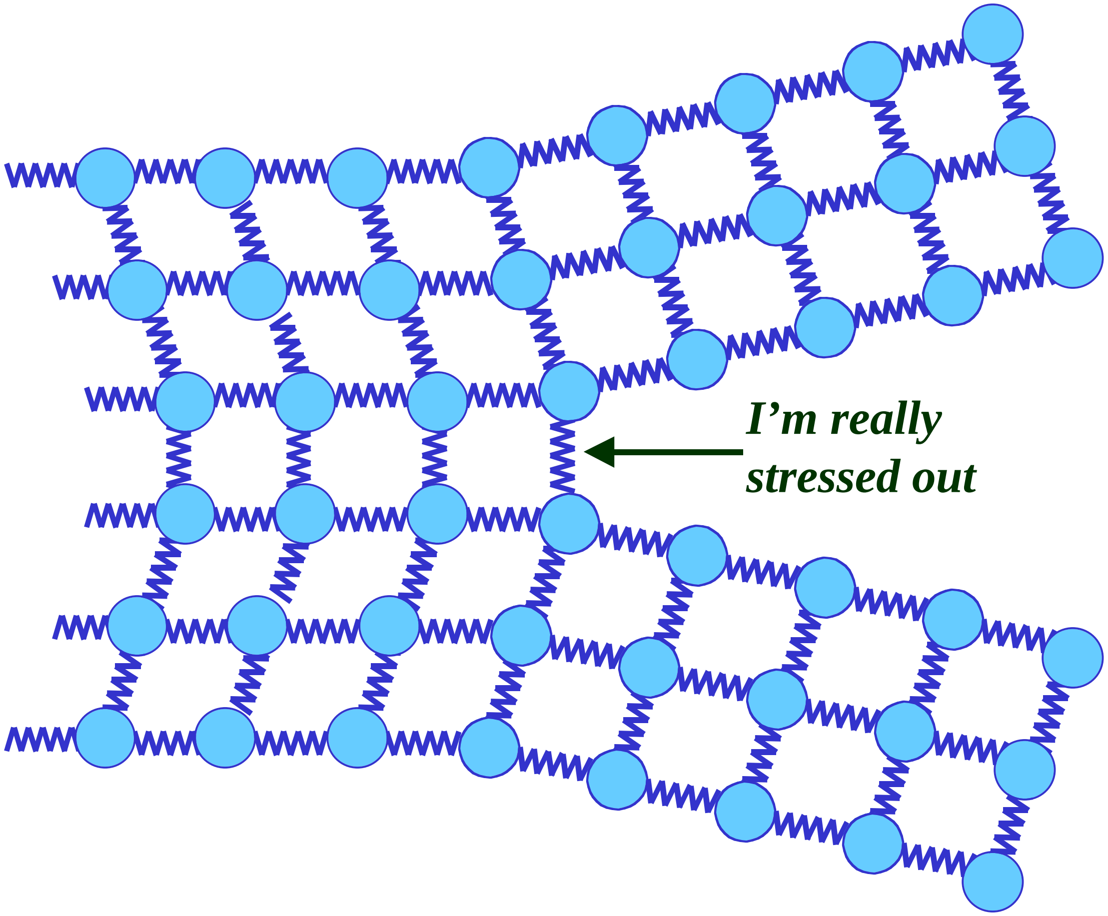
Cracks and Stress Concentration



- A crack acts as a stress concentrator.

- The stress concentration depends upon the size and shape of the defect.

$$\textit{Stress Concentration Factor} = 1+2\sqrt{\frac{L}{R}}$$



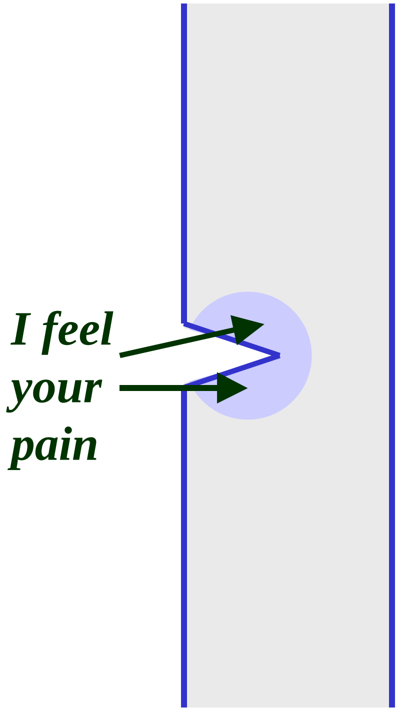
- The bonds near the tip of the crack are carrying more than their fair share of the stress and can fail.
- The crack becomes longer and thinner, the stress concentration even greater, and the next bonds in line also fail.
- Thus a crack can propagate catastrophically through a material

But surely such arguments apply to steel and kevlar as well as glass; what is different about these materials and why does glass fail more readily?

Strength and Toughness

If we let the energy that has to be used to produce a "real" fracture surface in a material be W, the work of fracture, Then the critical crack length is given by;

$$l_g = \frac{2WE}{\pi \sigma^2}$$

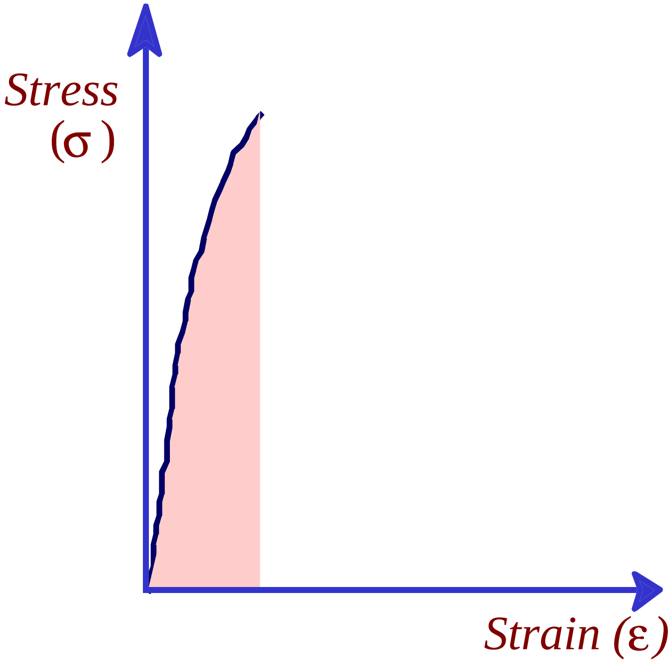


Strength and Toughness

- In window glass the molecular structure is perturbed to a relatively shallow depth during fracture and W is about 6G.

- Under any significant load the critical crack length is very short. The tensile strength of glass might be appreciable under a static load, but under stress the glass is in a fragile state, the critical crack length is small and slight perturbations can lead to crack propagation and failure.

- Brittle materials in general have a low work of fracture or energy to break, as reflected in the area under the stress strain curve.

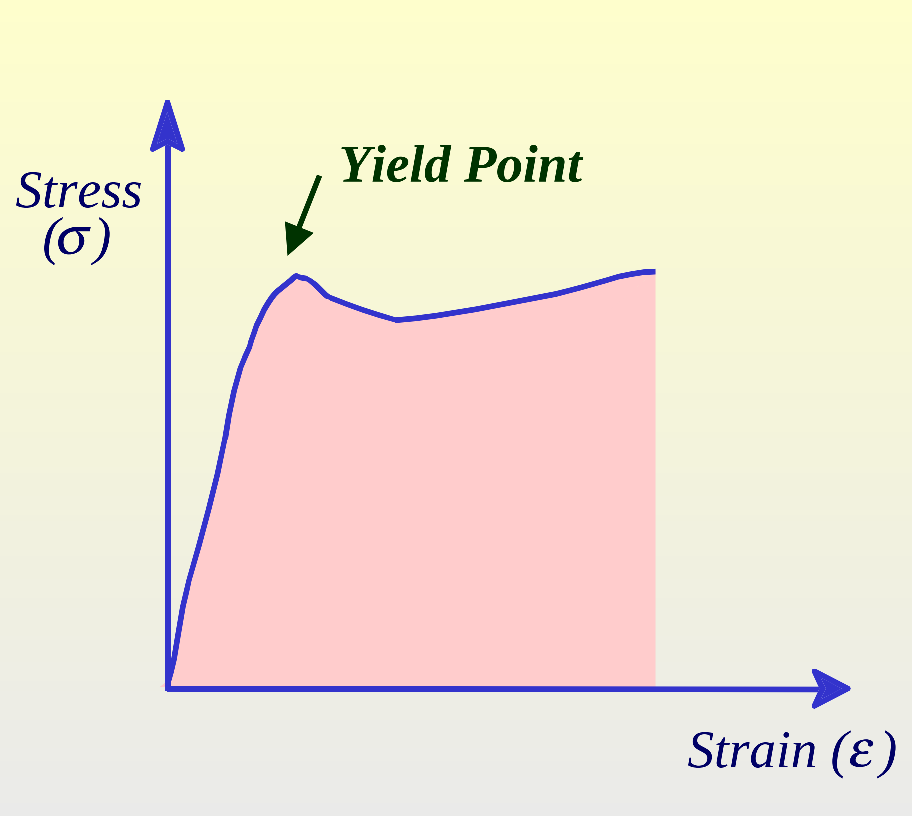


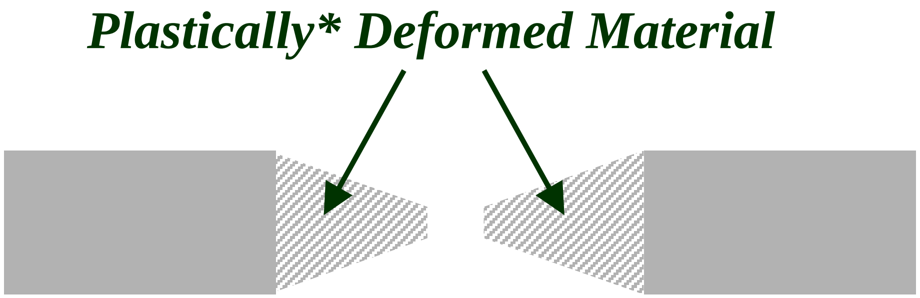
Strength and Toughness

- Mild steel and other ductile metals have an enormous work of fracture; W is of the order of 10^4 - 10^6 G and the critical crack length is very long.

- The structure of these materials is perturbed to a significant depth below the fracture surface, hence the high work of fracture.

- The stress strain plots of such a material display a yield point, where a neck forms and the material deforms plastically.



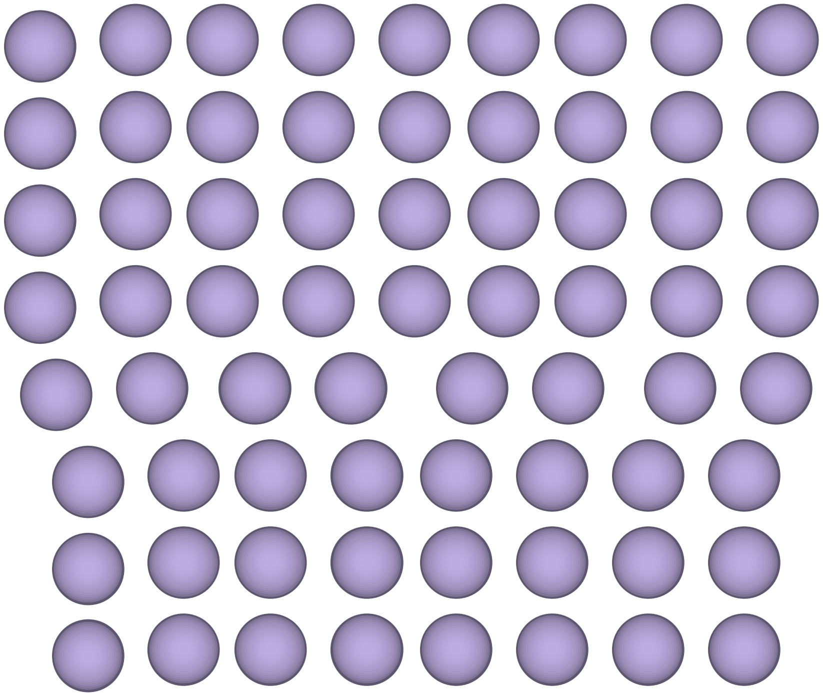


Strength and Toughness

- Ductile failure in metals involves slip between layers of atoms in the crystal structure.

- The elastic limit is reached at much lower stresses than you would calculate for a hypothetically perfect material and again the problem is defects.

- Here the principal "weakening" mechanism is not microscopic cracks, however, but defects within the crystal structure known as dislocations.



Strength and Toughness - Summary

All materials are weaker than they could be because of cracks, defects in the crystalline lattice, and so on.

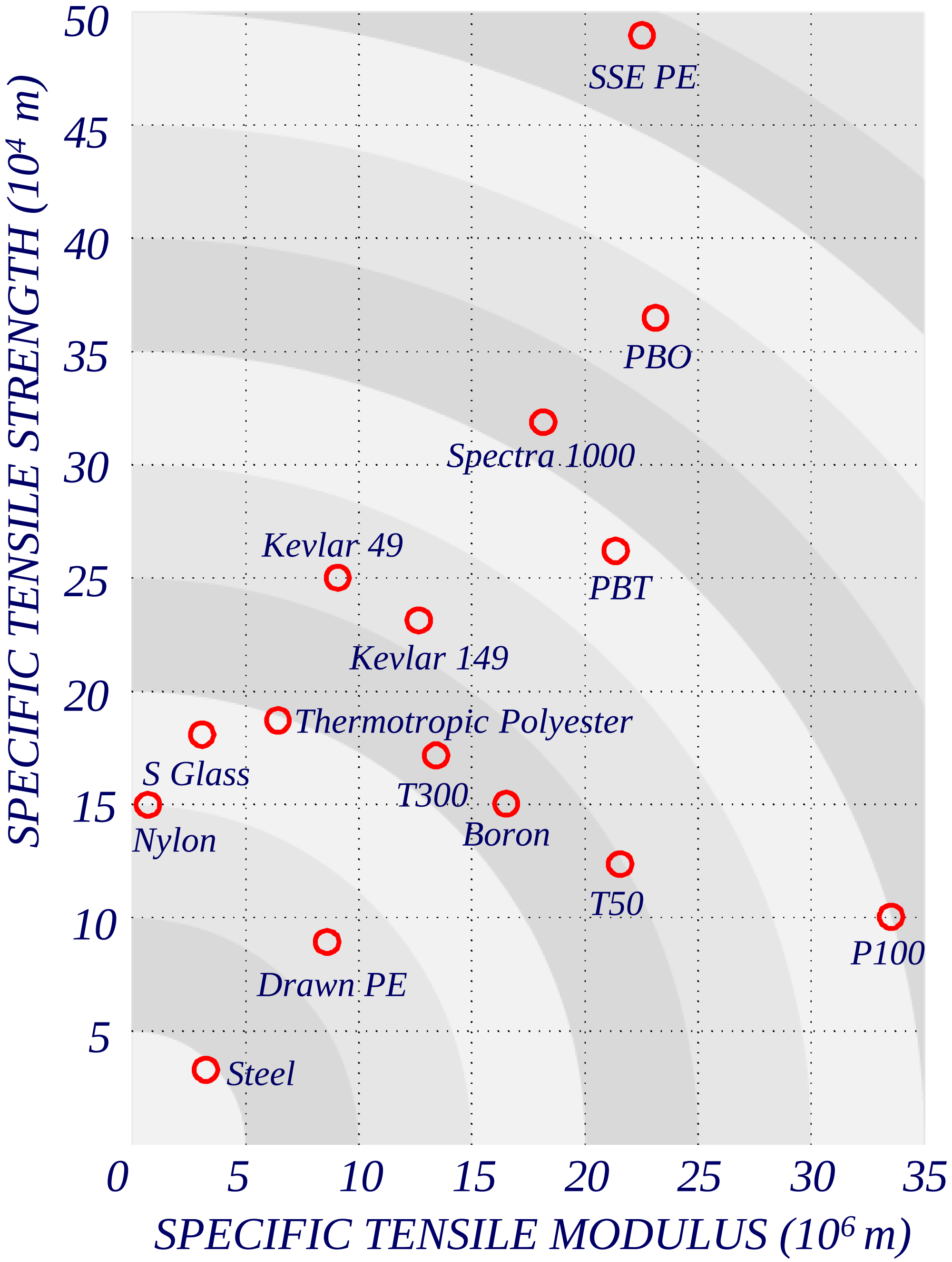
It is not necessarily the measured tensile strength that is the most critical factor in choosing a material for a structural application, but its work of fracture, its resistance to the growth of cracks.

This property also plays into impact strength. When you hit a ceramic vase with a hammer you are really just applying a load at a point. The energy is actually conducted away very quickly in the form of stress waves traveling at about the speed of sound (~E/ρ; about 11,000 mph in glass!). These reflect back and forth and accumulate at some spot, perhaps where there is a structural flaw or crack. Then if the material has a low work of fracture, it's history.

Polymers, in general, are relatively tough, but at least in their melt processed form not they are not as strong or as stiff as metals and ceramics, but they don't have to be if your making film wrap or a toothbrush.

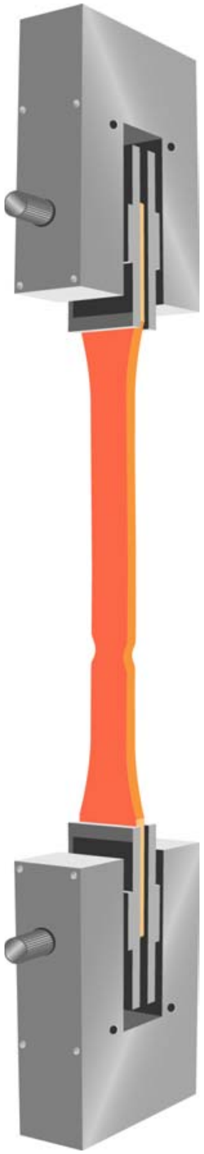
Strength and Modulus of Various Materials

In the form of oriented fibers, however, polymers can be made to be very strong and stiff.



Reproduced with permission from S. J. Krause, et al., Polymer, 29, 1354 (1988).

The Stress/Strain Characteristics of Polymers



In polymeric materials stiffness, strength and toughness vary over an extraordinary range.

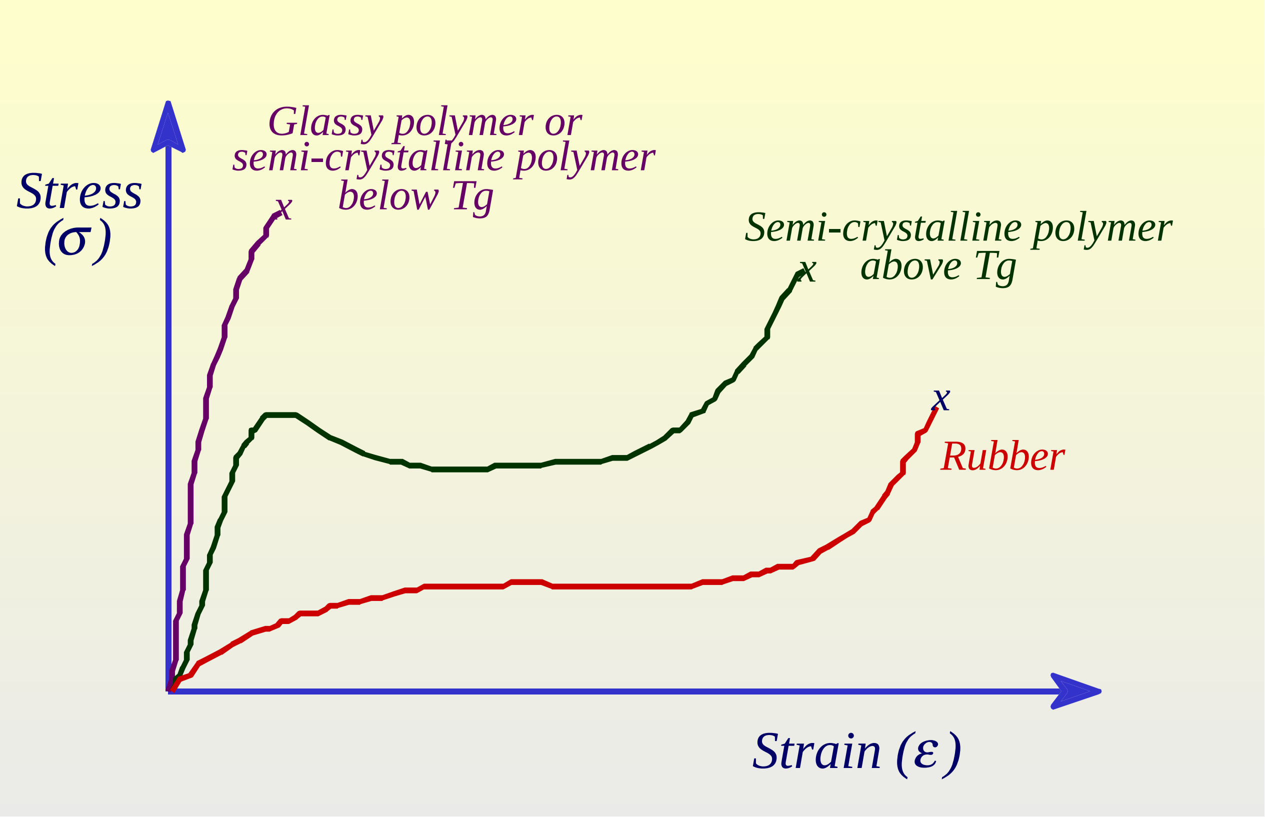
This is a reflection of structure, which we have seen ranges from the random coil, purely amorphous states, to chain folded semi-crystalline morphologies, to highly oriented fibers.

By and large, however, polymers tend to deform irreversibly far more readily than the other materials

This deformation can increase dramatically even if the temperature is raised fairly modest amounts (often less than $100^{0}C$).

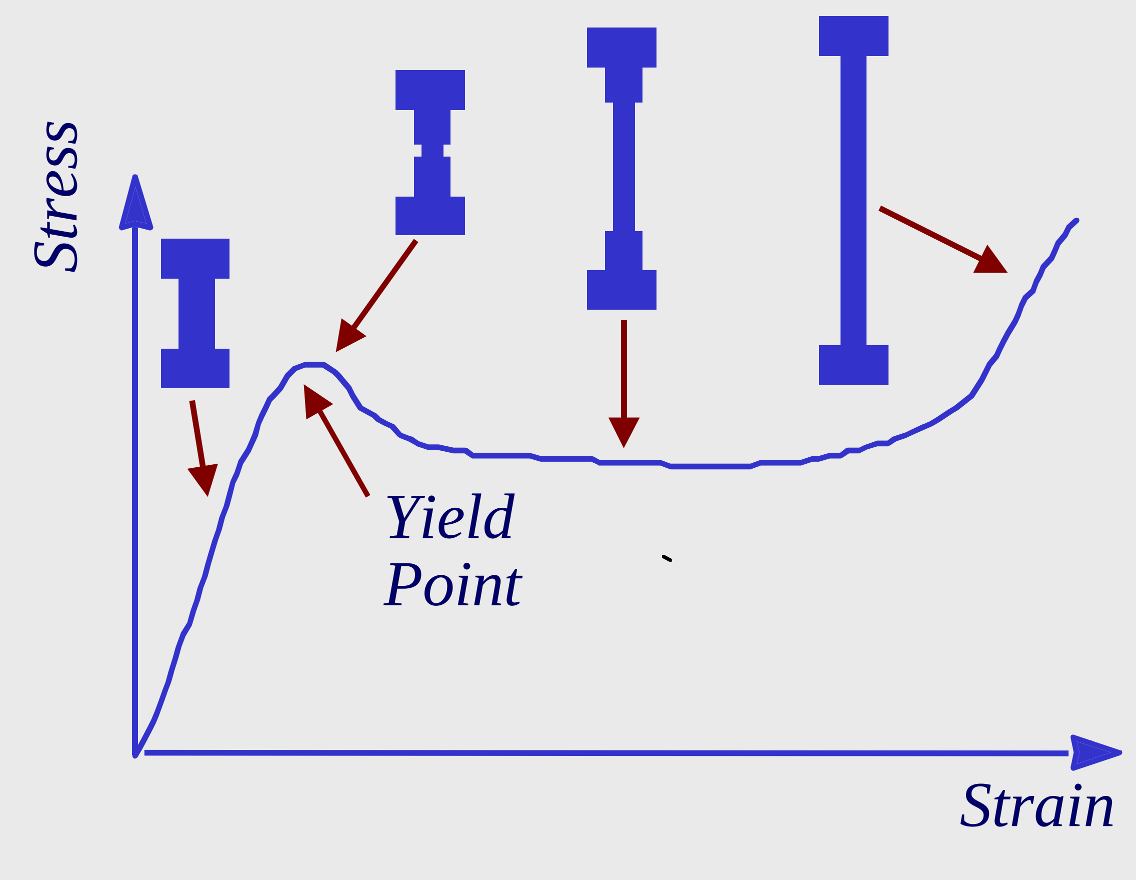
There is a time dependence to their behavior. We'll neglect that for now and start by surveying general stress/strain behavior.

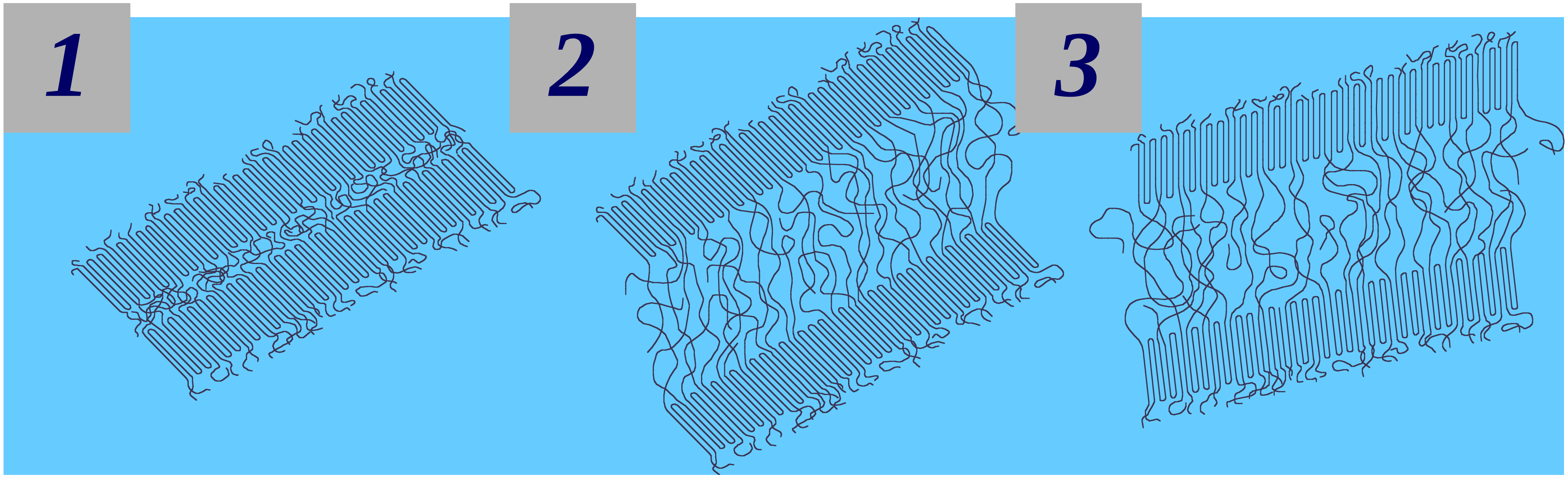
Stress / Strain Characteristics of Polymers



Yielding in Flexible Semi-Crystalline Polymers

Flexible semi-crystalline polymers such as polyethylene (where the Tg of the amorphous domains is below room temperature) usually display a a considerable amount of yielding or "cold-drawing", as long as they are not stretched too quickly.

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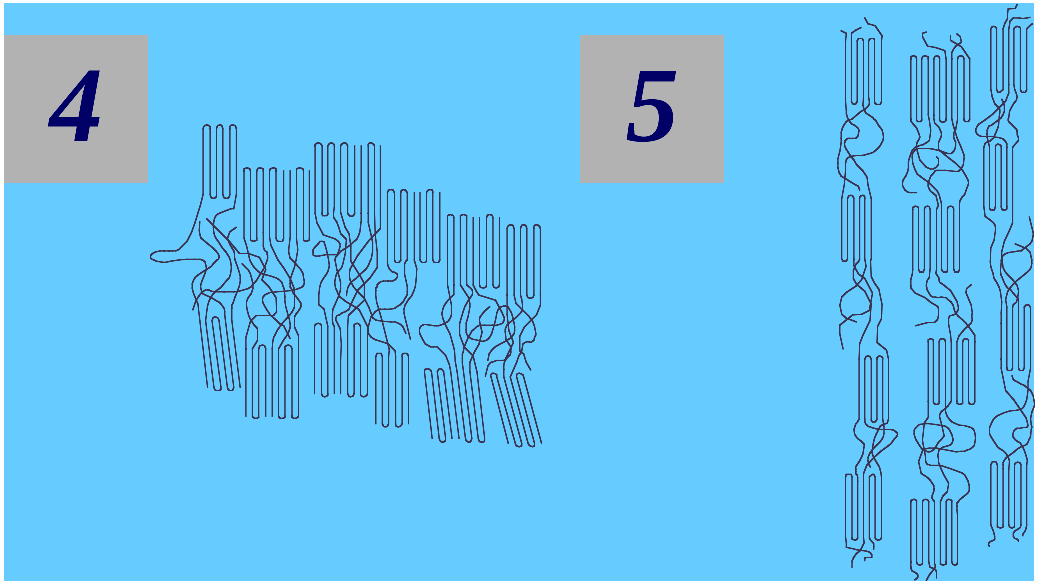
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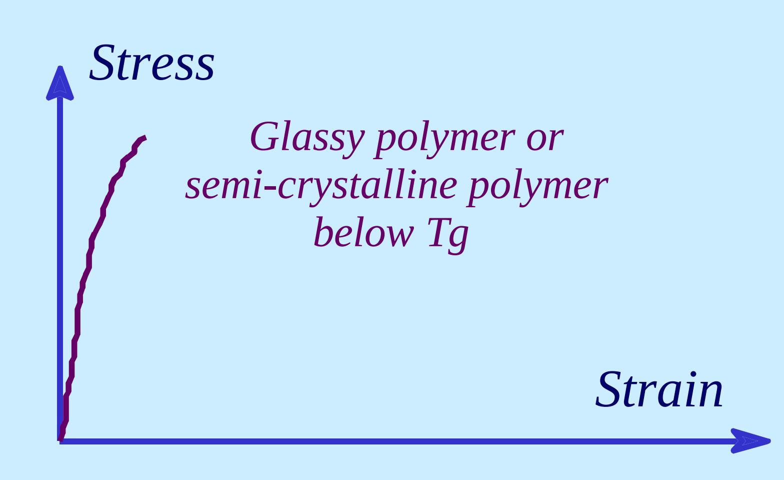
Yielding in Polymers



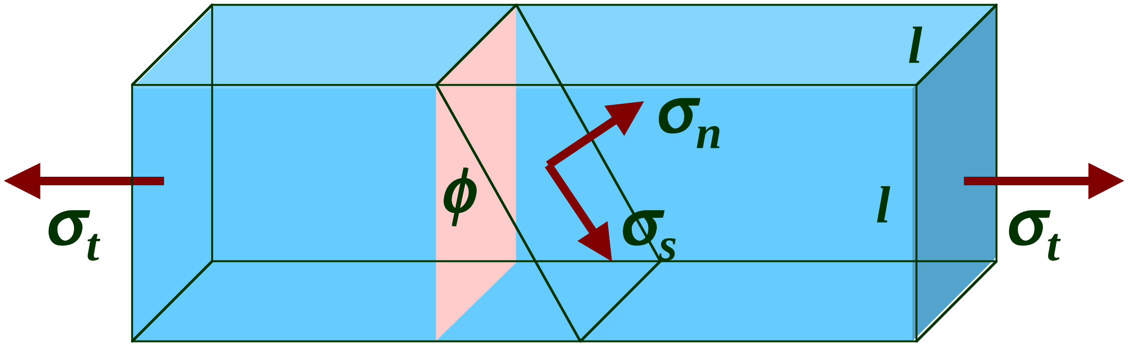
Polymers nearly always yield and plastically deform to some degree during failure.

The mechanism by which this occurs is differs according to structure and morphology.

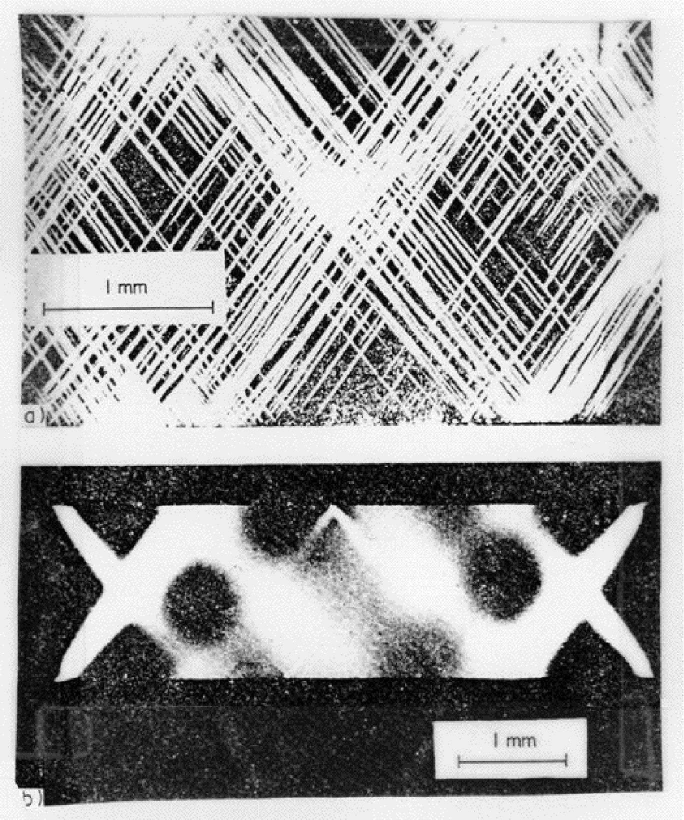
In rigid polymers you usually don't see a yield point; instead as the stress on the sample increases there is a deviation from Hookean behavior followed by permanent deformation of the sample. This can occur by shear yielding

In brittle polymers there is another yielding mechanism called crazing. The two processes are not mutually exclusive and both can show up together or one can precede the other.

Shear Yielding in Glassy Polymers



There are shear forces present in a material even when it is subjected to a simple tensile elongation.



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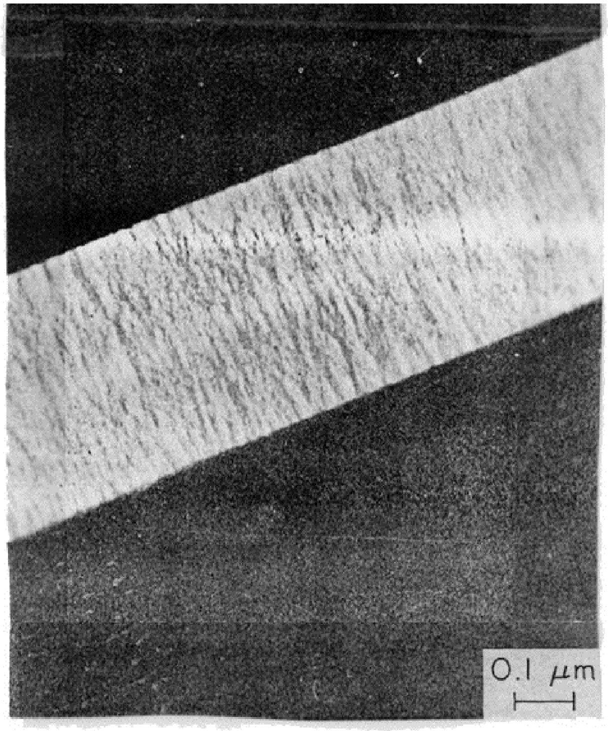
I’m Going Crazy and Cracking Up!



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In many brittle polymers at stresses just below fracture a “whitening” of the sample occurs.

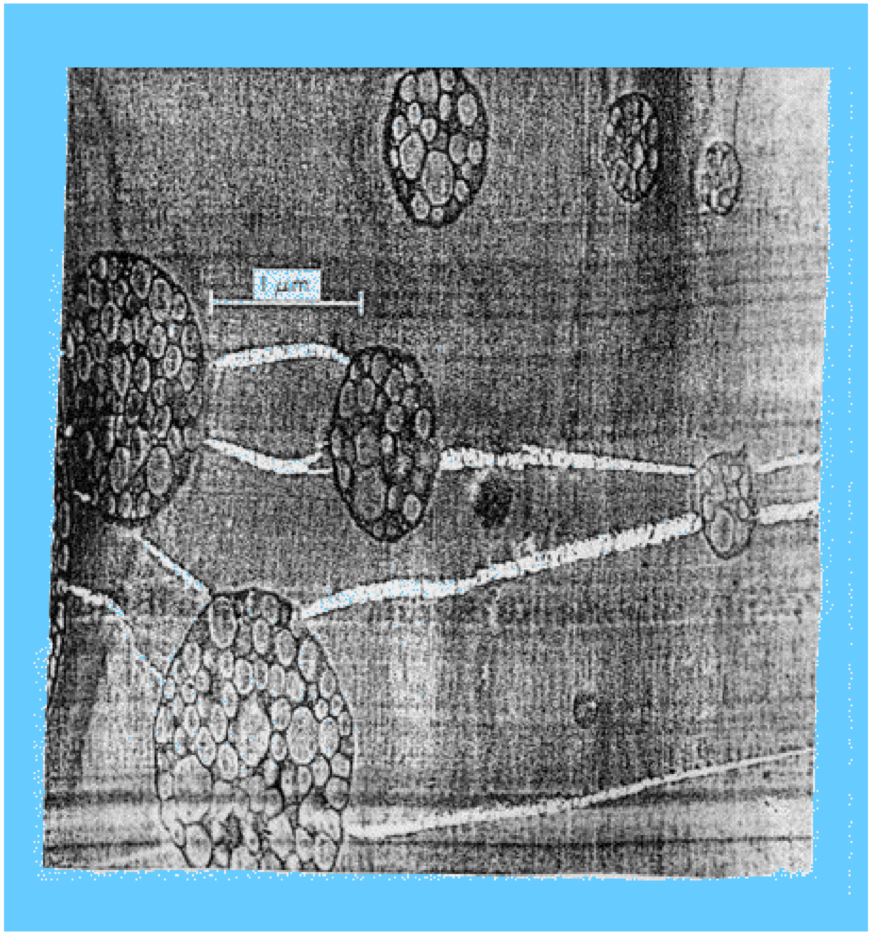
This is due to crazing, where microscopic crack-like entities form in a direction perpendicular to the applied stress. These tiny cracks scatter light, thus giving an opaque or white-like appearance to the sample.

If examined under the microscope tiny fibrils can be seen spanning the cracks, helping to hold them together. Obviously, the formation of these tiny cracks and fibrils absorbs energy, making these materials tougher than they otherwise would be.

Tough Polymers

- The formation of energy absorbing crazies in brittle polymers can be promoted by presence of small amounts of rubber in small phase separated domains.

- These domains act as stress concentrators, a result of the large mismatch between the modulus of the rubber and the rigid matrix, which, in turn, promotes the formation of crazes throughout the body of the sample.



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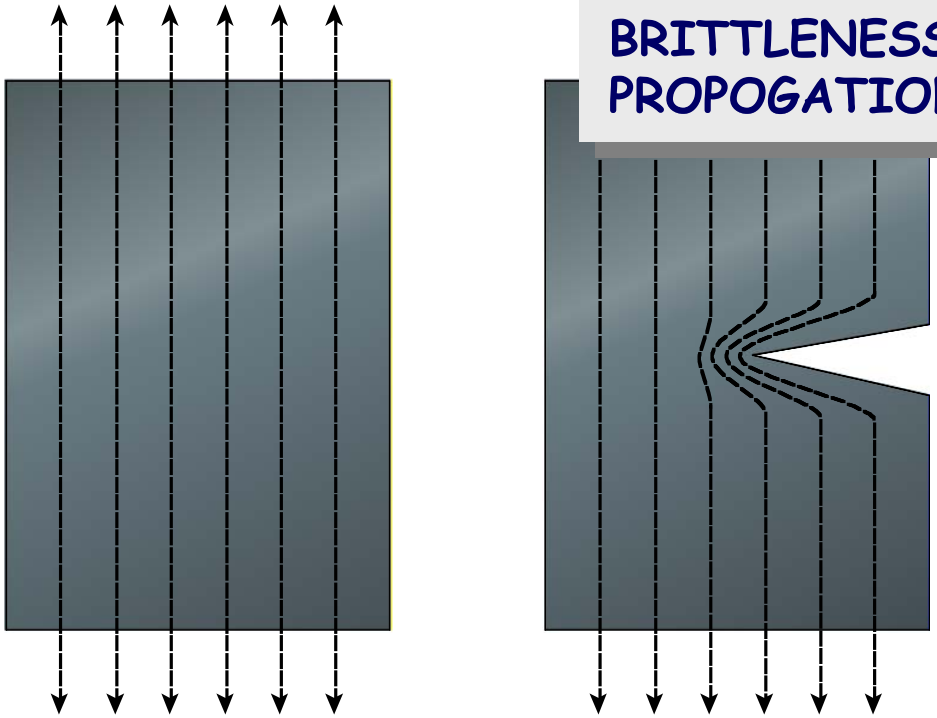
More Toughness - or how to Stop Cracks

Pliny - to determine if a diamond is genuine, it should be put on an anvil and hit very hard with a hammer

- Not a reliable test !!!

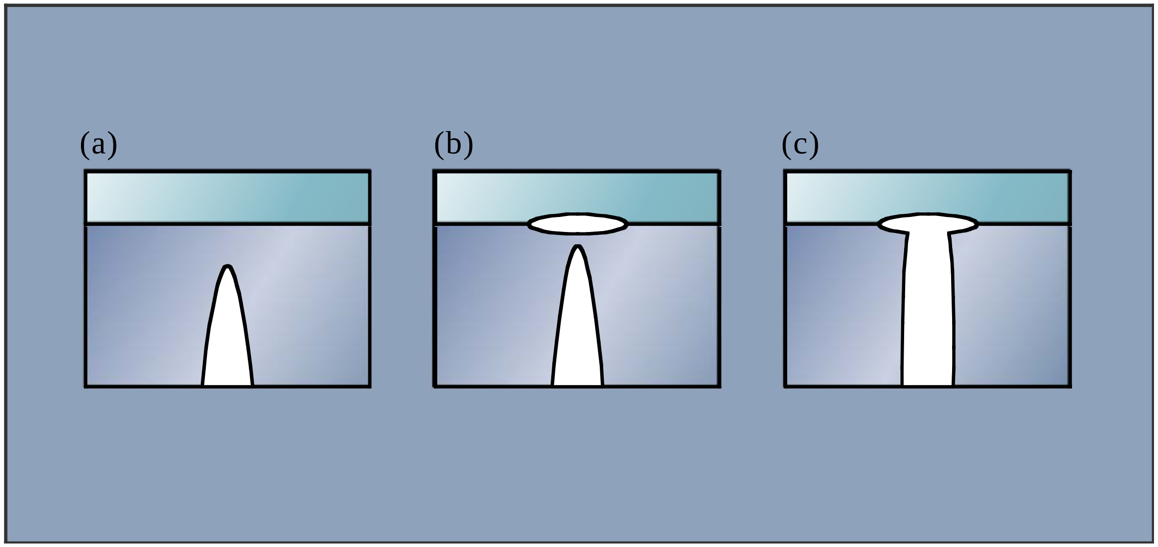
CONFUSES BRITTLENESS AND HARDNESS

BRITTLENESS - LACK OF RESISTANCE TO THE PROPOGATION OF CRACKS



Toughness - or how to Stop Cracks

Now consider two brittle materials;window glass (in the form of fibers) and a thermosetting polyester resin (high Tg). Disperse one in the other, but keep the interface weak.



Relaxation in Polymers

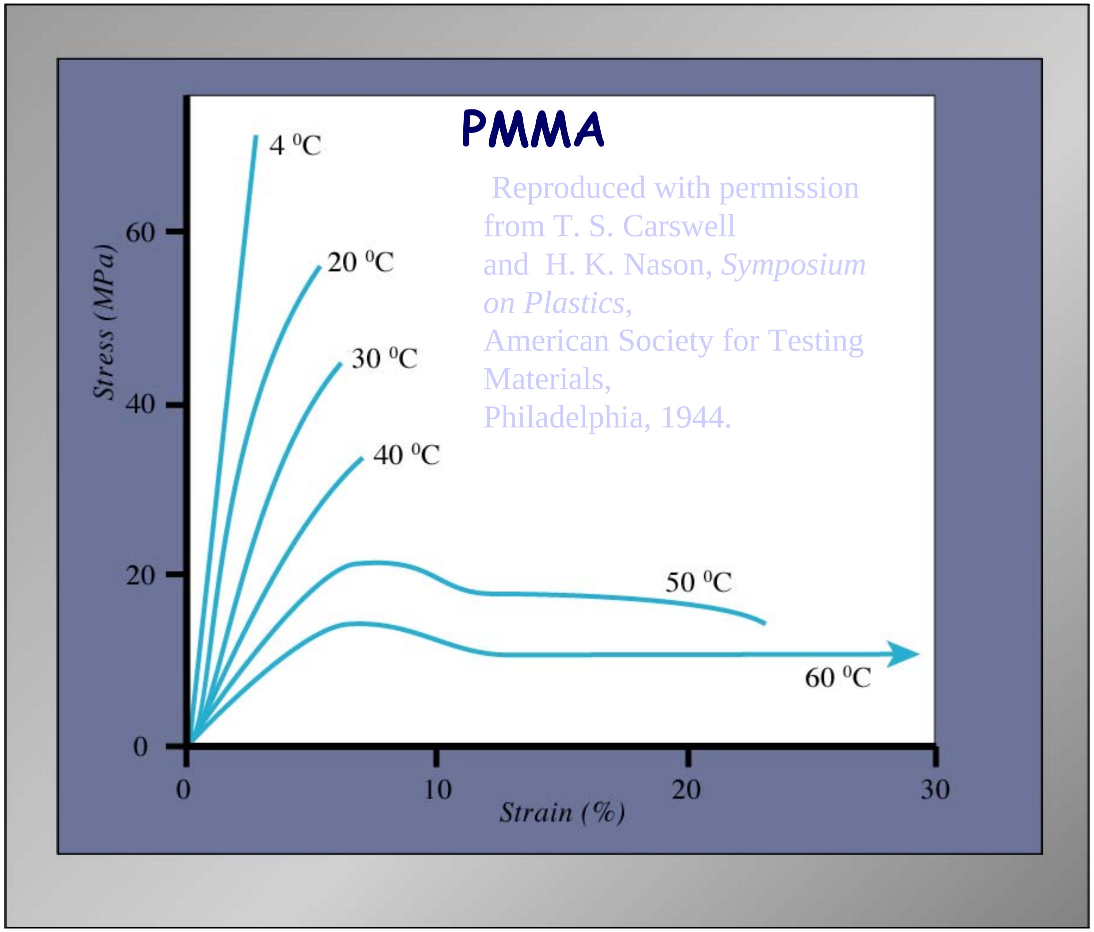
The processes of yielding we have briefly described depends upon specific relaxation processes.

By relaxation we mean any sort of time dependent molecular transition or rearrangement, such as a change in the conformation of a chain, crystalline slip, chain sliding, and so on.

We don't mean this

Yielding phenomena therefore depend upon the rate at which a polymer is being strained relative to the time required for these relaxations to occur - the relaxation rate.

The Effect of Heat and Plasticizers on the Mechanical Properties of Glassy Polymers



PMMA

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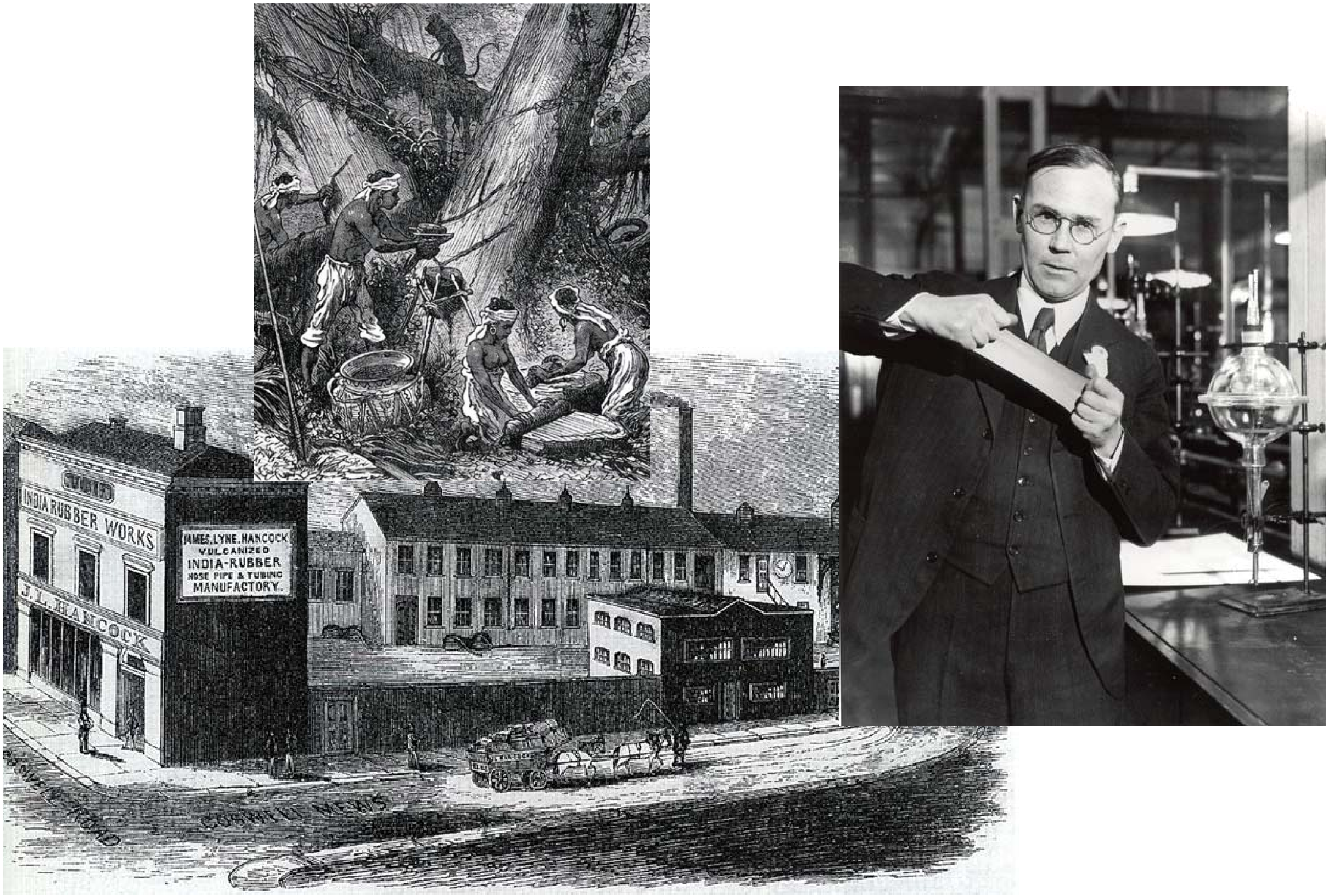
Questions ;

Which curve would best represent the behavior of pure PVC at room temperature?

What would happen if the PVC was now mixed with a plasticizer?

Rubber Elasticity

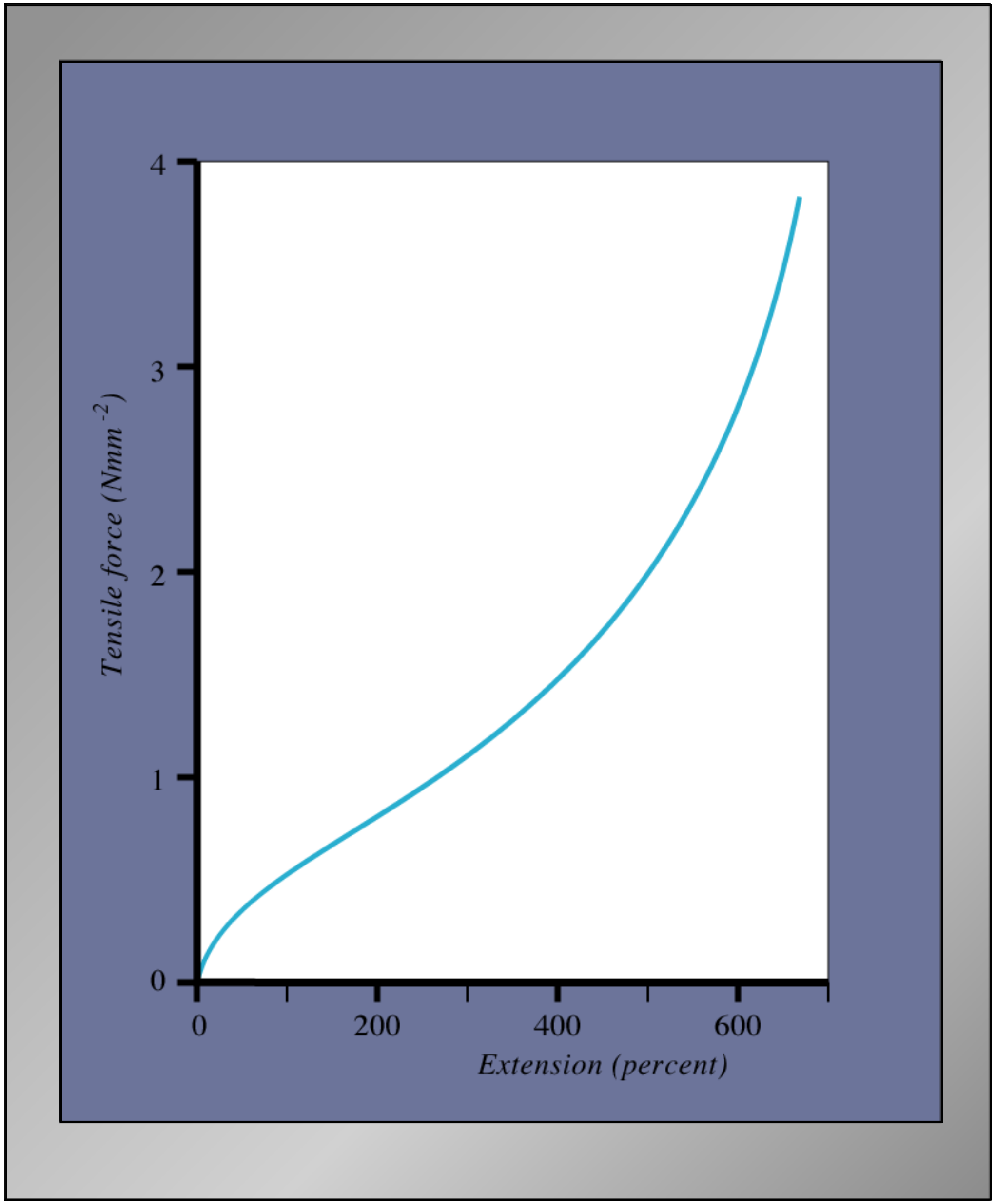


Linear and Non-Linear Behavior

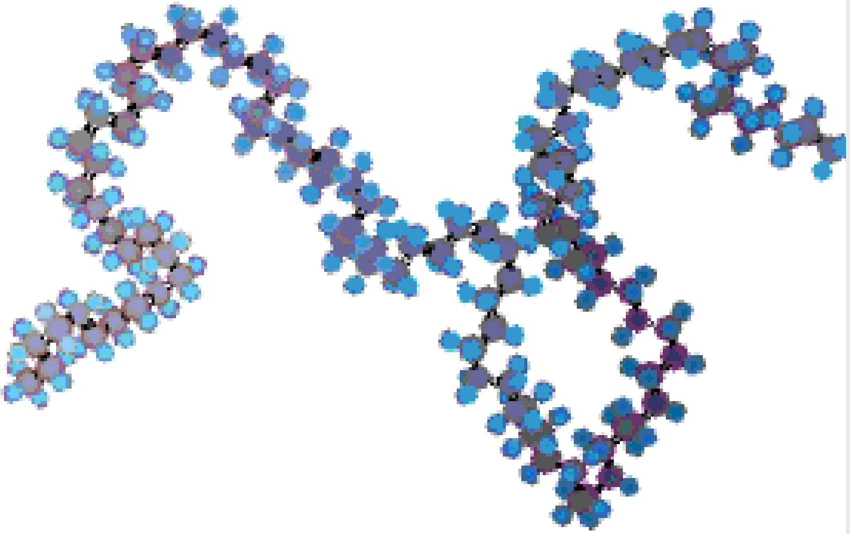
Rubbers also have strong stiff (covalent) bonds, but they are capable of stretching more than 500% elastically.

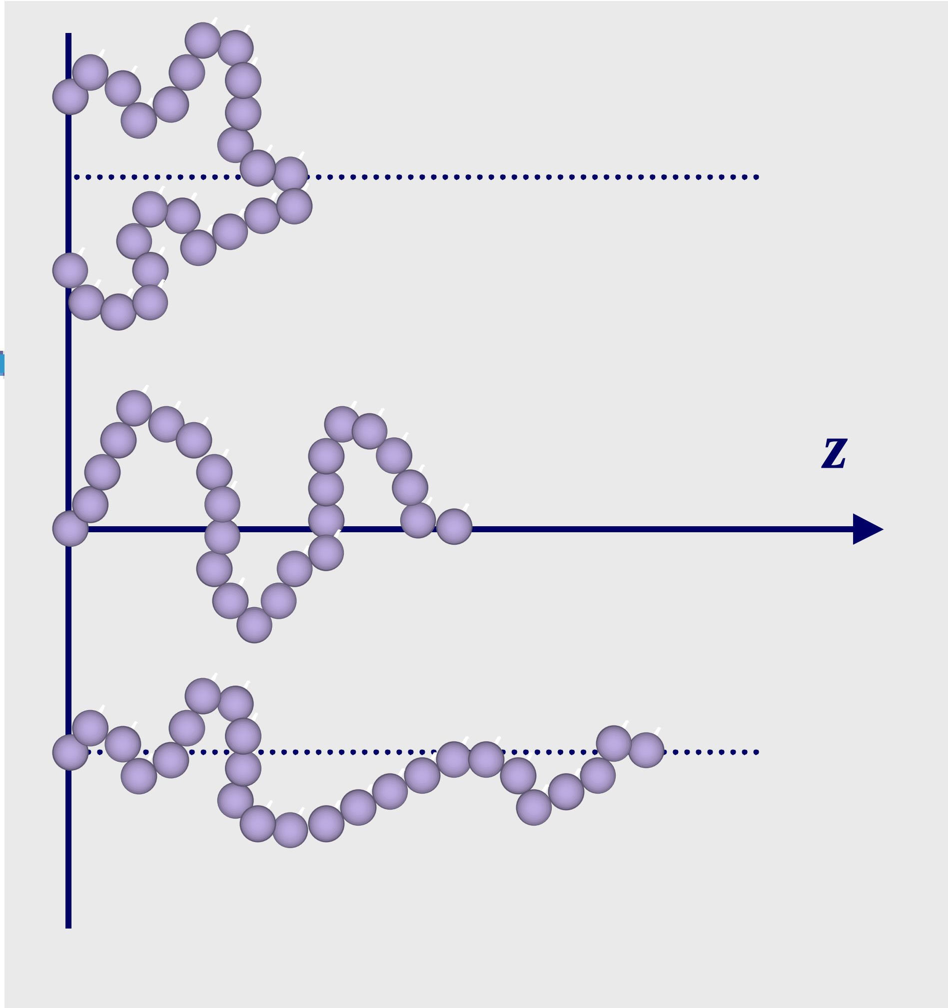
Instead of just minor deviations from Hooke's law we see behavior that is markedly non-linear.

The bonds in these materials cannot be stretching this much, so what's going on?



Chain Conformations and Entropy





Thermodynamics Revisited

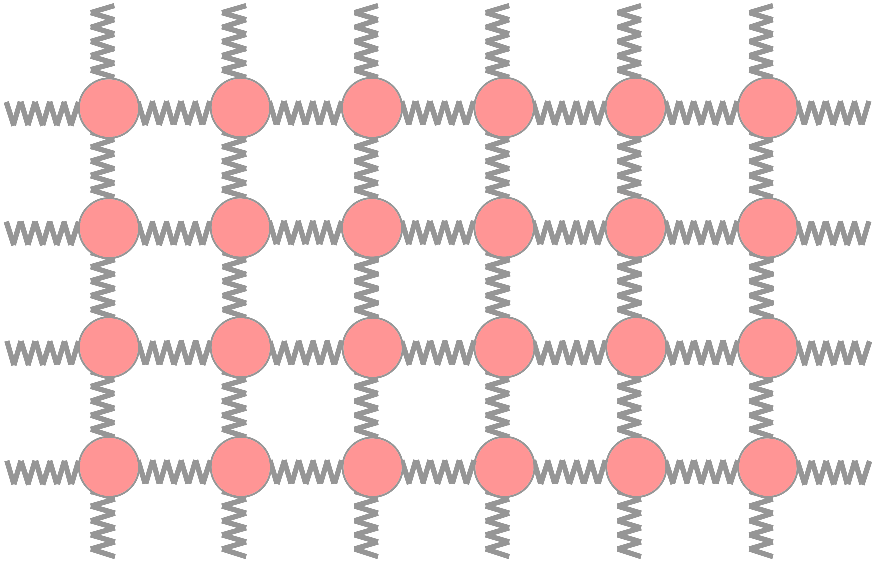
$$F = E - TS$$

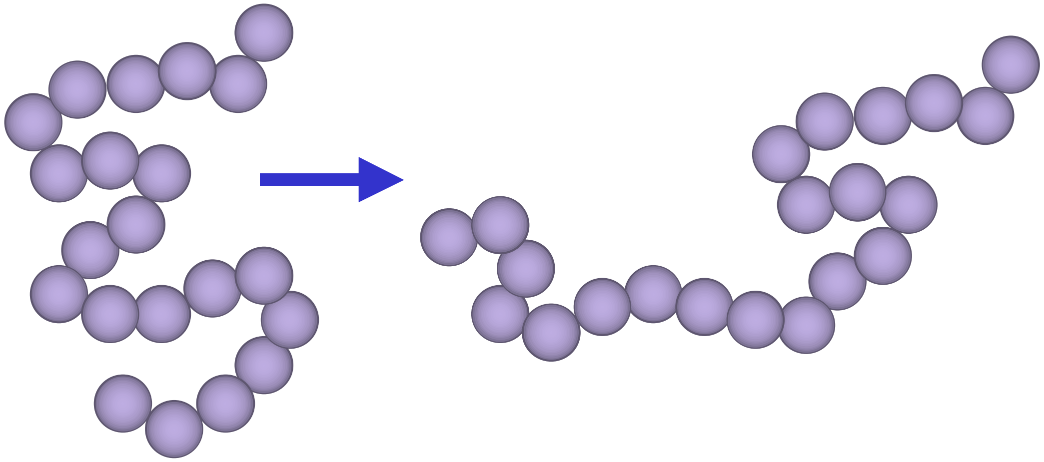
Stretching this sample, which we'll say has a length L, changes its free energy and the relationship of this change to the applied force, f, is given by

$$f = \left(\frac{\partial F}{\partial L}\right)_{V,T} = \left(\frac{\partial E}{\partial L}\right)_{V,T} - T\left(\frac{\partial S}{\partial L}\right)_{V,T}$$

If this relationship is not familiar or obvious to you, just keep in mind that energy has the dimensions of force times distance, so that differentiating with respect to distance gives you a force.

$$f \approx \left(\frac{\partial E}{\partial L}\right)_{V,T}$$





$$f \approx -T\left(\frac{\partial S}{\partial L}\right)_{V,T}$$

Networks

Elastomeric materials are produced in the form of networks to prevent the chains slipping past one another.

Networks are not perfect.

There are all sorts of defects in the resulting network; dangling ends and loops that are not part of the network, some chains that may not be cross-linked at all, and so on. These affect properties and you get things like compression set in cushions.