BIOEN 326 2013 LECTURE 22: MOLECULAR BASIS OF ELASTICITY

Estimating Young's Modulus from Bond Energies and Structures

First we consider solids, which include mostly nonbiological materials, such as metals, plastics, ceramics, and covalently bound solids like diamonds. We will consider the molecular structure of these materials and how this determines the materials properties. First, we learn to estimate the Young's modulus of these materials from the molecular structure, which determines their behavior at sufficiently small deformations. Next we ask what happens when we deform them beyond the point where the stress-strain relationship becomes nonlinear, meaning the ratio of stress to strain is no longer constant and the Young's modulus no longer applies.

Only mechanical testing experiments can provide the exact Young's modulus of a material, but one can estimate the Young's modulus from knowledge about the molecular structure of the material. This is useful when designing a material, determining the right mechanical test for a material, or simply understanding materials properties better.

In general, materials are made up of atoms or molecules, which we call **nodes** for the purposes of this discussion, and these interact with each other through what we call **bonds**. For diamond, the nodes are the carbon atoms, and the bonds are the covalent bonds between carbon atoms. For a collagen scaffold, a node is where two fibers are cross-linked, and the bond is the length of fiber between two cross-links.

Figure 1. Idealized material structure with cubic node geometry.

Consider now an idealized material that has the nodes in a square matrix as in Figure 1. Let r_0 be the equilibrium bond length in unstressed material. What do stress, strain, and the Young's modulus mean on the nanoscale level of single bonds? If we apply a stress, σ, to the material, how much force is applied to each bond? Consider a single bond that is parallel to the direction of force. How is it spaced from the bonds that are parallel to it? Because the matrix is square, each node and thus bond has a cross-sectional area of r_0^2, so the force per bond is $f = r_0^2\sigma$. We also remember what we learned last lecture: $f = \frac{dU}{dr}$, to obtain a way to calculate stress from the energy function $U(r)$.

$$\sigma = \frac{f}{r_0^2} = \frac{\frac{dU}{dr}(r)}{r_0^2}$$

Next we ask if the resulting strain on the material is ϵ, then how much does each bond stretch? The original bond length is r_0, so it stretches $r - r_0 = \Delta r = r_0\epsilon$ by the definition of strain. Thus,

$$\epsilon = \frac{\Delta r}{r_0} = \frac{r - r_0}{r_0}$$

We can combine this to relate stress to strain using the energy function. That is, if we know $U(r)$, then we calculate the value at which this is minimum to get r_0, and then can calculate both stress and strain for any bond length r. The ratio is of particular interest:

$$\frac{\sigma}{\epsilon} = \frac{f}{r_0^2}\frac{r_0}{\Delta r} = \frac{f}{r_0(r - r_0)} = \frac{\frac{dU}{dr}(r)}{r_0(r - r_0)}$$

Depending on the Energy function, this may not be a linear relationship. However, for sufficiently small deformations, we can use the linear approximation: $f = \frac{dU}{dr} = k(r - r_0)$, where $k = \frac{d^2U}{dt^2}(r_0)$. For these small deformations,

$$\frac{\sigma}{\epsilon} = \frac{k(r - r_0)}{r_0(r - r_0)} = \frac{k}{r_0} = \frac{\frac{d^2U}{dr^2}(r_0)}{r_0}$$

This is a constant relationship between stress and strain, and thus is the Young's modulus:

$$E = \frac{k}{r_0} = \frac{\frac{d^2U}{dr^2}(r_0)}{r_0}$$

Thus, we can use the full version of the energy function to relate stress to strain, and can use the linear spring form to estimate the Young's modulus.

Limitations:

If a material is stretched so that the bonds are stretched beyond the linear spring approximation, the linear approximation will not be valid, and the material will show nonlinear properties and eventually fail.

This derivation assumed that the material was a perfect square lattice, but most materials have different crystalline lattices or even noncrystalline lattices. This introduces some error to our calculation. The area may not be exactly r_0^2, and bonds may be angled relative to the direction of force. Indeed, the material may stretch as bond angles change as well as when bond length increases, as in Figure 2.

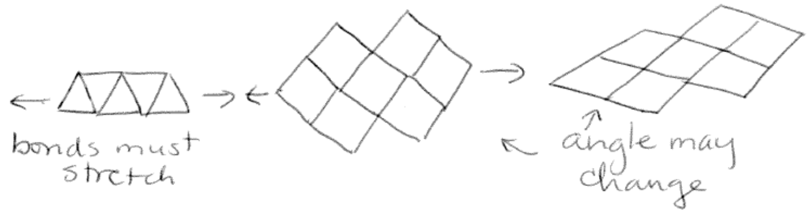


Figure 2. Other bond-node geometries affect these calculations.

This derivation also assumed that all bonds were the same. In fact, many materials, especially biological materials, have many different types of bonds. In this case, the weakest of the bonds is the primary determinant of the Young's modulus, just as the stiffness of springs in parallel is dominated by the softest springs. Thus, for mixed materials, we consider the mean length between the softer bonds.

Molecular Structure and Elasticity of Various Solids

Now we will consider the different types of bonds that make up materials, and learn their energy functions and typical parameters of these functions so we can estimate the Young's modulus.

Covalent solids:

Covalent solids are held together by covalent bonds. Covalent bond energy is approximated by a spring, with $U(r) = \frac{1}{2}k(r - r_0)^2$, where k is the spring constant of the bond. Since this bond energy is already a linear spring form, we obtain the same answer if we use the linear approximation or full function: $E = k/r_0$.

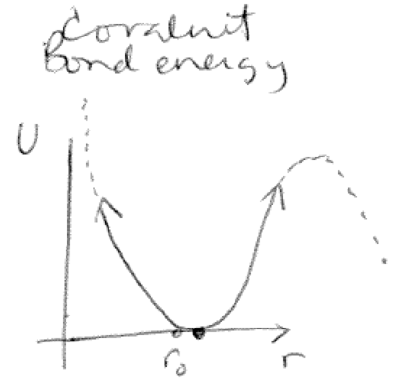


Figure 3. Covalent Bond energy

An example of a covalent solid is a diamond in which carbon atoms form a tetrahedryl lattice. For a typical covalent solid, $k = 150\,N/m$ and $r_0 = 1.5e - 10\,m$. Thus, $E \approx 10^{12}\,N/m^2$. Note that $10^9 N/m^2$ = 1 GPa, so we would expect a covalent solid to have a Young's modulus of around 1000 GPa. In fact, diamond has a modulus of E = 1200 GPa, so this estimate is good.

Metallic solids.

In metals, the electrons in the outer valence shells are shared by many atoms and thus are delocalized. Thus, while the atoms still form regular crystal structures like covalent solids, they tolerate irregularities so that the overall structure is more disordered. The bond stiffness in metallic solids is weaker than covalent, at about 15 – 75 N/m, so the Young's moduli of metals are several fold weaker than for covalent solids.

Ionic solids

Ionic solids include salts like NaCl and ceramics like ZrO2 (zirconia), Alumina, and hydroxyappetite, which forms the inorganic part of bone. The crystalline structures of these solids have alternating positive and negative ions.

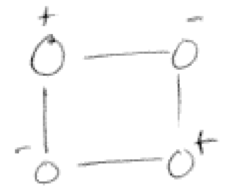


Figure 4. Ionic Solid

The bond force between each pair is a complicated sum of the following forces:

- The attractive force between that pair, which is $U = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r}\frac{1}{r}$, where q_1 and q_2 are the charges of the two ions (e.g. 1.6e-19 C for Na), $\epsilon_0 = 8.3e - 12\frac{C^2}{Nm^2}$ is the permittivity of free space, $\epsilon_r = 6$ is the dielectric constant of typical salts.
- The van der Waals repulsion between that pair of atoms
- The sum of attractive and repulsive forces of neighboring atoms, which are significant for quite some distance since they only drop with the inverse of the distance.

Calculating these forces from the information above is beyond the scope of this class, but in general, ionic bonds stiffnesses are known to be around 8 to 24 N/m and bond lengths are also longer than in covalent or metallic bonds, so salts are much softer. For example, the Young's modulus of NaCl is 40 GPa.

Van der Waal's solids

Finally, consider a van der Waal's solid, such as a hard plastic. These materials are made up of polymers that have many intramolecular covalent bonds, but these interact through intramolecular and intermolecular **van der Waal's** (VDW) bonds. As we will see below, the VDW bonds are weaker than the covalent bonds, so they determine the Young's modulus of VDW solids such as hard plastic.

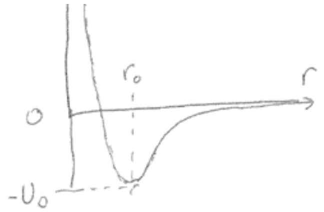
Element	radius (Å)	energy (J)
H	1.20	3.0E-22
C	1.70	7.2E-22
N	1.55	4.7E-22
O	1.52	4.1E-22

The **Lennard Jones Potential** approximates VDW energies:

$$U(r) = U_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right],$$

Here, $r_0 = r_i + r_j$ is the sum of the VDW radii of the two atom types. $U_0 = \sqrt{U_i U_j}$, where U_i is the bond energy for atom type i. For example, a N-C bond would have $r_0 = 1.55 + 1.7 = 3.25$Å and $U_0 = \sqrt{4.7E-22 * 7.2E-22} = 5.8E-22J$. While energy estimates vary by method and covelent connections, the table to the right provides values for some atom types for r_i and U_i .

Note from the equation and the figure that:



$U(0) = U_0(\infty^{12} - \infty^{6}) = \infty$

$U(r_0) = U_0(1-2) = -U_0$

$U(\infty) = U_0(0-0) = 0$

In the homework, you will show that VDW solids have Young's moduli of a few GPa.

Proteins are polypeptides, which are covalent polymers, but fold up into alpha helices and beta sheets, that are held together by hydrogen bonds. Finally, these secondary structure elements are held together by VDW interactions, at least in globular proteins. The VDW interactions are the softest of these, so globular proteins have a Young's modulus of a few GPa, and are fairly isotropic. For examples, the Young's modulus of microtubules and actin filaments have both been measured at around 2 GPa. However, proteins are not always globular, and can thus have a wide range of behaviors. We will consider many of these in the next few lectures.

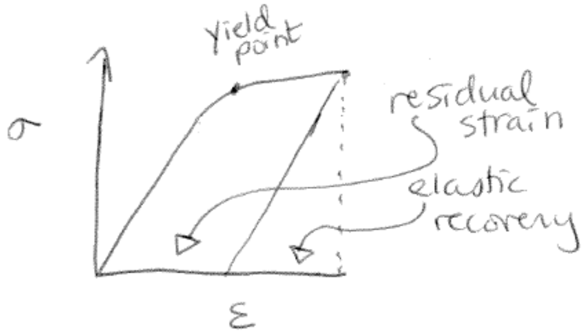
Hydrogels

Like plastics, hydrogels are made up of polymers. However, the polymers are hydrophilic and soak up water. We learned before that water causes viscosity in these materials. The presence of water between the polymers also prevents most of the intramolecular and intermolecular van der Waals bonding, so a mixture of these hydrophilic polymers would form a viscous liquid instead of a hard plastic. Cross-linking between the polymers creates nodes, so the polymers form bonds that can be addressed quantitatively as described above. Hydrogels are often very soft relative to other surfaces, and can tolerate large strains, even greater than 1. The next lectures will address the nonlinear behaviors that often arise for hydrogels, including biological tissues.

Review of Nonlinear Materials Properties and Failure

Nonlinear Materials Properties.

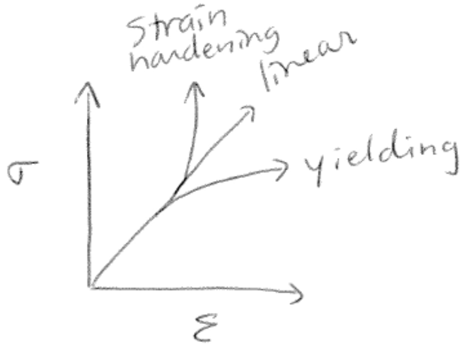
Hooke's law ($\sigma = E\epsilon$) applies below a critical point called the **proportional limit** characterized by the stress and strain at this point: σ_{PL} and ϵ_{PL}. Above the proportional limit, the stress-strain relationship becomes **nonlinear**, meaning the ratio of stress to strain is no longer constant, but either increases or decreases with further stress or strain. For some materials, the proportional limit is clearly defined, while for others, the boundary is less clear and can only be identified after defining an allowable deviation from linearity.



In the nonlinear regime above the proportional limit, we cannot define a Young's Modulus, since by definition that requires a constant ratio of stress to strain. Instead, we define the **tangent Young's modulus** as the slope of the stress/strain curve: $E_T = d\sigma/d\epsilon$.

If the tangent Young's modulus decreases with strain ($d^2\sigma/d\epsilon^2 < 0$), we refer to this as **yielding**.

If the tangent Young's modulus increases with strain ($d^2\sigma/d\epsilon^2 < 0$), we refer to this as **strain hardening**.



Below a critical point called the **elastic limit**, the material relaxes back exactly to its original shape when force is removed. The elastic recovery occurs because the bonds described above never break within this limit, but instead are simply stretched, so return to the original low-energy position in the absence of force, which is the equilibrium bond length. Usually, all deformations below the proportional limit are **elastic**, so one can usually guaranteed that the material is undamaged as long as the stress is still proportional to the strain during loading.

If a material is stretched beyond a critical point, the atomic or molecular bonds break. For covalent solids, metals, plastics and ceramics (the materials we discussed on Friday), this occurs at about the proportional limit; that is, the bonds break shortly beyond the point where they are stretched beyond the linear range. We will see that this is not the case for most gels and soft and biological materials.

For **ductile** materials, bonds can reform between two atoms or molecules that were not previously bonded. In this case, the material deforms substantially beyond the proportional limit. But, when the force is removed, it will not return to its original shape, since the molecular bonds have reformed into new connections that determine the shape.

The fractional change in length after stress is removed is called **residual strain**. Irreversible deformation like this is referred to as **plastic deformation**.

However, as the plastically deformed material is relaxed, there is a small amount of **elastic recovery** as the bonds return to their equilibrium length. However, due generally in the amount expected from the proportional limit.

The **yield point** (characterized by **yield stress $\boldsymbol{\sigma_Y}$** and **yield strain $\boldsymbol{\epsilon_Y}$**), is the point between the elastic and plastic regime. While the proportional limit can be identified while increasing the load on a material, the yield point can only be identified when the load is added and then removed. Thus, a material is repeatedly stretched and relaxed to increasingly greater strains to identify the yield point. The exact yield point is impossible to identify due to errors in measurements, so by convention, it is approximated by the elastic limit, which is defined as the stress and strain that will cause a permanent 0.2% deformation in the material upon relaxation.

If the relaxed material is now stressed again below the yield point, it behaves elastically.

For **brittle** materials, the rupture of bonds causes the material to **fracture**, or break catastrophically along the points of most stress. In brittle materials, bonds do not readily reform, so the material fails completely when the original bonds are overstretched.

Even ductile materials will fracture eventually, as the material is deformed in some way that does not allow bonds to reform.

The **maximum stress $\boldsymbol{\sigma_{MAX}}$** is the highest stress the material can withstand prior to fracture. Because some materials may reduce the strain prior to fracture, the maximum stress is not necessarily the stress at fracture. The **breaking strain $\boldsymbol{\epsilon_{MAX}}$** is the strain at fracture.

The **tensile strength** of a material is σ_{MAX} during tension, while the **compressive strength** is σ_{MAX} for compression. These are often not the same.

Molecular Basis of Plastic Deformation and Failure

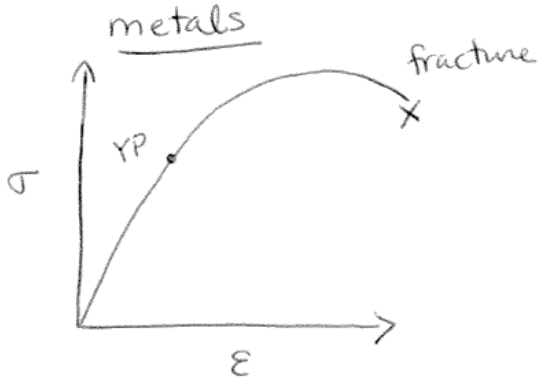
Above the proportional limit, different materials behavior very differently in terms of whether they yield or strain harden and where they fracture relative to their elastic limit (brittle vs ductile). Thus, we now consider specific materials.

Note that you can calculate the strain at the proportional limit by dividing the yield stress or by the Young's modulus, since the material are generally linear before they yield.

Metals

The shared electrons in metal atoms allows bonds to easily break and reform so that the material can rearrange along slip planes when exposed to shear stress:

Metals are usually polycrystalline, with many small regions that are crystalline and regular, but each small region is oriented randomly, which is why the crystalline materials is still isotropic. The stress needed to cause a small region to slip depends on its orientation relative to the stress, so that only a few ideally oriented ones slip at the plastic limit (yield point), but more and more slip as stress increases higher. Because of this, the stress-strain curve gradually slopes for typical metals:

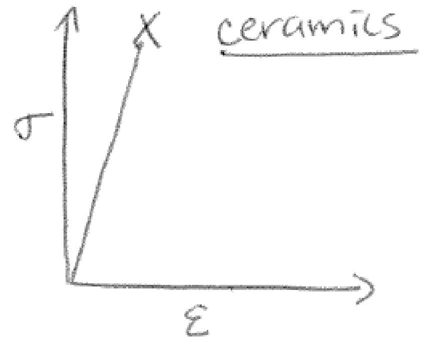


To understand how much deformation is allowed before slippage, note that the yeild stress of aluminum is 95 MPa, while the Young's modulus is 69 GPa, so the yield strain is about 95E6/69E9 ~ 0.1%. For stainless steel, the value is 180 GPa and 502 MPa, or 0.3%.

Thus, metals can only deform by 0.1% to 0.3% before they undergo plastic deformation, but do not fracture because they are ductile.

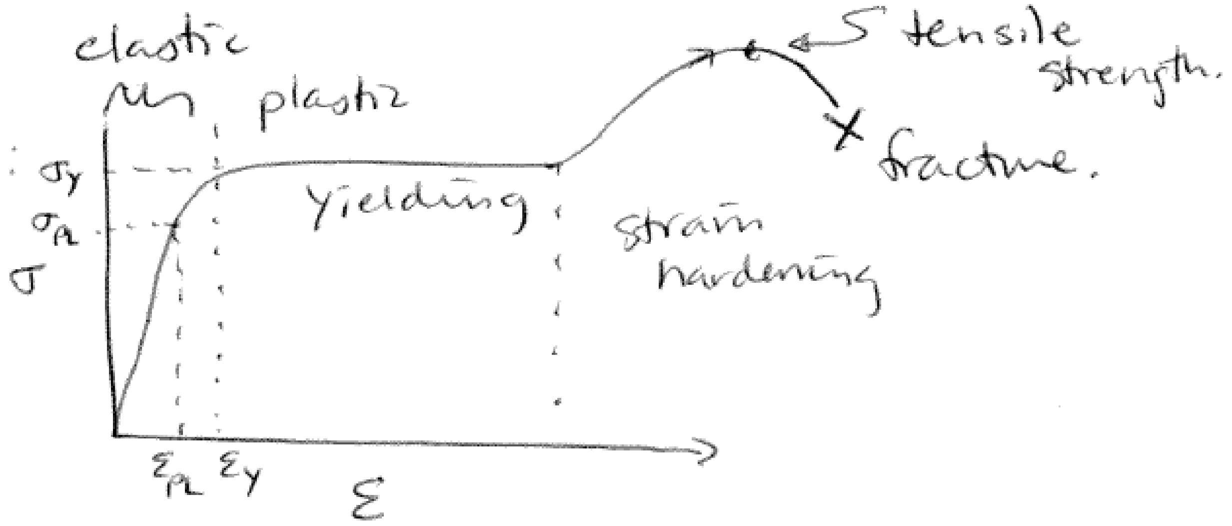
Ceramics.

In contrast, ceramics are generally resistant to slip along planes because of the electrostatic interactions. They also leave the proportional limit at about 0.1 to 0.3% strain. However, the resistance to slip means they are brittle and fracture when the bonds break. Some polymers are also brittle.



Amorphous polymers.

Most polymers are amorphous, with the covalently bonded polymers oriented randomly, and interactions within and between chains are primarily VDW interactions. Because VDW interactions are long range and packing is noncrystalline, the polymers can slide along each other, alowing yielding. The yielding is plastic because the VDW bonds have broken and reformed. Finally, because there is no crystaline organization, the orientation of the stress to the material doesn't matter like in metals, so the material continues to deform at the yield stress. Thus, the stress-strain curve flattens out and the tangent Young's modulus becomes nearly zero.



Nevertheless, above some point, the polymers become aligned in a way that limits further slipping, which causes the plastic to exhibit strain hardening.

However, as the material continues to stretch, the cross-section gets smaller due to the lateral strain. At sufficiently large deformations, this effect cannot be ignored. The **true stress** is the force divided by the actual cross-sectional area measured at that force. However, most graphs, including that above, display the **engineering stress**, which is defined to be the force applied divided by the original unstressed cross-sectional area. The engineering stress represents the direct measurement in a tensile test, without needing to measure the cross-sectional area at each point. It also can predict how a object will behave in an engineering application. As the cross-sectional area decreases, and the material is already yielding, the true stress will stay the same but the engineering stress will drop as shown in the sketch above, due to the ever smaller cross-section. In an engineering situation, this drop leads to catastrophic failure as the member supports less and less stress. As for all materials, sufficient stress and strain will eventually cause fracture.

Polymers typically have a much higher yield strain than do ceramics or metals, allowing 1 to 3% strain.