3.22 Mechanical Properties of Materials
Spring 2008

Problem Set #2

Due: Tuesday, March 4 by 5:00 PM

1. You did such an outstanding job in the engineering department at *Unique Unicycles* that they gave you a promotion to the R&D department. Your first assignment there is to study a new material developed by your competitors *Un-Unique Unicycles*. The material is a composite composed of unidirectional fibers in a polymer matrix (Fig. 1). While another research scientists determines what the fibers and matrix are, your boss Dr. Van Vliet asks you to determine the stiffness tensor components for such a structure in terms of Young's Modulus and Poisson's ratio.
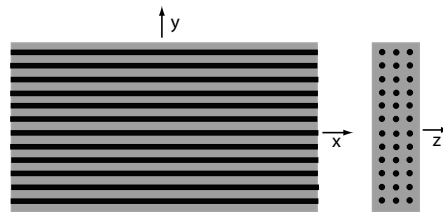

Figure 1: A composite material comprised of unidirectional fibers in a matrix.

Solution: From Fig. 1 we see that there is some symmetry to this structure. In particular, it is composed of three orthogonal axes with four-fold rotational symmetry along the x axis and two-fold rotational symmetry along the y and z axes. Therefore this structure is tetragonal and has six independent elastic constants.

Consider the strain if the composite is loaded by a force F along the x axis (which I will refer to as the 1-direction). If the fiber and the matrix are well bonded, they experience the same strain such that

$$\epsilon_{11} = \epsilon_{M11} = \epsilon_{F11}$$

where $\epsilon_{11}, \epsilon_{M11}$, and ϵ_{F11} is the strain in the composite, matrix and fiber, respectively.

However, the resulting stress in the fibers is different because of the different Young's moduli in the fibers and matrix. (Note that because we know nothing of the fiber or matrix microstructures we are treating them as isotropic.) The stress in the fiber σ_{F11} and matrix σ_{M11} are therefore

$$\sigma_{F11} = E_F \epsilon_{11} \text{ and } \sigma_{M11} E_M \epsilon_{11}$$

where E_M and E_F are the Young's moduli of the matrix and fiber, respectively.

The total applied force must be in equilibrium with the total force due to the stresses in the fiber and matrix. The internal force is given by multiplying the stress by the area of the fiber or matrix it acts on. If the total cross-sectional area of the composite is A, then the cross-sectional area of the fibers and matrix are given by the total area multiplied by the volume fraction of fiber or matrix. Thus the force acting on the fibers and matrix is given by

$$F_{11} = V_F A \sigma_F + V_M A \sigma_M$$

Substituting our definitions of strain and dividing by A gives

$$\sigma_{11} = (V_F E_F + V_M E_M)\epsilon_{11}$$

From this equation, we can see that the modulus of the composite along the x axis E_1 is

$$E_{11} = V_F E_F + V_M E_M$$

Now consider if the composite is loaded along the y axis (which I will refer to as the 2-direction). The fibers and matrix will experience different strains. The total strain ϵ_2 will be the sum of the strain in each component (multiplied by the volume fraction) such that

$$\epsilon_{22} = V_F \epsilon_{22F} + V_M \epsilon_{22M}$$

The stress applied σ will be distributed equally over both the fibers and matrix and therefore we can write

$$\epsilon_{22} = \frac{\sigma V_F}{E_F} + \frac{\sigma V_M}{E_M}$$

From this equation, we see that the modulus along the y axis E_2 is

$$E_{22} = \frac{E_F E_M}{V_M E_F + V_F E_M}$$

Futhermore, because the "unit cell" of the composite is the same along the y and z direction (e.g. the composite has a tetragonal structure), $E_{22} = E_{33}$.

We can also do a similar analysis to determine the shear moduli G_{12} and find

$$G_{12} = \frac{G_F G_M}{V_M G_F + V_F G_M}$$

where G_M and G_F are the shear moduli of the matrix and fibers, respectively. Again because of symmetry, we know that $G_{12} = G_{13}$.

For the shear modulus G_{23}, we know that the yz plane (or 23 plane) is an isotropic plane. Therefore

$$G_{23} = \frac{E_{22}}{2(1 + \nu_{23})}$$

where ν_{23} is Poisson's ratio that relates the strain in the 2 and 3 direction.

There will also be other Poisson effects in the composite. For example, the ϵ_{22} and ϵ_{33} will be equal to $-\nu_{12}\epsilon_{11}$ for an applied strain $\epsilon_{11} = \frac{\sigma_{11}}{E_{11}}$. (Note that because of symmetry $\nu_{12} = \nu_{13}$.)

With all of this information, we can begin to construct a compliance tensor for the composite

$$
S_{\mathrm{ij}} = \begin{vmatrix}
\frac{1}{E_{11}} & -\frac{\nu_{12}}{E_{11}} & -\frac{\nu_{12}}{E_{11}} & 0 & 0 & 0 \\
-\frac{\nu_{12}}{E_{22}} & \frac{1}{E_{22}} & -\frac{\nu_{23}}{E_{22}} & 0 & 0 & 0 \\
-\frac{\nu_{12}}{E_{22}} & -\frac{\nu_{23}}{E_{22}} & \frac{1}{E_{22}} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{G_{23}} & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{G_{12}} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{1}{G_{12}}
\end{vmatrix}
$$

Note the factors of two in S_{44}, S_{55} and S_{66}. These are a consequence of converting from mathematical strain to engineering strain.

With the exception of our Poisson ratios, the other terms in this tensor are in terms of the component properties and volumes. Let us now do this for the Poisson ratios.

Consider a sample section of the composite (Fig. 2) with a stress applied along the x axis. The sum of the change in length of the fibers (δ_{F}) and matrix (δ_{M}) in the y direction will equal the change in length of the composite (δ_{C}) along this direction. We can write these changes as

$$
\begin{aligned}
\delta_{\mathrm{F}} &= t_{\mathrm{F}}\epsilon_{22\mathrm{F}} = -t_{\mathrm{F}}\nu_{\mathrm{F}}\epsilon_{11\mathrm{F}} \\
\delta_{\mathrm{M}} &= t_{\mathrm{M}}\epsilon_{22\mathrm{M}} = -t_{\mathrm{M}}\nu_{\mathrm{M}}\epsilon_{11\mathrm{M}} \\
\delta_{\mathrm{C}} &= t_{\mathrm{C}}\epsilon_{22} = -t_{\mathrm{C}}\nu_{12}\epsilon_{11}
\end{aligned}
$$

We know that along the x axis, $\epsilon_{11\mathrm{F}} = \epsilon_{11\mathrm{M}} = \epsilon_{11}$ and therefore

$$
t_{\mathrm{C}}\nu_{12} = t_{\mathrm{F}}\nu_{\mathrm{F}} + t_{\mathrm{M}}\nu_{\mathrm{M}}
$$

or

$$
\begin{aligned}
\nu_{12} &= \frac{t_{\mathrm{F}}}{t_{\mathrm{C}}}\nu_{\mathrm{F}} + \frac{t_{\mathrm{M}}}{t_{\mathrm{C}}}\nu_{\mathrm{M}} \\
&= V_{\mathrm{F}}\nu_{\mathrm{F}} + V_{\mathrm{M}}\nu_{\mathrm{M}}
\end{aligned}
$$

Once again, because of symmetry $\nu_{12} = \nu_{13}$ as we have implied already in writing the compliance tensor as we did.

The Poisson ratio for the isotropic plane ν_{23} is a little more complicated but if similar principles are used, we find

$$
\nu_{23} = \frac{V_{\mathrm{M}}\nu_{\mathrm{M}}E_{\mathrm{F}} + V_{\mathrm{F}}\nu_{\mathrm{F}}E_{\mathrm{M}}}{V_{\mathrm{F}}E_{\mathrm{M}} + V_{\mathrm{M}}E_{\mathrm{F}}}
$$

With all the composites elastic constants now defined in terms of the volume fraction, Young's moduli, shear moduli, and Poisson's ratios of the matrix and fiber, we can compute the stiffness tensor C_{ij} by taking the inversion of the compliance tensor S_{ij}. This can be done by hand, but would be more easily done using some mathematical software such as Mathematica *or* Maple. *As you have found, the inversion is a large messy matrix which I will not present.*
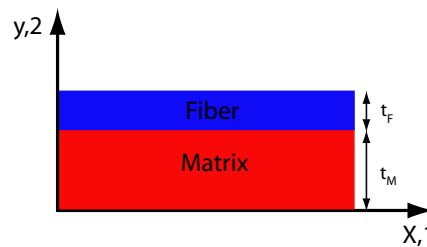

Figure 2: A sample section of the composite.

2. Two isotropic materials (A & B) are being considered for use in shoe insoles. When used as insoles the average strain with respect to time $\epsilon(t)$ of the materials is that presented in the spreadsheet posted on the MIT Server (2-2.xls).

   (a) Derive a model that accurately describes each material's response to the applied stress. Plot the result of your model along with the given data.

   Solution: Material A has an immediate response to the stress and strain is constant with time. We recognize this behavior as characteristic of a linear elastic solid. An appropriate model for its stress/strain behavior is therefore Hooke's Law ($\epsilon = \sigma/E$).

   For Material B, we see that there is an instantaneous response with the applied stress followed by a strain that is dependent on time. This appears to be a linear viscoelastic material. The constitutive models we have for these materials include the Maxwell Solid, Kelvin/Voight Solid, and Standard Linear Solid. We can eliminate the Maxwell Solid because it cannot very accurately predict this type of strain response with time, as discussed in lecture.

   The solution to the Kelvin/Voight model is

$$\epsilon = \frac{\sigma_\circ}{E}\left[1 - \exp\left(\frac{-t}{\tau}\right)\right]$$

   where $\sigma_\circ$ is the initial stress, E is the Young's modulus, t is the time, and τ is the relaxation time. If we plot this with our data for Material B (Fig. 3), we see that we can accurately predict the strain at later times, but not at earlier times especially the instantaneous strain we observe at $t = 0$ s. We therefore must consider another model.

   Because the Maxwell Solid can accurately model instantaneous strains, how about a

Standard Linear Solid that is a combination of the Maxwell and Kelvin/Voight Solids?
From the Maxwell Solid and Kelvin/Voight Solid we have

$$\frac{1}{3\eta}\sigma + \frac{1}{E}\frac{d\sigma}{dt} = \frac{d\epsilon}{dt}$$

and

$$\sigma = E\epsilon + 3\eta\frac{d\epsilon}{dt}$$

respectively. Taking the best parts of these two equations, we write an equation of the form

$$\sigma + \tau_\epsilon\frac{d\sigma}{dt} = E_R(\epsilon + \tau_\sigma\frac{d\epsilon}{dt}$$

where τ_ϵ and τ_σ are the relaxation times for fixed strain and stress, respectively, and E_R is the relaxed modulus. To understand E_R, look at the physical model of this system in Fig. 4. In this system, as time goes to infinity,

$$\epsilon = \frac{\sigma}{E_R} = \frac{\sigma}{E_1} + \frac{\sigma}{E_2}$$

or

$$\frac{1}{E_R} = \frac{1}{E_1} + \frac{1}{E_2}$$

where E_1 and E_2 are the respective moduli of the two springs.

Now imagine that a stress $\sigma_\circ$ is applied and held constant (as is the case in our problem). Our equation for this model becomes

$$\sigma_\circ = E_R(\epsilon + \tau_\sigma\frac{d\epsilon}{dt}$$

Integrating this equation from strain $\epsilon_\circ$ to ϵ and time 0 to t yields

$$\epsilon = \frac{\sigma_\circ}{E_R} + \left(\epsilon_\circ - \frac{\sigma_\circ}{E_R}\right)\exp\left(\frac{-t}{\tau_\sigma}\right)$$

Using this equation, we are able to fit the data perfectly (Fig. 3) finding $\tau = 2$ s and $\sigma_\circ/E_R = 0.153$.

(b) Characterize these materials, focusing on their elastic moduli and the relaxation time. Without having handled the materials, what class would each fall into?

Solution: Using our models, we know we can calculate the moduli of the two materials as long as we know the strain and stress. The strain is given to us from our data. The stress we will estimate based on the weight of a person and the "cross-sectional" area of a foot. For my estimations, I assumed a 170 lb. ($\sim$700 N) person and for simplicity treated a leg as a rod with a three inch diameter.

Because Material A is a linear elastic solid, its Young's modulus can be calculated from Hooke's Law. Doing so, we fine $E_A = 40$ GPa. The Young's Modulus for Material
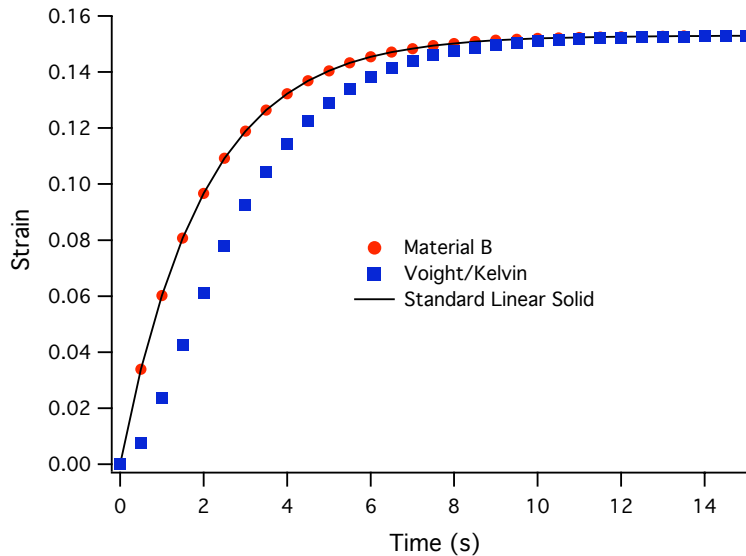
Figure 3: Strain as a function of time in Material B. Also plotted are the results given by the Voight/Kelvin Solid and Standard Linear Elastic Solid models.
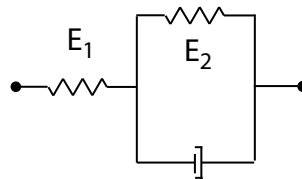

Figure 4: A physical model of a Standard Linear Elastic Solid.

B is obtained from our model. At $t = 0$ s, the strain ϵ is equal to the instantaneous strain $\epsilon_\circ$. Using the values we are given, we can solve for E in the same way we did for Material A to find E_B=4 GPa. (Note that depending how you defined your stress, you may get very different answers.)

The relaxtion time τ for Material A is zero because it is a linear elastic solid and reach maximum strain instantaneously. The relaxation time for Material B was determined to be $\tau = 2$ s when we fitted the data.

Based on the moduli and strain behavior of these materials, we can categorize Material A as a linear elastic solid that is most likely a metal and Material B as a linear viscoelastic solid such as a polymer.

(c) Which material is better suited for the job? Explain by showing the $\sigma(t)$ (given that you take a step every second) and the resulting strain for each material. Define a quantity for judging the effectiveness of each material in this application. What would this quantity

be for a material ideally suited for this application?

Solution: We can model the stress applied in one foot while we are walking as a sine wave such that

$$\sigma = \sigma_\circ \sin \omega t$$

where ω is the angular frequency. In a linear elastic solid, such as Material A, the strain would mirror the strain (with a reduced magnitude equal to the stress divided by the modulus) because the response is instantaneous. It can therefore be written as

$$\epsilon = \epsilon_\circ \sin \omega t.$$

What about the strain in Material B? Using a sine wave complicates the problem in this situation, so let's model our steps as a block wave. This means that the material is loaded at a constant stress $\sigma_\circ$ for a time $t = 1$ s. If we look at our strain data for Material B from $t = 0$ to 1 s (you should plot it in smaller time steps than 0.5 s to better resolve this), we see that the strain instantaneously increases to $\epsilon_\circ$ before increasing nearly linearly with time.

When the stress is removed (e.g. you step with the other foot), the material will instantly recover $\epsilon_\circ$ and then recover all the remaining strain over the next second (the time to take the other step).

So what metric can we use in determining each material's utility in shoe insoles? Continuing with our block wave approximation, let's plot the stress versus strain in each material for one step (Fig. 5). Material A reversibly follows a line between the origin and ($\sigma_\circ$, $\epsilon_\circ$) while Material B follows a circuit. The energy dissipated in this circuit is just the area inside the circuit. For Material A, this energy is zero, so clearly Material B is better suited for use in shoe insoles because it can dissipate some of the energy from walking.

Ideally the perfect material for an insole would dissipate as much energy as possible. Since $\sigma_\circ$ is set within the range of a human's weight, to do this we would want the material to reach maximum strain ϵ_∞ in the time it takes to take one step. The material must also be able to fully recover the strain in the same amount of time.

(d) A similar concept can be applied to measure the natural frequency of molecular chain rotation at the glass transition temperature of a polymer. Explain how you do this experimentally and the results you would expect.

Solution: At the glass transition temperature in polymer there is a large increase in the free volume, allowing for molecular motion to occur more easily. When a frequency similar to the natural frequency of the molecular chain rotation is applied, (nearly) complete damping will occur. If the applied frequency is too high, the chains will have insufficient time to move and the polymer will seem stiff. If the applied frequency is too low, the chains will have more time to move and the polymer will seem soft.
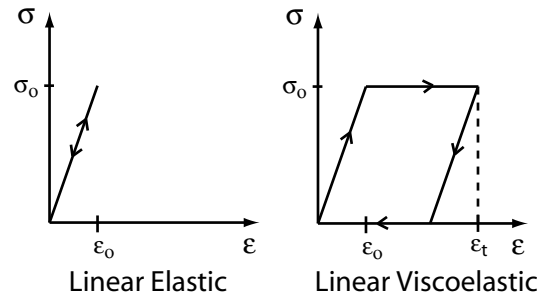
Figure 5: A schematic of the stress-strain behavior in a linear elastic and linear viscoelastic solid.

3. You are responsible for performing uniaxial tensile tests on three very different materials: a 316 stainless steel alloy, alumina (Al_2O_3), and high density polyethylene (HDPE). However, before performing the actual tests, you are asked to predict the elastic stress vs. strain responses of each of the materials based on the mechanical properties of these materials documented in the literature (e.g., material property databases such as matweb.com, linked on the MIT Server.)

   (a) Graph the engineering and true stress (MPa) versus engineering and true strain (%) response for all three materials on a single graph, up to an applied engineering strain value of .01 (or 1%) in strain increments of 0.0005.

   Solution: The Young's elastic moduli for these materials are approximately 210 GPa (steel); 370 GPa (alumina); and 1 GPa (HDPE); data source = matweb.com.Graphically, we need only plot the stress-strain response with these values as the slope. There is no measureable difference between the true and engineering stress and strain during purely elastic deformation, though technically the Poisson's effect does slightly decrease the cross-sectional area from which the true stress is calculated.

   (b) Remark on the differences in behaviors seen for each of the three materials as related to their relevant mechanical properties. Also, looking at the magnitude of the stresses at the maximum applied strain, do you expect all of these materials to deform elastically up to these strains? If not, what was the fallacy in solely using Hooke's law to predict the stress-strain behaviors for each of the materials?

   Solution: The requested maximum strain of 0.01 would induce the following stress magnitudes: 2.1 GPa (stainless steel); 3.7 GPa (alumina); 10 MPa (HDPE). The reasons for the differences among the values of E and the corresponding stress generated are attributable to the resistance to bond stretching in metal alloys (nondirectional) vs. oxides (ionic/covalent) and to organic polymer chain displacement (HDPE). At these levels of stress, the stainless steel would no longer behave elastically (yield stress at which plasticity commences is approximately 1 GPa); the alumina would fracture (tensile fracture stress is 0.3 GPa, and compressive fracture stress is 3 GPa); and the HDPE would likely plastically deform (tensile yield stress is on order of 10 MPa). The fallacy is that Hooke's Law cannot be assumed for any arbitrary strain level; it applied only in a stress state that corresponds to a state of elastic (reversible) deformation.

(c) All three samples were given to you as cylinders with identical initial dimensions of 10 cm length and 2 cm diameter. Show whether a uniaxial load frame of maximum load capability = 100 kN (standard capabilities of load frames such as Instrons available at MIT) will be sufficient to deform all three materials to the requested engineering normal strain of 1%. Here, neglect the possibility that the materials might not remain intact (all in one piece) to that applied strain.

Solution: The initial cross-sectional area of the cylinder is

$$A_o = \pi r^2 = 3.14x10^{-4}m^2 \tag{1}$$

If we neglect the above consideration that the material may yield or fracture at a strain of 0.01, we can compute the required force as $F = \sigma x A_o$. This would correspond to a required force of 6.6 x 10^5 N (stainless steel); 1.2 x 10^5 N (alumina); and 3.1 x 10^3 N. As 100 kN = 1 x 10^5 N, it is clear that such a load cell could only deform the HDPE, but not the SS or alumina. Luckily for us, none of these materials behave linearly elastic manner up to these strains.

4. Atomic interactions can be modeled using a variety of potential energy approximations. One very common potential form is the Lennard-Jones 6:12 potential:

$$U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

where ϵ and σ are constants specific to a given material (note: these terms are NOT equivalent to stress and strain, but this is the standard notation for the L-J parameters). Here, r is the interatomic spacing given in units of Angstroms, and $U(r)$ is given in units of eV atom^{-1}. A molecular dynamics simulation was performed by Zhang and coworkers [1] to study the properties of Al thin films in which the authors proposed a Lennard-Jones potential of the form above to model Al-Al interactions. The values used for the material parameters were: $\epsilon = 0.368$ and $\sigma = 2.548$ (we've rounded off the values in the paper for your problem set).

(a) What are the assumed units of ϵ and σ in Zhang and coworkers' potential for aluminum?

Solution: As discussed in class, ϵ must have units of energy in [kJ/mol] or [eV/atom]; and σ must have units of [m].

(b) Using the given material parameters and the form of the interatomic potential energy curve, plot $U(r)$ for aluminum from $r = 0$ to 3.5 Angstroms in increments of < 0.25 Angstroms.

Solution: Using Excel, the following plot of U(r) was generated. The scale of the x-axis was set so that it ranged from 2.25 to 4 angstroms, while the scale of the y-axis was set so that it ranged from -0.4 to 1eV in increments of 0.2 eV. This is much less preferable to graphing in Mathematica, MATLAB, or Maple!

(c) Determine the equation for and graph the interatomic forces F as a function of interatomic separation r for Al over the same range of r used in part (a), indicating units of $F(r)$. Also, analytically and graphically determine the equilibrium interatomic spacing, r_o. Mark this point on both the graphs produced in parts (a) and (b).

Solution: The interatomic forces between atoms can be determined from the interatomic potential energy function given the relationship: F = dU/dr. Taking the derivative of the
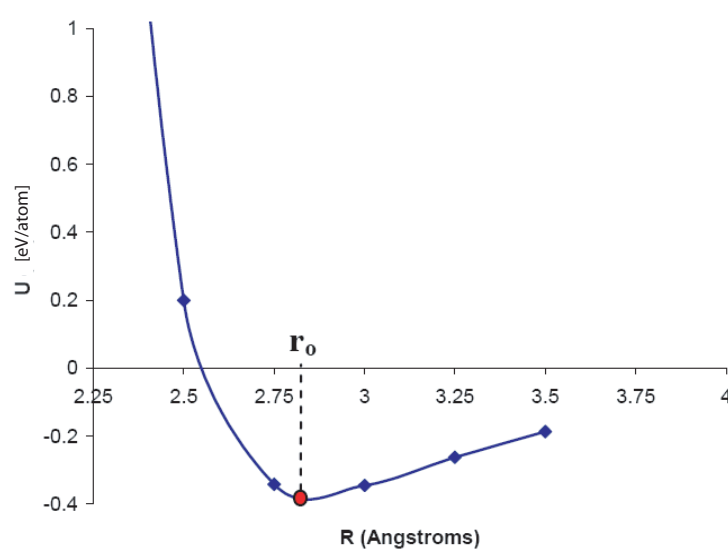
Lennard-Jones 6:12 form of U(r) with respect to r gives the following relationship:

$$F = -24\epsilon\{2(\sigma^{12}/r^{13} - \sigma^6/r^7 \tag{2}$$

*This function is then plotted for the same range of r values used in part (a) to obtain
The equilibrium interatomic spacing can be determined by setting F(r) equal to zero*
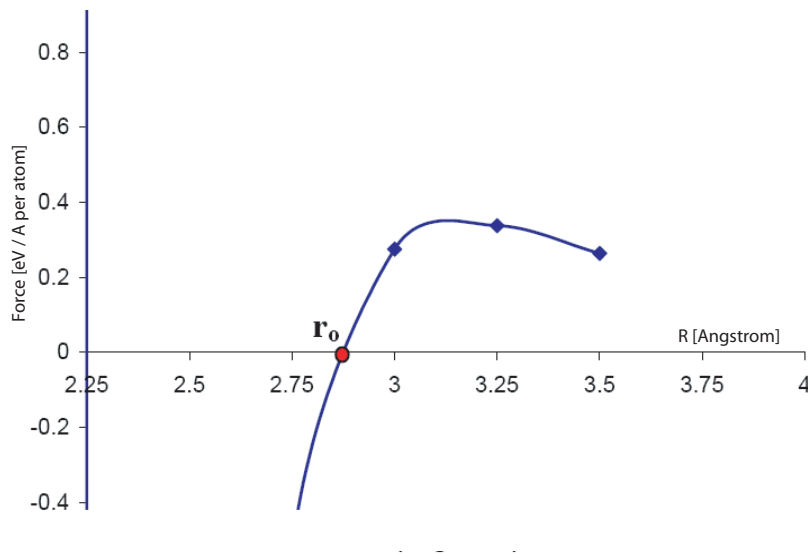
and solving for r (this can be easily done using a computer program or a graphing calculator). Doing this, one obtains an equilibrium interatomic spacing of ro=2.86 Angstroms (0.286 nm). This point is marked as a red dot on both the graphs for parts (a) and (b). Notice that the equilibrium interatomic spacing corresponds to the minimum

point on the potential energy curve U(r), whereas this corresponds to the zero point on the interatomic force curve F(r).

(d) Compare this equilibrium interatomic spacing to the literature value of atomic radius for aluminum, and from that comparison explain what you think Zhang and coworkers assumed in choosing the constants ϵ and σ that made r_o come out this way.

Solution: This is exactly twice the atomic radius of Al (0.143 nm). Zhang et al. actually chose the LJ constants so that this equilibrium interatomic spacing would reflect the interatomic distances in the close-packed or ¡110¿ direction of this fcc metal.

(e) Figure 6 shows interatomic energy curves [$V(r)$ is equivalent to our $U(r)$] for Mg that were calculated by Chavarria [2] (squares) and McMahan and coworkers [3] (dotted and solid curve). These data are shown in arbitrary units (a.u.) which is typical of computational/experimental results that have funny units peculiar to the computational programming units, but r turns out to be expressed in $\sim 2 \times$ Angstroms (i.e., 9 a.u. = 4.5 Angstroms). Comparing these curves with that calculated in part (a) for Al, explain whether you would expect magnesium to have a lower or higher elastic modulus than aluminum? Is this confirmed by the literature values of elastic properties and physical properties of Al and Mg?

Solution: From consideration of the atomistic basis for linear (small strain) elasticity we derived the following relationship in class, $E = d^U/dr^2/r_o$, where the term in the numerator represents the curvature of the interatomic potential energy curve at $r = r_o$, and the term in the denominator represents the interatomic equilibrium spacing. Thus, if and only if we assume the U(r) of two materials had the same curvature at the energy minimum, we see that a larger equilibrium interatomic spacing leads to a smaller elastic (or Youngs) modulus. Since magnesium is seen to have an equilibrium interatomic spacing of about 3 Angstroms (0.32 nm) which is larger that calculated for aluminum (r_o =2.8 A or 0.28 nm), we would expect magnesium to have a smaller elastic modulus (i.e., magnesium is more compliant than aluminum). The increase in equilibrium interatomic spacing can be attributed to the fact that Mg has a much lower density compared to Al, which in turn means larger interatomic separations between atoms. In fact, if we look up the actual values for Youngs modulus using MatWeb we find the moduli of aluminum and magnesium to be 68 GPa and 44 GPa, respectively. This is a pretty significant difference for two elements which lie right next to each other on the periodic table and have essentially the same melting temperatures!!!

(f) Again, considering the relationship between the Young's modulus, the equilibrium interatomic spacing, and $U(r)$ curvature, what effect do you think temperature has on the measured Young's modulus? Provide a conceptual explanation of your answer. (Hint: Think about what happens to atoms inside of a material as you heat it up.)

Solution: As temperature increases, atomic vibrations are caused which cause the equilibrium spacing between atoms to increase. Since the Youngs modulus decreases with increasing equilibrium spacing, an increase in temperature causes the elastic modulus to decrease. To see this another way, we can also note that the modulus is proportional to the slope of the interatomic force, F(r), curve. Taking our calculated F(r) graph for aluminum, we see that if we move our original equilibrium spacing from r_o=2.86 A to a higher value (lets say r_o'= 3.1 A), the slope of the curve greatly decreases which repre-
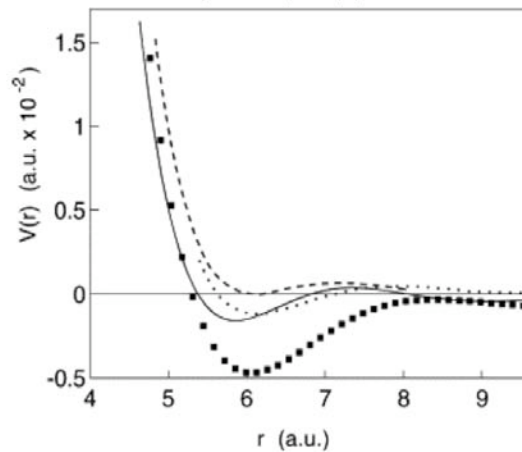
Courtesy of Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

Figure 6: Interatomic potential for magnesium as calculated by Chavarria [2] (squares) and McMahan and coworkers [3] (dotted and solid curves).

sents a decrease in the elastic modulus. Additionally, the atoms will vibrate more about this r_o, which means that the curvature at the bottom of the U(r) well will be decreased (the well gets wider), so the 2nd derivative of U(r), which is directly proportional to E, will decrease. Physically, the resistance to bond stretching decreases as the well curvature decreases.

Refs:

1. H. Zhang and Z. N. Xia, Nuclear Instruments & Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 160 (2000) 372-376.
2. G. R. Chavarria, Physics Letters A, 336 (2005) 210-215.
3. A. K. McMahan and J. A. Moriarty, Physical Review B, 27 (1983) 3235-3251.

5. The Worm Like Chain (WLC) model of rubber elasticity has been used to analyze the deformation of DNA under uniaxial loading. Bouchiat and coworkers used magnetic tweezers to extend lambda-DNA (λ-DNA) and applied the WLC model to infer its structure and resistance to bending. Table 1 is a subset of the experimental data Bouchiat and coworkers reported, with additional points (Bouchiat *et al.*,Biophys J. (1999) Fig. 2). Apply the WLC model to determine the following:

   (a) Graph these experimentally measured data as force on the chain vs. stretch of the chain, F_c vs. $\lambda_c = r/r_o$ where r_o is the distance between chain ends before force is applied, and indicate the region over which the experimentally measured data is fit reasonably well by the WLC model.

      Solution: One could note the values of L_p and L_c from the authors' fit to these data, and/or obtained your own fit to these data by executing a fit with these values as initial guesses of L_p and L_c. The better your "starting guess" for these values, the closer your

Table 1: A subset of the experimental data Bouchiat and coworkers reported, with additional points (Bouchiat *et al.*,Biophys J. (1999) Fig. 2)

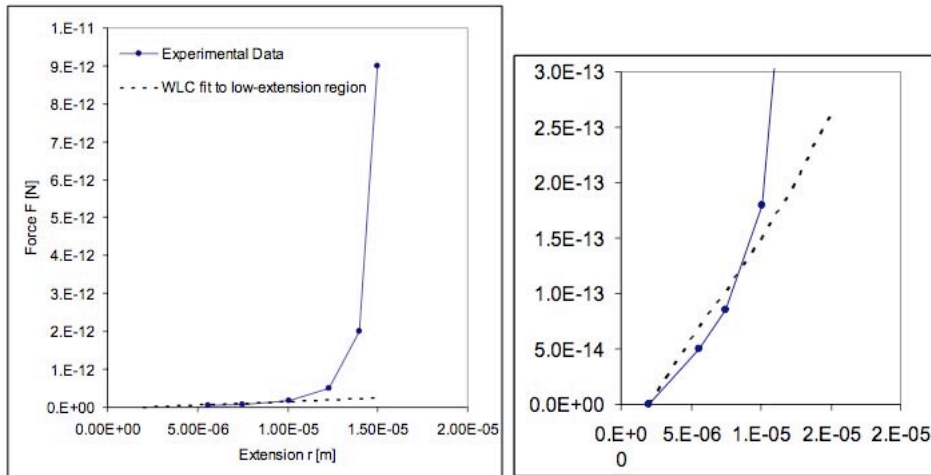| Applied force F (pN)	Extension r (μm)
0.05	5.6
0.085	7.5
0.18	10.1
0.5	12.3
2.0	14.0
9.0	15.0

fit will approximate the authors'. The solution below assumes ignorance of L_c and L_p, and compares the values obtained with that of the authors. Note that, in practice, L_c can actually be calculated from knowledge of the structure of a polymer chain; L_p can only be estimated from experiments like this one, or from measurements of the lengths over which thermal fluctuations of the chain are uncorrelated in space and time. (We did not cover the latter approach in class, but it is consistent with the definition of L_p that we discussed in class.)

The WLC model covered in class assumes a Gaussian distribution of chain end-end distances r, and thus predicts a fairly linear relationship between F and r. This linear relationship is observed only true for the low extension region and the high extension region, as the experimental data is highly nonlinear in between. The Gaussian assumption holds best in the low-extension region, however, because it is in this region that there is a "normal" distribution of chain end-end distances, unbiased by the application of force to these chains. For these data, the limit of a reasonable linear fit to the low extension data is at about the third data point, or F = 0.18 pN and r= 10 μm.

Note that this fit was achieved by identifying the values of L_c and L_p that minimized the error between the WLC-predicted force and the experimental value of force over these three points (L_c = 8.6 μm; L_p = 25.6 nm) for k_B = 1.38x10^{-23} J/K and T = 298 K (room temp). As this was linear, the value of $r_\circ$ was then identified via linear extrapolation ($r_\circ$ = 1.95 μm). This is an interesting deviation from our prediction that the force = 0 when r = 0, because although the time-space average value of r = 0 (if there is a statistical distribution of r), r was not equal to zero at the instant sampled by this experiment; the DNA chain ends were about 1 micron apart. Strictly speaking, r = 0 should be defined to either mean $< r >$= 0, the time-averaged, Gaussian value of most likely chain end-end distance in the absence of applied force; or as dr = 0, where dr is the change in chain end-end distance.

(b) The number of nucleotides in this λ-DNA.

Solution: The number of nucleotides that comprise this DNA is governed by the con-

tour length or fully extended length of this DNA sample. According to the above WLC fit to the low- extension region of the F-r response, $L_c = 8.6$ μm. We know right away that this is a poor estimate of L_c due to the Gaussian distribution P(r, n)dr, because the WLC force should tend toward infinity as $r = L_c$, and the experimental data indicates that this occurs at about 15 μm. Visually, the data indicate that $L_c \sim 15$ m.

The number of nucleotides in this polynucleotide is then equal to the number that can fit in this length; if we assume this is single stranded DNA, we divide Lc by the size of one nucleotide, and if we assume this is double stranded DNA, wed multiply that answer by two (2 nucleotides in one basepair). Youd need to check out the paper to be sure (as I didnt give you that information in the problem).

The length of a single nucleotide (and, for that matter, a single basepair) is 0.33 nm [Mandelkern M, Elias J, Eden D, Crothers D (1981). "The dimensions of DNA in solution". J Mol Biol 152 (1): 15361.]

Thus, the number of nucleotides in ssDNA would be 8600 nm/0.33 nm = 26,060 nucleotides; the number in dsDNA would be 52,121 nucleotides or 26,060 basepairs (bp).

Note that this is in contrast to the estimates from the authors of the paper, as they assumed the nonlinear form of the WLC model and found from their fit that $L_c = 15.6$ μm (which gives 47,272 nucleotides (for ssDNA); or 94,545 nucleotides or 47,272 basepairs (for dsDNA).

(c) The number of nucleotides that comprise a segment of the DNA that is significantly resistant to bending.

Solution: This length is equivalent to the persistence length L_p, which my fit in (a) determined to be 25.6 nm. The number of nucleotides in ssDNA would be 25.6 nm/0.33 nm = 77 nucleotides (rounding down to integer values), and would be 155 nucleotides in a dsDNA segment.

Contrast this with the authors estimate: $L_p = 51$ nm 154 nucleotides for ssDNA; again, we underestimate by a factor of two by fitting to only the Gaussian/low extension region.

(d) The effective entropic spring constant of λ-DNA, k_s. Note that this is often defined as the resistance to extension at large forces – why is this? Compare your value to that stated by the Bouchiat and coworkers, and explain why they expressed this stiffness in units of [N] instead of [N m^{-1}].

Solution: Although we could define the spring constant as the slope of the linear region in the low-extension region, the forces are so low in this region that they are essentially at the limit of measurable forces with existing instrumentation. As a result, there is a tendency to use more reliable data at higher forces/extensions. The entropic spring constant or slope to my fit shown in (a) is 2×10^{-8} N/m.

*At low forces/extensions, the linear term r/L_c dominates; at high forces/extensions, though, note that the quadratic term in our WLC equation dominates, or $F \sim kT/L_p[4(1r/L_c)] - 2$, which can be rewritten as $[F/(kT/L_p)] - 1/2 = 4(1r/L_c)$, where you can see that the LHS of the equality is unitless [N * m / N-m/K * K] and the units on the RHS of the equality are also unitless [m/m]. Thus, one can obtain Lp and Lc via a linear fit to these data so plotted. Smith/Bustamante did this to demonstrate the linearity of the relationship at high force, and as a check on their fit. If one plots force [N] vs. extension ratio r/ro or as r/L_c [m/m], the slope to the linear portion of this response, k, is in units of only [N], not [N/m]. This is often presented as such to compare the effective stiffness of chains of different contour length L_c.*

*To compare with Bouchiat et al.s estimate of k (1.3 pN, stated on the graph), we could multiply our k by our L_c, so k = 2E(-8) N/m*8.6E(-6) m =1.72E(-13) N = 0.172 pN. Our fit to the low-extension region underestimates their k by an order of magnitude, but of course wed expect that because we can visually see in (a) that the rate of change of F vs. r is much greater at large forces/extensions (and, also, our L_c is 2x too small like the Grinchs heart).*

(e) The minimal force required to break the phosphate ester bonds that join nucleotides in DNA?

Solution: Here, we know that the force applied up to the contour length L_c only serves to uncoil the coiled DNA, and no force is transferred to the primary bonds like the phosphate ester bonds. The force required to load and break these primary bonds must be greater than the force required to achieve the fully extended polynucleotide, so $F_{min} = F(r = L_c)$ or 10 pN.

(f) The stretch $\lambda_c = r/r_o$ at which the WLC prediction diverges from that of the Freely Jointed Chain (FJC) model, by graphing the FJC prediction on the graph in (a), and the reasons for this divergence.

Solution: Here, both WLC and FJC predict a linear relation between F and r, so

both only fit reasonably well to the first few points given in the experimental data table. Below, the best fit of the FJC equation to these 3 points is given in orange (where $L_c = 10$ μm and b = 92 nm). The WLC and FJC diverge from each other for increasing extension, r. Mathematically, this is because the quadratic r/L_c term in the WLC equation dominates. Physically, this is because the WLC incorporates the resistance to segment BENDING and ROTATION that the FJC model disallows (all segments rigid and straight over length b, between frictionless joints).