

3.032 Problem Set 4 Solutions

Fall 2007

Due: Start of Lecture, 10.19.07

1. A microelectronic sensor is to be made of conductive wires deposited on a thin Si wafer. During design considerations, it was decided that only metals having cubic symmetry were to be used as fibers (metallic wires) in this composite sensor. Another design criterion for the sensor is that the fibers of the sensor do not undergo any elastic (true) normal or shear strains $\geq 0.1\%$ and 0.01% , respectively, when subjected to a given stress state. (We will assume plane stress since the device is very thin.)

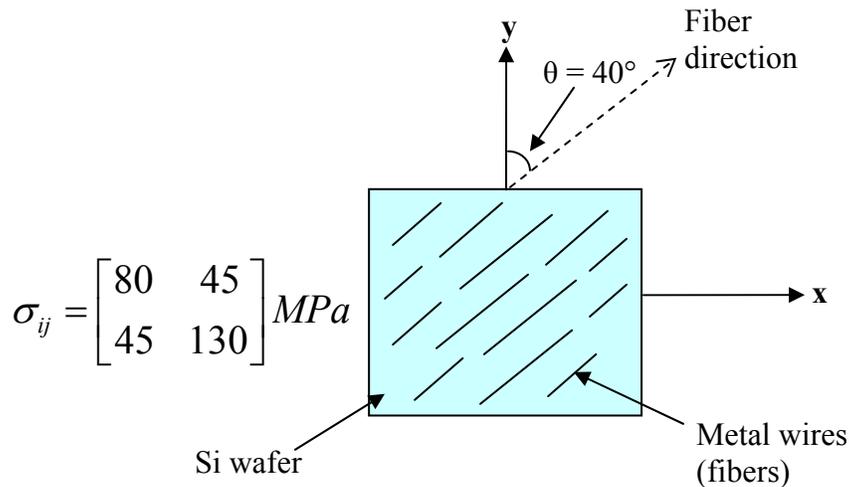
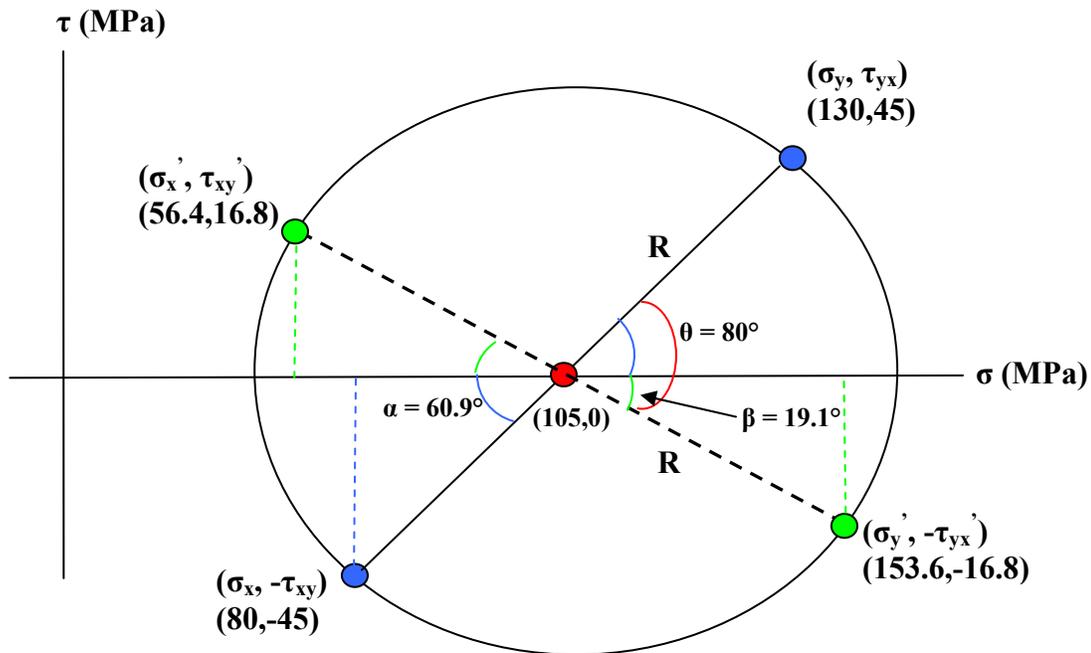


Figure 1: Orientation of composite sensor with respect to original loading conditions

- (a) The fibers in the sensor are subjected to an initial plane stress state, given below, with respect to the orientation seen in Fig. 1. Determine the stress state on the fibers by resolving the original stress state onto an axis-set aligned with the fibers (instead of aligned with the applied stress state σ_{ij} as shown in Fig. 1).

Solution: In order to resolve the original stress onto the orientation of the fibers, we need to rotate our original axes 40° in the clockwise direction. If we use a Mohr's Circle construction, this is the same as an 80° rotation in the same direction. This transformation is shown below where the solid line with blue endpoints represents the original stress state and the dotted line with green endpoints represents the new stress state:



In order to calculate our new stress state after the rotation, we need to determine the average stress (center of circle) and the radius:

$$\sigma_{avg} = (130 + 80) / 2 = 105 \text{ MPa}$$

$$R = \sqrt{\left(\frac{(130 - 80)}{2}\right)^2 + 45^2} = 51.48 \text{ MPa}$$

Next, we want to find the angle between our new stress state and the σ -axis so that we can calculate our new stress state through geometry of Mohr's circle. To determine this angle (labeled β , green line) we can subtract the total angle of rotation ($\theta = 80^\circ$, red line) by the angle between the original stress state and the σ -axis (labeled α , blue line). This last angle is the same as the orientation of principal normal stresses as we have seen before and can be calculated as follows:

$$\tan \alpha = \frac{45}{25}$$

$$\alpha = 60.9^\circ$$

$$\beta = 80 - 60.9 = 19.1^\circ$$

Finally we can calculate our new stress state σ_x' , σ_y' , and τ_{xy}' as follows:

$$\sigma_x' = \sigma_{avg} - R \cos \beta = 105 - 51.45 \cos(19.1^\circ) = 56.4 \text{ MPa}$$

$$\sigma_y' = \sigma_{avg} + R \cos \beta = 105 + 51.45 \cos(19.1^\circ) = 153.6 \text{ MPa}$$

$$\tau_{xy}' = R \sin \beta = 51.45 \sin(19.1) = 16.8 \text{ MPa}$$

Writing this in terms of a stress matrix we get

$$\sigma_{ij} = \begin{bmatrix} 56.4 & 16.8 \\ 16.8 & 153.6 \end{bmatrix} \text{ MPa}$$

- (b) Given the elastic compliance constants for various cubic crystals (see Hosford Table 2.2. below), calculate the complete strain tensor ϵ_{ij} for the stress state you determined in part (a) for all of the metallic and organic materials from which we might make these fibers (writing a small program would be ideal here!). Identify the metals that satisfy the design criterion that the fibers do not undergo elastic normal strains (ϵ_{ii}) equal or greater than 0.1% or true shear strains (ϵ_{ij}) equal to or greater than 0.01%. (Note: The units of s_{ij} are given in $(\text{TPa})^{-1} = 1 \times 10^{-12} \text{ Pa}^{-1}$).

Mechanical Behavior of Materials

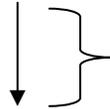
Material	S_{11}	S_{12}	S_{44}
Cr	3.10	-0.46	10.10
Fe	7.56	-2.78	8.59
Mo	2.90	-0.816	8.21
Nb	6.50	-2.23	35.44
Ta	6.89	-2.57	12.11
W	2.45	-0.69	06.22
Ag	22.46	-9.48	22.03
Al	15.82	-5.73	35.34
Cu	15.25	-6.39	13.23
Ni	7.75	-2.98	8.05
Pb	94.57	-43.56	67.11
Pd	13.63	-5.95	13.94
Pt	7.34	-3.08	13.07
C	1.10	-1.51	1.92
Ge	9.80	-2.68	15.00
Si	7.67	-2.14	12.54
MgO	4.05	-0.94	6.60
MnO	7.19	-2.52	12.66
LiF	11.65	-3.43	15.71
KCl	26.00	-2.85	158.6
NaCl	22.80	-4.66	78.62
ZnS	18.77	-7.24	21.65
InP	16.48	-5.94	21.74
GaAs	11.72	-3.65	16.82

Elastic compliances (TPa)⁻¹ for various cubic crystals

Table by MIT OpenCourseWare.

Solution: Looking at our stress state we see that $\sigma_x = \sigma_1 = 56.4 \text{ MPa}$, $\sigma_y = \sigma_2 = 153.6 \text{ MPa}$, and $\sigma_{xy} = \sigma_6 = 16.8 \text{ MPa}$. Knowing that $s_{11} = s_{22}$, $s_{21} = s_{12}$, $s_{44} = s_{66}$ for cubic crystals we can calculate each of the elements of strain through the equations given below. Note: the first equation is written out in its entirety for the reader to see how each of the strain values are calculated. The next three are the condensed versions which taken into account the terms that become zero (either because there is no applied stress in a certain direction or the value of s_{ij} is zero due to crystal symmetry).

$$\varepsilon_1 = s_{11}\sigma_1 + s_{12}\sigma_2 + s_{13}\sigma_3 + s_{14}\sigma_4 + s_{15}\sigma_5 + s_{16}\sigma_6$$


 Using same technique and eliminating zero terms

$$\varepsilon_1 = s_{11}\sigma_1 + s_{12}\sigma_2$$

$$\varepsilon_2 = s_{21}\sigma_1 + s_{22}\sigma_2$$

$$\varepsilon_3 = s_{31}\sigma_1 + s_{32}\sigma_2$$

$$\varepsilon_6 = s_{66}\sigma_6 = 2\varepsilon_{12}$$

Using the last three equations we can calculate the total normal and shear strains of the fibers made out of each of the various cubic metallic materials given in Table 2.2. We eliminate the materials from Si to GaAs (as listed in the chart) because they are non-metallic materials. Here is a table of the results (values rounded to three decimal places):

Material	$\varepsilon_1 = \varepsilon_{11}$ (%)	$\varepsilon_2 = \varepsilon_{22}$ (%)	$\varepsilon_3 = \varepsilon_3$ (%)	ε_6 (%)	$\varepsilon_{12} = \varepsilon_{21}$ (%)
Cr	0.010	0.045	-0.010	0.017	0.008
Fe	0.000	0.100	-0.058	0.014	0.007
Mo	0.004	0.040	-0.017	0.014	0.007
Nb	0.002	0.087	-0.047	0.060	0.030
Ta	-0.001	0.091	-0.054	0.020	0.010
W	0.003	0.034	-0.014	0.010	0.005
Ag	-0.020	0.288	-0.199	0.037	0.019
Al	0.001	0.211	-0.120	0.059	0.030
Cu	-0.012	0.198	-0.134	0.022	0.011
Ni	-0.002	0.102	-0.063	0.014	0.007
Pb	-0.136	1.207	-0.915	0.113	0.056
Pd	-0.015	0.176	-0.125	0.023	0.012
Pt	-0.006	0.095	-0.065	0.022	0.011
C	-0.017	0.008	-0.032	0.003	0.002

Therefore, considering our design criteria for total strain, the only materials that are possible candidates as metallic fibers in our microelectronic sensor are Cr, Mo, W and C. One should observe how small carbon's compliance values are compared to the metallic materials. This is the reason why carbon is popularly used as fiber reinforcements to increase the strength of composite materials which tend to have matrixes made up of very

compliant materials (such as in our example where it can be seen that Si has relatively high s_{ij} values compared to the other materials).

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

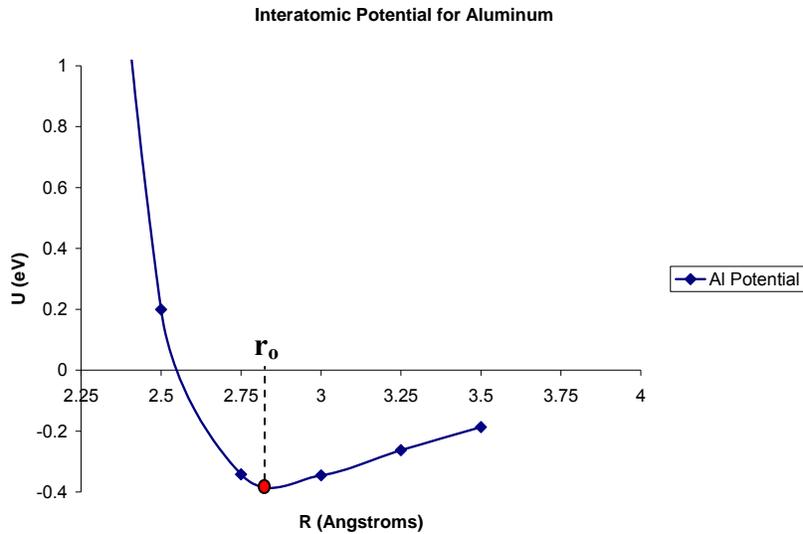
$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where σ and ϵ are constants specific to a given material (note: they are **NOT** equivalent to stress and strain, but this is the standard notation for the L-J parameters). The parameters σ and ϵ are related to the equilibrium bond length and the bond strength, respectively. Here, r is the interatomic spacing given in units of Angstroms (1 Angstrom = 10 nm = 10^{-10} m), and $U(r)$ is given in units of eV/atom.

A molecular dynamics simulation was performed by Zhang *et al.* [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 pset).

- (a) What are the assumed units of σ and ϵ in Zhang et al's potential for aluminum?
- (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.
- Tips:*
- We strongly suggest you use a scientific programming language such as Mathematica, Matlab, or Maple here to graph and take derivatives of $U(r)$, as this will be a big help in prep for Lab 2. If you didn't take 3.016 or use this in another class, now is your chance to learn – e.g., by working with a classmate who did. You must include your own program and output in the pset, of course, not a duplicate of someone else's program.*
 - Since $r = 0$ will give you an error, use a very low value for your starting point instead, i.e., $r = 0.001$ A.*
 - In order to make your graph more readable, you may want to adjust the scale of your axes so that it only emphasizes the points around the equilibrium interatomic spacing, r_0 .*

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 0.2eV.



- (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_0 . Mark this point on both the graphs produced in parts (a) and (b).

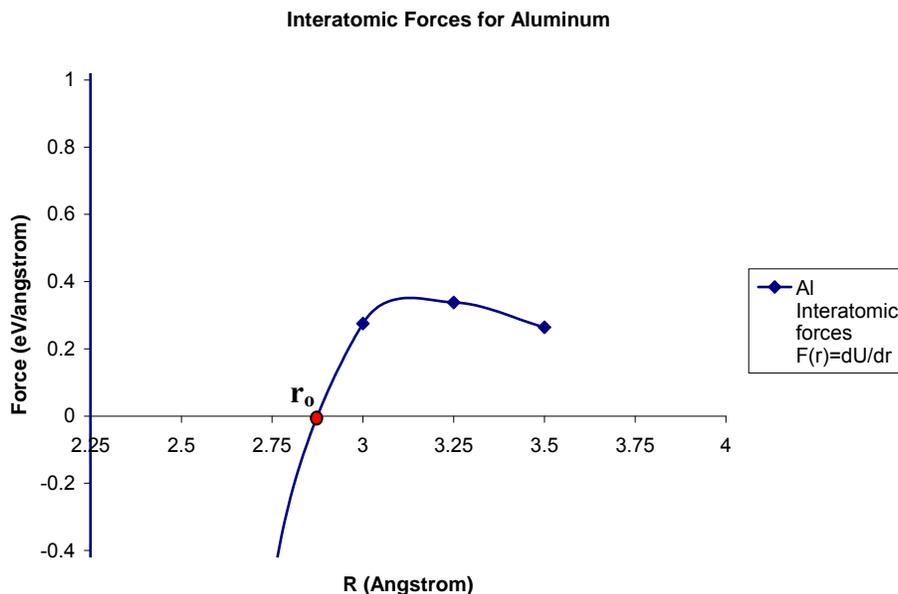
*Solution: The interatomic **forces** between atoms can be determined from the interatomic potential energy function given the relationship:*

$$F = \frac{\partial U}{\partial r}$$

Taking the derivative of the Lennard-Jones 6:12 form of $U(r)$ with respect to r gives the following relationship

$$F(r) = \frac{\partial U}{\partial r} = -24\epsilon \left[2 \left(\frac{\sigma^{12}}{r^{13}} \right) - \left(\frac{\sigma^6}{r^7} \right) \right]$$

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 $r_0=2.86$ 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 et al. assumed in choosing the constants σ and ϵ that made r_0 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 $\langle 110 \rangle$ direction of this fcc metal.

- (e) Figure 2 below shows interatomic energy curves [$V(r) = \text{our } U(r)$] for Mg that were calculated by Chavarria [2] (squares) and McMahan *et al.* [3] (dotted and solid curve). These data are shown in “arbitrary units” or “a.u.” which is typical of computational / experimental results that have funny 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, would you expect magnesium to have a lower or higher elastic modulus than aluminum? Is this confirmed by the literature values of elastic properties of Al and Mg? *Hint: One can compare the shape or curvature of the Al and Mg potential energy curves by normalizing energies by the minimum or binding energy U_b or (U/U_b) and distances by r_0 or (r/r_0) .*

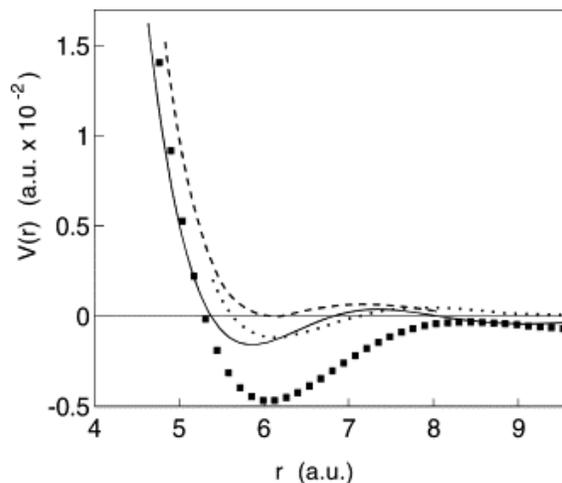


Figure 2: Interatomic potential for magnesium as calculated by Chavarria [2] (squares) and McMahan et al. [3] (dotted and solid curve).

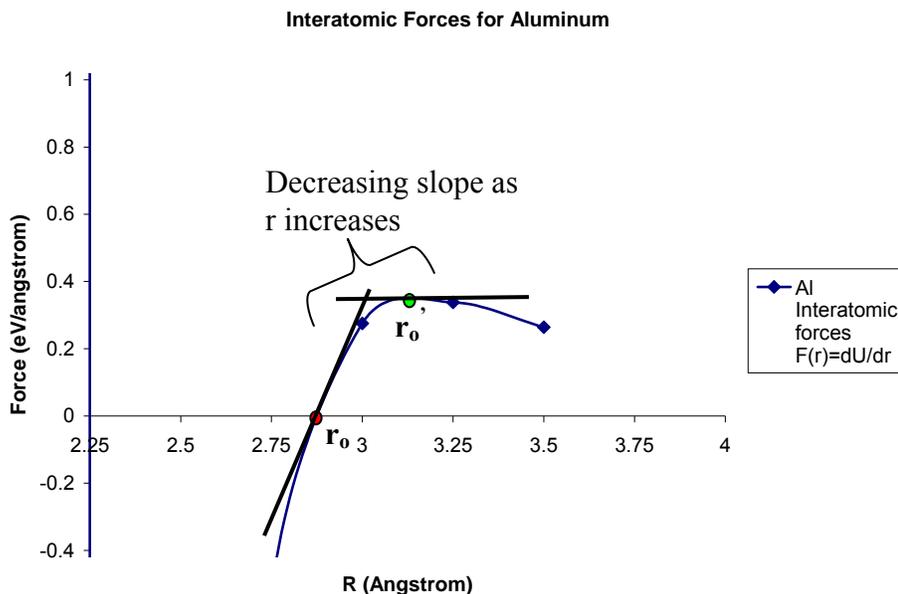
Solution: From consideration of the atomistic basis for linear (small strain) elasticity we derived the following relationship in class:

$$E = \frac{\partial^2 U}{\partial r^2} \bigg|_{r_0}$$

where the term in the numerator represents the curvature of the interatomic potential energy curve at $r = r_0$, 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 Young's) modulus. Since magnesium is seen to have an equilibrium interatomic spacing of about 3 Angstroms (0.32 nm) which is larger than calculated for aluminum ($r_0 = 2.8 \text{ \AA}$ 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 Young's 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 and the equilibrium interatomic spacing and $U(r)$ curvature, what effect do you think temperature has on the 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 Young's 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 $r_0 = 2.86 \text{ \AA}$ to a higher value (let's say $r_0 = 3.1 \text{ \AA}$), the slope of the curve greatly decreases which represents a decrease in the elastic modulus. Additionally, the atoms will vibrate more about this r_0 , 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.

3. Poly(dimethylsiloxane) or PDMS is a crosslinked elastomer that is commonly used to build optical/electronic/biomedical devices via soft lithography (borrowing from microelectronics processing approaches to make flexible, patterned surfaces). The glass transition temperature of pure PDMS is -120°C , and crosslinking can be induced by exposure to UV light.

At molecular weights on the order of 10^6 g/mol or degree of polymerization (DP) ~ 60 , PDMS is said to exhibit a viscoelastic response with Young's elastic modulus E reported to be about 2 MPa for short times / high strain rates. At very low molecular weights ($<10^2$ g/mol) or DP, PDMS acts as a Newtonian fluid of viscosity $\eta \sim 10^{-2}$ poise (1 poise = $0.1 \text{ N}\cdot\text{s}/\text{m}^2 = 0.1 \text{ Pa}\cdot\text{s}$). Note that this viscosity increases with molecular weight as shown in Fig. 3a.

(a) Briefly discuss why it is confusing that PDMS is widely described as a rubber elastic polymer, but is also widely reported to exhibit measurable elastic moduli E .

Solution: Rubber elasticity is governed by entropy $dU(dS)$ and expressed by the relationship between chain extension, contour length, etc, whereas E is a measure of linear elastic behavior for a material for which $dU(dW)$ and is only weakly dependent on entropic effects. Further, elastomers tend to exhibit highly nonlinear stress-strain responses under uniaxial tension, and E would be obtained by a linear fit to some portion of the stress-strain curve.

(b) Let us assume PDMS is reasonably described as a linear viscoelastic (LVE) material up to at least 100% normal strain. You've built a microfluidics device of 1 mm-high channels inside PDMS ($M_w = 10^6$ g/mol), then placed a sheet of glass on top that applied a constant compressive stress σ_0 of 1 MPa to keep it sealed (Fig. 3b).

Assuming that $E = 2$ MPa and η is given by Fig. 3a, determine and graph $\epsilon(t)$ of this PDMS for both Kelvin-Voigt and Maxwell models of the linear viscoelastic response. Note the magnitude of strain at $t = 0$ s and $t = \text{infinity}$ for both assumptions.

Solution:

Let $s = \text{stress } \sigma$; $e = \text{strain } \epsilon$, and $h = \text{viscosity } \eta$. The Maxwell model, a spring and dashpot in series, has the constitutive law $de/dt = 1/E(ds/dt) + s/h$, so if $s = s_0$ then $ds/dt = 0$ and $de/dt = s_0/h$.

The graphical prediction is that $e(t=0) = s_0/E$ and then $e(t)$ is a straight line of slope s_0/h for all t thereafter; $e(t = \text{infinity}) = \text{infinity}$.

The Kelvin-Voigt model, a spring and dashpot in parallel, has the constitutive law $de/dt = s/h - Ee/h$, so if $s = s_0$ then the solution of the differential equation $de/dt + Ee/h = s_0/h$ is:

$$e(t) = s_0/E[1 - \exp[-Et/h]].$$

The graphical prediction is that $e(t=0) = 0$ and increases to approach a constant strain of s_0/E at $t = \text{infinity}$.

(c) You've noticed that as soon as you apply this stress to the device, the pressure required to move fluid through the channels at a fixed velocity increased; you checked this pressure level the next day and it had leveled off. Considering this observation and your results in (b), which LVE model do you think best captures the deformation of your PDMS, and why?

Solution: This means that the channel got smaller (shorter) right away, which could be predicted by either model though instantaneously by the Maxwell model, and then steadied to a constant size (height). The Voigt model correctly predicts this leveling off of size because it predicts a constant strain (normalized change in thickness of the PDMS) at long times.

(d) According to the model you find most appropriate in (c), what is the channel height you would expect at $t = 1$ min after you applied the sealing stress to this PDMS device?

(a)

(b)

Image removed due to copyright restrictions. Please see Fig. 1 in Friedman, Emil M., and Porter, Roger S. "Polymer Viscosity-Molecular Weight Distribution Correlations via Blending: For High Molecular Weight Poly(dimethyl Siloxanes) and for Polystyrenes." *Transactions of the Society of Rheology* 19 (1975): 493-508.

Figure 3: (a) Experimentally measured viscosity of PDMS as function of molecular weight [4].

(b) Sealed microfluidics device comprising PDMS between 2 glass plates. Visible channels of PDMS were originally 1 mm high before the top glass plate was put on top to exert a constant stress of 1 MPa.

Solution: For the K-V model, if we assume $E = 2$ MPa and $h = 5 \times 10^6$ poise or 0.5 MPa-s from the graph in Fig. 3a, then $e(t) = s_0/E[1 - \exp[-Et/h]] = -0.5[1 - \exp(-4t)]$ where I include the negative sign to note that the stress is compressive. Thus, $e(t=60 \text{ s}) = -0.5$. This means a 50% decrease in the channel height, or a height of 0.5 mm after only 1 minute.

Incidentally, you should have noticed that this exponential really quickly decays for these values of E and h . The characteristic time it takes to decay is sometimes expressed as h/E , or 0.25

seconds for these values, or the time it takes for the strain to attain $[1-1/e]$ *(steady-state value), or $63\%*s_0/E = 0.32$ s for these values.

References

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. Mcmahon and J. A. Moriarty, *Physical Review B*, **27** (1983) 3235-3251.
4. Friedman, E. M. and R. S. Porter, *Trans. Soc. Rheol.* **19** (1975) 493–508.