## Section 5 DRAFT Mechanical Properties of Materials

## Interatomic Potentials

Atoms attract each other. The evidence for this is that all substances become liquid or solid at sufficiently low temperatures. So if the potential energy of a pair of atoms is zero at infinite separation, it becomes negative as they approach each other.

Atoms have sizes and do not interpenetrate (since solids have finite volume). So they must repel at short enough separations. The simplest repulsive potential is a "hard sphere" potential,



However, realistically, atoms are not infinitely rigid. Analytic approximations include the Lennard-Jones, or *12-6* potential,

$$U = a \left( \frac{b^{12}}{r^{12}} - \frac{b^6}{r^6} \right)$$

and the Morse potential,

$$U = c \left(1 - e^{-d(r - r_e)}\right)^2$$



In these plots the constants have been chosen to give the same equilibrium separation (1) and the same well-depth (1), and the third parameter in the Morse potential is chosen to give the same curvature at the bottom.

From the interatomic potential, we can immediately obtain a number of interesting properties of any material, including:

- Theoretical strength
- Hooke's Law
- Elastic stiffness moduli
- Thermal Expansion

First, let us put some numbers in. Typical atomic diameters are about  $3\text{\AA} = 0.3\text{nm} = 3 \times 10^{-8}\text{cm}$ , so there are about  $(\frac{1}{3} \times 10^{8})^{3} = -4 \times 10^{22} \text{cm}^{-3}$ . A typical metal weighs say 8g cm<sup>-1</sup>, so a typical atom weighs about  $2 \times 10^{-22}$ g or about  $2 \times 10^{-25}$ kg.

A typical chemical bond energy is ~eV (we know this because photochemistry exists, and because chemical batteries give a volt or two.) This is  $\sim 1.6 \times 10^{-19}$ J. So our interatomic potential in suitable units is



Atomic separation, r, (Å)

The *equilibrium separation* is at the bottom, at r = 2Å. *Theoretical Strength*: The force is maximum at the inflection point, at r = 2.17Å. This force will tear the atoms apart. This defines the *theoretical strength*. The force is D[*U*,*r*] at r = 2.17, which is 0.9 eV/Å = 0.9×  $(1.6 \times 10^{-19}) \times 10^{10}$ Jm<sup>-1</sup> = 1.4nN.

This force applied on a 3Å square is a stress of  $\sigma = F/A = 1.6 \times 10^{10}$ Pa = 16GPa = 160 tonnes per square cm. *This is vastly beyond the strength of any real materials.* 

Atomic Vibration Frequency: The bottom of the potential U(r) approximates to the parabola  $U(x) = \frac{1}{2}kx^2$ , where x is a small displacement from the equilibrium potential, and the curvature  $k = 8 \text{eV}\text{Å}^{-2} = 128 \text{Jm}^{-2}$ . Taking the mass as above, the vibration frequency in this harmonic approximation (see W&O) is \_\_\_\_\_\_

$$v = 2\pi\omega = 2\pi\sqrt{\frac{k}{m}} = 2\pi\sqrt{\frac{128}{2\times10^{-25}}} = 5\times10^{12} \text{ Hz}$$

This frequency corresponds to a wavelength of light of about  $60\mu m \sim 160 \text{cm}^{-1}$  – far infra-red – and is therefore called "optical". Of course materials can also sustain lower, "acoustic" vibrational frequencies (see W&O).

*Hooke's Law*: First published 1660, as an anagram of the Latin, *Ut tensio, sic vis.* "As the extension, so the force, or F = kx.

A force constant k (Nm<sup>-1</sup>) is appropriate for describing a structure, such as a coil spring. For a material such as rubber or steel, we define *material constants*, and *stress* and *strain*.

**Engineering stress and strain:** For a wire under tension, the *stress* is the force per unit area,  $\sigma = F/A$  Pa.

The *strain* is the fractional extension,  $\varepsilon = \Delta L/L$ .

**Young's Modulus:** Hooke's Law relates the stress and strain by a *modulus of elasticity*, here the Young's modulus *Y*:  $\sigma = Y\epsilon$ . Young's modulus is often called *E*.

Other engineering quantities: Shear stress, shear strain, shear modulus *G*. Poisson's ratio  $v = -\varepsilon_{\parallel}/\varepsilon_{\perp}$ , typically  $v = \frac{1}{3}$ .Bulk modulus *B*, given by  $P = B \Delta V/V$ , and often called *K*. See, e.g., http://en.wikipedia.org/wiki/Elastic\_modulus

Lennard-Jones potential, with the parameters above:  $F = -\frac{dU}{dr} = kx \text{ for small } x$ , i.e. for small displacements from the equilibrium position, with  $k = 8 \text{eV}\text{Å}^{-2}$ . This converts to  $\sigma = F/(3\text{\AA})^2 = k/(3\text{\AA})^2 \times \epsilon(3\text{\AA}) = Y\epsilon$ , so Y = 8/3  $\text{eV}\text{\AA}^{-3} = 8 \times 1.6 \times 10^{-19} / (3 \times 10^{-10})^3 = 5 \times 10^{10} \text{Jm}^{-3} = 50 \text{GPa}$ . Y = 50 GPa is in the right ballpark.

The bulk modulus requires the stress *P* to be applied in all directions, and the volumetric strain  $\Delta V/V$  is  $3\Delta L/L$ , so in this approximation (neglecting Poisson's ratio),  $B = \frac{1}{3}Y$ .

Engineering stress and strain, and moduli and Poisson's ratio, are a mess (too many constants and complicated relationships), and only valid for infinitesimal strain.

*Stress and Strain in Physics and Mathematics*: Stress is force per unit area. Force is a vector, and the unit area is a vector (the unit normal). So stress is a *higher-rank* object, a tensor. Scalars are zeroth-rank tensors; vectors are firstrank tensors, and stress is a second-rank tensor.

That is, a force in the *x*-direction,  $F_x$ , may be applied to a surface whose normal is in the *x*-direction – this results in a *normal stress*  $\sigma_{xx}$ . Or it may be applied to surfaces whose normals are in the *y*- or *z*- directions – this gives the *shear stresses*  $\sigma_{xy}$  and  $\sigma_{xz}$ . Thus tensor stress has nine components,

$$\overline{\boldsymbol{\sigma}} = \begin{pmatrix} \boldsymbol{\sigma}_{xx} & \boldsymbol{\sigma}_{xy} & \boldsymbol{\sigma}_{xz} \\ \boldsymbol{\sigma}_{yx} & \boldsymbol{\sigma}_{yy} & \boldsymbol{\sigma}_{yz} \\ \boldsymbol{\sigma}_{zx} & \boldsymbol{\sigma}_{zy} & \boldsymbol{\sigma}_{zz} \end{pmatrix} = \boldsymbol{\sigma}_{ij}$$

Similarly, the *x*-face of a cube may be displaced in the *x*, *y* or *z* directions, so strain is also a second-rank tensor,

$$\overline{\varepsilon} = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \sigma_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{pmatrix} = \varepsilon_{ij}$$

Each of the nine stress components depends on each of the nine strain components, so Hooke's Law may be written as,

$$\sigma_{ij} = c_{ijkl} \varepsilon_{kl}$$

where  $\overline{c}$  is a *fourth-rank* tensor (3×3×3×3) with 81 components, the elastic stiffness constants.

Fortunately, the requirement of static equilibrium and symmetry arguments reduce the number of independent components and elastic constants enormously. Static equilibrium requires  $\sigma_{ij} = \sigma_{ji}$ , and for an isotropic material (rubber, steel, etc) there are only two independent  $c_{ijkl}$ , not 81.

To go any further with tensor stress and strain, and to handle finite strains properly, requires the same maths – tensor analysis – as General Relativity.

*Voigt Notation*: A step back towards engineering methods was introduced by Voigt. Since there are only six independent stress components, Voigt labelled them 1-6, as  $xx \rightarrow 1$ ,  $yy \rightarrow 2$ ,  $zz \rightarrow 3$ ,  $yz \rightarrow 4$ ,  $zy \rightarrow 5$ ,  $xy \rightarrow 6$ . Then Hooke's Law is written as

$(\sigma_1)$		$(c_{11})$	<i>c</i> <sub>12</sub>	<i>c</i> <sub>12</sub>	0	0	0	×	$\left( \boldsymbol{\varepsilon}_{1} \right)$
$\sigma_2$		<i>C</i> <sub>12</sub>	$c_{11}$	<i>c</i> <sub>12</sub>	0	0	0		ε2
$\sigma_3$		<i>C</i> <sub>12</sub>	<i>c</i> <sub>12</sub>	<i>C</i> <sub>11</sub>	0	0	0		ε3
$\sigma_4$		0	0	0	C <sub>44</sub>	0	0		ε4
$\sigma_5$		0	0	0	0	<i>C</i> <sub>44</sub>	0		ε <sub>5</sub>
$\left(\sigma_{6}\right)$		0	0	0	0	0	$(c_{44})$		$\left(\epsilon_{6}\right)$

or

$$\sigma_I = c_{IJ} \varepsilon_J$$

(we use capital *I* and *J* for Voigt subscripts 1-6, to distinguish from tensor subscripts *i*, *j*, *k*, *l* that are 1-3).

The zero values of  $c_{IJ}$  come from fundamental symmetry arguments. The re-appearance of the subscripts 1, 2 and 4 comes from assuming cubic symmetry ( $x \equiv y \equiv z$ ). And in isotropic (spherical) symmetry,  $c_{44} = \frac{1}{2}(c_{11} - c_{12})$ . We conclude by calculating Young's modulus using this version of Hooke's Law:

A wire in tension has only one stress component,  $\sigma_1$ . It has a longitudinal tensile strain,  $\varepsilon_1$ . Poisson's ratio gives its lateral contraction, the two strains  $\varepsilon_2 = \varepsilon_3 = -v\varepsilon_1$ . So Hooke's Law becomes,

$$\begin{pmatrix} \sigma_{1} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \times \begin{pmatrix} \varepsilon_{1} \\ -\nu\varepsilon_{1} \\ -\nu\varepsilon_{1} \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

Each line of this matrix equation can be read off as a simple equation. The second or third lines give,

$$0 = c_{12}(\varepsilon_1 - v\varepsilon_1) - c_{11}v\varepsilon_1$$

Rearranging,

$$v = \frac{c_{12}}{c_{11} + c_{12}}$$

Then the first line reads

$$\sigma_1 = c_{11}\varepsilon_1 - 2c_{12}\nu\varepsilon_1 = \left(c_{11} - \frac{2c_{12}}{c_{11} + c_{12}}\right)\varepsilon_1$$

So

$$Y = c_{11} - \frac{2c_{12}}{c_{11} + c_{12}}$$

Similarly, we may find  $B = \frac{1}{3}(c_{11} + 2c_{12})$ .

**Thermal Expansion:** Thermal energy is average kinetic energy per atom ( $300K \equiv 25meV$  per degree of freedom). This lifts the material up the potential energy curve.

Very approximately, we solve for the maximum and minimum separations as a function of energy above the minimum. Averaging the two gives the average separation:



We see that the thermal expansion is close to linear, and is about a 1% expansion for 1000K. That is, the thermal expansion coefficient  $\alpha$  is about  $10^{-5}$ K<sup>-1</sup> (compare actual values of  $1.7 \times 10^{-5}$  for copper,  $1.18 \times 10^{-5}$  for iron).

*Quantum mechanics will show later why*  $\alpha \rightarrow 0$  *as*  $T \rightarrow 0$ *.* 

Thermal expansion is often attributed to atoms jiggling about at high temperature. This calculation shows that this is not true. It is due to atoms jiggling about at high temperature <u>in an anharmonic potential.</u>