NOTES 3: ATOMIC BONDING AND ELASTICITY THEORY

Ground-State Potential Energy of Solid

• We have introduced energy as key metric in solids and a rule to account for it during changes of a solid or system: the 1st law of thermodynamics

$$dU = TdS - PdV + \sum_i X_i dY_i$$

The rule applies to small changes in the solid relative to an unperturbed equilibrium state U_o. We could write in a rough sense $dU = U - U_0$ where U is the perturbed energy of the solid. Therefore, before getting into the perturbation of solids, it is helpful to calculate the magnitude of U_o, which will help in understanding the strength of solids as well as in gauging the size of the perturbations. (this is similar to the situation in electrostatics where before finding the energy of a distribution of charges it is important to first define the zero energy condition; because of the Coulombic nature of the force, this is conveniently chosen with all charges at infinity).

To understand U_0 and dU we need to understand the nature of the bonds that occur between atoms in solids at the microscopic level. Thanks largely to the field of quantum chemistry, these bonds were understood to be one of three general types, or a combination thereof: (1) the ionic bond, (2) the covalent bond, and (3) the metallic bond. Note that this makes no statement about the solid microscopic morphology – be it crystalline, amorphous, or something inbetween. In fact, a great deal of engineering can be done with solids without ever knowing their morphological state.

Ionic Bonding

• In ionic solids the atoms are considered to be independent with only a small force between them until one or more electrons are *tranferred* between pairs. One atom is called the *anion* and the other atom is called the cation.   This allows us to make the following assumptions, the first two founded in electrostatics:

(1) There is a collection of positive and negative charged atoms or molecules with equal number of each (charge neutral system)

(2) Zero of energy is defined with all atoms (or molecules) at infinity (so infinitely separated)

(3) The ions interact through two competing forces:

- Repulsive at close separation owing to overlap of the nuclear wave functions and inability (from Pauli exclusion) of electrons and nucleons to occupy same space/spin state [Note this is the first truly quantum-mechanical force of several to be used for the solid-state; the strong repulsion as atoms
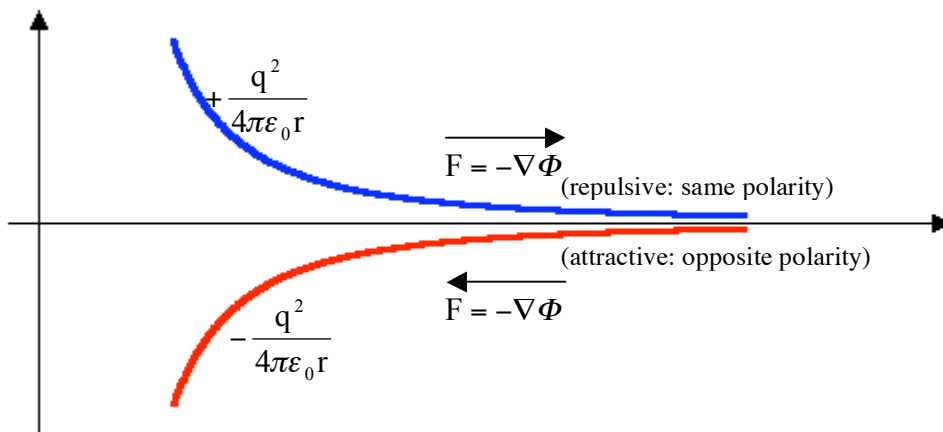
approach each other has no classical analog in classical electromagnetism or gravitational mechanics; when it is arises entirely from Pauli exclusion, it is called the "exchange" interaction]

- Long-range Coulomb force owing to the net charge + or - on each ion. This must have the form

$$\mathbf{F} = \frac{q_1 q_2}{4\pi\varepsilon_0 r_{ij}^2}\mathbf{r} = \pm\frac{q^2}{4\pi\varepsilon_0 r_{ij}^2}\mathbf{r} \text{ corresponding to a potential } \pm\frac{q^2}{4\pi\varepsilon_0 r_{ij}}$$

where $\mathbf{r}$ is the unit vector pointing between the two atoms, the *top sign* applies when q_1 and q_2 have the same polarity, and the *bottom sign* applies when they are opposite.
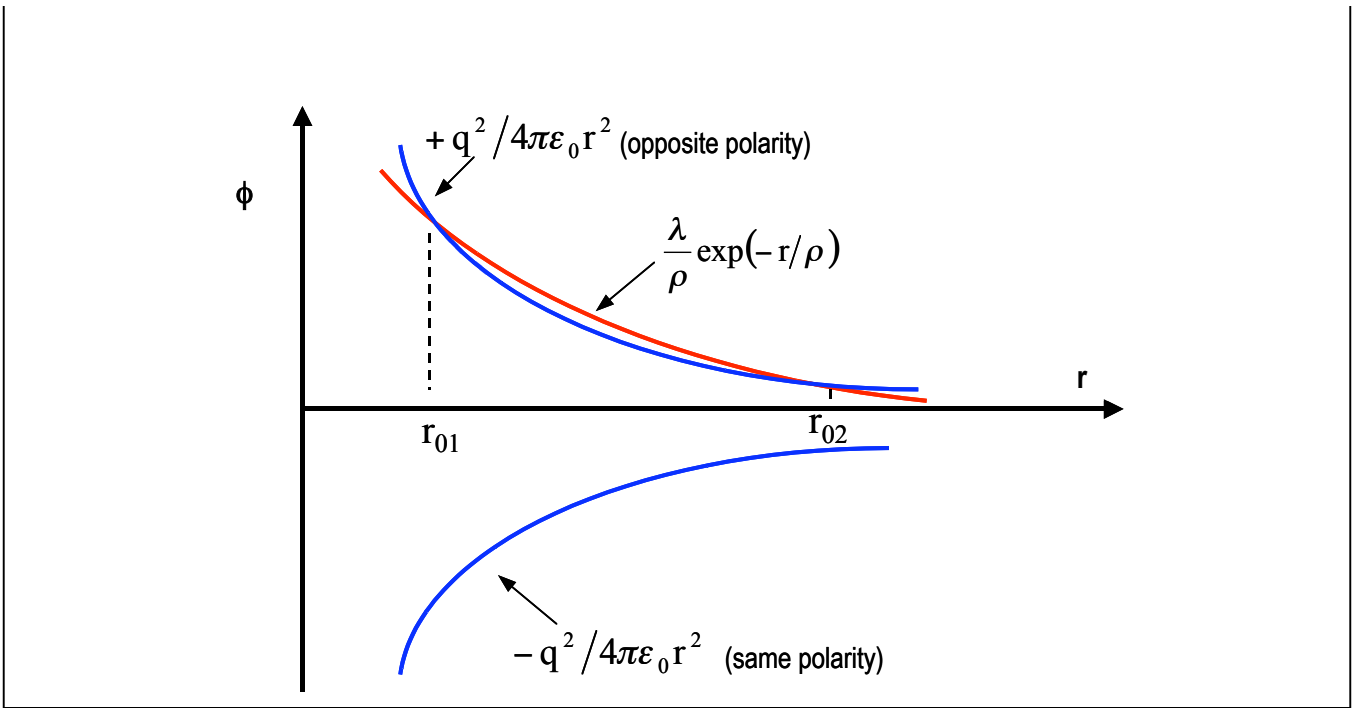
• A particularly useful form for the repulsive force is $F \propto \exp\left(-r_{ij}/\rho\right)$, which corresponds to an electrostatic potential: $\phi_R = \lambda\exp\left(-r_{ij}/\rho\right)$ where λ is a constant having units of energy.

• Given these potentials, the equation describing the electrostatic energy of one atomic ion in the presence of a neighbor is: (two body problem): $\phi = \lambda\exp\left(-r/\rho\right)\pm\frac{q^2}{4\pi\varepsilon_0 r}$

$+\dfrac{q^2}{4\pi\varepsilon_0 r}$

$F = -\nabla\Phi$ (repulsive: same polarity)

(attractive: opposite polarity)

$-\dfrac{q^2}{4\pi\varepsilon_0 r}$

$F = -\nabla\Phi$

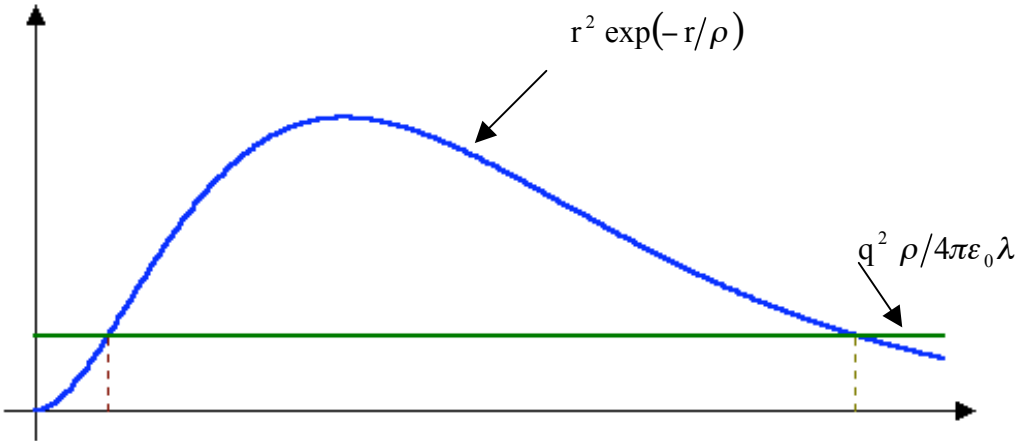Aside: Quick review of relationship between forces and potentials

Stable (or quasistable) point will be where $|F| = \dfrac{d\phi}{dr} = 0 \rightarrow \dfrac{\lambda}{\rho}\exp\left(-r/\rho\right) = \mp\dfrac{q^2}{4\pi\varepsilon_0 r^2}$

This is an *implicit* equation with graphical solution as follows:

The figure shows ϕ versus r with curves labeled $+q^2/4\pi\varepsilon_0 r^2$ (opposite polarity), $\frac{\lambda}{\rho}\exp(-r/\rho)$, and $-q^2/4\pi\varepsilon_0 r^2$ (same polarity), with marks at r_{01} and r_{02}.

er point determines the solution, and a solution exists only for the (bottom) + sign corresponding to opposite charge. Note: there may be two solutions ! To better understand this possibility, re-write

implicit derivative equation as $r^2 \exp\left(\dfrac{-r}{\rho}\right) = \rho q^2/4\pi\varepsilon_0\lambda$

The curve is labeled $r^2 \exp(-r/\rho)$ and the horizontal line is labeled $q^2\,\rho/4\pi\varepsilon_0\lambda$.

So yes, there are two possible solutions! Which solution is correct one? Go back and look at ϕ:
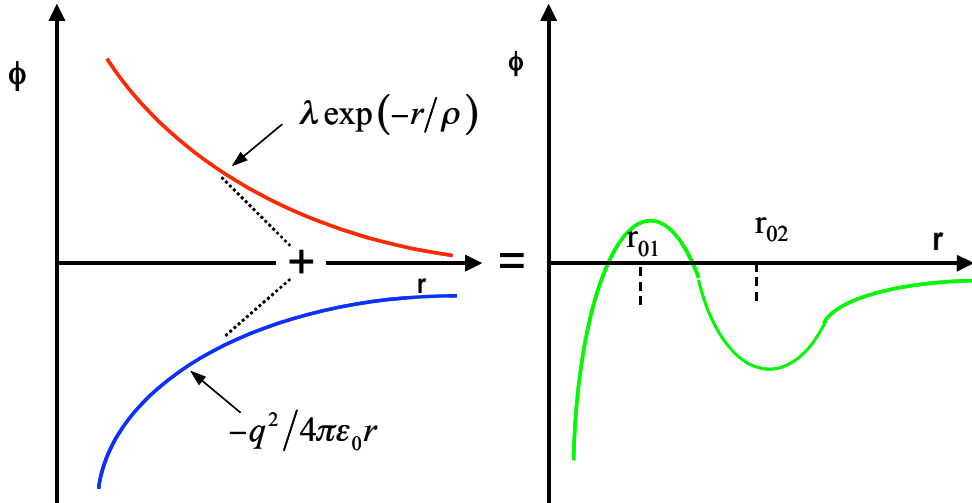
Of the two possible solutions, r_{01} is unstable and r_{02} is stable. Point at r_{02} is stable because force is restorative. That is, at $r = r_{01}$, or r_{02}, $F(r) = 0$

- At $r = r_{01} + \delta$, $F = -\nabla \phi > 0$, so that force points toward larger r_{01} increasing separation

  $r = r_{01} - \delta$, $F = -\nabla \phi < 0$, so that force points toward smaller r_{01} further decreasing separation

- At $r = r_{02} \pm \delta$, $F = -\nabla \phi \gtrless 0$, so that any deviation in r from r_{02} gives rise to force that draws atoms back to stable point.

Easier way to establish stability is through 2nd derivative.

Suppose we have zero slope point r_0: so that $\dfrac{d\phi}{dr} = 0$

- Stability occurs if $\left.\dfrac{d^2\phi}{dr^2}\right|_{r=r_0} > 0$ • Instability occurs if $\left.\dfrac{d^2\phi}{dr^2}\right|_{r=r_0} < 0$

Approximate Value of parameters

- X-ray diffraction shows that the size of many ionic molecules is $r_0 \approx 3\,\text{Å}$

- Particle scattering $\rightarrow$ atomic diameter $\approx 1\,\text{Å}$ $\rightarrow \rho \approx 0.5\,\text{Å}$

- So we can estimate

$$\lambda \equiv \frac{q^2 \rho \exp\left(\dfrac{r_0}{\rho}\right)}{4\pi\varepsilon_0 r_0^2} \equiv \frac{\left(1.6\times10^{19}\right)^2\left(0.5\times10^{-10}\right)\exp(6)}{4\pi\left(8.85\times10^{-12}\right)\left(3\times10^{-10}\right)^2} = 5.7\times10^{-17}\,\text{J}\,(322\text{eV})$$

(The magnitude of these quantities does not change much in solids if they are ionic)

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At stable point $\dfrac{\lambda}{\rho}\exp\left(\dfrac{-r}{\rho}\right) = \dfrac{q^2}{4\pi\varepsilon_0 r^2}$

So that $\phi = \lambda\exp\left(\dfrac{-r_0}{\rho}\right) - \dfrac{q^2}{4\pi\varepsilon_0 r_0} = \dfrac{q^2}{\rho\left(4\pi\varepsilon_0 r_0^2\right)} - \dfrac{q^2}{4\pi\varepsilon_0 r_0}$

$$\phi = \dfrac{q^2}{4\pi\varepsilon_0 r_0}\left(\dfrac{\rho}{r_0} - 1\right) = 4.8\left(\dfrac{\rho}{r_0} - 1\right)\left[eV\right]$$

$\phi \cong -4.0eV$ (comparable to known binding energy of many molecules)
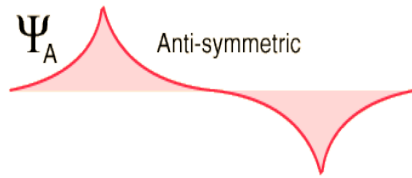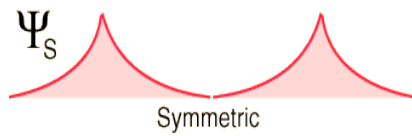
Covalent Bonding

- Very different from Ionic bonding. There are no ions formed…just a distortion in the electron "clouds", around the atoms that leads to competing repulsive and attractive terms.
- Overlap of wavefunctions is responsible for the bonding:
– as in ionic bonds, there is a strong tendency for atoms to interact with other atoms in such a way as to fill their outer electronic shells completely $\Rightarrow$ inert-gas state.
– If the atoms are in the middle part of the periodic table, there are simply too many electrons to gain or lose completely.
– So for these atoms, the electrons are commonly shared between the atoms.
- But Pauli exclusion principle prohibits electrons from occupying the same spatial-spin wavefunction.
$\Rightarrow$ There will be a repulsion between electron clouds that prevents them from getting too close. In quantum-mechanical terms, this is called the "exchange" interaction.

Good example of covalent bonding: the hydrogen molecule: H_2

Wavefunction of the 2 electrons around 2 H atoms is either antisymmetric or symmetric.

- Pauli exclusion principle $\Rightarrow$ wavefunctions for 2 identical fermions must be antisymetric
o Electron spin can be symmetric (parallel spin) OR anitsymmettric (opposite spin) $\Rightarrow$ space part of the wavefunction must be opposite so that entire wavefunction is antisymmetric

Spatial wavfunction for distant hydrogens: Hydrogens close to each other:

Ψ_S Symmetric

Ψ_S $|\Psi_S|^2$ Bonding

Ψ_A Anti-symmetric

Ψ_A $|\Psi_A|^2$ Anti-bonding
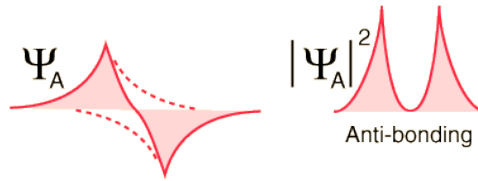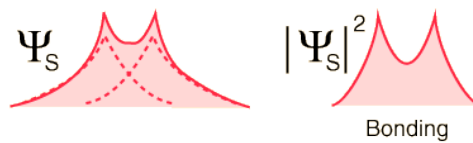
Electron charge density is high between nuclei for symmetric ⇨net attractive force because of electrostatics ⟹ bonding. In other words, the symmetric combination of spatial wavefunctions creates a distortion of the atomic charge distributions such that the nuclei of each H atom "experiences" a slightly greater electron number than one (i.e., the number of protons in each nucleus). So there is a net attractive force inward on each nucleus toward the overlap region. For the hydrogen molecule, the exchange interaction thus leads to a minimum in the total potential energy curve as shown below. And it has only been explained successfully using quantum mechanics.

Potential energy U
U_A
0.1   0.2 r (nm)
4.52 eV U_S
0.074 nm = r_0
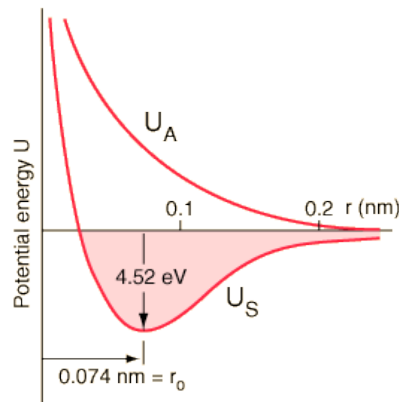
Directionality of covalent bond:

Electron Domain theory: 3 dimensional distribution of the outermost electrons about a given atom and how electrons will pair with other electrons from bonding atoms.

- Valence electrons bind as pairs with opposite spin – an electron domain (bonding or antibonding) bonding – paired electrons are shared, anti-bonding – electrons belong exclusively to a particular atom
- Electron domains arrange themselves to be as close as possible to a central atom and also avoid other electron domains
- Electron distribution – result of bonding and antibonding electron domains
  Molecular shape – result of only the bonding electron domains

Example: C forms the diamond structure as a result of the tetrahedrally coordinated bonds (same for many group IV elements).

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3.1.3. Metallic Bonding

The third type of bond common to solids is what occurs in metals – the class of solids characterized by high electrical conductivity and a related mechanical property called *ductility*. Similar to the covalent and ionic bond, in the metallic bond the atoms strive to achieve a full outer electron shell. But rather than transferring an electron to a neighboring atom or sharing an electron, the atoms all donate electrons to the solid as a whole, creating a background of electrons that are free to move about the solid unattached to any particular atom or group of atoms. The number of electrons donated by each atom is equal to its valence (i.e., the number of electrons in its outermost partially filled shell in its neutral state). Every atom in the metallic solid is "cationic" in the sense that they donate electrons and acquire a positive charge and, therefore, repel each other. But they remain fixed in the solid state because of the collective attraction with the background of "free" electrons.

A subtlety of metallic bonding is the fact that the atoms are not locked-in to specific locations as in ionic or covalent solids since the cohesion is between the atoms and the "free" electrons that are in constant motion. This helps explain the natural ductility of metals – the ability to deform without cracking or changing physical property. And of course ductility is one of the reasons that metals became the basis for tool making, machines, and other developments in the rise of human technology and the industrial revolution.

Important Points on Atomic Bonding in Solids

(1) Some of the most important solids, particularly elemental materials (e.g., diamond, S, and Ge) display purely covalent behavior. But compound solids (i.e., composed of two or more elements), usually display a mix between ionic and covalent behavior. Good examples are the compound semiconductors GaAs, InP, and their ternary and quaternary alloys. Largely because of the importance of these materials in electronics and optoelectronics, metrics have been developed to quantify the degree of ionicity or covalency of materials. A particularly useful metric is Phillips fractional ionic character , ζ ,summarized in Table 8 of Chapter 3 in Kittel: $\zeta = 0$ being purely covalent and $\zeta = 1.0$ being purely ionic. When the material has ζ around 0.5, it may display either ionic or covalent behavior depending on the nature of the external force. For example, in response to external mechanical forces, GaAs displays a similar response as Si, largely because of its tetrahedral covalent bonding. But in response to infrared radiation, GaAs can display a very strong optical absorption owing to the small but significant polar nature of the Ga-to-As bond, as we shall soon see in the coverage of optical lattice waves and phonons.

(2) The key common result from the ionic and covalent bonding analysis is they both result in the same *asymmetric* type of binding potential – very steep as r approaches zero, but more gradual as r goes to infinity. This asymmetry leads to universal properties of solids, such as nonzero thermal expansivity (as we have already seen from the thermodynamic analysis). But it also corresponds to a high degree of nonlinearity in the interatomic potential, which causes mixing between elastic waves once the atoms are put into motion (i.e., given kinetic energy associated with heat, or with acoustical energy).

(3) As might be expected, the single bond energy for covalent solids is often less than the single bond energy in ionic solids{e.g., NaCl bond $U_0 \sim 4.0$ eV; silicon "single" bond: $U_0 = 1.8$ eV (see Table 7 of Chapter 3, Kittel)}. So why are covalent solids generally so much stronger ?

Answer: the number of bonds per atom and their spatial orientation. For example, through hybridization of the atomic wavefunctions, a single Si atom forms 4 tetrahedrally-oreinted covalent bonds with each nearest neighbor, $\Rightarrow$ a net U_0 of 7.2 eV (but be careful on the counting !). The Si is essentially "locked in a cage" of four spatially opposing bonds.

Elasticity Theory

As we have just seen for ionic and covalent solids, the atomic binding is always characterized as a competition between quantum or nuclear repulsion under compressive forces, and internuclear (usually electrostatic) attraction under tensile (i.e., expansive) forces on the solid. These competing internal forces always conspire to create a microscopic potential energy for each atom as shown qualitatively in the previous sections on ionic and covalent bonding.

To get the cohesive energy of the solid, we need to sum over the binding energy of each atomic bond. Conceptually, this is the reduction in potential energy in the actual solid-state configuration compared to having all the atoms of the solid separated to infinity. The most accurate way to calculate this quantity is by knowing the exact average location of each atom, as is possible in a crystalline solid. This will be carried out in detail in Notes#5 once we go over some crystal lattice theory.

Response of Solid to External Mechanical Force: Strain

But interestingly, the U_0 energy was known to be important even before the advent of the atomic picture, particularly in explaining the reaction of the solid dU to external mechanical and thermal forces. To demonstrate this, we write the total U_0 as a sum over all relative position vectors $\mathbf{r}^{ij}$

(being careful to not count any vector twice): $U = \sum\limits_{i,j;i \neq j} U\left(\mathbf{r}^{ij}\right)$ where the $\mathbf{r}^{ij}$ connects the ith and jth

atom relative to some fixed coordinate system, or the ith and jth reference points (the viewpoint before the discovery of atoms). But the $\mathbf{r}^{ij}$ are themselves a function of position, defined by the lattice type in a crystalline solid or the chosen reference points in an amorphous solid. So it is smart to factorize the energy deviation in terms of: (1) an atom *(or reference-point)*-independent contribution that accounts for the universal binding behavior derived for both ionic- and covalent-type bonds, and (2) an atom- (or reference point)-dependent term that accounts for the distribution of atoms and their reaction to the external force.

$$r^{ij} = \left|\mathbf{r}^{ij}\right| \qquad \mathbf{r}^{ij} = r_x^{ij}(x,y,z)\mathbf{x} + r_y^{ij}(x,y,z)\mathbf{y} + r_z^{ij}(x,y,z)\mathbf{z}$$
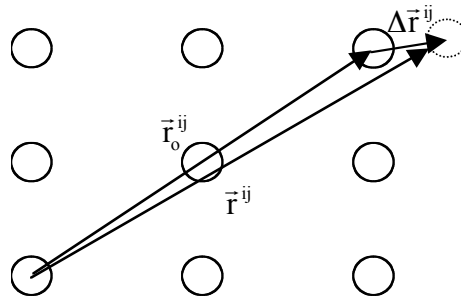
The site-independent factor is defined by a Taylor's series expansion in three dimensions:

$$U\left(\mathbf{r}_0^{ij} + \Delta\mathbf{r}\right) = U\left(\mathbf{r}_0^{ij}\right) + \sum_{(m=x,y,z)} \left.\frac{\partial U}{\partial r_m^{ij}}\right|_{r_0} \Delta r_m^{ij} + \frac{1}{2}\sum_{(m,n=x,y,z)} \frac{\partial^2 U}{\partial r_m^{ij} \partial r_n^{ij}} \Delta r_m^{ij} \Delta r_n^{ij} + ...$$

From equilibrium condition, $\dfrac{\partial U}{\partial r_n^{ij}} = 0$ for all n = x, y, and z., so the 2$^{\text{nd}}$ term is always zero. So what

remains is an expression for $\Delta U\left(\mathbf{r}_0^{ij} + \Delta\mathbf{r}\right) \approx \dfrac{1}{2}\sum\limits_{(m,n=x,y,z)} \dfrac{\partial^2 U}{\partial r_m^{ij} \partial r_n^{ij}} \Delta r_m^{ij} \Delta r_n^{ij}$ (*)

This is an example of what is called a "quadratic form" in linear algebra. And it has the special property that the potential energy function (such as the ionic and covalent forms we have inspected already) should be well-behaved – no singularities or no multiple values. So the order of differentiation should not matter; i.e., $\partial^2 U/(\partial r_m \partial r_n) = \partial^2 U/(\partial r_n \partial r_m)$. So there are six independent terms (generalized spring constants)

$$\frac{\partial^2 U}{\partial r_x^2}, \frac{\partial^2 U}{\partial r_y^2}, \frac{\partial^2 U}{\partial r_z^2}, \frac{\partial^2 U}{\partial r_x \partial r_y}, \frac{\partial^2 U}{\partial r_x \partial r_z}, \frac{\partial^2 U}{\partial r_y \partial r_z}$$

The site-dependent contribution is defined by expanding the $(\Delta r_n)^{ij}$ factors with respect to a cartesian coordinate system

$$\Delta r_x^{ij} = \frac{\partial \Delta r_x^{ij}}{\partial x^{ij}} \Delta x_0^{ij} + \frac{\partial \Delta r_x^{ij}}{\partial y^{ij}} \Delta y_0^{ij} + \frac{\partial \Delta r_x^{ij}}{\partial z_z^{ij}} \Delta z_0^{ij} \ ; \text{ and similar for } \Delta r_y^{ij} \text{ ; and } \Delta r_z^{ij}$$

This leads to a matrix representation:

$$\begin{bmatrix} \Delta r_x^{ij} \\ \Delta r_y^{ij} \\ \Delta r_z^{ij} \end{bmatrix} = \begin{pmatrix} \dfrac{\partial \Delta r_x}{\partial x} & \dfrac{\partial \Delta r_x}{\partial y} & \dfrac{\partial \Delta r_x}{\partial z} \\ \dfrac{\partial \Delta r_y}{\partial x} & \dfrac{\partial \Delta r_y}{\partial y} & \dfrac{\partial \Delta r_y}{\partial z} \\ \dfrac{\partial \Delta r_z}{\partial x} & \dfrac{\partial \Delta r_z}{\partial y} & \dfrac{\partial \Delta r_z}{\partial z} \end{pmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix} \equiv \sum_{m,n=x,y,z}^{3} \varepsilon_{mn} \Delta n$$

This 3x3 matrix is, in fact the gradient of $\Delta \mathbf{r}$ – an operation that ignores the bodily motion of the solid as a whole, which is not interesting from a solid-state perspective. [As shown in some books on vector calculus, the gradient of a vector is a 2nd rank tensor (similar to the definition of the dielectric constant tensor earlier): And a 2nd rank tensor is a matrix]. And it does not depend on location in the sample. It is often called the *deformation* matrix with unitless elements ε_{mn}

An even more useful quantity results from symmetrizing the deformation matrix:

$$1/2 \cdot \begin{pmatrix} 2\dfrac{\partial \Delta r_x}{\partial x} & \dfrac{\partial \Delta r_x}{\partial y} + \dfrac{\partial \Delta r_y}{\partial x} & \dfrac{\partial \Delta r_x}{\partial z} + \dfrac{\partial \Delta r_z}{\partial x} \\ \dfrac{\partial \Delta r_y}{\partial x} + \dfrac{\partial \Delta r_x}{\partial y} & 2\dfrac{\partial \Delta r_y}{\partial y} & \dfrac{\partial \Delta r_y}{\partial z} + \dfrac{\partial \Delta r_z}{\partial y} \\ \dfrac{\partial \Delta r_z}{\partial x} + \dfrac{\partial \Delta r_x}{\partial z} & \dfrac{\partial \Delta r_z}{\partial y} + \dfrac{\partial \Delta r_y}{\partial z} & 2\dfrac{\partial \Delta r_z}{\partial z} \end{pmatrix} \equiv \begin{pmatrix} e_{xx} & e_{xy} & e_{xz} \\ e_{yx} & e_{yy} & e_{yz} \\ e_{zx} & e_{zy} & e_{zz} \end{pmatrix}$$

This is called the strain matrix, and it has the special properties of being unitless and insensitive to externally applied torque and any resulting angular bodily motion. More importantly from an analytic standpoint, like the generalized spring constants $\partial^2 U/(\partial r_m \partial r_n)$, *there are only six independent elements in the strain matrix* (the deformation matrix had nine, in general).

Through some fancy algebra (an obligatory exercise in continuum mechanics; not necessarily solid-state engineering), it is now possible to substitute the Δr_m terms back in to (*) and sum over all the ij atomic pairs:

$$\Delta U = \sum_{i,j} \Delta U \left(\mathbf{r}_0^{ij} + \Delta \mathbf{r} \right) \approx \frac{1}{2} \sum_{i,j} \sum_{(m,n=x,y,z)} \frac{\partial^2 U}{\partial r_m^{ij} \partial r_n^{ij}} \Delta r_m^{ij} \Delta r_n^{ij} \qquad \Delta U = \frac{1}{2} \sum_{(M,N=1)}^{6} C_{MN} e_M e_N \cdot \Delta V_0$$

	36 stiffness	six independent strain terms
	coefficients	
	(or moduli of elasticity)	

Note: since the strain terms are unitless, the CMN must have units of force/unit-area (i.e., pressure)

Convention for six terms: $\quad e_1 \equiv e_{xx} = \varepsilon_{xx} \qquad e_2 \equiv e_{yy} = \varepsilon_{yy} \qquad e_3 \equiv e_{zz} = \varepsilon_{zz}$

$$e_4 = e_{yz} = \varepsilon_{yz} + \varepsilon_{zy} \qquad e_5 = e_{xz} = \varepsilon_{xz} + \varepsilon_{zx} \qquad e_6 = e_{xy} = \varepsilon_{xy} + \varepsilon_{yx}$$

Important comments about elasticity theory:

(1) The formalism to this point does not care about the microscopic morphology of the solid (i.e., crystalline vs amorphous). It only cares that the material contains bonds in which the potential energy has the characteristic minimum we found for both ionic and covalent bonds.

(2) The need for six independent strain terms is unique to solids. The first three e_1, e_2, and e_3 can be thought of as the usual compression (if the e's are < 0) or tensional (if the e's are > 0) deformations, just as occurs in gases or liquids.

(3) But the last three e_4, e_5, and e_6 are a consequence of a "shear" response. In other words, application of a force along a certain direction leads to a response in an orthogonal direction. So these are called the *shear* strain terms.

Properly Characterizing the Applied Force: Stress

With the mathematical description of strain comes a need to properly represent the external force on a solid. This exercise is guided by analogy with gases and liquids – the useful mechanical and thermodynamic intensive variable for gases and liquids is the pressure (force/unit area). To get a quantity having units of pressure, we simply need the linear transformation using the stiffness

coefficient matrix: $\qquad\qquad\qquad P_M = \dfrac{\Delta U}{\Delta V_0 \cdot e_M} = \displaystyle\sum_{N=1}^{6} C_{MN} e_N$

And just like the strain, there are six unique stress terms in general.

and $\quad \Delta U' = \dfrac{1}{2} \displaystyle\sum_{M=1}^{6} P_M e_M$ (energy density)

So $\quad d\left(\Delta U_{total}\right) = TdS - \displaystyle\sum_{M=1}^{6} P_M de_M \Delta V_0$ in quasi-equilibrium

Important Note from our Engineering Approach:

(1) from our thermodynamic reasoning, the stiffness coefficients C_{MN} are just (inverse) generalized susceptibilities relating change in stress to change in strain.

(2) For all solids, the stiffness coefficients as defined above are symmetric $C_{MN} = C_{NM}$

(3) When solid has high degree of symmetry, most C_{MN} vanish. For example, in both an isotropic solid and one having cubic symmetry

$$
\begin{bmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \\ P_5 \\ P_6 \end{bmatrix}
=
\begin{bmatrix}
C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{44}
\end{bmatrix}
\bullet
\begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix}
$$

For the isotropic solid, C_{11}, C_{12} and C_{44} are correlated, so there are only two indepenedent parameters. But for cubic solids, C_{11}, C_{12} and C_{44} are independent parameters

In a hexagonal System (e.g., GaN, AlN, and other important materials at UCSB !)

$$
\begin{bmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \\ P_5 \\ P_6 \end{bmatrix}
=
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\
C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & C_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & C_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\bullet
\begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix}
$$

<u>There are 5 independent coefficients in this system</u>.

(4) By matrix inversion get: $\quad e_M = \sum_{N=1}^{6} S_{MN} P_N$

> ***S → elastic compliance coefficients (or elastic constants) with*** $S_{MN} = S_{NM}$

Note: In practice, the compliance matrix is usually easier to deal with than the stiffness matrix.

(5) Clearly, the form of the C and S matrices depends strongly on the symmetry (and thus the underlying crystallinity as we shall soon see). But again, the elasticity theory handles isotropic solids as well as it does symmetric ones, which is why it is so useful in solid-state engineering.

(6) And it even applies to fluids (gases and liquids) as a special case:

$$
\begin{bmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \\ P_5 \\ P_6 \end{bmatrix}
=
\begin{bmatrix}
C_{11} & 0 & 0 & 0 & 0 & 0 \\
0 & C_{11} & 0 & 0 & 0 & 0 \\
0 & 0 & C_{11} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\bullet
\begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix}
$$

where $C_{11} \approx 1/(3\kappa)$, κ being the compressibility from macroscopic thermodynamics

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Fluids support no shear strain, and therefore can apply no shear stress. This provides even deeper insight into why solids are so important in engineering !

How Elasticity is Often Characterized: Young's Modulus and Poisson's Ratio

Clearly, the (tensor) mathematics of elasticity theory is rather tedious. But as is often the case in engineering, great simplification occurs through practical implementation. Perhaps the most important simplification is based on the fact that practical applied macrosocopic forces are easily *uniaxial* (i.e., in one direction of space), such as from a screw. And nature gives us a great contrast in the compressibility of solids and air (see 1st HW problem on copper vs air). So the mechanical boundary condition on solids in air is well approximated as "free". A uniaxial pressure, i.e., stress, then means: All P_M equal to zero except one, call it P_N

$$Y = \frac{P_N}{e_N}\bigg|_{P_N} \quad N \to (xx, yy, or\ zz)$$

$Y \to$ Young's modulus

$P_N \to$ tensile (elongation) means positive P_N (mnemonic tool: positive means toward greater Δr)

$$\sigma = -\frac{e_M}{e_N}\bigg|_{P_N} \quad \begin{array}{l} M = (xx, yy, or\ zz \neq N) \\ N = (xx, yy, or\ zz) \end{array}$$

$\sigma \to$ Poisson's ratio (turns out less $< 1/2$, but can be < 0): Note: sign is important: defined to be positive for the normal solid where for e_N in tension (>0), $e_N < 0$.

Constructing the Compliance Matrix for a Generic (Isotropic) Solid

We start with a cube of material in which compressive forces are applied sequentially

(A) Compressive forces along each facet of area A
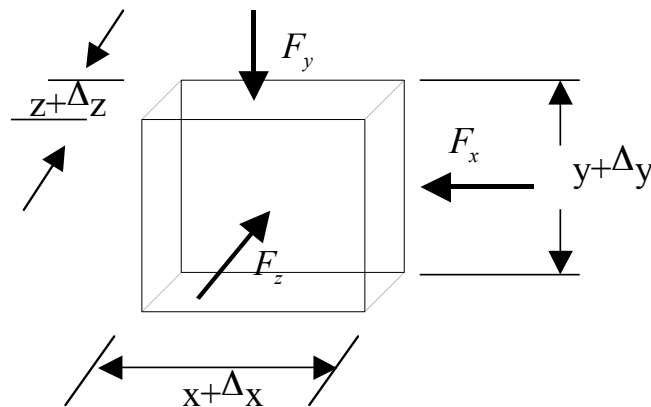
The strain along any axis will have three contributions.
For example, along x axis:

$$\left(\frac{\Delta x}{x}\right)_1 = -F_x / (AY) \equiv {-P_{xx}}\big/{Y}$$

$$\left(\frac{\Delta x}{x}\right)_2 = \sigma \left(\frac{\Delta x}{x}\right)_1 = \sigma F_x / (AY) = \sigma F_y / (AY) \equiv {+\sigma P_{yy}}\big/{Y}$$

$$\left(\frac{\Delta x}{x}\right)_3 = \sigma \left(\frac{\Delta x}{x}\right)_1 = \sigma F_x / (AY) = \sigma F_z / (AY) \equiv {+\sigma P_{zz}}\big/{Y}$$

So that total strain along the x axis is:

$$e_{xx} = \left(\frac{\Delta x}{x}\right)_1 + \left(\frac{\Delta x}{x}\right)_2 + \left(\frac{\Delta x}{x}\right)_3 = \frac{-1}{Y}\left(P_{xx} - \sigma P_{yy} - \sigma P_{zz}\right)$$

Following convention, we reverse all the signs for forces in tension and we already have one part of the compliance matrix:

$$
\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ ? \\ ? \\ ? \end{bmatrix}
=
\begin{bmatrix}
1/Y & -\sigma/Y & -\sigma/Y & ? & ? & ? \\
? & ? & ? & ? & ? & ? \\
? & ? & ? & ? & ? & ? \\
? & ? & ? & ? & ? & ? \\
? & ? & ? & ? & ? & ? \\
? & ? & ? & ? & ? & ?
\end{bmatrix}
\bullet
\begin{bmatrix} P_{xx} \\ P_{yy} \\ P_{zz} \\ ? \\ ? \\ ? \end{bmatrix}
$$

By deduction, it can be seen that if sequential forces are applied along the y and z axes, the matrix fill will in as follows

$$
\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ ? \\ ? \\ ? \end{bmatrix}
=
\begin{bmatrix}
1/Y & -\sigma/Y & -\sigma/Y & ? & ? & ? \\
-\sigma/Y & 1/Y & -\sigma/Y & ? & ? & ? \\
-\sigma/Y & -\sigma/Y & 1/Y & ? & ? & ? \\
? & ? & ? & ? & ? & ? \\
? & ? & ? & ? & ? & ? \\
? & ? & ? & ? & ? & ?
\end{bmatrix}
\bullet
\begin{bmatrix} P_{xx} \\ P_{yy} \\ P_{zz} \\ ? \\ ? \\ ? \end{bmatrix}
$$

(B) Shear forces at angle to facets
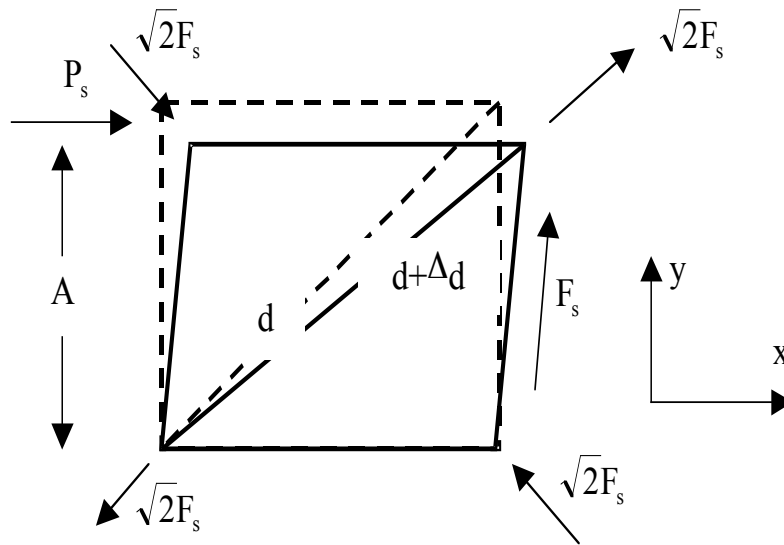
Note: Shear results from the combination of tensional and compressional stresses acting at right angles to each other. Good example: attach a cube to the ground, then pull horizontally on the top surface. In order that the cube not move, the ground must apply an equal and opposite horizontal force. The result is that the cube is in a state of *shear*.

Δd has two contributions:

(1) tensile stress along diagonal is applied over area $\sqrt{2} \cdot A$

$$\left(\frac{\Delta d}{d}\right)_1 = \frac{\sqrt{2}F_S}{\sqrt{2}A}\frac{1}{Y} = \frac{P_S}{Y}$$

(2) compressional stress along oppostite diagonal applied

over area of $\sqrt{2} \cdot A$

$$\left(\frac{\Delta d}{d}\right)_2 = \frac{\sigma}{Y}\frac{\sqrt{2}F_S}{\sqrt{2}A} = \frac{\sigma P_S}{Y}$$

Strain:

$$\frac{\Delta d}{d} = \left(\frac{\Delta d}{d}\right)_1 + \left(\frac{\Delta d}{d}\right)_2 = \frac{1+\sigma}{Y}P_S$$

But there are two opposing F_S terms so that $(\Delta d/d)_{tot} = 2(1 + \sigma)\,P_S/Y$. We have filled in another

entry to the compliance matrix !

$$\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ ? \\ ? \\ e_{xy} \end{bmatrix} = \begin{bmatrix} 1/Y & -\sigma/Y & -\sigma/Y & ? & ? & ? \\ -\sigma/Y & 1/Y & -\sigma/Y & ? & ? & ? \\ -\sigma/Y & -\sigma/Y & 1/Y & ? & ? & ? \\ ? & ? & ? & ? & ? & ? \\ ? & ? & ? & ? & ? & ? \\ ? & ? & ? & ? & ? & 2(1+\sigma)/Y \end{bmatrix} \cdot \begin{bmatrix} P_{xx} \\ P_{yy} \\ P_{zz} \\ ? \\ ? \\ P_{xy} \end{bmatrix}$$

Successive application of such "pure" shear forces in the xz and yz planes would naturally create identical ($\Delta d/d$) strain terms for "pure" shears P_{yz} and P_{xz} And in normal solids, this exhausts the possibilities of external forces, so that the total compliance matrix for an isotropic solid is given by:

$$\begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{xz} \\ e_{xy} \end{bmatrix} = \begin{bmatrix} 1/Y & -\sigma/Y & -\sigma/Y & 0 & 0 & 0 \\ -\sigma/Y & 1/Y & -\sigma/Y & 0 & 0 & 0 \\ -\sigma/Y & -\sigma/Y & 1/Y & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(1+\sigma)/Y & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(1+\sigma)/Y & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(1+\sigma)/Y \end{bmatrix} \cdot \begin{bmatrix} P_{xx} \\ P_{yy} \\ P_{zz} \\ P_{yz} \\ P_{xz} \\ P_{xy} \end{bmatrix}$$

As you might expect, this relatively simple form of the compliance matrix leads to an equally simple form of the stiffness matrix upon inversion of the matrix. It turns out (see HW#2 as well) for the isotropic solid:

$$\begin{bmatrix} P_{xx} \\ P_{yy} \\ P_{zz} \\ P_{yz} \\ P_{xz} \\ P_{xy} \end{bmatrix} = \begin{bmatrix} 2\mu_L + \lambda_L & \lambda_L & \lambda_L & 0 & 0 & 0 \\ \lambda_L & 2\mu_L + \lambda & \lambda_L & 0 & 0 & 0 \\ \lambda_L & \lambda_L & 2\mu_L + \lambda & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu_L & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu_L & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu_L \end{bmatrix} \cdot \begin{bmatrix} e_{xx} \\ e_{yy} \\ e_{zz} \\ e_{yz} \\ e_{xz} \\ e_{xy} \end{bmatrix}$$

where λ_L and μ_L are the Lame constants. So an isotropic solid has only two independent parameters needed to describe its elastic behavior. A fluid has only one. Any anisotropic solid

requires more than two (e.g., simplest case being solid of cubic symmetry, three parameters required).