

## Lecture 7: Bonding in solids and elastic strain

- **Covalent Crystals (electrons shared between neighboring atoms)**
- **Metallic Bonding (delocalized electrons 'shared' among all atoms in crystal)**
- **Van der Waals crystals (electric dipole-dipole interactions)**
- **Introduction to elastic strain**

### Review: Ionic solids

**Definition:** charged ions held together because coulomb attraction between opposite charges overcomes repulsion between like charges

**Examples:** NaCl, KCl, many other salts and ceramics

**Key concepts:** madelung constant and madelung energy

Total potential energy of crystal:  $U_{tot} = \frac{-N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0}\right)$

Madelung energy=prefactor term (term inside parenthesis  $\sim 1$ )

$R_0$  = equilibrium atomic separation (found by finding minimum of potential energy); N=# of ion pairs

Madelung constant= $\alpha$ =sum of coulomb terms from every other ion; this parameter contains the messy arithmetic involved in describing ionic solids, and it is also the configuration-dependent term in the expression for the total potential energy

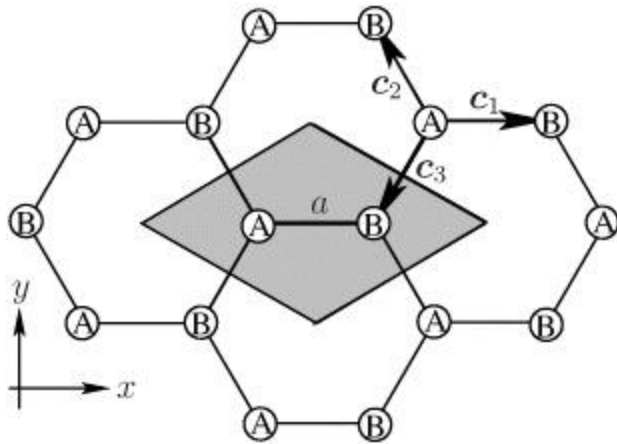
### Covalent bonding

Most commonly encountered in Column-4 elements (C, Si, Ge...) and nearby columns too (e.g. GaAs). In column-4, atoms are 4 electrons short of a full shell, which they can attain by sharing electrons with 4 neighbors.

Most common manifestation in this class—diamond lattice. Each atom is tetrahedrally bonded to 4 other atoms. Technologically, this is one of the most important bonding schemes because it is implicated in Si, GaAs, GaN (see HW1) just to name several examples. Biologically, this is also one of the most important bonding schemes, because carbon can make covalent bonds in several different ways.

Example: graphene—sp<sup>2</sup> hybridized carbon forms bonds with 3 other carbons.

Identify primitive lattice vectors in honeycomb lattice (and explain why the obvious suspects are not it)



### Metallic bonding

Metals are characterized by ductility and electrical conductivity, both of which can be understood by metallic bonding which features delocalized electrons (one or two from each atom) which are free to move around the entire solid. Metals also tend to crystallize in relatively close-packed structures—FCC, HCP, and BCC. If the atoms are imagined as hard spheres, FCC and HCP allow for the highest packing fraction possible and BCC is close.

Q: why is ductility related to metallic bonding

A: Compare to covalent bonding (which is very directional) or ionic bonding (which requires a specific configuration for electrostatic stability), metallic bonding doesn't prefer one configuration of atoms relative to another.

Example of metallic bonding in action—cold welding. This is where two metals are joined to each other in vacuum without using heat or molten components. Vacuum is needed to avoid the formation of a native oxide on the metal surface (pretty much every metal oxidizes a tiny bit). When two unoxidized pieces of metal are brought into contact in such a way that large surface areas contact each other (either because the metal pieces are really flat, or because they are smushed together hard enough, or because they are soft enough to easily conform to each other), they will actually fuse. This is cold welding.

### Van der Waals solids

Van der Waals interactions are very important in our everyday life. For example, the adhesive in sticky tape works via van der Waals interactions, and vdW interactions also allow geckos to stick to smooth surfaces like glass.

The important things to remember about van der Waals interaction are:

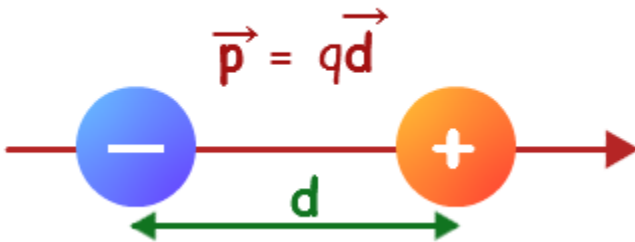
- It is a dipole-dipole interaction (permanent dipole/permanent dipole, permanent dipole/induced dipole, or induced dipole induced dipole)
- It is a very short-range interaction and is only appreciable if two objects are very close (within several atomic radii) to one another
- When an atomic lattice is held together by van der Waals interactions, the resulting potential energy landscape that each atom is subjected to is called the 'lennard jones potential.'

The textbook explains VdW interactions using neutral, non-reactive atoms, such as Xenon.

Consider two atoms a distance  $r$  apart

The average charge distribution is spherically symmetric, but at any instant, there might be more charge on one side than on the other, producing an instantaneous dipole.

Review: derivation of electric field from dipole (this is not derived in class, we just use the result)



The electric potential of this charge distribution in the far-field regime is given by:

$$\Phi(\mathbf{r}) = \frac{q}{|\mathbf{r} - \mathbf{r}_+|} - \frac{q}{|\mathbf{r} - \mathbf{r}_-|}$$

Where  $\mathbf{d} = \mathbf{r}_+ - \mathbf{r}_-$

Define a position relative to the center of mass of the two charges (assuming they have the same mass):

$$\mathbf{R} = \mathbf{r} - \frac{\mathbf{r}_+ + \mathbf{r}_-}{2}, \hat{\mathbf{R}} = \mathbf{R}/R$$

Rewrite  $\mathbf{r}$  in terms of  $\mathbf{R}$  and plug into equation for electric potential

$$\begin{aligned} \Phi(\mathbf{R}) &= \frac{q}{\left| \mathbf{R} + \frac{\mathbf{r}_- - \mathbf{r}_+}{2} \right|} - \frac{q}{\left| \mathbf{R} + \frac{\mathbf{r}_+ - \mathbf{r}_-}{2} \right|} \\ \Phi(\mathbf{R}) &= \frac{q}{\left| \mathbf{R} - \frac{\mathbf{d}}{2} \right|} - \frac{q}{\left| \mathbf{R} + \frac{\mathbf{d}}{2} \right|} \end{aligned}$$

Take out a factor of  $\mathbf{R}$  from absolute value using definition of unit vector above

$$\begin{aligned} \Phi(\mathbf{R}) &= \frac{q}{\left| R\hat{\mathbf{R}} + \frac{R\mathbf{d}}{2R} \right|} - \frac{q}{\left| R\hat{\mathbf{R}} + \frac{R\mathbf{d}}{2R} \right|} \\ \Phi(\mathbf{R}) &= \frac{q}{R \left| 1 + \frac{\mathbf{d} \cdot \hat{\mathbf{R}}}{2R} \right|} - \frac{q}{R \left| 1 + \frac{\mathbf{d} \cdot \hat{\mathbf{R}}}{2R} \right|} \end{aligned}$$

Taylor expand each term to first order noticing that  $\frac{\mathbf{d} \cdot \hat{\mathbf{R}}}{2R} \ll 1$  (use:  $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$ )

$$\Phi(\mathbf{R}) \approx \frac{q}{R} \left[ 1 + \mathbf{d} \cdot \frac{\hat{\mathbf{R}}}{2R} - 1 + 1 + \mathbf{d} \cdot \frac{\hat{\mathbf{R}}}{2R} \right]$$

$$\Phi(\mathbf{R}) \approx \frac{q\hat{\mathbf{R}}}{R} \left[ 1 + \mathbf{d} \cdot \frac{\hat{\mathbf{R}}}{2R} - 1 + 1 + \mathbf{d} \cdot \frac{\hat{\mathbf{R}}}{2R} \right]$$

$$\Phi(\mathbf{R}) \approx \frac{q(\mathbf{d} \cdot \hat{\mathbf{R}})}{R^2}$$

Define a new **dipole moment vector,  $\mathbf{p} = q\mathbf{d}$**

$$\Phi(\mathbf{R}) = \frac{\mathbf{p} \cdot \hat{\mathbf{R}}}{R^2} = \frac{pcos\theta}{R^2} \quad (\theta \text{ is the angle between dipole vector and observation point})$$

The electric field is given as  $E(\mathbf{R}) = -\nabla\Phi(\mathbf{R})$

$$E(\mathbf{R}) = \frac{2pcos\theta}{R^3} \hat{\mathbf{R}} + \frac{psin\theta}{R^3} \hat{\boldsymbol{\theta}}$$

This can be re-expressed in a coordinate free form as:

$$E(\mathbf{R}) = \frac{3(\mathbf{p} \cdot \hat{\mathbf{R}})\hat{\mathbf{R}} - \mathbf{p}}{R^3}$$

**This is the result we will use: that the electric field from a dipole falls off as  $1/r^3$**

First we will do a sketchy derivation, then we will follow the derivation in the textbook.

Consider one atom which has a dipole moment  $\mathbf{p}_1$

It will provide an electric field  $E_1 \propto p_1/r^3$  a distance  $r$  away

Another atom will feel this electric field and it will be polarized into an **induced** dipole. The dipole moment of the induced dipole will be **proportional** to the electric field via a polarizability constant  $\alpha$  which will depend on what type of atom you are considering.

$$p_2 = \alpha E \sim \frac{\alpha p_1}{r^3}$$

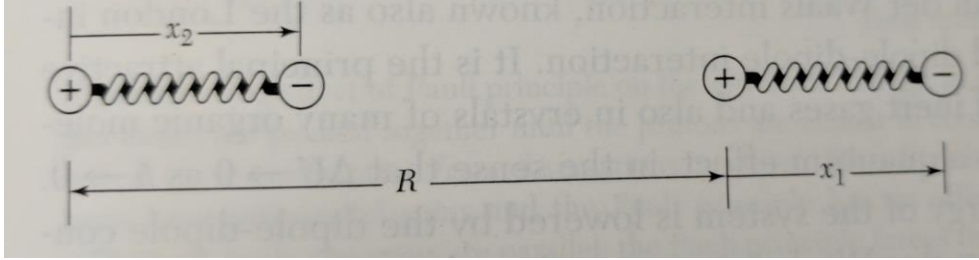
The energy stored in an electric field is proportional to  $E^2$  so the energy of the dipole-dipole interaction is given by multiplying the field originating from each of them:

$$U \propto \frac{p_1}{r^3} \frac{\alpha p_1}{r^3} = \alpha p_1^2 / r^6$$

This is an important piece of information to remember: the potential energy from dipole-dipole interaction falls off as  $1/r^6$

Now for the full derivation in your textbook:

Consider two oscillators (springs) with + and - charge on either end; basically, two dipoles whose dipole moment oscillates as the spacing between the charges oscillates



The coulomb interaction within this system is:

$$U = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2}$$

(if the charges in the image above are labeled A, B, C, D from left to right, the terms in the equation above from left to right are coulomb interaction between AC, BD, AD, and BC)

Again, we will use the taylor expansion for  $\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n$  for  $|x| < 1$

And we work in the limit where  $|x_1|, |x_2| \ll R$

Note: we need to expand to **second** order, because we will get zero otherwise

$$U \approx \frac{e^2}{R} + \frac{e^2}{R} \left[ 1 + \frac{x_2 - x_1}{R} + \left( \frac{x_2 - x_1}{R} \right)^2 - 1 + \frac{x_1}{R} - \left( \frac{x_1}{R} \right)^2 - 1 - \frac{x_2}{R} - \left( \frac{x_2}{R} \right)^2 \right]$$

$$U \approx \frac{e^2}{R} \left[ -\frac{2x_1x_2}{R^2} \right] = \frac{-2e^2x_1x_2}{R^3}$$

Change coordinates (s=symmetric; a=antisymmetric):

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2)$$

$$x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2)$$

Write  $x_1, x_2$  in terms of the new coordinates:

$$x_1 \equiv \frac{1}{\sqrt{2}}(x_s + x_a)$$

$$x_2 \equiv \frac{1}{\sqrt{2}}(x_s - x_a)$$

This gives  $U = \frac{e^2(x_s^2 - x_a^2)}{R^3}$

Also, define momenta in terms of symmetric and antisymmetric modes:

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a)$$

$$p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a)$$

Total Hamiltonian including kinetic energy terms (function of momentum) and potential energy terms (electrostatic and from spring):

$$\mathcal{H} = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{1}{2}Cx_2^2 - \frac{e^2(x_s^2 - x_a^2)}{R^3}$$

(C is a spring constant term; next steps just involve putting everything in terms of position and momentum variables that have s and a subscripts)

$$\begin{aligned} &= \frac{1}{4m}(p_s^2 + 2p_s p_a + p_a^2 + p_s^2 - 2p_s p_a + p_a^2) + \frac{1}{4}C(x_s^2 + 2x_s x_a + x_a^2 + x_s^2 - 2x_s x_a + x_a^2) \\ &\quad - \frac{e^2}{R^3}(x_s^2 - x_a^2) \\ &= \frac{1}{2m}(p_s^2 + p_a^2) + x_s^2 \left( \frac{1}{2}C - \frac{e^2}{R^3} \right) + x_a^2 \left( \frac{1}{2}C + \frac{e^2}{R^3} \right) \\ &= \left[ \frac{1}{2m}p_s^2 + \frac{1}{2} \left( C - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[ \frac{1}{2m}p_a^2 + \frac{1}{2} \left( C + \frac{2e^2}{R^3} \right) x_a^2 \right] \end{aligned}$$

Thus, the Hamiltonian has reduced to two de-coupled harmonic oscillators with frequency

$$\omega = \left[ \left( C \pm \frac{2e^2}{R^3} \right) / m \right]^{1/2}$$

Define a frequency of the harmonic oscillator if the coulomb term were absent,  $\omega_0 = \sqrt{C/m}$

Expand the square root to get an approximate expression for  $\omega$  in terms of  $\omega_0$  (use:  $(1+x)^{1/2} \approx 1 + \frac{1}{2}x - \frac{1}{8}x^2 + \dots$ )

$$\omega \approx \omega_0 \left[ 1 \pm \frac{1}{2} \left( \frac{2e^2}{CR^3} \right) - \frac{1}{8} \left( \frac{2e^2}{CR^3} \right)^2 + \dots \right]$$

The zero point energy of the interacting system is given by  $\frac{\hbar\omega_a}{2} + \frac{\hbar\omega_s}{2}$  where the two terms come from the fact that the Hamiltonian reduces to two oscillators with two different frequencies. In the absence of the coulomb term in the Hamiltonian, the zero point energy would be given by  $\hbar\omega_0$  (twice the ordinary ZPE because there are two harmonic oscillators)

The *difference* in potential energy is given by:

$$\Delta U = \hbar\omega_0 - \frac{\hbar\omega_0}{2} \left[ 1 + \frac{1}{2} \left( \frac{2e^2}{CR^3} \right) - \frac{1}{8} \left( \frac{2e^2}{CR^3} \right)^2 + 1 - \frac{1}{2} \left( \frac{2e^2}{CR^3} \right) - \frac{1}{8} \left( \frac{2e^2}{CR^3} \right)^2 + \dots \right] = -\frac{\hbar\omega_0}{8} \left( \frac{2e^2}{CR^3} \right)^2$$

$$\equiv -\frac{A}{R^6}$$

The key things to note are:

- Change in zero point energy is negative, indicating that coupling between dipoles saves energy

- The  $\sim 1/R^6$  dependence is still there

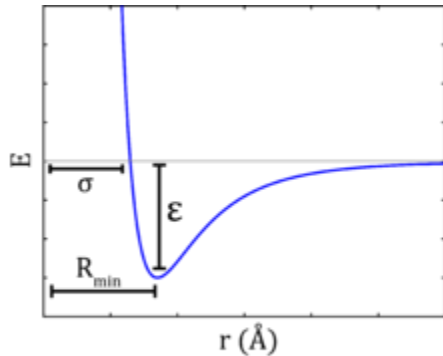
We have shown how two dipoles attract each other when they are close by, but we need to remember that we are dealing with atoms and they cannot get arbitrarily close together—this originates from Pauli exclusion. Just as we did for the potential in an ionic solid, we need to add an empirical term to the potential energy to account for this repulsion at small interatomic separations. It is customary to use  $U_{repulse} = B/R^{12}$

Putting this all together, we get the Lennard-Jones potential:

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

We have introduced two new parameters such that  $4\epsilon\sigma^6 = A$ ,  $4\epsilon\sigma^{12} = B$

In the Lennard-Jones potential, the 2<sup>nd</sup> term is physically motivated by dipole-dipole attraction, derived above. The first term is just an empirical term to make sure that atoms cannot get too close together and that beyond a certain point, it is more difficult to compress the solid than to stretch it apart (at small compression or stretching, the force will be identical because the minimum of the potential is quadratic to first order)



Using the potential, we can get expressions for the equilibrium lattice constant and the cohesive energy:

Find total potential energy by adding contribution from all atoms

$$U_{tot} = \frac{1}{2} N (4\epsilon) \left[ \sum_j \left[ \left( \frac{\sigma}{p_{ij}R} \right)^{12} - \left( \frac{\sigma}{p_{ij}R} \right)^6 \right] \right]$$

Where  $p_{ij}$  is the distance, in terms of the nearest neighbor distance  $R$ , between the reference atom  $i$  and every other atom  $j$ . One needs to choose a crystal structure before evaluating these sums, and your textbook gives values for the FCC and HCP structures.

$$\frac{dU_{tot}}{dR} = 0 = -2N\epsilon \left[ \frac{(12)(12.13)\sigma^{12}}{R^{13}} - (6)(14.45)\sigma^6/R^7 \right]$$

(the first term in the parenthesis comes from the derivative, and the 2<sup>nd</sup> term comes from the sum over all  $p_{ij}$  for a HCP or FCC lattice)

Solving for R above gives

$$\frac{R_0}{\sigma} = 1.09$$

The cohesive energy is found by plugging in the value for the equilibrium separation,  $R_0$ , into the equation for  $U_{tot}$

$$U_{tot} = -2.15 * 4N\epsilon$$

Quantum mechanical corrections can reduce this cohesive energy.

In your textbook, vdw solids are discussed in the context of things like solid Xenon. While this is an important textbook example, in recent years, a very important class of materials has come into research prominence, known as van der waals solids. There are materials, such as graphene, which can be reduced to a single unit cell thickness using everyday implements like scotch tape. Then, people can bring two different films (e.g. graphene and hexagonal boron nitride) close enough together that they will stick and make a new franken-material. The composite van-der-waals-bound material will often have properties that are completely different from its constituents.

### **Elastic strains**

For this portion of the course, we will pretend that a material is not made up of discrete atoms and view it as a continuous medium. We will develop a formalism for describing and analyzing elastic strains (elastic=like a spring, linear dependence between force and displacement; strain=how much we stretch the solid)

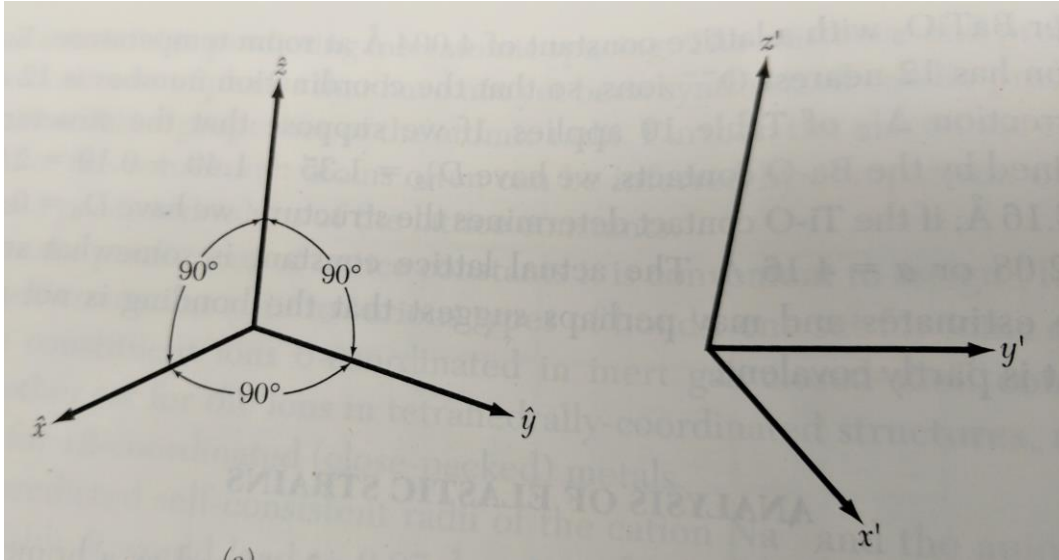
The purpose of this section is two-fold:

- Describe the aggregate mechanical properties of materials
- Build a formalism needed to describe the transmission of elastic waves in solids (e.g. when we say 'the speed of sound in diamond is 12,000 m/s, what does this actually mean?')

**Stress:** force applied to a unit area

**Strain:** deformation resulting from stress





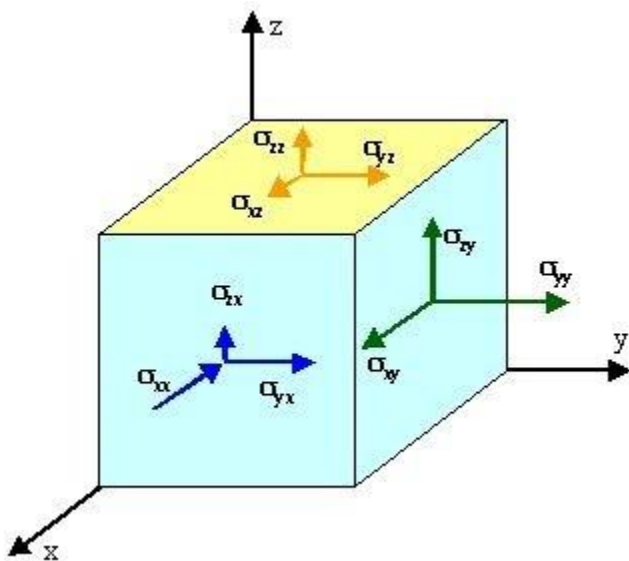
We imagine 3 orthogonal vectors  $\hat{x}, \hat{y}, \hat{z}$  embedded in a solid before we have deformed it. After we have deformed the solid, these vectors might be of different length and they might be pointing in different directions. We describe these deformed vectors  $x', y', z'$  in the following way:

$$x' = (1 + \epsilon_{xx})\hat{x} + \epsilon_{xy}\hat{y} + \epsilon_{xz}\hat{z}$$

$$y' = \epsilon_{yx}\hat{x} + (1 + \epsilon_{yy})\hat{y} + \epsilon_{yz}\hat{z}$$

$$z' = \epsilon_{zx}\hat{x} + \epsilon_{zy}\hat{y} + (1 + \epsilon_{zz})\hat{z}$$

The components  $\epsilon_{\alpha\beta}$  define the deformation. They are dimensionless and have values much smaller than 1 in most instances in solid state physics. How one 'reads' these vectors is (for example)  $\epsilon_{xx} \rightarrow$  force along x, deformation along x;  $\epsilon_{xy} \rightarrow$  shear xy-plane along x or y direction (depending which unit vector it is next to)



epsilons...)

(pretend the sigma's in the image above are

The new axes have new lengths given by (for example):

$$\mathbf{x}' \cdot \mathbf{x}' = 1 + 2\epsilon_{xx} + \epsilon_{xx}^2 + \epsilon_{xy}^2 + \epsilon_{xz}^2$$

Usually we are dealing with tiny deformations so 2<sup>nd</sup> order terms are often dropped.