Mon. Sept. 24

- Our free electron model worked well to approximate many physical phenomena involving conductors, but it has many limitations

- For example, how do we explain the behavior of insulators and semiconductors?

- to understand these effects, we need to know the details of the microscopic solid - i.e. what are the forces holding the solid together + how do they influence behavior?

- many solids consist of highly symmetric repeating units - these symmetries make modelling practical

- in other words, we are interested in <u>crystals</u>

- what binds a crystal?

- first, the crystal is typically the lowest energy state (at least locally)

- Ex: non-crystaline solids may be glasses

- let's just name the types of bonds:

  - ionic
  - covalent
  - metallic
  - molecular
  - hydrogen

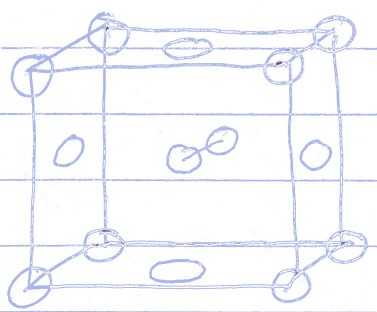
  } all are electrostatic phenomena

- as a starting point, let's take an inert gas & cool it until it solidifies

- the inert gasses have very low melting points; atoms are weakly bound; transparent & electrically insulating; very high ionization energies

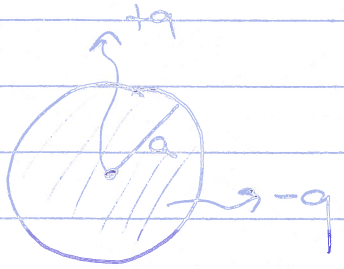
- let's use the example of argon (Ar)

- Ar atoms pack tightly in a solid in a "face-centered cubic" (fcc) crystal (melting temp. ~ 80K)



FCC

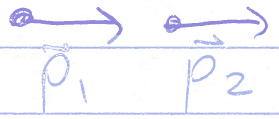
- What actually binds two atoms of Ar together?
- charge distribution of Ar is roughly symmetric (assume it is)
- +q nucleus + -q charge shell (combined charge of electrons)



- from Gauss' law: $\oint \vec{E} \cdot d\vec{a} = \frac{Q_{enc}}{\epsilon_0}$
- the field of nucleus holds electrons in orbit, but outside?
- $r > a$, we have $\oint \vec{E} \cdot d\vec{a} = \frac{Q_{enc}}{\epsilon_0} = 0$
- and so $\vec{E} = 0$
- how does one atom affect another (via electrostatics) if $\vec{E} = 0$?

- the answer is that the charge density does not stay constant in time & so the atom becomes a fluctuating dipole, $\langle E \neq 0 \rangle$

- a non-zero field induces a dipole in a nearby atom & the two attract

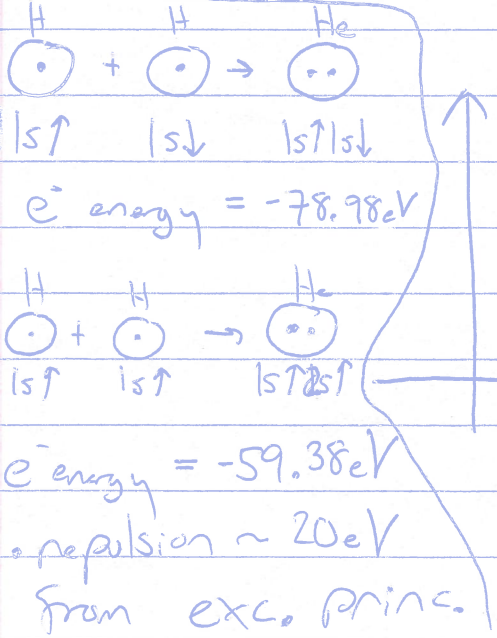


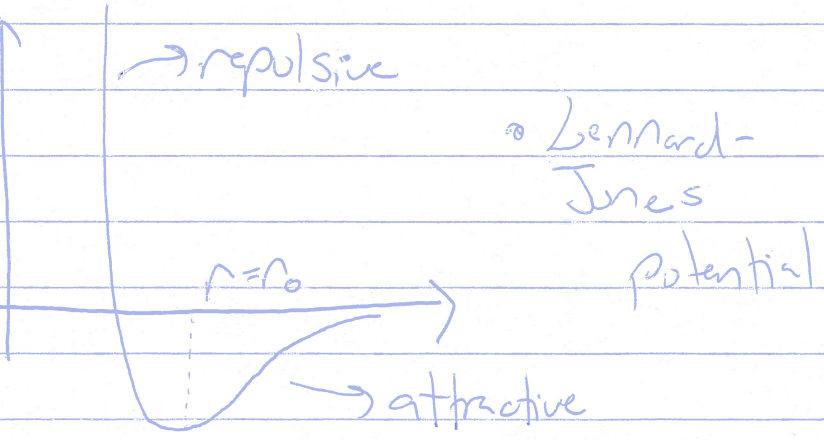
- this attractive force goes like $1/r^6$, where r is the distance between atoms

- by Pauli exclusion principle, there is a repulsive term also $1/r^{12}$

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

repulsion:





• Lennard-Jones potential

- What is significant about r_0?

- When summing over all interacting atoms in crystal, we can determine the lattice constant by setting

$$\frac{dU_{tot}}{dr} = 0$$

- which gives $\frac{r_0}{a} \sim 1.09$

- Measured values:

Ne	Ar	Kr	r_0/a
1.14	1.11	1.10	

- Ionic crystals: e.g. NaCl

- energy is needed to ionize a Na atom

Energy in: $Na + \sim 5.1eV \rightarrow Na^+ + e^-$

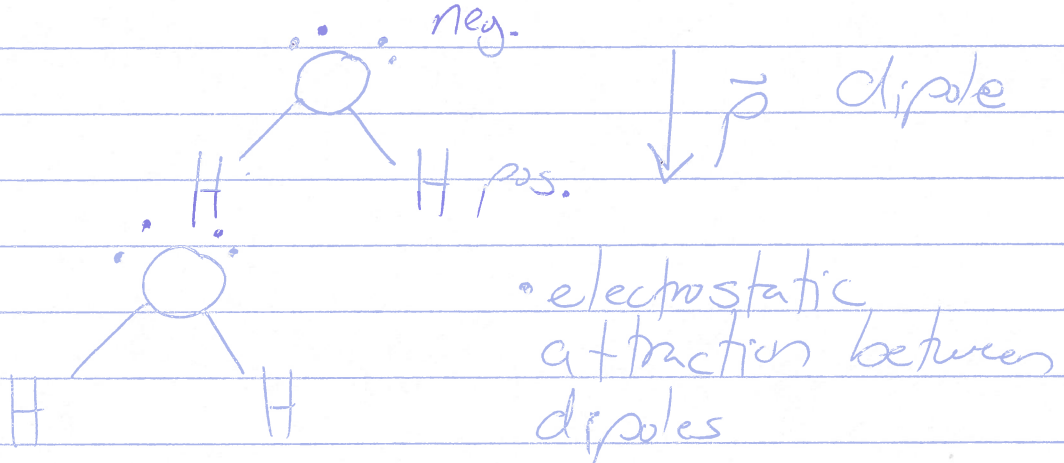
out: $e^- + Cl \rightarrow Cl^- + \sim 3.6eV$

out: $Na^+ + Cl^- \rightarrow NaCl + \sim 7.9eV$

"Cohesive energy" $\sim 7.9eV$ (needed to separate ions)

total: $(7.9 + 3.6 - 5.1)eV = 6.4eV$

Hydrogen bonding: arising from permanent dipoles in molecules



- electrostatic attraction between dipoles

- eg. ice from water is due to H-bonding

- Metallic bonding: why are the valence electrons "loosly" bound in a metal? The ionic (+) charge is screened by other electrons (core electrons)

- Na atoms have a single valence electron - how does the valence electron contribute to bonding?

- Again, the total energy is reduced when the electrons have a larger volume to move - more atoms, lower energy

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